Biochar Modified by Nano-manganese Dioxide as Adsorbent and Oxidant for Oxytetracycline

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Abstract

Biochar has limited capacity to adsorb oxytetracycline (OTC). Here we have used bamboo willow biochar (BC) as a carrier to produce nMnO₂-loaded biochars (MBC) by a co-precipitation method. Their chemical compositions, morphological features, specific surface area, and surface functional groups were observed or determined. Batch experiments were conducted to assess the effects of reaction time, initial OTC concentrations, pH, salt concentrations, and natural organic matter (NOM) on OTC removal. Kinetics and isotherms indicated that OTC was mainly adsorbed via chemical interactions, and mono- and multi-layer adsorption occurred on the surface. MBC removed 19–25 times more OTC than BC, and the removal was highest at near-neutral pH, not influenced by NaCl (2, 10 mM), slightly reduced by NOM (0–20 mg L⁻¹), and enhanced by NaHCO₃ (2, 10 mM). Besides being an adsorbent, MBC acted as an oxidant and degraded 58.5% of OTC at 24 h.

Keywords Biochar · Oxytetracycline · Nano-manganese dioxide · Adsorption · Degradation

Antibiotics in aquatic environments is a vital class of contaminants of emerging concern due to their extensive usage and environmental implications (Peiris et al. 2017). Being a member of tetracycline antibiotics (TCs) family, oxytetracycline (OTC) has been widely used in aquaculture and animal husbandry (Chen and Huang 2011; Jia et al. 2016). The high persistence and recalcitrance of OTC could induce antibiotic resistance genes and cause its bioaccumulation in the aquatic ecosystem (Jeong et al. 2010; Yuan et al. 2019). Thus, OTC immobilization in or removal from the aquatic environment is highly desirable.

Biochar (BC) as an adsorbent for antibiotics has been intensively investigated (Peiris et al. 2017). Its adsorption capacity for antibiotics, however, is generally low (Zhou et al. 2017). For example, BC produced from *Robinia*

pseudoacacia had an OTC adsorption of 10–15 mg g⁻¹ (Xiao et al. 2019). Thus, modifications of BC have been proposed to enhance its performance. The synthesis of BC-based nanocomposites, for example, has recently become a research hotspot (Gao et al. 2018; Liang et al. 2017; Narvaez et al. 2019). Nano-MnO₂ (nMnO₂)-modified BC showed great potential for removing heavy metals and organic contaminants (Narvaez et al. 2019). For example, Gao et al. (2018) reported that MnO₂-BC nanocomposites effectively removed di-n-butyl phthalate and OTC from aqueous solutions. Recently Jung et al. (2019) found the catalytic degradation of bisphenol A in water by MnO₂-modified BC. The large surface area and oxidative capacity of nMnO₂ contributed to the enhanced adsorption and abiotic decomposition (Mahamallik et al. 2015; Song et al. 2019). Biochar averted the agglomeration of nMnO₂, thus enabling the efficient use of nMnO₂ (Jung et al. 2019).

Despite the above signs of progress, systematic studies are rare on how does the assembling of nMnO₂-BC composites affect their adsorptive and oxidative ability for antibiotics under various environmental conditions. This study aimed to (1) synthesize nMnO₂-BC nanocomposites with different BC/MnO₂ ratios; (2) assess their potential for OTC removal as influenced by pH, salt compositions and contents, and organic carbon content; and (3) reveal the dual functions of MBC on adsorbing and degrading OTC.

