Tetracycline Degradation in the UV-heterogeneous Fenton-like System With BiFeO₃ Catalyst

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1 Tetracycline degradation in the UV-heterogeneous Fenton-like system with BiFeO₃
2 catalyst

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15

16 **ABSTRACT**

17 Surplus tetracycline (TC) in the water body causes damage to the ecology balance
18 and human health. Therefore, an efficient strategy was proposed, namely, the UV-
19 heterogeneous Fenton-like system with BiFeO₃ (BFO) catalyst, to eliminate TC
20 pollution. This work successfully integrated the photocatalytic oxidation system with
21 the heterogeneous Fenton-like system, cooperating with the photolysis of H₂O₂. These
22 coupled effects could boost the reduction of Fe (III) to Fe (II) and depress the

recombination of photogenerated charges, further promoting the generation of reactive species, and ultimately facilitating the TC degradation and mineralization. The catalytic of the prepared BFO was stable with no secondary pollution, and BFO could be recovered by an extra magnet to reuse. Compared with other advanced oxidation processes, this system showed an outstanding performance in TC degradation and mineralization, and TC and TOC removal efficiencies could reach 100% and 74.92%, respectively. Moreover, the possible mechanisms for TC degradation involved that TC was degraded by oxidation species generated by the synergistic effect in this system, such as superoxide radicals ($\cdot\text{O}_2^-$), hydroxyl radicals ($\cdot\text{OH}$), and positive holes (h^+). Intermediate products in the TC degradation process mainly were products at $m/z=459$, $m/z=445$, and $m/z=134$.

Keywords: Tetracycline degradation; BiFeO_3 ; UV-Fenton; Photocatalysis;

1. Introduction

In recent decades, tetracycline (TC) (Fig. S1), a typical antibiotic, is extensively employed in treating bacterial infections for humans, and the disease prevention and growth promotion for livestock (Sarmah et al., 2006). However, owing to the overuse and misuse of TC and the incomplete metabolism in the body, most of TC was discharged into the environment system. Residual TC in the water body could break the balance of the aquatic ecosystem and cause the drug resistance in microorganisms, due to its genotoxicity and neurotoxicity, and even increase the possibility of developing superbacteria, which might subsequently cause damage to human health (Xia et al.,

2019). Therefore, much attention is supposed to be paid to the treatment of TC pollution in the aqueous environment.

Many advanced oxidation processes (AOPs) are effective and eco-friendly methods to remove antibiotics through the generation of highly reactive radicals (Anjali and Shanthakumar, 2019). Among AOPs, the heterogeneous Fenton-like method could produce corresponding reactive species by the reaction between solid catalysts and H_2O_2 , such as hydroxyl radical ($\cdot\text{OH}$) radicals, to degrade antibiotics. Moreover, this method broadens the pH range of the application and lessens the production of iron sludge versus the homogeneous Fenton method (Chen et al., 2020; Karthikeyan et al., 2011). The photocatalytic oxidation method is considered as a green, mild and effective AOP to eliminate antibiotics by the generation of superoxide radicals ($\cdot\text{O}_2^-$), $\cdot\text{OH}$ radicals, and other reactive species (Nguyen et al., 2020). And in this method, the optical property and stability of the photocatalyst are critical factors in the removal of antibiotics.

In the photocatalytic process, the photocatalyst under the light irradiation generates electron-hole pairs (e^- - h^+). And then, negative electrons (e^-) and positive holes (h^+) diffuse to the surface of the photocatalyst to degrade antibiotics, or react with other substances to form reactive radicals, achieving antibiotic removal (Nosaka and Nosaka, 2017). Some traditional semiconductor photocatalysts, such as TiO_2 , ZnO , and ZnS , are limited in the employment of photocatalytic methods, due to the wide band gap and the fast recombination of photogenerated e^- - h^+ pairs (Rajeshwar et al., 2008). Recently, ABO_3 materials as photocatalysts have become highly interested since the band gap and

the optics property could be altered by changing the cations in A and B-sites. ABO_3 materials mainly include titanates, tantalates, ferrites, and others (Zhou et al., 2018). Among these materials, BiFeO_3 (BFO) has captured much attention, because its multiferroic property aids the separation of photogenerated e^- - h^+ pairs, and its considerable chemical stability avoids secondary pollution and achieves the reusability (Irfan et al., 2019).

