α-Ketoglutaric Acid-Modified Chitosan Resin as Sorbent for Enhancing Methylene Blue Removal from Aqueous Solutions

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ABSTRACT: In this study, cross linked chitosan resin (CCR) was prepared by cross linking chitosan with glutaraldehyde, and then α-ketoglutaric acid-modified chitosan resin (KCR) was obtained by modifying CCR with α-ketoglutaric acid. The sorption behavior of methylene blue (MB) on KCR and CCR from aqueous solution was investigated. The effect of various experimental parameters (e.g. initial pH, sorbent dose, dye concentration, contact time, and temperature) was examined. The maximal MB sorption ratio on KCR and CCR was respectively reached beyond pH 8 and at pH 8. The MB removal ratio on KCR and CCR increased with increasing sorbent dose but decreased with increasing dye concentration. The isothermal data of MB sorbed on KCR and CCR followed the Langmuir model. The MB sorption process could be described by the pseudo-second-order kinetic model. The thermodynamic study indicated that the MB sorption process was spontaneous and exothermic.

Key words: Methylene blue, Sorption, α-Ketoglutaric acid-modified chitosan resin, Kinetics, Thermodynamics

INTRODUCTION

Dyes represent an important group of water pollutants which appear in the effluents discharged from textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and foodstuff industries. Dye wastewater discharge into environmental water bodies deteriorates the water quality, and may cause a significant impact on human health due to mutagenic, teratogenic or carcinogenic effects of some dyes or their metabolites (Gregory *et al.,* 1991; McKay *et al.,* 1985). Due to water resource shortage and socio-economic development, China is facing serious problems of water supply and water pollution. A few biological (Michniewicz *et al.,* 2008; Shaw *et al.,* 2002), physical (Ciardelli *et al.,* 2000; Hassani *et al.,* 2008; Hu *et al.,* 2005), and chemical methods (He, 2008; Koch *et al.,* 2002; Qiu *et al.,* 2005; Shen *et al.,* 2006) have been employed for dye wastewater treatment. In all these methods, the sorption has been found to be economical and effective dye wastewater treatment technology as it can remove various dyes with lower treatment cost. Interaction of the dye molecules with the sorbent can be result from covalent, columbic, hydrogen bonding or weak van der Waals forces (Jayswal and Chudasama, 2007). Chitosan, produced commercially by deacetylation of chitin, is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine. The reactive amino group in chitosan can provide easy derivatization of this polysaccharide with some functional reagents for wider application. Recently, chitosan (Wong *et al.,* 2008) or its derivatives had been used as sorbents for removing dyes from aqueous solution, These chitosan derivatives included chitosans-higher fatty acid glycidyl (Shimizu *et al.,* 2005), *N,O*-carboxymethyl-chitosan (Wang and Wang, 2008), cross linked quaternary chitosan (Rosa *et al.,* 2008), poly(methylmethacrylate) grafted chitosan (Singh *et al.,* 2009), chitosan-

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ethylene glycol diglycidyl ether (Azlan *et al.,* 2009), poly(methacrylic acid)-modified chitosan (Xing *et al.,* 2009), cetyl trimethyl ammonium bromide modified chitosan (Chatterjee *et al.,* 2009), poly(acrylamide) grafted chitosan, and poly(acrylic acid) grafted chitosan (Kyzas and Lazaridis, 2009).

In the present work, chitosan was cross linked with glutaraldehyde and subsequently treated with α-ketoglutaric acid to form Schiff's base. Lastly, Schiff's base was reduced to produce α-ketoglutaric acid-modified chitosan resin (KCR). The comparative study with KCR and cross linked chitosan resin (CCR) as sorbents for removal of methylene blue (MB) from aqueous solution was conducted in a batch system.

