High removal efficiency of tetracycline (TC) by biochar-supported zerovalent iron composite prepared by co-pyrolysis of hematite and pinewood

Jun Shi, Xianni Yang, Changai Zhang, Xue Feng, Xiaofei Kong, Xiaozhi Wang and Shengsen Wang

College of Environmental Science and Engineering, Yangzhou University, Yangzhou, P.R. China; School of Environmental and Natural Resources, Zhejiang University of Science & Technology, Hangzhou, P.R. China; Science and Technology Service Centre of Dongchangfu District, Liaocheng, Shandong Province, P.R. China; Shuifa Utilities Group Co., Ltd, Jinan, P.R. China

ABSTRACT
There is a need to prepare a high-efficient sorbent to remove the recalcitrant tetracycline (TC) in wastewater. Herein, biochar-supported zerovalent iron (BC/ZVI) was fabricated in nitrogen ambience via one-step co-pyrolysis of hematite and pinewood. X-ray diffractometer pattern indicated pinewood catalyzed conversion of hematite to ZVI, which was otherwise transformed to FeO, Fe_3O_4, and ZVI without biomass. Batch sorption results indicated that TC removal capacities at pH 5 were 8.02, 177.70 and 301.39 mg g^{-1} by BC, ZVI and BC/ZVI, respectively. Overall, BC/ZVI showed excellent TC removal capacity through the complexation with Fe ions, surface adsorption and degradation. Thus, the agricultural and industrial wastes were converted via a one-step co-pyrolysis to a value-added product for highly efficient removal of TC in wastewater.

1. Introduction

Tetracycline (TC) represents one of the widely used antibiotics with increasing demands due to its low cost and excellent resistance to bacterium [1]. However, overuse and improper disposal of antibiotics to soil and water has cause a big concern to ecological environment [1]. Therefore, efforts have been devoted to seek for efficient techniques to remove TC from water, which include photocatalysis [2], adsorption [3] and advanced oxidation [4]. As is well accepted, adsorption and degradation are a low-cost and efficient method to remediate TC contamination [5].

Recently, zerovalent iron (ZVI) has been recognized as an adsorbent and catalyst to retain and degrade TC simultaneously [6,7]. There are many successful attempts to use ZVI for TC removal. Low redox potential and strong reducibility enable ZVI to reduce and degrade TC [8]. Meanwhile, ZVI could react with oxygen and water to generate free radicals, which could attack organic molecules to facilitate its degradation [9]. On other hand, TC molecule could readily complex with ferric and ferrous iron derived from ZVI as a result of surface corrosion [10]. Pan et al. [9] found that ZVI and Fe^{2+} promoted production of hydroxyl radical (-OH), enhancing degradation of antibiotics. However, the passivation of ZVI due to reaction with oxygen and water could result in a layer of iron oxides, inhibiting electron transfer from ZVI to target organics [11]. Besides, high tendency of aggregation of small-sized ZVI is another drawback for practical application, which hinder contact and reaction between ZVI and pollutants [12].

Immobilization of ZVI with carbonaceous materials not only well disperse ZVI nanoparticles but enhance electron transfer and manipulate ZVI oxidation [12]. Biochar (BC) derived from biomass has abundant porosity with large surface area and abundant functional groups [5], which is useful to immobilize ZVI nanoparticles and enhance ZVI reactivity. Traditionally, biochar-supported ZVI (BC/ZVI) composites were usually fabricated by borohydride reduction; instead, a novel route was developed through co-pyrolysis of pinewood biomass and natural hematite in which hematite was reduced by reducing gases from carrier and decomposition of biomass [13]. To date, there are limited researches concerning TC removal by using BC/ZVI composites synthesized via co-pyrolysis approach.

TC removal mechanisms of ZVI could be complicated after its immobilization with BC. This largely depended on the properties of BC, which are affected by precursor feedstock and pyrolysis temperature [14]. A temperature of greater than approximately 700°C is usually needed to obtain BC/ZVI composites [15]. The BC prepared at this temperature is characterized by good conductivity, which favor electron transfer and thus passivation of ZVI. As a result, the ability of ZVI to degrade TC could be greatly enhanced. Besides, BC could adsorb TC via pore filling and...
partition mechanisms [16]. Yet, the TC removal mechanisms by BC/ZVI composites have not been systematically investigated.

