

Study on Adsorption Behavior Between Cr(VI) and Crosslinked Amphoteric Starch

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ABSTRACT: Crosslinked amphoteric starches (CASs) with quaternary ammonium cationic and carboxymethyl anionic groups were prepared by a hemidry reaction. Their adsorption behavior for Cr(VI) was investigated, and was found to follow the Langmuir isotherm. The adsorption process was found to be dependent on initial pH, concentration of Cr(VI), dose of CAS, and temperature. The adsorption capacity decreased with increasing degree of substitu-

tion of anionic groups. The thermodynamic study indicated that the adsorption process was exothermic, and the enthalpy changes (ΔH^0), the entropy changes (ΔS^0), and free energy changes (ΔG^0) for CASs were determined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 263–267, 2003

Key words: adsorption; amphoteric starch; crosslinking; metal ion; thermodynamics

INTRODUCTION

Over the past few years, removal of heavy metal ions from sewage and industrial wastewater has been the center of increased attention. Although existing treatment methods, such as chemical precipitation, ion exchange, and chitisan adsorption,¹ have been proved effective, they still have some disadvantages: the traditional precipitation process does not always reduce metal ion concentrations to the presently required discharge level (0.2 mg/L); synthetic ion-exchange resins are often quite expensive; and the process of producing chitisan itself pollutes the environment. Starch is renewable and biodegradable, and modified starch is capable of adsorbing heavy metal ions, so low-cost modified starch for removal of heavy metal ions has been documented. Crosslinked starch xanthate had been proved to effectively remove heavy metal cations from wastewater²; insoluble carboxyl-containing starch products, obtained by grafting acrylonitrile onto a highly crosslinked starch, showed effective adsorption of heavy metal cations³; and Chan^{4–6} reported the mass transport process for the adsorption of Cr(VI) onto crosslinked cationic starch, as well as the adsorption of Cu²⁺ and Ga²⁺ onto insoluble amphoteric starch containing quaternary ammonium cation and phosphate anion. However, none of these studies investigated the relationship between the adsorption capacity and the degree of substitution (DS) of modified starch, which is very important in actual applica-

tion, and the adsorption behavior between Cr(VI) and amphoteric starch with carboxymethyl anionic groups has not been investigated so far in the relevant literature.

This study investigates the effect of initial pH value, initial concentration, and the dose on the adsorption of Cr(VI) with a series of crosslinked amphoteric starches with the same DS of quaternary ammonium cationic groups and different DS of carboxymethyl anionic groups. The dynamic and thermodynamic characteristics are also reported.

EXPERIMENTAL

Materials

Corn starch, of food-grade quality, was dried at 105°C before use. 3-Chloro-2-hydroxypropyltrimethylammonium chloride (65% aqueous solution), epichlorohydrin, chloroacetic acid, and diphenylcarbazine (analytical reagent-grade) were used as received. Analysis of Cr(VI) concentration was performed with a model 721 spectrophotometer (Shang Hai Third Analytical Instrument Factory, China).

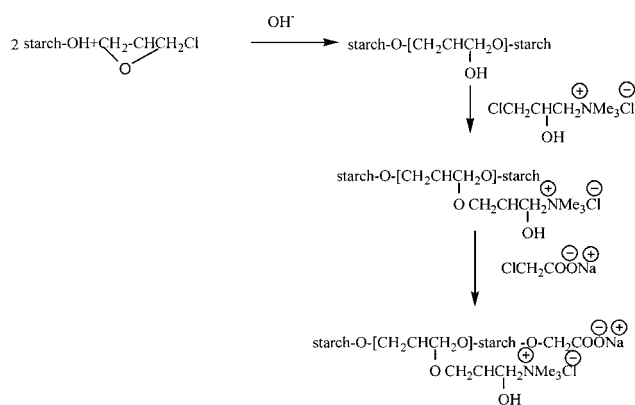
Synthesis of crosslinked amphoteric starch

The processes for preparing crosslinked starch were previously described.⁷ Crosslinked amphoteric starch (denoted as CAS) was prepared by a hemidry reaction: the crosslinked starch was first etherified by 65% 3-chloro-2-hydroxypropyltrimethylammonium chloride,⁷ then carboxymethylated⁸ by chloroacetic acid; the final products were washed and neutralized to pH 6.5 with 80% ethanol solution containing hydrochloric

