



# Chloramphenicol interaction with functionalized biochar in water: sorptive mechanism, molecular imprinting effect and repeatable application



Mohammad Boshir Ahmed<sup>a</sup>, John L. Zhou<sup>a,\*</sup>, Huu Hao Ngo<sup>a</sup>, Wenshan Guo<sup>a</sup>, Md Abu Hasan Johir<sup>a</sup>, Kireesan Sornalingam<sup>a</sup>, M. Sahedur Rahman<sup>b</sup>

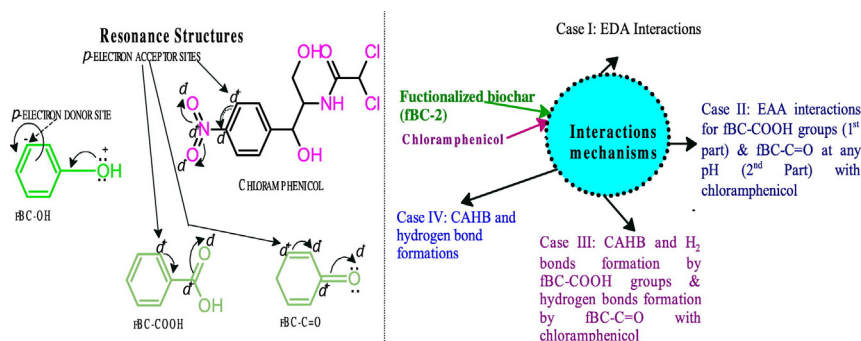
<sup>a</sup> School of Civil and Environmental Engineering, University of Technology Sydney, 15 Broadway, NSW 2007, Australia

<sup>b</sup> Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Rajshahi 6205, Bangladesh

## HIGHLIGHTS

- Functionalized biochar showed excellent removal efficiency of chloramphenicol.
- Removal decreased as deionized water > lake water > synthetic wastewater.
- H-bonds formation and EDA interactions were the main sorptive mechanism.
- Regenerated functionalized biochar exhibited excellent reusability.
- Molecular imprinting effect was observed in fBC.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 1 February 2017

Received in revised form 26 July 2017

Accepted 26 July 2017

Available online xxxxx

Editor: Ajit Sarmah

### Keywords:

Functionalized biochar

Chloramphenicol

Electron-donor interactions

H-bond

Reusability

Molecular imprinting effect

## ABSTRACT

Biochar and functionalized biochar (fBC-1 and fBC-2) were prepared and applied to remove antibiotic chloramphenicol from deionized water, lake water and synthetic wastewater. Results showed that chloramphenicol removal on biochar was pH dependent and maximum sorption occurred at pH 4.0–4.5. The sorption data of chloramphenicol fitted better with the Langmuir isotherm model than the Freundlich isotherm model with the maximum Langmuir sorption capacity of 233  $\mu\text{M g}^{-1}$  using fBC-2. Chloramphenicol sorption on fBC-2 followed the trend: deionized water > lake water > synthetic wastewater. The presence of humic acid decreased the sorption distribution coefficient ( $K_d$ ) while the presence of low ionic strength and soil in solution increased  $K_d$  value significantly. The mechanism of sorption on fBC mainly involved electron-donor-acceptor (EDA) interactions at pH < 2.0; formation of charge assisted hydrogen bond (CAHB) and hydrogen bonds in addition to EDA in the pH 4.0–4.5; and CAHB and EDA interactions at pH > 7.0. Additionally, solvent and thermal regeneration of fBC-2 for repeatable applications showed excellent sorption of chloramphenicol under the same condition, due to the creation of a molecular imprinting effect in fBC-2. Consequently, fBC-2 can be applied with excellent reusability properties to remove chloramphenicol and other similar organic contaminants.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Antibiotics are widely produced and used in large quantities to treat diseases caused by microorganisms as they can selectively act on

\* Corresponding author.

