Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads

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Abstract

The adsorption of reactive dye (Reactive Red 189) from aqueous solutions on cross-linked chitosan beads was studied in a batch system. The equilibrium isotherms at different particle sizes (2.3–2.5, 2.5–2.7 and 3.5–3.8 mm) and the kinetics of adsorption with respect to the initial dye concentration (4320, 5760 and 7286 g/m^3), temperature (30, 40 and 50 °C), pH (1.0, 3.0, 6.0 and 9.0), and cross-linking ratio (cross-linking agent/chitosan weight ratio: 0.2, 0.5, 0.7 and 1.0) were investigated. Langmuir and Freundlich adsorption models were applied to describe the experimental isotherms and isotherm constants. Equilibrium data fitted very well to the Langmuir model in the entire saturation concentration range (0–1800 g/m^3). The maximum monolayer adsorption capacities obtained from the Langmuir model are very large, which are 1936, 1686 and 1642 g/kg for small, medium and large particle sizes, respectively, at pH 3.0, 30 °C, and the cross-linking ratio of 0.2. The pseudo first- and second-order kinetic models were used to describe the kinetic data, and the rate constants were evaluated. The experimental data fitted well to the second-order kinetic model, which indicates that the chemical sorption is the rate-limiting step, instead of mass transfer. The initial dye concentration and the solution pH both significantly affect the adsorption capacity, but the temperature and the cross-linking ratio are relatively minor factors. An increase in initial dye concentration results in the increase of adsorption capacity, which also increases with decreasing pH. The activation energy is 43.0 kJ/mol for the adsorption of the dye on the cross-linked chitosan beads at pH 3.0 and initial dye concentration 3768 g/m^3. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption capacity; Adsorption rate; Reactive dye; Chitosan; Cross-linked chitosan

1. Introduction

Dyes are widely used in industries such as textiles, leather, paper, plastics, etc. to color their final products. Since many organic dye compounds are harmful to human beings, the

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Nomenclature

b Langmuir constant defined in Eq. (2) (m^3/g)

C_e equilibrium aqueous solution concentration (g/m^3)

C_0 initial aqueous solution concentration (g/m^3)

k_1 rate constant of pseudo first-order kinetic model defined in Eq. (4) (per min)

k_2 rate constant of pseudo second-order kinetic model defined in Eq. (5)
           (kg/g per min)

n Freundlich constant defined in Eq. (3)

q amount of adsorption at time t (g/kg)

q_e amount of adsorption at equilibrium (g/kg)

Q maximum monolayer amount of adsorption (g/kg)

Q_f parameter of Freundlich equation defined in Eq. (3) $((g/kg)(g/m^3)^{-1/n})$

R^2 correlation coefficient

t time (min)

V volume of the solution (m^3)

W amount of the dry chitosan used (kg)

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removal of color from process or waste effluents becomes environmentally important. The adsorption process is one of the efficient methods to remove pollutants from wastewater. Many studies have been made on the possibility of adsorbents using activated carbon [1–3], peat [4,5], chitin [3,6], silica [7] and others [5,8–13]. However, the adsorption capacity of the adsorbents is not very large, to improve adsorption performance new absorbents are still under development.

Chitosan is the deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose. Recently, chitosan that is used as an adsorbent has drawn attentions due to its high contents of amino and hydroxy functional groups showing high potentials of the adsorption of dyes [3,14–17], metal ions [16,18–20] and proteins [21,22]. Other useful features of chitosan include its abundance, non-toxicity, hydro-philicity, biocompatibility, biodegradability and anti-bacterial property [23]. The adsorption of reactive, acidic and direct dyes in neutral solutions using chitosan shows large adsorption capacities [3,14–17]. The effect of pH may be an important factor on the dye-binding capacity of chitosan because at low pH, the amino groups of chitason are much easier to be cationized and they adsorb the dye anions strongly by electrostatic attraction [23]. Moreover, it is also useful to study the dye-binding capacity of chitosan below pH 7, since acetic acid is often used as a stimulator in the dying process, in which the pH of the dye solution is normally adjusted from 3 to 4. However, chitosan formed gel below pH 5.5, and could not be evaluated. The acid effluent could severely limit the use of chitosan as an adsorbent in removing dyes and mental ions due to chitosan's dissolution tendency in the acid effluent.

To overcome such a problem, some cross-linking agents are used to stabilize chitosan [24,25] in acid solutions. Cross-linked chitosan is insoluble in an acid solution of pH 1–7 and its mechanical properties are improved. Yoshida et al. [15] used Denacol EX841 as a cross-linking agent and has shown that the adsorption capacity of Acid Orange II (acid dye) on the cross-linked chitosan fibers in acid solution of pH 3, 4 is very large. It

indicates that the ability of acid dye removal by cross-linked chitosan appears technically feasible.

To our knowledge, the adsorption of dyes in the solutions using cross-linked chitosan was little studied. In this work, epichlorohydrin (ECH) was selected as a convenient base cross-linking agent. An advantage of ECH is that it does not eliminate the cationic amine function of chitosan [24], which is the major adsorption site attracting the anion dyes during adsorption. The aim of this paper was to study the adsorption behavior of dyes using cross-linked chitosan beads in both acidic and alkaline solutions. We investigated the equilibrium and kinetics of adsorption of Reactive Red 189 (RR 189) on the chitosan from solutions of pH 1, 3, 6 and 9. The Langmuir and Frenudlich equations were used to fit the equilibrium isotherm. The adsorption rates were measured and determined quantitatively in correlation with initial dye concentration, temperature, solution pH value and the ECH/chitosan weight ratio. These results will be useful for further applications in color removal from wastewater.