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Materials and Methods

OTC (> 98% purity) from Aladdin Reagent (Shanghai) Co, Ltd was used to prepare a stock solution of 500 mg L⁻¹ with methanol (HPLC-grade) and ultra-pure water and stored in a refrigerator at 4°C in the dark for use within a week. Branches of bamboo willow (*Salix fragilis* L.) were collected from a farm in Dongying City of Shandong Province, China, as feedstock to produce biochar in the field via an aerobic carbonization process and a fire and water coupled method (Xiao et al. 2019). The retention time was 0 min. The formed biochar was homogenized, ground, and passed through a 60-mesh sieve, then dried at 80°C and labeled as BC. nMnO₂ modified BC (MBC) was synthesized using the co-precipitation method (Liang et al. 2017; Mahamallik et al. 2015). Briefly, BC (5.22 g) was dispersed in 300 mL of MnSO₄ solution (6, 12, 24 mM) and ultra-sonicated for 1 h. Then, 10 mL KMnO₄ solution (4, 8, 16 mM) were dropwise added with continuous stirring. In the end, the suspension was stirred for a further 30 min, then filtered, washed with ultra-pure water three times, and dried in a vacuum oven at 80°C for 12 h to obtain MBC samples with BC/MnO₂ ratios of 40:1, 20:1, and 10:1.

The ash content of BC and MBC was obtained by heating in a muffle furnace at 800°C for 4 h. The C, H, and N contents of BC and MBC were analyzed using an elemental analyzer (Elementar Micro cube, Germany). The specific surface areas (S_{BET}) of the samples were determined by N₂ adsorption at 77 K using an Autosorb-1 gas analyzer (Quantachrome Autosorb-iQ, USA), and applying the Brunauer–Emmett–Teller equation. A scanning electron microscope (SEM) (Hitachi S4800, Japan) was used to observe the surface morphology of the samples. A Fourier transform infrared (FTIR) spectrometer (Thermo Fisher Nicolet iS50, USA) was used to record the spectra of BC and MBC with a resolution of 2 cm⁻¹ over the 400–4000 cm⁻¹ wavenumber region. The zero point charge (pH_{pzc}) of MBC was determined by salt titration (Jang et al. 2018).

Batch experiments were carried out in triplicate to investigate the effect of pH, salt species and concentrations, and NOM on OTC sorption by BC and MBC. Briefly, BC and MBC (20 mg) were added to OTC solutions (30 mL) at 25°C. Except for the isothermal experiment to study the effect of initial concentrations, OTC concentration was 100 mg L⁻¹. The suspensions of BC- and MBC-OTC were shaken at 120 rpm on an oscillator, sampled and filtered through a 0.45 µm filter. The sampling times in the kinetic experiment were 0, 5, 15, 30, 60, 120, 240, 480, 720, 960, and 1440 min. The initial concentrations of OTC in the isotherm experiment were 10, 20, 50,

100, 150, 200, 250, 300 mg L⁻¹. The solution pH was adjusted to 3–11 with 0.1 M HCl and NaOH. Salts (NaCl and NaHCO₃) at 2 and 10 mmol L⁻¹, being the typical ion concentrations in freshwater and brackish aquaculture water, were used as background electrolytes. Humic acid from Yuanye Biotechnology Co, Ltd was used (0–20 mg L⁻¹) as a NOM. Further, OTC adsorption on MBC was differentiated from OTC degradation by nMnO₂ via the addition of 4 mg mL⁻¹ oxalic acid to the suspensions to dissolve nMnO₂ in MBC and thus immediately quench OTC oxidation by nMnO₂ (Rubert and Pedersen 2006).

Sorption kinetics were evaluated by the pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich models, as follows:

$$Q_t = Q_e(1 - \exp(-k_1 t)) \quad (1)$$

$$Q_t = k_2 Q_e^2 t / (1 + k_2 Q_e t) \quad (2)$$

$$Q_t = (\ln(ab))/b + (\ln t)/b \quad (3)$$

where Q_e (mg g⁻¹) and Q_t (mg g⁻¹) represent the OTC adsorption capacity at equilibrium time and time t (min), respectively; k_1 (min⁻¹) and k_2 (mg g⁻¹ min^{-1/2}) are the rate constant of the PFO and PSO, respectively; a is the chemical adsorption rate constant; b is the surface covering constant.

The Langmuir and Freundlich models were used to fit isotherm adsorption data, and the equations are:

$$Q_e = Q_m K_L C_e / (1 + K_L C_e) \quad (4)$$

$$Q_e = K_F C_e^{1/n} \quad (5)$$

where Q_e (mg g⁻¹) is the amount of OTC adsorbed at equilibrium, Q_m (mg g⁻¹) is the maximum adsorption capacity under monolayer coverage; C_e (mg L⁻¹) is OTC concentration at equilibrium; K_L (L mg⁻¹) and K_F (mg¹⁻ⁿ Lⁿ g⁻¹) are the Langmuir and Freundlich constants, respectively; $1/n$ is the adsorption intensity.

