Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.833879

52 (2014) 7733–7742
December

Taylor & Francis
Taylor & Francis Group

Adsorption of congo red by cross-linked chitosan resins

Li-Xuan Zeng, Yu-Fei Chen, Qiu-Yun Zhang, Yuan Kang, Ji-Wen Luo*

Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education; School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China
Tel. +862 0 39310213; email: luojw@scnu.edu.cn

Received 24 May 2013; Accepted 30 July 2013

ABSTRACT

In this study, cross-linked chitosan resins were prepared through inverse suspension and were used to adsorb congo red (CR). FT-IR spectra and SEM technique characterized the chitosan resins. The influences of contact time, temperature, adsorbent dose, initial concentration of CR, and pH of CR solution on the adsorption behavior were investigated. The results showed that the chitosan beads made from 5% chitosan in 2% aqueous acetic acid had smooth surface and strong mechanical strength. When the contact time was 60 min, temperature was 50℃, adsorbent dose was 0.02 g, initial concentration of CR was 80 mg/L, and pH of CR solution was 7, the best adsorption capacity was obtained. The adsorption behavior can be fitted well by the Langmuir isotherm and also obeyed the pseudo-second-order kinetic expression. The intra-particle diffusion studies indicate that the diffusion step was not the only rate-limiting step. Thermodynamic studies illustrated that the adsorption reactions are exothermic and spontaneous in nature.

Keywords: Chitosan; Crosslink; Resins; Congo red; Adsorption

1. Introduction

Nowadays, extensive use of synthetic dyes has produced large volumes of dye wastewater. A very small amount of dye in water is highly visible and it can affect aquatic life and food webs with carcinogenic and mutagenic effects [1]. Congo red (CR), 1-naphthalenesulfonic acid, 3, 3′-(4, 4′-biphenylenebis (azo)) bis (4-amino-) disodium salt, is a benzidine-based anionic diazo dye prepared by coupling tetrazotized benzidine with two molecules of napthionic acid. This synthetic dye which can be metabolized to benzidine is known as a human carcinogen; it is toxic to many organisms and causes the possible risk of harm to the unborn child [2]. Because of the high steady structure and the good water-solubility as sodium salt form in general, CR is difficult to be biodegraded and photodegraded.

Generally, there are several treatments of dyeing effluent such as adsorption, coagulation–flocculation, oxidation–ozonation, reverse osmosis, membrane filtration, photo-catalytic degradation, biological degradation, and electrochemical processes [3,4]. Adsorption is the most popular treatment technique due to its simplicity and high efficiency. Activated carbon has been recognized as the most popular adsorbent for the removal of dyestuffs from wastewater, but the adsorption process is expensive and difficult for adsorbent regeneration [5]. Therefore, the alternative low-cost adsorbents, such as clay minerals [6], hen feathers [7–9], bottom ash [10], eggshell waste

---

*Corresponding author.

[11], de-oiled soya [12], and biosorbent eggshell membrane [13] have been used for the removal of CR from aqueous solutions. However, low adsorption capacities of these adsorbents toward dyes limit their applications in practical field.

Chitosan is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin, which is a polysaccharide consisting predominantly of unbranched chains of β-(1→4)-2-acetoamido-2-deoxy-d-glucose. Chitin is the second most abundant polymer in nature after cellulose. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects, and other crustaceans [14]. Chitosan has good characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. The application of biopolymers such as chitin and chitosan is one of the emerging adsorption methods for the removal of dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites even at low concentrations [14]. However, chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values. To improve the chitosan's performance as an adsorbent, cross-linking reagents have been used such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether, and isocyanates. Cross-linking agents can stabilize chitosan in acid solutions and enhance its mechanical properties [15]. The resins morphology of chitosan can improve the adsorption capacity and regeneration. But there is little report about cross-linked chitosan resins as absorbent.

The aim of this study is to prepare the cross-linked chitosan resins and investigate the adsorption behavior of the chitosan resins toward CR dye.

2. Material and methods

2.1. Materials

Chitosan was purchased from Jinan Haidebei Marine Bioengineering Co. Ltd., (Shandong, China). The molecular weight (MW) of chitosan was 2.0×10^5 and the degree of deacetylation was 80%. Other chemicals were of analytical grade.

2.2. Preparation of cross-linked-chitosan resins

Chitosan resins were prepared through inverse suspension when formaldehyde and epichlorohydrin were used as a cross-linking agent [16]. Chitosan solution was prepared in 2% acetic acid and dispersed in 100 ml of paraffin liquid and then Tween 80 containing PEG2000 was added. The dispersion was stirred at 1,000 r/min for 1 h, 10 ml of 40% formaldehyde was added followed by stirred at room temperature for 2 h, then 10% NaOH/ethanol(V/V = 1:1) solution was added followed by stirred slowly for 2 h. After the reaction, the beads were washed by petroleum ether and ethanol absolute step by step and then suspended in 0.067 mol/L NaOH solution. About 8 ml of epichlorohydrin was added into the mixture and stirred at 300 r/min at 45˚C for 3.0 h. The product was washed with deionized water and suspended in 0.5 mol/L HCl to remove the protecting group for 12 h and then suspended in 5% NaOH solution for 5 h. After the process, the product was washed with ethanol absolute and deionized water, then the cross-linked chitosan resins were obtained. The wet resins were put into a vacuum oven for 24 h to dry to the constant weight.