2. Materials and methods

2.1. Chemicals

Chitosan (α-type, degree of deacetylation: 85.5%, molecular weight: 220,000) was supplied by OHKA Enterprises Co. ECH (weight ≥ 98%) to be used as the cross-linking agent was purchased from Fluka. The commercial reactive dye (RR 189) was supplied by a local manufacturer, Dyexel Chemical Corp., and used as received. Fig. 1 displays the structure of RR 189. The buffer solution to adjust the pH of the aqueous solutions contained sodium acetate-3-hydrate (wt. > 99%, RDH) and acetic acid (ACS grade, TEDIA).

2.2. Chitosan bead making experiments [24,26]

About 10.0 g of chitosan were dissolved in 300 cm^3, 5 wt.% of acetic acid solution, and the aqueous solution was diluted to 1.0 dm^3 by strong stirring overnight. The chitosan-dissolved solution was poured into a burette equipped with a micro-pipette tip ((2–200 × 10^{-3} cm^3, Gilson) and 10 cm^3 (containing 0.1 g dry chitosan) were dropped into a 100 cm^3 aqueous solution containing sodium hydroxide (10 wt.%) and ethanol (2 wt.%). The chitosan droplets formed a bead shape in the solution. It was left in the aqueous solution for more than 24 h.
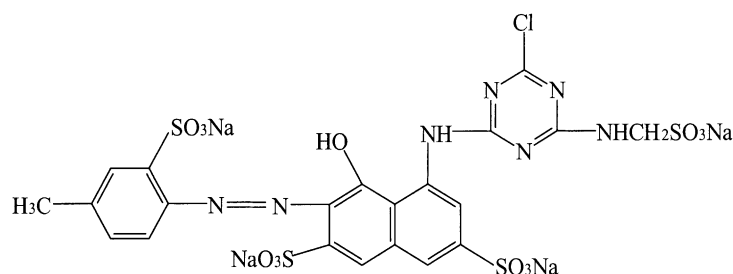

Fig. 1. The structure of reactive dye (RR 189).

The filtered chitosan beads were washed by deionized water and stored in distilled water for use. The diameter of the beads was controlled via the various tips of the micro-pipette. In this way, we prepared wet non-cross-linked chitosan beads with three different diameters (mm): small (2.3–2.5), medium (2.5–2.7)and large (3.5–3.8).

2.3. Cross-linking experiments [24,26]

The wet non-cross-linked chitosan beads (containing 0.1 g dry chitosan) were put in 50 cm^3, 1N sodium hydroxide solution in a flask, some cross-linking agent, ECH was added and shaken at 50 °C for 6 h with a water bath (Deng Yng Corp., Taiwan). Cross-linked chitosan beads with different weight ratios of ECH to chitosan (cross-linking ratio) of 0.2, 0.5, 0.7and 1.0 were prepared in this work.

2.4. Batch equilibrium studies

The RR 189 was dissolved in deionized water to the required concentrations. The pH of dye solutions was adjusted by buffer solutions of acetic acid/acetate. The pH was adjusted to 1.0, 9.0 by concentrated HCl, NaOH, respectively. In experiments of equilibrium adsorption isotherm, the chitosan beads (containing 0.1 g dry chitosan) and the dye solution (50 cm^3) were placed in a 125-cm^3 flask, which contained the buffer solution with the desired pH value and shaken for 5 days using a bath to control the temperature at 30 ± 1 °C. The dye concentration of the solutions was analyzed at wavelength 534 nm by an UV–VIS spectrometer (JASCO V-530) under pH 6.0. The amount of adsorption at equilibrium q_e (g/kg) was computed as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium solution concentrations (g/m^3), respectively, V the volume of the solutions (m^3) and W the weight of chitosan used (kg).

2.5. Batch kinetic studies

In experiments of batch kinetic adsorption, chitosan beads (containing 0.1 g dry chitosan) and dye solution (50 cm^3) were placed in a 125-cm^3 flask and shook by a shaker in a water bath to control temperature. Every other period of time, 0.1 cm^3 of dye solution was taken out to dilute to 10 cm^3 with pH 6.0 buffer solutions, and its concentration was determined at wavelength 534 nm. The experiment parameters included initial dye concentration, temperature, pH, and the cross-linking ratio.

