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4 **Heterogeneous Photocatalytic Degradation of Sulfamethoxazole in Water Using a Biochar-**  
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6 **Supported TiO<sub>2</sub> Photocatalyst**  
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## ABSTRACT

The present study reports an effective heterogeneous photocatalytic degradation of sulfamethoxazole (SMX) in water using a biochar-supported  $\text{TiO}_2$  (biochar/ $\text{TiO}_2$ ). The biochar was used as a low cost and effective support for  $\text{TiO}_2$  to lower the recombination rate of electrons and electron holes during photocatalysis, allow efficient attachment of  $\text{TiO}_2$ , increase adsorption capacity and help easy separation of the photocatalyst after use. The biochar/ $\text{TiO}_2$  showed much higher adsorption of SMX than the commercial  $\text{TiO}_2$  powder due to the hydrophobic interaction between the biochar and SMX. Particularly this study focused on the effects of water quality and operating conditions on the photocatalytic oxidation of SMX. The addition of low concentration of bicarbonate made drastic enhancement in SMX removal and mineralization while the final effluent showed high biotoxicity. On the contrary, the presence of nitrate exhibited slight enhancement in SMX removal efficiency. The photocatalyst loading and UV irradiation time also played their important roles in enhancement of SMX removal and mineralization. In overall the photocatalytic oxidation of SMX using the biochar/ $\text{TiO}_2$  at the selected catalyst loading and irradiation time (5 g biochar-supported  $\text{TiO}_2 \text{ L}^{-1}$ , 6 h) resulted in the high removal and mineralization of SMX and negligible toxicity.

**Keywords:** sulfamethoxazole, pharmaceutical compound, photocatalysis, advanced oxidation, biochar,  $\text{TiO}_2$

## 1. Introduction

Sulfamethoxazole (SMX) is an antibiotic that has been extensively used for the treatment of human and animal diseases (Avisar et al., 2009). It has been detected in the ng/L-µg/L range in discharges from wastewater treatment plants (WWTPs), rivers and groundwater (Avisar et al., 2009; Çalışkan & Göktürk, 2010; Dirany et al., 2011). **Many drugs interact with transport blood proteins. This interaction may affect the functions of proteins and lead to various illnesses (Duman et al., 2013; Tunç et al., 2013a; Tunç et al., 2013b).** Due to the antibiotic-resistant pathogens and toxic effects on the aquatic ecosystem and human health at low levels, SMX needs to be effectively removed in various water resources (Yao et al., 2012).

To date, various methods such as biological treatment, chemical oxidation, membrane separation, and adsorption have been studied for the removal of SMX in wastewater and water (Adams et al., 2002; Beltrán et al., 2008; Castiglioni et al., 2005; Domínguez et al., 2011; Kim et al., 2009; Kim et al., 2005; Tambosi et al., 2010; Ternes et al., 2002; Thiele-Bruhn, 2003; Yao et al., 2012). Unfortunately, these conventional methods cannot achieve the complete or effective removal of SMX due to its low concentrations and biorefractory nature (Akhtar et al., 2011; Zhang et al., 2010). Compared with the conventional methods, the photocatalytic oxidation using photocatalysts (e.g., TiO<sub>2</sub>) has shown high potential to degrade SMX under UV light irradiation (Abellan et al., 2007; Beltrán et al., 2008). ·OH and electron holes generated from UV light-excited TiO<sub>2</sub> effectively can oxidize SMX via direct or indirect routes (Kim & Kan, 2015). For instance, the commercial photocatalyst TiO<sub>2</sub> (e.g. Degussa P25) is currently used to treat aqueous contaminants under UV light irradiation. However, current photocatalytic oxidation using commercial TiO<sub>2</sub> exhibited critical shortcomings such as quick recombination of electrons and electron holes, difficult separation of the nano to micro-scale TiO<sub>2</sub> powders after treatment, and

low reactivity with low concentration of contaminants in water (Abellan et al., 2007; Beltrán et al., 2008). The quick recombination of electrons and electron holes lowers photocatalytic efficiency while the separation of fine  $\text{TiO}_2$  powder after treatment increases energy consumption. Very dilute SMX in wastewater and water would result in low reactivity, slow reaction and poor removal efficiency. These problems have limited the scale-up and practical application of  $\text{TiO}_2$ -mediated photocatalytic oxidation for water and wastewater purification.

To overcome these limitations, the present study suggested a biochar-supported  $\text{TiO}_2$  (biochar/ $\text{TiO}_2$ ) as an effective photocatalyst to eliminate SMX in water. Previous studies have been attempted to immobilize photocatalyst onto various supports such as activated carbon, graphene, carbon nanotube, zeolite, glass, silica and honeycombs; however, they exhibited high costs and lack of treatability (Cao et al., 2015; Jang et al., 2015; Ragupathy et al., 2015; Sampaio et al., 2015; Shan et al., 2010; Vaiano et al., 2015; Wang et al., 2015). In this study the biochar made from pyrolysis of agricultural wastes was used as a low cost and effective support for  $\text{TiO}_2$ . The biochar had excellent conductivity which would lower quick recombination of electrons and electron holes during the photocatalysis for enhancing photocatalytic oxidation. Efficient attachment of  $\text{TiO}_2$  onto the biochar was allowed due to the large specific surface area, rich functional groups and easy surface modification of the biochar. The biochar-supported  $\text{TiO}_2$  was also easily separated and reused after treatment of SMX in water. In addition to the support for  $\text{TiO}_2$ , the biochar demonstrated high adsorption capacity of SMX which allowed SMX to undergo phase transfer from a dilute solution onto the biochar surface where the SMX was immobilized and concentrated. This led to much more efficient photocatalytic oxidation of SMX rather than dilute aqueous phase.

The objective of this study was to effectively remove SMX in water by photocatalytic oxidation using the biochar-supported TiO<sub>2</sub> (biochar/TiO<sub>2</sub>). To the best of our knowledge, there have been no studies for photocatalytic oxidation of antibiotics (i.e., SMX) using a biochar-supported TiO<sub>2</sub> photocatalyst. This study presents the effects of key parameters (i.e., catalyst loading and irradiation time) and water quality (i.e., bicarbonate and nitrate) on photocatalytic oxidation of SMX in water along with the characterization and adsorption capacity of the biochar/TiO<sub>2</sub>. Possible mechanisms associated with photocatalytic oxidation of SMX by the biochar/TiO<sub>2</sub> are also addressed.