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acid, then dried. The nitrogen content and the DS of quaternary ammonium cationic groups in the CAS were measured according to the Kjeldahl method; the amount and the DS of the carboxymethyl anionic group were measured according to the procedure proposed by Eyler and Diephuis.⁹

The above reaction process may be described by the following scheme:



Adsorption of Cr(VI)

The adsorption experiments of this study were carried out in a series of dyeing tubes containing the desired dose of CAS and 50 mL of dichromate aqueous solution at the desired concentration and initial pH (adjusted with dilute hydrochloric acid or 0.1N NaOH) in a constant temperature bath. After shaking for a certain time, the tubes were removed and the concentration of Cr(VI) after the adsorption was analyzed by spectrophotometer.

RESULTS AND DISCUSSION

It was previously demonstrated by Chan¹⁰ that an insoluble amphoteric starch containing tertiary amine cationic (DS = 0.73) and phosphate anionic (DS = 0.15) groups was effective in removing Cr(VI) from relatively high concentrations of Cr(VI). In practice, industrial wastewaters usually contain 20–100 mg/L Cr(VI). In the present study, various CASs with quaternary ammonium cationic groups and carboxymethyl anionic groups were studied for the adsorption of Cr(VI) at such concentrations.

Effect of pH

In the adsorption experiments, three kinds of CASs were used, of which the DS of quaternary ammonium cationic groups were all 0.3, whereas the DS of carboxymethyl anionic groups were 0.19, 0.23, and 0.29, respectively. The three crosslinked amphoteric starches were denoted as CAS1, CAS2, and CAS3, respectively. The adsorption capacity Q (mg/g) on the adsorbents

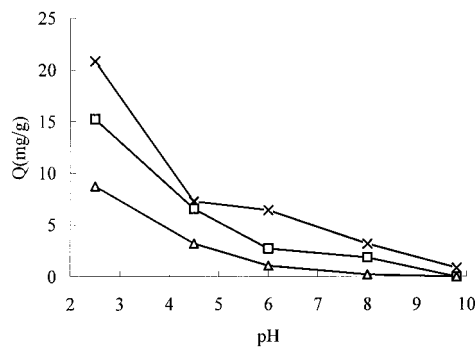
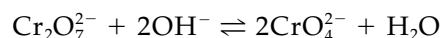


Figure 1 Effect of initial pH value of solution on adsorption capacity: CAS1 (×); CAS2 (□); CAS3 (△). Conditions: $[\text{Cr}_2\text{O}_7^{2-}] = 50$ mg/L; $t = 4$ h; $T = 15^\circ\text{C}$; dose of CAS1, CAS2, and CAS3, all 30 mg.

for initial pH values of solution ranging from 2.5 to 10 at 50 mg/L Cr(VI) and 15°C is shown in Figure 1.

The figure shows that the adsorption capacity of the three adsorbents all decreased as the initial pH value of solution increased from 2.5 to 10. At the same pH value, as the DS of the anionic group increased, the adsorption capacity of the adsorbent decreased [i.e., Q (CAS1) > Q (CAS2) > Q (CAS3)]. The quaternary ammonium group in CAS adsorbs Cr(VI) by electrostatic attraction. In alkaline conditions, carboxymethyl groups exist in the form of $-\text{COO}^-$, which prevented the adsorption of Cr(VI) onto the CAS. The higher the DS of the anionic group, the stronger the repulsion. Moreover, the following reaction occurs:



As a consequence, the forward reaction is favored, and because the same quantity of $\text{Cr}_2\text{O}_4^{2-}$ ion is absorbed, CAS has a higher adsorption capacity when absorbing the $\text{Cr}_2\text{O}_7^{2-}$ ion. However, at low pH, the carboxymethyl groups exist primarily in the form of $-\text{COOH}$ and repulsion is weaker, so we selected the initial pH 2.5 as the test condition for experimental study.

Effect of the dose

The adsorption capacity Q on the adsorbents for adsorbent doses ranging from 10 to 60 at 50 ppm Cr(VI) and 15°C is shown in Figure 2.

