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Study on adsorption behavior of crosslinked cationic starch maleate for chromium(VI)

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Abstract

Crosslinked cationic starch maleates (CCSM) containing quaternary ammonium cationic groups were prepared by a dry reaction. The adsorption behavior of crosslinked cationic starch maleates for Cr(VI) was investigated. Physicochemical factors such as equilibrium time, temperature, and initial solution pH affecting magnitude of Cr(VI) adsorption were studied. Their adsorption behavior was found to follow langmuir isotherm. The adsorption capacity decreased with increasing DS of anionic maleic groups. The thermodynamic investigation demonstrated that the adsorption process was exothermic, and thermodynamic parameters were calculated at different DS.

Keywords: Crosslinked amphoteric starch; Adsorption; Cr(VI); Thermodynamics

1. Introduction

Water pollution due to chromium compounds remains a serious environmental problem. Chromium ions are often found in the environment as a result of their industrial uses, such as electroplating, metal finishing, leather tanning, pigments, etc. Chromium(VI) compounds are known to be much more toxic than chromium(III) ones. Removal methods, such as chemical precipitation, ion exchanger, membrane separation (Kozlowski & Walkowiak, 2002), and adsorption, have been effective, especially adsorption using sorbents is one of the most popular techniques (Crini, 2005).

Recently modified biopolymers as cheaper and more effective sorbents have been investigated. Among these, starch is renewable, biodegradable, and relatively inexpensive, which makes it attractive as an environmentally friendly material for industrial uses. In order to form water-insoluble crosslinked networks, starch can be crosslinked by a reaction between the hydroxyl groups of the chains with a coupling agent. Crosslinked starch xanthate and carboxyl-containing starch derivatives had been used as effective adsorbents to remove heavy metal ions from wastewater (Kim & Lim, 1999; Kweon, Choi, Kim, & Lim, 2001; Wing, Swanson, & Doane, 1976). Chan et al. (1993, 1999) reported the mass transport process for the adsorption of chromium(VI) onto crosslinked cationic starch with high degree of substitution (0.73). Xu, Zhang, and Lu (2003) investigated adsorption behavior between Cr(VI) and crosslinked amphoteric starch containing tertiary amine cationic ($DS = 0.3$) and carboxymethyl anionic groups ($DS = 0.19, 0.23, 0.29$). However, most of the commercially available starch derivatives have a low degree of substitution ($DS < 0.2$), and high degree of substitution means high cost. Moreover the adsorption behavior between chromium(VI) and amphoteric starch with maleic groups, which is prepared by dry process, has not been reported so far in the literatures.

In the present study, chromium(VI) adsorption behavior on a novel crosslinked amphoteric starch containing tertiary amine cationic ($DS = 0.2$) and maleic anionic ($DS = 0.02, 0.04, 0.07$) groups from aqueous solution was

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investigated. The dynamic and thermodynamic characteristics were also reported.