## 2. Material and methods

### 2.1. Chemical and reagent

The biochar used as a support for TiO<sub>2</sub> was obtained from Hawaii Natural Energy Institute (Honolulu, HI). As described by Lopez et al. and Budai et al. (Budai et al., 2014; Lopez et al., 2014), it was produced by flash carbonization of corn cob at 873 K (the specific surface area of 134 m<sup>2</sup>/g). Ethanol (C<sub>2</sub>H<sub>6</sub>O, 100%) and hydrochloric acid (HCl, 37% v/v) were purchased from Fisher Scientific (Waltham, MA, USA). Titanium isopropoxide (Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, 97%, Sigma-Aldrich, MO, USA) was used as the TiO<sub>2</sub> precursor without any further purification. TiO<sub>2</sub> nano powder (21 nm, specific surface area of 35-65 m<sup>2</sup>/g, Sigma-Aldrich, MO, USA) was used to compare its photocatalytic capacity with the biochar/TiO<sub>2</sub> prepared for this study. Sulfamethoxazole (SMX), sodium bicarbonate (NaHCO<sub>3</sub>), and sodium nitrate (NaNO<sub>3</sub>) were purchased from Sigma-Aldrich (St. Louis, MO, USA). *Daphnia magna* was obtained from National Institute of Environmental Research (Incheon, Republic of Korea). The biological toxicity test kit (Toxi-Chromotest™) was purchased from Environmental Biodetection Products

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4 Inc. (Brampton, Ontario, Canada).  
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## 6 7 2.2. Preparation and characterization of biochar-supported TiO<sub>2</sub> (biochar/TiO<sub>2</sub>) 8

9 The biochar/TiO<sub>2</sub> was prepared using the sol-gel method modified from that reported by  
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11 Wang et al. (2008). The raw biochar was grounded and sieved to make the 30 x 40 mesh size  
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13 (425 – 600 µm) similar to the size of commercial granular activated carbon used for water  
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15 treatment. The biochar was washed with deionized (DI) water, and dried in an oven at 343 K for  
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17 12 h. The acid-treated biochar was prepared by the methods reported by Kan and Huling (Kan &  
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19 Huling, 2009). The raw biochar (5 g) was suspended in nitric acid at pH 3 for 4 d to increase the  
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21 acidic surface oxides and to lower the pH at point of zero charge (pH<sub>PZC</sub>) (i.e., the pH at which  
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23 positive and negative surface charges are approximately equal). The initial pH<sub>PZC</sub> of the biochar  
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25 was 5.5-5.8 and was lowered to 4.1-4.5 through the acid treatment process. After filtration, the  
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27 acid treated-biochar was washed with DI water multiple times. The acid treated-biochar was  
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29 dried in an oven at 343 K for 24 h, and stored in a desiccator for further use. 2.5 g acid treated-  
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31 biochar was dispersed in 60 mL ethanol followed by addition of 20 mL titanium isopropoxide  
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33 (97%) was added. The mixture was stirred at ambient temperature for 1 h before adding a  
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35 solution containing 8 mL of 37% (v/v) HCl and 20 mL ethanol (100%) with constant stirring for  
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37 1 h. The solution was vacuum filtered, then washed with ethanol before drying in the oven at 373  
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39 K for 24 h. The dried sample was milled and heated at 598 K for 1 h to yield the biochar/TiO<sub>2</sub>  
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41 (specific surface area of 383 m<sup>2</sup>/g). The scanning electron microscopy (SEM) images and Energy  
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43 dispersive X-ray (EDX) spectroscopy data were obtained with Hitachi HT7700 field emission  
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45 scanning electron microscope (10 kV) with an Oxford INCA PentaFET-x3 Si (Li) EDX detector  
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47 system (Oxford instruments, Oxford, United Kingdom) for EDX analysis. Powder X-ray  
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diffraction (XRD) patterns of the powdered sample were performed on a Bruker D8 Discover (Bruker, Billerica, MA, USA) with a Cu K $\alpha$  radiation source.

### 2.3. Adsorption of SMX onto the Biochar/TiO<sub>2</sub>

The adsorption capacities of the biochar/TiO<sub>2</sub> and commercial TiO<sub>2</sub> nano powder (Sigma-Aldrich, MO, USA) were investigated before the photocatalytic reactions occurred since many (photo-) catalytic reactions are mass transfer or adsorption limited. The batch experiments for adsorption isotherm were conducted by suspending 0.25-2 g of the biochar/TiO<sub>2</sub> in a series of flasks containing 0.1 L of SMX solutions at the concentration of 10 mg/L at 293 K. The initial pH of SMX solution (pH = 4.0) was adjusted by adding 0.1 M HCl or 0.1 M NaOH since the optimum pH for the adsorption of SMX solution was found to be 4 (please see Fig. S2). The adsorption process was carried out by shaking at the constant speed (200 rpm) at room temperature (293 K) for 24 h to ensure equilibrium was reached although most of adsorption occurred within 1- 4 h. The post-adsorption SMX solution was sampled after equilibrium in replicate and analyzed. The differences between initial and final concentrations were used to calculate the mass of SMX adsorbed to the biochar/TiO<sub>2</sub>. Similar to the adsorption of SMX onto the biochar/TiO<sub>2</sub>, the batch experiments for adsorption of SMX onto the raw biochar (0.25-2g) and the commercial TiO<sub>2</sub> (0-5g) were conducted in a series of flasks containing 0.1 L of 10 mg/L SMX solutions at 293 K.

The Langmuir and Freundlich isotherm models were used to interpret the batch isotherm data. The nonlinear form of Freundlich and Langmuir isotherms are given in Eq. 1 and 2, respectively (Kiran Kumar & Venkata Mohan, 2012; Han et al., 2013):

Freundlich isotherm: 
$$q_e = k_f (C_e)^{1/n} \quad (1)$$

Langmuir isotherm:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $q_e$  indicates an adsorption capacity in  $(\text{mg/g})(\text{L/mg})^{1/n}$ ,  $1/n$  is an indicator of adsorption effectiveness (dimensionless),  $q_m$  is the maximum adsorption capacity (mg/g) corresponding to complete monolayer coverage of the surface,  $q_e$  is the amount of SMX adsorbed per unit mass of adsorbent at equilibrium (mg/g),  $C_e$  is the liquid-phase concentration of SMX at equilibrium (mg/L) and  $K_L$  is the Langmuir constant (L/mg) related to the sorption/desorption energy.

