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Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids

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HIGHLIGHTS

- Biochar derived from eucalyptus saw dust was modified by various organic acid.
- Carboxyl group was introduced onto biochar surface after the activation.
- Pseudo-second-order kinetics was the most suitable adsorption model.
- The isotherm model is in good agreement with Langmuir model.
- The maximum monolayer adsorption capacity was 178.57 mg g^{-1}.

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ABSTRACT

Biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids at low temperatures was utilized as adsorbent to remove methylene blue (MB) from aqueous solutions. Fourier transform infrared spectroscopy analysis showed that the carboxyl group was introduced on the biochar surface. Adsorption experiment data indicated that eucalyptus saw dust modified with citric acid showed higher MB adsorption efficiency than that modified with tartaric and acetic acids. Pseudo-second-order kinetics was the most suitable model for describing MB adsorption on biochar compared with pseudo-first-order, Elovich, and intraparticle diffusion models. The calculated values of ΔG^0 and ΔH^0 indicated the spontaneous and endothermic nature of the adsorption process. MB adsorption on biochar followed the Langmuir isotherm. The maximum adsorption capacities for eucalyptus saw dust modified with citric, tartaric, and acetic acids were 178.57, 99.01, and 29.94 mg g^{-1}, respectively, at 35 °C.

1. Introduction

Biochar is a stabilized, recalcitrant organic carbon compound obtained when biomass is heated to temperatures between 300 °C and 1000 °C under low (preferably zero) oxygen concentrations (Xie et al., 2015). Biochar is an effective adsorbent derived from agricultural and industrial solid wastes (Rafatullah et al., 2010) and is frequently applied to remove various pollutants, including dyes, pesticides, and heavy metals, from aqueous solutions (Mohan et al., 2014). At present, biochar is considered a cheap alternative to activated carbon for wastewater treatment because it is abundant and can be readily obtained to prepare adsorbents. The adsorption capacity of biochar depends on the following characteristics: Brunauer–Emmett–Teller (BET) surface, pore volume, and surface functional groups; in particular, the main functional groups play a key role in the adsorption of specific contaminants (Rivera-Utrilla et al., 2011). As the adsorption capacity of crude precursors is low for pollutants, it should be improved by adopting appropriate technical methods.

Several technologies, including chemical, physical, and biological treatments, are employed to modify crude precursors for biochar preparation (Bhatnagar et al., 2013). As a commonly employed technology, chemical treatment, such as acid modification, is frequently utilized to prepare biochar with special functional groups and improved adsorption capacity (Bhatnagar et al., 2013). However, biochar preparation through chemical agent modification typically involves high-temperature pyrolysis under nitrogen flow. Strong acids and alkalis could also cause secondary pollution of the environment during preparation. Compared with

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strong acids, alkalis, and salts, organic acids are environment friendly and have been successfully used as modification agent for biochar preparation at low temperatures by using different types of precursors, such as soybean straw (Zhu et al., 2008), kenaf core fibers (Sajab et al., 2011), and lawny grass (Chen et al., 2011). An advantage of the modification method is the use of low toxicity reactants. At present, citric acid is extensively used to modify various waste biomass materials for the adsorption of heavy metal ions and dyes. A previous study reported that biochar prepared from corncob modified with citric acid was more effective than that modified with nitric acid, with Cd(II) adsorption capacities of 55.2 and 19.3 mg g^{-1}, respectively (Leyva-Ramos et al., 2005). Tartaric acid is another important chemical agent used to modify swede rape straw (*Brassica napus* L.) (Feng et al., 2012), rice husk (Wong et al., 2003), and bagasse (Low et al., 2013) to prepare biochar for the adsorption of pollutants from wastewater containing dyes or heavy metal ions. Furthermore, oxalic acid (Feng et al., 2013) is employed as modification agent to prepare biochar. A common characteristic of biochar modified with organic acids is the introduction of the carboxyl group on the biochar surface through esterification. However, the effects of different types of organic acids on the characteristics of biochar and the differences in the adsorption capacities for pollutants from aqueous solution must be further elucidated.

Eucalyptus has been extensively used as raw material for the paper and wood processing industries. In the end of 2013, the eucalyptus plantation area in Guangxi Province, China was approximately 2 million hectares and produced a considerable amount of by-products, such as saw dust, which should be further treated. In our previous study, eucalyptus wood biochar prepared at low-temperature pyrolysis exhibited the maximum methylene blue (MB) adsorption capacity of only 2.0 mg g^{-1} (Sun et al., 2013). Patnukao and Pavasant (2008) analyzed biochar prepared from eucalyptus bark powder treated with 85% phosphoric acid at an impregnation ratio of 1:1 by weight and activation time of 1 h at 500 °C. The prepared biochar demonstrated the maximum MB adsorption capacity of 427 mg g^{-1}. Moreover, biochar modified with phosphoric acid, a medium-strong acid, presents high adsorption capacity, but the preparation involves high-temperature pyrolysis (from 350 °C to 1000 °C) under nitrogen or argon flow (Al Bahri et al., 2012; Myglovets et al., 2014). Few studies have reported the preparation of biochar derived from eucalyptus saw dust modified with various organic acids at low activation temperatures for dye removal. Thus, scholars must determine the systematic adsorption data and differences in the adsorption capacity, processes, and mechanisms of biochar derived from eucalyptus saw dust modified with typical organic acids.