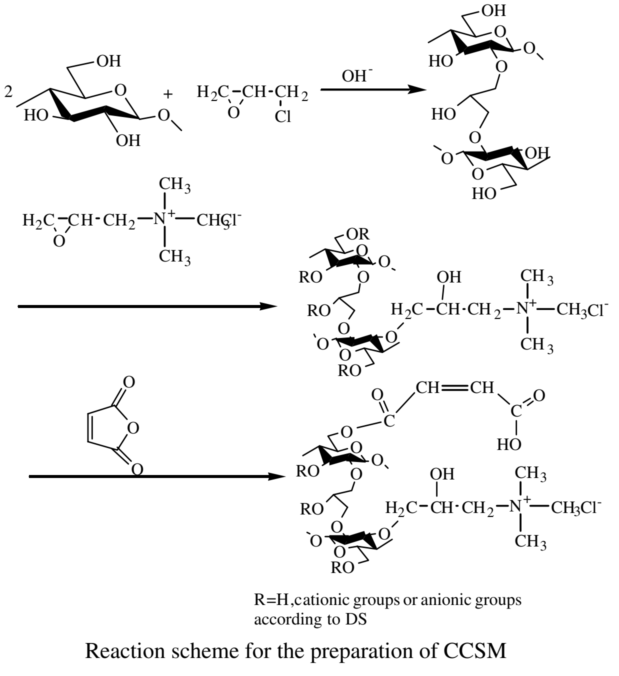
2. Experimental

2.1. Materials

Food-grade quality corn starch was dried at 105 °C before used. 2,3-Epoxypropyltrimethyl-ammonium chloride, epichlorohydrin, ethanol, and maleic anhydride (analytical reagent grade) were obtained from Shenyang reagent No.1 factory (Shenyang, China). $K_2Cr_2O_7$, NaOH, and other chemicals were of analytical reagent quality purchased from Liaodong chemical company (Dalian, China). US-VIS-NIR recording spectrophotometer (Shimadzu UV-3100 instrument) was used to analyze the content of chromium(VI) in the aqueous solution.

2.2. Preparation of crosslinked amphoteric starch

Crosslinked starch was obtained by the reaction of epichlorohydrin and starch. Crosslinked cationic starch maleate (denoted as CCSM) was prepared by a dry process: the crosslinked starch was etherified by 2,3-epoxypropyltrimethylammonium chloride (Ju, 1998), then esterified by maleic anhydride (Minkema, 1959); the products were washed with 80% ethanol solution and neutralized to pH 7.0 with 0.1 N hydrochloric acid, then dried. The nitrogen content and the DS of quaternary ammonium cationic groups in the CCSM were analyzed using the Kjeldahl method. The DS of the maleic anionic groups was determined using the method of Wurzburg with minor modification (Chan Kong-Chong, Jie Xing, David Lee Phillips, & Harold Corke, 2001).



Reaction scheme for the preparation of CCSM

2.3. Structural characterization

Fourier transform-infrared (FT-IR) spectra were obtained from KBr pellets of native starch and CCSM with a Thermo Nicolet FT-IR Spectrometer (Model-Nexus 470FTIR).

2.4. Adsorption procedure

The adsorption experiments in this study were carried out according to the method of Xu et al. (2003): 50 mL of dichromate aqueous solution with desired concentration and the desired dose of CCSM were placed in a series of dyeing tubes in a thermostated water bath. Initial pH was adjusted with dilute hydrochloric acid and 0.2 N sodium hydroxyl aqueous solution. After shaken for the definite time, the tubes were removed and the concentration of chromium(VI) in the aqueous solution after the adsorption was analyzed by US-VIS-NIR recording spectrophotometer. The adsorption capacity of the CCSM was calculated by the following expression:

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

where Q is the adsorption capacity of the CCSM (mg/g), C_0 and C_t (mg/L) are the concentration of chromium(VI) at the initial time and at time t, respectively, V is the total volume of the aqueous solution and m is the weight of CCSM. Three kinds of CCSM were used in this adsorption experiment, and they were designated as CCSM1, CCSM2, and CCSM3. Their DS of quaternary ammonium cationic groups were all 0.2, while the DS of maleic anionic groups were 0.02, 0.04, and 0.07, respectively.

3. Results and discussion

3.1. The FT-IR spectra of native starch and CCSM

The FT-IR spectra of native starch and CCSM are shown in Fig. 1. The native starch showed a typical broad hydroxyl peak around 3400 cm^{-1}. The FT-IR spectrum of CCSM showed new peaks around 1730 and 1480 cm^{-1} for the carboxylic acids of maleate groups and C–N bonds of quaternary ammonium cationic groups, respectively.

3.2. Morphological study of native starch and CCSM

Scanning electron microscopy (SEM) was used to study the changes of the granule morphology before and after modification. As shown in Fig. 2, the different surface morphology between native starch and CCSM is clearly visualized in the scanning electron micrographs. Because CCSM were prepared by dry process, some damage to the starch granules was observed.