MATERIALS & METHODS

Chitosan (MW: 8×10^4, degree of deacetylation: 85%) was purchased from Koyo Chemical Co. Ltd., Japan. MB (Sigma Chemical Co., St. Louis, MO, USA), a basic dye of phenothiazine type (C.I.No 52015, FW= 373.9, λ_{max} = 670 nm) in highest grade available, was used without further purification. The standard dye stock solution was prepared by dissolving accurately weighted MB in distilled water to the concentration of 500 mg/L. All experimental solutions were obtained by diluting the dye stock solution in accurate proportions to different initial concentrations. All other chemicals were of analytical or biological grade.

The synthesis of KCR contained two steps, chitosan cross linked by glutaraldehyde and cross linked chitosan modified by α-ketoglutaric acid. In the first step, 300 ml of 2% (w/v) chitosan solution prepared with 1% (v/v) HCl solution was poured into 300 ml paraffin oil containing 1.0 ml Tween-80 with vigorous stir at ambient temperature. Thirty minutes later, 30 ml of 5% (v/v) glutaraldehyde solution and 6.0 g $CaCO_3$ powder were continuously added into the reaction system and stirred for 1 h at 40 °C. The reaction mixture was then adjusted to pH 10.0 with 10% (w/v) NaOH solution and stirred for 3 h at 60 °C. After that, the product was filtered by vacuum and washed continuously with petroleum ether and ethanol to remove paraffin oil and Tween-80. Then the product was poured into 400 ml of 0.2 mol/L

HCl to dissolve $CaCO_3$ and form pore network. Cross linked chitosan resin (CCR) was obtained by washing with de-ionized water to remove excessive HCl and dried in an infrared drier. In the second step, dry CCR was suspended in 150 ml of 6% (w/v) α-ketoglutaric acid solution, and then the pH of the solution was adjusted to 4.5-5.0 using sodium hydroxide solution and stirred for 1 h at 37 °C. Afterwards, sodium borohydride was added to the stirred mixture and the pH of the polymeric solution was adjusted to 6.5-7.0 using hydrochloric acid solution. The reaction system was further stirred for 24 h and reaction was terminated by 95% alcohol. The precipitated polymer was filtered, washed three to four times with ethanol and diethyl ether, respectively. KCR was dried in an infrared drier. The chemical principle of CCR and KCR synthesis was presented in Fig. 1.

Except for the experiments of sorption thermodynamics conducted at different temperature, other removal experiments were carried out in a rotary shaker at 150 rpm and ambient temperature using 250 ml shaking flasks containing 100 ml of desired concentrations and initial pH values of MB solution. The initial pH value of the solution was previously adjusted with diluted HNO_3 or NaOH using a pH meter. Different dose of KCR or CCR was respectively added to each flask, and then the flasks were covered with aluminum foil to avoid the photo degradation of MB and volume change of the solution during the experiments. After shaking the flasks for predetermined time intervals, the sample was separated by sedimentation/centrifugation and the residual concentration of MB in the supernatant solution was estimated by spectrophotometer. The MB sorption amount was calculated by the mass balance equation.