3. Results and discussion

3.1. Equilibrium adsorption

Fig. 2 shows the equilibrium adsorption of RR 189 at pH 3.0, 30 °C, cross-linking ratio 0.2 on the cross-linked chitosan beads for three different particle sizes and one size
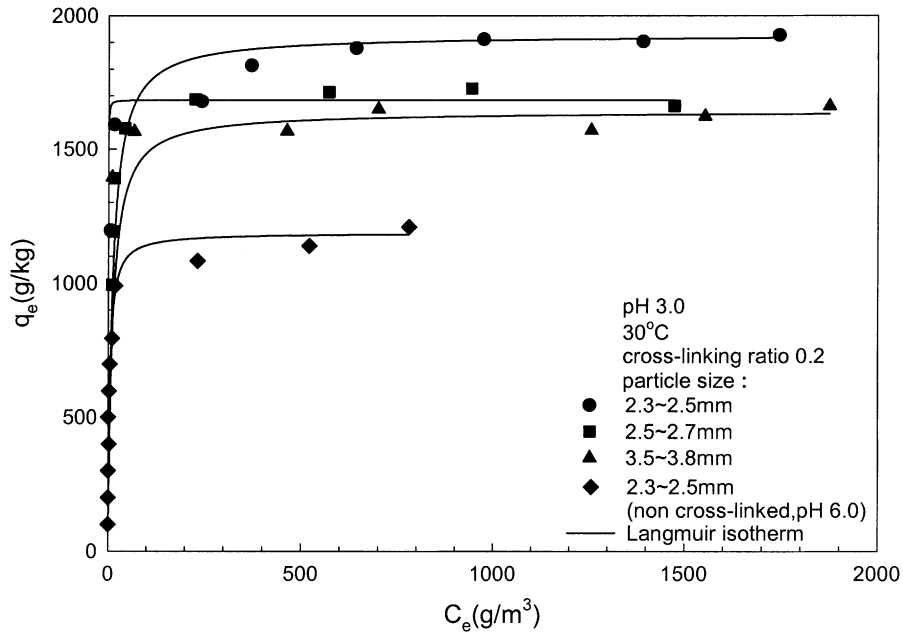
Fig. 2. Equilibrium adsorption of RR 189 on chitosan beads at different particle size.

of the non-cross-linked chitosan beads (pH 6.0). It is seen that the saturation adsorption of the cross-linked chitosan beads at pH 3.0 is much larger than that of non-cross-linked chitosan beads at pH 6. This may suggest that at low pH chitosan free amino groups are protonated, causing them to attract anionic dyes [23]. Chitosan forms gel below pH 5.5 and the dye-binding capacity could not be evaluated. The cross-linked chitosan beads have excellent adsorption ability of RR 189 below pH 5.5. The shape of the isotherms looks rectangular because at low equilibrium dye concentration C_e, the equilibrium adsorption density q_e of the cross-linked chitosan beads reaches almost the same q_e as those at high equilibrium dye concentrations. It indicates that the cross-linked chitosan beads have a high adsorption density even at low equilibrium dye concentration. The rectangular shape of the isotherms was also obtained by Yoshida et al. [15]. Fig. 2 also shows that the adsorption capacity decreases slightly with increasing diameter of the chitosan bead. This might suggest that the adsorption took place mainly on the outer surfaces of the particles due to steric hindrance of large dye molecules. The dye uptake increases with a decrease in the particle size since the effective surface area is higher for the same mass of smaller particles.

3.1.1. Langmuir isotherm

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solutes and adsorbent, and is important in the design of adsorption system. The widely used Langmuir isotherm [27] has found successful application in many real sorption
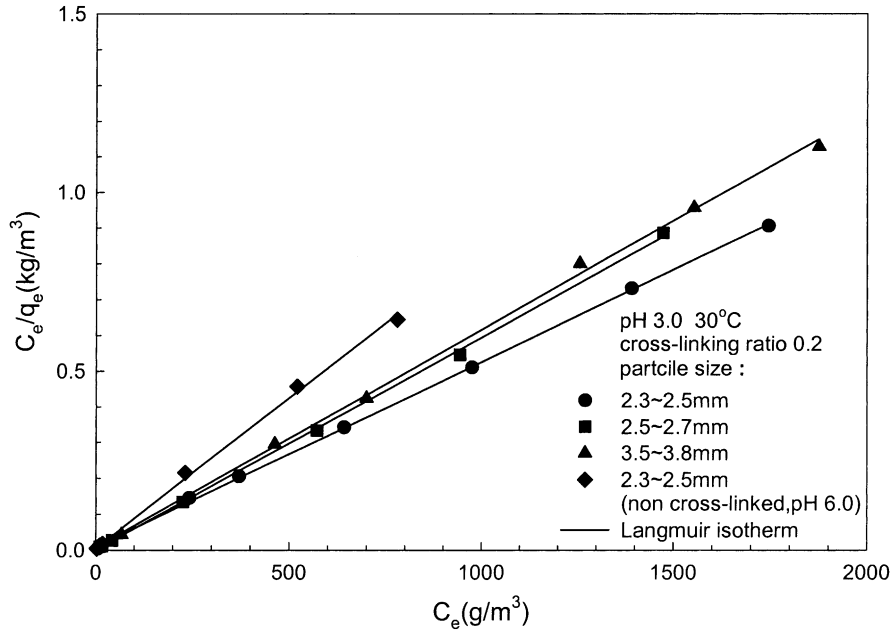
Fig. 3. Langmuir plot at different particle size on chitosan.

processes and is expressed as:

$$q_e = \frac{QbC_e}{1 + bC_e} \tag{2}$$

where Q (g/kg) is the maximum amount of the dye per unit weight of chitosan to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e, and b the Langmuir constant related to the affinity of binding sites (m^3/g). Q represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance. A linearized plot of (C_e/q_e) versus C_e is obtained from the model as shown in Fig. 3. Q and b are computed from the slopes