The nonlinear forms of Freundlich and Langmuir models (Eqs. 1 and 2) were used to estimate the model parameters. A trial and error procedure was performed using the solver function in Microsoft Excel to minimize the sum of squared errors which was the sum of squared errors  $((q, \text{measured} - q, \text{calculated})^2)$ .

#### 2.4. Photocatalytic oxidation of SMX using the biochar/TiO<sub>2</sub> photocatalyst under UV light irradiation

All of the experiments except the effect of catalyst loading were conducted in glass reactors (12.5 cm diameter, 6.5 cm height) filled with 100 mL of 10 mg/L SMX solution and 0.5 g of the biochar/TiO<sub>2</sub> at 293 K under UV-C irradiation. Unless otherwise stated, the photocatalytic oxidations were performed at pH 4. A 15 W UV lamp (Nuaire, Plymouth, MN, USA) was used as UV-C light source (254 nm) to irradiate vertically into the glass reactor. The lamp was placed vertically at a distance of 20 cm from the glass reactor. Before turning the lamp, the suspension was magnetically stirred for 30 min to establish the adsorption-desorption equilibrium under dark condition. The pH of SMX solution with 0.5 g of the biochar/TiO<sub>2</sub> was about 4.5 while the pH values with biochar/TiO<sub>2</sub> (0.25, 0.75 and 1g) were varied from 4.2 to 4.8 due to the acidic nature of the biochar/TiO<sub>2</sub> before adjusting the pH to 4 for the photocatalytic

oxidation. Adjusting to pH 4 for the photocatalytic oxidation tests was to keep “non-ionic (neutral) SMX” based on its pKa and make consistent conditions for the photocatalytic oxidation tests. The photocatalytic oxidation of SMX was initiated by stirring magnetically the mixture (SMX solution with the biochar/TiO<sub>2</sub>) and turning on the UV lamp. The effects of the catalyst loading (0.25 – 1.0 g per 0.1 L SMX solution), nitrate concentration (0-1 M), bicarbonate concentration (0 – 0.1 M) and UV irradiation time (1– 6 h) on the oxidation of SMX were investigated. Besides, the photolysis (UV irradiation alone) of SMX was also performed and compared with the photocatalytic oxidation of SMX at the selected conditions (10 mg/L SMX, initial pH of 4, temperature of 293 ± 2K). For all of the experiments, SMX concentration and Chemical oxygen demand (COD) were monitored while the toxicity of the photocatalytically treated solutions was also evaluated.

## 2.5. Analytical methods

HPLC analysis for SMX concentration in water was carried out on a Waters 2690 separations module with a Waters 996 Photo Diode Array at 235 nm using a Phenomenex Aries Peptide column (3.6 µm XB-C18, 150 x 4.60 mm). The mobile phase was 67 % v/v nanopure water (0.1% v/v formic acid) and 33 % v/v HPLC grade methanol which was applied as an isocratic run with a constant flow rate of 0.75 ml/min. The runs lasted for ten minutes with a three-minute delay between injections to allow for the column to equilibrate. COD was measured with Chemetrics low range (10-150 mg/L) COD vials (Midland, VA, USA) to indicate the mineralization of SMX and SMX oxidation products generated by the photocatalytic oxidation.

It was found that the biochar/TiO<sub>2</sub> kept some SMX while the aqueous phase had negligible SMX after the photocatalytic oxidation of SMX. Thus, the overall removal efficiency

of SMX (considering removal of SMX from both aqueous phase and biochar/TiO<sub>2</sub>) was evaluated by using Eq. 3:

$$\text{Overall removal (\%)} = \frac{(\text{Initial amount of SMX} - \text{amount of SMX in aq} - \text{amount of SMX in biochar/TiO}_2)}{\text{Initial amount of SMX}} \times 100 \quad (3)$$

(Initial amount of SMX, mg of initial SMX before the photocatalytic oxidation; amount of SMX in aq, mg of SMX remaining in aqueous phase after photocatalytic oxidation; amount of SMX in biochar/TiO<sub>2</sub>, mg of SMX remaining in biochar/TiO<sub>2</sub> after photocatalytic oxidation)

The toxicity of the SMX and its oxidation products were tested using 24 h born *Daphnia magna* at various dilutions (Chahbane et al., 2007) based on the procedure as Organization for Economic Cooperation and Development (OECD) Guideline 202. The *Daphnia magna* species were cultivated in the laboratory to be put into the solution for culturing in an incubator for 24-48 h. The incubator was set at 293 K in a 16 h light – 8 h dark cycle. The toxicity tests were conducted with five *Daphnia magna* in each beaker with 50 mL of reaction solution after different dilution ratios. The results were evaluated on the basis of immobilization percentage obtained by counting the number of survived *Daphnia magna* after 24 and 48 h.

Toxi-Chromotest™ (Environmental Bio detection Products Inc., Brampton, Ontario) was also used to test the toxicity of SMX and the SMX oxidation products. This biotoxicity test is one of the US Environmental Protection Agency (EPA)'s certified biotoxicity methods, and relies on colorimetric analysis to measure the toxicant-based inhibition of β-galactosidase synthesis by *E. coli* as described in detail by Schalie et al. (van der Schalie et al., 2006). The *E. coli* bacteria in the test kit were rehydrated in a solution containing the inducers for β-galactosidase production and excretion. The rehydrated bacteria were then exposed to the toxicant and incubated at 310 K for 3 h. The presence of a toxin would lead to a reduction in

enzyme production. After incubation a colorant (blue chromogen agent) was added to the bacteria, which was hydrolyzed by the enzyme, producing a blue color. After additional incubation at 310 K for 30 min for color development, the solution was measured by a spectrophotometer at 615 nm. The minimum inhibition concentration (MIC) is defined as the concentration that results in 20% inhibition of the  $\beta$ -galactosidase. Samples were considered nontoxic if they measured below the MIC.

### 3. Results and discussion

#### 3.1. Characterization of the biochar-supported TiO<sub>2</sub>

The SEM images of biochar and biochar/TiO<sub>2</sub> present the structures of biochar and biochar/TiO<sub>2</sub>, respectively (Fig. 1). The images exhibited that tiny TiO<sub>2</sub> granules were well dispersed on the biochar with little agglomeration. The XRD patterns of the TiO<sub>2</sub> and biochar/TiO<sub>2</sub> showed that the diffraction peaks at  $2\theta=25.3, 37.8, 48.1$  and  $54.1$  in the biochar-TiO<sub>2</sub> were attributed to anatase-TiO<sub>2</sub> (Fig.2) (Zhao et al., 2010), which confirmed that the majority of TiO<sub>2</sub> in the biochar/TiO<sub>2</sub> sample was anatase-TiO<sub>2</sub>. The EDX analysis of the biochar/TiO<sub>2</sub> is also provided in Table S1.

