Application of Chitosan-Coated Quartz Sand for Congo Red Adsorption from Aqueous Solution

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ABSTRACT: The preparation, characterization, and environmental application of chitosan-coated quartz sand for Congo red adsorption have been investigated. The absorbent was characterized by Fourier transform infrared spectrophotometer (FTIR) and scanning electron microscope (SEM). The experiments were carried out in a batch system to optimize operation variables: contact time, Congo red concentration, absorbent dosage, temperature, and pH. The optimum conditions for Congo red adsorption were pH 5, 45°C and contact time of 4 h. An amount of 1 g of chitosan-coated quartz sand could successfully remove 96% of the dye form 50 mg/L Congo red solution. The adsorption kinetics and equilibrium isotherms showed that the sorption processes were better fitted by pseudo-second order equation and Langmuir equation, respectively. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1766–1772, 2012

Key words: chitosan; quartz sand; absorption; coated; Congo red

INTRODUCTION

Colored compounds comprising pigments and dyes are used widely in the textile, plastic, food, dye, paper, printing, pharmaceutical, and cosmetic industries.[1] Thus, effluents from these industries contain various kinds of synthetic dye stuffs. Congo red is a benzidine-based dye (Fig. 1). That is expected to metabolize to benzidine, which is a known human carcinogen.[2] Various physical and chemical techniques, other than adsorption, like coagulation, chemical oxidation, froth floatation, oxidation or ozonation, membrane separation, and solvent extraction processes have been used by a number of researchers for the removal of organics as well as inorganics from the wastewater; however, these processes are effective and economic only in the case where the solute concentrations are relatively high.[3] Also, these treatments involve high operational cost and aerobic digestion. Adsorption is a physiochemical wastewater treatment in which dissolved molecules are attached to the surface of an adsorbent by physical/chemical forces.[4] This technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents, and it proved to be an effective and attractive process for the removal of nonbiodegradable pollutants (including dyes) from wastewater.[5] To decrease the cost of treatment, some attempts have been made to find low cost adsorbents.

Chitosan (CS), a naturally occurring linear polymer of glucosamine (Fig. 2), has exhibited excellent adsorption capacity for anionic dyes because chitosan molecules contain a large number of active amine (—NH$_2$) groups. CS-based adsorbents are versatile materials in view of their use in different forms; from powder or beads to film types. Recent papers reported that CS-based adsorbents that are usually used in the form of films have shown the highest adsorption capacity for numerous dyes. However, low density of CS films limits their commercial application as an adsorbent. In previous studies, various types of solids have been coated with chitosan such as bentonite,[6] perlite,[7] montmorillonite,[8] alumina,[9] activated clay,[10] calcium alginate, and silica.[11] Quartz sand is a low-cost material with a simple component, which is wildly used in water treatment. Embedding chitosan with quartz sand can provide physical support and increase the accessibility of binding sites. The aim of this study is to investigate the adsorption behavior of chitosan-coated quartz sand toward Congo red dye.

MATERIALS AND METHODS

Materials

Chitosan (CS, >90% deacetylation) was purchased from Zhejiang Ocean Biochemical. Congo red (CR)
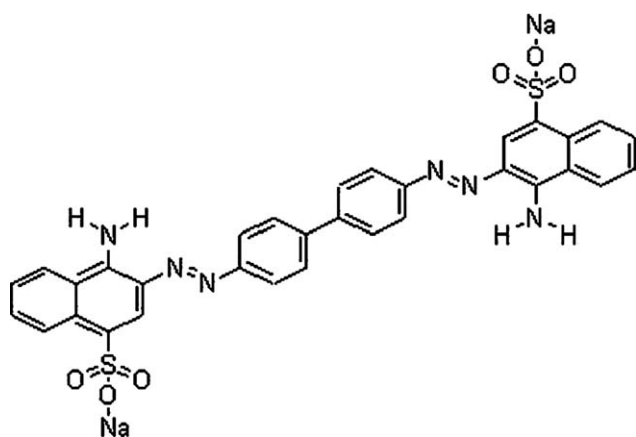
Figure 1 Molecular structure of Congo red.

and quartz sand (QS) were commercially available. Sodium hydroxide and glacial acetic acid were analytically pure. All solutions were prepared by distilled water.