2.3. Characterization of cross-linked chitosan resins

The surface morphology of the beads was observed under a scanning electron microscope (SEM) (JEOL, JSM-6700F, Japan) after coated with gold.

FT-IR spectrum was measured by a Nicolet FT-IR 5,700 spectrophotometer (Madison, America) by a KBr pellets method. The spectra were collected for each measurement over the spectral range 4,000–400 cm^{-1} with a resolution of 4 cm^{-1}.

2.4. Adsorption behavior for CR

The adsorption behavior of chitosan resins for CR was investigated. About 0.02 g chitosan resins were added into 10 mL of 50 mg/L CR solution with pH value 6.6 ± 0.1. The experiments were performed in temperature-controlled water bath at 200 r/min and 25˚C. At required time intervals, 5 mL of the reaction solution was quickly taken out and then determined by the UV–vis spectrophotometer with the analytical wavelength of 498 nm at room temperature.

3. Results and discussion

3.1. Effect of chitosan concentration on the formation bead

In order to obtain the optimal cross-linked resins, the effect of the chitosan concentration on resins quality was studied. As shown in Fig. 1, when the chitosan concentration was 3%, the obtained beads had a rough surface (Fig. 1(a)) with friable mechanical strength. When chitosan concentration reached 5.5%, the largest number of the beads were obtained, but the surface of the bead was little rough (Fig. 1(c)) because the solution of the chitosan is too viscous to

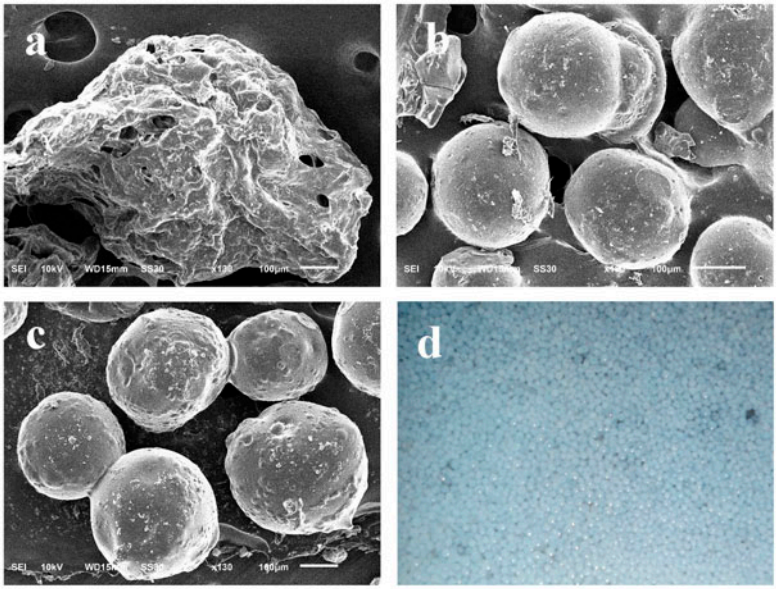

Fig. 1. SEM photographs of the beads when chitosan concentration was (a) 3%, (b) 5%, (c) 5.5%, and (d) bead photo of 5% chitosan concentration.

stir evenly. While chitosan concentration was 5%, the appropriate number of the microspheres were formed, the bead surface was very smooth (Fig. 1(b) and (d)), and its mechanical strength was strong enough. As mentioned above, 5% chitosan concentration was choosen to carry out the adsorption study.

3.2. Characterization of resins

Structure analyses of the resins were performed by FT-IR spectroscopy, as shown in Fig. 2. In the spectrum of chitosan, the peaks at 663 and 1,596 cm^{-1} were attributed to the stretching vibration of amino-group, the band at 1,654 cm^{-1} was due to the bending vibration of acid amides, the two peaks at 2,877 and 2,918 cm^{-1} were belonged to the stretching vibration of C–H and $-CH_2$, respectively, and the band at 3,423 cm^{-1} was ascribed to the stretching vibration of O–H. By comparison, in the FT-IR spectrum of the cross-linked chitosan resins, the adsorption bands of amino groups at 663 and 1,596 cm^{-1} weakened. There was a new peak at 1,741 cm^{-1}, which was attributed to the stretching vibration of –C=N, it illustrates the intramolecular or external cross-linking happened between the aldehyde and the amino groups of chitosan [17–20]. In addition, it can be found that the adsorption band at 1,452, 2,877, and 2,918 cm^{-1} which corresponded to the vibration of C–H and $-CH_2$ were stronger significantly, further indicating the success of the cross-linking reaction. After the adsorption of CR, the vibration peak at 1,596 cm^{-1} of amino groups disappeared, revealing that the interaction happened between chitosan resins and CR, and the adsorption site was mainly at the amino group. In addition, a new adsorption band at 1,560 cm^{-1} occurred because CRs has a lot of C=C groups. The results further reveal the effective adsorption of CR on the chitosan resins.

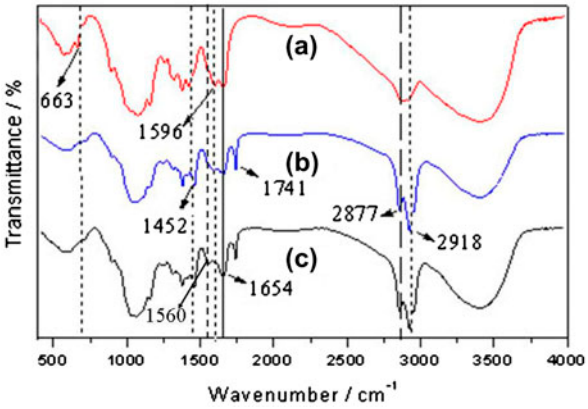

Fig. 2. (a) FT-IR spectra of chitosan, (b) cross-linked chitosan resins before adsorption, and (c) cross-linked chitosan resins after adsorption.