OTC concentration was analyzed by HPLC (Agilent 1260 Infinity II) with a reversed-phase C-18 column (100 mm × 4.6 mm, 4 µm) and a diode array detector (DAD) at 355 nm. The instrument parameters were as follows: 0.01 M oxalic acid (85%) and acetonitrile (15%) (v:v) as the mobile phase; the flow rate at 1 mL min⁻¹; the injection amount of 20 µL; and column temperature at 30°C. Two standard samples were used for quality assurance/control in OTC analysis. The difference between the concentrations of OTC initially added and those remaining in solution at the end of the reaction, both analysed by HPLC, were used to calculate the amount of OTC removed by BC and MBC. Inductively coupled plasma mass spectrometry (ICP-MS,

Agilent 7800) was used to determine the concentration of dissolved Mn from the sorption experiment.

Results and Discussion

As Mn-loading increased, C and N contents of MBC decreased (Table 1), whereas ash content rose. Meanwhile, the increase in H/C and O/C indicated that MnO_2 loading weakened BC aromaticity. The near-spherical particles on the surface of MBC (20:1) (Fig. 1a) and energy-dispersive X-ray spectroscopic (EDS) patterns (Fig. 1b) confirmed the existence of nMnO_2 . Figure 2a shows the main functional groups of BC and MBC, including $-\text{OH}$ (3424 cm^{-1}), $\text{C}=\text{O}/\text{C}=\text{C}$ ($1561\text{--}1577\text{ cm}^{-1}$, $1421\text{--}1437\text{ cm}^{-1}$), $\text{C}-\text{O}$ (1039 cm^{-1}) and aromatic $\text{C}-\text{H}$ (875 cm^{-1}) (Liang et al. 2017; Wei et al. 2019; Wu et al. 2019). After nMnO_2 loading, the absorption band of $\text{C}=\text{O}/\text{C}=\text{C}$ and $\text{C}-\text{H}$ weakened sequentially, further proving the weakening of BC aromaticity. Meanwhile, $\text{Mn}-\text{O}$ peaks at 518 cm^{-1} gradually enhanced. As Liang et al. (2017) and Gao et al. (2018) reported, these simultaneous changes suggest that the aromatic ring of BC is the site to bind MnO_2 .

Figure 3 shows that nMnO_2 loading on biochar greatly enhanced its removal capacity for OTC. As expected, the removal capacity further increased with the reaction time and OTC concentration. Calculated from the PSO equation, the equilibrium adsorption capacities at the initial OTC concentration of 100 mg L^{-1} were 8.31 mg g^{-1} for BC, 114.13 mg g^{-1} for MBC (40:1), 128.56 mg g^{-1} for MBC (20:1), and 144.09 mg g^{-1} for MBC (10:1). The parameters in Table 2 show that the Elovich model fitted on adsorption data best ($R^2 > 0.95$), suggesting that OTC was mainly adsorbed onto BC and MBC via chemical action (Yuan et al. 2019).

The fitting results of isotherm adsorption (Table 3) showed that OTC removal by BC was more in line with the Freundlich model, indicating heterogeneous multilayer adsorption. It is similar to the reports of Yuan et al. (2019) and Zhou et al. (2017). Both the Langmuir and Freundlich models fit OTC removal on MBC, which suggested that both monolayer and multilayer adsorption would occur at the surface (Jang et al. 2018). The maximum adsorption capacity of MBC for OTC, obtained from the Langmuir model, reached 292.53 (MBC40:1), 360.50 (MBC20:1), and 383.39 mg g^{-1} (MBC10:1), which were about 19, 24, and 25 times higher than that of BC (14.56 mg g^{-1}), respectively.

