



# Enhanced adsorption performance of tetracycline in aqueous solutions by methanol-modified biochar



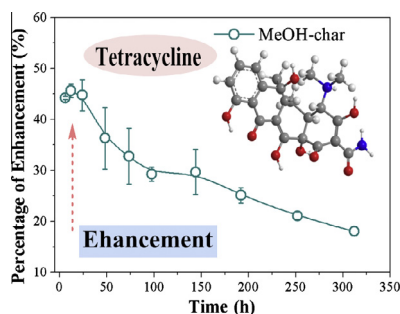
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## HIGHLIGHTS

- The MeOH-biochar showed significant increase in adsorption capacity to tetracycline.
- The inherent organic pollutants in biochar decreased after methanol modification.
- The filtration volume has a 2-fold of enhancement after methanol modification.
- The improvement of adsorption to TC attributes to the change in O-containing groups.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Tetracycline (TC), a commonly used personal care and veterinary drug, is produced in large-scale, during which high concentrations of wastewater is discharged into environment and difficult to biodegrade. Adsorption is a cost-effective and environment-friendly approach to TC wastewater. In this study, ubiquitous rice husk biochar was modified by methanol to improve TC adsorption capacities and reduce the inherent organic compound content in the biochar. The modified biochar showed approximately 45.6% enhancement of adsorption capacity in 12 h and 17.2% in equilibrium time compared with Ori-char. X-ray photoelectron spectroscopy suggested that the main factor responsible for the enhancement of TC adsorption is the change in O-containing groups in the modified biochar, which affects  $\pi$ - $\pi$  electron-donor-acceptor interactions between the biochar and TC. The fixed bed experiment show that the effective filtration volume of MeOH-char is 1059 bed volumes, which is approximately 2-fold of that of Ori-char.

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## 1. Introduction

Tetracycline (TC) is among the most commonly used personal care and veterinary drugs available in the market today. Recent reports on the recurrent detection of TC residues from wastewater treatment facility effluents [1], soils [2], sediments [3], and aquatic environments [4] have raised concerns for global public health. The reported concentrations for antibiotics residue in domestic

effluents are usually at  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  level [5], higher concentrations in hospital and pharmaceutical manufacturing wastewater can up to  $100\text{--}500 \text{ mg L}^{-1}$  [6]. The spread of these bioactive compounds can potentially lead to long-term adverse consequences on various ecosystems, including acute and chronic toxicity and propagation of antibiotic resistance in microbes [7]. Compared with current treatment technologies for TC removal, such as oxidation, enzymatic, photocatalytic, and photoelectrocatalytic degradation, and biodegradation by activated sludge [8–12], adsorption from pharmaceutical manufacturing wastewater or remediation of the contaminated environment using biochar is a more practical and environment-friendly approach.

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Pyrolytic biochar, a type of carbonaceous material, is massively produced during the pyrolysis of lignocellulosic biomass to obtain biofuel [13]. Pyrolytic biochar reportedly boosts soil fertility [14] and serves as a long-term sink of atmospheric carbon dioxide [15,16] in terrestrial ecosystems. Currently, biochar is used to control the fate and toxicity of organic compounds, including hydrophobic organic compounds [17], pesticides [18], and antibiotics [19], because of its strong sorption affinities for various contaminants and low cost. For example, biochar from rice straw can be utilized to reduce the risk posed by pentachlorophenol [20]. Dairy manure biochar can be a potentially unique amendment for simultaneously immobilizing atrazine and lead [21].

Biochar can efficiently remove TC from aqueous solutions [19]. However, several critical concerns must be addressed before biochar can be widely used to treat higher concentrations of wastewater or remediate TC-contaminated water and environment. On the one hand, the adsorption capacity and affinity to TC must be enhanced to ensure TC immobilization, particularly for high concentrations of wastewater. Considering that multiple groups (e.g., phenol, amino, alcohol, and ketone) in the TC molecule may cause specific interactions with the corresponding structures on the surface of the biochar, deliberately modifying the surface of biochar to enhance the interaction between them is a rational endeavor for improvement of TC adsorption. For instance,  $\pi$ - $\pi$  electron-donor-acceptor (EDA) interactions may occur between enone structures and the protonated amino group of TC ( $\pi$ -electron-acceptors) and the polarized electron-rich structure ( $\pi$ -electron-donors) of carbonaceous adsorbents [22]. Cation- $\pi$  bonding could also occur between the protonated amino group on ring C4 of TC and  $\pi$ -electron-rich structures [22]. Furthermore, several moieties included in the TC molecule can function as H acceptors (carbonyl and dimethylamino groups) or act as either H acceptors or H donors (amino, amide carbonyl, and hydroxyl groups) [23], which can form H bonds with biochar. On the other hand, biochar contains different organic compounds that are produced during the thermochemical decomposition of biomass. Some studies have demonstrated the very low environmental risks of biochar use [24], but risk evaluation data of long-term and massive usage of biochar in the environment are still unavailable. Pretreatment of biochar by solvents will improve the removal of organic compounds in biochar [25]. In addition, the adsorption performance of modified biochar in a continuously operated fixed bed is also a key factor influenced its practical application.

