

Removal of Cu(II) from Aqueous Solutions by Chelating Starch Derivatives

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ABSTRACT: Two chemically modified starch derivatives, crosslinked amino starch (CAS) and dithiocarbamates modified starch (DTCS), were prepared and used for the removal of Cu(II) from aqueous solutions. CAS was found to be effective for the adsorption of Cu(II), which tended to form a stable amine complex. Adsorption of Cu(II) onto DTCS was higher than that onto CAS. Experiments showed that the adsorption processes of Cu(II) on both CAS and DTCS were endothermic, and followed Freundlich isothermal adsorption. For both adsorbents, dynamic modeling of their

adsorption showed that the first-order reversible kinetic model described the adsorption process. The adsorption rate constants of CAS and DTCS were 1.578 and 10.32 h⁻¹, respectively. From the results of the thermodynamic analysis, free energy ΔG , enthalpy ΔH , and entropy ΔS of the adsorption process were calculated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3881–3885, 2004

Key words: starch; synthesis; copper; adsorption; modeling

INTRODUCTION

Removal of toxic heavy metal ions from industrial and mining wastewaters has received much attention in recent years because they cause health problems in human beings and animals.

Various methods, such as ion-exchange, reverse osmosis, and electrodialysis techniques, have been developed for the removal and recovery of heavy metal ions from sewage and industrial wastewater.¹ In spite of their effectiveness at ion removal, they are often quite expensive. Traditional chemical precipitation can be envisaged, but the generation of precipitated bulky hydroxides and colloidal particles is a major disadvantage.

The search for an effective and economic method of removing toxic heavy metal ions requires the consideration of unconventional materials and processes. In this respect, many natural polysaccharides and their derivatives containing various functional groups may have some potential. Recently, chitin and its derivatives,^{2,3} modified cellulose,^{4,5} and modified starch ethers^{6,7} have been studied with respect to their ability to remove heavy metal ions from aqueous solutions.

Starch is a natural low-cost polymer that can be highly crosslinked with epichlorohydrin or other agents to make it water insoluble. Chemical modification of the crosslinked starch with various reactive monomers yields ionomer products that can be used

to remove heavy metal ions from wastewater.⁸ Xanthation of a crosslinked starch yields insoluble starch xanthate, which has been shown to effectively remove heavy metal cations from wastewater.^{9,10} Insoluble starch products, containing tertiary amine or quaternary ammonium, have been shown to effectively remove heavy metal anions from wastewater.¹¹

In this work, we prepared two starch derivatives, crosslinked amino starch (CAS) and dithiocarbamate starch (DTCS), and their dynamic adsorption behaviors were investigated.

EXPERIMENTAL

Materials

Corn starch powder (industrial grade) was dried 2 h at 105°C before use. Epichlorohydrin (ECH), perchloric acid, ethylenediamine (EDA), potassium hydroxide, sodium chloride, carbon disulfide, and copper sulfate were all of analytical grade. The solvents, alcohol, and acetone were of technical grade (Shanghai Chemicals Co., China). All aqueous solutions and standards were prepared using deionized water.

Preparation of the samples

Corn starch powder (100 g) was slurried in water (150 mL) containing sodium chloride (1.5 g) and ECH (7 mL) in a stirred glass reaction kettle equipped with a reflux condenser. To this, slurry potassium hydroxide (6 g) in water (40 mL) was slowly added over 15 min, and the mixture was stirred for 18 h at 25°C. The pH value was adjusted to 6–7 with HCl (0.1M), and the

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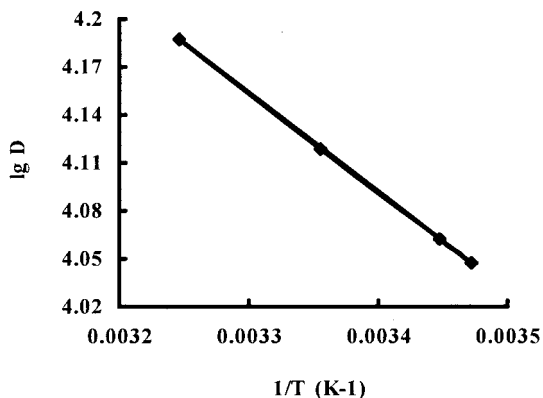


Figure 3 Effect of temperature on distribution ratio (CAS).

removal of Cu(II) ions was observed with the increase of temperature in the range of 283 to 308 K, which indicated that the adsorption processes were chemical adsorption behaviors.

Kinetics studies

The relationship between $-\ln(1 - F)$ and time is observed in Figures 1 and 2, and the nearly straight line observed indicates that the adsorption reactions can be approximated to a first-order kinetics, by the following expression:

$$-\ln(1 - F) = kt \tag{1}$$

where k is the equilibrium constant, and

$$F(t) = \frac{C_0 - C_t}{C_0 - C_e} \tag{2}$$

where C_0 , C_t , and C_e (all in mg/L) represent concentrations of Cu(II) ions initially, in aqueous solutions at any time t , and at equilibrium, respectively.