Table 1 The specific surface area, ash content, and element compositions of biochars

Samples	Specific surface area ($\text{m}^2\text{ g}^{-1}$)	Ash (%)	Elemental compositions on ash-free base (%)					
			C	H	N	O	H/C	O/C
BC	262.2	20.08 ± 0.39	82.21 ± 0.01	2.34 ± 0.01	0.65 ± 0.01	14.80	0.028	0.180
MBC (40:1)	285.9	22.03 ± 0.54	80.90 ± 0.90	2.83 ± 0.13	0.58 ± 0.03	15.69	0.035	0.194
MBC (20:1)	299.5	22.46 ± 0.19	80.39 ± 0.00	2.74 ± 0.02	0.55 ± 0.01	16.32	0.034	0.203
MBC (10:1)	278.6	23.82 ± 0.39	79.43 ± 0.17	2.88 ± 0.03	0.54 ± 0.01	17.14	0.036	0.216

Fig. 1 SEM images and EDS patterns of MBC (20:1)

Fig. 2 FTIR spectra of BC/MBC (40–10:1) and MBC₂₀ before and after OTC adsorption

Fig. 3 Effect of reaction time (a) and OTC concentrations (b) on OTC adsorption on BC and MBC (40–10:1)

Table 2 Kinetics fitting parameters for OTC adsorption onto BC and MBC

Samples	Pseudo-first order model			Pseudo-second order model			Elovich model		
	Q_e (mg g ⁻¹)	k_1 (min ⁻¹)	R^2	Q_e (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	R^2	a	b	R^2
BC	7.86	0.209	0.799	8.31	0.0293	0.886	233.40	1.414	0.991
MBC (40:1)	105.15	0.012	0.782	114.13	0.0002	0.874	10.24	0.058	0.956
MBC (20:1)	118.43	0.015	0.800	128.56	0.0002	0.889	15.17	0.056	0.970
MBC (10:1)	131.43	0.013	0.869	144.09	0.0001	0.935	11.31	0.045	0.979

Environmental conditions in water bodies would affect OTC removal by BC and MBC. Based on the tradeoff of preparation cost and adsorptive performance

of MBC, MBC₂₀ was chosen as the scavenger to assess the effects of pH, salts, and NOM on OTC removal from water.

Table 3 Isothermal fitting parameters of OTC adsorption onto BC and MBC

Samples	Langmuir			Freundlich		
	Q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	K_F (mg ¹⁻ⁿ L ⁿ g ⁻¹)	$1/n$	R^2
BC	14.56	0.1077	0.779	4.3985	0.2376	0.977
MBC (40:1)	292.53	0.0299	0.974	28.7714	0.4397	0.973
MBC (20:1)	360.50	0.0296	0.995	28.9789	0.5053	0.982
MBC (10:1)	383.39	0.0973	0.937	73.2574	0.3967	0.965

pH can affect OTC adsorption by changing the surface charge of biochar and the ionization degree of OTC (Jia et al. 2016; Aghababaei et al. 2017). With ionization constants of $pK_{a1} = 3.22$, $pK_{a2} = 7.46$, and $pK_{a3} = 8.94$, OTC can exist as cation (OTC⁺), zwitterion (OTC⁰), or anion (OTC⁻ or OTC²⁻), depending on ambient pH. The maximum removal of OTC by MBC₂₀ occurred at pH 5 (Fig. 4a), indicating that the π - π electron-donor-acceptor (EDA) interaction between neutral OTC molecule and MBC₂₀ played an important role in adsorption. In other words, OTC acted as an electron

acceptor due to the strong electron-withdrawing ability of its ketone group, whereas the aromatic rings of BC made it an electron donor. As pH was lowered to 3 or raised to 11, the removal capacity decreased. This decrease was due to the electrostatic repulsion between MBC₂₀ and OTC under strong acidic and alkaline conditions (Yuan et al. 2019). With a pH_{pzc} of 9.18, MBC₂₀ was positively charged on the acidic side of pH_{pzc} and negatively charged at $pH > 9.18$.

