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Removal of levofloxacin from aqueous solution using rice-husk and wood-chip biochars

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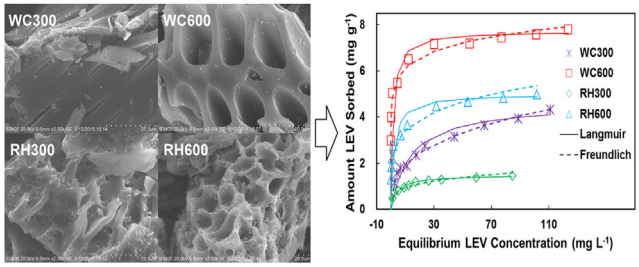
HIGHLIGHTS

- Rice husk and wood chip biochars showed fast sorption kinetics to LEV.
- Maximum LEV sorption capacities of the biochars were between 1.49 and 7.72 mg g^{-1}.
- Adsorption of LEV onto wood-chip biochar was spontaneous and exothermic.
- Adsorption of LEV onto rice-husk biochar was spontaneous and endothermic.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential for rice husk (RH) and wood chip (WC) biochars to remove levofloxacin (LEV) from aqueous solution was evaluated. The physical and chemical properties of the biochars were characterized using various tools and techniques. Furthermore, batch sorption experiments were conducted to determine the sorption ability of the biochars to LEV. The pseudo-second order kinetic model described the sorption kinetic data better than the pseudo-first order kinetic model and the Elovich equation because the process involved both surface adsorption and pore diffusion. For the isotherms, the Langmuir equation fitted the data better than the Freundlich equation. The maximum Langmuir sorption capacities of the biochars to LEV ranged from 1.49 to 7.72 mg g^{-1}. Thermodynamic parameters obtained from the experiments showed that the adsorption of LEV onto the WC biochar was spontaneous and exothermic, while its adsorption onto the RH biochar was spontaneous and endothermic under tested conditions. A mixture of 0.025 M phosphate buffer (80%, pH 3.0) and acetonitrile (20%) effectively desorbed the LEV from the biochars with a recovery rate up to 80%. Findings from this work indicate that biochars can be used as an alternative adsorbent to effectively remove emerging contaminants including LEV from aqueous solutions.

1. Introduction

A considerable fraction of antibiotics have been released into the soil and water environment because they are not only widely used

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in human and veterinary medicine to treat or prevent microbial infections, but also as husbandry growth promoters in aquaculture and livestock operations (Sarmah et al., 2006; Luo et al., 2011). The presence of antibiotics in the environment can alter the microbial communities, leading to the antibiotic resistance of some bacteria (Xiao et al., 2008; Girardi et al., 2011); further, they pose potentially toxic risks to aquatic organisms and may be absorbed eventually by humans through the food chain and drinking water (Luo et al., 2011). Fluoroquinolone antibiotics, which have been widely used in controlling many bacterial pathogens, could even be genotoxic (Hu et al., 2007). It is thus critical to develop efficient and cost-effective approaches to remove antibiotics from water.

Adsorption is one of the most efficient and attractive methods for removing pollutants from water and is characterized by easy process control and low cost requirements (Inyang et al., 2011, 2014). Sorption of antibiotics have been conducted using various materials, including resins, activated carbon, and carbon nanomaterials (Yang et al., 2011; Tian et al., 2013a, 2013b; Chen et al., 2014, 2015). These materials can effectively remove the antibiotics from water; however, they may not be economically feasible in some large-scale applications (Tong et al., 2011). Therefore, there is an urgent need to develop other environmental-friendly and low-cost adsorbents for the removal of antibiotics from water.

Biochar, which can be produced from various waste biomass materials in an oxygen-limited environment, has recently received major attention as an alternative low-cost and effective adsorbent for environmental pollutants. Many studies have shown that biochar has strong sorption ability for organic and inorganic contaminants in soil and water (Mohan et al., 2014; Xie et al., 2015). For example, wood chip (WC) and rice husk (RH) biochars have been effective in removing various pollutants including tetracycline (Liu et al., 2012), ammonium nitrogen (Kizito et al., 2015), dyes (Zou et al., 2013), heavy metals (Agrafioti et al., 2014; Cope et al., 2014). However, only very little work has been done to examine the removal mechanisms and effectiveness of fluoroquinolone antibiotics from water using biochar (Yao et al., 2013).