E-mail address: [junliang.zhou@uts.edu.au](mailto:junliang.zhou@uts.edu.au) (J.L. Zhou).

bacteria and pathogens without affecting human cells and tissues (Ahmed et al. 2015; Ahmed et al. 2017b; Boxall et al. 2003; Liao et al. 2013). Considering the different classes of antibiotics, chloramphenicol antibiotics have been commonly employed in veterinary clinics since the 1950s. Chloramphenicol, however, has geno-toxic effects and causes severe side effects such as aplastic anaemia, leukopenia, agranulocytosis and anaemia (Zhao et al. 2015). Although chloramphenicol has been banned since the 1990s in many countries for use in food-producing animals, it is still widely used due to its low cost and easy availability (Zhao et al. 2015; Nie et al. 2015). The occurrence and fate of chlorinated pollutants in the environment is recognized as an important problem due to the adverse effects on human health through the formation of emerging antibiotic-resistant bacteria and antibiotic-resistant genes (Mi et al. 2014; Chen et al. 2017). Low removal efficiencies of these organic contaminants have been reported through different biological treatment technologies (Ahmed et al. 2017a). Moreover, they are not easily degraded in the metabolite system and thus, they have been frequently detected in surface water, groundwater, and even in drinking water (Maskaoui and Zhou 2010; Chen and Zhou 2014). Several chemical methods have been applied to remove chloramphenicol from water (Lofrano et al. 2016; Nie et al. 2015; Wu et al. 2016; Xia et al. 2016). In addition, physicochemical methods have been applied for the removal of chloramphenicol (Dai et al. 2016; Fan et al. 2010; Qin et al. 2016; Zhu et al. 2016). Generally, adsorption by porous materials such as engineered activated carbon, resin, graphene oxide and carbon nanotubes is an expensive process. For this reason, biochar has received increasing interest due to its low cost (Ahmed et al. 2015), high hydrophobicity, aromaticity and multifunctional applications such as reduction of soil acidity, carbon sequestration and water remediation (Ahmed et al. 2016a; Chen et al. 2016; Dai et al. 2017; Das and Sarmah 2015; Mandal et al. 2017; Sorrenti et al. 2016). However, biochar properties depend on biomass origin, chemical composition, physical properties, and pre and post-treatment processes (Suliman et al. 2017). Biochar properties including surface functionality can be further improved through different modification methods (Ahmed et al. 2016b).

Adsorption of antibiotic onto biochar is expected to be heavily influenced by solution conditions and antibiotic speciation under different pH values (Ji et al. 2009a; Ji et al. 2009b; Ji et al. 2011; Taheran et al. 2016; Teixidó et al. 2011). Different species can interact with biochar through different mechanisms such as  $\pi$ - $\pi$  electron-donor-acceptor (EDA) interaction, nucleophilic addition, electrostatic attraction, cation bridging, cation/anion exchange, pore filling, partitioning into un carbonized fraction and formation of the charge assisted hydrogen bond (CAHB) with surface oxygen groups (Liao et al. 2013; Teixidó et al. 2011). For example, during the removal of tetracycline and chloramphenicol using charcoal, Liao et al. (2013) found that  $\pi$ - $\pi$  EDA interaction, cation- $\pi$  bond in conjunction with hydrogen bonding interaction were the main mechanisms while surface diffusion was less likely to be involved. However, so far no studies clearly described the sorption behavior of chloramphenicol using carbonaceous materials such as carbon nanotubes, graphene or graphene oxide, and biochar. In addition, research is lacking on the potential regeneration and repeatable application of carbonaceous sorbents. The physicochemical properties of chloramphenicol are shown in Table A.1.

Therefore this study aimed to use biochar and fBC for removing chloramphenicol. Specifically the objectives were to (i) evaluate the interaction mechanism and performance of biochar and fBC for removing chloramphenicol; (ii) study the impact of humic acid, soil and salt concentrations on the sorptive behavior of chloramphenicol; (iii) assess the sorption performance in different water matrices for removing chloramphenicol; and (iv) examine the desorption and repeatable application of fBC with special emphasis on the molecular imprinting effects (by creating sorptive template on/in fBC) during regeneration from different water.

