Chemical Engineering Journal 245 (2014) 99–106

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Highly enhanced adsorption of congo red onto graphene oxide/chitosan fibers by wet-chemical etching off silica nanoparticles

Qiuju Du *, Jiankun Sun, Yanhui Li *, Xiaoxia Yang, Xiaohui Wang, Zonghua Wang, Linhua Xia

Laboratory of Fiber Materials and Modern Textile, The Growing Base for State Key Laboratory, Qingdao University, 308 Ningxia Road, Qingdao, Shandong 266071, China

HIGHLIGHTS

- Graphene oxide/chitosan/silica fibers were prepared by a wet spinning technique.
- Porous fibers were produced through wet-chemical etching off silica nanoparticles.
- The maximum adsorption capacity of the porous fibers can reach 294.12 mg/g.
- The adsorption process was characterized by kinetics and isotherm analysis.

ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 25 January 2014
Accepted 2 February 2014
Available online 10 February 2014

Keywords:
Graphene oxide
Chitosan
Fibers
Adsorption
Congo red

ABSTRACT

Graphene oxide/chitosan/silica fibers were prepared by a wet spinning technique. Silica nanoparticles were etched off from the graphene oxide/chitosan/silica fibers to produce graphene oxide/chitosan fibers with porous structure. The morphology and functional groups of the porous graphene oxide/chitosan fibers were characterized using scanning electron microscopy and Fourier-transform infrared spectroscopy, respectively. Adsorption experiments with the porous graphene oxide/chitosan fibers were performed based on various parameters, such as initial congo red concentration, solution pH, adsorbent dose and contact time. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models were employed to discuss the adsorption behavior. The results indicated that the equilibrium data were perfectly represented by the Langmuir isotherm. The maximum adsorption capacity reached 294.12 mg/g. The kinetics data were analyzed using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models and the pseudo-first-order model best described the adsorption of congo red onto the porous graphene oxide/chitosan fibers.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Waste effluents from textiles, dyeing, rubber, printing, paper, plastics, and related industries contain various dyes. Most dyes have aromatic rings in their structures, which make them highly toxic, non-biodegradable, carcinogenic and mutagenic for human being and aquatic life [1]. So the removal of various dyes from industrial wastewaters before discharging into natural water bodies is extremely important to environmental safety.

Different physico-chemical processes such as photo-catalytic degradation [2], coagulation [3], flocculation [4], ion-exchange [5], membrane nanofiltration [6], electrochemical oxidation [7] and catalytic ozonation [8] have been used to treat wastewater containing dyes. However, the application of these technologies has been limited due to poor efficiency. The adsorption is an attractive technology due to its simple operation and effectiveness in removing dyes in low concentration. Among various adsorbents, carbon related materials such as activated carbon [9], carbon nanotubes [10], graphene [11] and biomaterials like chitosan [12] are the most popular research objects due to their high removing efficiency and adsorption capacity.

Graphene, a single-atom-thick and two-dimensional sheet of hexagonally arrayed sp^2-bonded carbon atoms, has unique physical and chemical properties which make it ideal candidate for widespread applications in drug delivery [13], nanoelectronics [14], sensors [15], nanocomposites [16], hydrogen storage [17], batteries [18], supercapacitors [19], and solar cells [20]. In recently, due to its large specific surface area and abundant functional groups, graphene has been suggested and proven to be an effective adsorbent to remove fluoride [21], methylene blue [11], phenol [22], arsenate [23], diethyl phthalate [24], 1-naphthol [25], Cr(VI) [26], Cu(II) [27] and lead [28] from aqueous solutions. With

---

* Corresponding authors. Tel.: +86 532 85953156 (Y. Li).
E-mail addresses: duqiuju999@gmail.com (Q. Du), liyanhui@tsinghua.org.cn (Y. Li).

http://dx.doi.org/10.1016/j.cej.2014.02.006
1385-8947/© 2014 Elsevier B.V. All rights reserved.

increasing application of graphene in wastewater treatment, public concern has also been paid on the potential ecological and environmental risks caused by this newborn nanomaterial. Chang et al. reported that high concentration of graphene oxide (GO) in A549 adenocarcinomic human epithelial cells could reduce the viabilities of cells [29]. Chen et al. studied the toxicity of GO on human cells and zebrafish and found that GO had a slight toxicity to organisms since it could induce minor (about 20%) cell growth inhibition and slight hatching delay of zebrafish embryos at a dosage of 50 mg/L [30]. Sasidharan et al. showed that pristine graphene could accumulate on the cell membrane to cause high oxidative stress and lead to apoptosis [31].

The toxicity to organic cells will undoubtedly increase the doubts in applying micro-sized graphene as adsorbent in wastewater treatment. In order to eliminate the harm caused by graphene, the most effective method is to prepare macroscopic graphene structures. The graphene and GO macro-structures have been successively prepared though wet-spinning method [32], one-step dimensionally confined hydrothermal strategy [33], and electrophoretic self-assembly method [34].

