



Effect of a magnetic field on the adsorptive removal of methylene blue onto wheat straw biochar



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HIGHLIGHTS

- Adsorption of MB by wheat straw biochar was enhanced by a magnetic field.
- The biochar pyrolyzed at 200 °C outperformed those pyrolyzed at higher temperatures.
- The surface acidic functional groups were sensitive to the external magnetic field.
- Kinetic study indicated a chemisorption process of adsorption.
- The $q_{\max}$ value was enhanced by 34.1% under the external magnetic field.

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ABSTRACT

Biochar pyrolyzed from wheat straw was innovatively used for the adsorptive removal of cationic dye methylene blue through exposure to a magnetic field. The adsorption capability of the biochar pyrolyzed at 200 °C exceeded that of samples pyrolyzed at higher temperatures. The surface acidic functional groups of wheat straw biochar were deduced to be more sensitive to the effects of the external magnetic field. The enhancement of the magnetic field achieved by increases in the initial dye concentration, and a decrease in the biochar dosage and solution pH, were more significant compared with those caused by other conditions. Kinetic experiments indicated that chemisorption occurred during adsorption. The $q_{\max}$ values for dye adsorption without, and with, an external magnetic field were found to be 46.6 and 62.5 mg/g, respectively. These demonstrated that wheat straw biochar could be used for the efficient adsorption of pollutants when assisted by an external magnetic field.

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1. Introduction

Large amounts of agricultural wastes including: wheat straw, rice husk, and cornstalk, are generated annually. So, these products are readily available as a low-cost resource for adsorption, as a biomass energy source, and as a precursory material for biochars. Recently attention has been paid to the utilization and application of biochar, which is derived from the biomass via incomplete combustion operations such as pyrolysis and carbonization (Ahmad et al., 2014; Chen and Chen, 2009; Mohan et al., 2014). As a stable carbon-rich material, the application of biochar for solving environmental problems can span several categories including: carbon sequestration, soil management, pollution remediation, and agricultural by-product/waste recycling. Among these uses, biochar as an adsorbent for the removal of environmental pollutants has

emerged as a promising technology (Lee et al., 2010; Lehmann, 2007; Xie et al., 2014; Inyang et al., 2012; Zhou et al., 2014). Currently, low-temperature pyrolysis is usually applied to convert biomass, typically agricultural biomass, into biochars (Keiluweit et al., 2010; Das et al., 2013), which helps to avoid organic leaching and secondary pollution from the raw biomass. Meanwhile, the surface area of the biochars usually increases with an increase in pyrolytic temperature at up to 700 °C (Ahmad et al., 2014). As such, it was deemed both reasonable, and feasible, to promote the application of biochar for practical decontamination purposes.

Concurrently, the magnetic field-exposure method has demonstrated its capability for enhancing the adsorptive removal of pollutants from water as static magnetization is convenient, simple, and cost-effective. Basically, the magnetic field is capable of affecting the behavior and physico-chemical properties of water (Patkowski et al., 2014). Thus, it is not surprising that many studies have focused on the effect of the external magnetic field on the properties of both adsorbent and adsorbate materials. On the one

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hand, the exposure to the magnetic field can affect the adsorbent significantly. Zhang and his co-workers reported that magnetic treatment is capable of enhancing the ζ potential of Ca-rectorite suspensions in the absence of Cu and of reducing that of the suspension, also in the presence of Cu (Zhang et al., 2004). Bel'chinskaya proved that the surface of materials became less homogeneous under a magnetic field, with increased surface area of sorbent and enhanced adsorption of formaldehyde (Bel'chinskaya et al., 2009). On the other hand, as most of the irradiation from the magnetic field is impinging upon the solution containing adsorbate, the effect of the magnetic field on the adsorbate might be as important as that on the adsorbent. Under a magnetic field, the increased mobility of methylene blue molecules onto magnetic clay has been confirmed, which facilitated the penetration of dye molecules to the adsorption sites (Aline et al., 2014). Similar behavior of the adsorption of methyl blue onto organo-bentonite was also seen elsewhere (Hao et al., 2012). Furthermore, a static magnetic field was integrated with the conventional adsorption process by activated carbon for the treatment of biologically-treated palm-oil mill effluent and as a result, the decreases in color, TSS, and COD were considerably enhanced (Rafie et al., 2014). In short, static magnetization may be an alternative to enhance the adsorption capability of biochar.