In this work, BC/ZVI composites were prepared in nitrogen ambience and characterized using X-ray diffraction. TC removal capacity by BC/ZVI was analyzed under different experimental conditions. The objectives of this study were to (1) synthesize and characterize BC/ZVI composites, (2) determine TC removal ability under different experimental conditions and (3) ascertain possible TC removal mechanisms by BC/ZVI composites.

2. Materials and methods

2.1 Reagents

Tetracycline hydrochloride (TC) was purchased from Aladin Industrial Corporation. Hydrochloric acid (HCl), sodium hydroxide (NaOH), ferric chloride hexahydrate (FeCl₃·6H₂O), tert-butyl alcohol (TBA) and hematite of analytical grade were obtained from Sinopharm Chemical Reagent Co., Ltd. Ethylenediaminetetraacetic acid (EDTA) was bought from Sigma-Aldrich Co., Ltd. Powered pinewood biomass was provided by a local furniture store. Deionized (DI) water of 18.2 MΩ was used to prepare solutions.

2.2 Preparation of BC/ZVI composites

The procedure to prepare the composites was similar to our recent work [17]. Specifically, 1.0 g of hematite and 5.0 g of biomass (mass ratio of 1: 5) were suspended in 50 mL DI water, which were then well stirred and sonicated for 30 min. Subsequently, the mixture was oven dried at 60°C for 24 h. The dried mixture was pyrolyzed at 800°C in a tube furnace for 1 h under nitrogen ambience with flow rate of 400 mL min⁻¹. The resulting BC/ZVI composites were washed with ethanol and DI water at least three times and dried in a vacuum oven at 60°C overnight. In a similar manner, biomass also pyrolyzed individually under the same condition, which was named BC. For zero-valent iron, we use sodium borohydride to reduce ferric chloride and then calcinate in a nitrogen atmosphere, which was denoted as ZVI. The sorbents were characterized by an X-ray diffractometer (XRD) (Bruker D8 Advance, Germany) to identify the form of Fe and C.

2.3 Batch sorption experiment

Kinetics: 0.01 g BC, BC/ZVI, or ZVI (1 g L⁻¹ dosage) were added to centrifuge tube containing 10 mL TC (400 mg L⁻¹) solution. The centrifuge tubes were shaken on a rotator (150 rpm) and sampled at time intervals (30, 60, 120, 240, 480, 720 and 1440 min). The subsamples were filtered through a 0.22-µm membrane filter and the TC concentration in the filtrate was analyzed by an UV-visible spectroscopy (SHIMADZU 2450, Japan) at wavelength of 357 nm [18].

Performance of sorbents was evaluated at various initial TC concentrations, which were 5, 10, 15, 20 and 50 mg L⁻¹ for BC, and 25, 50, 100, 150, 200, 250, 300 and 400 mg L⁻¹ for both BC/ZVI and ZVI. To implement the sorption experiment, 0.01 g sorbents (BC, BC/ZVI and ZVI) were added into centrifuge tube containing 10 mL fresh TC solution. The sorption was terminated after 24 h, and the samples were filtered and analyzed following the same procedure as above. Same reaction time and TC analysis protocol were used in the subsequent experiments unless otherwise specified.

Solution pH was an important factor which could affect surface charge of the sorbents and protonation of TC [1]. To assess TC removal, efficiency at different pH, 0.01 g sorbents (BC/ZVI and ZVI) were added into TC solutions at pH of 3, 5, 7–9 (± 0.2), which were adjusted using 0.1 M HCl or 0.1 M NaOH.

To further explore the mechanisms of TC removal by ZVI and BC/ZVI, TBA (50 mM) was used to capture -OH radical to identify the participation of degradation mechanism. 0.01 g sorbents (BC/ZVI and ZVI) were added into 10 mL TC solution containing 1 mL TBA solution (50 mM).

EDTA has greater ability to complex Fe(II) and Fe(III) than TC, and thus was introduced to reaction solution to ascertain the contribution of complexation mechanism for TC removal. And 0.01 g sorbents (BC, BC/ZVI and ZVI) were added into 10 mL TC solution followed by addition of 1.0 mL EDTA with different concentration (1, 5 and 10 mM). In addition, in order to verify the effect of complexation, we added Ca²⁺ ions to the adsorbed solution to test whether the removal effect has been increased.