3.3. Influence of contact time on CR removal

The influence of contact time on the adsorption behavior of CR ($C_0 = 50$ mg/L) was examined at 25˚C. Fig. 3 shows that the adsorption amount of CR onto

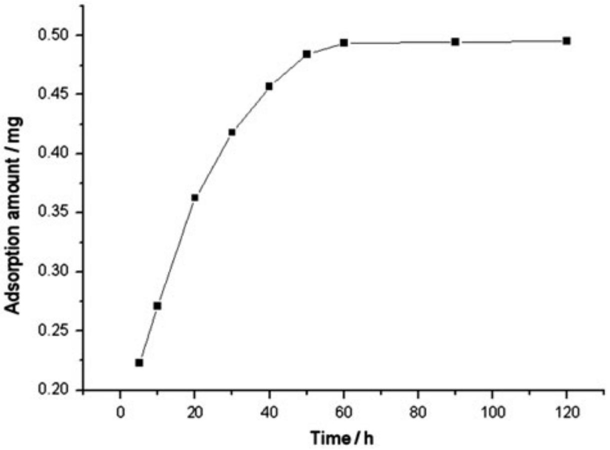

Fig. 3. Influence of the adsorption time on adsorption capacity of cross-linked chitosan resins for CR. Adsorption condition—dye concentration: 50 mg/L; sample dose: 0.02 g/10.00 mL; pH: 6.6 ± 0.1; temperature: 25℃.

cross-linked chitosan resins rapidly increased at the initial stage and then enhanced gradually until it reached equilibrium. The removal efficiency increased from 44.64 to 98.74% and the adsorption amount increased from 0.22 to 0.49 mg. It could be due to the fact that the contact opportunity between the dye molecules and adsorbent increased with the increasing contact time until the available adsorption sites got diminished. As shown in Fig. 3, the maximum adsorption capacity was observed at 60 min.

3.4. *Influence of temperature on CR removal*

The influence of temperature on adsorption capacity of cross-linked chitosan resins was investigated at 25, 30, 35, 40, 45 and 50℃, respectively, the stirring time was 60 min. The adsorption capacity of CR on cross-linked chitosan resins increased from 0.315 to 0.464 mg with an increase of temperature from 25 to 50℃, indicating that higher temperature facilitated to the adsorption of CR on cross-linked chitosan resins. It could be due to the fact that increasing temperature may produce a swelling effect within the internal structure of cross-linked chitosan resins, which facilitated the penetration of dye molecules into the internal structure of cross-linked chitosan resins [16]. However, the adsorption amount of CR on cross-linked chitosan resins decreased from 0.464 to 0.453 mg with an increase of temperature from 50 to 55℃. The reason may be due to the fact that the swelling effect of cross-linked chitosan resins and the diffusion of the solution may play a very small role in the adsorption capacity of CR after 50℃ for the adsorption process was an exothermic process; higher temperature than 50℃ was not conducive to the adsorption.

3.5. *Influence of initial concentration on CR removal*

The influence of initial concentration (20, 30, 40, 50, 60, 80 and 100 mg/L) on CR adsorption amount was investigated. The adsorption amount increased until the initial concentration of CR solution reached 80 mg/L, thereafter the adsorption reached a plateau and then the adsorption amount kept stable. The findings were probably caused by the increasing concentration of CR, which could accelerate the diffusion of CR molecules onto the adsorbent as a result of an increase of the driving force of concentration gradient. With the progress of adsorption, the availability of adsorption sites of the adsorbent got diminished; it made the adsorption capacity constant.

3.6. *Influence of adsorbent dose on CR removal*

The effect of different cross-linked chitosan resins dose (0.005, 0.01, 0.02, 0.03, 0.04, 0.05, and 0.08 g) on CR adsorption amount was examined. The removal efficiency (%) decreased greatly until the dose of the cross-linked chitosan resins reached 0.03 g; thereafter the adsorption capacity reached a plateau and then increased gradually. Removal efficiency (%) decreased from 82.46 to 65.35% and adsorption amount decreased from 0.41 to 0.32 mg with the increase of adsorbent dose. The above results demonstrate that the decrease of adsorption amount may be due to the fact that some of the adsorption sites remained unsaturated when adsorbent dose was increased. On the other hand, the contact opportunity between the dye molecules and adsorbent declined, which weakened the adsorption ability of the cross-linked chitosan resins [21]. Moreover, the removal efficiency increased from 65.35 to 66.62% and adsorption amount increased from 0.32 to 0.33 mg when cross-linked chitosan resins dose was more than 0.03 g; it can be explained that large amount of CR were adsorbed as the number of available adsorption sites increased, resulting in the increase of the removal efficiency [21].

3.7. *Influence of pH on CR adsorption*

CR is an acid–base indicator and its pH of the solution ranges from 6.0 to 7.0; it may discolor when the pH of the solution is less than 6, therefore, the influence of pH ranging from 6.0 to 14.0 on the removal of CR was investigated as Fig. 4 shows.