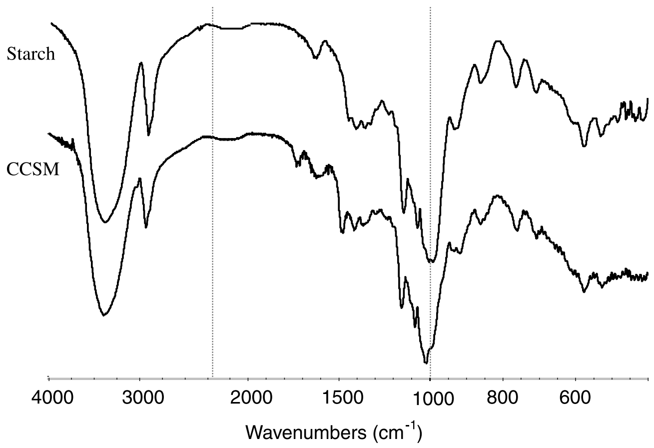


Fig. 1. FT-IR spectra of native starch and CCSM.

3.3. Comparison between native starch and CCSM in chromium(VI) adsorption

Native starch itself appeared to adsorb minor amounts of chromium(VI) ions. As shown in Fig. 3, adsorption capacity of native starch was much lower in comparison with CCSM. Adsorption capacity of native starch was only 1.7 mg/g, while those of CCSM1, CCSM2, and CCSM3 were 33.3, 26.3, and 22.8 mg/g, respectively. It may be explained that physical entrapment of the chromium(VI) ions would be the characteristics for the ion-adsorption of native starch, while strong electrostatic attraction would be the characteristics for the ion-adsorption of CCSM.

3.4. Effect of adsorption time on residual concentration of Cr(VI)

Fig. 4 shows the influence of time on residual concentration of chromium(VI) solution. Chromium(VI) solution is dichromate aqueous solution. It is clear that time has evident influence on the residual concentration of chromium(VI) solution within 20 min. However, the decrease in the residual concentration of chromium(VI) solution is very small beyond 20 min. Therefore, the adsorption at 20 min reaches equilibrium. The results show that although the DS of the anionic groups is different, the equilibrium time is almost the same. As the DS of maleic anionic group increased, residual concentration of Cr(VI) increased. It could be accounted for that the cationic