Pretreatment of quartz sand

The quartz sand was sieved to obtain 20–40 mesh size particle (diameter 0.45–1 mm), dipped in $0.1M$ HCl for 24 h, and then washed with distilled water. After that, the quartz sand was heated for 2 h at a constant temperature of 80°C. Then the quartz sand was prepared.

Preparation of chitosan-coated quartz sand

Four grams of CS powder was added into 100 mL acetic acid solution (2%, v/v), and then stirred for 1 h to get CS solution (4%, w/v). Pretreated quartz sand (30 g) was mixed with 25 mL chitosan solution. The obtained suspension was homogenized with a stirrer, and then spread over a glass plate. When dried, the material was immersed in NaOH solution (2% w/v) till natural shedding. Subsequently, the chitosan-coated quartz sand (CS-Q) obtained was washed with distilled water, dried in air.

Characterization of CS-Q

The samples were grounded into powder for the preparation of KBr pellets. IR spectra of the pow-

dered samples were recorded on Nicolet-360 FTIR spectrometer with KBr pellet. The spectrum was corrected for the background noise.

Micrographs of these samples were taken by Nova400NanoSEM. Before observation of SEM, all samples were fixed on aluminum stubs and coated with gold.

Batch adsorption studies

A stock solution of 200 mg/L CR was prepared freshly each time the adsorption experiment was conducted. The stock solution was then diluted to 50 mg/L (unless otherwise stated). In general, adsorption experiments were conducted by adding 1 g of CS-Q (unless otherwise stated) into 50 mL CR solutions in 250 mL glass vials. The batch adsorption was carried out on a shaker at 120 rpm under room temperature (25°). After adsorption, the solutions were filtered and analyzed at a wavelength of 498 nm using UV–Visible spectrophotometer. According to the decreasing of CR concentration in the adsorption, absorbance and decolorization rate were calculated.

RESULTS AND DISCUSSION

Characterization of CS-Q

The infrared spectra of chitosan (CS), quartz sand (QS), and chitosan-coated quartz sand (CS-Q) are shown in Figure 3. It was found that the major peaks of chitosan at 898, 1096, 1598, 1640, and 3440 cm^{-1} belonging to pyranose ring, glucoside, amino, acetamide, and hydroxyl groups, respectively. The absorption bands at 723 and 1020 cm^{-1} in quartz sand are attributed to the symmetric Si—O—Si stretching and asymmetric Si—O stretching, respectively. Compared with spectra of quartz sand, the absorption bands of chitosan-coated quartz sand at 3455 cm^{-1} and 1438 cm^{-1} become stronger with the addition of chitosan. The peak at 3455 cm^{-1} is due to stretching vibration of —OH, which indicates surface property of sand becomes more hydrophilic, whereas the peak of 1438 cm^{-1} suggests the involvement of amine groups in the binding of SiO_2 molecules. No significant shift in wavenumber was observed for the peak at 1020 cm^{-1} and 723 cm^{-1}
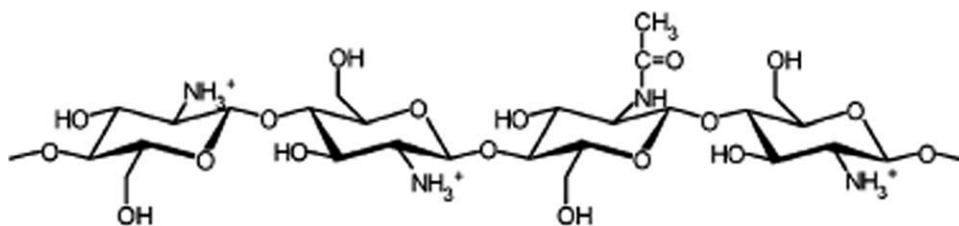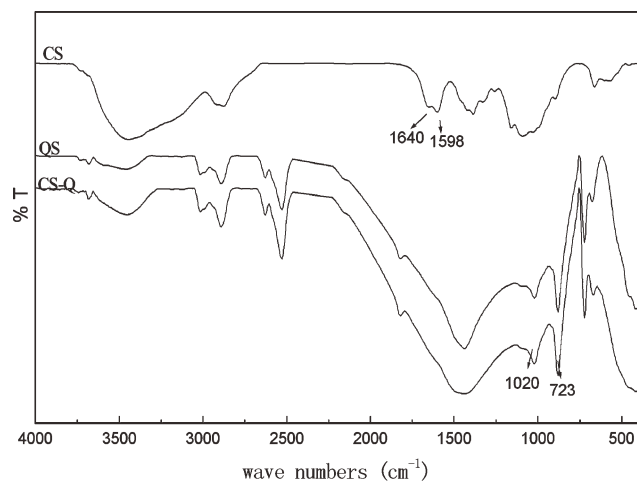