3. Results and discussion

3.1 Sorbent characterization

XRD diffraction pattern of BC demonstrated the characteristic graphitic carbon at 2θ = 26.55° and 54.75° (Figure 1) [19]. This confirmed that biomass tended to be graphitized more intensively at higher temperatures, e.g. 800°C. With respect to hematite (α-Fe₂O₃), calcination process in the hydrogen gas promoted its phase transformation to Fe₃O₄, FeO and FeO at 800°C, corresponding to peaks at 2θ = 35.85°, 42.28° and 44.79°, respectively [13]. Instead, hematite was completely converted to FeO in the presence of biomass, because the decomposition of biomass could generate more reducing syngas such as CO and H₂ [13]. Besides, a minor Fe carbide peak was observed, an indication of the interaction between Fe and C during calcination process.
3.2 Contact time effect on TC adsorption

Total TC removal by BC, BC/ZVI and ZVI over time indicated that the TC removal increased rapidly in the first 240 min and then slowly thereafter. BC/ZVI exhibited well TC removal after 30 min reaction, further increasing time, BC/ZVI could remove more TC and reached to equilibrium after 480 min. TC adsorption of ZVI was inferior to BC/ZVI, while TC adsorption of BC was obvious, about 8.02 mg g$^{-1}$. Total TC adsorption of BC/ZVI was 301.39 mg g$^{-1}$, which were higher than that of ZVI (177.70 mg g$^{-1}$). Adsorption results were fitted by pseudo-first-order and pseudo-second-order model respectively and shown in Figure 2 and the parameters were concluded in Table 1. According to $R^2$, pseudo-second-order model was more fitted for TC, indicating chemisorption occurred during reaction [18]. During adsorption, TC molecules were
immobilized on sorbents surface through intra-particle diffusion and mass transfer could be the rate-limiting step; once active sites of sorbents were occupied by TC molecules, reaction was not obvious and trend to stable [20,21].

### 3.3 Initial concentration effect on TC adsorption

TC adsorption isotherm was shown in Figure 3, both BC/ZVI and ZVI exhibited increasing TC adsorption while TC concentration increased. In a similar research from Fu et al. [10], NZVI could adsorbed 4137.3 mg g⁻¹ TC when initial TC concentration increased to 1000 mg L⁻¹. In our study, BC presented a quite low adsorption capacity, about 8.02 mg g⁻¹. Removal ability of ZVI and BC/ZVI to TC gradually increased with the increase of TC concentration. At the initial concentration of 400 mg L⁻¹, removal capacity of ZVI and BC/ZVI were 152.70 and 308.26 mg g⁻¹, respectively. Adsorption isotherm of TC by BC, ZVI and BC/ZVI indicated that Freundlich model was better fitted than Langmuir model owing to the high coefficient of determination (0.9505, 0.9868 and 0.9047, respectively).

### Table 1. Fitted parameters for kinetic models for TC adsorption by BC, BC/ZVI and ZVI.

|          | Pseudo-first-order model | Pseudo-second-order model |
|----------|--------------------------|---------------------------|
|          | $K_1$ (min⁻¹) | $q_e$ (mg g⁻¹) | $R^2$ | $K_2$ (min⁻¹) | $q_e$ (mg g⁻¹) | $R^2$ |
| BC       | 0.0343          | 2.34 | 0.8827 | 0.0206          | 2.50 | 0.9425 |
| ZVI      | 0.0079          | 105.96 | 0.7300 | 0.0554          | 120.93 | 0.8353 |
| BC/ZVI   | 0.0029          | 251.21 | 0.7893 | 0.0133          | 282.27 | 0.8445 |

**Figure 3.** TC adsorption isotherms and fitted models for BC (a), ZVI and BC/ZVI (b) (TC = 5–400 mg L⁻¹, $T = 25 ± 0.5°C$).
respectively) (Table 2). The results suggested a multilayer interaction between the sorbents and TC in the heterogeneous-phase adsorption process [22].

Due to the agglomeration and surface passivation, removal capacity of ZVI was limited. BC/ZVI effectively reduced the agglomeration of ZVI, enhanced hydrophobicity and specific surface area and made more active sites reacting with TC. Meanwhile, functional groups like –OH on the surface of BC may connect with –NH2 on the surface of TC through hydrogen bond, furtherly increasing TC removal [23].

Synergistic effects may also exist between BC and ZVI. The graphite-like structure of BC and the functional groups can transfer electron to iron, accelerating the electron transfer of iron and TC [24]. Due to the synergistic effect, BC/ZVI presented 1.7 times adsorption capacity than ZVI.

