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Removal of methylene blue from aqueous solutions by chemically modified bamboo

Jian-Zhong Guo [a], Bing Li [a,*], Li Liu [a], Kangle Lv [b,*]

[a] Zhejiang Provincial Key Laboratory of Chemical Utilization of Forestry Biomass, Zhejiang A & F University, Lin'an, Zhejiang 311300, PR China
[b] Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, South-Central University for Nationalities, Wuhan 430074, PR China

HIGHLIGHTS

- The carboxyl group and diethylenetriamine modified bamboo was firstly synthesized.
- The absorbent showed the prominent adsorption capacity and strong removal ability.
- The adsorption kinetics was systematically investigated and mechanism was proposed.
- Electrostatic interaction is responsible for the strong adsorption.

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ABSTRACT

Chemically modified bamboo (CMB) was utilized for removing methylene blue (MB) from aqueous media in the present study. The adsorbent was characterized by Fourier transform infrared (FTIR) spectra and elemental analysis, which confirms that carboxyl groups and diethylenetriamine were successfully introduced into the surface of bamboo. The effects of initial MB concentration (100–900 mg L^{-1}), contact time (15–315 min), the pH of the solution (3–10), temperature (298–318 K), adsorbent dosage (0.4–2.6 g L^{-1}) and salt concentration on the adsorption efficiency of CMB towards MB were investigated. It was found that the adsorption of MB in CMB fits Langmuir mode well, and the maximum adsorption capacity of CMB achieved 606 mg g^{-1} at 298 K, which is much higher than those obtained from previously investigated bioadsorbents. The adsorption kinetics can be described by pseudo-second-order kinetic model, and the adsorption of MB on CMB was an exothermic process. The results of the present study suggest that CMB is an effective biosorbent for removal of organic pollutants from aqueous solutions.

1. Introduction

Synthetic dyes are widely used in many industries to colorize substances such as in textiles, leather, paper, wool, printing and cosmetics. Discharge of wastewater containing dye compounds into water sources has caused serious environmental impact because dyeing effluent will deplete the dissolved oxygen content in water and also inhibit sunlight from reaching to the water sources. Some of the dye wastewater is usually poisonous, carcinogenic, and teratogenic to human beings (Bhattacharyya and Sharma, 2005). Thus, the removal of dyes from waste water is necessary before discharging into downstream bodies of water. Methylene blue (MB), a heterocyclic aromatic compound, was widely used in a range of different fields, especially in textile industry. The wastewater containing MB has significant adverse impacts on flora, fauna and aquatic ecosystems (Ghosh and Bhattacharyya, 2002). Moreover, MB is often used as a probe molecule for identifying the adsorption capacity of adsorbents (Bestani et al., 2008). Therefore, investigating the removal of MB from wastewater is both practical and significant.

Various methods, including adsorption (Waranusantigul et al., 2003; Li et al., 2013), flocculation (Fang et al., 2010), membrane filtration, electrolysis, biological treatments, and oxidation have been employed for the removal of dyes from wastewaters. Among all of the treatments proposed, the adsorption of dye molecules onto a substrate (adsorbent) is increasingly considered as a simple, effective and low-cost method for treating the wastewater. The success of an adsorption technology depends on the choice of an appropriate adsorbent. In recent years, the research of adsorbents prepared from agricultural by-products has been intensively investigated due to relatively cheap and high adsorption capacities (Waranusantigul et al., 2003).

* Corresponding authors. Tel.: +86 571 63732775; fax: +86 571 63732772.
E-mail addresses: libingzjfc@163.com (B. Li), lvkangle@mail.scuec.edu.cn (K. Lv).

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Bamboo is well-known to be one of the fastest growing plants in the world with a growth rate ranging from 30 to 100 cm d^{-1} during the growing season. It is plentiful, inexpensive, and a renewable natural resource. Bamboo was usually utilized to produce biochar as a stable adsorbent for removing contaminant from wastewater (Liao et al., 2012). The utilization of chemically modified bamboo to treat contaminated water is rare. Hameed et al. reported that nitric acid-treated bamboo waste is efficient to the removal of MB with maximum MB adsorption capacity of 87.72 mg g^{-1} (Hameed and Tan, 2010).

The chemical compositions of bamboo were cellulose (45–52%), lignin (22–30%), and pentosan (17–25%). Therefore it contains a large amount of easily available hydroxyl groups, which indicates broad potential application in adsorption, especially after chemically modified. Up to now, a series of strategies for modification of surface reactive hydroxyl groups were reported such as condensation, etherification (Sajab et al., 2011) and copolymerization (Deng and Ting, 2005).