Table 1
Langmuir and Freundlich isotherm constants at different particles sizes (30 °C; cross-linking ratio, 0.2)

Particle sizes (mm)	Langmuir			Freundlich		
	Q (g/kg)	b (m^3/g)	R^2	Q_f (g/kg)	n	R^2
pH 3.0 (cross-linked)						
Small: 2.3–2.5	1936	0.0609	1.000	1169	14.22	0.859
Medium: 2.5–2.7	1686	1.5987	0.999	1001	12.13	0.704
Large: 3.5–3.8	1642	0.0945	0.999	1345	37.37	0.779
pH 6.0 (non-cross-linked)						
Small: 2.3–2.5	1189	0.2413	0.999	516	7.28	0.770

and intercepts of different straight lines representing the different particle sizes. Table 1 lists the calculated results. The fits are quite well for all the three different particle sizes under the concentration range studied (correlation coefficient, $R^2 > 0.999$). Table 1 indicates that the computed maximum monolayer capacity Q of RR 189 on the cross-linked chitosan beads has a large value ($Q > 1640$ g/kg) and increases with decreasing particle sizes. Table 2 lists the comparison of maximum monolayer adsorption capacity of some dyes on various adsorbents. Compared with some data in literature, Table 2 shows that the cross-linked chitosan beads studied in this work have relatively high adsorption capacity of RR 189 at pH 3.0.

3.1.2. Freundlich isotherm

The well-known Freundlich isotherm [28] used for isothermal adsorption is a special case for heterogeneous surface energy in which the energy term in the Langmuir equation varies as a function of surface coverage strictly due to variation of the sorption. The Freundlich equation is given as:

$$q_e = Q_f C_e^{1/n} \tag{3}$$

Table 2
Comparison of the maximum monolayer adsorption capacities of some dyes on various adsorbents

Dyes	Adsorbent	Maximum monolayer adsorption capacities (g/kg)	Reference
RR 189	Chitosan bead (cross-linked)	1642–1936	This work
RR 189	Chitosan bead (non-cross-linked)	1189	This work
Acid Orange II	Chitosan fiber (cross-linked)	1226–1678	[15]
RR 222	Chitosan (non-cross-linked)	299–380	[3]
RR 222	Chitosan (non-cross-linked)	1026–1106	[16]
RR 222	Chitosan (non-cross-linked)	1653	[17]
RR 222	Chitin	∼100	[3]
RR 222	Activated carbon	∼50	[3]
RB 222	Chitosan (non-cross-linked)	1009	[17]
RB 222	Chitosan (non-cross-linked)	54–87	[3]
RY 145	Chitosan (non-cross-linked)	117–179	[3]
RY 145	Chitosan (non-cross-linked)	885	[17]
Deorlene Yellow	Activated carbon	∼200	[1]
Telon Blue	Activated carbon	∼160	[1]
Astrazone Blue	Silica	∼25	[7]
Mordant Yellow 5	Chitin	52	[6]
AB 25	Chitin	183	[6]
AB 158	Chitin	216	[6]
Direct red 84	Chitin	44	[6]
RY 2	Bacteria	52–124	[11]
RY 2	Activated sludge	333	[13]
RB 2	Rice husk	130	[10]
RB 2	Activated sludge	250	[13]
RB 2	Earth	260	[9]
Remazol Black B	Fungus	286–588	[12]
Acid Blue 29	Peat, fly ash	14, 15	[5]
Basic Blue 29	Peat, fly ash	46, 54	[5]
Disperse Red 1	Peat, bentonite, slag, fly ash	23–50	[5]

where Q_f is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity. Q_f and $1/n$ can be determined from the linear plot of $\ln(q_e)$ versus $\ln(C_e)$. Table 1 lists the calculated results. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. Values, $n > 1$ represent favorable adsorption condition [29]. From Table 1, the exponent n is larger than 10 for adsorption of RR 189 on the different particle sizes of the cross-linked chitosan beads. However, the low correlation coefficients ($R^2 < 0.859$) show poor agreement of Freundlich isotherm with the experimental data.

3.2. Kinetics of adsorption

3.2.1. Effect of initial dye concentration

Fig. 4 shows that the effect of initial RR 189 concentration on the adsorption kinetics of the cross-linked chitosan at pH 3.0, 30 °C and particle size 2.3–2.5 mm. An increase in the initial dye concentration leads to an increase in the adsorption capacity of the dye on chitosan. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial dye concentration. Fig. 4 also shows that most of the dye is adsorbed to achieve adsorption equilibrium in about 8 h, although the data were measured in 48 h. The adsorption density at an initial dye concentration of 7286 g/m^3 is 1.2 times larger than that at 4320 g/m^3.