We considered that besides antibiotics could be degraded by the BFO-based photocatalytic oxidation process, Fe (III) in BFO could be reduced by e^- to transform into Fe (II) in this system, so further adding H_2O_2 on the basis of BFO could form the heterogeneous Fenton-like system. Therefore, the cycle between the reduction of Fe (III) in photocatalytic system and the generation of Fe (III) in heterogeneous Fenton-like system was established, which was beneficial to the proceeding of above two systems, ultimately boosting the removal of antibiotics (Moztahida et al., 2019). Moreover, in this coupled oxidation system, added H_2O_2 under the light irradiation could produce $\cdot\text{OH}$ radicals, further promoting the degradation of antibiotics. Additionally, BFO with magnetism could be recycled by an extra magnetic field, avoiding secondary pollution and reducing the operating costs (Sudhaik et al., 2018). Therefore, this coupled oxidation process has the hope to be an efficient strategy for the treatment of TC pollution.

In this work, BFO was prepared by the simple and facile sol-gel method and was analyzed by various characterizations. The UV-heterogeneous Fenton-like system was established to dispose of TC pollution. To evaluate TC removal performance in this

system, the treatment efficiencies of TC under different oxidation systems, the apparent rate constant, and the effects of pH value, H₂O₂ dosage, and catalyst dosage on the TC degradation and mineralization were investigated. Moreover, the successive TC treatment experiment was conducted to discuss the stability and reusability of the prepared BFO. Also, possible mechanisms and intermediate products were explored by the free radicals capturing experiment, the electron spin resonance technique, and the liquid chromatography coupled with tandem mass spectrometry.

2. Materials and methods

2.1. Materials

TC (>98%) and bismuth (III) nitrate pentahydrate were obtained from TCI (Shanghai) Development Company and Shanghai Macklin Biochemical Company, respectively. Methanol and acetonitrile were HPLC grade and obtained from Shanghai Xingke Solvents Company. Other chemicals were analytical grade.

2.2. Preparation of photocatalyst

Firstly, 4.25 g Bi(NO₃)₃·5H₂O, 3.54 g Fe(NO₃)₃·9H₂O, and 8.41 g C₆H₈O₇·H₂O were dissolved in the 100 mL nitric acid solution and were stirred to obtain a reddish-brown solution. Secondly, the mixture was heated in the water bath at 70 °C until the solution was transformed into a sticky gel. And then, the gel was dried in an oven at 100 °C. Finally, the above gel was calcined in a muffle furnace at 600 °C for 1 h at the heating rate of 5 °C/min. The obtained red-brown solid was the prepared photocatalyst.

2.3. Characterization

X-ray Diffraction (XRD, RIGAKU, Smartlab9) and X-ray Photoelectron Spectroscopy (XPS, TMO, K-Alpha) were used to analyze the crystal structure, the elemental composition, and the elemental valence state of the prepared photocatalyst. The morphology of the prepared photocatalyst was observed by the Scanning Electron Microscopy (SEM, Hitachi, SU-1510) and Transmission Electron Microscopy (TEM, JEOL, JEM 2100F). The optical property of the obtained photocatalysts was explored by the Diffuse Reflectance Spectroscopy (UV-Vis DRS, Hitachi, UV-3600). The specific surface area of materials was measured by the Brunauer-Emmett-Teller (BET, Quantachrome, Autosorb-IQ-AG-MP). The magnetic property was analyzed by the Vibrating Sample Magnetometer (VSM, Quantum Design, PPMS-9T). Total organic carbon (TOC) in the TC mineralization process was measured by the Total Organic Carbon analyzer (TOC, SHIMADZU, TOC-L). Possible intermediate products were analyzed by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS, Agilent, Agilent-1260, Agilent Q-TOF).