**Figure 2** Molecular structure of chitosan.

Figure 3 FTIR spectra of CS, QS, and CS-Q.

corresponds to Si—O and Si—O—Si groups; therefore, it is likely that no chemical interaction occurs between SiO_2 molecules and chitosan molecules.

Figure 4 shows SEM micrographs of quartz sand and chitosan-coated quartz sand. The image of quartz sand show rugged and porous surface structure and the pores with diameter smaller than 1 μm can be clearly observed on the surface, which favor the load of chitosan onto quartz sand. Layer-by-layer structure could be seen clearly on both images of CS-Q, suggesting that chitosan combined with quartz sand successfully. The presence of layer structure provides suitable sites for Congo red adsorption.

Effect of contact time on adsorption

To investigate the effect of contact time on adsorption capacities of CR, 1 g adsorbent and 50 mL CR solution (initial concentration 50 mg/L) were used. It is observed from Figure 5 that the adsorption of CR onto CS-Q is rapid from the beginning of the experiment and thereafter it proceeds at a slower rate and finally reaches to equilibrium. As illustrated
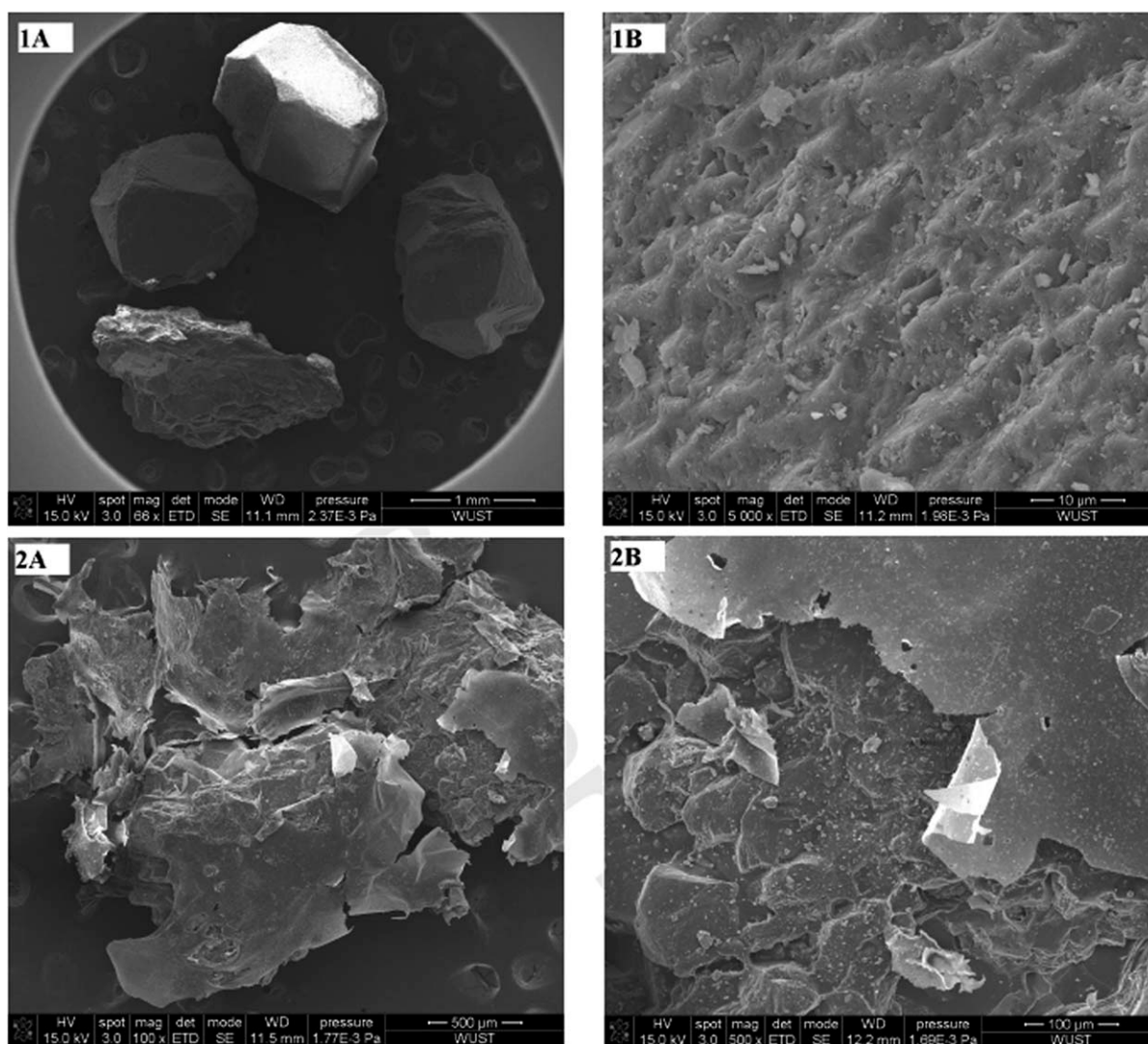
Figure 4 SEM micrographs of quartz sand (1) and chitosan-coated quartz sand (2).