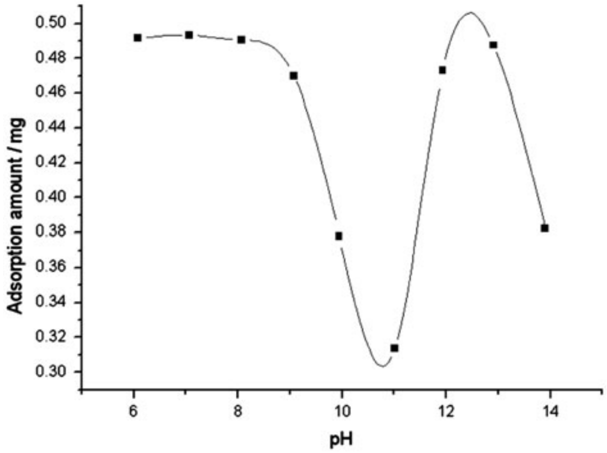

Fig. 4. Influence of pH on adsorption capacity of cross-linked chitosan resins for CR. Adsorption conditions—dye concentration: 50 mg/L; sample dose: 0.02 g/10.00 mL; temperature: 25℃, stirring time: 60 min.

It can see that there was no significant change of adsorption amount when the pH rose from 6.0 to 8.0, whereas the adsorption amount decreased rapidly when the pH was at the range of 8–11 and reached a least adsorption amount when the pH was 11. The adsorption amount increased gradually when the pH was above 11 and decreased rapidly again when the pH was above 13. Since cross-linked chitosan resins were suspended in 0.5 mol/L HCl solution originally, the amine groups of the chitosan molecules were protonated well. During adsorption, protonation of amine groups is necessary for its interaction with negatively charged CR molecules [22], as mentioned in FT-IR result, so there was a high adsorption capacity of cross-linked chitosan resins for CR from initial pH 6.0 to 8.0. Another reason may due to the fact that pH could change the surface charge of an adsorbent and could promote or depress the ionization of adsorbent of CR [23]. Ionic strength played a major role in the electrical double-layer structure of hydrated particle. The thickness of the electrical double layer decreased as the ionic strength increased, resulting in a decrease in adsorption [24]. At lower pH values, hydrogen ion promoted the ionization of CR anion, the surface charge of CR molecular increased, and the adsorption amount increased. At higher pH values, hydrogen ion depressed the ionization of CR anion with the decrease of the surface charge of CR molecular, the adsorption amount also decreased [25]. The adsorption amount decreased when the pH value was bigger than 13, which probably resulted from the increases of viscidity of the solution and the diffusion rate of the CR molecular decreased when the pH increased.

3.8. Adsorption isotherms

To investigate the interaction of adsorbate molecules and adsorbent surface, two well-known models, the Freundlich and Langmuir isotherms, were chose to explicate dye–resins interaction in this study [25]. Adsorption experiments were investigated in following conditions: 20, 30, 40, 50, 60, 80 and 100 mg/L initial concentration of CR; sample dose: 0.02 g/10.00 mL; pH: 6.68; stirring time: 60 min; temperature: 25℃. The results were showed in Table 1.

The Freundlich isotherm illustrates the non-ideal adsorption of a heterogeneous system and reversible adsorption [26]. The model can be expressed as the following equation which was linearized by taking logarithms:

$$L_g q = l_g K_F + \frac{1}{n} l_g C_e \tag{1}$$

where q is the amount of the dye adsorbed per unit of adsorbent (mg/g), C_e is the concentration of the dye solution at adsorption equilibrium (mg/l), K_F ($\mathrm{mg}^{1-1/n}\,\mathrm{l}^{1/n}\,\mathrm{g}^{-1}$) and n is the Freundlich adsorption isotherm constants. The adsorption of this model can be characterized as a favorable and a physical process if n=1. The fitting results of Freundlich isotherm model can be showed in Fig. 5.

A basic assumption is that sorption takes place at specific homogeneous sites within the sorbent. Once a dye molecule occupies a site, no further sorption can take place at that site. It can be shown as the following equation:

$$\frac{C_e}{q} = \frac{1}{aQ} + \frac{C_e}{Q} \tag{2}$$

where q is the maximum amount of adsorption which completes monolayer coverage on the adsorbent surface (mg/g), a is the Langmuir constant (l/mg).

The Langmuir isotherm is based on the assumption of a structurally homogeneous adsorbent and the monolayer coverage. Then the theoretical monolayer capacity of the sorbent can be determined from the parameters of the linearized form of Langmuir sorption isotherm as in Eq. (3). In Fig. 6, the linearized form of Langmuir sorption isotherm was tested by the plots of C_e/Q versus C_e for CR [27].