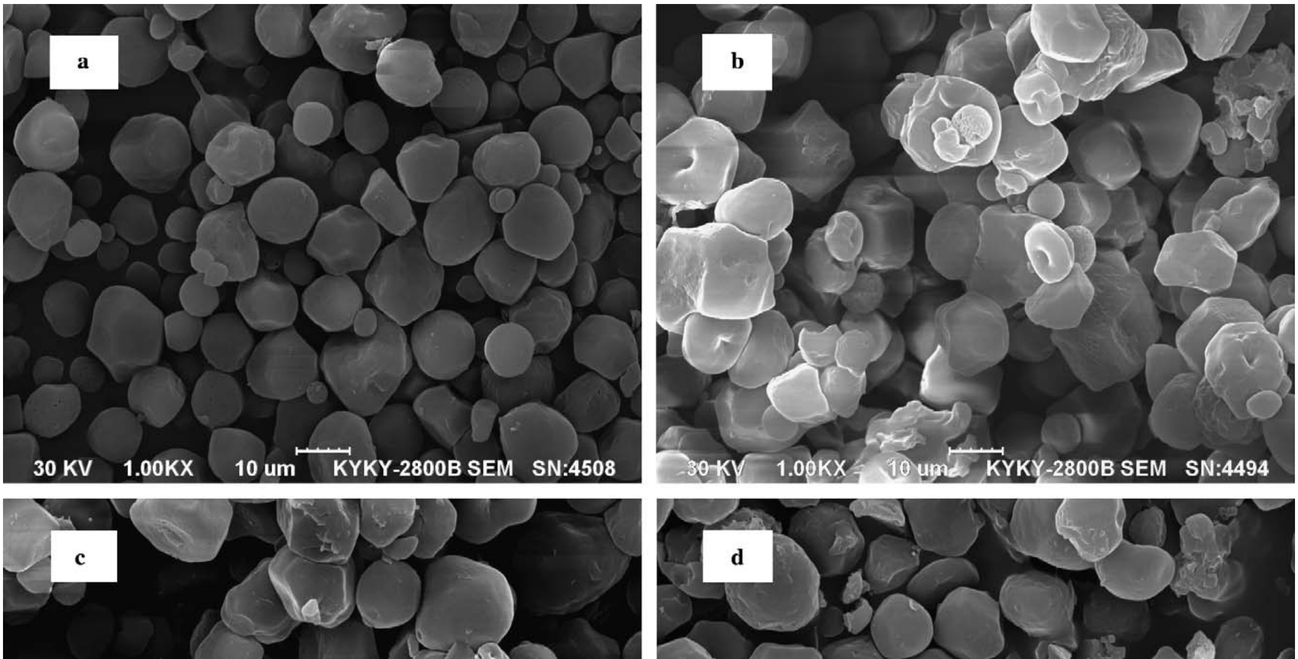


Fig. 2. SEM pictures of different starch granules (a, native starch; b, CCSM1; c, CCSM2; d, CCSM3).

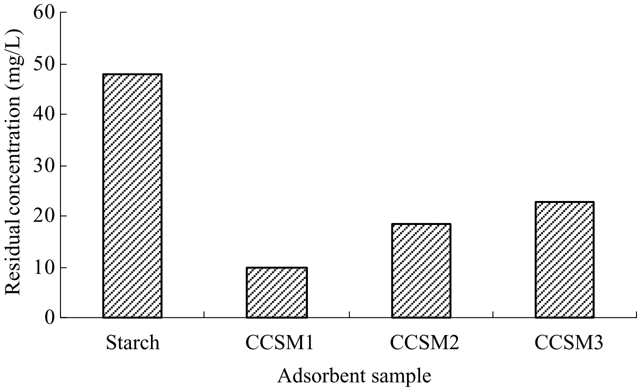


Fig. 3. Effect of different adsorbent sample on the residual concentration of chromium(VI) solution. (the dose of starch and all CCSM are 60 mg; $T = 15$ °C, pH 4, [Cr(VI)] = 50 mg/L, time = 20 min).

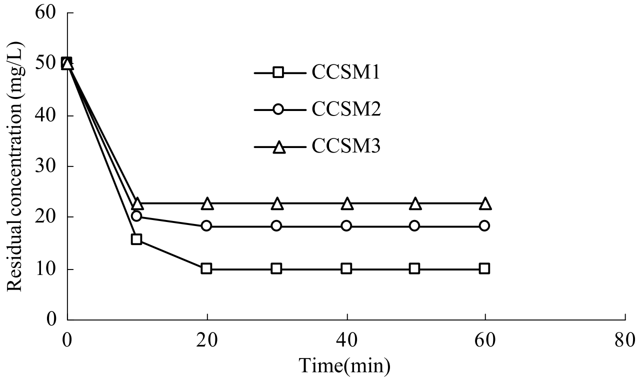


Fig. 4. Time influence on the residual concentration of Cr(VI) (the dose of all CCSM are 60 mg; $T = 15$ °C, pH 4, [Cr(VI)] = 50 mg/L).

quaternary ammonium groups in CCSM absorb chromium(VI) by electrostatic attraction and anionic maleic groups prevented the adsorption of Cr(VI) onto CCSM. The higher DS of anionic group is, the stronger the repulsive force is between CCSM and chromium(VI).