#### 3.2. Adsorption of SMX onto the biochar-supported TiO<sub>2</sub>

In the present study, the biochar/TiO<sub>2</sub> showed high adsorption capacity of SMX due to the hydrophobic interaction between SMX and the biochar/TiO<sub>2</sub>. Compared with the biochar/TiO<sub>2</sub>, the raw biochar showed higher adsorption of SMX because the raw biochar had more carbon sites for  $\pi$ - $\pi$  interaction for adsorption of SMX than the biochar/supported TiO<sub>2</sub> (Table 1, Fig. S3). The nonlinear adsorption isotherms in Fig. S3 and the adsorption isotherms

parameters in Table 1 support that Langmuir isotherm is the better-fitted model for adsorption of SMX onto the raw biochar and the biochar/TiO<sub>2</sub>. However, the commercial TiO<sub>2</sub> powder exhibited little adsorption of SMX since it had no sites for  $\pi$ - $\pi$  interaction for adsorption of SMX (Fig. S4). The adsorption capacities of SMX onto the biochar/TiO<sub>2</sub> were found to be 0.6 – 2.4 mg SMX per g biochar/TiO<sub>2</sub> at the selected conditions (0.25-2 g biochar-supported TiO<sub>2</sub>, 100 mL of 10 mg/L SMX, pH 4). The K<sub>d</sub> (solid-water distribution coefficient) was 176 L/kg which were higher than those for the biochar made from bamboo, sugarcane and hardwood (i.e., 60 – 104 L/kg) reported by Yao et al. (Yao et al., 2012). This adsorption capacity of the biochar/TiO<sub>2</sub> would enhance the overall photocatalytic oxidation efficiency since the previous studies showed the synergy of adsorption and photocatalytic (also catalytic) reaction to enhance overall reaction efficiency (Jiang et al., 2010; Kim et al., 2015; Liu et al., 2014).

### 3.3. Photocatalytic oxidation of SMX using the biochar-supported TiO<sub>2</sub>

There have been a number of studies on the heterogeneous photocatalysis of SMX under UV-A (320 nm <  $\lambda$  < 400 nm) and UV-B (280 nm <  $\lambda$  < 320 nm) irradiation (Abellán et al., 2009; Hu et al., 2007). Compared with the photocatalytic processes using UV-A and UV-B, the photocatalytic processes for SMX under UV-C ( $\lambda$  < 280 nm) irradiation have been rarely studied because UV-C ( $\lambda$  < 280 nm) irradiation has been used for disinfection of wastewater and drinking water (Lonnen et al., 2005). However, the photocatalytic process using UV-C exhibited higher oxidation of pharmaceutical compounds, phenol, and salicylic acid than UV-A and UV-B (Matthews & McEvoy, 1992; Sommer et al., 1998). Fig. 3 compares the direct photolysis of SMX, the photocatalytic oxidation of SMX using the commercial TiO<sub>2</sub> powder (0.1 g and 0.5 g TiO<sub>2</sub>) and the biochar/TiO<sub>2</sub> (0.5 g biochar/TiO<sub>2</sub> containing 0.015 g TiO<sub>2</sub>) under UV-C light

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4 irradiation. The direct photolysis and photocatalytic oxidation using commercial  $\text{TiO}_2$  powders  
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6 (0.5 and 1 g) led to nearly complete removal of SMX in 3h. On the other hand, the photocatalytic  
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8 oxidation using the biochar/ $\text{TiO}_2$  exhibited 75% removal efficiency of SMX (considering the  
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10 residual SMX in the aqueous phase and the biochar/ $\text{TiO}_2$  after the photocatalytic reaction)  
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12 calculated by Eq. 3. Higher removal of SMX by the direct photolysis was made because the  
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14 SMX had high absorption of UV-C light at 250-270 nm (maximum absorption at 260 nm  
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16 (Nasuhoglu et al., 2011)) which was quite close to the major wavelength (254 nm) of UV-C light  
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18 from the UV lamp for this study. On the contrary, the presence of  $\text{TiO}_2$  resulted in lowering the  
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20 removal of SMX by the biochar/ $\text{TiO}_2$ . Since  $\text{TiO}_2$  also absorbs effectively UV-C light at 250-260  
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22 nm, SMX and  $\text{TiO}_2$  would compete for the photons in the UV-C light which caused less efficient  
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24 removal of SMX.  
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31 However, the COD removal of SMX (as an indicator for mineralization of SMX) by the  
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33 biochar/ $\text{TiO}_2$  was almost four times higher than that by the direct photolysis. It indicated the  
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35 biochar/ $\text{TiO}_2$  resulted in effective oxidation of SMX and its oxidation products leading to high  
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37 mineralization of SMX (~ high removal of COD) because  $\text{TiO}_2$ -mediated photocatalysis was  
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39 heavily dependent on OH radical-driven oxidation. In addition, the SMX removal by the  
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41 commercial  $\text{TiO}_2$  nano-powder (0.5 - 1 g  $\text{TiO}_2$ , average size of 21 nm) also exhibited lower  
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43 removal of COD than the biochar- $\text{TiO}_2$ . The lower removal of COD by the commercial  $\text{TiO}_2$   
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45 powders indicated the less photocatalytic oxidation efficiency due to the higher recombination  
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47 rate of electrons and electron holes generated from the  $\text{TiO}_2$  surface by the UV light irradiation.  
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49 Compared with the commercial  $\text{TiO}_2$  powder, the biochar/ $\text{TiO}_2$  had its advantage to lower the  
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51 recombination rate of electrons and electron holes because of high conductivity of biochar.  
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4 It was also interesting that increase of the biochar/TiO<sub>2</sub> loading resulted in slight decrease  
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6 in SMX removal efficiency (Fig. 4). The actual amount of TiO<sub>2</sub> in the biochar/TiO<sub>2</sub> were found  
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8 to be 3 - 3.4% of total mass of the biochar/TiO<sub>2</sub>. As mentioned in Nasuhoglu et al and Abellán  
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10 et al. (Abellan et al., 2007; Nasuhoglu et al., 2011), the direct photolysis by UV light is more  
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12 effective mechanism to remove SMX itself than TiO<sub>2</sub>-mediated photocatalytic oxidation. The  
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14 higher loading of biochar/TiO<sub>2</sub> led to higher absorption of UV light (photons) onto the TiO<sub>2</sub> in  
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16 the biochar/TiO<sub>2</sub> while lowering the contact between UV light and SMX and decreasing the  
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18 photolysis efficiency of SMX. However, the higher loading of biochar/TiO<sub>2</sub> enhanced the COD  
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20 removal efficiency due to the higher generation of OH radicals.  
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26 Various water bodies such as wastewater, groundwater, landfill leachate and surface  
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28 water include environmental constituents such as bicarbonate, nitrate, and natural organic matter  
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30 (NOM). This study investigated particularly the effects of bicarbonate and nitrate on  
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32 photocatalytic oxidation of SMX using the biochar/TiO<sub>2</sub>. Fig. 5A shows the effect of nitrate  
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34 concentration on the photocatalytic oxidation of SMX. Nitrate is abundant in surface and ground  
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36 water, and is known as an electron scavenger to prevent the recombination of electron holes and  
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38 electrons for enhancing photocatalytic oxidation efficiency (Bems et al., 1999). However, the  
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40 presence of high concentration of nitrate (1 M) made only slight enhancement of SMX removal  
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42 (by the factor of 1.2). Besides, the biotoxicity tests showed low biotoxicity (0-27% inhibition)  
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44 with 0 – 0.25 M nitrate and high biotoxicity (44-64% inhibition) with 0.5-1 M nitrate.  
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51 Fig. 5B demonstrates that the SMX removal was significantly improved by the presence  
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53 of bicarbonate ion. The slight addition of bicarbonate (0.02 M bicarbonate) to the mixture of  
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55 aqueous SMX and biochar/TiO<sub>2</sub> drastically increased the SMX removal efficiency from 75% to  
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57 90%. Other studies reported the generation of carbonate radical (CO<sub>3</sub><sup>•-</sup>) during the TiO<sub>2</sub>-mediated  
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photocatalytic oxidation in the presence of bicarbonate/carbonate (Canonica et al., 2005; Chen et al., 1975; Hu et al., 2007; Mazellier et al., 2002) as listed in Eq. 4 and 5.