After the calculation, we can get the correlation coefficients of Langmuir isotherm model ($R = 0.9998$) for CR indicated a good agreement with the experimental data. The applicability of Langmuir sorption model suggested the monolayer coverage of CR on the surface of resins. We can also get the value of Q

Table 1
Concentration and adsorption capacity

C_e (mg/L)	Q (mg/g)	C_e/Q (g/L)	l_gC_e	l_gQ
0.043636	9.978182	0.004373	−1.360155	0.99905
0.189091	14.905455	0.012686	−0.723329	1.173345
0.661818	19.669091	0.033648	−0.179261	1.293784
1.716364	24.141818	0.071095	0.234609	1.382769
3.098182	28.450909	0.108896	0.491107	1.454096
16.880000	31.560000	0.534854	1.227372	1.499137
35.789091	32.105455	1.114736	1.553751	1.506579

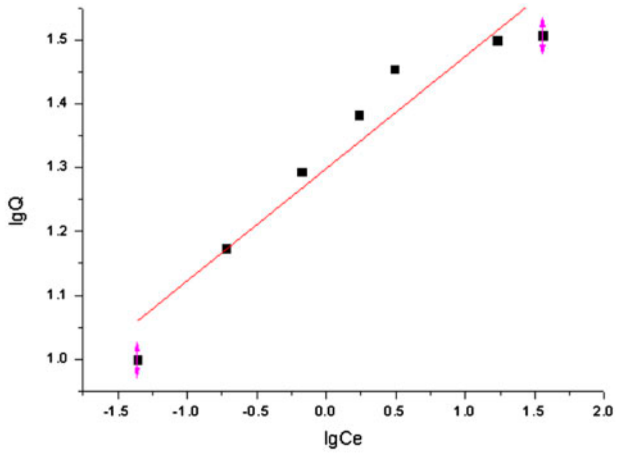

Fig. 5. Freundlich isotherm model.

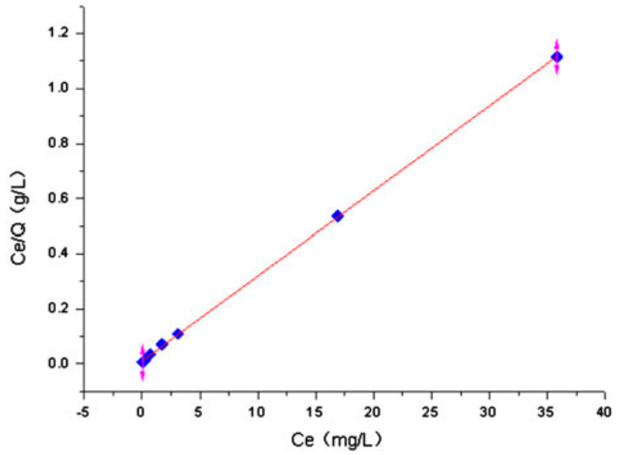

Fig. 6. Langmuir isotherm model.

(2.8 mg/g) and the Langmuir constant *a* (32.47 L/mg). The linearity of the plot as well as the values of correlation coefficients ($R = 0.9130$) for CR showed the linearity of the Freundlich sorption equation. The values of $1/n$ (0.1758) also illustrate the favor ability of Freundlich isotherm model. The comparison on the basis of the regression coefficient (R) obtained from the Langmuir and Freundlich equations demonstrate that the Langmuir model yielded a much better applicability than the Freundlich model. However, the experimental evidences pointed out the applicability of Freundlich isotherm, which explain surface heterogeneity and a multilayer coverage of the CR on the surface of resins.

3.9. Adsorption kinetics

Several adsorption kinetic models have been applied to examine the controlling mechanism of dye adsorption from different concentration aqueous solution [16,28]. The kinetics of adsorption can be described by the first-order Lagergren equation that is given by Eq. (3) [29].

$$\ln(Qe_{\exp} - Q_t) = \ln Q_{e1} - k_1 \times t/2.303 \tag{3}$$

where $Qe_{\exp}$ and Q_t are the amounts of CR adsorbed (mg/g) at equilibrium and time (t), respectively. Q_{e1} is the amount of dye adsorbed equilibrium-calculated data, expressed as mg/g sample. k_1 is the first-order-rate constant. The adsorption rate constant (k_1) was calculated from the plot of ln ($Qe_{\exp} - Q_t$) against t.

The pseudo-second-order kinetic is represented as equation by Eq. (4) [30].

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{e2}^2} + \frac{1}{Q_{e2}} t \tag{4}$$

where t and Q_t are, respectively, time (min) and the amount of dye adsorbed by cross-linked chitosan resins at time t (mg/g). Q_{e2} is the amount of dye adsorbed equilibrium-calculated data, expressed as mg/g sample. k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). The initial adsorption rate, h (mg g^{-1} min^{-1}) at $t \to 0$ is defined as:

$$h = k_2\, Qe^2 \tag{5}$$

h, Qe and k_2 can be obtained by linear plot of t/qt versus t.

Both models have been applied to describe the adsorption of CR adsorbed on the cross-linked chitosan resins in our work. The calculated results are given in Table 2. The first-order kinetic curves of dye adsorption from different concentration aqueous solution did not fit very well with the experimental data. While, the pseudo-second-order equation provided an excellent fit between the predicted curves and the experimental data (Fig. 7). This supports the assumption of the model that the adsorption is due to chemisorptions. The curves also illustrate that, at the beginning, the adsorption of CR increased rapidly then slowed at the end of the reaction. The initial adsorption rate, h (mg g^{-1} min^{-1}) also shows that low concentration of CR on cross-linked chitosan resins adsorption was 2.4, 5.3, 6.9 times faster than that of high concentration, respectively. It illustrates that the contact time is critical when the resins are applied in high concentration solution.

The model proposed by Weber and Morris has been applied to gain a deeper knowledge about the mechanism of dye adsorption onto cross-linked chitosan resins. In this model, described by Eq (6) [31].

$$Q_t = k_p\, t^{1/2} \tag{6}$$

where Q_t and k_p are the amount adsorbed at time t (mg/g) and Intra-particle rate constant (mg/g $\text{min}^{1/2}$), respectively.

