Carbohydrate Polymers 102 (2014) 755–761

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

# Mechanical and dye adsorption properties of graphene oxide/chitosan composite fibers prepared by wet spinning

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ARTICLE INFO

*Article history:*
Received 12 March 2013
Received in revised form 28 October 2013
Accepted 30 October 2013
Available online 7 November 2013

*Keywords:*
Graphene oxide
Chitosan
Fibers
Adsorption
Fuchsin acid

ABSTRACT

Graphene oxide/chitosan composite fibers were prepared by a wet spinning method, and their mechanical properties were investigated. Experimental results showed that the introduction of graphene oxide at 4 wt% loading can improve the tensile strengths of chitosan fibers. Batch adsorption experiments were carried out to study the effect of various parameters, such as the initial pH value, adsorbent dosage, contact time and temperature on adsorption of fuchsin acid dye. The Langmuir model was used to fit the experimental data of adsorption isotherm, and kinetic studies showed that the adsorption data followed the pseudo-second order model. Thermodynamic studies indicated that the adsorption of fuchsin acid dye on graphene oxide/chitosan fibers was a spontaneous and exothermic process. Our results indicate that the graphene oxide/chitosan fibers have excellent mechanical properties and can serve as a promising adsorbent for the removal of dyes from aqueous solutions.



## 1. Introduction

The discharge of effluents containing dyes into the environment, even at low concentrations, can cause harmful environmental and public problem. These dyes usually have complex aromatic structures which are stable and non-degradable under light or heat, and in presence of oxidizing agents. Therefore, legislation is drawing up more stringent limits on the concentrations of the discharged effluents from dyestuff manufacturing and textile industries.

Various treatment processes such as coagulation, flocculation, reverse osmosis, photo-degradation processes and ion-exchange have been used to remove dyes from wastewaters. However, high energy consumption, complicated design and multiple operations have limited applications of those techniques in industry. Moreover, those methods may generate harmful substances and become ineffective at low dye concentration. In this regard, adsorption appears to be an attractive method for treatment of dye effluents due to its low cost, simplicity of operation, as well as the availability of a wide range of adsorbents (Chatterjee, Lee, Lee, & Woo, 2009). Adsorption technology can handle trace amounts of dye molecules and do not bring other contaminants (Crini & Badot, 2008). To date, numerous adsorbents have been used for the removal of dyes, such as clay (Liu & Zhang, 2007), Kaolin (Nandi, Goswami, & Purkait, 2009), perlite (Dogan, Alkan, & Onager, 2000), and activated carbon (El Qada, Allen, & Walker, 2008).

Chitosan, β-(1-4) acetyl-D-glucosamine, is a linear biopolymer of glucosamine. It can be produced commercially by chemical deacetylation of chitin, a major component of the exoskeleton of crustaceans (such as crabs, lobster and shrimp) and cell walls of fungi and algae, therefore it is the second most abundant biological resource after cellulose. Due to its high contents of amino and hydroxyl functional groups, chitosan based materials have been widely used to remove dyes and metal ions from aqueous solutions. Chitosan gel-beads can effectively adsorb $Cu^{2+}$, $Hg^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Ni^{2+}$, and dyes (Paulino, Guilherme, Reis, Tambourgi Nozaki, & Muniz, 2007; Wong, Szeto, Cheung, & McKay, 2004; Wu, Tseng, & Juang, 2010; Zhao et al., 2007) from wastewaters. Modification of chitosan by chemical methods such as insertion of new functional groups, cross-linking and grafting with polymers (Laus & de Fávere, 2011; Singh, Sharma, Tripathi, & Sanghi, 2009), can substantially improve adsorption capacities of chitosan gel-beads. However, few investigations have been focused on the use of chitosan fibers as adsorbents for dye removal because of their weak mechanical properties.

Graphene, a new carbon material with $sp^2$-hybridized single-atom-layer structure, has attracted considerable attention. Graphene possesses a two dimensional structure with specific magnetism (Singh & Yakobson, 2009), and has high carrier

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http://dx.doi.org/10.1016/j.carbpol.2013.10.094

concentration and mobility (Morozov et al., 2005), high mechanical strength (Lee, Wei, Kysar, & Hone, 2008) and thermal conductivity (Balandin et al., 2008). Graphene oxide (GO), as the most important derivative of graphene, has similar properties to graphene and contains abundant hydroxyl, epoxide groups, carbonyl and carboxyl groups (—COOH). These oxygenous groups can make GO easily disperse into some polar solvents and improve the interfacial interaction between GO and polar molecules through strong interaction, and thus the mechanical properties of polar molecules can be changed (Chen et al., 2012).