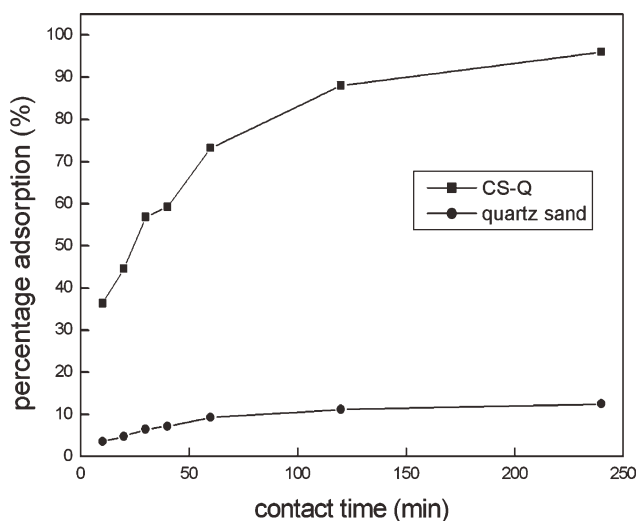
Figure 5 Influence of contact time on adsorption.

Figure 6 Influence of CR concentration on adsorption.

in Figure 5, the removal efficiency of CR onto CS-Q by adsorption for 1 h can reach up to 73%. The percentage of CR adsorption increases to 88% in the condition of double time. However, the percentage of CR removal by quartz sand was only 9% at 2 h, it indicate that the adsorption capacities of CR onto CS-Q was mainly attributed to chitosan. According to recent paper,[6] there are four common steps involved in an adsorption process. The first step is bulk diffusion process in which adsorbates migrate from bulk solution onto the surface of the adsorbent. Second is the film diffusion where the adsorbates diffuse through boundary layer to the adsorbent surface. Pore diffusion or intraparticle diffusion then takes place which allows adsorbates to diffuse from the surface to the inner part of the adsorbent particles and finally adsorbed on the active sites. That is why the adsorption becomes slower near the equilibrium. Figure 5 also shows that percentage of CR adsorption can reach to 96% after adsorption for 4 h. Based on the above results, 4 h was fixed as equilibrium time throughout this study.