3.5. *Effect of solution pH on the residual concentration of Cr(VI) solution*

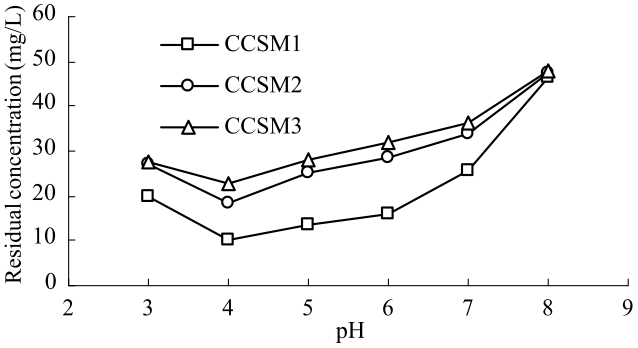


Fig. 5. Solution initial pH influence on residual concentration of the Cr(VI) solution (the dose of all CCSM are 60 mg; $T = 15$ °C, time = 20 min, [Cr(VI)] = 50 mg/L).

Fig. 5 shows influence of the initial pH values raging from 3.0 to 8.0 on the residual concentration of Cr(VI) between 50 mg CCSM sample and 50 mL of 50 mg/L Cr(VI) solution. The adsorption temperature is 15 °C and the time is 20 min. The residual concentration of Cr(VI) solution decreases with increasing pH from 3.0 to 4.0 and reach a minimum, then increases from pH 4.0 to 8.0. This indicated that the initial pH value of the solution affects the adsorption between Cr(VI) and CCSM. When pH value of the solution is 3, the sum of quaternary ammonium groups in CCSM decreases a little because of hydrolyzation of CCSM. So the residual concentration of Cr(VI) decreases with increasing pH from 3.0 to 4.0. With the pH value increasing from 4.0 to 8.0, the residual concentration of Cr(VI) gradually increases. It was explained that the sum of maleic groups existing in the form of COO^- increased when pH values of Cr(VI) solution increased, so the repulsive effect between CCSM and Cr(VI) got stronger. Moreover, the following reaction occurs in aqueous solution:

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$$

When pH values of Cr(VI) solution increased, the amount of CrO_4^{2-} groups in aqueous solution tended to increase. The sum of active sites is fixed, and electrostatic attraction is main effect between CCSM and Cr(VI). The adsorption capacity for $Cr_2O_7^{2-}$ is stronger than that for CrO_4^{2-} on CCSM. So the optimal pH condition for the adsorption of Cr(VI) is about 4.0.

3.6. *Effect of the dose of CCSM on the residual concentration of Cr(VI)*

As shown in Fig. 6, the residual concentration of Cr(VI) gradually decreases when the dose of CCSM increases from 20 to 60 mg. When the dose is over 60 mg, the trend becomes weak. The reason is that when the dose increases there is a stronger interaction between maleic anionic groups of CCSM and Cr(VI), even among CCSM molecules, some active sites would be unoccupied or be

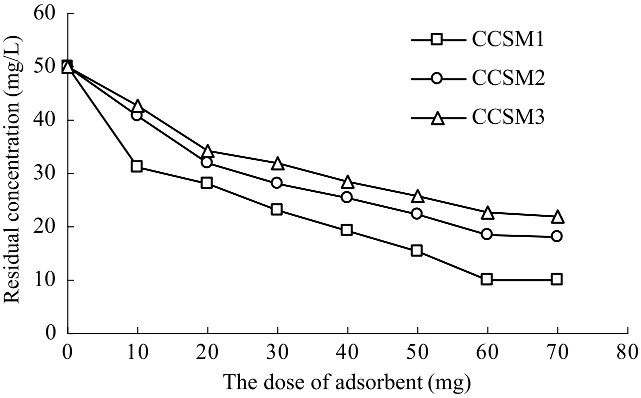


Fig. 6. The dose of CCSM influence on the residual concentration Cr (VI) solution ($T = 15$ °C, pH 4, [Cr(VI)] = 50 mg/L, pH 4, time = 20 min).

