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# Adsorption of Cr(VI) from aqueous solution by crosslinked cationic konjac glucomannan with different degree of substitution

# Adsorption of Cr(VI) from aqueous solution by crosslinked cationic konjac glucomannan with different degree of substitution

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**Abstract.** Chromium has numerous industrial applications, such as metallurgy, processing of leather, producing chromic acid, acting as catalyst and electroplating. These activities cause Cr(VI) contamination in air, soil and water resources. Developing efficient and cost- effective adsorbents for removing Cr(VI) is of utmost importance. Crosslinked cationic konjac glucomannan (CCKGM) with different degrees of substitution (DS) 0.226, 0.391 and 0.456, were prepared by reaction of 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride, konjac glucomannan (KGM) and epichlorohydrin and used to adsorb Cr(VI) ions from the aqueous solutions. Then the adsorption behaviour of CCKGM to Cr (VI) was explored. The adsorption effect of CCKGM on Cr(VI) is affected by pH, Cr(VI) initial concentration, adsorbent dose and temperature. With the increase of DS, adsorption capacity increased. The adsorption capacity was 31.52 mg/g, 58.82 mg/g and 62.59 mg/g corresponding to DS 0.226, 0.391 and 0.456, respectively. Adsorption can get equilibrium within several minutes and follows Langmuir isothermal adsorption. The process is exothermal and low temperature is favourable for adsorption. CCKGM has potential to be used as adsorbents for Cr (VI).

## 1. Introduction

Environmental pollution caused by toxic heavy metal in industrial effluents is one of the most pressing problems in the world. 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 use, such as electroplating, metal finishing, leather tanning, pigments etc. Chromium(VI) compounds are known to be 1000 times more toxic than chromium(III) and cause allergy,skin ulveration and damage to the liver, kidneys and blood cells.

Strict legislation on the discharge of these toxic products makes it necessary to develop various efficient technologies for the removal of pollutants from wastewater [1]. Different technologies and processes are currently used. Biological treatments [2], membrane processes [3], advanced oxidation processes [4], chemical and electrochemical techniques [5, 6] and adsorption procedures [7-9] are the most widely used for removing metals from industrial effluents. Among all the treatment propositions, adsorption is one of the most popular methods. It is now recognized as an effective, efficient and economic method for water decontamination application and separation analysis. Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Polysaccharides which are abundant, renewable and biodegradable resources are

able to associate by physical and chemical interaction [10,11]. So much attention was focused on chitin starch [12,13]. Crosslinked starch xanthate and carboxyl-containing starch derivatives had been used as effective adsorbents to remove heavy metal ions from wastewater. Xu reported the mass transport process for the adsorption of chromium(VI) onto crosslinked amphoteric starch [14].

Konjac glucomannan (KGM) is a high molecular weight water-soluble non-ionic polysaccharide found in tubers of the amorphophallus konjac. KGM is a linear random copolymer of β-(1,4) linked D-glucose and D-mannose in the molar ratio of 1:1.6 with a low degree of acetyl groups [15,16]. It is more attractive for industrial use owing to its renewability, biodegradability and economy. At present, many investigations related to KGM are focused on isolating and characterizing properties of solution and solid, it is mainly used in biochemical, medical and food fields [17-20].

Recently, the investigation of carboxymethyl KGM used to adsorb Cu2+, Pb2+ and Cd2+ ions from the aqueous solutions was carried out by our group, the results showed KGM modified by anion etherifying agent can be used as an high effective and fast metal ion adsorbent. But the researches on KGM modified by cationic etherifying agent and its adsorption of heavy metal ions, especially Cr(VI) ion, have not been reported so far.

The objective of this study was focused on the development of konjac glucomannan modified by 3-chloro-2-hydroxypropyl-trimethylammonium chloride(HAT) and epichlorohydrin (ECH) for removal of Cr(VI)ions. The effects of pH, adsorbent dose, initial concentration of Cr(VI), adsorption time and temperature on adsorption capacity were investigated. In order to provide a new method and theoretical evidences for waste-water treatment, the characterization of isothermal adsorption and adsorption thermodynamics were also studied.