Being a common organic component in water, humic acid (HA) had a competitive effect on OTC adsorption onto

Fig. 4 Effect of pH (a), NOM (b), and salts (c) on OTC removal by MBC₂₀, and Mn²⁺ release (d) at different times of reaction

MBC₂₀ (Fig. 4b). HA can complex with cationic or zwitterionic OTC species through electrostatic attraction (mainly carboxylic groups) to hinder its mobility (Zhao et al. 2012), and may also compete with OTC for active sites on MBC₂₀ via van der Waals forces or π - π EDA interaction (Xie et al. 2014).

Figure 4c showed the effect of salt species and concentrations on OTC removal. NaCl had little inhibition on OTC removal by MBC₂₀, indicating that Na⁺ and Cl⁻ had no electrostatic screening effect on OTC adsorption, and Na⁺ did not compete with OTC at the adsorptive sites of MBC₂₀ (Song et al. 2019). In contrast, NaHCO₃ enhanced OTC removal, which was concentration-dependent. HCO₃⁻ was able to precipitate the Mn²⁺ released from MBC (discussed below), thereby reducing interference of Mn²⁺ and increasing OTC removal.

Figure 4d demonstrated that OTC removal by MBC was accompanied by Mn²⁺ release, suggesting that nMnO₂ acted as an oxidant during OTC removal (Gao et al. 2012; Mahamallik et al. 2015). After 24 h reaction at pH 5.0, Mn²⁺ release reached 2.97 mg L⁻¹ (about 8.91% of the theoretical value of loaded MnO₂), much higher than the 0.10 mg L⁻¹ in control (Mn release without OTC). Meanwhile, OTC degradation by nMnO₂ at 24 h, estimated from the changes in OTC total (i.e. OTC in solution and OTC bound to MBC), was 58.5%. At 4 h, the amount of OTC bound to MBC₂₀ reached the maximum, approximately 38.0% of the total. Similarly, Song et al. (2019) reported that Mn²⁺ competed with tetracycline (TC) for adsorption and hindered the migration of electrons to TC, thus reducing TC adsorption on MnO₂ surface. After 4 h Mn²⁺ release quickly increased, suggesting that the Mn originally complexed with OTC and bound to MBC₂₀ was gradually released with the degradation of OTC (Rubert and Pedersen 2006). According to Chen and Huang (2011), during its oxidative degradation by MnO₂, OTC did not undergo isomerization. Instead, N-demethyl products with higher polarity were produced. Besides, N-demethyl derivatives, formaldehyde and hydroquinone products would also form. Importantly, the derivatives from OTC degradation have lower toxicity and pose less threat to the environment (Chen and Huang 2011).

The FTIR spectra (Fig. 2b) provided further evidence of the mechanisms of OTC removal by MBC₂₀. The reduced intensity of the C=O/C=C peak at 1421 cm⁻¹ confirmed the presence of π - π EDA interaction between MBC and OTC (Aghababaei et al. 2017; Yuan et al. 2019). Furthermore, the decrease in the Mn-O bond at 518 cm⁻¹ demonstrated that during OTC adsorption, nMnO₂ was partly reduced to Mn²⁺ for release into the solution (Fig. 4d).

Though it was not intended to recover and reuse MBC because of its low value, MBC₂₀ still showed reusability. Its OTC removal capacity was 140, 106, 70, 53, and 37 mg g⁻¹ at the 1st, 2nd, 3rd, 4th, and 5th use, respectively.

