Carbohydrate Polymers 95 (2013) 501–507

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Methylene blue adsorption on graphene oxide/calcium alginate composites

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ARTICLE INFO

Article history:
Received 1 April 2012
Received in revised form
28 November 2012
Accepted 24 January 2013
Available online 4 March 2013

Keywords:
Graphene oxide
Calcium alginate
Methylene blue
Adsorption

ABSTRACT

Graphene oxide has been used as an adsorbent in wastewater treatment. However, the dispersibility in aqueous solution and the biotoxicity to human cells of graphene oxide limits its practical application in environmental protection. In this research, a novel environmental friendly adsorbent, calcium alginate immobilized graphene oxide composites was prepared. The effects of pH, contact time, temperature and dosage on the adsorption properties of methylene blue onto calcium alginate immobilized graphene oxide composites were investigated. The equilibrium adsorption data were described by the Langmuir and Freundlich isotherms. The maximum adsorption capacity obtained from Langmuir isotherm equation was 181.81 mg/g. The pseudo-first order, pseudo-second order, and intraparticle diffusion equation were used to evaluate the kinetic data. Thermodynamic analysis of equilibriums indicated that the adsorption reaction of methylene blue onto calcium alginate immobilized graphene oxide composites was exothermic and spontaneous in nature.

1. Introduction

Dyes are widely used in the synthesis, printing, textile, pulp mill, food and cosmetic industries. The estimated annual production of commercially available dyes is approximately 7×10^5 t, including more than 100,000 kinds of dyes (Sharma & Uma, 2010). In China, dyeing wastewater has been released into the environment in large quantities, causing pollution of water and soil. Some dyes and their degradation products are not easily biodegradable and have a toxic, carcinogenic, or mutagenic influence on human beings (Chen, Chen, & Diao, 2010). Therefore, it is necessary to remove dyes prior to their discharge. Several methods such as membrane separation, flocculation, coagulation, ozonatioin, aerobic or anaerobic treatment and adsorption have been explored to remove dyes from dyeing wastewater (Slokar & Le Marechal, 1998). However, among these methods, adsorption is the most widely used technology because it is simple, low cost and effective for removing dyes from waste streams. Various adsorbents, such as rice husk (Li, Du, et al., 2011), garlic peel (Hameed & Ahmad, 2009), pyrolyzed petrified sediment (Aroguz, Gulen, & Evers, 2008), coir pith carbon (Kavitha & Namasivayam, 2007), activated clay (Weng & Pan, 2007), carbon nanotubes (Yao, Xu, Chen, Xu, & Zhu, 2010), activated desert plant (Bestani, Benderdouche, Benstaali, Belhakem, & Addou, 2008), and activated carbon (Karagöz, Tay, Ucar, & Erdem, 2008), have been studied for adsorption of dyes from aqueous solutions.

Graphene and graphene oxide (GO), new types of carbon nanomaterials, have attracted enormous research interests not only in electronics (Eom et al., 2009) and mechanics (Lee, Wei, Kysar, & Hone, 2008), but also in wastewater treatment. It has been used for the adsorption of fluoride ions (Li, Zhang, et al. 2011), heavy metals (As (Mishra & Ramaprabhu, 2011), Cu (Yang et al., 2010), Pb and Cd (Deng, Lü, Li, & Luo, 2010), etc.), dyes (methylene blue (Liu et al., 2012), methyl violet, orange-G, rhodamine-B (Ramesha, Vijayakumar, Muralidhara, & Sampath, 2011), etc.) and express good adsorption property. Nevertheless, in very recent work, Wang et al. (2011) demonstrated that GO has the obvious toxicity to human fibroblast cells when the dose is higher than 50 μg/mL. Based on the hemolysis and WST-8 viability assay results, Liao et al. showed that GO has the toxicity to suspended erythrocytes and human skin fibroblasts (Liao, Lin, Macosko, & Haynes, 2011). So, the difficulty of separating nanosized GO from the effluent may result in the loss of the adsorbent and harmful effects on human being as well as the fauna and flora. These disadvantages may limit its practical application in environmental protection in the future.

Sodium alginate, a water-soluble linear polysaccharide, is a natural occurring carbohydrate polymer composed of α-L-guluronate and β-D-mannuronate residues and has hydrophilic, biocompatiblity, and nontoxic (Liu, Chen, Zhong, & Wu, 2009). The gelling

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http://dx.doi.org/10.1016/j.carbpol.2013.01.094

properties of sodium alginate are mainly achieved by the exchange of sodium ions from the guluronic acid residues with the divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, etc.). The divalent cations bind to the α-L-guluronic acid blocks between two different chains resulting in a three-dimension network (Sarmento et al., 2006). Calcium alginate has been widely used to immobilize activated carbon (Kim, Jin, Park, Kim, & Cho, 2008), carbon nanotubes (Li et al., 2010), titanian nanoparticles (Mahmoodi, Hayati, Arami, & Bahrami, 2011), and maghemite nanoparticles (Rocher, Siaugue, Cabuil, & Bee, 2008) to create adsorbents to remove heavy metals and dyes from aqueous solutions. However, to our knowledge, no study on preparing calcium alginate immobilized graphene oxide (GO/CA) composites used for the removal of dyes has been reported.

In this work, GO/CA fibers were prepared using a sol-gel method and characterized by scanning electron microscope (SEM), transmission electron microscope (TEM) and Fourier Transform infrared spectroscopy (FTIR). The adsorption equilibrium and kinetic studies have been investigated to observe the effects of various process parameters such as pH, contact time, and temperature on methylene blue (MB) removal.