## 2. Materials and methods

### 2.1. Reagents and instruments
KGM powder was obtained from Shiyan Huaxianzi Konjac Productions Co., Ltd. Hubei Province, China and dried at 60℃ in vacuum oven before used; HAT were provided by Dow Company Americas (aqueous solution with w(HAT)=69%), ECH and ethanol (analytical reagent grade) were obtained from Beijing Chemical Factory (Beijing, China). K2Cr2O7, NaOH, and other chemicals were of analytical reagents purchased from Beijing Chemical Factory (Beijing, China). US-VIS-NIR recording spectrophotometer (a model of UV-1700 made in Japan) was used to analyze the content of chromium(VI) in the aqueous solution.

### 2.2. Preparation of crosslinked cationic konjac glucomannan (CCKGM)
10g KGM was dispersed in 30 mL isopropyl alcohol and increased temperature to 40℃ and kept constant, 15g NaOH solution (45wt.% in mass basis) was added slowly while stirring and certain amount of ECH was then added gradually at 40℃. After 1.0 h, the temperature was increased to 50℃, the defined HAT was dropped, and mechanical stirring was continued for 1.5 h at 50℃. The mixture was then allowed to cool, neutralized with hydrochloric acid, washed with 50 wt% alcohol to remove impurities, filtered and dried. The nitrogen content and the DS of quaternary ammonium cationic groups in the CCKGM were analyzed using element analysis (German elementar strucment). The degree of substitution (DS) and reaction yield (R) were calculated according to equations (1) and (2).

$$DS = \frac{162.15 \times W(N)}{1401 - 151.64 \times W(N)} \tag{1}$$

$$R = \frac{DS_{\text{test}}}{DS_{\text{theory}}} \times 100\% \tag{2}$$

During the experiment, only changing the content of cationic etherifying agent, three kinds of CCKGM with different DS were prepared and named CCKGM1, CCKMG2 and CCKGM3.

The preparation route was shown as Fig.1 and the preparation conditions and reaction results were shown in Tab. 1.
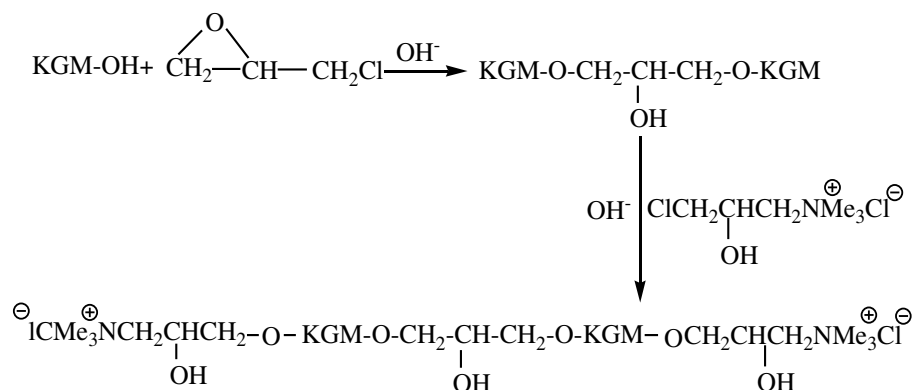


**Figure 1.** Preparation scheme of CCKGM

**Table 1.** Reaction conditions and reaction results of KGM with HAT.

| Sample | T (°C) | Time (h) | n(KGM):n(HAT) :n(NaOH):n(ECH) | DS | R (%) |
|--------|--------|----------|-------------------------------|-------|-------|
| CCKGM1 | 50 | 1.5 | 1:0.8:1.5:1 | 0.226 | 28.3 |
| CCKGM2 | 50 | 1.5 | 1:1.3:1.5:1 | 0.391 | 30.1 |
| CCKGM3 | 50 | 1.5 | 1:1.0:1.5:1 | 0.456 | 45.6 |