It is supposed that the adsorption capacity would increase if the DS of the cationic group increased or the dose of adsorbent was increased, given that the active site on CAS to adsorb Cr(VI) is the quaternary cationic group. Figure 2 shows that when the dose varies from 10 to 60 mg, the adsorption capacity gradually increases. However, when the dose reaches a certain degree, the trend becomes weak, which may be explained as follows: when the dose increases, a stronger interaction occurs between the carboxymethyl an-

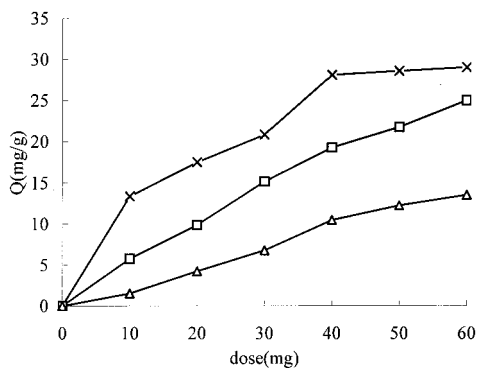


Figure 2 Effect of dose on adsorption capacity: CAS1 (×); CAS2 (□); CAS3 (△). Conditions: $[Cr_2O_7^{2-}] = 50 \text{ mg/L}$; $t = 4 \text{ h}$; $T = 15^\circ\text{C}$; $\text{pH} = 2.5$.

ionic group and Cr(VI), even among CAS molecules, and thus some active sites would be unoccupied or be occupied by other anionic group. Thus, we selected a dose of 60 mg as the test condition for experimental study.

Effect of adsorption time

The residual concentrations of Cr(VI) for adsorption times ranging from 5 to 60 min at 15°C are shown in Figure 3.

The results indicate that the adsorption reaches equilibrium within 1 h. The adsorption consists of three steps: (1) Cr(VI) from the bulk solution diffuses through a liquid film surrounding the particle surface; (2) Cr(VI) diffuses through the particle to the adsorption active site; and (3) Cr(VI) is adsorbed onto the adsorption active site. Because the adsorption is a physical process, step 3 is rapid, and is thus not considered in the kinetic analysis. Consequently, steps 1 and 2 are considered as the rate-limiting steps. The results show that the equilibrium time is almost the same, and independent of the DS of the anionic group. Thus, the particle size determines the equilibrium rate

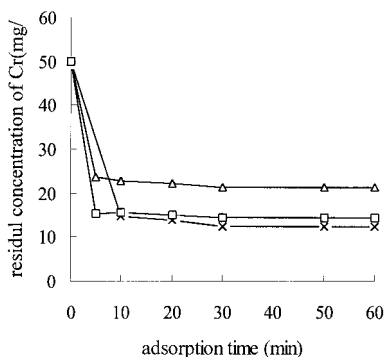


Figure 3 Effect of adsorption time on residual concentration of [Cr]: CAS1 (×); CAS2 (□); CAS3 (△). Conditions: $[Cr_2O_7^{2-}] = 50 \text{ mg/L}$; $\text{pH} = 2.5$; $T = 15^\circ\text{C}$; dose of CAS1, CAS2, and CAS3, all 60 mg.

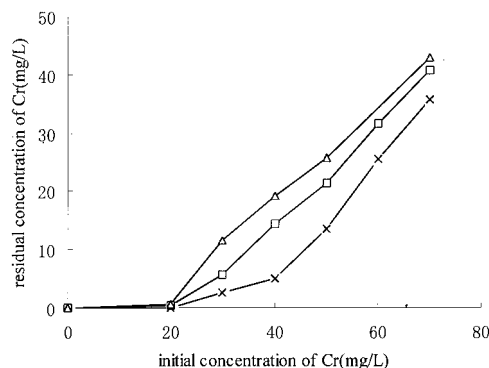


Figure 4 Effect of initial concentration of Cr(VI) on residual concentration of [Cr]: CAS1 (×); CAS2 (□); CAS3 (△). Conditions: $\text{pH} = 2.5$; $t = 1 \text{ h}$; $T = 15^\circ\text{C}$; dose of CAS1, CAS2, and CAS3, all 60 mg.

in steps 1 and 2. When the particle size of the three adsorbents is the same, there is no difference in the equilibrium time.