In this study, GO/chitosan fibers were prepared by a wet spinning method and used as adsorbents for removal of fuchsin acid. The effect of GO addition (loading) on the mechanical properties of the GO/chitosan fibers was investigated. The effect of various experimental parameters on fuchsin acid adsorption, such as the initial dye concentration, contact time, pH, and temperature were studied in detail.

## 2. Materials and methods

### 2.1. Materials

Chitosan (CS > 90.0% deacetylation, viscosity <100cps) was purchased from Qingdao Lanji Tech. Co., Ltd., China. The expandable graphite was supplied by Henglide Graphite Company (Qingdao, China). Fuchsin acid (Chemical formula: $C_{20}H_{17}N_3Na_2O_9S_3$, MW: 585.55 g/mol, AR) was purchased from Tianjin Chemical Reagent Manufacturing Co., Ltd., China. Potassium permanganate, sulfuric acid (98 wt%), hydrochloric acid, sodium nitrate, hydrogen peroxide (30 wt%), acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Other chemical reagents were of analytical grade and all solutions were prepared with deionized water.

### 2.2. Preparation of GO

GO was prepared from expandable graphite using a modified Hummers' method (Hummers & Offeman, 1958). Briefly, expandable graphite (5.0 g), sodium nitrate (5.0 g) and potassium permanganate (30.0 g) were mixed in concentrated sulfuric acid (230 mL) in an ice bath. The mixture was stored at 273 K for 24 h. Next, the mixture was stirred and slowly diluted with deionized water at 308 K and kept for 30 min. Then, the reaction temperature of the suspension was rapidly increased to 371 K and maintained for 15 min. 30% $H_2O_2$ solution was added dropwise to reduce the residual $KMnO_4$ untill no bubbles appeared. The mixture was washed with 5% HCl to remove metal ions and rinsed with deionized water to remove acid. After further centrifugation treatment, different concentrations of GO solutions were prepare through diluting GO with appropriate deionized water.

### 2.3. Preparation of GO/chitosan fibers

GO/chitosan fibers were prepared using a wet spinning method (Speakman & Hamberlain, 1944). In short, chitosan powders were added into the solutions with different GO concentrations (the weight ratio of GO: chitosan was 0%, 2%, 4%, and 6%, respectively). 10% v/v acetic acid was slowly added into the mixture. The mixture was stirred vigorously to make chitosan disperse homogeneously. After vigorously stirred for 6 h, the homogeneous and stable GO/chitosan solutions were obtained. The GO/chitosan solutions were filtered and left standing for at least 30 min under vacuum to remove air bubbles. After filled a certain volume of $N_2$, the GO/chitosan solutions were injected through a 0.5 mm diameter spinneret into the coagulation bath containing 2 M aqueous solution of NaOH and finally collected on a rotating spool. The coagulated fibers were rinsed by deionized water and dried to a constant weight at room temperature.

### 2.4. Characterization of GO/chitosan fibers

The surface morphologies of GO/chitosan fibers were characterized by scanning electron microscope (SEM, JSM 6700F, JEOL Ltd., USA), operating at an accelerating voltage of 5.0 kV. The mechanical properties of the chitosan fibers and GO/chitosan fibers were investigated through measuring the strain–stress curves using the Single Column Mechanical Test Instruments (Instron 5843).

### 2.5. Batch adsorption experiments

Batch adsorption experiments were conducted with GO/chitosan fibers for the removal of fuchsin acid dye from aqueous solution. The desired concentration of dye was obtained by diluting a stock solution of fuchsin acid (1000 mg/L). The batch adsorption experiments were conducted in 50 mL conical flasks with 20 mL of solutions and 10 mg fibers and performed for 3 days in a temperature-controlled water bath shaker (SHZ-82A). The concentration of fuchsin acid dye was measured using a UV-vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd, China) at $\lambda_{max}$ 517 nm.

The adsorption capacity of fuchsin acid dye adsorbed by GO/chitosan fibers at equilibrium, was evaluated using the following equation:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

where $C_0$ and $C_e$ are initial and equilibrium concentrations of fuchsin acid (mg/L), respectively, $m$ is the mass of adsorbent (g), $V$ is volume of the solution (L).

The dye removal percentage $Q$ (%) at time $t$ is calculated by the following equation:

$$Q = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where $C_t$ (mg/L) is the concentration of fuchsin acid dye at time $t$.