*2.3. Adsorption procedure*

The adsorption experiments in this study were carried out according to the reference [14]. 50 mL of dichromate aqueous solution with desired concentration and the desired dose of CCKGM were placed in a series of comparison tubes in a thermostat water bath. Initial pH was adjusted with dilute HCl and 0.2 N NaOH aqueous solution. After shaken for the definite time, the tubes were removed and the concentration of Cr(VI) in the aqueous solution after the adsorption was analyzed by US-VIS-NIR recording spectrophotometer. The adsorption capacity of Cr(VI) on CCKGM was calculated by the equation (3).

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

(3)

where C0 and Ct are the concentrations of Cr (VI) ions before and after adsorption respectively (mg/L); V is the total volume of the aqueous solution (L); and m is the dry weight of CCKGM (g).

## 3. Results and discussion

*3.1. Comparison between native KGM and CCKGM in chromium(VI) adsorption*

Native KGM itself appeared to adsorb minor amounts of chromium(VI) ions. As shown in Fig.2, adsorption capacity of native KGM was much lower in comparison with CCKGM. Adsorption capacity of native KGM was only 1.7 mg/g, while those of CCKGM1, CCKGM2, and CCKGM3 were 31.52 mg/g, 58.82 mg/g and 62.59 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 KGM while strong electrostatic attraction would be the characteristics for the ion-adsorption of CCKGM.
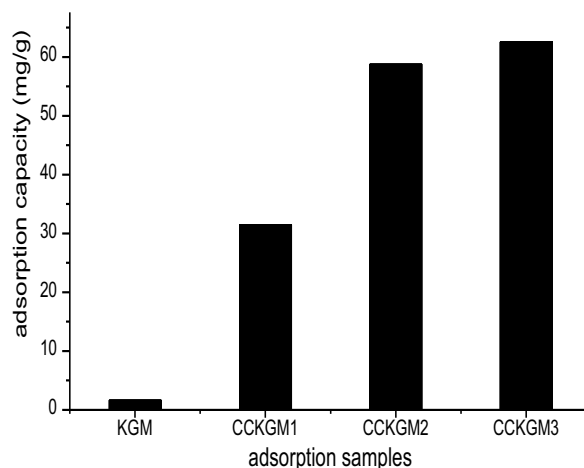
**Figure 2.** Effect of different adsorbent samples on the residual concentration of chromium(VI) solution (the dose of KGM and all CCKGM are 60mg; T =20 ℃, pH=4, [Cr(VI)]=50mg/L, t=20min).

*3.2. Isotherm adsorption*
The Langmuir isotherm data together with the Freundlich data are often used to investigate adsorption behavior of heavy metal ions on polysaccharide. The Langmuir model is expressed as

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b}$$

(4)

where Ce is equilibrium concentration of the metal ion in aqueous solution (mg/L), Qe is adsorption capacity (mg/g), Qm is the maximum adsorption capacity (mg/g), and b is Langmuir constant (L/mg).

From the correlation coefficients listed in Tab.2, we could draw the conclusion that the adsorption of Cr (VI) ions onto CCKGM was well followed as Langmuir isotherm equation under the concentration range studied. It indicated the monolayer coverage of CCKGM by the ions, and all the adsorption sites supplied nearly same action to metal ions. This could reflect indirectly that ligand ion exchange was predominant in the adsorption process. A higher DS value of the cationic group led to a higher Qm and b, it corresponded to the above-mentioned conclusion that a higher DS resulted in a higher adsorption capacity.