3.2.2. Effect of temperature

Fig. 5 shows the effect of temperature on adsorption of RR 189 onto the cross-linked chitosan at pH 3.0, particle size 2.3–2.5 mm, cross-linking ratio 0.2 and initial dye
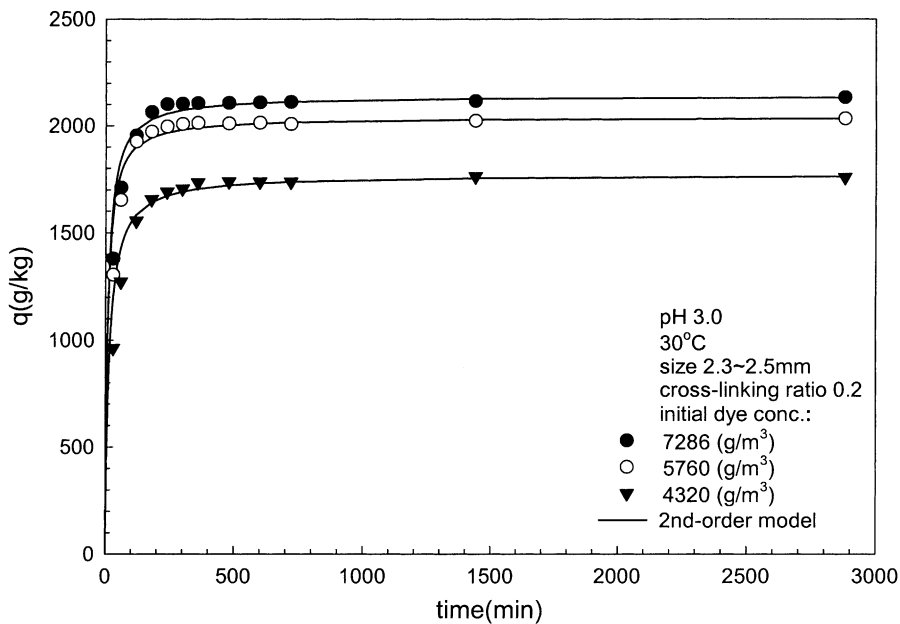

Fig. 4. Adsorption kinetics of RR 189 on cross-linked chitosan beads at different initial dye concentration.
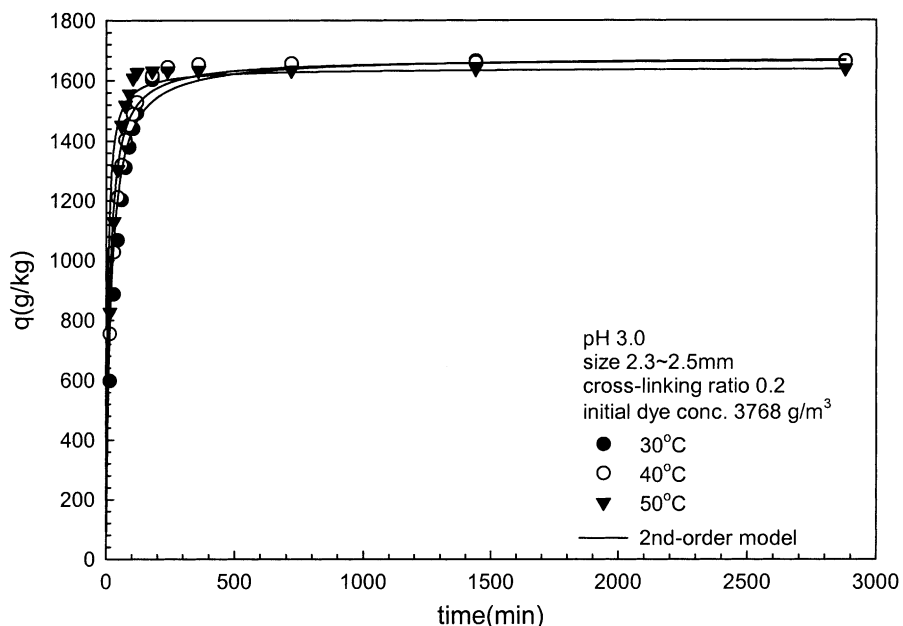
Fig. 5. Adsorption kinetics of RR 189 on cross-linked chitosan beads at different temperature.

concentration $3768\,g/m^3$. Below and above the equilibrium time, the adsorption density q in Fig. 5 shows different trends at different temperatures. Below the equilibrium time, an increase in the temperature leads to an increase in dye adsorption rate dq/dt and q, which indicates a kinetically controlling process. After equilibrium time, the decrease of sorption capacity with increasing the temperature indicates that the adsorption of RR 189 onto chitosan is controlled by an exothermic process [23]. Similar temperature effect on the adsorption trend has also been shown in the case of sorption of acid blue 25 onto peat [34]. However, it can be seen from Fig. 5 that these effects are insignificant. Normal wastewater temperature variations do not significantly affect the overall decolorization performance [23]. However, a significant effect of temperature on the equilibrium isotherm was observed in the low dye concentration range ($<1\,mol/m^3$) for adsorption of Acid Orange II (acid dye) on cross-linked chitosan [15]. Our data shows that the time to reach adsorption equilibrium is about 240, 200 and 120 min at 30, 40 and 50 °C, respectively.