During the adsorption, there are a series of resistances to mass transfer involved in the reaction. These may be either “external resistance”, in which the resistance is encountered by solute molecules as they diffuse through a solute film onto the adsorbent particle surface, or “internal resistance”, in which the resistance is encountered by solute molecules as they diffuse through the liquid filling the pores on the way to the adsorption sites. The external resistance is characterized by the external mass transfer coefficient and the internal resistance can be assessed by internal pore and solid diffusivities. It is suggested that the multiple regions of the plot between q_t and $t^{1/2}$ represent the external mass transfer followed by intraparticle diffusion in macro, meson, and microspore.

The multi-linearity stages were explained by Lorenc-Grabowska and Gryglewicz [32]. The initial stage is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second stage describes the gradual adsorption stage, where intra-particle diffusion rate is rate limiting. The last stage refers to the final equilibrium stage in which the intra-particle diffusion starts to slow down and level out as the extremely low dye concentration left in solution. Fig. 8 shows the plots of uptake for CR versus square root time on cross-linked chitosan resins. The plot shows that more than one process affects the CR adsorption and none of the lines passed through the origin. This indicates that the intra-particle diffusion was involved in the adsorption process, but was not the only rate-limiting step. As can be seen in Fig. 8, the diffusion of the adsorbate through the solution to the external surface of adsorbent affects the rate of adsorption. The intra-particle diffusion occurs in two stages. The CR molecule enters the wider macrospores rapidly and then penetrates into smaller macrospores slowly.

3.10. Thermodynamics analysis

According to thermodynamics temperature coefficient formula [33]:

$$\ln A = \Delta H/RT + 2.303\ \Delta S/R \tag{7}$$

where A is the allocation coefficient, $A = C_s/C_e$, and C_s (mg/L) is the equilibrium concentration of CR adsorbed on cross-linked chitosan resins, while C_e (mg/L) is the equilibrium concentration of CR in aqueous solution. ΔH is the enthalpy change, ΔS the

Table 2
Adsorption kinetic parameters for the adsorption of CR on cross-linked chitosan resins

Concentration (mg/L)	Pseudo-first order			Pseudo-second order			
	Q_{e1} (mg/g)	k_1 (1/min)	R^2	Q_{e2} (mg/g)	h mg $(\text{g min})^{-1}$	k_2 (g/mg min)	R^2
20	20.55	0.0045	0.717	25.27	9.74	0.015	0.999
30	15.71	0.0077	0.823	22.77	4.01	0.0077	0.994
40	10.55	0.0125	0.901	19.63	1.81	0.0047	0.981
50	7.59	0.0127	0.825	14.05	1.40	0.0071	0.989

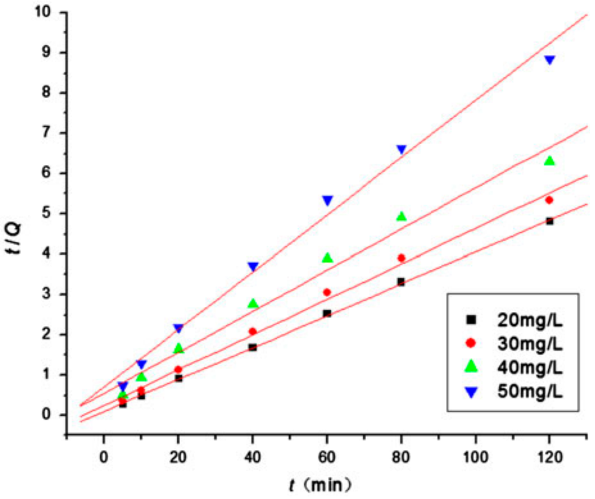

Fig. 7. The pseudo-second-order kinetics for the adsorption of CR on cross-linked chitosan resins (adsorbent dosage 0.02 g, initial pH 6.5–7) linear expression.

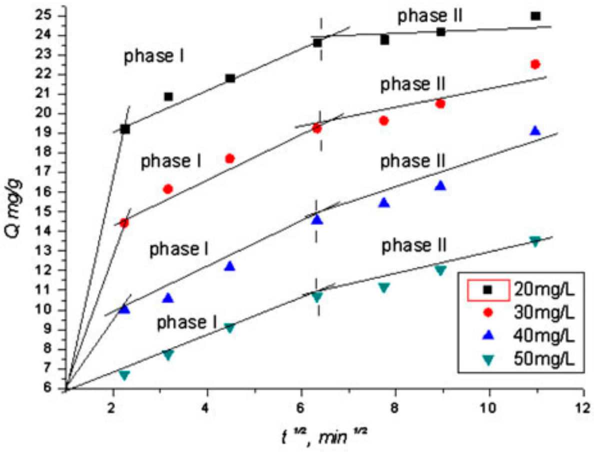

Fig. 8. The intra-particle diffusion kinetics for adsorption of CR on cross-linked chitosan resins (adsorbent dosage 0.02 g, initial pH 6.5–7) linear expression.

entropy change, R the gas law constant (8.314 J/mol K), and T is the absolute temperature (K).