2.4. Photocatalysis experiment

TC degradation experiments were carried out in the XPA-7 photocatalytic reactor (Xujiang Electromechanical Plant, China) (Fig. S2). A 300 W mercury lamp (with 365 nm filter) was used as the light source, and it was preheated for 5 min before the reaction. Samples were taken and filtered through the 0.22 μm filter, and then were determined by the UV-vis spectrophotometer at 357 nm (Yang et al., 2018b). Also, TOC at 1, 3, 6, and 10 h was measured. The following formula was used to calculate TC or TOC removal efficiencies.

$$RE = (C_0 - C_t)/C_t \times 100\%$$

where C_0 is the initial concentration of TC or TOC, and C_t is the TC or TOC concentration at different sample points, and RE is the TC or TOC removal efficiency.

2.4.1. TC degradation and mineralization under different oxidation systems

To estimate TC degradation and mineralization performances in the UV-heterogeneous Fenton-like system, TC treatment experiments were conducted under different oxidation systems, including the single system (UV system, BFO system, and H_2O_2 system), the dual system (UV + H_2O_2 system, BFO + H_2O_2 system, and UV + BFO system) and the triple system (UV + BFO + H_2O_2 system). Corresponding operation conditions included the followings: The concentrations of TC, BFO, and H_2O_2 were 40 mg/L, 2g/L, and 9.8 mmol/L, respectively.

2.4.2. Influencing factors

To explore the effects of crucial influencing factors on the TC degradation and mineralization in the UV-heterogeneous Fenton-like system, TC treatment experiments were conducted under various operational conditions, including initial solution pH values (pH at 4, 7, and 10), H_2O_2 dosages (4.9, 9.8, 19.6, and 49.0 mmol/L) and catalyst dosages (0.5, 1.0, and 2.0 g/L).

2.4.3. The stability and reusability of BFO in successive TC treatment process

The successive photocatalytic experiment (5 cycles) was conducted to evaluate the stability and reusability of the prepared photocatalyst. When a cycle finished, the photocatalyst was washed with deionized water and dried in the oven at 105 °C. And then, BFO was reused in the next cycle. Operation conditions during 5 cycles were the

same, and the concentrations of TC, BFO, and H₂O₂ were 40 mg/L, 2g/L, and 9.8 mmol/L, respectively.

2.4.4. Possible mechanisms and intermediate products in the TC degradation process

To explore possible mechanisms and to determine reactive species for TC degradation in the UV-heterogeneous Fenton-like system, active species trapping experiments were conducted by using sodium thiosulfate, sodium oxalate, isopropanol, and ascorbic acid as the scavengers of e⁻, h⁺, ·OH, and ·O₂⁻, respectively (Huang et al., 2016; Liu et al., 2016a). Moreover, the electron spin resonance (ESR) technique was employed to further demonstrate whether or not reactive species were produced.

To demonstrate possible intermediate products in the TC degradation process, samples were firstly extracted by Solid Phase Extraction (SPE), and then were analyzed by LC-MS/MS. The sample was extracted through the Oasis HLB cartridge (Waters, Milliford, MA), and the steps in SPE were as follows: first, the cartridge was activated by adding 5 mL of methanol and 5 mL of deionized water in turn. Second, each sample was passed through the cartridge at the flow rate below 3 mL/min. Next, 5 mL of 5% methanol was used to rinse the cartridges. Then, enabling 10 mL of methanol to pass through the cartridge at the flow rate below 1 mL/min to elute samples, and these samples flushed with high purity N₂ (99.9%) to dryness, and finally diluted with methanol for LC-MS/MS analysis. LC-MS/MS equipped with a C18 column (150 mm × 4.6 mm, 5 μm). And the isocratic mobile phase was made up of 5% methanol, 20% acetonitrile, and 75% deionized water (including 0.4% formic acid) at a flow rate of 1 mL/min, with the sample injection volume of 10 μL, with the column temperature of

45 °C. The mass spectrometer analysis (m/z 50-600) was conducted in positive ionization mode by electrospray ionization, and the capillary voltage was 4000 V. Data were analyzed by Mass Hunter software (mass error below 1 ppm).

