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Adsorption study of environmentally relevant concentrations of chlortetracycline on pinewood biochar

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HIGHLIGHTS

- Activated pinewood has considerable potential for adsorption of CTC from water.
- CTC follows the Langmuir model for adsorption on raw and activated biochar.
- In lower pH, adsorption on biochar is enhanced due to lower electrostatic repulsion.

GRAPHICAL ABSTRACT

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ABSTRACT

The presence of pharmaceutically active compounds (PhACs) in water and wastewater has raised concerns because of potential environmental impacts and thus their removal is of high importance. The adsorption behavior of chlortetracycline (CTC) from aqueous solution on raw and activated pinewood biochar was studied at 298 K. The effect of initial pH of the solution was studied by performing the experiment at three different pHs (1, 5 and 9). At each pH, CTC showed varied electrostatic charge (+1, 0 and −1, respectively) which affected its adsorption. The results indicated that CTC followed Langmuir isotherm and the related parameters were calculated. Also, it was observed that the maximum adsorption occurred at pH 1. The adsorption capacity of CTC for raw and activated biochar was at least 2.1 and 208.3 mg/g adsorbent, respectively. The characteristics of biochars were studied using zeta potential analyzer, laser size analyzer and scanning electron microscopy (SEM). The results showed that raw and activated biochars are promising candidates for removal of CTC from water due to the acidic character of pinewood that can result in better interaction with ionizable compounds at lower pHs.

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1. Introduction

Chlortetracycline (CTC) is a broad-spectrum antibiotic from the family of tetracyclines that is commonly used as veterinary medicine for poultry, swine, and livestock for preventing, controlling, and treating animal health issues as well as increasing their growth rates (Puicharla et al., 2014). This pharmaceutically active compound (PhAC) can enter the environment through the application of animal manure to agricultural fields and thereafter it can go to rivers, ground waters and lakes by surface runoff (Hoese et al., 2009). The concentration of CTC is reported from several ppb in the effluent of municipal wastewater treatment plant to several ppm in pharmaceutical production wastewater (Guoxin et al., 1995; Karthikeyan and Meyer, 2006). Generally, PhACs can enter the human body through the drinking of contaminated water which has raised concerns over potential human health risks (Taheran et al., 2016). Antibiotic resistance can also develop to chlortetracycline in human and animals which in turn necessitates the prescription of higher dosages of antibiotics and finally invention of new compounds (Davis et al., 2006). Therefore, removal of this compound from water and wastewaters should be considered to avoid potential problems.

There are different methods including physical (membrane separation, adsorption), chemical (ozonation, chlorination, UV irradiation) and biological (microbial or enzyme bioreactor) for removal of PhACs from aqueous media (Chang et al., 2012; Chang et al., 2009; de Godos et al., 2012; Gómez-Pacheco et al., 2011; Hao et al., 2012; L. Ji et al., 2010; Kang et al., 2010; Sungpyo Kim et al., 2005; Yang et al., 2011). Among them, adsorption onto carbonaceous materials is of interest because of its feasibility, scale-up capability and reasonable capital and operational costs (Liu et al., 2012). Ji et al. studied the removal of tetracycline with carbon nanotube and compared it with graphite and activated carbon. They observed that single-walled carbon nanotube has higher adsorbent to solution distribution coefficient compared to multi-walled carbon nanotube, activated carbon and graphite (Liangliang Ji et al., 2009a). Choi et al. used granular activated carbons (GAC) made from coal or coconut for removal of CTC and achieved >80% removal efficiency for both carbon sources (Choi et al., 2008). Gao et al. investigated the adsorption capacity of graphene oxide for tetracycline and achieved 313 mg/g maximum adsorption capacity (Gao et al., 2012). Recently, biochars produced by pyrolysis of different biomass has attracted the attention of researchers for removal of PhACs because they are cost effective, porous and environmentally friendly and have functional groups. For example, Zhang et al. used corn straw biochar for sorption of tetracycline and observed that, the corn straw biochar is not an ideal sorbent for immobilization of tetracycline though its performance for simazine is acceptable (Zhang et al., 2012; Zhang et al., 2013). In another study, Liu et al. enhanced the adsorption capacity of rice-husk biochar with acid and alkali treatment and achieved >58.8 mg/g adsorption on alkali treated biochar (Liu et al., 2012). Among different sources of biochar, pinewood biochar is of high interest. Pine trees account for the majority of forest trees in Canada and other regions and each year millions of them are cut and transported to all around the world for industrial uses which leaves lots of biomass in the form of wooden chips. Therefore, availability and low cost make pinewood biomass as a promising source for production of biochar which is also a value adding process for wooden residues. To the best of our knowledge, there is no report on adsorption of chlortetracycline on pinewood biochar and in this study the adsorption behavior of this compound is investigated at different pHs on raw and activated biochar.