The effect of pH on fuchsin acid removal was studied by changing the initial solution pH from 4.0 to 10.0 using small amounts of 1 M $HNO_3$ or 1 M NaOH solution and the initial concentration of the fuchsin acid was 90 mg/L. The effect of adsorbent dosage was conducted by shaking 20 mL of 90 mg/L dye solution containing different amounts of GO/chitosan fibers at 293 K. The GO dosage was chosen from 0.25 to 1.5 g/L in a step size of 0.25 g/L. The adsorption isotherm studies were carried on with different initial dye concentrations (50–150 mg/L, a step size of 20 mg/L) at 293 K. The contact time study was performed with initial fuchsin acid concentration of 90 mg/L and 0.01 g GO/chitosan fibers at room temperature (293 K).

To evaluate the thermodynamic properties, 0.01 g GO/chitosan fibers were added into 20 mL solutions with initial fuchsin acid concentration ranging from 50 to 150 mg/L in a step size of 20 mg/L. The samples were shaken at 293, 313 and 333 K, respectively.

## 3. Results and discussion

### 3.1. Characterizations of GO/chitosan fibers

Fig. 1 shows the SEM images of the fibers with different weight ratio of GO:chitosan. It can be seen that all the fibers have uniform diameters (Fig. 1a–d). With increasing GO contents from 0% to 6%, the fiber surface becomes rough, which could be due to interaction between the chitosan and GO.

