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Application of goethite modified biochar for tylosin removal from aqueous solution

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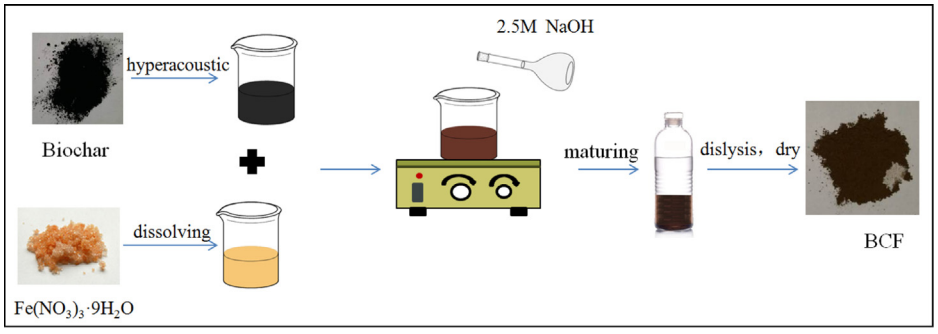
HIGHLIGHTS

- Goethite biochar composite (BCF) was simplified created with higher sorption for tylosin (TYL) in aqueous.
- Goethite loaded on biochar played a key role in TYL remove.
- The removal efficiency of BCF was greater than pure BC film.

GRAPHICAL ABSTRACT



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ABSTRACT

Recent investigations have shown frequent detection of pharmaceuticals in soils and waters posing potential risks to human and ecological health. Here, we report the enhanced removal of tylosin (TYL) from water by a novel goethite biochar (BCF) composite. Characterization by scanning electron microscopy (SEM) images showed good dispersion of goethite nanoparticles on the biochar surface. The coating was constructed by well-crystallized cubic phase goethite nanoparticles as examined by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis. To evaluate the feasibility of BCF composite as a potential adsorbent for antibiotic removal, batch sorption experiments were conducted using TYL as the model antibiotic molecule. The results showed that this adsorbent showed rapid and high sorption of TYL. According to the Henry and Freundlich model, the maximum capacities of TYL on BCF were 8132.89 L/kg and 5386.76 (μg/g)/(mg/L)^n respectively. Besides, the sorption capacity of TYL on BCF was obviously affected by pH and ionic strength. The sorption mechanisms of TYL on BCF were contributed to hydrophobic, electrostatic, H-bonding, cation exchange and π-π EDA interaction. The present work suggests that BCF composite, owing to their simple preparation procedures, high sorption capacity, low cost, and environmentally benign nature, have great potential as the next-generation adsorbent in the removal of antibiotics and other emerging contaminants.

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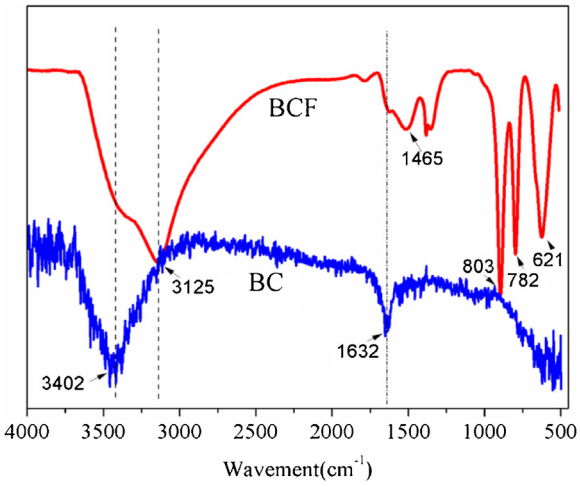

Fig. 1. FTIR spectrum of biochar (BC) and biochar-goethite complexes (BCF).

1. Introduction

Tylosin (TYL), a macrolides antibiotic, is widely applied for the treatment of bacterial, protozoal and fungal infections in human therapy, livestock production and aquaculture [1]. Residues of TYL and metabolites discharged from municipal wastewater treatment plants and agricultural runoff have a high potential to enter surface-water and groundwater [2,3]. Concerns arising from exposure to TYL in aquatic environments include acute and chronic toxic effects and microorganism antibiotic resistance [4]. However, the removal of TYL by existing water treatment technologies is incomplete [5]. To date, many technologies, such as photocatalytic degradation, membrane filtration, ion-exchange and sorption, have been explored for the removal of antibiotics from aqueous solution [6–8]. Compared to other techniques, sorption is considered simpler and more economical, and remains one of the most attractive methods for antibiotic removal [9].