The linear relation coefficient r ($r = 0.929$) can be obtained by linear plot of ln A vs. T^{-1} (shown in Fig. 9). The linear results show that $\Delta H = -26.51$ (kJ/mol), $\Delta S = -42.88$ (J/mol K). We can see enthalpy change and entropy change of cross-linked chitosan resins for CR is negative, which means all the adsorption reactions are exothermic and entropy values decrease. According to thermodynamics formula $\Delta G = \Delta H - T\Delta S$, ΔG, Gibbs free energy change, at room temperature ($T = 25$°C) also can be obtained ($\Delta G = -13.73$ (kJ/mol)). Negative Gibbs free energy change demonstrated that the adsorption of CR with cross-linked chitosan resins carried out spontaneously.

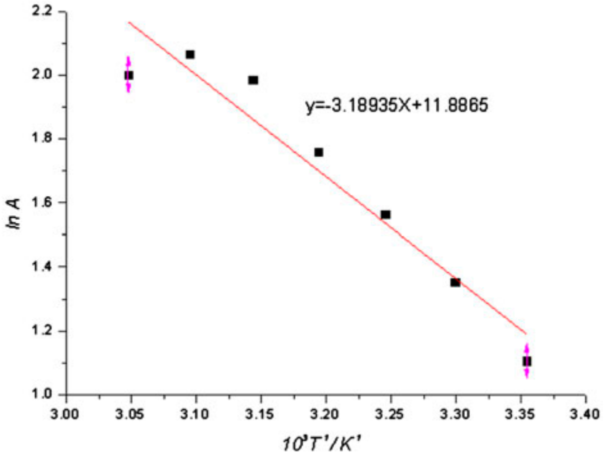

Fig. 9. Thermodynamics plots of adsorption.

3.11. *The effect of salt ionic strength on adsorption capacity of cross-linked chitosan resins for CR*

On account of the high percentage of salts in industrial wastewater since real time, the effect of salt ionic strength on adsorption capacity of cross-linked chitosan resins for CR was studied in our work.

Tables 3 and 4 show the results for adsorption of CR on cross-linked chitosan resins by adding different salt ionic compounds, respectively. We can see from the tables, with the increasing ionic strength of the solution, the extent of the adsorption is increased. This might be explained by the screening effect of added salt resulting in the increase of the electrostatic attractive interactions between CR molecule and cross-linked chitosan resins. The results also show that

Table 3
The effect of NaCl concentration on adsorption capacity of cross-linked chitosan resins for CR (pH = 6.5–7)

Number	NaCl concentration (mol/L)	NaCl weight (g)	pH	Q (mg/g)
1	0	0	6.9	14.72
2	0.10	0.0585	6.25	21.36
3	0.20	0.117	6.58	19.85
4	0.40	0.234	6.14	21.03
5	0.60	0.351	6.61	21.09
6	0.80	0.468	6.40	21.25
7	1.00	0.585	6.21	21.31
8	2.00	1.17	6.14	20.23

Table 4
The effect of $NaSO_4$ concentration on adsorption capacity of cross-linked chitosan resins for CR (pH = 6.5–7)

Number	$NaSO_4$ concentration (mol/L)	$NaSO_4$ weight (g)	pH	*Q* (mg/g)
1	0	0	6.90	14.69
2	0.10	0.146	6.70	21.71
3	0.20	0.288	6.70	21.74
4	0.40	0.578	6.74	20.41
5	0.60	0.861	6.73	20.72
6	0.80	1.128	6.70	20.14
7	1.00	1.43	6.71	19.36
8	2.00	2.86	6.54	19.00

both Cl^- and SO_4^{2-} contribute to strong the attractive forces between the CR molecule and cross-linked chitosan resins surface.

4. Conclusions

Cross-linked chitosan resins with smooth surface and strong strength were prepared via inverse suspension method and they could adsorb CR effectively. The adsorption sites were oxhydryl groups and amino groups. The results showed that the contact time, temperature, adsorbent dose, initial concentration, and pH of the CR solution have significant influences on the adsorption process, and the temperature effect was more obvious. Langmuir isotherm and the pseudo-second-order kinetic expression can describe the adsorption process of chitosan resins for CR removal well. Thermodynamic studies illustrated that the adsorption reactions are exothermic and spontaneous in nature. The effect of salt ionic strength on adsorption capacity of cross-linked chitosan resins for CR also shows that the cross-linked chitosan resins could be applied in the industrial wastewater treatment.

Acknowledgments

This work is supported by the scientific research of fund project for young teachers of the South China Normal University and open fund of State Key Laboratory of pulp and paper engineering of the South China University of Technology.

References

[1] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol. 97 (2006) 1061–1085.

[2] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: Kinetic study and equilibrium isotherm analyses, Chemosphere 61 (2005) 492–501.

[3] V.K. Gupta, R. Jain, A. Mittal, T.A. Saleh, A. Nayak, S. Agarwal, S. Sikarwar, Photo-catalytic degradation of toxic dye amaranth on TiO2/UV in aqueous suspensions, Mat. Sci. Eng. C-Mat. 32 (2012) 12–17.

[4] Z.M. Shen, W.H. Wang, J.P. Jia, J.C. Ye, X. Feng, A. Peng, Degradation of dye solution by an activated carbon fiber electrode electrolysis system, J. Hazard. Mat. 84 (2001) 107–116.

[5] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions, Bioresour. Technol. 87 (2003) 129–132.

[6] N. Miyamoto, R. Kawai, K. Kuroda, M. Ogawa, Adsorption and aggregation of a cationic cyanine dye on layered clay minerals, Appl. Clay Sci. 16 (2000) 161–170.