## 2. Materials and methods

### 2.1. Chemicals

The standards of chloramphenicol (purity >98%), potassium chloride, sodium chloride (>99.6%), calcium chloride (>97%), and organic solvents such as methanol, acetonitrile and formic acid of HPLC grade were purchased from Sigma-Aldrich, Australia. Peptone, beef extract, humic acid, tannic acid, sodium lignin sulphonates, Na-laryl sulphate, acacia gum powder, arabic acid, ammonium sulphate,  $K_2HPO_4$ ,  $NH_4HCO_3$ , and  $MgSO_4 \cdot 3H_2O$  were of analytical-grade. Phenanthrene (98%) and *para* amino benzoic acid (PABA, >99%) were also purchased from Sigma-Aldrich. A Zorbax Bonus RP  $C_{18}$  column (5.0  $\mu$ m, 2.1  $\times$  1.50 mm) was purchased from Agilent Technologies. *Eucalyptus globulus* wood was donated by New Forest Asset Management Pty Ltd., Portland, Victoria, Australia. The soil sample was collected from the surface horizon (0–10 cm) at Willy Park, NSW, Australia. The soil was air dried, sieved (<1.0 mm), and stored at room temperature for further use.

### 2.2. Preparation of biochar and fBC

Biochar and fBC were prepared according to our previous study (Ahmed et al. 2017b). Briefly, 50 g of bamboo or eucalyptus wood biomass was pyrolyzed at 380 °C at a heating rate of 10–11.4 °C min<sup>-1</sup> under nitrogen flow at 2.5 psi for 2 h, to obtain biochar samples coded BBC380 and EGBC380, respectively. Activation of BBC380 and EGBC380 was carried out through chemical activation method by soaking 15 g of each biochar in 30 mL of 50% ortho-phosphoric acid ( $oH_3PO_4$ ) for 3 h at 50 °C. The mixture was then heated at 600 °C for 2 h. After that, the prepared activated biochar was left to cool, washed and the pH adjusted to 7, followed by drying overnight at 100 °C, to obtain the activated biochar fBC-1 (prepared from bamboo) and fBC-2 (prepared from eucalyptus wood). Average biochar particles size ranged from 75 to 1000  $\mu$ m. As activated biochar was enriched with different functional groups (such as —COOH, —OH, C=O, C=C) on its surface, the prepared activated biochar was termed as fBC.

### 2.3. Chloramphenicol sorption on biochar and fBC under different pH and different concentrations of humic acid, salt, soil and competitors

Interactions of biochar and fBC with chlorinated chloramphenicol in deionized water were studied in batch method at different pH (1.6 to 9) to calculate  $K_d$ . Sorption was carried out in PTFE-lined screw cap glass vials with a capacity of 50 to 100 mL. Sorbents were pre-equilibrated at a specific pH followed by adding the required amount of sorbate solution with the same pH. Batch sorption isotherm experiments were conducted at pH ranging from 4.0 to 4.5 at 25 °C with initial chloramphenicol concentrations of 0.774 to 154.7  $\mu$ M L<sup>-1</sup> at room temperature using 50–60 mg L<sup>-1</sup> of fBC and 100 mg L<sup>-1</sup> of biochar for 40 h. These conditions made it possible to calculate the maximum sorption at different pH values. The control experiments without sorbents were also executed.

To study the effects of salts, soil and humic acid on  $K_d$ , the sorption experiments were conducted by mixing humic acid or soil or salts with chloramphenicol (3.1  $\mu$ M L<sup>-1</sup>) overnight, before fBC-2 (being the best sorbent) was introduced. The sorption experiments were performed at pH 4.0–4.5 and 25 °C. Humic acid stock solution was prepared by dissolving the desired amount of humic acid in NaOH solution and stored for further use. Chloramphenicol sorption was also carried out in the presence of competitors (PABA and phenanthrene). The  $\pi$ -electron donor (phenanthrene) and  $\pi$ -electron acceptor (PABA) were chosen to unravel the possible EDA, electron acceptor-acceptor (EAA) and electron donor-donor (EDD) interactions mechanisms. The initial concentrations of chloramphenicol, phenanthrene and PABA were 3.1  $\mu$ M L<sup>-1</sup>, 1.0 mg L<sup>-1</sup> and 1.0 mg L<sup>-1</sup>, respectively at different pH (~1.85, 4.0–4.5 and 9.0–10.5). Control experiments (no

Download English Version:

<https://daneshyari.com/en/article/5750815>

Download Persian Version:

<https://daneshyari.com/article/5750815>

[Daneshyari.com](https://daneshyari.com)