Among the current available adsorbents, biochar has been greatly studied due to its outstanding properties like high sorption capacity, low cost, geological abundance, and environmentally benign nature [3]. Biochar is analogous to black carbon and derived from burning plant residues [10]. It is an ubiquitous geosorbent that is long lasting in the natural environment and thus influences the environmental behavior of antibiotics [11]. Rajapaksha et al. [12] investigated the removal of sulfamethazine by tea waste biochars and found that the π-π interaction and cation exchange were the primary sorption mechanisms. Teixidó et al. [13] found that sorption of sulfamethazine by black carbon was via π-π electron donor-acceptor interaction. Li et al. [14] indicated that sorption of sulphamethoxazole (SMX) by the biochar derived from rice straw was mainly via π-π electron donor-acceptor, while the electrostatic interaction might control the sorption of SMX by the biochar derived from alligator flag.

TYL adsorptions have been studied on clays, humic substances and soils [1,15–17]. Their ionization (cationic and neutral) depends on the pH of the media as is shown in Fig. 1 [16]. Hence, the sorption of TYL is complex. The adsorption of TYL is known to be governed by surface complexation or cation exchange mechanisms [15,16]. Among many different parameters, pH, ionic speciation, ionic strength, soil texture, cation exchange capacity (CEC), and soil organic carbon (SOC) were considered as the most important factors influencing the sorption of TYL to clays, goethite, humic acid and soils [1,2,15–17].

Goethite (a-FeOOH) is a wide spread soil mineral and a major component of many ores, sediments and soils and it is one of the most thermodynamically stable iron oxide which has been extensively researched especially the structure (including surface structure), the sorption capacity to anions, organic/organic acid (especially for the soil organic carbon) and cations in the natural environment and its potential application in environmental protection [4,18]. However, separation of goethite from an aqueous medium often requires centrifugation which is rather tedious and expensive. Recently, biochar (BC) which can be rapidly separated by filtration field have been developed for the sorption of antibiotics and exhibited high sorption capacities [19,20].

The objective of this work was to develop and evaluate a new method to prepare goethite-biochar composites for the removal of TYL from aqueous solution. The goethite-biochar adsorbents were prepared through co-precipitation of the iron metal ions onto biochar. The adsorbents were tested for TYL sorption capacity in batch experiments. The specific objectives of this work were to: (1) characterize the goethite-biochar composites, and (2) determine the sorption ability and mechanisms of the goethite-biochar composites for TYL in aqueous solution.

2. Materials and methods

2.1. Reagents

Tylosin tartrate (purity > 95%) was purchased from Sigma-Aldrich Corporation (St. Louis, MO). Acetonitrile and formic acid (HPLC grade, Merck Chemicals Co. AQ5) were used as received. Pure water was prepared by Milli-Q® water machine (Millipore Co., Guangzhou, China). All the other chemicals were analytical reagent grade and used without further purification.

Primary stock solutions of TYL at 1000 mg/L were prepared with pure water and stored at 4 °C for a maximum of 1 month. The work solutions were prepared by diluting stock solution using 0.01 M KNO_3 solution.

2.2. Preparation of goethite-biochar composites(BCF)

Pristine biochar (palm, obtained from fast pyrolysis at 600 °C) was supplied by Guangdong institute of eco-environment and soil sciences. The sample was milled through a 200-mesh sieve, stirred by 2 mol/L hydrochloric acid (HCl) for 12 h to remove the salt, and centrifuged to remove floater on the surface. After that, the residue was washed with deionized water until the aqueous phase was neutral, and dried at 105 °C for 24 h.

A typical procedure for the preparation of BCF was as follows (Scheme 1) [21]: Briefy, 4 g of biochar was added to 800 mL distilled water, agitated with a magnetic stirrer, and continuously purged with N_2 gas for 30 min. The composite dispersion was sonicated until it became clear with no visible particulate matter. Then 50 g $Fe(NO_3)_3{\cdot}9H_2O$ was dispersed into the solution. 5 M KOH was added into the suspension until red colloid was generated. The yielding ferrihydrite-biochar complex was aged at 60 °C in a capped Teflon container for 60 h and then was dialyzed with double distilled deionized water until the pH of the supernatant reached 8.5 close to the point of zero charge. After that, the solid was freeze-dried and employed as sorbent.

2.3. Characterization

Fourier transform infrared (FTIR) spectra were recorded with a KBr pellet in the mid-infrared region using a Nicolet 6700 Infrared Detector (Thermo Fisher Scientific, USA). The Brunauer-Emmett-Teller (BET) surface area of the samples was determined by nitrogen adsorption at 77 K (GEMINT VII 2390, USA). The constituents of the samples were identified using an X-ray powder diffractometer (XRD) (XD-2X/M4600, Beijing Purkinje General Instrument Co.,