The aim of the study is to improve the adsorption capacity of bamboo by chemical modification. The whole synthetic process was illustrated in Fig. 1. Firstly, alkaline treated bamboo powders (BP) was crosslinked with epichlorohydrin, forming epoxy ethers. Secondly, diethylenetriamine was grafted onto the surface bounded epoxy ethers by amination reaction. Thirdly, amine groups and hydroxyl groups were reacted with chloroacetic acid, forming the new biosorbent. The property of the prepared biosorbent was evaluated by adsorption of MB dye from aqueous solution.

2. Materials and methods

2.1. Materials

BP was obtained from Lin'An City, China. Before experiment, BP was washed with distilled water, followed by drying at 60 °C for 6 h. Then, it was ground into particles with diameters of 100–250 μm. All other reagents used in this work were of A.R. grade reagents. The deionized water was used in all experiments.

2.2. Chemical modification of bamboo

Prior to the chemical treatment, 30 g of BP were pretreated by soaking in 120 mL 1 mol L^{-1} NaOH solution for 2 h under magnetic stirring, which was then rinsed with deionized water until the pH of the filtrate is about 7, and followed by drying at 333 K for 10 h.

The obtained alkaline treated BP were immersed in epichlorohydrin and heated to 353 K for 1 h under stirring. Then the powder was filtered, washed with deionized water, and dried at 333 K for 10 h.

The crosslinked BP, 25 mL of diethylenetriamine, and 40 mL of deionized water were mixed under stirring at 333 K for 4 h. The reaction mixture was then filtered, washed with deionized water to neutral pH and dried at 333 K.

The above-mentioned product was dispersed in 300 mL ethanol–water solution (water:ethanol = 1:2, v/v), and then 45 g chloroacetic acid dissolved in 50 mL ethanol was added dropwise into the mixture under agitation at 318 K for 3 h. The pH of solution was maintained higher than 10 during the reaction by addition of NaOH solution. The mixture solution was filtrated, and washed by diluted hydrochloric acid and water, till the pH of the filtrate is about 7. After dried at 333 K for 10 h, the cake was ground to particles sizes in range of 60–150 μm. The final product was named as chemical modified bamboo (CMB).

2.3. Instrument analysis

The FTIR spectra of CMB and BP were obtained with an ABB Bomen MB 102 Spectrophotometer with pressed potassium bromide in the scanning range of 4000–400 cm^{-1}. The nitrogen, carbon, hydrogen contents of BP and CMB were obtained with an Elementar Vario EL II elemental analyzer.

2.4. Adsorption isotherms

50 mg of CMB was added into flask containing 50 mL of MB solution. After shaken at certain temperature overnight to establishment the adsorption–desorption equilibrium, the solution was filtered through a 0.45 μm membrane, and the filtrate was analyzed to get the MB equilibrium concentration. The concentration of MB in filtrate was determined by a UV–visible spectrophotometer (model UV754GD, Shanghai) at an absorbance wavelength of 665 nm.

The amount of adsorption q_e (mg g^{-1}), was calculated using Eq. (1).

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

where C_0 and C_e (mg L^{-1}) are the liquid phase concentrations of MB at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

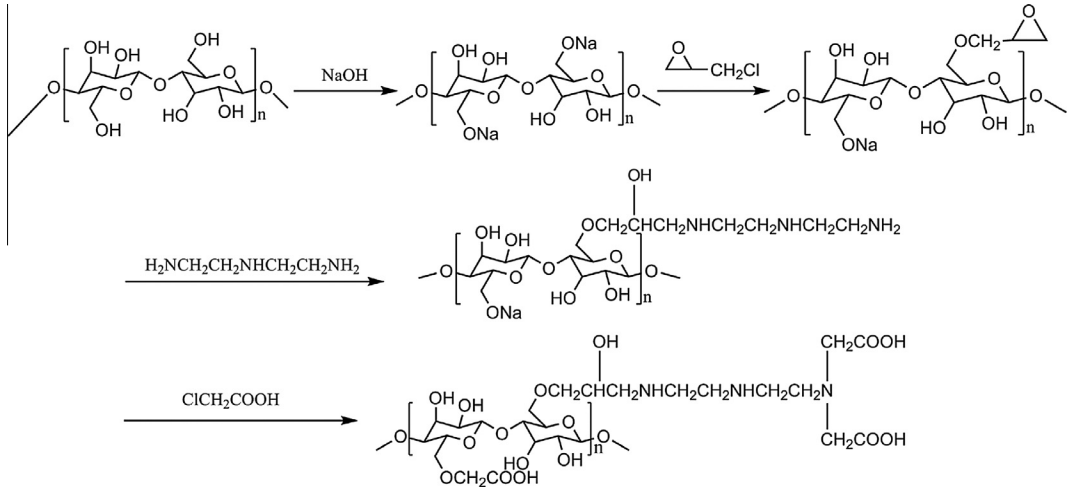

Fig. 1. Synthetic reactions of CMB.