Effect of initial CR concentration on adsorption

The effect of the initial CR concentration on dye removal were carried out by vibrating 50 mL various dye concentrations of CR solution and adding 1 g adsorbent at room temperature for 4 h. The test show that the amount of CR molecule adsorbed onto CS-Q increased from 1.004 mg/g to 3.523 mg/g with an increase from 20 to 200 mg/L in the initial concentration of dye solution, whereas percentage adsorption decreased from 97.41% to 35.25% (Fig. 6). The adsorbing capability increasing with the initial CR concentration is due to the increase in the driving force of the concentration gradient with the higher initial dye concentration.[12] The adsorption of dyes by CS-Q is
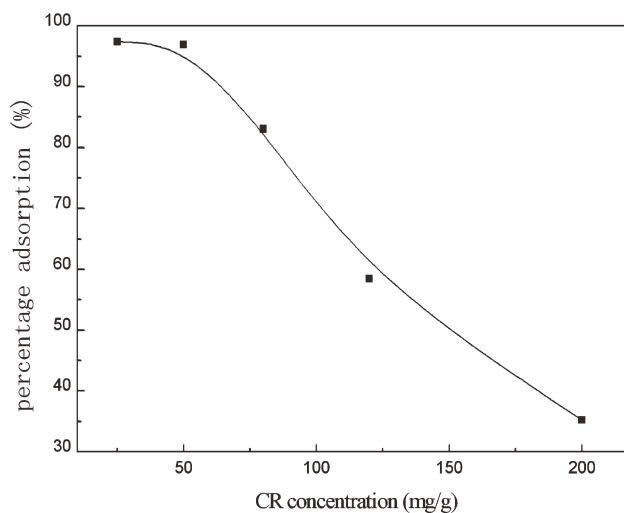
very intense and reaches equilibrium very quickly at low initial concentration. This is because, in the case of lower concentrations, the ratio of initial number of dye molecules to the available adsorption sites is low and subsequently the molecules form itself into monolayer coverage at the outer interface of the adsorbent. In the case of higher concentrations, the removal of dyes depends on the concentration gradient and the diffusion of exchanging molecules within CS-Q, because of the number of available adsorption sites is a constant.[13] So, the amounts of unadsorbed molecules increase with the initial dye concentration, leading to the decrease of adsorption.

Effect of CS-Q dosage on adsorption

To investigate the effect of CS-Q dosage on adsorption capacities of CR, 50 mL CR solution (initial concentration 50 mg/L) were used. The results show in Figure 7, the percentage adsorption increase with
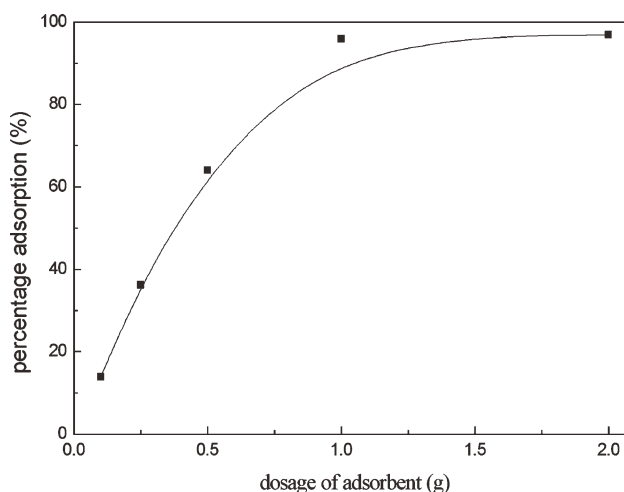

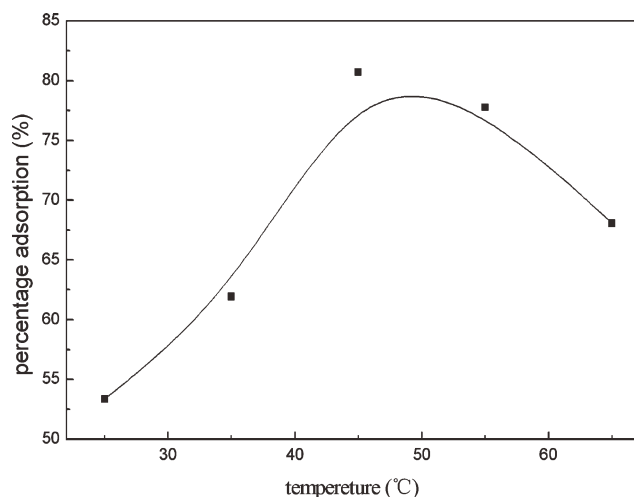**Figure 7** Influence of dosage of adsorbent on adsorption.