In the present work, methanol was used to modify the carbonyl group, an important O-containing group involved in TC adsorption, of rice husk-derived biochar and simultaneously wash off inherent organic compounds in the material. The main concerns regarding the massive application of biochar were addressed, and the underlying relationships between the physicochemical characteristics of modified biochar were clarified. This work provides information on the massive application of biochar in TC removal from hospital and pharmaceutical manufacturing wastewater as well as contaminated soil and water.

## 2. Materials and methods

### 2.1. Chemicals

TC hydrochloride (purity > 98.5%) was purchased from Sangon Biotech Co., Ltd. (Shanghai). All other chemicals used in these experiments were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd., China. The biochar was donated by Anhui Yineng bioenergy Co., Ltd. It was produced by fast pyrolysis of rice-husk at 723–773 K in the absence of air.

### 2.2. Modification and characterization of biochar

As previously described [19], raw biochar was first pretreated with 3 mol L<sup>-1</sup> NaOH solution at a rate of 1:10 (w/v), followed by rinsing with deionized water. Considering that biochar cannot be immediately modified under most practical conditions, modification and subsequent testing were performed after 20 d of storage in air. We also conducted an experiment on the effect of aging time on TC adsorption in the latter part of this work.

An adaptation of a procedure from the literature [26] was used to modify carboxyl groups with methanol under acidic conditions. The basic chemical reactions include both esterification (Fig. S1a) and the reaction between the carbonyl groups of biochar and methanol (Fig. S1b).

To compare the effects of organic solvent on the cleaning of alkaline-treated biochar, cyclohexane was used to wash the biochar via steps similar to those adopted for biochar modification. All separated solid samples were freeze-dried and stored in desiccators before use. Elemental analysis, X-ray photoelectron spectroscopy (XPS) and Brunauer, Emmett and Teller (BET) surface area (SA) determinations of the biochar samples are described in Supporting Information (SI).

### 2.3. Batch adsorption experiments

The adsorption kinetic experiment was performed using a batch protocol. An aqueous solution containing TC at the desired concentration was prepared in 0.01 mol L<sup>-1</sup> HCl solution without pH adjustment. Afterward, 100 mg of biochar was transferred to a 250 mL vial containing 100 mL of 100 mg L<sup>-1</sup> TC solution (measured during preliminary experiments to achieve detectable levels). Suspensions were mixed in the dark (to minimize the possible photodegradation of TC) at 303 K by end-over-end rotation (150 rpm) until equilibrium was achieved. The control experiment was conducted using TC solution without biochar. All sample aliquots were obtained at successive time intervals and immediately filtered through 0.22  $\mu$ m microporous membranes.

Solutes were determined directly by a UV-vis spectrometer (UV-2401, Shimadzu, Japan) at a wavelength of 270 nm. The TC amount adsorbed by the biochars was calculated by the difference between the initial sorbate concentration and the equilibrium concentration. All experiments were performed in duplicate for each data point.

Extraction of water-soluble substances from biochar samples was conducted by soaking 250 mg of biochar in 25 mL of NaOH solution (3 mol L<sup>-1</sup>), followed by placing on end-over-end rotation operating at 180 rotates per minute (rpm) under 303 K for 8 h. Then the suspension was transferred to 50 mL centrifuge tubes and centrifuged at 8000 rpm for 20 min using table-top high-speed centrifuge (model TG16-WS). The supernatant was filtered through 0.22  $\mu$ m microporous membranes, followed by adjusting the pH to weak acid. The total organic C content (TOC) of biochar extracts was determined using TOC analyzer (TOC-V<sub>cpN</sub>, Shimadzu, Japan).

### 2.4. Fixed bed adsorption experiment

The fix-bed adsorption experiments were performed at room temperature (298 K) using the dry biochar samples packed in two separate columns (200 mm in length, 9.0 mm in diameter). Columns were filled with approximately 1.0 g Ori-char and MeOH-char particles, respectively. Then, feeding solution containing 5.0 mg L<sup>-1</sup> TC was down-flow through the column by vacuum filtration at a constant flow rate of 25 mL h<sup>-1</sup>. The effluent samples were collected at successive time intervals and analyzed by the UV-vis spectrometer at 270 nm.

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