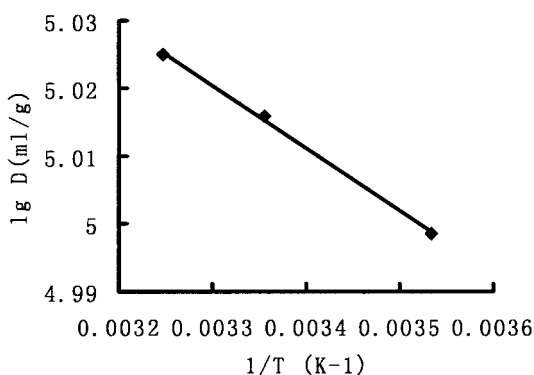


Figure 4 Effect of temperature on distribution ratio (DTCS).

TABLE II
Thermodynamic Parameters for Adsorption of Cu(II) on Adsorbents

	ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
CAS	11.91	-23.50	118.9
DTCS	1.765	-28.62	101.9

From experimental data adsorption rate constants for CAS and DTCS were calculated and are shown in Table I. It can be seen that the adsorption rate of DTCS was higher than that of CAS at any temperature. A reasonable explanation is that the functional group of DTC binds Cu(II) ions more easily than CAS. The adsorption rate of both CAS and DTCS is relatively high, and perhaps the reason is that most functional group are dispersed on the surface layers of the adsorbents, especially for DTC groups.

Thermodynamic studies

To explain the effect of temperature on adsorption thermodynamic parameters, free energy ΔG , enthalpy ΔH , and entropy ΔS were calculated. To calculate values of these parameters, the following equations were used:

$$D = \frac{Q_e}{C_e} \tag{3}$$

$$\log D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{R} \tag{4}$$

$$\Delta G = \Delta H - \Delta ST \tag{5}$$

where R is the gas constant and D is the distribution ratio between Cu(II) and the adsorbent in aqueous solution.

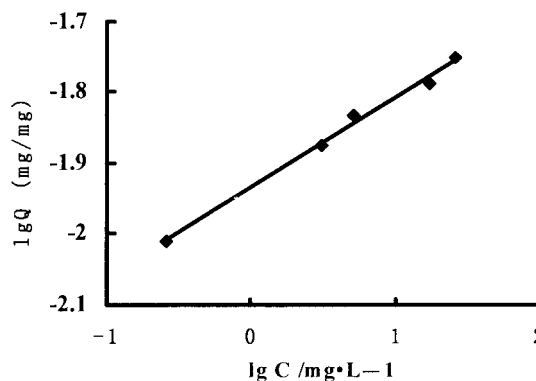


Figure 5 Freundlich isothermal adsorption curve (CAS).

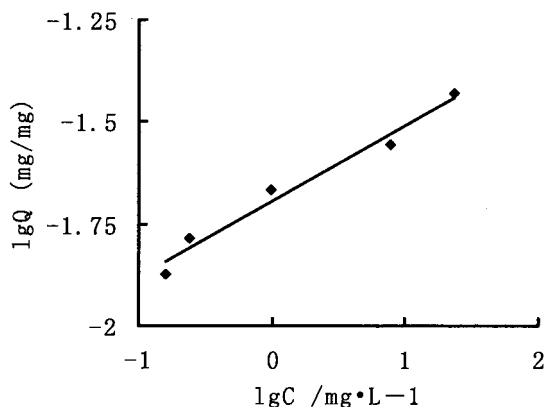


Figure 6 Freundlich isothermal adsorption curve (DTCS).

The relationship between $\log D$ and $1/T$ for CAS and DTCS is shown as Figures 3 and 4, respectively. According to eqs. (3)–(5) and the slopes and intercept of linear lines in Figures 3 and 4, thermodynamic parameters of CAS and DTCS were calculated, and are shown in Table II.

The results show that both adsorptions are endothermic, although that of CAS is more temperature dependent.

Apparent activation energy

The apparent activation energy E_a can be calculated by using the following Arrhenius expression:

$$\log k = -\frac{E_a}{2.303RT} + B \quad (6)$$

where k is the adsorption rate constant and B is a related constant.

According to the Arrhenius expression, and experimental data of different temperatures, values of E_a of CAS and DTCS were calculated as 11.07 and 9.98 kJ/mol, respectively, which indicates that adsorption for Cu(II) was easier onto DTCS than onto CAS.