### 3.4 Effect of pH on TC adsorption

TC removal capacity was affected by solution pH. With the pH increased, TC removal showed an overall decrease (Figure 4). TC removal by BC/ZVI increased from 279.24 mg g⁻¹ at pH of 3 to 301.39 mg g⁻¹ at pH of 5. With the pH further increased, removal capacity by BC/ZVI decreased to 43.06 mg g⁻¹. TC presented more negative charges at the higher pH, which resulted in the electrostatic repulsion with BC/ZVI [25]. Removal capacity by ZVI decreased from 296.45 to 54.94 mg g⁻¹ with the increment of pH from 3 to 9. At a higher pH, more Fe(OH)₂/Fe(OH)₃ produced on the surface of ZVI, reactive sites reduced [26], resulting in a quite low removal capacity of ZVI. In addition, electrostatic interaction has also become the main reason for the significant reduction in TC removal at high pH. At pH>9.7, the solution is mainly in the form of TC²⁻, which leads to the repulsion between the adsorbent and TC and inhibits effective adsorption [1].

### 3.5 TC removal mechanisms

To further verified the removal mechanisms of TC by BC, ZVI and BC/ZVI. The ZVI in the material will react with oxygen in the aqueous solution to generate H₂O₂ and Fe³⁺ (Equation (1)). The resulting H₂O₂ will further react with Fe²⁺ to generate ·OH (Equation (2)), which are then used for the removal of TC [1]. When 1 mM concentration of EDTA was added into the solution, the removal of TC by the three materials increased (Figure 5). This may be because the TC group forms a more stable ternary complex with carbon-based materials and metal ions (Fe³⁺/Fe²⁺), thereby increasing the amount of TC adsorption [27]. But when the concentration continues to increase, for the BC/ZVI material, the removal amount is lower than the control group. This may be because EDTA will also complex

![Figure 4](image-url). TC removal capacity at different solution pHs between 3 and 9.
with Fe\(^{2+}/Fe^{3+}\) in the material, thereby inhibiting the activity of the Fenton reaction and reducing the formation of •OH in the solution.

\[
\begin{align*}
Fe^0 + O_2 + 2H^+ &\rightarrow H_2O_2 + Fe^{2+} \quad (1) \\
Fe^{2+} + H_2O_2 &\rightarrow Fe^{3+} + OH^- + •OH \quad (2)
\end{align*}
\]

Then we use TBA to verify that the hydroxyl radicals in the material are the main TC removal mechanism [28]. After adding TBA, the removal of TC by ZVI and BC/ZVI decreased (Figure 6). The removal of TC by ZVI decreased from 158.95 to 147.53 mg g\(^{-1}\), while the removal of TC by BC/ZVI decreased from 303.55 to 265.66 mg g\(^{-1}\). The existence of TBA is mainly to react the •OH in the solution. Therefore, the hydroxyl radicals are also a main reaction mechanism of BC/ZVI to remove TC. In addition, we simulated the addition of Ca\(^{2+}\) (20 mg L\(^{-1}\)) to the removal solution to verify that complexation is a reasonable mechanism for the removal of TC. When Ca\(^{2+}\) (20 mg L\(^{-1}\)) are present in the solution, the removal of TC by BC/ZVI has increased from 301.39 to 403.55 mg g\(^{-1}\) (Figure 7). Ca\(^{2+}\) is easier to complex with TC in aqueous solution than Fe\(^{2+}\). This also proves from the side that complexation is indeed a dominant mechanism in the removal of TC.

4. Conclusion
The BC/ZVI composite was synthesized via a copyrolysis of hematite and pine power at 800°C. Adsorption results indicated that BC, ZVI and BC/ZVI presented the excellent adsorption capacity at the initial

Figure 5. Effect of EDTA on TC removal by BC, ZVI and BC/ZVI.

Figure 6. Effect of TBA on TC removal by BC, ZVI and BC/ZVI.

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concentration of 400 mg L\(^{-1}\) and pH of 5. Compared to BC and ZVI, removal capacity of BC/ZVI was more than 37 and 1.7 times better at the pH of 5. Removal mechanisms of TC mainly involved complexation. Fe(II)/Fe(III) can be complexed with TC. TC combined with the surface groups of BC and adsorb to the active site. Meanwhile, oxidation of ZVI resulted in the production of -OH, which promoted the degradation of TC. In the whole reaction process, Fe(II) and Fe(III) transformed into each other. This allowed TC to be efficiently degraded. In addition, we used industrial waste to synthesize BC/ZVI and presented a high removal capacity of TC; thus, BC/ZVI was a promising sorbent.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Figure 7. The effect of Ca\(^{2+}\) on the removal of TC by BC/ZVI.
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