3.2.3. Effect of pH

Fig. 6 shows the effect of pH on adsorption of RR 189 onto chitosan at 30 °C, particle size 2.3–2.5 mm, cross-linking ratio 0.2, and initial dye concentration $4665\,g/m^3$. It indicates that the adsorption capacity increases significantly with decrease in pH. After 6 h of adsorption, the adsorption density q at pH 1.0 (1715 g/kg) is more than twice of that (755, 690 g/kg) at pH 9.0 (cross-linked, non-cross-linked). It can be seen that the pH of aqueous solution plays an important role in the adsorption of RR 189 onto chitosn. Similar results are also mentioned in [15,23]. After 6 h of adsorption, the adsorption capacity is almost the same
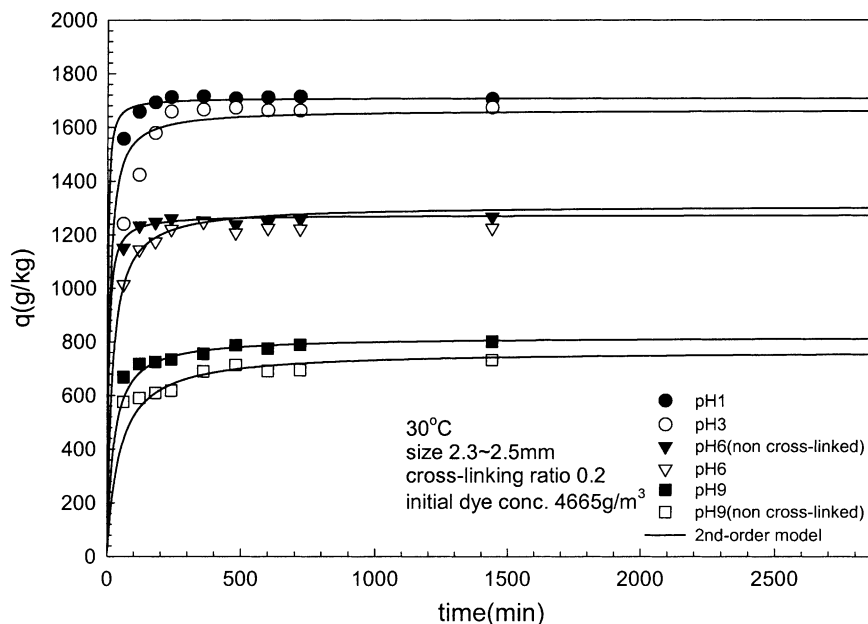
Fig. 6. Adsorption kinetics of RR 189 on chitosan beads at different pH.

for both the cross-linked and the non-cross-linked chitosan at pH 6.0, and relatively slight differences are obtained for the two chitosans at pH 9.0 in this work. Fig. 6 also shows that the time to reach adsorption equilibrium is about 3–4 h.

The pH effect shown in Fig. 6 might suggest possible mechanisms of adsorption of RR 189 on chitosan. Two possible mechanisms are compared: (a) electrostatic interaction between the protonated amine groups ($-NH_3^+$) of chitosan and anionic dye; (b) the chemical reaction between the reactive groups (–Cl) of RR 189 and either the amine groups ($-NH_2$) or the hydroxy groups (–OH) of chitosan. In mechanism (b), HCl is eliminated to form covalent bond between chitosan and dye. If reaction (b) dominates the adsorption of RR 189 on chitosan, then decreasing the pH of solutions should retarded the forward reaction of mechanism (b) because HCl is produced. However, this contradicts with the results obtained in Fig. 6. Besides, at low pH, most amine groups are protonated to form groups $-NH_3^+$ resulting in a low possibility of formation of the covalent bond between chitosan and dye. At lower pH more protons will be available to protonate amine groups of chitosan molecules, thereby increasing the electrostatic attraction of dye molecules to active sites and causing the observed increase in dye adsorption. This explanation agrees with our data on pH effect. Thus, the main reaction involving the adsorption of RR 189 on chitosan may follow mechanism (a) but not mechanism (b).

3.2.4. Effect of ECH/chitosan weight ratio

Fig. 7 shows the effect of cross-linking agent, ECH, on adsorption of RR 189 onto chitosan at pH 1.0, 30 °C, particle size 2.3–2.5 mm and initial dye concentration 5640 g/m³.
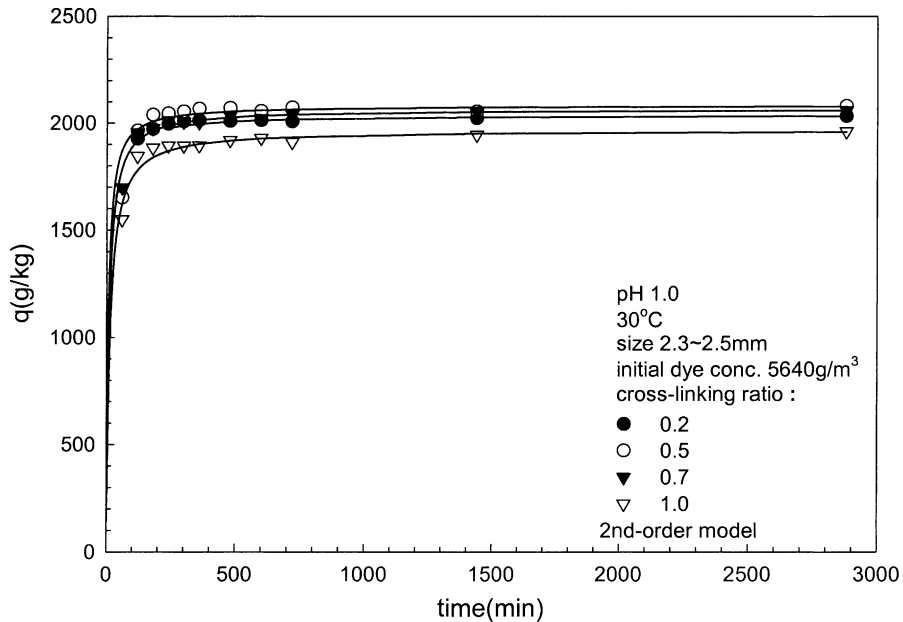
Fig. 7. Adsorption kinetics of RR 189 on cross-linked chitosan beads at different cross-linking ratio.