The overarching objective of this work was to evaluate the potential of using WC and RH biochars as adsorbents for the removal of fluoroquinolone antibiotics from aqueous solutions. An emerging kind of fluoroquinolone antibiotic, levofloxacin (LEV), was selected to represent antibiotic contaminants. Batch experiments and mathematical simulations were conducted to determine the mechanisms and characteristics of LEV adsorption onto the biochars. Characteristics of the biochars were analyzed using scanning electron microscope (SEM), elemental analyzer (EA), X-ray fluorescence (XRF), inductively-coupled plasma emission spectroscopy (ICP-OES), surface area analyzer (BET), Fourier transform infrared spectroscopy (FTIR), and point of zero charge (PZC) method. The specific objectives were as follows: 1) develop a simple and easy-to-operate method for preparing low-cost LEV sorbents; 2) evaluate the LEV removal ability and sorption mechanisms of WC and RH biochars; and 3) determine the effects of initial solution pH, contact time, initial LEV concentration, and temperature on the adsorption of LEV onto the biochars.

2. Materials and methods

2.1. Materials

Levofloxacin (LEV) (>98.5%) was obtained from Dalian Meilun Biology Technology, Ltd (China); chemical structures and properties of LEV are reported in Fig. S1 (supporting information). Acetonitrile (HPLC grade) was purchased from Tedia Company, Inc., and other the chemicals of analytic grade were obtained locally.

Two different feedstock materials, containing rice husk (RH) and wood chip (WC) from the pine trees, were collected from Fujian province, China. They are cheap and easy available biomass feedstocks in China and commonly used to represent the herbs- and woody biomass feedstocks in previous studies (Mohan et al., 2014; Xie et al., 2015; Inyang et al., 2016). These raw rice husk and wood chip were washed with deionized (DI) water to remove the dirt, and dried in an oven at 80 °C for 24 h and then were ground to powder in a disintegrator. Biochar is generally obtained through slow pyrolysis in an oxygen-limited environment under different temperature ranging from 200 °C to 600 °C (Mohan et al., 2014). Previous literature indicate that the pyrolysis temperature is one of the key factors determining the physicochemical properties of biochars (Mohan et al., 2014; Sun et al., 2014; Xie et al., 2015). Thermal decomposition of functional groups of cellulose, hemicellulose and lignin occurs generally at 150–300 °C and carbon skeletons at 300–500 °C. Therefore, the powders of RH and WC were used to produce biochars at 300 and 600 °C as described by Ding et al. (2014). The biochars, cooling to room temperature in the muffle, were rinsed with DI water several times to remove impurities and then were sieved through a 100-mesh sieve to obtain a uniform size. The samples were oven dried (100 °C) for 12 h. The biochar samples acquired at different temperatures were referred to as RH300, RH600, WC300, and WC600.

2.2. Characterization of biochars

The contents of C, H and N in the biochars were determined using an elemental analyzer (EA, Vario MICRO, Elementar) via high-temperature catalyzed combustion. The content of main mineral elements (K, Ca and Mg) in biochars was determined using inductively-coupled plasma emission spectroscopy (ICP-OES, Optima 5300, PerkinElmer, USA) after ashing the samples at the temperature of 550 °C and dissolution with 7% hydrochloric acid (w/w). Silicon was obtained using X-ray fluorescence (XRF, ARL-9800, ARL, Co., Switzerland) after ashing at 550 °C. Specific surface areas of the samples were measured with a surface area analyzer (BET, ASAP20, Micromeritics Ltd., USA) using the N_2 adsorption methods. The surface physical morphology was examined using a scanning electron microscope (SEM, S-3400N II, Hitachi, Ltd., Tokyo, Japan). FTIR spectra were recorded on a NEXUS870 FTIR (USA) instrument in the absorption mode in the range 4000–400 cm^{-1} with a resolution of 0.2 cm^{-1}. The pH of the solutions were measured by a pH meter (Mettler Toledo E-201-C). The point of zero charge (PZC) was determined by salt addition method (Mustafa et al., 2002).

2.3. Batch adsorption experiments

Adsorption experiments were carried out at 30 °C, unless otherwise stated, by adding 20 mL LEV solution of desired concentration mixing 0.2 g WC or RH biochar in 50 mL polyethylene centrifuge tubes. Solution pH was adjusted to the desired pH value using 0.1 mol L^{-1} HCl or NaOH. The effect of pH on the LEV removal was investigated in the pH range of 2–9, with an initial LEV concentration of 100 mg L^{-1}. The adsorption kinetics were investigated with an initial LEV concentration of 40 and 75 mg L^{-1} for RH300 and RH600 respectively at pH 8.0, while the adsorption kinetics were investigated with an initial LEV concentration of 50 and 150 mg L^{-1} for WC300 and WC600 respectively at pH 6.5 from 5 to 600 min. Different initial concentrations were used for the kinetic study because the adsorption ability of the four biochars differed greatly. The isotherm adsorption experiments were performed in the initial LEV concentration range from 7.5 to 100 mg L^{-1} and from 15 to 150 mg L^{-1} at pH 8.0 for RH300 and RH600 respectively, while the initial LEV concentration range was from 15 to 150 mg L^{-1} and

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