Effect of concentration of Cr(VI)

The residual concentrations of Cr(VI) for an initial concentration of Cr(VI), ranging from 20 to 70 mg/L at 15°C and pH 2.5, are shown in Figure 4.

The residual concentration of Cr(VI) of CAS1, CAS2, and CAS3 increases from <0.1 to 36, 0.5 to 41, and 0.6 to 43 mg/L, respectively, with increasing initial concentration of Cr(VI). These results imply that CAS has a higher adsorption capacity when the initial concentration of Cr(VI) is 50–60 mg/L; the adsorption capacities of CAS1, CAS2, and CAS3 are 30.68, 27.04, and 25.48 mg/g, respectively. The three curves of residual concentration of Cr(VI) versus initial concentration of Cr(VI) are all concave upward; moreover, they share a common trend, which implies that the type of adsorption isotherms for the three adsorbents would be the same, independent of the DS of the anionic groups.

Adsorption isotherms

Adsorption isotherms of the adsorption capacity per equilibrium concentration (Q/C_e) of Cr(VI) versus the equilibrium concentration (C_e) of CAS1, CAS2, and CAS3 are shown in Figure 5. The relationship between C_e/Q and C_e is linear, which indicates that the adsorption behavior follows the Langmuir adsorption isotherm. The Langmuir adsorption isotherm is expressed as

$$Q = Q_0 b C_e / (1 + b C_e)$$

where C_e is equilibrium concentration of the metal ion in solution (mg/L), Q is adsorption capacity (mg/g), Q_0 is the maximum adsorption capacity (mg/g), and b

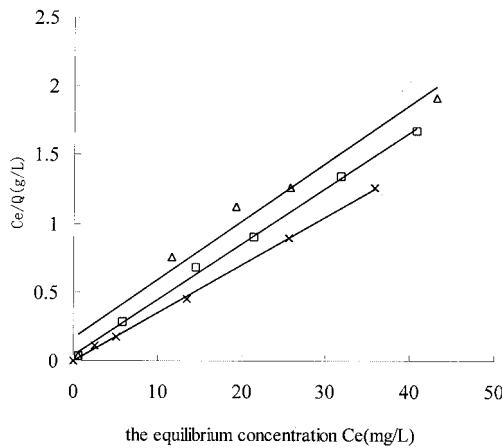


Figure 5 Langmuir adsorption isotherm for CAS1 (×), CAS2 (□), and CAS3 (Δ). Conditions: pH = 2.5; $t = 1$ h; $T = 15^\circ\text{C}$; dose of CAS1, CAS2, and CAS3, all 60 mg.

is the Langmuir constant (L/mg). The adsorption parameters for CAS1, CAS2, and CAS3 are listed in Table I.

These results indicate that CAS1 has a greater adsorption capacity than that of CAS2; and CAS2, greater than that of CAS3 (i.e., the higher DS of the anionic group leads to lower adsorption capacity). The same conclusion is drawn from the Langmuir constant b : when the DS of the anionic group increased, b decreased from 24.86 to 0.26 L/mg.

Adsorption thermodynamics

The adsorption behavior of adsorbed Cr(VI) on the adsorbents at different temperatures, ranging from 35 to 55°C , was also investigated (Fig. 6). The results show that the adsorption capacity decreases with increasing temperature, which implies that the adsorption process was exothermic. To certify this conclusion, the curves of $\log(Q/C_e)$ versus $1/T$ for CAS1, CAS2, and CAS3 are shown in Figure 7. Because the relation between $\log(Q/C_e)$ and $1/T$ for CAS1, CAS2, and CAS3 is linear, the changes of apparent enthalpy (ΔH^θ) and entropy (ΔS^θ) were calculated from the Van't Hoff equation:

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

TABLE I
Langmuir Parameters for CAS1, CAS2, and CAS3 at 15°C

Sample	b (L/mg)	Q_0 (mg/g)	r^a
CAS1	24.86	28.78	0.9994
CAS2	0.88	27.90	0.9988
CAS3	0.26	23.30	0.9847

^a The related coefficient.