RESULTS & DISCUSSION

The influence of solution pH on MB sorption was shown in Fig. 2. The percentage of MB sorbed on CCR increased as the initial pH increased from pH 2 to pH 8 and then slightly decreased as the initial pH unceasingly increased from pH 8 to pH 10. But for KCR, the MB removal amount increased as initial pH increased from pH 2 to pH 8. Beyond pH 8, the maximal MB sorption ratio on KCR was reached and its
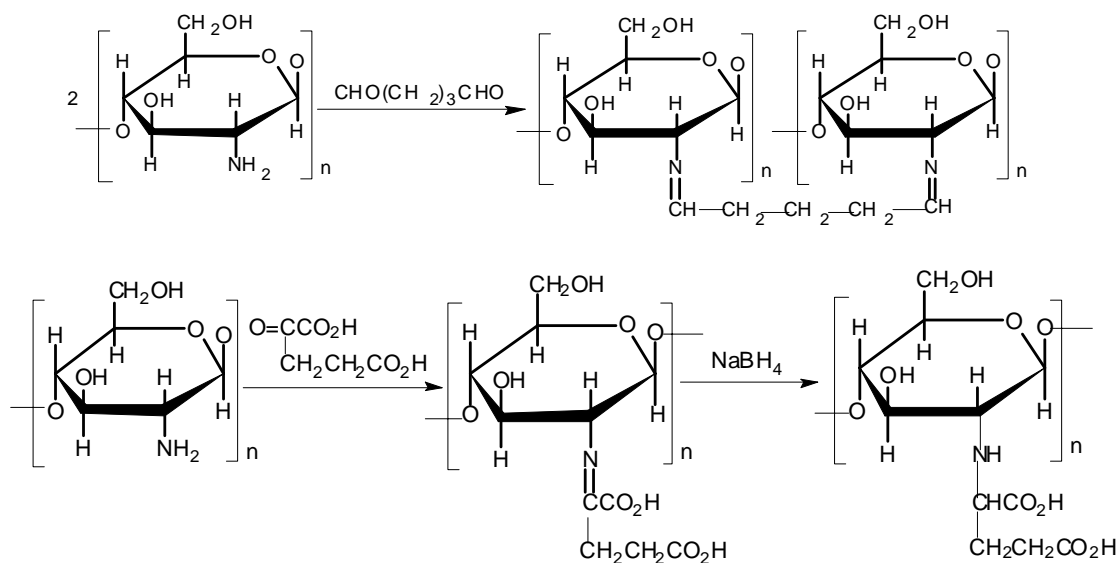
Fig. 1. Synthetic route of CCR (above) and KCR (below)

value only fluctuated between 98.41-99.43%. For these reasons, the pH 8 was selected for the other experiments. The effect of sorbent dose on the MB removal was presented in Fig. 3. Along with the sorbent dose increased from 1.0 to 6.0 g/L, the percentage of MB sorbed on CCR kept steady increase from 15.25 to 60.41%. But for KCR, the MB sorption amount increased as sorbent dose increased from 1.0 to 3.0 g/L. After that, the MB sorption ratio on KCR held almost no variety and its value only fluctuated between 98.41-99.90%. So, the sorbent dose of 3.0 g/L was chosen for the further experiments.
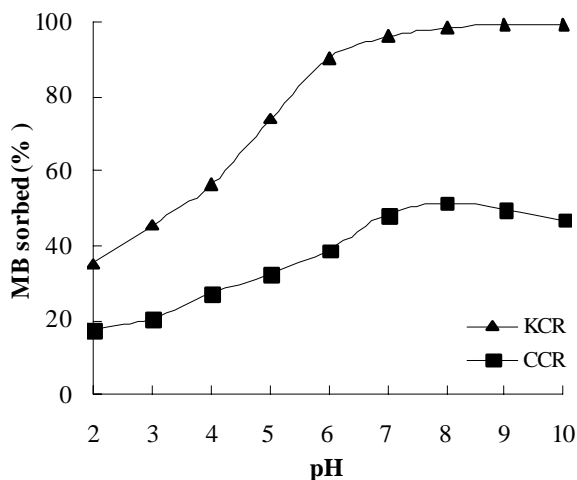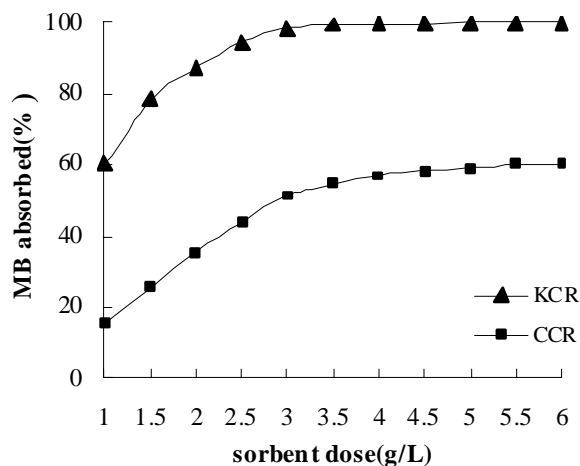