The previous studies showed that carbonate radicals effectively oxidized the aniline-based compounds such as SMX (Canonica et al., 2005; Hu et al., 2007). Therefore, the bicarbonate concentration led to more effective photocatalytic oxidation of SMX. However, when the toxicity of the SMX oxidation products generated by the photocatalytic oxidation in the presence of 0.02 M bicarbonate was examined by 24 h immobilization test with *Daphnia magna*, it showed a maximum toxicity of 100%. The biotoxicity using the *E. coli* expressing  $\beta$ -galactosidase (Toxi-Chromotest™) also confirmed the 100% toxicity of the SMX oxidation treated by the photocatalytic oxidation with the bicarbonate. Such high toxicity of the SMX oxidation products would limit the practical application of the photocatalytic oxidation in the presence of bicarbonate.

Finally, the effect of UV irradiation time on the removal of SMX and COD were examined at the selected conditions (0.5 g biochar/TiO<sub>2</sub> per 0.1 L solution which is 5 g/L, initial pH of 4, 6 h UV irradiation). Fig. 6 presented that the SMX removal efficiency reached 91% while the COD removal efficiency as an indication of SMX mineralization also increased to 81% for the photocatalytic oxidation with 6 h UV irradiation. Thus, these results indicated effective decomposition of the SMX and SMX oxidation products with increasing UV irradiation time during the photocatalytic oxidation. The highest removal capacity of SMX in this study (2.3 g SMX degraded per m<sup>3</sup> of reactor per h, Fig. 6) was compared with those from others'

investigation at similar conditions (100 mL of 10 mg/L SMX, 6-15 watt UV lamp). The SMX removal capacity in this study was higher than the commercial TiO<sub>2</sub> powder (1 g SMX degraded/m<sup>3</sup><sub>reactor</sub>-h), similar to the TiO<sub>2</sub>/hydroxyapatite (2 g SMX degraded/m<sup>3</sup><sub>reactor</sub>-h), but lower than the excessive concentration of TiO<sub>2</sub> powder (5-10 g SMX degraded/m<sup>3</sup><sub>reactor</sub>-h)(Xekoukoulotakis et al., 2011). In addition, the biochar/TiO<sub>2</sub> in this study showed easy separation after use due to its size and weight while the tiny TiO<sub>2</sub> powders were found to cause extensive aggregation and required high energy consumption for separation of TiO<sub>2</sub> powder after use. Surprisingly the biotoxicity tests using the *Daphnia magna* and the *E. coli* expressing  $\beta$ -galactosidase (Toxi-Chromotest™) exhibited minimal inhibition of the SMX oxidation products generated by the photocatalytic oxidation with 6 h UV irradiation. Particularly only 20% immobilization of *Daphnia magna* was obtained after the 6 h photocatalytic oxidation which is acceptable in drink water as described in US EPA guideline (2002). The negligible biotoxicity from the reaction effluent containing SMX oxidation products was mainly due to the high conversion (91%) and mineralization (81%) of SMX resulting in the accumulation of nontoxic final products such as sulfate, nitrate and small organic acids (i.e., oxalic, maleic, formic, and acetic acids).

The possible mechanisms associated with photocatalytic degradation of SMX under UV light irradiation (< 400 nm) using TiO<sub>2</sub> was already explored by other studies (Hu et al., 2007). The photocatalytic oxidation is based on absorption of UV light for generating the excited electrons to the conducting band of TiO<sub>2</sub> and the electron holes to the valence bands of TiO<sub>2</sub>. The photogenerated electron at the surface of TiO<sub>2</sub> is scavenged by electron acceptors such as O<sub>2</sub> while the photogenerated hole can react with OH<sup>-</sup> or H<sub>2</sub>O at the surface of TiO<sub>2</sub>. These reactions generate •OH or •O<sub>2</sub><sup>-</sup> respectively which can oxidize SMX. As Hu et al. (2007) reported, the

major oxidation products by the photocatalytic oxidation of SMX included 3-amino-5-methylisoxazole, hydroxylated and dihydroxylated SMX, and organic acids (i.e., oxalic, maleic, formic, and acetic acids).