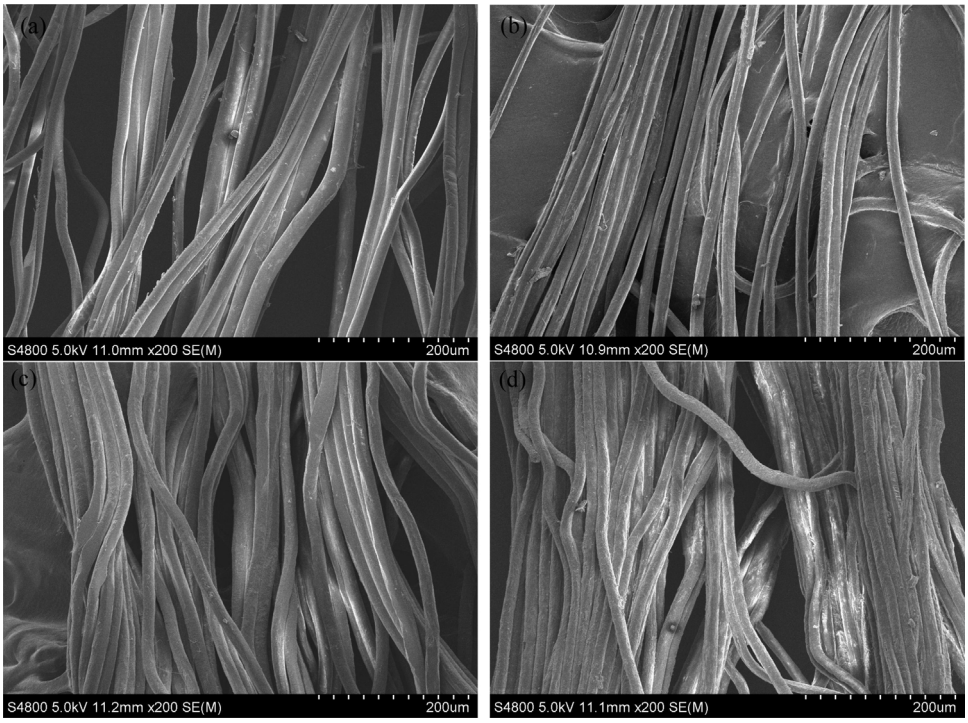


**Fig. 1.** SEM images of the fibers: (a) chitosan fibers, (b) 2 wt% GO, (c) 4 wt% GO, (d) 6 wt% GO.

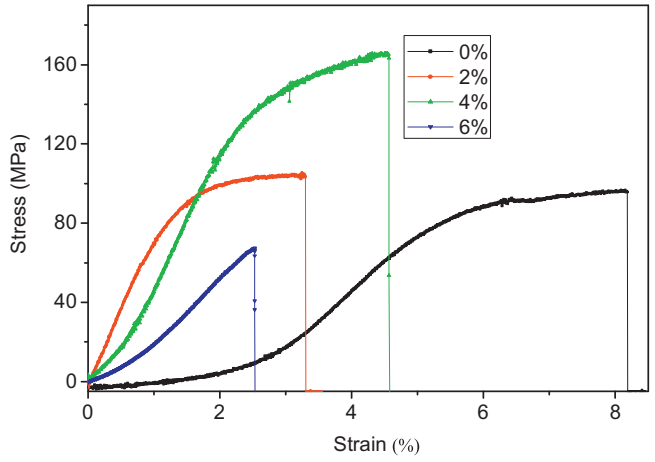


**Fig. 2.** Typical stress–strain curves of GO/chitosan fibers with different GO contents.

### 3.2. Mechanical properties of the fibers

Mechanical properties of the fibers are important for practical applications. Typical stress–strain curves of the chitosan and GO/chitosan fibers are presented in Fig. 2. The Young's modulus of GO/chitosan fibers is higher than that of chitosan fibers. The result is similar to a previous report on polymer fibers reinforced by inorganic nano-fillers (Sa & Kornev, 2009). The tensile strength of chitosan fibers is only 96.7 MPa, and can be improved after adding GO into chitosan. The tensile strength of GO/chitosan fibers increases to 105.2 MPa at a GO loading of 2 wt% and reaches the maximum value of 165.8 MPa at 4 wt% GO. This phenomenon is because when appropriate amounts of GO is dispersed homogeneously into the chitosan matrix with a strong GO-chitosan interaction, there exists effective load transfer from the matrix to single-layer GO sheets which enhances tensile strength and also help absorb more energy before fracture (Chen et al., 2012). With further increasing GO content to 6%, the tensile strength of GO/chitosan fibers decreases abruptly to about 67.3 MPa. The rapidly decreased tensile strength may be attributed to the phase separation effect at very high GO content.

SEM images in Fig. 3 show cross-section morphologies of the fractured chitosan and GO/chitosan fibers after mechanical tests. The cross section of the chitosan fiber (Fig. 3a) looks loose and has some grooves. Comparing with the chitosan fiber, the surface of fractured GO/chitosan fibers (Fig. 3b and c) also shows grooves, but the groove density has increased apparently due to strong interaction between the GO and chitosan, which causes higher tensile strengths in GO/chitosan fibers. Fig. 3d shows a relatively smooth surface of the 6% GO/chitosan fiber. It indicates that high GO content leads to heterogeneous dispersion of GO in the chitosan matrix, resulting in poor tensile strength of the fiber.

### 3.3. Fuchsin acid adsorption

#### 3.3.1. Effect of pH value

The pH value of adsorption medium is one of the most important parameters that influences adsorption property of an adsorbent. Fig. 4a shows the effect of the initial pH on the adsorption of fuchsin acid onto GO/chitosan fibers. The underlying mechanism is likely to be the ionic electrostatic interactions between the dye ions and the amino groups from the fibers. In aqueous solution, the fuchsin acid can be ionized and converted to anionic dye ions with sulfonate groups (Zhou et al., 2011).

$$\text{Dye—SO}_3\text{Na} \rightarrow \text{Dye—SO}_3^- + \text{Na}^+$$

in acidic solution, the amine groups (—$NH_2$) of chitosan can be protonated by hydrogen ions ($H^+$).

$$\text{Chitosan—NH}_2 + \text{H}^+ \rightarrow \text{Chitosan—NH}_3^+$$

the removal of fuchsin acid by GO/chitosan fibers occurs mainly due to the electrostatic interaction between the protonated amine