Citric, tartaric, and acetic acids containing different numbers of carboxyl groups are typical environment-friendly, organic, and low-cost compounds extensively used in the food industry. This work aims to (i) prepare and characterize biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids, (ii) investigate the effect of various key parameters on adsorption performance, kinetics constants, and equilibrium concentrations of the prepared biochar, and (iii) elucidate differences in the adsorption processes and mechanisms of MB on the modified biochar.

2. Methods

2.1. Materials

Eucalyptus saw dust, with size less than 5 mm, was obtained from timber processing plants in Liuzhou, Guangxi Province, China. MB, citric acid, tartaric acid, and acetic acid were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Preparation of modified biochar

Eucalyptus saw dust were first washed with tap water to remove sand and silt and then dried in a forced air oven (DHG-9030A, China) at 50 °C for 24 h. The dried saw dust was crushed to powder with a stainless steel grinder (RHP-2000A, China) and sieved using a standard screen of 60 mesh to retain particles with size less than 0.25 mm. The sieved powder without any acid modification was called BC-E. Meanwhile, another part of the sieved powder was subjected to acid modification based on the method reported by Gong et al. (2006). Citric acid was utilized to determine the optimal impregnation ratio and acid concentration. Briefly, 2.0 g of the sieved powder was mixed with 0.6 M citric acid solution at impregnation ratios of 1:8, 1:10, and 1:12 (saw dust powder/acid, w/v) in a 50 mL beaker. The mixture was stirred using a magnetic stirrer at 150 rpm for 30 min at room temperature. Afterward, the supernatant of the mixture was discarded, and the wet material was dried in the forced air oven at 50 °C for 24 h. The temperature of the oven was then increased to 120 °C and maintained for 90 min. The reacted products were washed repeatedly with distilled water to remove excess citric acid and added with 0.1 M lead (II) nitrate until the liquid did not become turbid. The products were subsequently dried in the oven at 50 °C for 24 h. Subsequently, 2.0 g of the sieved powder was mixed with 0.3, 0.9, and 1.2 M citric acid at the optimal impregnation ratio to optimize acid concentration. The optimal impregnation ratio and acid concentration were determined by comparing the MB adsorption efficiency of the different biochar samples prepared. Briefly, 0.1 g of the biochar sample was added to a series of 250 mL Erlenmeyer flask containing 200 mL of MB solution with a fixed initial MB concentration of 15 mg L^{-1}. The Erlenmeyer flasks were oscillated in a shaker (SHZ-82A, China) at 180 rpm and 30 °C for 120 min. Based on the results, the sieved powder was also modified with tartaric and acetic acids. The final biochar samples modified with citric, tartaric, and acetic acids were named BC-CA, BC-TA, and BC-AA, respectively.

2.3. Analytical methods

The specific surface area and porous texture of BC-CA, BC-TA, and BC-AA were measured by nitrogen adsorption at 77 K by using a surface area and porosimetry system (ASAP 2020M+C, USA). The biochar samples were also characterized through Fourier transform infrared spectroscopy (FT-IR; Nicolet iS10, USA) within the spectral range of 400–4000 cm^{-1}. Elemental analysis was conducted using an elemental analyzer (Vario MAX, Germany). The pH of the solution was adjusted using 1 M HCl or NaOH and measured using a pH meter (PHB-4, China). MB concentration was measured at 665 nm by using a UV–visible spectrophotometer (UV-5200, China) after filtration with microfilters of 0.45 μm pore size.

2.4. Adsorption kinetics studies

The effects of biochar dosage (0.1, 0.15, and 0.2 g), temperature (25, 30, 35, and 40 °C), and pH (approximately 5.0, 7.0, and 9.0) on the efficiency of MB adsorption on BC-CA, BC-TA, and BC-AA were investigated using a series of batch experiments at a fixed MB solution volume of 200 mL, initial MB concentration of 15 mg L^{-1}, and shaking speed of 180 rpm. Adsorption kinetics study was conducted as follows. Briefly, 0.15 g of BC-CA, BC-TA, and BC-AA were added to a series of 250 mL Erlenmeyer flasks containing 200 mL of MB solutions with different initial MB concentrations (15, 20, 25,