Ecotoxicology and Environmental Safety 157 (2018) 300–306

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Removal of methylene blue from aqueous solution by modified bamboo hydrochar

Wei-Cong Qian[a], Xi-Ping Luo[a], Xing Wang[a], Ming Guo[a], Bing Li[a,b,c,*]

[a] Zhejiang Provincial Key Laboratory of Chemical Utilization of Forestry Biomass, Zhejiang A & F University, Lin'an, Zhejiang 311300, PR China
[b] Zhejiang Provincial Collaborative Innovation Center for Bamboo Resources and High-efficiency Utilization, Zhejiang A & F University, Lin'an, Zhejiang 311300, PR China
[c] Zhejiang provincial Collaborative Innovation Center of Agricultural Biological Resources Biochemical Manufacturing, Hangzhou, Zhejiang 310023, PR China

ARTICLE INFO

Keywords:
Methylene blue
Adsorption
Hydrochar
Dye

ABSTRACT

Four hydrochars (labeled as HC, AHC, MHC, and MAHC, respectively) were prepared by hydrothermal carbonization of bamboo with and without chlorane or followed by NaOH modification. Various techniques were adopted to characterize the physicochemical properties of hydrochars and the removal of methylene blue (MB) by these hydrochars from aqueous solution was investigated. The MB adsorption isotherm and kinetic onto MAHC and MHC can be preferably interpreted by Langmuir adsorption mode and the pseudo-second-order model, respectively. Thermodynamic parameters implied that adsorption was a spontaneous and exothermic process. The adsorption capacity of MAHC was 655.76 mg g^{-1}, which was 2–3 times compared to that of MHC (268.93 mg g^{-1}) at 303 K. The high adsorption capacity of MAHC for MB suggests that hydrothermal carbonization in acidic medium followed by alkaline treatment has the potential application to produce efficient MB adsorbents used in wastewater treatment.

1. Introduction

The wet biomass can be converted into energy-dense, carbon-rich, value-added hydrophilic solid material, known as hydrochar, by hydrothermal carbonization (HTC) technology at moderate temperatures (180–350 °C) in the presence of water under autogenous pressures for several hours (Jain et al., 2016; Nizamuddin et al., 2017; Owsianiak et al., 2016; Liu et al., 2017). The detailed chemistry of the HTC reaction mechanism is not yet fully understood due to the complexity of biomass. In general, the reaction mechanisms simultaneously occur in the HTC process of biomass, such as hydrolysis, dehydration, decarboxylation, polymerization and aromatization (Funke et al., 2010; Lei et al., 2016; Fakkaew et al., 2015). Moreover, the elemental compositions and physicochemical properties of hydrochar depend on the type of feedstock and different HTC processing conditions (Guo et al., 2016; Ghanim et al., 2016; Xu et al., 2013). Therefore, it is possible to produce suitable properties of hydrochar by altering feedstock type and optimizing the carbonization conditions to meet different practical applications.

Though hydrochar has lower carbon content and less aromatic structure, it has the remarkable feature as an adsorbent for the environmental contaminant removal due to substantial oxygen-containing functional groups (hydroxyl, phenolic, carbonyl, or carboxylic) on its surface (Li et al., 2016; Han et al., 2017; Tran et al., 2017). However, the main disadvantages of hydrochar are its low surface area and poor porosity, which can decrease its adsorption capacities for pollutants. Hence, improving surface area and porosity of hydrochar presents a challenge as efficient adsorbents. Some work shows the content of carbon and HHV of hydrochar increased with the decrease of initial pH, and large pore volume and high surface area was founded during acidic feedwater (Ghanim et al., 2017; Braghiroli et al., 2015; Reza et al., 2015; Zhou et al., 2017). Indeed, the addition of acid in HTC of biomass may act as catalyst of hydrolysis reactions, decrease activation energy and modify the reaction rate and the characteristics of hydrochar, respectively (Ghanim et al., 2017; Braghiroli et al., 2015; Reza et al., 2015). In addition, cold alkali modification of hydrochar as an efficient, simple and low-cost approach may increase the oxygen based functional groups on hydrochar surface and increase the sorption capacities of alkaline modified hydrochar compared with those of pristine hydrochar for removing cationic pollutants from aqueous (Sun et al., 2015; Petrović et al., 2016; Regmi et al., 2012).

Bamboo is one of the fastest growing plants, which is distributed widely in China (Guo et al., 2014). It can be employed to produce bamboo charcoal as an effective adsorbent to remove contaminant from wastewater due to the abundance and short growth cycle of bamboo (Hameed et al., 2007; Li et al., 2017). In this study, we focused on

* Corresponding author at: Zhejiang Provincial Key Laboratory of Chemical Utilization of Forestry Biomass, Zhejiang A & F University, Lin'an, Zhejiang 311300, PR China.
E-mail address: libingzjfc@163.com (B. Li).

https://doi.org/10.1016/j.ecoenv.2018.03.088
Received 4 February 2018; Received in revised form 26 March 2018; Accepted 28 March 2018
0147-6513/

following main objectives: (i) to prepare four hydrochars by HTC of bamboo in deionized water and acidic medium, or followed by NaOH modification; (ii) to compare physicochemical properties of NaOH-modified and unmodified hydrochars using Fourier Transformed infrared (FT-IR) spectroscopy, elemental analysis, BET (Brunauer–-Emmett–Teller) surface area analysis and Boehm titration method; (iii) compare the potential application of the four hydrochars as adsorbents for MB removal.