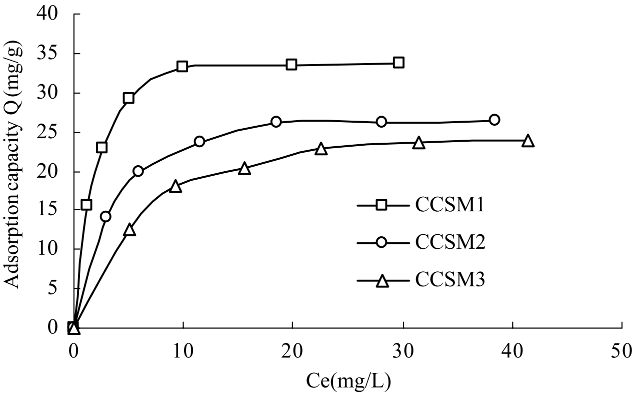


Fig. 7. Langmuir adsorption isotherm of Cr(VI) on the CCSM.

occupied by the other anionic groups. Thus we selected a dose of 60 mg as an optimal dose.

3.7. Adsorption isotherms of Cr(VI)

Adsorption isotherms of Cr(VI) on the CCSM are shown in Fig. 7. The experiments were conducted using 50 mL of Cr(VI) aqueous solution where concentrations were ranging from 20 to 70 mg/L, and 60 mg of CCSM was employed at initial pH 4.0 and adsorption temperature 15 °C, and adsorption time is 20 min. The adsorption capacity of CCSM increases slightly when the initial concentration of Cr(VI) is over 50 mg/L (i.e., equilibrium concentration of CCSM1, CCSM2, and CCSM3 is 10, 18.6, and 22.6 mg/L, respectively). So we selected the initial concentration of 50 mg/L as the test condition for experimental study. The Cr(VI) adsorption isotherms of CCSM fit well the Langmuir model. The Langmuir model is expressed as

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

where C_e is equilibrium concentration of the metal ion in aqueous solution (mg/L), Q is adsorption capacity (mg/g), Q_0 is the maximum adsorption capacity (mg/g), and b is Langmuir constant (L/mg). The adsorption parameters for CCSM1, CCSM2, and CCSM3 are listed in Table 1. These results indicate that CCSM1 has a higher adsorption capacity compared to CCSM2, while the adsorption capacity of CCSM2 is greater than that of CCSM3. This is because higher DS of anionic group leads to lower adsorption. The Langmuir constant b decreases in the order CCSM1 > CCSM2 > CCSM3. The larger the constant b is, the higher the adsorption energy is, which is reflected by a fast increase in adsorption at low Cr(VI) concentration.

Table 1
Parameters of the Langmuir equation

Adsorbent	Q_0 (mg/g)	b (L/g)	R^2
CCSM1	35.71	0.67	0.9973
CCSM2	28.09	0.44	0.9981
CCSM3	27.10	0.20	0.9975

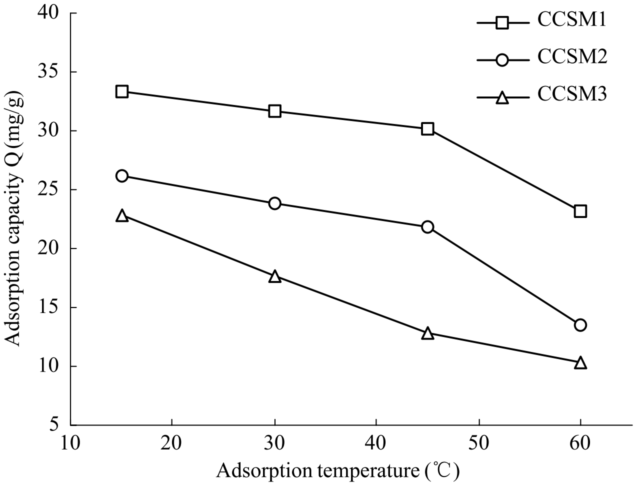


Fig. 8. Effect of temperature on the Cr(VI) adsorption capacity (the dose of all CCSM are 60 mg; time = 20 min, pH 4, [Cr(VI)] = 50 mg/L).