Figure 8 Influence of temperature on adsorption.

CS-Q dosage. This can be attributed to increased adsorbent surface and availability of more adsorption sites. However, if the adsorbent dosage increases to a certain amount, the percentage adsorption increases rarely with the CS-Q dosage. This may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to CR molecules and an increase in diffusion path length. The odds of contact between CR molecules and effective group of adsorbent decreased, leading to the decrease of adsorption efficiency. Therefore, 1 g is chosen as the dosage of CS-Q.

Effect of temperature on adsorption

The effect of temperature on dye removal was carried out in the 50 mL dye solution (50 mg/L), by adding 1 g adsorbent under various temperature for 4 h. Figure 8 shows that uptake of Congo red by CS-Q appear to increase (25–45°C) firstly and then decrease (45–65°C) with an increase in temperature. An increase in temperature is followed by an increase in the diffusivity of the dye molecule, moreover, the dimensions of the chitosan pores increased with temperature, which reduce the contribution of intraparticle diffusion resistance.[14] So, the increase with the temperature seems to decrease the impact of the boundary-layer effect. Thus, the adsorption increases as the temperature increases from 25 to 45°C. According to recent literature, the adsorption of organic compounds (including dyes) is an exothermic process (negative value of enthalpy change) which is responsible for reduction in adsorption as the temperature is increased. Besides, when temperature is increased, the physical bonding between CR molecules and the active sites of the CS-Q will weaken, and the interaction forces between CR molecules and the solvent

become stronger than CR molecules and CS-Q because of the increasing solubility of the dyes.[15] Consequently, the dyes are more difficult to adsorb, and the adsorption is step-down while the temperature increases from 45 to 65°C.

Effect of pH on adsorption

Figure 9 shows the percentage adsorption of initial CR at different pH solution. It can be observed that the adsorption efficiency of the adsorbents increases with an increase in pH of the initial solution from 3 to 4 and keep constant from 4 to 6. This may be attributed to the fact that pH affects the surface charge of the adsorbent. Chitosan is a weak base and is insoluble in water and organic solvents; however, it is soluble in dilute aqueous acidic solution which can convert the amine group in CS-Q into a soluble form $R-NH_3^+$.[16] So, chitosan is polycationic in acidic medium: the free amino groups are protonated and this facilitates electrostatic interaction between the adsorbent and the anionic ($R-SO_3^-$) group in the CR molecule.[17] Consequently, high adsorption capacity of CR on adsorbent occurs when pH is around 4–6. Below this range, a large excess of competitor anions limits adsorption efficiency.[18] That is why the percentage adsorption decreases from 96% to 89.89% with pH decrease from 4 to 3. However, the percentage adsorption decreases from 96.01% to 59.22% with increases in initial pH of CR solution from 6 to 12 due to successive deprotonation of positive charged groups on the adsorbent and electrostatic repulsion between negatively charged sites on the absorbent and CR molecules. Moreover, the decrease in percentage adsorption could also be interpreted by enhanced formation of OH^- ions that compete with the dye anionic species for the adsorption sites.
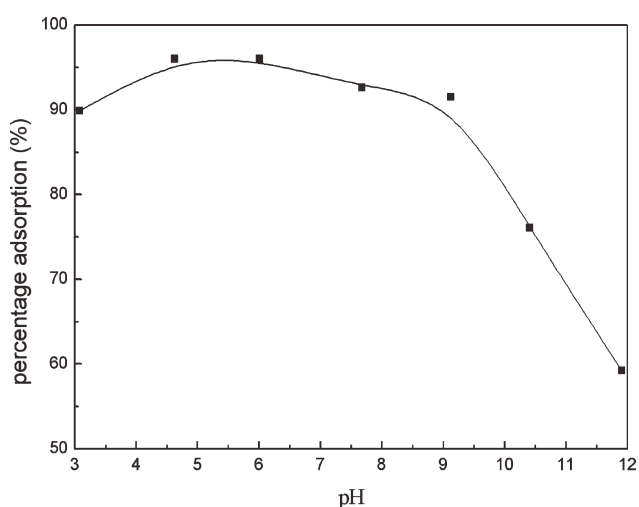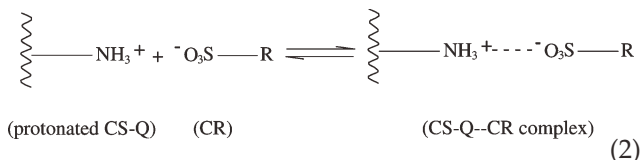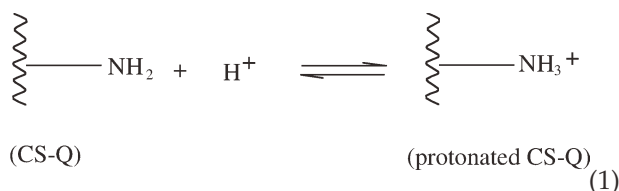