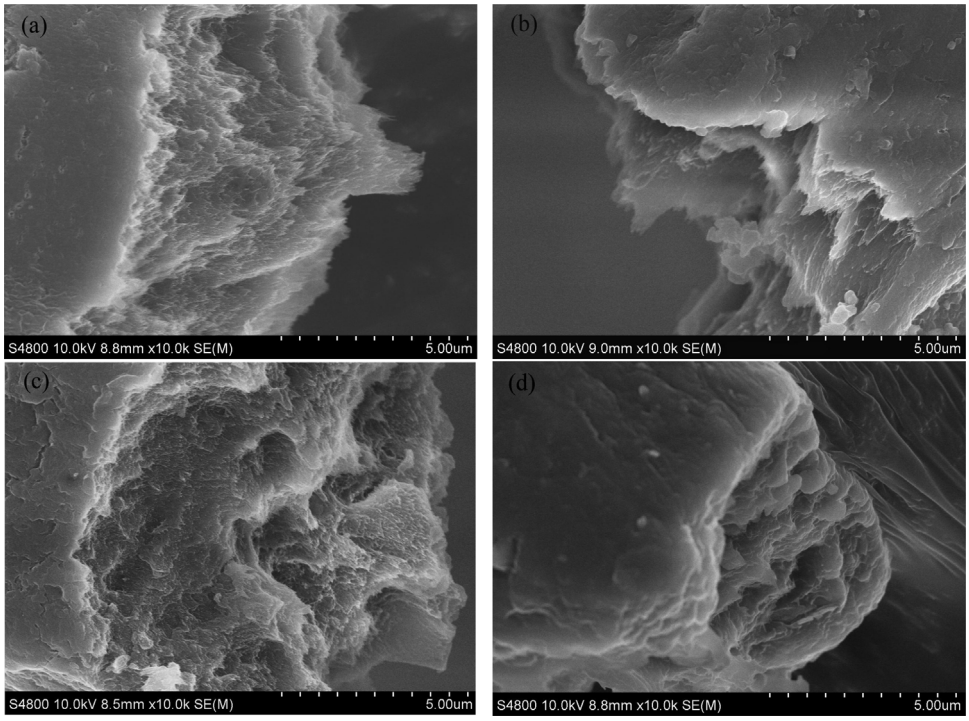


**Fig. 3.** SEM photographs of the fractured surface of the fibers: (a) chitosan fibers, (b) 2 wt% GO, (c) 4 wt% GO, (d) 6 wt% GO.