2. Experimental

2.1. Materials

Graphene oxide was prepared from expandable graphite (Henglide Graphite Co., Ltd., Qingdao, China) by a modified Hummers method (Hummers & Offeman, 1958). Expandable graphite (2.5 g) was mixed with a mixture of H_2SO_4 (115 mL, 98 wt %), $KMnO_4$ (15 g) and $NaNO_3$ (2.5 g) in ice bath. The obtained mixture was then kept at 0 °C for 24 h. Then the mixture was 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, and the color turned into yellow as 30% H_2O_2 was added to the mixture. Then, the mixture was centrifuged and washed with HCl (5%) and deionized water several times. After drying under room condition, graphene oxide (GO) was obtained.

5 g sodium alginate (AR, Aibi Chemistry Preparation Co., Ltd., Shanghai, China) was dissolved into 350 mL deionized water and stirred for 5 h. 0.26 g GO was added into 50 mL deionized water and ultransonicated for 30 min. Then the GO solution was slowly dropped into the viscous solution of sodium alginate and stirred continuously to form a homogeneous mixed solution. Then, the mixed solution was rapidly injected into 1000 mL 10% $CaCl_2 \cdot 2H_2O$ (AR, Basf Chemical Co., Ltd., Tianjin, China) to form GO/CA fibers. The obtained GO/CA fibers were washed several times with deionized water and then dried in a vacuum freeze drying machine (FD-1-50, Boyikang Laboratory Apparatus Co., Ltd, Beijing, China).

2.2. Characterization of adsorbents

The morphology and surface structure of GO and GO/CA fibers were examined with JSM 6700F scanning electron microscope (SEM) and JEM-2100F transmission electron microscope (TEM). Functional groups of GO and GO/CA were analyzed by a Perkin-Elmer-283FTIR spectrometer over the wave range from 4000 to 400 cm^{-1}.

2.3. Batch adsorption experiments

MB was purchased from Tianjin Red Cliff Chemical Reagent Factory in China and the stock solution (1000 mg/L) was prepared by dissolving the MB in deionized water.

Adsorption experiments were carried out using batch equilibration techniques in a temperature-controlled water bath shaker (SHZ-82A). For adsorption equilibrium experiments, a fixed adsorbent dose (25 mg) was weighed into 100 mL conical flasks containing 50 mL of different initial concentrations (30–80 mg/L) of MB. The mixture was shaken for 5 h at 25 °C until equilibrium was obtained. Then the adsorbent was separated from solution by centrifugation at 7000 rpm for 6 min. The concentration of MB in the solution was measured using a UV–vis spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co., Ltd., China) at 663 nm. The adsorption capacity was calculated using the following equation:

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

where C_0 and C_e were initial and equilibrium concentrations of MB (mg/L), respectively, m was the mass of adsorbent (g) and V was volume of the solution (L).

The effect of pH on the adsorption of MB was studied in a pH range of 3.4–10.2 using 50 mL of solutions with MB concentrations of 60 mg/L. The effect of adsorbent dose on the adsorption of MB was conducted by adding different amounts of adsorbents (0.01–0.10 g) into 50 mL of solutions with MB concentration of 80 mg/L. The effect of contact time on the adsorption of MB was carried out in a 2000 mL glass beaker at 25 °C. The aqueous solution (1000 mL) with GO/CA (0.5 g) and MB (40 mg/L) was shaken continuously. The recording time was started when GO/CA was added to the beaker. Aqueous samples (5 mL) were taken from the solution at predetermined time. The filtrate was analyzed and the amount of adsorbed MB at time t, q_t (mg/g), was calculated by:

$$q_t = \left(\frac{C_0 - C_t}{m}\right) \times V \tag{2}$$

where C_t (mg/L) is the MB concentration at time t.

To evaluate the temperature effect on the adsorption, 25 mg adsorbents were added into 50 mL solutions with initial MB concentration ranging from 30 to 80 mg/L. The samples were shaken at 25, 40 and 55 °C, respectively, until the equilibrium was obtained.

GO/CA utilized for the adsorption of initial dye concentration of 80 mg/L was separated from the MB solution. The MB adsorbed GO/CA was washed with deionized water for the removal of any unabsorbed dye. And then, it was put into 50 mL deionized water with pH 1.5. Finally they were shaken for 420 min. The amount of dye desorbed was determined as mentioned before.

3. Results and discussion

3.1. Characterization of materials

Fig. 1a shows the TEM image of GO, it can be seen that GO is transparent film due to its single-atom layered structure. The surface of GO film is wrinkled due to the crumpling and scrolling of graphene sheets. Fig. 1b shows that the dried GO/CA fibers have belt-like structrue. Most GO sheets are embedded into CA. GO/CA composites have a very rough surface and lots of raised strips.

The functional groups of GO and GO/CA were characterized by FT-IR spectra and shown in Fig. 2. The strong peak at 3426 cm^{-1} is assigned to stretching vibration of OH groups. The bands at 1625 and 1400 cm^{-1} indicate the existence of asymmetric and symmetric stretching vibration of C=O groups. The band at 1110 cm^{-1} can be attributed to the appearance of C—O groups. The bands at 621 cm^{-1} reflect the C—H bending vibrations. The peak around at 475 cm^{-1} may correspond to C—O stretching vibration.

3.2. Adsorption isotherms of GO and GO/CA

The adsorption isotherm is usually used to study how the adsorption molecules distribute between the liquid phase and the