Figure 9 Influence of pH on adsorption.

Based on the results obtained from the pH study, the mechanism of CR adsorption process can be represented by the following equations:

$$\text{(CS-Q)} \qquad \text{(protonated CS-Q)} \tag{1}$$

$$\text{(protonated CS-Q)} \quad \text{(CR)} \qquad \text{(CS-Q--CR complex)} \tag{2}$$

However, CR also contains amino ($-NH_2$) and azo ($-N=N-$) groups. Therefore, binding of CR on CS-Q surface via hydrogen bonding and Van der Waals forces cannot be ruled out.[19]

Adsorption isotherm

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence, two important isotherms were selected in this study, which were namely Langmuir and Freundlich isotherms. The Langmuir isotherm model assumes monolayer coverage of adsorbate on a homogeneous adsorbent surface. This model does not consider surface heterogeneity of the sorbent. It assumes adsorption will take place only at special site on the adsorbent. The Freundlich isotherm model is an empirical equation that describes the surface heterogeneity of the sorbent. It considers multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.[20]

The Langmuir isotherm is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{bq_{\max}C_e} \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), $q_{\max}$ (mg g^{-1}) and b (mg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. $q_{\max}$ and b are calculated from the slopes and intercepts of the straight lines of plot of $1/q_e$ versus $1/C_e$.

The Freundlich adsorption isotherm can be expressed as follows:

$$\ln q_e = \ln k_f + \frac{1}{n}\ln C_e \tag{4}$$

where k_f and n are Freundlich adsorption isotherm constants, being indicative of the extent of the

TABLE I
Adsorption Isotherm Constants for Adsorption of Congo Red on Chitosan-Coated Quartz Sand at 25°C

Dye	Freundlich adsorption model			Langmuir adsorption model		
	n	k	R^2	q_0	B	R^2
CR	5.0100	1.4798	0.8464	3.5625	0.3772	0.9986

adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. k_f and $(1/n)$ can be determined from the linear plot of $\ln q_e$ versus $\ln C_e$.

Table I shows the calculated values of Freundlich and Langmuir model's parameters. The values of R^2 of Langmuir and Freundlich models are 0.9986 and 0.8464, respectively. It can be concluded that the Langmuir isotherm best represents the equilibrium adsorption of CR on chitosan-coated quartz sand, which suggests the monolayer coverage of the dye on the surface of the adsorbent. Similar behavior was also found for the adsorption of CR onto chitosan/montmorillonite nanocomposite.[8]

Kinetics of adsorption

To investigate the adsorption kinetics of CR onto CS-Q, two different kinetics models, pseudo first-order and pseudo second-order rate models were used in this study.

The pseudo-first-order rate equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{5}$$

In the above equation, q_e and q_t denote the amount adsorbed at equilibrium and at any time t, respectively, and k_1 is the first-order rate constant.

The pseudo-second-order rate equation is represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e} \tag{6}$$

In the above equation, q_e and q_t denote the amounts adsorbed at equilibrium and at any time t, respectively, and k_2 is the second-order rate constant.