In summary, biochar produced from *Salix fragilis* L. and further loaded with nMnO₂ (MBC) was an inexpensive and high efficient scavenger to remove OTC from water. More OTC was removed at near-neutral pH than at either acidic or alkaline conditions. NaCl as an electrolyte apparently had little effect on OTC removal, but NaHCO₃ enhanced the removal. DOM slightly reduced OTC removal by MBC. FTIR spectra suggested that π - π EDA interaction was involved in OTC removal by MBC; the release of Mn²⁺ from MBC indicated that nMnO₂ acted as an oxidant for the degradation of OTC, thus contributing to OTC removal. In other words, OTC removal was the combined result of its adsorption onto MBC and its degradation by nMnO₂.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Aghababaei A, Ncibi MC, Sillanpää M (2017) Optimized removal of oxytetracycline and cadmium from contaminated waters using chemically-activated and pyrolyzed biochars from forest and wood-processing residues. *Bioresour Technol* 239:28–36
- Chen WR, Huang CH (2011) Transformation kinetics and pathways of tetracycline antibiotics with manganese oxide. *Environ Pollut* 159(5):1092–1100
- Gao J, Hedman C, Liu C et al (2012) Transformation of sulfamethazine by manganese oxide in aqueous solution. *Environ Sci Technol* 46:2642–2651
- Gao ML, Zhang Y, Gong XL et al (2018) Removal mechanism of di-n-butyl phthalate and oxytetracycline from aqueous solutions by nano-manganese dioxide modified biochar. *Environ Sci Pollut Res* 25:7796–7907
- Jang HM, Yoo S, Choi YK et al (2018) Adsorption isotherm, kinetic modeling and mechanism of tetracycline on *Pinus taeda*-derived activated biochar. *Bioresour Technol* 259:24–31
- Jeong J, Song WH, Cooper WJ et al (2010) Degradation of tetracycline antibiotics: mechanisms and kinetic studies for advanced oxidation/reduction processes. *Chemosphere* 78(5):533–540
- Jia MY, Wang F, Jin X et al (2016) Metal ion-oxytetracycline interactions on maize straw biochar pyrolyzed at different temperatures. *Chem Eng J* 304:934–940
- Jung KW, Lee SY, Lee YJ et al (2019) Ultrasound-assisted heterogeneous Fenton-like process for bisphenol A removal at neutral pH using hierarchically structured manganese dioxide/biochar nanocomposites as catalysts. *Ultrason Sonochem* 57:22–28
- Liang J, Li XM, Yu ZG et al (2017) Amorphous MnO₂ modified biochar derived from aerobically composted swine manure for adsorption of Pb(II) and Cd(II). *ACS Sustain Chem Eng* 5:5049–5058

- Mahamallik P, Saha S, Pal A (2015) Tetracycline degradation in aquatic environment by highly porous MnO₂ nanosheet assembly. *Chem Eng J* 276:155–165
- Narvaez OMR, Hernandez JMP, Goonetilleke A et al (2019) Biochar-supported nanomaterials for environmental applications. *J Ind Eng Chem* 78:21–33
- Peiris C, Gunatilake SR, Mlsna TE et al (2017) Biochar based removal of antibiotic sulfonamides and tetracyclines in aquatic environments: a critical review. *Bioresour Technol* 246:150–159
- Rubert KF, Pedersen JA (2006) Kinetics of oxytetracycline reaction with a hydrous manganese oxide. *Environ Sci Technol* 40:7216–7221
- Song Z, Ma YL, Li CE (2019) The residual tetracycline in pharmaceutical wastewater was effectively removed by using MnO₂/graphene nanocomposite. *Sci Total Environ* 651:580–590
- Wei J, Tu C, Yuan GD et al (2019) Assessing the effect of pyrolysis temperature on the molecular properties and copper sorption capacity of a halophyte biochar. *Environ Pollut* 251:56–65
- Wu J, Lu J, Zhang C, Zhang ZH et al (2019) Adsorptive removal of tetracyclines and fluoroquinolones using Yak dung biochar. *B Environ Contam Tox* 102:407–412
- Xiao L, Feng LR, Yuan GD et al (2019) Low-cost field production of biochars and their properties. *Environ Geochem Health*. <https://doi.org/10.1007/s10653-019-00458-5>
- Xie MX, Chen W, Xu ZY et al (2014) Adsorption of sulfonamides to demineralized pine wood biochars prepared under different thermochemical conditions. *Environ Pollut* 186:187–194
- Yuan L, Yan M, Huang ZZ et al (2019) Influences of pH and metal ions on the interactions of oxytetracycline onto nano-hydroxyapatite and their co-adsorption behavior in aqueous solution. *J Colloid Interface Sci* 541:101–131
- Zhao YP, Gu XY, Gao SX et al (2012) Adsorption of tetracycline (TC) onto montmorillonite: cations and humic acid effects. *Geoderma* 183–184:12–18
- Zhou YY, Liu XC, Xiang YJ et al (2017) Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: adsorption mechanism and modelling. *Bioresour Technol* 245:266–273

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