**Table 2.** Langmuir parameters for CCKGM1, CCKGM2 and CCKGM3

|          | Qm(mg/g) | b(L/g) | R*     |
|----------|----------|--------|--------|
| CCKGM1   | 41.84    | 0.084  | 0.9892 |
| CCKGM2   | 67.79    | 0.442  | 0.9941 |
| CCKGM3   | 77.38    | 1.615  | 0.9922 |

Note: R * is the correlation coefficient of Langmuir isothermal adsorption plots.
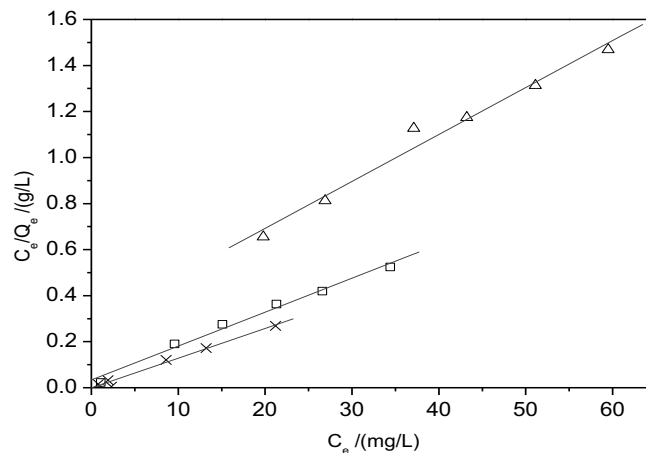
**Figure 3.** Langmuir adsorption isotherm for CCKGM1, CCKGM2 and CCKGM3: (△)CCKGM1; (□)CCKGM2; (X) CCKGM3 (pH=3.78; t=1 h; T=20 °C; the dose of CCKGM1, CCKGM2, CCKGM3 each was 50 mg).

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, RL, which is used to predict if an adsorption system is "favorable" or "unfavorable". The separation factor, RL is defined by:

$$R_L = \frac{1}{1 + bC_0}$$
(5)

where C0 is the initial concentration of metal ions (mg/L), and b is the Langmuir adsorption equilibrium constant (mL/mg). Because b values were all beyond zero, RL values were in the range 0＜RL＜1, which indicated that the adsorption of Cr (VI) ions of CCKGM was favorable. Thus, CCKGM was favorable adsorbent for Cr (VI) ions.

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

Fig.4 showed that the time profiles of residual concentration of chromium(VI) changed with the initial concentration of 60 mg/L. It was clear that time had evident influence on the residual concentration of chromium(VI) solution within 20 min. However, the decrease in the residual concentration of chromium(VI) solution was very small beyond 20 min and was independent of DS. In process application, the rapid adsorption phenomenon was an advantage because short adsorption time could directly affect operation cost.
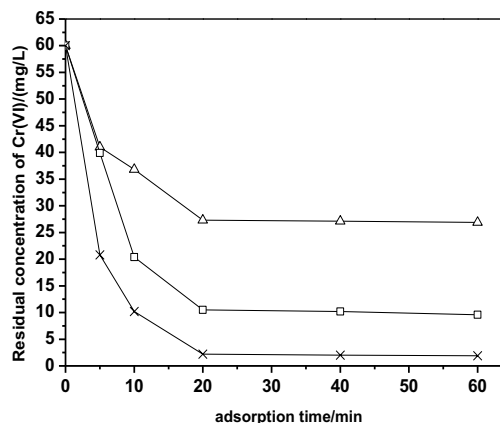


**Figure 4.** Effect of adsorption time on residual concentration of Cr(VI) (△)CCKGM1; (□)CCKGM2; (×)CCKGM3 (pH=3.78; T=20 °C; the dose of CCKGM1, CCKGM2, CCKGM3 each was 50 mg; the initial concentration of Cr(VI) was 60 mg/L).