Fig. 3. The effect of sorbent dose on MB sorbed on KCR and CCR(MB concentration: 300 mg/L; contact time: 50 min; pH: 8)

The influence of dye concentration on the MB sorption was shown in Fig. 4. When the dye concentration was increased from 100 to 500 mg/L, the MB sorption percentage on CCR continuously decreased from 60.67 to 34.77%, but the MB sorption ratio on KCR kept basically unchangeable and fluctuated between 99.90-98.56% over a range from 100 to 300 mg/L of MB concentration. With further increase of dye concentration, the MB sorption percentage on KCR obviously decreased. With the data in Fig. 4. The Langmuir equation was employed to study the sorption isotherm of MB on KCR and CCR.
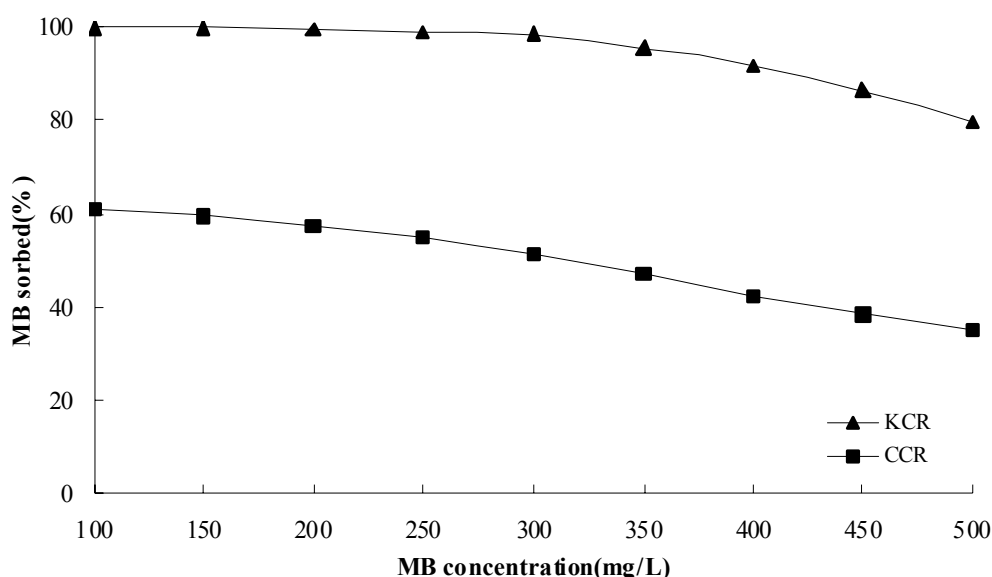

Fig. 2. The influence of initial pH on MB sorbed on KCR and CCR(MB concentration: 300 mg/L; sorbent dose: 3.0 g/L; contact time: 50 min)

Fig. 4. The influence of MB concentration on MB sorbed on KCR and CCR (sorbent dose: 3.0 g/L; contact time: 50 min; pH: 8)

The linear Langmuir equation was expressed as follows:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m \tag{1}$$

where C_e is the equilibrium concentration of the MB solution (mg/L), q_e is the amount of MB sorbed at equilibrium (mg/g), Q_m is the sorption capacity of sorbent and represents a practical sorption limitation when the sorbent surface is fully covered with monolayer sorbet molecules and a is Langmuir constant. The Q_m and a values can be calculated from the slope ($1/Q_m$) and intercept ($1/aQ_m$) of linear plot of C_e/q_e versus C_e. Based on the experimental data in Fig. 4, the Langmuir equations of MB on KCR and CCR were respectively described as:

$$C_e/q_e = 0.0075\ C_e + 0.01,\ R^2 = 0.9991 \tag{2}$$

$$C_e/q_e = 0.0131\ C_e + 1.1534,\ R^2 = 0.9829 \tag{3}$$

The effect of contact time on MB sorption was presented in Fig. 5. The MB sorption rate was very rapid at the initial stage of sorption. It was caused by the fast diffusion and sorption of dye molecule onto the external surface of sorbent. After a very rapid sorption, MB uptake rate slowly declined with lapse of time and reached equilibrium value at about 50 min. This process was controlled by the pore diffusion velocity of dye into the intra-particle matrix of sorbent.