In order to remain economical for wastewater and water treatment the biochar/TiO<sub>2</sub> catalyst must be stable throughout multiple photocatalytic reactions. The three cycles of the photocatalytic reactions using the same catalyst resulted in the removal of SMX (90 – 92%) which confirms high stability of the biochar/TiO<sub>2</sub> catalyst over the multiple reactions (Fig. S5).

#### 4. Conclusions

The biochar/TiO<sub>2</sub> was prepared by using the surface-modified biochar and a simple sol-gel method for TiO<sub>2</sub> synthesis, and exhibited tiny TiO<sub>2</sub> granules well dispersed on the biochar with little agglomeration. The biochar/TiO<sub>2</sub> also exhibited the higher adsorption capacity of SMX than the commercial TiO<sub>2</sub> powder and the biochar made from various agricultural wastes while it showed better fit to Langmuir isotherm.

The biochar/TiO<sub>2</sub> showed much higher mineralization of SMX than the photolysis (by UV irradiation only) and the photocatalysis using the commercial TiO<sub>2</sub> powder. The higher loading of biochar-TiO<sub>2</sub> also led to enhancement in mineralization of SMX due to the higher generation of OH radicals. The addition of bicarbonate (~ 0.02 M) contributed to significant enhancement of SMX removal while the presence of nitrate made only slight enhancement of SMX removal. However, the SMX oxidation products generated by the photocatalytic oxidation with the bicarbonate showed the maximum toxicity of 100%. When the UV irradiation time increased up to 6 h, both SMX removal efficiency and mineralization enhanced (91 %, 81%) at the selected conditions (5 g biochar/TiO<sub>2</sub> per L, pH 4). It led to high decomposition of SMX and its oxidation products, negligible toxicity and accumulation of non-toxic products.

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11 analysis of biotoxicity.  
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## Figures and Figure Captions

**Fig.1.** SEM images of biochar (A) and biochar-supported TiO<sub>2</sub> (B).

**Fig. 2.** XRD patterns of (a) TiO<sub>2</sub> and (b) biochar-supported TiO<sub>2</sub>.

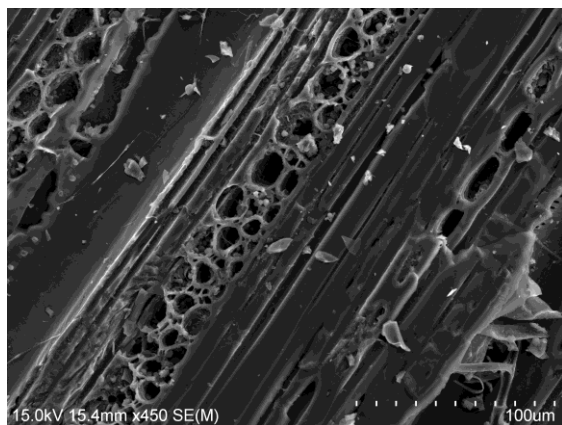
**Fig. 3.** Removal of sulfamethoxazole (SMX) and COD using photolysis and photocatalysis. Conditions: [SMX]<sub>0</sub>, 10 mg/L; SMX solution, 0.1 L; biochar-supported TiO<sub>2</sub> loading, 0.5 g; initial pH, 4; UV irradiation time, 3 h.

**Fig. 4.** Effect of the photocatalyst loading on removal of sulfamethoxazole (SMX) and COD. Conditions: [SMX]<sub>0</sub>, 10 mg/L; SMX solution, 0.1 L; initial pH, 4; UV irradiation time, 3 h.

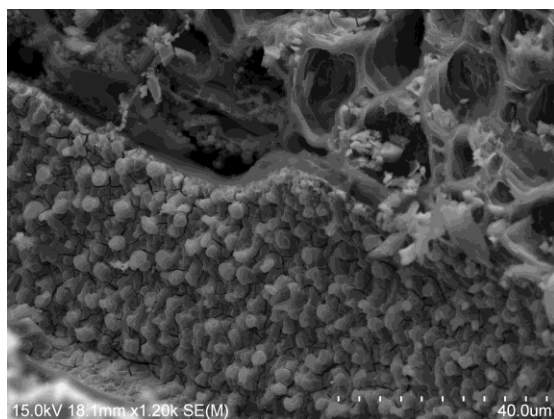
**Fig. 5.** Effect of nitrate (A) and bicarbonate (B) concentration on removal of sulfamethoxazole (SMX). Conditions: [SMX]<sub>0</sub>, 10 mg/L; SMX solution, 0.1 L; photocatalyst (biochar-supported TiO<sub>2</sub>) loading, 0.5 g; initial pH, 4; UV irradiation time, 3 h.

**Fig. 6.** Effect of irradiation time on removal of sulfamethoxazole (SMX). Conditions: [SMX]<sub>0</sub>, 10 mg/L; SMX solution, 0.1 L; photocatalyst (biochar-supported TiO<sub>2</sub>) loading, 0.5 g; initial pH, 4.

(A)

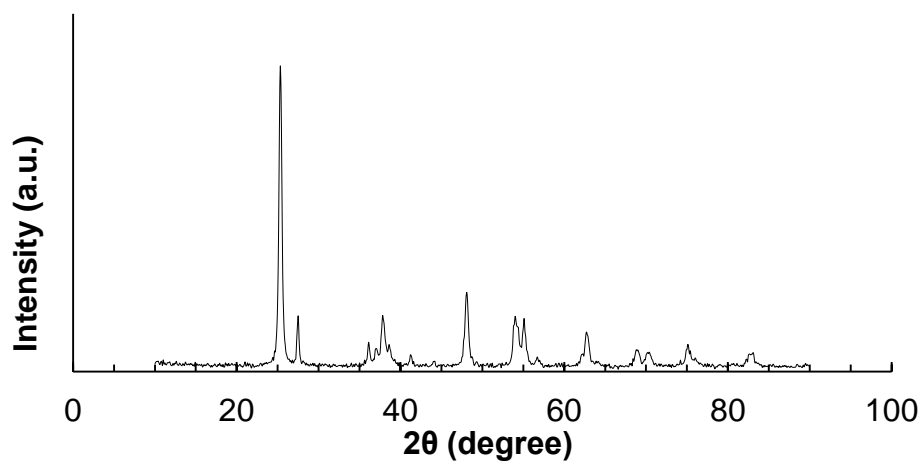


(B)