[7] V.K. Gupta, A. Mittal, D. Jhare, J. Mittal, Batch, bulk removal of hazardous colouring agent rose Bengal by adsorption techniques using bottom ash as adsorbent, RSC Adv. 2 (2012) 8381–8389.

[8] A. Mittal, V. Thakur, V. Gajbe, Evaluation of adsorption characteristics of an anionic azo dye Brilliant Yellow onto hen feathers in aqueous solutions, Environ. Sci. Pollut. R. 19 (2012) 2438–2447.

[9] A. Mittal, V. Thakur, V. Gajbe, Adsorptive removal of toxic azo dye amido black 10B by hen feather, Environ. Sci. Pollut. R. 20 (2013) 260–269.

[10] K.G. Bhattacharyya, A. Sharma, Azadirachta indica leaf powder as an effective biosorbent for dyes: A case study with aqueous congo red solutions, J. Environ. Manage. 71 (2004) 217–229.

[11] R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li, L. Zou, Use of rice husk for the adsorption of congo red from aqueous solution in column mode, Bioresour. Technol. 99 (2008) 2938–2946.

[12] Y.Z. Fu, T. Viraraghavan, Removal of congo red from an aqueous solution by fungus *Aspergillus niger*, Adv. in Environ. Res. 7 (2002) 239–247.

[13] K. Vijayaraghavan, Y.-S. Yun, Bacterial biosorbents and biosorption, Biotechnol. Adv. 26 (2008) 266–291.

[14] W.S.W. Ngah, I.M. Isa, Comparison study of copper ion adsorption on chitosan, Dowex A-1, and Zerolit 225, J. Appl. Polym. Sci. 67 (1998) 1067–1070.

[15] M.S. Chiou, P.Y. Ho, H.Y. Li, Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads, Dyes Pigm. 60 (2004) 69–84.

[16] K.G. Bhattacharyya, A. Sarma, Adsorption characteristics of the dye brilliant green, on neem leaf powder, Dyes Pigm. 57 (2003) 211–222.

[17] P.K. Dutta, J. Dutta, V.S. Tripathi, Chitin and chitosan: Chemistry, properties and applications, J. Sci. Ind. Res. India 63 (2004) 20–31.

[18] R. Jayakumar, R.L. Reis, J.F. Mano, Chemistry and applications of phosphorylated chitin and chitosan, E-Polym. (2006) no. 035.

[19] C.K.S. Pillai, W. Paul, C.P. Sharma, Chitin and chitosan polymers: Chemistry, solubility and fiber formation, Prog. Polym. Sci. 34 (2009) 641–678.

[20] F. Shahidi, R. Abuzaytoun, Chitin, chitosan, and co-products: Chemistry, production, applications, and health effects, Adv. Food Nutri. Res. 49 (2005) 93–135.

[21] N. Sankararamakrishnan, A. Dixit, L. Iyengar, R. Sanghi, Removal of hexavalent chromium using a novel cross linked xanthated chitosan, Bioresour. Technol. 97 (2006) 2377–2382.

[22] J. Luo, B. Liu, X. Wang, Y. Pan, R. Sun, Preparation and characterization of chitosan monomer/organic rectorite nanocomposite, Curr. Nanosci. 8 (2012) 387–392.

[23] E.N. El Qada, S.J. Allen, G.M. Walker, Adsorption of methylene blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm, Chem. Eng. J. 124 (2006) 103–110.

[24] B. Liu, X. Wang, C. Pang, J. Luo, Y. Luo, R. Sun, Preparation and antimicrobial property of chitosan oligosaccharide derivative/rectorite nanocomposite, Carbohydr. Polym. 92 (2013) 1078–1085.

[25] A. Martin, N. Tabary, L. Leclercq, J. Junthip, S. Degoutin, F. Aubert-Viard, F. Cazaux, J. Lyskawa, L. Janus, M. Bria, B. Martel, Multilayered textile coating based on a beta-cyclodextrin polyelectrolyte for the controlled release of drugs, Carbohydr. Polym. 93 (2013) 718–730.

[26] J.P. Chen, S.N. Wu, K.H. Chong, Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption, Carbon 41 (2003) 1979–1986.

[27] L. Wang, A. Wang, Adsorption characteristics of congo red onto the chitelsan/montmorillonite nanocomposite, J. Hazard. Mater. 147 (2007) 979–985.

[28] V.P. Vinod, T.S. Anirudhan, Adsorption behaviour of basic dyes on the humic acid immobilized pillared clay, Water Air Soil Pollut. 150 (2003) 193–217.

[29] V. Vimonses, S. Lei, B. Jin, C.W.K. Chow, C. Saint, Adsorption of congo red by three Australian kaolins, Appl. Clay Sci. 43 (2009) 465–472.

[30] P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: A case study of acid yellow 36, Dyes Pigm. 56 (2003) 239–249.

[31] M.A. Fontecha-Camara, M.V. Lopez-Ramon, L.M. Pastrana-Martinez, C. Moreno-Castilla, Kinetics of diuron and amitrole adsorption from aqueous solution on activated carbons, J. Hazard. Mater. 156 (2008) 472–477.

[32] E. Lorenc-Grabowska, G. Gryglewicz, Adsorption characteristics of congo red on coal-based mesoporous activated carbon, Dyes Pigm. 74 (2007) 34–40.

[33] M. Alkan, O. Demirbas, M. Dogan, Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite, Microporous Mesoporous Mater. 101 (2007) 388–396.