The pseudo-second-order rate equation was used to study the kinetic model of MB sorption. The linear pseudo-second-order rate equation was expressed as follows:

$$t/q_t = 1/k_{ad}\ q_e^2 + t/q_e \tag{4}$$

where q_e and q_t refer to the MB sorption amount at equilibrium and time t (min), respectively (mg/g), and k_{ad} is the rate constant. Based on the experimental data in Fig. 5. the pseudo-second-order rate equations of MB sorbed on KCR and CCR were respectively described as:

$$t/q_t = 0.0095\ t + 0.032,\ R^2 = 0.9987 \tag{5}$$

$$t/q_t = 0.0182\ t + 0.0622,\ R^2 = 0.9957 \tag{6}$$

The excellent linear correlation coefficient showed that the experimental data in Fig. 5 conformed well to the pseudo-second-order rate kinetic model. The experimental results under different temperatures indicated that the MB sorption ratio on KCR and CCR decreased slightly along with increasing experimental temperature. The thermodynamic parameters were obtained from the following Van't Hoff and Gibbs-Helmholtz equations:

$$\ln (q_e/C_e) = -\triangle H^\circ /RT + \triangle S^\circ /R \tag{7}$$

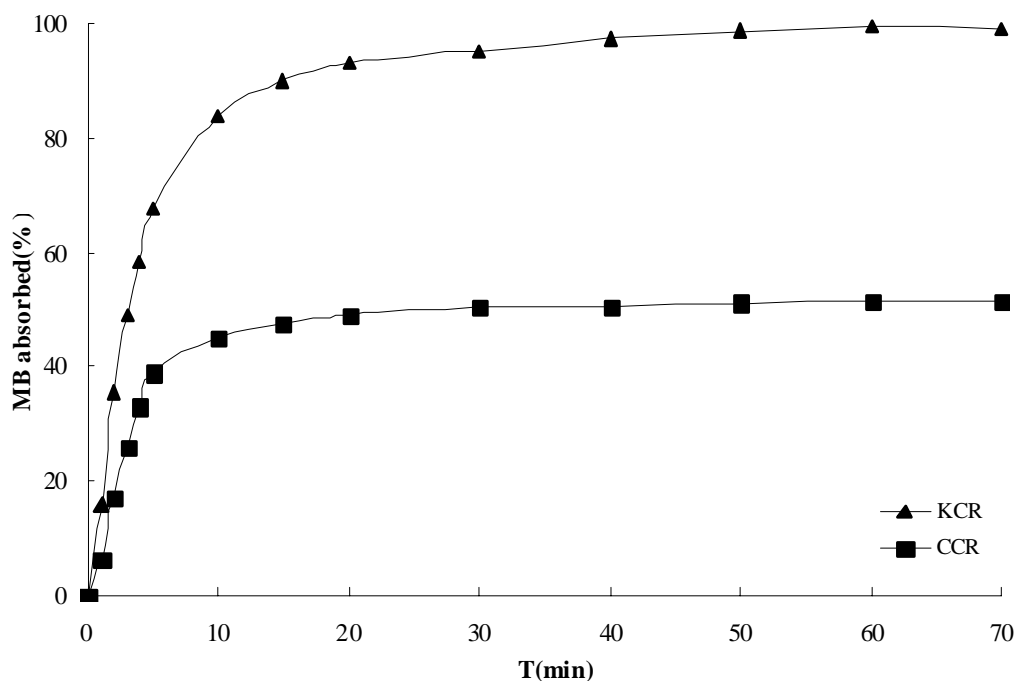$$\triangle G^\circ = \triangle H^\circ - T\triangle S^\circ \tag{8}$$

Fig. 5. The influence of contact time on MB sorbed on KCR and CCR (MB concentration: 300 mg/L; sorbent dose: 3.0 g/L; pH: 8)