2. Materials and methods

2.1. Materials

Bamboo sawdust with diameter less than 60 mesh from a local factory in Lin'an City, China was used as the feedstock biomass. All other reagents are A.R. grade ones in this study. The preparation of initial concentrations of MB solution was conducted by adding directly a required amount of MB powder in deionized water.

2.2. Preparation of hydrochar

Hydrothermal carbonization of bamboo was performed in a Teflon-lined stainless steel autoclave. Actually, 20.0 g of dried bamboo combined with 80 mL deionized water or 80 mL of 1 M hydrochloric acid solution was added to a 500 mL teflon vessel, which was then sealed in the autoclave, which was then held at 473 K for 24 h in an electric furnace and cooled in air atmosphere to room temperature. Then, the solid-phase material was separated from liquid by vacuum filtration, and subsequently washed with deionized water. Finally, the hydrochar samples were dried for 24 h to remove residual moisture at 353 K and the obtained dry samples were labeled as HC and AHC, respectively, where A refers to hydrothermal carbonization in acid medium.

2.3. NaOH modification of hydrochar

The obtained hydrochars were mixed with 0.25 M 100 mL NaOH solution and the mixture was stirred for 1 h at room temperature. Using vacuum filtration, the solid products were collected, then washed with deionized water until the pH value of the filtrate is reduced to 7–8. The NaOH modified hydrochars were obtained by dried the products overnight at 373 K, which were henceforth denoted as MHC and MAHC, respectively.

2.4. Characterization

Elemental composition (C, H and N) of the samples was assessed by means of an elemental analyzer (vario EL III). The average pore volume and specific surface area of hydrochars was obtained by the nitrogen adsorption-desorption isotherms under the condition of 77 K with an ASAP 2010.

2.5. Batch adsorption studies

Adsorption isotherms of MB onto the modified hydrochar samples were determined by adding 40 mg adsorbent to 150 mL stoppered glass bottles containing 50 mL of MB solution at 303 K, 313 K and 323 K, respectively. MB initial concentrations in the glass bottles were ranged from 50 to 350 mg L^{-1} for MHC and 100–900 mg L^{-1} for MAHC. The equilibrium states of the solutions were achieved for 24 h at certain temperatures (303–323 K) under a water bath thermostatic oscillator (SHY-2A, China). Then, the obtained solutions were filtered using a 0.45 μm membrane, and the MB concentrations were measured from the calibration curve of MB solutions at a maximum adsorption wavelength of 665 nm by using a UV754GD type UV–visible spectrophotometer (Shanghai, P.R. China). The adsorption capacity of the adsorbent was defined by Eq. (1) (Guo et al., 2014; Mohammadi et al., 2011).

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

where V was the solution volume (L), W was the adsorbent mass used (g), and C_e and C_o were the equilibrium and initial MB concentration, respectively.

The kinetics of MB adsorption onto the modified hydrochars were examined by adding 40 mg of each adsorbent to 150 mL stoppered glass bottles containing 50 mL MB solution for MHC and MAHC, for which the concentrations were 300 and 500 mg L^{-1}, respectively, at a desired temperature (303–323 K) and different time intervals. The glass bottles were then shaken at 110 rpm under a water bath thermostatic oscillator. After adsorption, the samples were withdrawn and filtered immediately and the residual MB concentration was measured by UV–visible spectrophotometer and calculated from the calibration curve.

To examine the effect of pH on the adsorption of MB onto MHC and MAHC, respectively, the initial pH of MB solution was conducted in the range from 2 to 13. The solution pH was adjusted with 0.1 M NaOH or HCl solutions. Cationic concentrations of (Ca^{2+}, Mg^{2+} and K^{+}) from 0 to 0.1 mol L^{-1} was studied to reveal the possible impact of ion-exchange mechanism of MB adsorption. The MB concentration and temperature of adsorption were fixed at 300 and 600 mg L^{-1} at 303 K for MHC and MAHC, respectively. Batch experiments were executed in triplicate, and the parameters were fitted by Origin Pro 9.1 software.

3. Results and discussion

3.1. Characterization

Several main properties including surface area, pore volume, average pore diameter and elemental compositions of solid materials were summarized in Table 1. As expected, the elemental contents of the solid materials changed significantly after the HTC process of bamboo (Li et al., 2016). Hydrochars had higher carbon contents and lower oxygen and hydrogen contents relative to bamboo. The atomic ratios of O/C and H/C of hydrochars were lower than those of raw bamboo due to removal of polar compositions and the formation of aromatic structures by the decarboxylation and dehydration reactions during the HTC process according to Van Krevelen diagrams (Cai et al., 2016). It was apparent that AHC had a slightly higher C content, but a relatively lower O, N and H contents in comparison to HC, which indicated the more obvious dehydration trend and the higher aromaticity in

Table 1
Main physicochemical characteristics and elemental compositions of the solid materials.

Samples	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	C(%)	H(%)	N(%)	O(%)[a]	H/C	O/C
Bamboo	–	–	–	49.29	6.23	0.19	44.29	1.506	0.675
HC	7.916	0.031	3.788	63.66	5.50	0.34	30.50	1.030	0.360
AHC	31.602	0.110	3.778	67.90	4.40	0.29	27.41	0.772	0.303
MHC	1.398	0.005	3.804	58.37	5.81	0.29	35.53	1.186	0.457
MAHC	26.249	0.089	3.781	60.19	4.84	0.19	34.78	0.958	0.434

[a] O = 100–(C + H + N).