In Fig. 7, the uptake in adsorption equilibria is similar to each other for cross-linking ratio at 0.2, 0.5 and 0.7, and decreases slightly at ratio 1.0. The chemical cross-linking reaction mainly takes place between the –OH group of chitosan and the chemical cross-linking agent, ECH [24]. The $-NH_3^+$ group of chitosan is the active site to uptake dye RR 189. Thus, the cross-linking ratio would not significantly reduce available adsorption active sites. However, the increase in the cross-linking ratio does increase the steric hindrance for the dye molecule to diffuse through the chitosan beads. This might explain the uptake decreases slightly for cross-linking ratio at 1.0. Fig. 7 indicates that the ECH/chitosan weight ratio is only a minor factor in the adsorption of RR 189 onto chitosan in the range we studied. It also shows that the time to reach adsorption equilibrium is about 4 h for the four different cross-linking ratios.

3.3. Rate constant studies

In order to investigate the mechanism of adsorption, the pseudo first-order and pseudo second-order equations were used to test the experimental data of initial concentration, temperature, pH and the ECH cross-linking ratio. The first-order rate expression of Lagergren and Annadurai and Krishnan [30,31] is given as:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

where q_e and q are the amounts of dye adsorbed on adsorbent at equilibrium and at time t, respectively (g/kg), and k_1 is the rate constant of first-order adsorption (per min). A

straight line of $\log(q_e - q)$ versus t suggests the applicability of this kinetic model to fit the experimental data. The equilibrium adsorption density q_e is required to fit the data, but in many cases q_e remains unknown due to slow adsorption processes. Also, in many cases, the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [30,32].

The second-order kinetic model [32,33] is expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 (kg/g per min) is the rate constant of second-order adsorption. If second-order kinetics are applicable, the plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand and the equilibrium adsorption density, q_e, can be calculated from Eq. (5). Also, it is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step [32,33], which may involve valency forces through sharing or exchange of electrons between dye anions and adsorbent.

The slopes and intercepts of plots of $\log(q_e - q)$ versus t were used to determine the first-order rate constant k_1 and equilibrium adsorption density q_e. Table 3 lists the calculated results. A comparison of results with the correlation coefficients (R^2) is shown in Table 3.

Table 3
Comparison of the first- and second-order adsorption rate constants, and calculated and experimental q_e values for different initial dye concentrations, temperatures, pH and ECH/chitosan weight ratios

| Parameters	$q_{e,exp}$ (g/kg)	First-order kinetic model			Second-order kinetic model		
		k_1 (per min)	$q_{e,cal}$ (g/kg)	R^2	k_2 (kg/g per min)	$q_{e,cal}$ (g/kg)	R^2
Initial dye concentration (pH 3.0) (g/m^3)							
4320	1760	0.0059	541	0.794	3.390E−5	1772	1.000
5760	2034	0.0054	375	0.645	5.527E−5	2040	1.000
7286	2134	0.0056	440	0.684	4.823E−5	2140	1.000
Temperature (°C) (pH 3.0)							
30	1664	0.0071	508	0.761	3.337E−5	1679	1.000
40	1662	0.0040	253	0.710	4.573E−5	1673	1.000
50	1639	0.0091	144	0.578	9.626E−5	1644	1.000
pH							
1	1715	1.538	1278	0.969	7.366E−5	1710	1.000
3	1672	0.467	438	0.624	1.533E−4	1661	1.000
6	1248	1.255	1072	0.949	4.242E−5	1309	1.000
6 (non-cross-linked)	1266	0.243	113	0.396	1.688E−4	1274	1.000
9	812	0.134	167	0.681	5.084E−5	818	1.000
9 (non-cross-linked)	756	0.109	223	0.678	2.814E−5	765	0.992
ECH/chitosan weight ratio (pH 1.0)							
0.2	2034	0.0026	162	0.478	6.428E−5	2039	1.000
0.5	2082	0.0022	124	0.304	6.968E−5	2084	1.000
0.7	2060	0.0029	222	0.623	5.134E−5	2066	1.000
1.0	1962	0.0023	234	0.544	3.972E−5	1968	1.000
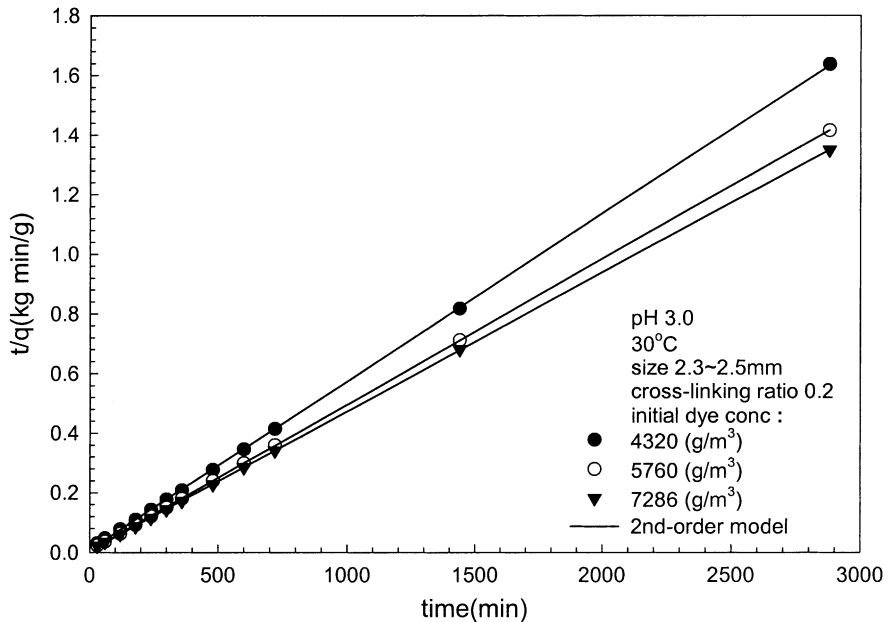
Fig. 8. Plot of the pseudo second-order model at different initial dye concentration.