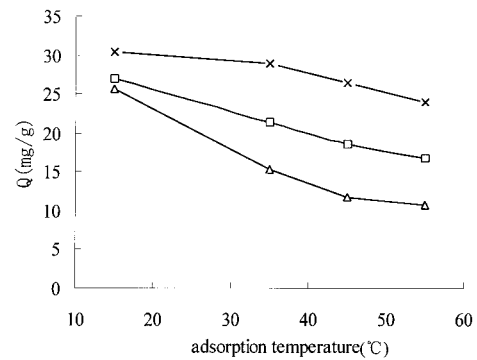


Figure 6 Effect of adsorption temperature on adsorption capacity: CAS1 (×); CAS2 (□); CAS3 (Δ). Conditions: $[\text{Cr}_2\text{O}_7^{2-}] = 50$ mg/L; pH = 2.5; $t = 1$ h; dose of CAS1, CAS2, and CAS3, all 60 mg.

The change of free energy (ΔG^θ) was calculated from the thermodynamic equation: $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$. The values of ΔH^θ , ΔS^θ , and ΔG^θ are listed in Table II. The results show that as the temperature increases, the value of Q decreases. The adsorption process was exothermic because of the negative value of ΔH^θ , and was more temperature dependent for CAS3. In addition, the negative values of ΔS^θ and ΔG^θ demonstrated a decrease in entropy and an increase in the feasibility of adsorption at lower temperatures.

CONCLUSIONS

Crosslinked starches containing a quaternary ammonium cationic group and a carboxymethyl anionic group can be used to effectively remove Cr(VI) in wastewater, especially wastewater containing lower initial concentrations of Cr(VI).

The adsorption capacity of crosslinked amphoteric starch with the same DS of quaternary ammonium cationic groups decreased with the increasing DS of carboxymethyl anionic groups. The adsorption capac-

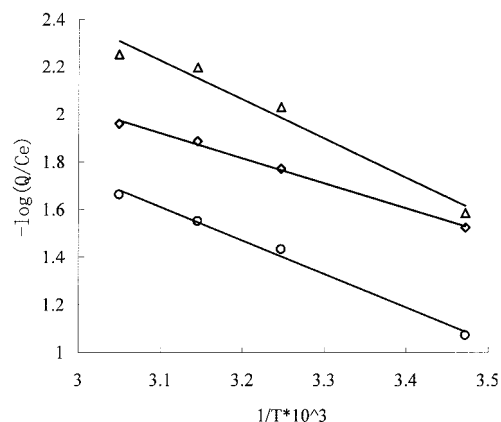


Figure 7 Plot of $1/T \times 10^3$ versus $-\log(Q/C_e)$ for CAS1 (×), CAS2 (□), CAS3 (Δ). Conditions: $[\text{Cr}_2\text{O}_7^{2-}] = 50$ mg/L; pH = 2.5; $t = 1$ h; dose of CAS1, CAS2, and CAS3, all 60 mg.

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 ⁻¹ /K ⁻¹)
CAS1	15	30.68	-8.5	-26.9	-63.9
	35	29.12	-7.4		
	45	26.52	-6.6		
	55	23.92	-5.9		
CAS2	15	27.04	-3.5	-19.9	-57.1
	35	21.32	-2.3		
	45	18.72	-1.7		
	55	17.16	-1.2		
CAS3	15	25.68	-9.7	-31.3	-74.9
	35	15.30	-8.2		
	45	11.79	-7.5		
	55	10.77	-6.7		

ity was dependent on pH, initial concentration of Cr(VI), the dose of adsorbent, and the adsorption temperature. The adsorption capacities of CAS1, CAS2, and CAS3 were 30.68, 27.04, and 25.48 mg/g, respectively; at 15°C, the adsorption followed the Langmuir adsorption isotherm.

Because the adsorption process was exothermic, lower temperatures facilitated the adsorption. Enthalpy changes (ΔH^θ) for the three adsorbents under investigation were -26.9, -19.9, and -31.3 kJ/mol, respectively. Moreover, the negative value of ΔG^θ indicated an increase in the feasibility of adsorption at lower temperatures.

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