Adsorption isotherms

Typical adsorption isotherms for Cu(II) onto CAS and DTCS are presented in Figures 5 and 6, respectively. As seen from the figures, adsorption of Cu(II) onto CAS and DTCS fits a Freundlich isotherm, which is expressed as

$$\log Q = \log k + n \log C \quad (7)$$

where Q is the amount of Cu(II) adsorbed per unit weight, k and n are Freundlich constants, and C is the equilibrium concentration of Cu(II) in aqueous solution.

From experimental data, the Freundlich constant n for CAS and DTCS was calculated as 7.9239 and 5.5072, respectively, values that were in the range of 2 to 10, suggesting that adsorption for Cu(II) onto both adsorbents was unhindered.¹²

Characterization of the adsorbents

Figure 7 shows that the IR spectra of DTCS exhibit bands at 1493.88, 1286.25, and 956.96 cm^{-1} (assigned to N=C=S), and bands at 1650 and 1370 cm^{-1} (assigned to N—H) were weakened compared

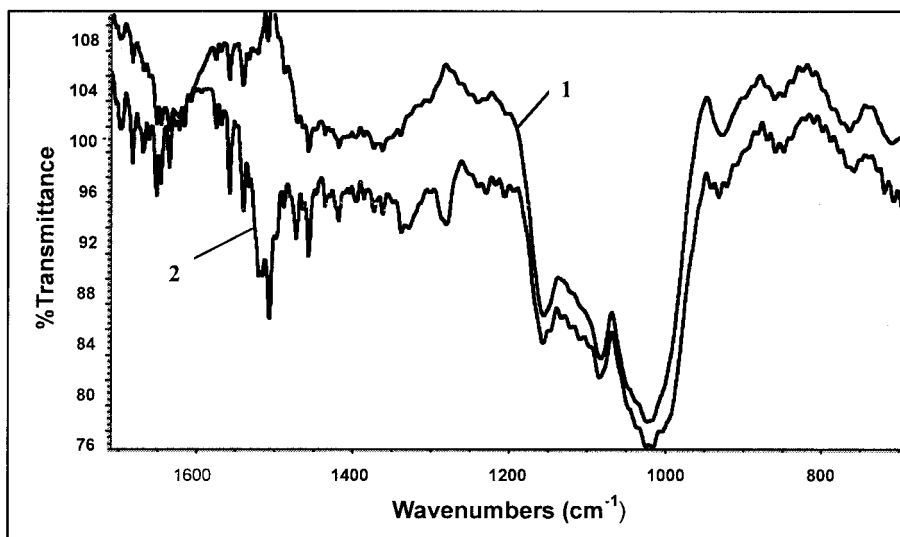


Figure 7 IR spectra of some CAS and DTCS: 1, CAS; 2, DTCS.

TABLE III
Results of Elemental Analysis

Sample	Contents of elements (%)			
	C	H	N	S
CAS	41.16	6.83	3.50	
CAS-Cu	36.84	6.57	3.10	
DTCS	38.56	6.31	3.26	3.96
DTCS-Cu	36.68	6.26	3.01	3.65

with those of CAS IR spectra. These changes provided evidence of DTC group formation.

Elemental analysis

Elemental analyses for adsorbents and formed complexes with Cu are shown in Table III.

As may be observed, the amino content in CAS is 2.49 mmol g⁻¹, that is, the degree of substitution of DTC is 45%. From elemental analysis results and adsorption equilibration experimental data, the ratio between the amino group in CAS and Cu adsorbed was determined as 1.9, near 2 : 1, attributed to the fact that hydroxyl group on the starch skeleton complexed some Cu. The ratio between DTC group in DTCS and Cu adsorbed is 0.83, with evidence of bonds between amino group and Cu.

Adsorption equilibrium

According to adsorption equilibrium experiments above, CAS and DTCS were both applied for Cu(II) removal from aqueous solutions, and the concentration of Cu(II) was measured every minute.

In our studies, CAS was found to exhibit a smaller adsorption capacity than that of DTCS, and showed a significant release of Cu(II) ion after 3 h of chelating reaction. DTC-Cu was stable within the 4 h Cu(II)

uptake experiment. A time of 2 h was sufficient for Cu(II) removal by CAS and 1 h by DTCS. Thus, DTCS was a better adsorbent for Cu(II) removal, either in chelating capacity or uptake rate.

CONCLUSIONS

We prepared Cu(II) adsorbents, CAS and DTCS, and their adsorption behaviors were investigated. As a result, the following conclusions were obtained.

1. Adsorption rates for Cu(II) on both adsorbents were very rapid.
2. Adsorption processes for Cu(II) on both adsorbents fit a Freundlich isotherm.
3. Adsorptions for Cu(II) from aqueous solution were endothermic reactions.
4. DTCS was very effective for the adsorption of Cu(II) and more efficient in capacity, stability, and adsorption rate than was CAS, which was also a good adsorbent for Cu(II) ion.

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