*3.4. Effect of adsorbent dose*

Fig.5 showed the effect of adsorbent dose on adsorption capacity under the condition of pH=3.78, C0=100 mg/L and t=60 min. The adsorption capacity of Cr(VI) adsorbed by different CCKGM followed the same trend, that is, adsorption capacity decreased with increasing of CCKGM dose in the range of 30 mg to 80 mg, which is contrary to the theory analysis. The reason was the quantity of Cr(VI) ions around activity sites of the single adsorbent decreased as the concentration of Cr(VI) kept constant, namely, the contact chance of CCKGM active site with Cr(VI) ion decreased. Because adsorption capacity is defined as the metal ion mass (mg) adsorbed by per gram adsorbent, so adsorption capacity decreased. As far as improving Q was concerned, increasing the DS of the absorbents was more effective and economical than increasing the absorbents dose.
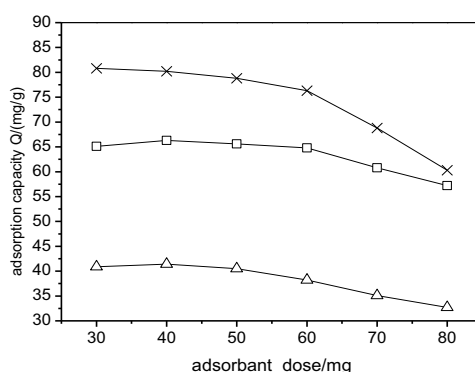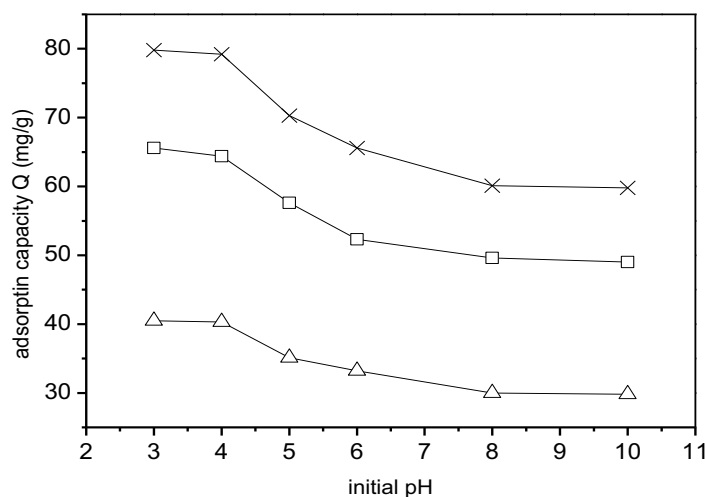


**Figure 5.** Effect of dose on adsorption capacity for CCKGM1,CCKGM2 and CCKGM3:($\triangle$) CCKGM1; ($\square$)CCKGM2; ($\times$) CCKGM3 (pH=3.78, t=1 h, T =20 ℃); the initial concentration of Cr(VI) was 100 mg/L.

*3.5. Effect of pH on the adsorption*

Metal-ion adsorption was known to be dependent on the pH of solution (see Fig.6). The adsorption capacity changed little with pH from 3.0 to 4.0, while decreased significantly as the pH increased from 4 to 10, because of the reaction of equation (6) in the aqueous solution.

$$Cr_2O_7^{2-}+2OH^- \rightleftharpoons 2CrO_4^{2-}+H_2O \tag{6}$$
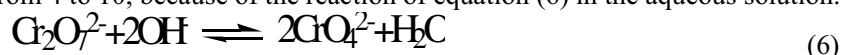
In acid media, Cr2O72- is the main form, the amount of $CrO_4^{2-}$ groups in aqueous solution tended to increase when pH values of Cr(VI) solution increased and $CrO_4^{2-}$ is the main form. The sum of active sites was fixed, and electrostatic attraction was the main effect between CCKGM and Cr(VI). The adsorption capacity for Cr2O72- was stronger than that for $CrO_4^{2-}$ on CCSM. So the optimal pH condition for the adsorption of Cr(VI) was about 4.0.