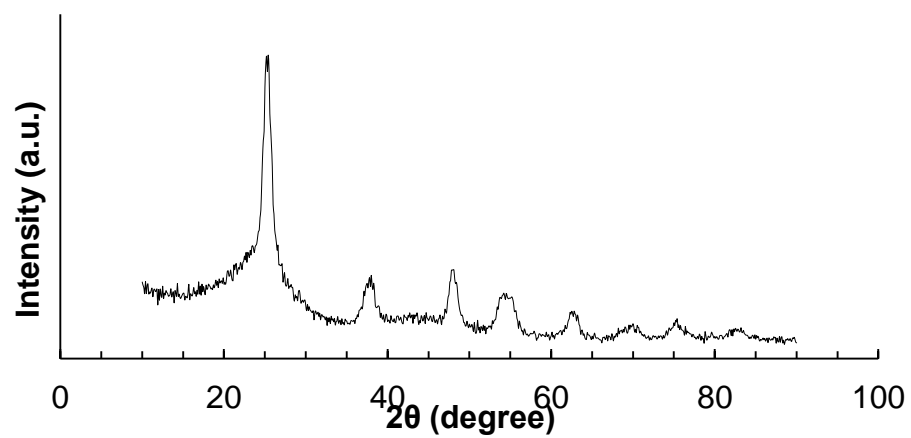


**Fig.1.** SEM images of biochar (A) and biochar-supported  $\text{TiO}_2$  (B).

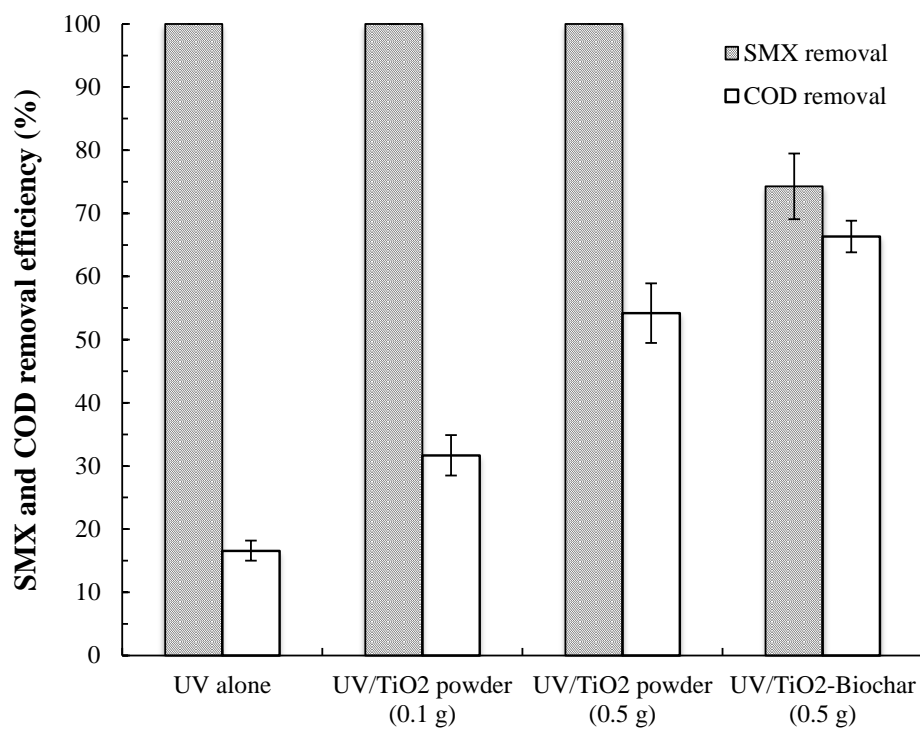
(a)



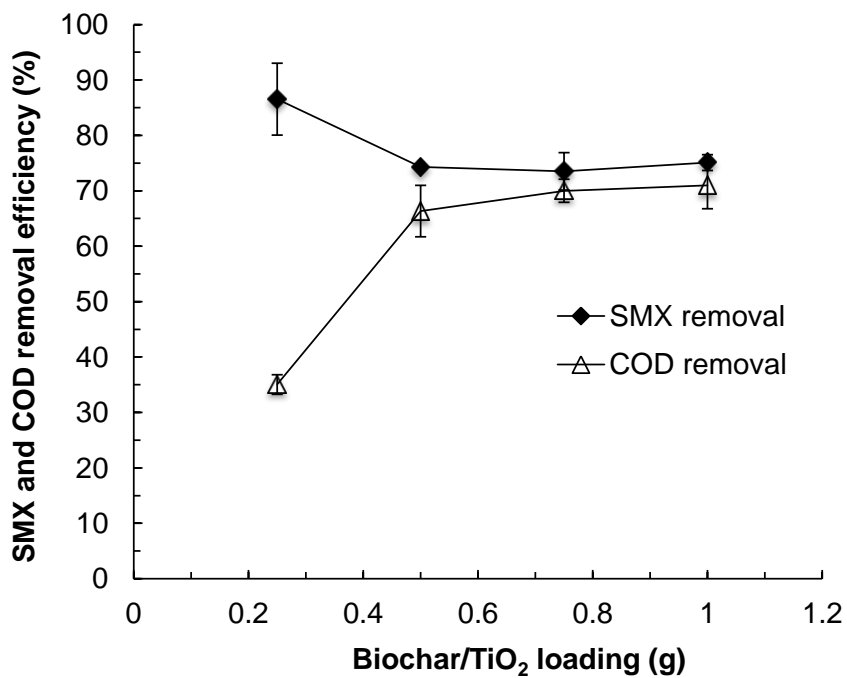
(b)