The calculated parameters of the pseudo-first order and second order kinetics parameters are given in Table II. On comparing the R^2 values obtained for first-order and second-order kinetics, it can be easily concluded that the ongoing reaction proceeds via a pseudo-second-order mechanism rather than a pseudo-first-order mechanism. It indicates that chemisorption might be the rate-limiting step that controls these adsorption processes.[21] The

TABLE II
Adsorption Parameters of Kinetic for the Adsorption of 50 mg/L Congo Red on Chitosan-Coated Quartz Sand

Dye	$q_{e(exp)}$ (mg/g)	Pseudo first-order rate models			Pseudo second-order rate models		
		k_1 (min^{-1})	q_{e1} (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	q_{e2} (mg/g)	R^2
CR	2.2242	1.8424×10^{-2}	1.6692	0.9960	1.5615×10^{-2}	2.4612	0.9979

adsorption of CR probably takes place via surface exchange reactions until the surface functional sites are fully occupied; thereafter, dye molecules diffuse into the polymer network for further interactions and/or reactions.

CONCLUSIONS

This study demonstrates that CS-Q is a promising absorbent for the removal of CR from aqueous solution. This is due to the rapid uptake of CR and a very high percentage adsorption of 96%. The adsorption process however was affected by several physicochemical factors such as contact time, CR concentration, CS-Q dosage, temperature, and pH. The kinetic study indicated that the CR adsorption obeyed pseudo-second-order model better than pseudo-first-order model. The adsorption process was better fitted by the Langmuir than the Freundlich model.

References

1. Chiou, M. S.; Ho, P.; Ho, Y.; Li, H. Y. Dyes Pigments 2004, 60, 69.
2. Mall, I. D.; Srivastava, V. C.; Agarwal, N. K.; Mishra, L. M. Chemosphere 2005, 61, 492.
3. Gupta, V. K.; Suhas. J Environ Manage 2009, 90, 2313.
4. Sharma, P.; Kaur, H.; Sharma, M.; Sahore, V. Environ Monit Assess 2011, 62, 233.
5. Aksu, Z. Process Biochem 2005, 40, 997.
6. Ngah, W. S. W.; Ariff, N. F. M.; Hanafiah, M. A. K. M. Water Air Soil Pollut 2010, 206, 225.
7. Hasan, S.; Krishnaiah, A.; Ghosh, T. K.; Viswanath, D. S.; Boddu, V. M.; Smith, E. D. Ind Eng Chem Res 2006, 45, 5066.
8. Wang, L.; Wang, L. J Hazard Mater 2007, 147, 979.
9. Boddu, V. M.; Abburi, K.; Talbott, J. L.; Smith, E. D.; Haasch, R. Water Res 2008, 43, 633.
10. Chang, M. Y.; Juang, R. S. J Colloid Interface Sci 2004, 278, 18.
11. Vijiaya, Y.; Popuri, S. R.; Boddu, V. M.; Krisnaiah, A. Carbohydr Polym 2008, 72, 261.
12. Crini, G. Dyes Pigments 2008, 77, 415.
13. Knorr, D. J Food Sci 1983, 48, 36.
14. Gaffar, M. A.; El-Rafie, S. M.; El-Tahlawy, K. F. Carbohydr Polym 2005, 56, 387.
15. Cestari, A. R.; Vieira, E. F. S.; Pinto, A. A.; Lopes, E. C. N. J Colloid Interface Sci 2005, 292, 72.
16. Cotoruelo, L. M.; Marques, M. D.; Diaz, F. J.; Rodriguez-Mirasol, J.; Rodriguez, J. J.; Cordero, T. Transp Porous Med 2010, 83, 573.
17. Crini, G.; Badot, P. M. Prog Polym Sci 2008, 33, 399.
18. Yigitoglu, M.; Temocin, Z. Fibers Polym 2010, 11, 996.
19. Ngah, W. S. W.; Ariff, N. F. M.; Hanafiah, M. A. K. M. Water Air Soil Pollut 2010, 206, 225.
20. Vimonsesa, V.; Lei, S.; Jin, B. Chem Eng J 2009, 148, 354.
21. Chiou, M. S.; Kuo, W. S.; Li, H. Y. J Environ Sci Health A 2003, 38, 31.