Chitosan (CS) is a naturally biodegradable and non-toxic biomaterial. It has showed excellent adsorption capacity for anionic dyes and heavy metal ions because CS molecules contain a large number of active amine ($-NH_2$) groups and hydroxyl groups in its monomers. Moreover, it exhibits excellent chelating and bead-, fiber- and film-forming properties [35] and has been considered as an ideal support material. In this study, CS was used as a carrier to fit the micro-sized GO and silica nanoparticles to prepare GO/CS/ silica fibers (GO/CS/SI) by wet spinning method. Then, silica nanoparticles were etched off from GO/CS/SI by diluted HF solution to produce GO/CS fibers (GO/CS/ETCH). The morphology and physicochemical properties of GO/CS were characterized by SEM and TGA analysis. The adsorption properties of congo red onto GO/CS/ETCH were studied through investigating the influencing parameters such as initial concentration, solution pH, adsorbent dose and contact time.

2. Materials and methods

2.1. Materials

The expandable graphite was supplied by Henglide Graphite Company (Qingdao, China). CS (CS > 90.0% deacetylation, viscosity <100 cps) was purchased from Qingdao Lanji Tech. Co., Ltd., China. Congo red ($C_{32}H_{22}N_6O_6S_2Na_2$) was purchased from Tianjin Chemical Reagent Manufacturing Co., Ltd., China. Silica nanoparticles were bought from Sigma–Aldrich Co. LLC. All other reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Preparation of GO

GO was prepared by oxidizing expandable graphite using modified Hummers method reported in our previous study [11]. Briefly, $KMnO_4$ (30 g), $NaNO_3$ (5 g) and expandable graphite (5 g) were sequentially added into the stirred H_2SO_4 solution (230 mL) at 0 °C. After kept at 0 °C for 24 h, the mixture was vigorously stirred at 35 °C for 30 min and slowly diluted with deionized water. The reaction temperature was rapidly increased to 98 °C and kept for 15 min. Then, 30% H_2O_2 was added to the mixture and the color turned into yellow. The mixture was purified by centrifuging with HCl (5%) and deionized water to obtain GO.

2.3. Preparation of GO/CS

GO/CS/ETCH were prepared by a wet-spinning procedure. 40 g CS was dissolved into 960 mL of 10% v/v acetic acid solution. Then, 2.1 g GO and 40 g silica nanoparticles were added into the CS solution, respectively. The mixture was vigorously agitated for 5 h to form a homogenous solution and pre-filtered using a filter-press (Wuxi Textile Machinery Co., Ltd., China) to remove the large particles and air bubbles. The mixture was passed through a wheel-powered metering pump by gravitational force, and then pumped to a stainless steel spinneret with hole diameter of 0.5 mm. The spinneret was immersed in a coagulation bath containing 2 M NaOH solution. The obtained fibers were washed several times with 40% methanol solution and dried in air. The dried fibers were then immersed into 30% HF solution for 48 h to etch off silica nanoparticles. GO/CS/ETCH fibers were obtained with deionized water washing and air drying. The pure CS and GO/CS (without adding silica nanoparticles) and GO/CS/SI fibers were prepared using the same procedure as above.

2.4. Characterization of the fibers

The morphology and structure of GO/CS/ETCH were characterized by scanning electron microscope (SEM, Hitachi S4800). The compositional characteristics of the samples were analyzed using energy dispersive spectroscopy (EDS). The Brunauer–Emmett–Teller (BET) surface area and porous properties of AC were determined from the N_2 adsorption at -196 °C using a Micrometric ASAP 2000 system. The surface functional groups were determined by a Perkin–Elmer-283B Fourier-transform infrared spectrometer (FTIR) within the wavenumber range from 400 to 4000 cm^{-1}.

2.5. Batch adsorption experiments

Batch adsorption experiments were carried out on a water bath temperature controlled shaker (SHZ-82A, Ningbo Jiangnan Instrument Factory, China) at 20 °C using 250 mL glass conical flask. All experiments were repeated at least three times to ensure accuracy of the obtained data. The effect of congo red concentration on the adsorption was tested by adding 70 mg GO/CS/ETCH into 100 mL solution with congo red concentration ranging from 20 to 200 mg/L at pH 5.0.

The influence of pH on congo red removal was studied by varying the solution pH from 3.1 to 10.0 using HNO_3 or NaOH solution with appropriate concentration. The initial congo red concentration, adsorbent dose and temperature were 80 mg/L, 0.7 g/L and 20 °C, respectively.

The effect of GO/CS/ETCH dosage on the adsorption was conducted by adding different GO/CS/ETCH amounts (0.1–1.1 g/L) into 100 mL solution with initial congo red concentration of 80 mg/L. The solution pH and temperature were controlled at 5.0 and 20 °C, respectively.

At the end of the adsorption, the supernatant solution was collected by quietly placing the sample for 30 min. The equilibrium concentration of congo red was analyzed at 497 nm using a by ultraviolet and visible spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd., China). The adsorption capacity of congo red onto GO/CS/ETCH was evaluated using the following equation:

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

where C_0 (mg/L) is the initial concentration of congo red, C_e the equilibrium concentration (mg/L), m the mass of adsorbent (g) and V is the volume of solution (L).

The kinetic studies were carried out by adding 70 mg GO/CS/ETCH into 100 mL solution with initial congo red concentration of 80 mg/L. The solution pH and temperature were controlled at 5.0 and 20 °C, respectively. At predetermined time, t, the congo red concentration in the supernatant, C_t (mg/L), was examined.

Download English Version:

https://daneshyari.com/en/article/147444

Download Persian Version:

https://daneshyari.com/article/147444

Daneshyari.com