Although a number of low-cost adsorbents such as: natural materials, agricultural, and industrial, wastes are capable of removing methylene blue efficiently (Rafatullah et al., 2010), significantly enhanced uptake of methylene blue onto biochar under an external magnetic field has rarely been reported to date. Our previous study has indicated that wheat straw biochar was more sensitive to an external magnetic field than biochars including sugarcane bagasse biochar and cornstalk biochar. In this study, for the first time, wheat straw biochar was prepared and used for the significantly enhanced adsorptive removal of the cationic dye methylene blue under a static magnetic field. The effects of the pyrolytic temperature on biochar adsorption, magnetic pre-treatment time, and initial dye concentration were investigated. The adsorption kinetics and isotherms were also studied as was the mechanism responsible for the effect of the external magnetic field.

2. Methods

2.1. Materials

Methylene blue (mass fraction > 98.5%, chemically pure) was purchased from Tianjin Chemical Reagent Research Institute. The other chemicals used were of analytical grade. Deionised (DI) water was used throughout the study. A pair of permanent magnets (30 mm × 19 mm × 6 mm, Beijing Fengrui Magnetic Material Factory) were used to provide the magnetic field.

2.2. Preparation of biochar from wheat straw

Wheat straw was collected from farmland in Zhengzhou, Henan Province. The collected biomass was washed, dried, crushed, and sieved through a 40 mesh sieve. The wheat straw biochar was prepared in a furnace by pyrolyzing the biomass at a constant temperature for 3 h. Meanwhile, to maintain an oxygen-limited atmosphere, the pre-treated biomass was put into a ceramic pot, in a compressed state, and covered with a tight-fitting lid. For demineralisation, the resultant wheat straw biochar was placed in a 4 mol/L HCl solution for 12 h and separated by filtration. Then the residues were rinsed with DI water until a neutral solution pH was achieved: the product was then oven-dried overnight at 80 °C. The treated biochars were finally preserved in a desiccator until further use.

2.3. Characterization

The acidic functional groups, including carboxyl, lactonic, and phenolic groups on the raw wheat straw and the biochars pyrolyzed at 200, 400, and 600 °C, were determined using Boehm's titration method (Abdulkarim and Abu Al-Rub, 2004; Strelko et al., 2002; Valdés et al., 2002).

2.4. Batch adsorption experiments assisted by external magnetic field

Adsorption trials of methylene blue (MB) onto the produced wheat straw biochar were conducted in a series of cylindrical flasks. The stock solutions of MB (500 mg/L) were prepared in DI water. All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. A desired amount of wheat straw biochar (200 mg) was added to a conical flask containing 500 mL of MB solution with a concentration of 10 mg/L. Constant and vigorous stirring was maintained by mechanical agitation for 24 h. After adsorption, samples were collected and filtered through a 0.45 μ m pore-size membrane before analysis. For the effect of magnetic pre-treatment, only the MB solution was treated by the magnetic field for a desired period before adding the wheat straw biochar into the pre-treated solutions.

The reaction temperature was held constant at 25 °C except when studying the adsorption isotherm at different temperatures. All solution pHs were maintained at neutral except during the pH effect study itself. Solution pH adjustment was effected by the addition of a dilute HCl, or NaOH, solution.

2.5. Analysis methods

The concentration of MB was analyzed using an UVmini-1240 spectrophotometer (Shimadzu) by monitoring emissions at the wavelength of maximum absorption (664 nm). The percentage removal of MB was given by:

$$\text{Removal percentage} = (1 - C_t/C_0) \times 100\% \quad (1)$$

The adsorption capacities (q_e , q_t) were calculated as follows:

$$q_t = (C_0 - C_e)V/W \quad (2)$$

$$q_t = (C_0 - C_t)V/W \quad (3)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min); C_0 is the initial concentration of MB in solution, while C_e and C_t (mg/L) are the concentrations of MB at equilibrium and t (min), respectively; V (L) is the volume of solution, and W (g) is the mass of adsorbent used.

3. Results and discussion

3.1. Effect of the pyrolytic temperature of biochars on the adsorption of MB

The surface chemistry of the biochars pyrolyzed at different temperatures differs gradually from low temperature to high temperature due to the loss of O- and H-containing functional groups. The resulting surface polarity and aromaticity are important characteristics affecting the sorption of organic contaminants (Chen et al., 2008). Considering the significant loss of organic matter from the raw wheat straw (WS) during pyrolysis, the adsorption performance of the raw WS and of the biochars pyrolyzed at 200, 400, and 600 °C was compared and the results are presented in Fig. 1. The biochars pyrolyzed at 200, 400, and 600 °C were referred to as BC200, BC400, and BC600, respectively. Typically, the adsorptive

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