The correlation coefficients for the first-order kinetic model were low. Also, the calculated q_e values obtained from the first-order kinetic model do not give reasonable values, which are too low compared with experimental q_e values. This suggests that the adsorption of dye RR 189 onto the cross-linked chitosan is not a first-order reaction.

The slopes and intercepts of plots of t/q versus t were used to calculate the second-order rate constant k_2 and q_e. The straight lines in plot of t/q versus t (Fig. 8) show a good agreement of experimental data with the second-order kinetic model for different initial dye concentrations. The similar straight-line agreements are also observed for data at different temperature, pH and ECH/chitosan weight ratio although their plots are not shown in this paper. Table 3 lists the computed results obtained from the second-order kinetic model. The correlation coefficients for the second-order kinetic model are equal to 1.000 for almost all the cases. Also, the calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system we studied belongs to the second-order kinetic model. The similar phenomena are also observed in biosorption of dye RB2, RY2 and Remazol black B on biomass [12,13]. According to the pseudo second-order model, the adsorption rate dq/dt is proportional to the second-order of $(q_e - q)$. Since the cross-linked chitosan beads in our experiments have relatively high equilibrium adsorption density q_e, the adsorption rates become very fast and the equilibrium times are short. Such short equilibrium times coupled with high adsorption capacity indicate a high degree of affinity between the dye RR 189 and the cross-linked chitosan beads [12].

The rate constant k_2 at different temperature (30, 40, 50 °C) listed in Table 3 was applied to estimate the activation energy of the adsorption of RR 189 on cross-linked chitosan beads.

Assume that the correlation among the rate constant k_2, temperature T and activation energy E_a follows the Arrhenius equation, which induces the following expression:

$$\ln k_2 = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \text{const} \tag{6}$$

where R is the gas constant. The slope of plot of $\ln k_2$ versus $1/T$ is used to evaluate E_a, which is 43.0 kJ/mol for the adsorption of RR 189 on cross-linked chitosan beads in temperature range 30–50 °C, at pH 3.0, particle size 2.3–2.5 mm, cross-linking ratio 0.2 and initial dye concentration 3768 g/m^3. This activation energy (43.0 kJ/mol) seems to be small and the adsorption rate is not very sensitive to temperature in the range we studied.

4. Conclusions

This study investigates the adsorption of reactive dye RR 189 on cross-linked chitosan beads, including the effects of particle sizes on the isotherm, and the effects of the initial dye concentrations, temperature, pH and the ECH/chitosan weight ratio on the kinetics of the adsorption processes. The following results are obtained:

1. The cross-linked chitosan beads have a high adsorption capacity to remove dye RR 189. The maximum monolayer adsorption capacities of cross-linked chitosan beads with diameters 2.3–2.5, 2.5–2.7 and 3.5–3.8 mm are 1936, 1686 and 1642 g/kg, respectively, at pH 3.0, 30 °C and ECH/chitosan weight ratio 0.2. Compared with conventional adsorbents, the cross-linked chitosan beads under study are much more effective.
2. A decrease in the pH of solutions leads to a large increase in the adsorption capacity of dye RR189 on the cross-linked chitosan beads. The results improve the adsorption ability of chitosan for the removal of color from acid solutions, in which non-cross-linked chitosan dissolves.
3. The Langmuir equation agrees very well with the equilibrium isotherm for the three particle sizes and the entire concentration range we studied. However, to fit the isotherm data by the Freundlich equation gives a low correlation coefficient.
4. Both the initial dye concentration and the pH of aqueous solutions significantly affect the adsorption capacity of dye RR189 on the cross-linked chitosan. However, the adsorption of the dye on chitosan is slightly influenced by the temperature and the ECH/chitosan weight ratio.
5. The pseudo second-order kinetic model agrees very well with the dynamical behavior for the adsorption of dye RR189 on cross-linked chitosan beads under several different initial dye concentrations, temperatures, pH and the ECH/chitosan ratios in the whole ranges we studied. On the contrary, the pseudo first-order kinetic model fits the experimental data poorly for the entire range under study. This suggests that the rate-limiting step may be the chemical adsorption but not the mass transport.

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