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Short Communication

Adsorptive removal of chloramphenicol from wastewater by NaOH modified bamboo charcoal

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ABSTRACT

This study described the adsorption of chloramphenicol (CAP) in wastewater on the renewable bioresource of bamboo charcoal (BC). Results showed that CAP adsorption on BC ($\text{Ln}\, q_e = 1.272\, \text{Ln}\, C_e + 1.971$) and H_2SO_4 modified BC ($\text{Ln}\, q_e = 1.851\, \text{Ln}\, C_e + 0.659$) were very slight, and on NaOH modified BC was significantly increased ($\text{Ln}\, q_e = 0.344\, \text{Ln}\, C_e + 6.490$). The adsorbents were characterized by N_2 adsorption–desorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). It is revealed that BC and modified BC had very small surface areas of less than 1 $m^2\,g^{-1}$, H_2SO_4 treatment led to minimal variation in surface functional groups, and NaOH treatment increased the percentage of surface graphitic carbon and other oxygen-containing groups. The increased adsorption of CAP on NaOH modified BC was mainly ascribed to the enhancement of the π–π interaction between the adsorbent and adsorbate.

1. Introduction

Adsorption by carbonaceous materials, particularly activated carbon (AC), has been extensively used for wastewater purification (Yin et al., 2007). However, the regeneration of AC saturated with contaminants is inconvenient because of the difficult desorption of contaminants from the micropores (<2 nm) and mesopores (2–50 nm) (Ania et al., 2005). Besides, AC is mostly made from the non-renewable source of coal, which implies the decreasing application in the future. Bamboo charcoal (BC) is an environmentally friendly, low-cost and renewable bioresource with porous structure. Adsorption of contaminants on BC has attracted great attention in recent years (Hameed et al., 2007; Wang et al., 2008; Zhao et al., 2008). Researchers modified the adsorbents by heating under elevated temperatures and certain atmosphere to create more micropores and mesopores for physical adsorption (Yin et al., 2007; Pietrzak and Bandosz, 2007), or by impregnating in certain solution to produce more characteristic surface functional groups for chemical adsorption (Shim et al., 2001; Pan and Xing, 2008). Compared with heating at high temperature, impregnation is more convenient and economical to increase adsorption. It has been addressed that acidic treatment led to the increase in metals uptake and the decrease in organic adsorption, while basic treatment gave contrary results (Shim et al., 2001). However, a detailed characterization of BC and acid/base modified BC was lacked.

Antibiotics belong to a group of antimicrobial compounds commonly used to treat the diseases caused by microorganisms (Martinez, 2008). However, the biodegradability of antibiotics is difficult, resulting in their nearly breakthrough in traditional wastewater treatment plants. Adsorptive removal by porous materials provides an option for the removal of antibiotics in the effluent from wastewater treatment plant or other water bodies (Yu et al., 2009). Till now, most studies used non-renewable adsorbents for antibiotics adsorption (Lee et al., 2004; Yu et al., 2009). In this study, commercial BC was modified by H_2SO_4 or NaOH. The adsorptive removal of chloramphenicol (CAP), a representative antibiotic, by BC and modified BC from wastewater was investigated and compared. Besides, a series of characterization, including N_2 adsorption–desorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were conducted to reveal the structure and surface properties of the adsorbents.

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2. Methods

2.1. Chemicals and materials

CAP (98%) was purchased from Acros organics, Belgium. Representative massive commercial BC in market (Quzhou Eidolon Bamboo Charcoal Products Co., Ltd., China) sold for indoor air purification was used. According to the manufacturer, BC was produced by water evaporation between 100 and 150 °C, pre-carbonization between 150 and 270 °C, carbonization between 270 and 450 °C, and calcination at above 450 °C. The massive BC was ground and sieved with 100 mesh screen. After washed for several times with deionized (DI) water, the BC particles were dried at 105 °C for 3 h (denoted as BC). One fraction of BC particles were immersed in 10% H_2SO_4 with constant stirring for 6 h at 60 °C, then washed with DI water to constant pH and dried at 105 °C for 3 h (denoted as BC–H_2SO_4). The other fraction was immersed in 10% NaOH for 6 h at 60 °C likewise (denoted as BC–NaOH). DI water (18.2 mΩ cm) was obtained from a Millipore Milli-Q system. All the other reagents were above analytical grade.

2.2. Characterization

N_2 adsorption–desorption was conducted at 77 K using Brunauer–Emmett–Teller (BET) surface area apparatus (Micromeritics ASAP2020). FTIR spectra were recorded on an IR spectrophotometer (VERTEX 70, Bruker) using KBr as background. TGA was performed on a Diamond thermogravimetic/differential thermal analysis (TG/DTA) instrument (Perkin–Elmer Instruments) from 30 to 950 °C at 10 °C min^{-1} under N_2 atmosphere. XPS analysis was conducted on an 800SIMS KROTOS Electron Energy Spectrometer. The C1s peaks were deconvolved by XPSpeak 4.1 software.