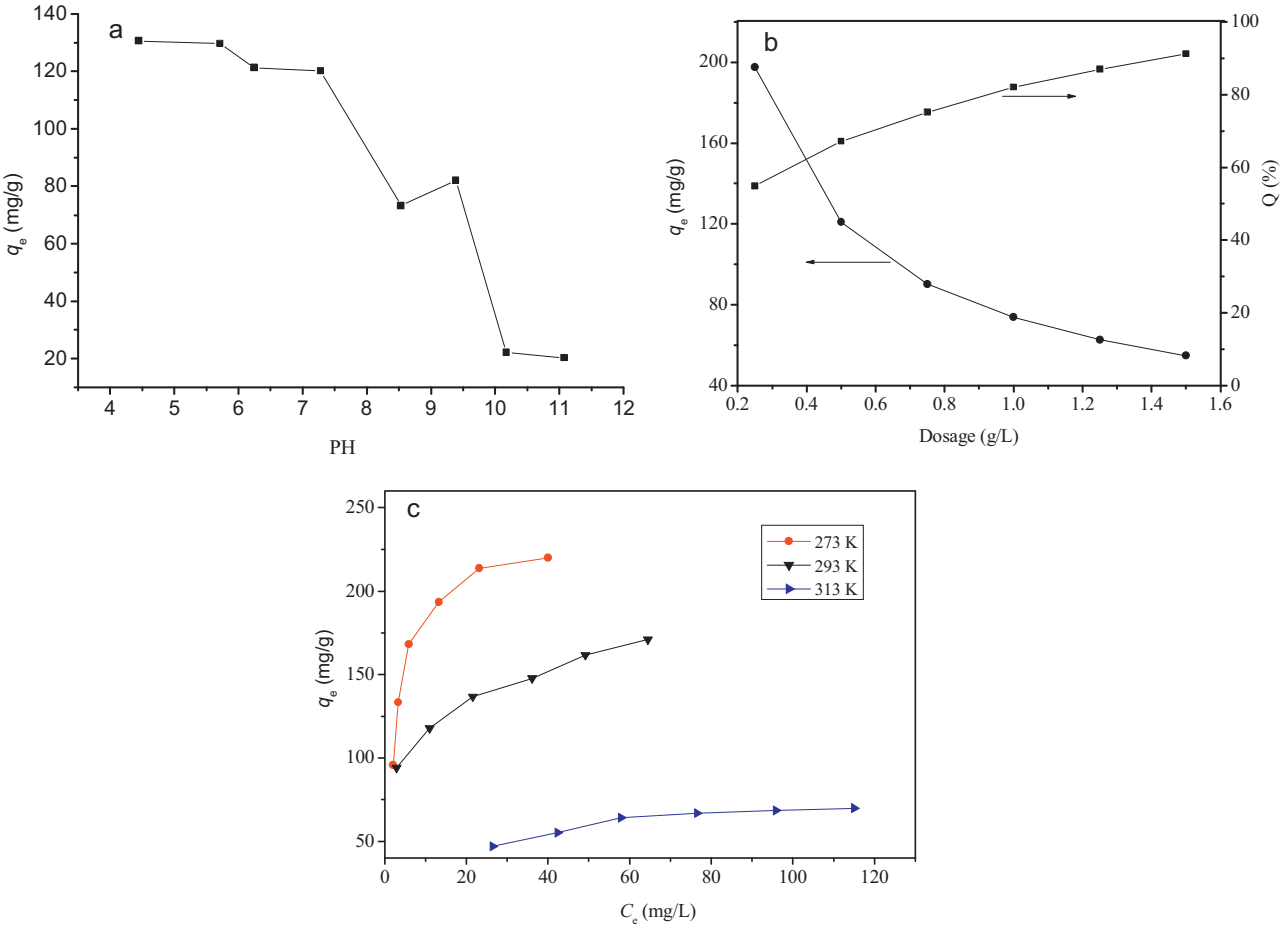


**Fig. 4.** Effect of different factors on fuchsin acid adsorbed by the 6 wt% GO/chitosan fibers: (a) pH effect, (b) dosage effect, (c) temperature effect.

groups on chitosan ($-NH^{3+}$) and the $SO^{3-}$ groups of anionic dyes structures.

$$\text{Chitosan}-NH_3^+ + \text{Dye}-SO_3^- \rightarrow \text{Chitosan}-NH_3^+\cdots SO_3^--\text{Dye}$$

on the other hand, GO prepared by acid oxidation has a large quantity of oxygen containing functional groups (Li et al., 2013) which is favorable for improving the dye adsorption capability of the fibers.

Within the acidic pH range (Fig. 4a), more amine groups are protonated and the electrostatic interaction between the protonated amine groups and the $SO^{3-}$ groups become stronger, which renders the fibers a higher dye adsorption capacity. In basic pH range, the decreased dye adsorption capacity is probably due to (1) successive deprotonation of the positive charged on the adsorbent, (2) increased electrostatic repulsion between negatively charged sites on the adsorbent (Chatterjee et al., 2009) and dye anions, and (3) more adsorption sites combined with hydroxyl ions (Wang & Wang, 2007).

### 3.3.2. Effect of adsorbent dosage

The effect of adsorbent dosage on fuchsin acid removal is shown in Fig. 4b. As the adsorbent dosage increases from 0.25 to 1.5 g/L, the fuchsin acid removal percentage by GO/chitosan fibers (6 wt% GO) increases from 54.9% to 91.3%, whereas the adsorption capacity decreases from 197.6 to 54.8 mg/g. The increased dye removal percentage at increasing adsorbent dosage is due to increased active sites and surface area for adsorption at higher adsorbent dosage (El Qada, Allen, & Walker, 2006). Almost all active sites are completely exposed and utilized at lower adsorbent dosage, while the active sites of at higher adsorbent dosage are much more than the saturated threshold adsorption point and only part of active sites can be occupied by dye, leading to the decrease of adsorption capacity (Li et al., 2003).

### 3.3.3. Effect of temperature

The effect of temperature on the adsorption of fuchsin acid dye onto the chitosan fibers and GO/chitosan fibers was carried out at different temperatures of 273, 293, and 313 K, respectively. Fig. 4c shows that the equilibrium adsorption capacity of fuchsin acid decreases as the temperature increases. As the temperature increases from 273 to 313 K, the maximum adsorption of GO/chitosan fibers decreases from 220.0 to 69.9 mg/g. This result demonstrates that the adsorption fuchsin acid onto the GO/chitosan fibers is an exothermic process.

## 3.4. Adsorption isotherm

The adsorption isotherm is the most important design parameter in describring the interactive behavior between the adsorbent and adsorbate. Fig. 5 shows the adsorption isotherm of fuchsin acid adsorbed by GO/chitosan fibers. The adsorption capacity increases sharply in the initial stage for low $C_e$, which indicates that there are plenty of readily accessible active sites. With further increasing $C_e$, the increased trend of $q_e$ becomes slow. This may be due to the less active sites being available at the end of the adsorption process and the difficulty of dye diffusion into the micropores on the adsorbent.

The Langmuir equation is the most commonly used model to describe the adsorption isotherm data. It supposes that adsorption takes place on a homogeneous surface by a monolayer and equivalent sorption energies (Langmuir, 1918). The Langmuir equation is expressed as:

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

where $C_e$ (mg/L) is the equilibrium concentration of fuchsin acid, $q_{max}$ (mg/g) represents the maximum adsorption capacity. $k_L$ (L/mg) is Langmuir constant related to the energy of adsorption,