**Figure 6.**   Effect of initial pH of solution on adsorption capacity for CCKGM1, CCKGM2 and CCKGM3:(△) CCKGM1;(□) CCKGM2; (×) CCKGM3 ( t=1 h; T=20℃; the dose of CCKGM1, CCKGM2, CCKGM3 each was 50 mg; the initial concentration of Cr(VI) was 100 mg/L)

### 3.6. Effect of the Cr(VI) initial concentration

In general, the concentration of Cr(VI) in industry wastewater is lower than 100 mg/L. So the effect of Cr(VI) initial concentration in the range 50~100 mg/L on adsorption capacity were studied under the condition of T=20℃, pH=3.78, m=50 mg/L and t=60 min. The results showed in Fig.7 indicated that the adsorption capacity was directly influenced by Cr(VI) initial concentration and increased with Cr(VI) initial concentration. As the initial concentration was 100 mg/L, the adsorption capacity of three kinds of CCKGM was respectively 40.5 mg/g, 65.6 mg/g and 78.8 mg/g, higher than 30.2 mg/g, 49.2 mg/g and 48.9 mg/g with the initial concentration 50 mg/L. The active sites in CCKGM were more than Cr(VI) with the low Cr(VI) concentration. While as the concentration was high, there were enough Cr(VI) contacted with CCKGM active sites, which resulted in adsorption capacity high, but the proportion of Cr(VI) unabsorbed increased.
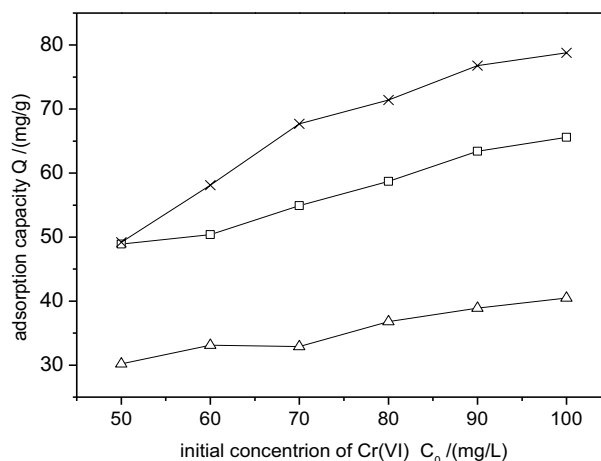


**Figure 7.**   Effect of initial concentration of Cr(VI) on adsorption capacity for CCKGM1, CCKGM2 and CCKGM3(△) CCKGM1; (□)CCKGM2; (×) CCKGM3 (pH=3.78; t=1 h; T=20 ℃; the dose of CCKGM1, CCKGM2, CCKGM3 each was 50 mg).

### 3.7. Thermodynamic studies

Effect of temperature on the Cr(VI) adsorption capacity is shown in Fig.8. The Cr(VI) adsorption capacities with various temperatures (20–60°C) were determined when initial solution concentration and pH were 60 mg/L and 3.78, respectively, and the dose of each CCKGM was 50 mg. The results showed that the adsorption capacity decreased with increasing temperature, which implied that the adsorption process was exothermic. For verification of the conclusion, the curves of log (Q/Ce) versus 1/T for CCSM1, CCSM2, and CCSM3 were shown in Fig.9. the results of ΔH and ΔS calculated according to the equation(7) and ΔG according to the equation (8) were listed in Tab.3.
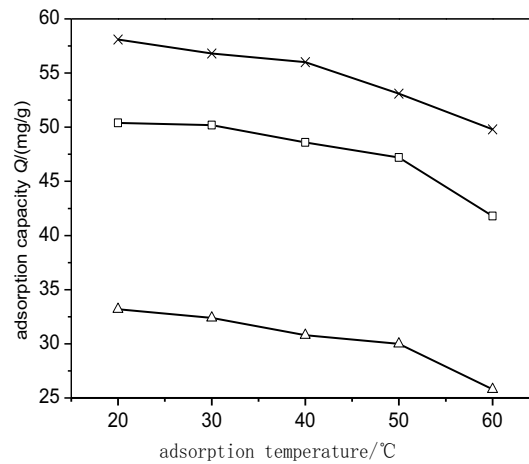
**Figure 8.** Effect of temperature on adsorption capacity. (△)CCKGM1; (□)CCKGM2; (×)CCKGM3

$$\lg(\frac{Q}{C_e}) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

(7)

$$\Delta G = \Delta H - T\Delta S$$

(8)