2.3. Adsorption of CAP by BC and modified BC

The adsorption experiments were carried out in 30-mL serum bottle. For the adsorption kinetics, 25 mL of solution containing 20 mg L^{-1} CAP was mixed with 0.2 g of adsorbents in the bottle. The bottles were sealed and placed in a shaking table at 150 rpm in dark (25 ± 1 °C). At regular time intervals, three bottles were sacrificed for CAP analysis. With respect to adsorption isotherms, similar procedure was used with initial CAP concentrations at 5, 10, 15, 20, 50, 100 mg L^{-1} (equilibrium for 30 min). CAP concentration in solution after filtration was analyzed at 279 nm on a Cary 50 ultraviolet visible spectrophotometer (Varian, USA). The solution from the mixing of DI water and adsorbent was used as reference. The correlation coefficient of the fitted line for CAP analysis was above 0.999.

3. Results and discussion

3.1. Adsorption time courses and isotherms of CAP on the adsorbents

Fig. 1a reveals that the adsorption proceeded quickly and reached equilibrium within 15 min. This was probably resulted from the relatively low initial concentration of CAP and the absence of micropores in the adsorbent. The data of adsorption isotherms in Fig. 1b are analyzed by Freundlich models ($\text{Ln}\, q_e = 1/n \text{Ln}\, C_e + \text{Ln} K_F$), where C_e is the equilibrium concentration of CAP (mg L^{-1}) and q_e is the equilibrated adsorbed amount of CAP (mg kg^{-1}). K_F and n are Freundlich constants which reflect the adsorption capacity and the affinity between adsorbent and adsorbate, respectively. A higher value of K_F indicates a larger adsorption capacity and a larger value of n represents more affinitive adsorption (Pietrzak and Bandosz, 2007). The logarithmic form of Freundlich adsorption isotherms for CAP on the three adsorbents are presented on Table 1. Compared with pristine BC, the adsorption capacity and affinity increased significantly after treatment by NaOH, suggesting that basic modification could effectively enhance the interaction between adsorbent and adsorbate. The approximately equivalent values of K_F and n for BC–H_2SO_4 and BC indicate negligible influence of H_2SO_4 treatment on BC characteristics. It is noteworthy that only the adsorption isotherms for BC–NaOH fitted Langmuir model ($C_e/Q_e = 0.00036C_e + 0.0023$, $R^2 = 0.942$).

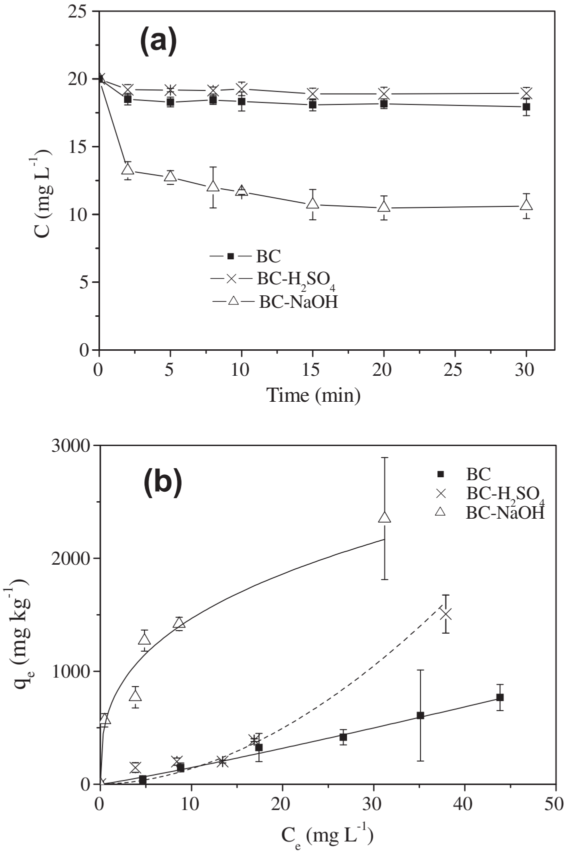

Fig. 1. Adsorption (a) time courses and (b) isotherms of CAP on BC and modified BC.

Table 1
Freundlich adsorption isotherms of CAP on BC and modified BC.

Samples	Freundlich equation	n	K_F	R^2
BC	$\text{Ln}\, q_e = 1.272 \text{Ln}\, C_e + 1.971$	0.79	7.17	0.980
BC–H_2SO_4	$\text{Ln}\, q_e = 1.851 \text{Ln}\, C_e + 0.659$	0.54	1.93	0.930
BC–NaOH	$\text{Ln}\, q_e = 0.344 \text{Ln}\, C_e + 6.490$	2.91	658	0.936

3.2. Surface structure, crystalline and functional groups

The adsorption–desorption isotherms of N_2 on the adsorbents at 77 K indicates that the commercial and modified BC had little micropores and very small BET surface areas (<1 $m^2\,g^{-1}$). The XRD patterns give no characteristic carbon peaks, mostly due to the lower carbonization temperature. The peaks at $2\theta = 20°–30°$ imply the stacking structure of aromatic layers (graphite 0 0 2), and the broadening is originated from the small dimensions of crytallites perpendicular to aromatic layers (Takagi et al., 2004). The DTG curve measurement demonstrates a much larger peak around 70 °C for BC–NaOH than for the other adsorbents, which indicated the presence of much more water loosely adsorbed and a more