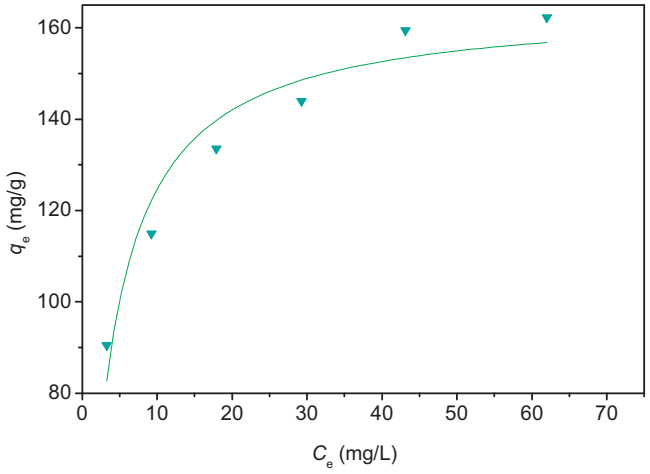


**Fig. 5.** The Langmuir isotherm of fuchsin acid adsorbed by the 6 wt% GO/chitosan fibers.

representing the affinity between adsorbent and adsorbate. $q_{max}$ and $k_L$ were calculated by using the Langmuir equation to fit the adsorption isotherm data and they were 175.4 mg/g and 0.16 L/mg, respectively. The higher determination coefficient $r^2$ (0.9982) of the Langmuir equation suggests that the Langmuir equation can be used to fit the experimental adsorption data and evaluate the maximum dye adsorption capacity.

The Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter ($R_L$), which is defined as follows (Weber & Chakravorti, 1974):

$$R_L = \frac{1}{1 + k_L C_0} \tag{4}$$

where $C_0$ is the highest initial concentration of fuchsin acid (mg/L), $R_L$ value indicates that the Langmuir isotherm is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) and irreversible ($R_L = 0$). The calculated $R_L$ value is 0.04, indicating the adsorption of fuchsin acid onto the GO/chitosan fibers is favorable (Chen, Chen, & Diao, 2010).

## 3.5. Kinetic studies

In order to evaluate the kinetic mechanism that controls the adsorption process, the pesudo-first-order Lagergren equation and the pseudo-second-order rate equation were applied to analyze the experimental data. The pesudo-first-order equation was expressed as follows (Dogan, Alkan, Demirbas, Ozdemir, & Ozmetin, 2006):

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

where $k_1$ is the Lagergren rate constant of adsorption (1/min), $q_e$ and $q_t$ are the amounts of fuchsin acid adsorbed at equilibrium and at time $t$ (min), respectively. The values of $k_1$ and $q_e$ can be calculated from the slope of the plots of $\log(q_e - q_t)$ versus $t$ (Fig. 6a) and they are 4.111/min and 258.4 mg/g, respectively. The determination coefficient $r^2$ is only 0.8854. The lower value of $r^2$ indicates that the adsorption of fuchsin acid onto GO/chitosan fibers does not follow the pseudo-first-order kinetic model.

The linearized-integral form of the pseudo second-order model is expressed as follows (Ho & Chiang, 2001):

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

where $k_2$ (g/(mg min)) is the rate constant of pseudo-second-order adsorption. From the slopes and intercepts of straight portion of the linear plots obtained by plotting $t/q_t$ against $t$ (Fig. 6b), the values of