The negative value of ΔH indicated that the adsorption process was exothermic and low temperature made the adsorption easy. Moreover, the negative values of ΔS and ΔG demonstrated a decrease in adsorption energy and an increase in the feasibility of adsorption process at lower temperature.
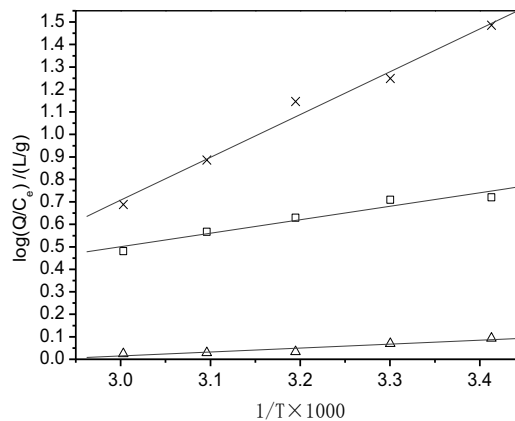


**Figure 9.** Plot of 1/T×103 versus log(Q/Ce) for (△)CCKGM1; (□)CCKGM2; (×)CCKGM3 (pH=3.78; t=1 h; the initial concentration of Cr(VI) was 60 mg/L; the dose of CCKGM1, CCKGM2, CCKGM3 each was 50 mg).

**Table 3.** Results of entropy ($\triangle S$), free energy ($\triangle G$) and enthalpy ($\triangle H$) of three kinds of CCKGM

| sample | T (°C) | Q (mg/g) | $\triangle G$ (kJ/mol) | $\triangle H$ (kJ/mol) | $\triangle S$ (J/mol) |
|--------|--------|----------|-----------|-----------|-----------|
| CCKGM1 | 20 | 33.2 | -0.212 | -1.46 | -4.26 |
|        | 30 | 32.4 | -0.169 |        |        |
|        | 40 | 30.8 | -0.127 |        |        |
|        | 50 | 30.0 | -0.084 |        |        |
|        | 60 | 25.4 | -0.041 |        |        |
| CCKGM2 | 20 | 50.4 | -1.827 | -5.00 | -10.83 |
|        | 30 | 50.2 | -1.719 |        |        |
|        | 40 | 48.6 | -1.610 |        |        |
|        | 50 | 47.2 | -1.502 |        |        |
|        | 60 | 41.8 | -1.394 |        |        |
| CCKGM3 | 20 | 58.1 | -3.642 | -15.84 | -41.63 |
|        | 30 | 56.8 | -3.226 |        |        |
|        | 40 | 56.0 | -2.810 |        |        |
|        | 50 | 53.1 | -2.394 |        |        |
|        | 60 | 49.8 | -1.977 |        |        |

## 4. Conclusion

Cationic konjac glucomannan could effectively remove Cr(VI) ions from water solutions. Adsorption capacity was affected by solution pH, initial concentration of metal ions, adsorbent dose and DS of cationic group. The adsorption capacity increased with DS and the value was respectively 31.52 mg/g, 58.82 mg/g and 62.59 mg/g corresponding to the DS 0.226,0.391 and 0.456. The adsorption process could be finished within several minutes and followed Langmuir isothermal adsorption under the concentration range studied. The process was exothermal and low temperature was favorable for adsorption. CCKGM had potential to be used as absorbent for Cr (VI).

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