Table 1. The thermodynamic parameters of MB sorbed on KCR and CCR

Sorbent	$\triangle H^{\circ}$ (kJ/moL)	$\triangle S^{\circ}$ (J/mol·K)	$\triangle G^{\circ}$ (kJ/moL)				
			293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
KCR	-28.99	-15.01	-24.59	-24.44	-24.29	-24.14	-23.99
CCR	-7.71	22.53	-14.31	-14.54	-14.77	-14.99	-15.22

$$\ln(qe/Ce) = 3486.7/T - 1.8049$$
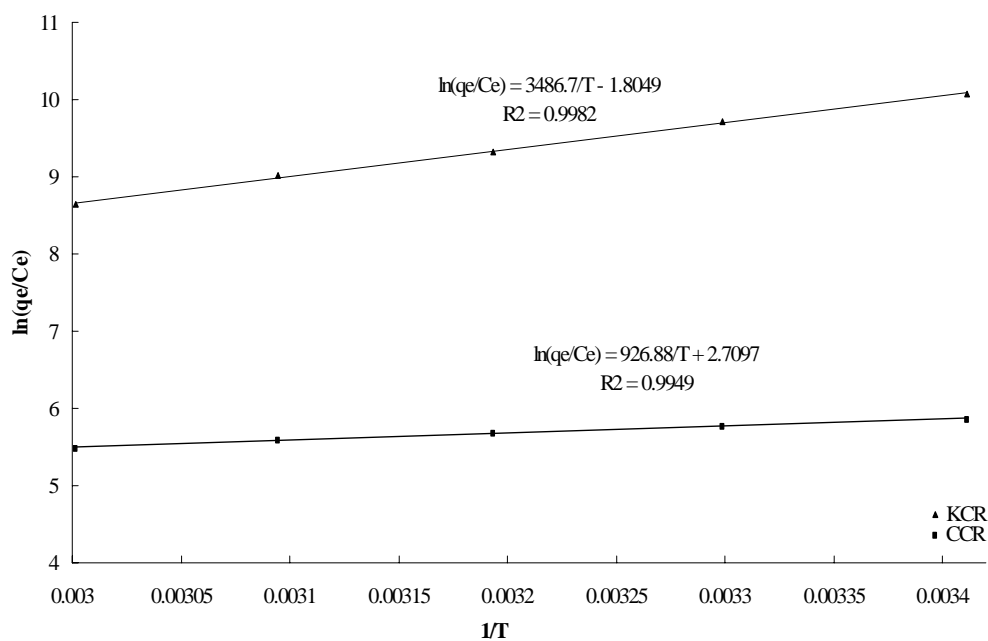$$R2 = 0.9982$$

$$\ln(qe/Ce) = 926.88/T + 2.7097$$
$$R2 = 0.9949$$

Fig. 6. The plot of ln (q_e/C_e) vs. 1/T for the sorption of MB by KCR and CCR

where q_e/C_e is the equilibrium constant (ml/g), $\triangle S^\circ$ is standard entropy change (J/mol·K), $\triangle H^\circ$ is standard enthalpy change (J/mol), T is the absolute temperature (K), and R is the gas constant (8.314 J/mol·K). $\triangle G^\circ$ is the standard free energy change (kJ/mol). The $\triangle H^\circ$ and $\triangle S^\circ$ values can be calculated from the slope ($-\triangle H^\circ/R$) and intercept ($\triangle S^\circ/R$) of the linear plot of $\ln(q_e/C_e)$ versus $1/T$. The $\triangle H^\circ$ and $\triangle S^\circ$ values as well as $\triangle G^\circ$ values under different temperatures, which were respectively obtained from Fig. 6 and Eq. 8, were presented in Table 1. The negative values of $\triangle G^\circ$ and $\triangle H^\circ$ indicated that the MB sorption on KCR and CCR were spontaneous and exothermic. Lower temperatures were favorable for the sorption process.

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