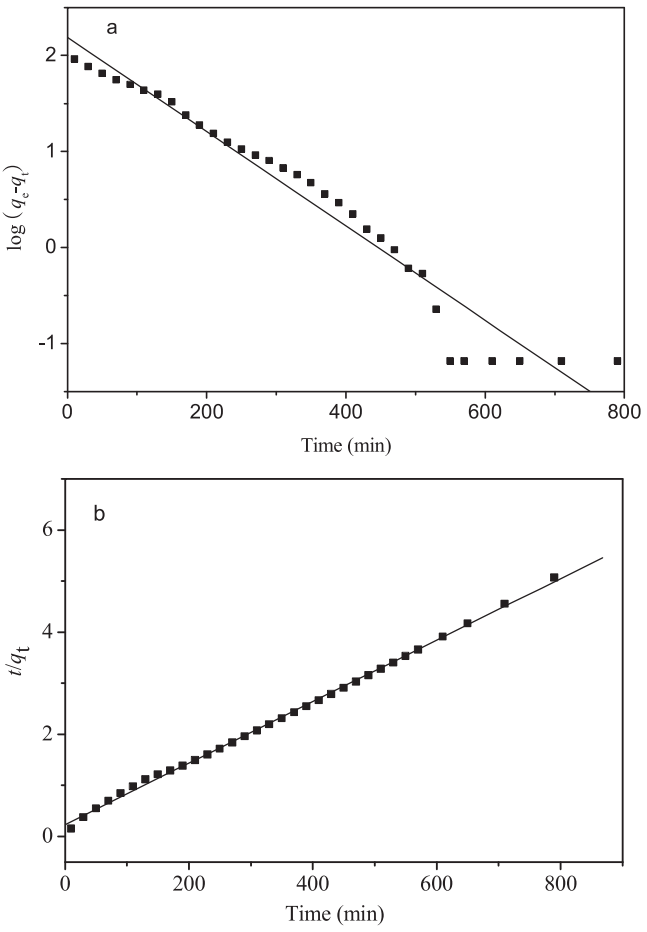


**Fig. 6.** Adsorption kinetics of fuchsin acid adsorbed by the 6 wt% GO/chitosan fibers: (a) pseudo-first-order and (b) pseudo-second-order models.

$k_2$ and $q_e$ can be calculated and are 4.16 g/(mg min) and 159.0 mg/g, respectively. The high determination coefficient of $r^2$ (0.9950) and the similiarity between the calculated capacity and the experimental capacity at equilibrium indicates that the adsorption of fuchsin acid onto GO/chitosan/fibers fits the pseudo-second-order model well. It is more likely to predict the behavior over the whole experimental range of adsorption and demostrates that the overall rate of fuchsin acid dye adsorption is controlled by the chemical process through sharing of electrons or by covalent forces through exchanging of electrons between adsorbent and adsorbate (Malik, Strelko, Streat, & Puziy, 2002).

### 3.6. Thermodynamic studies

In order to evaluate the effect of temperature on the adsorption process, the thermodynamic parameters such as Gibbs free energy ($\Delta G^0$), standard enthalpy change ($\Delta H^0$) and standard entropy change ($\Delta S^0$) are calculated at various temperatures using the following equations:

$$\Delta G^0 = -RT\ln\ k_L \tag{7}$$

$$\ln\ k_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

where $R$ (8.3145 J/(mol K)) is the universal gas constant, $k_L$ (L/g) is the Langmuir constant and $T$ (K) is the absolute temperature (in Kelvin). The values $\Delta H^0$ of and $\Delta S^0$ can be calculated from the slopes and the intercept of the linear straight by plotting $\ln K_0$ against $1/T$. According to Eq. (9), the values of $\Delta G^0$ can be calculated. Table 1 shows the values of $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$ at different initial dye concentrations and temperatures.

**Table 1**
Thermodynamic parameters for fuchsin acid adsorbed by GO/chitosan fibers.

| Temperature (K) | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (J/(mol K)) |
|---|---|---|---|
| 273 | −13.71 | −34.57 | −76.39 |
| 293 | −12.18 | | |
| 313 | −10.66 | | |

The negative values of $\Delta G^0$ indicate that the adsorption of fuchsin acid dye onto GO/chitosan/fibers is a spontaneous and feasible process. The values of $\Delta G^0$ (between 0 and 20 kJ/mol) indicate that the adsorption process is physisorption. However, the absolute value of $\Delta G^0$ decreases with increasing the temperature, suggesting that the adsorption of fuchsin acid becomes less favorable at higher temperature. The negative standard enthalpy change ($\Delta H^0$) suggests that the adsorption is an exothermal reaction, the negative standard entropy change ($\Delta S^0$) reveals the decreased randomness at the solid-solution interface during the adsorption progress. As temperature increases, the increased mobility of dye molecules causes the molecules to escape from the solid phase to the liquid phase. Therefore, the amount of fuchsin acid adsorbed by the fibers decreases.

## 4. Conclusion

A composite material, GO/chitosan fiber, has been prepared by a wet spinning method. The tensile strength of the GO/chitosan fibers reaches 165.8 MPa, which has been improved compared with pure chitosan fibers with a tensile strength of 96.7 MPa. The adsorption properties of fuchsin acid dye by the GO/chitosan fibers have been studied in detail through investigating related factors such as the initial pH, adsorbent dosage, contact time and temperature. The results suggest that the initial pH of the solution is one of the most important factors that affect the adsorption capacity of fuchsin acid dye onto the GO/chitosan fibers. The experimental data can be well fitted with the Langmuir isotherm equation. Kinetic studies show that adsorption process followed the pseudo-second order reaction model. Thermodynamic investigations indicate that the adsorption reaction is a spontaneous and exothermal process.

## Acknowledgements

This work was supported by the Natural Science Foundation of Qingdao (12-1-4-2-23-jch), Science & Technology Development Program of Shandong Province (2012GSF111819), and National Key Basic Research Development Program of China (973, 2012CB722705).

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