3.8. Thermodynamic studies

Effect of temperature on the Cr(VI) adsorption capacity is shown in Fig. 8. The Cr(VI) adsorption capacity with various temperatures (15–60°C) were determined when initial solution concentration and pH were 50 mg/L and 4.0, respectively, and the dose of all CCSM is 60 mg. The results show that the adsorption capacity decreases with increasing temperature, which implies that the adsorption process is exothermic. For verification of the conclusion, the curves of $\log(Q/C_e)$ versus $1/T$ for CCSM1, CCSM2, and CCSM3 were shown in Fig. 9. ΔH^θ and ΔS^θ were calculated according to the following equation:

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

The change of adsorption free energy (ΔG^θ) was calculated from the thermodynamic equation:

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta.$$

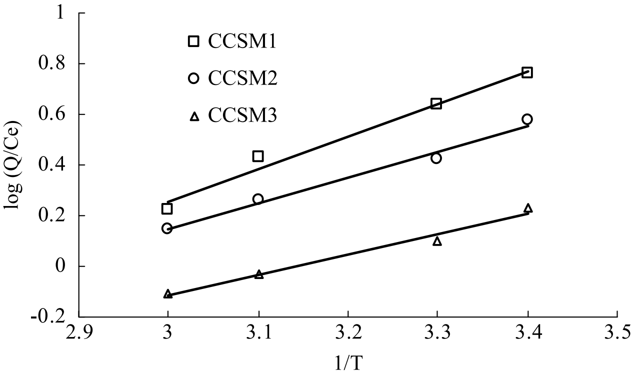


Fig. 9. Plot of $1/T \times 10^3$ versus $\log(Q/C_e)$ for CCSM.

Table 2
Thermodynamic values at various temperature for CCSM1, CCSM2, and CCSM3

Temperature (°C)	Q (mg/g)	ΔG^{θ} (kJ/mol)	ΔH^{θ} (kJ/mol)	ΔS^{θ} (J/K/mol^{-1})
CCSM1				
15	33.6	−16.3	−24.7	−30.1
30	32.5	−15.6		
45	30.1	−15.1		
60	23.2	−14.7		
CCSM2				
15	26.3	−12.5	−19.5	−24.2
30	23.8	−12.2		
45	21.9	−11.8		
60	15.3	−11.4		
CCSM3				
15	22.8	−9.4	−15.5	−21.2
30	17.6	−9.1		
45	12.9	−8.8		
60	10.4	−8.4		

The values of ΔH^{θ}, ΔS^{θ}, and ΔG^{θ} are listed in Table 2. The negative value of ΔH^{θ} indicates that the adsorption process is exothermic and low temperature makes the adsorption easy. The adsorption process of CCSM3 is more dependent on temperature than those of CCSM1 and CCSM2. Moreover, the negative values of ΔS^{θ} and ΔG^{θ} demonstrated a decrease in adsorption energy and an increase in the feasibility of adsorption process at lower temperature.

4. Conclusion

The adsorption between Cr(VI) ion and crosslinked cationic starch maleate (CCSM) with quaternary ammonium was investigated. The results demonstrated that crosslinked cationic starch maleate (CCSM) with a low degree of substitution (DS < 0.2) can be effective for the Cr(VI) removal. The adsorption process is dependent on the initial pH of solution, the dose of adsorbents and the adsorption temperature. The adsorption process fits well the langmuir isotherm. The maximum adsorption capacity decreases with the increasing DS of the maleic anionic group in CCSMs, and reaches 35.71, 28.09, and 27.10 mg/g, respectively, for CCSM1, CCSM2, and CCSM3 (50 mg/L initial concentration). The adsorption processes are exothermic, the apparent enthalpies (ΔH^{θ}) are −24.7, −19.5l, and −15.5 kJ/mol for CCSM1, CCSM2, and CCSM3, respectively. Moreover, the negative values of ΔG^{θ} indicated that the feasibility of adsorption increases at low temperature.

Acknowledgment

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