**Fig. 2.** XRD patterns of (a) TiO<sub>2</sub> and (b) biochar-supported TiO<sub>2</sub>.



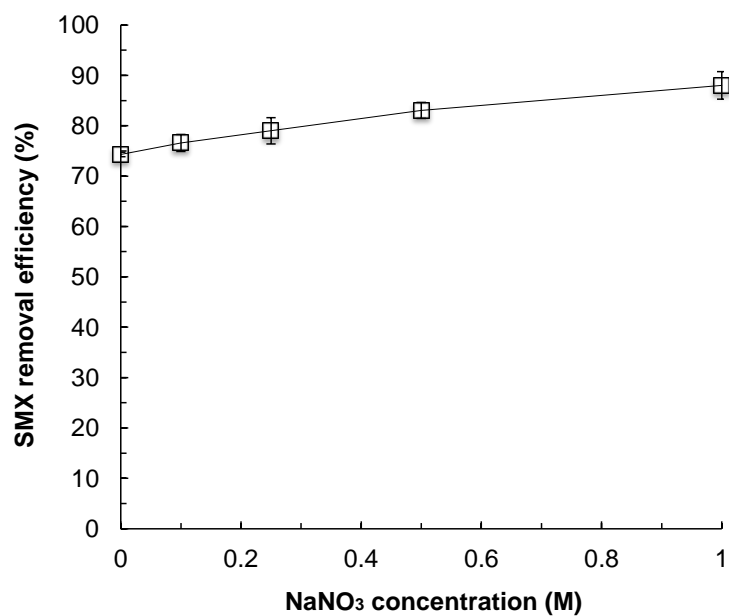
**Fig. 3** Removal of sulfamethoxazole (SMX) and COD using photolysis and photocatalysis. Conditions:  $[SMX]_0$ , 10 mg/L; SMX solution, 0.1 L; biochar-supported TiO<sub>2</sub> loading, 0.5 g; initial pH, 4; UV irradiation time, 3 h.



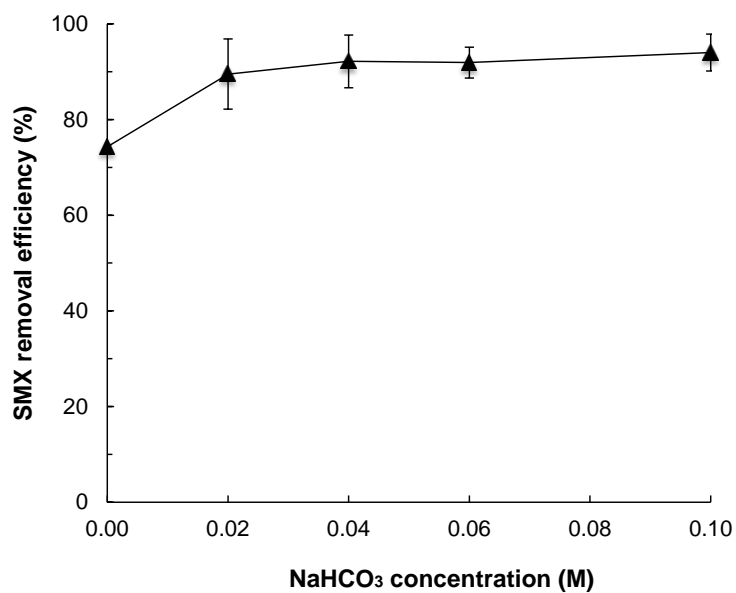
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Conditions: [SMX]<sub>0</sub>, 10 mg/L; SMX solution, 0.1 L; initial pH, 4; UV irradiation time, 3 h.

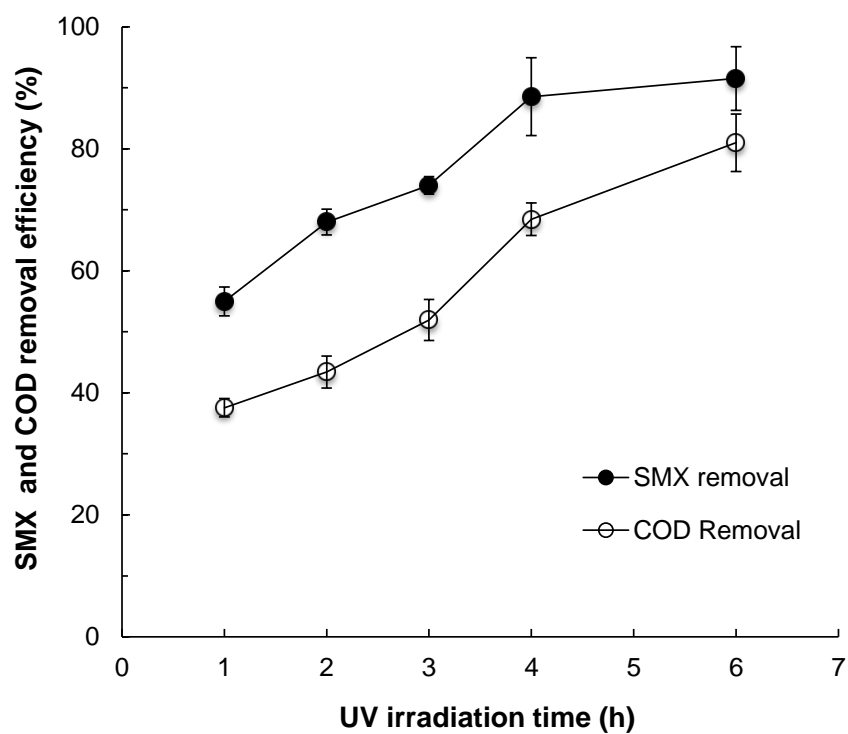
(A)



(B)



**Fig. 5.** Effect of nitrate (A) and bicarbonate (B) concentration on removal of sulfamethoxazole (SMX). Conditions:  $[\text{SMX}]_0$ , 10 mg/L; SMX solution, 0.1 L; photocatalyst (biochar-supported  $\text{TiO}_2$ ) loading, 0.5 g; initial pH, 4; UV irradiation time, 3 h.



**Fig. 6.** Effect of irradiation time on removal of sulfamethoxazole (SMX). Conditions:  $[SMX]_0$ , 10 mg/L; SMX solution, 0.1 L; photocatalyst (biochar-supported  $TiO_2$ ) loading, 0.5 g; initial pH, 4.

**Table 1**  
Freundlich and Langmuir isotherm model parameters for adsorption of SMX on the raw biochar and biochar/TiO<sub>2</sub>. Conditions: Initial SMX (10 mg/L, 0.1 L); raw biochar and biochar/TiO<sub>2</sub> (0.25-2 g); initial pH, 4; 293 K.

Samples	Freundlich		R <sup>2</sup>	Langmuir		R <sup>2</sup>
	k <sub>f</sub> (mg/g)(L/mg) <sup>1/n</sup>	n ( - )		q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	
Biochar/TiO <sub>2</sub>	0.94	2.28	0.97	2.44	0.63	0.99
Raw biochar	0.71	1.30	0.97	12.2	0.052	0.99

\* k<sub>f</sub> indicates an adsorption capacity in (mg/g)(L/mg)<sup>1/n</sup>; 1/n is an indicator of adsorption effectiveness (dimensionless), q<sub>m</sub> is the maximum adsorption capacity (mg/g), and K<sub>L</sub> is the Langmuir constant (L/mg).