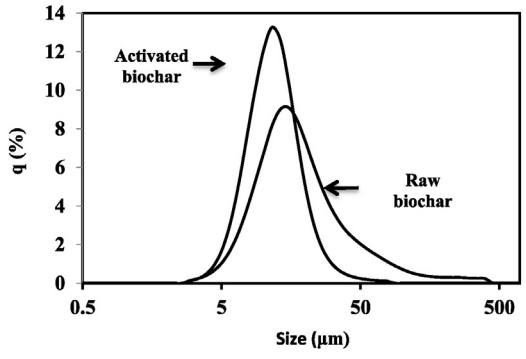

Fig. 1. Particle size distribution of biochars (q: amount of each size by volume).

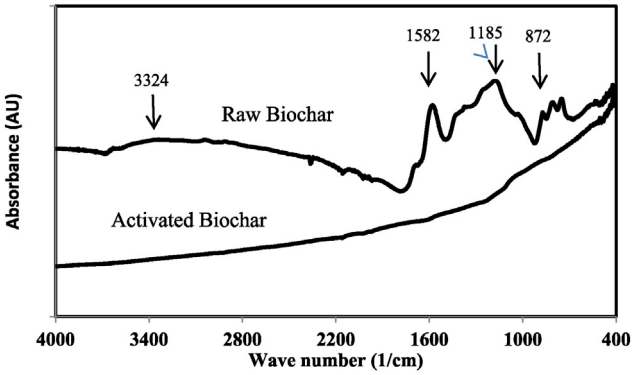

Fig. 2. FTIR spectra of raw and activated biochars.

2. Materials and methods

2.1. Materials

Chlortetracycline (CTC, purity > 97%) was purchased from Toronto Research Chemicals (TRC-Canada). HPLC grade water was prepared in the laboratory using milli-Q/Millli-Ro Milli pore system (Massachusetts, USA). Sodium hydroxide and hydrogen chloride (purity > 97%) were purchased from Fisher Scientific. Biochar was donated by Pyrovac Inc. (Quebec, Canada) derived from pine white wood (80%) purchased from Belle-Ripe in Princeville and the rest was spruce and fir (20%). This biochar was produced at 525 °C under atmospheric pressure for 2 min and used as obtained from the reactor outlet.

2.2. Biochar characterization

Supplied biochar was grinded by a Retsch RS 200 vibratory disc mill at 750 rpm for 60 s. For activated biochar, this process was performed again for 30 s after activation due to agglomeration. Particle size distribution of biochar was measured by a LA-960 laser particle size analyzer (Horiba, Japan). For this analysis, about 0.5 g of samples was dispersed into 100 ml of water and the mixture was introduced into sample space. The zeta potential of biochar and activated biochar were measured by zetasizer nano ZS (Malvern instruments Inc., UK) at different pH. Prior to analysis, a 200 ppm mixture of biochar or activated biochar in water was prepared and injected into sample holder. For each sample, measurement was done 30 times and the average value was reported. Fourier-transform infrared-attenuated total reflectance (FTIR-ATR) spectra were recorded on a Nicolet iS50 spectrometer (Thermo scientific, USA) at 0.04 cm^{-1} resolution and in the range of 400–4000 cm^{-1}. Morphological characteristics of biochar and activated biochar were investigated by an EVO® 50 scanning electron microscope (Zeiss, Germany). For this analysis, small amounts of the samples were transferred to the stub for gold coating by a SPI Module sputter coater. Energy-dispersive X-ray analysis (EDS) was performed by Inca 250 X-ray analyzer (Oxford instrument, UK). The BET specific surface areas were obtained from the N_2 adsorption isotherms recorded at 77 K ((Autsorb-1, Quantachrome Instruments) at the relative pressure range from 0.05 to 0.3. Powder X-ray diffraction (XRD) patterns of raw and activated biochar were collected using D5000 diffractometer (Siemens, Germany). The diffractometer was operated at 40 kV and 40 mA using Cu Kα

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