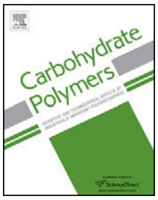
Carbohydrate Polymers xxx (2013) xxx–xxx

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

Yanhui Li[a,*], Jiankun Sun[a], Qiuju Du[a], Luhui Zhang[b], Xiaoxia Yang[a], Shaoling Wu[a], Yanzhi Xia[a], Zonghua Wang[a], Linhua Xia[a], Anyuan Cao[b,*]

[a] *Laboratory of Fiber Materials and Modern Textile, The Growing Base for State Key Laboratory, Qingdao University, 308 Ningxia Road, Qingdao, Shandong 266071, China*
[b] *Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing 100871, China*

ARTICLE INFO

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

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

---

[*] Corresponding authors. Tel.: +86 532 85951842.
E-mail addresses: liyanhui@tsinghua.org.cn (Y. Li), anyuan@pku.edu.cn (A. Cao).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.10.094

Please cite this article in press as: Li, Y., et al. Mechanical and dye adsorption properties of graphene oxide/chitosan composite fibers prepared by wet spinning. *Carbohydrate Polymers* (2013), 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 λ_{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.

Please cite this article in press as: Li, Y., et al. Mechanical and dye adsorption properties of graphene oxide/chitosan composite fibers prepared by wet spinning. *Carbohydrate Polymers* (2013), http://dx.doi.org/10.1016/j.carbpol.2013.10.094