3. Results and discussions

3.1. Characterizations

The XRD result of the prepared material (Fig. S3) demonstrated that the diffraction peaks at 22.2°, 31.8°, 39.3°, 45.6°, 51.1°, and 56.8°, corresponding to the perovskite phase of bismuth ferrite (JCPDS PDF No. 86-1518) (Xue et al., 2015), indicating that the prepared photocatalyst was BFO. And the valence states of elements were analyzed by XPS. As shown in Fig. S4, the prepared photocatalyst contained three elements: Bi, Fe, and O. Two strong peaks were located at 158.78 eV and 164.09 eV, and their energy separation was 5.31 eV, which conformed to Bi 4f 7/2 and Bi 4f 5/2 in the trivalent oxidation state (Luo et al., 2007). The peaks at 710.75 eV, 724.24 eV, and 718.15 eV were indexed to Fe 2p 3/2, Fe 2p 1/2, and the satellite peak, respectively, which suggested Fe with +3 valence state (Reddy et al., 2018). Moreover, the peak at 530.9 eV was ascribed to the O²⁻ coordinated to Bi³⁺, and the peak at 529.6 eV was attributed to the O²⁻ interacted with the Fe³⁺ (Bhoi and Mishra, 2018). These results further confirmed that BFO was prepared successfully.

The morphology of the material was observed by SEM and TEM. Fig. S5 illustrated that it was relatively smooth and composed of nearly rhombic nanoscale particles, with about 20 nm in average particle size. And most particles agglomerated

to form large clusters, possibly due to electrostatic potential and magnetic attraction (El-Desoky et al., 2015). Elemental mapping images (Fig. S6) suggested that Bi, Fe, and O elements were uniformly distributed in BFO.

The optical property of BFO was investigated by UV-vis DRS. In Fig. S7, BFO displayed a strong absorption band at 360-550nm, and the absorption edge was around 635 nm. Based on the Kubelka-Munk theory (Kubelka and Munk, 1931), the band gap energy of BFO was estimated to be 2.1 eV (the inset of Fig. S7), which is consistent with reported values (Papadas et al., 2015; Zhang et al., 2017). Additionally, the surface area was 20.6 m²/g from BET results. And Fig. S8 showed magnetic hysteresis loops at room temperature with the maximum magnetic field of 20 kOe. The saturation magnetization value was 12.5 emu/g, and the prepared BFO could be conveniently separated by an extra magnet from the system (the inset of Fig. S8).

3.2. TC degradation and mineralization under different oxidation systems

Figure 1 illustrated the results of the TC degradation and mineralization under different oxidation systems. After the reaction, the removal efficiencies of TC and TOC under the single UV system were all lower than 10%, and they were lower than 20% in the single H₂O₂ system. Both systems had poor performances in TC degradation and mineralization. In the single BFO system, due to the absorption, the TC removal efficiency was about 54%, but the absorption could not achieve TC degradation.

Compared with signal systems, the removal efficiencies of TC and TOC in the UV + H₂O₂ system were improved to 84% and 36%, respectively. This was because the irradiation of UV light boosted the generation of ·OH radicals, which can break the

structure of TC to realize a high TC degradation (Eq. (6)). But the low TOC removal efficiency indicated low mineralization. The BFO + H₂O₂ system, as the heterogeneous Fenton-like system, promoted the generation of ·OH radicals, achieving the higher TC degradation (73%) and mineralization (50%). TOC removal efficiencies in the BFO + H₂O₂ system were lower than those in the single BFO system, possibly because in the heterogeneous Fenton-like system, the adsorbed TC was degraded to intermediate products, and they subsequently desorbed into the solution. The UV + BFO system, as the photocatalysis system, achieved the higher removal efficiencies of TC (87%) and TOC (74%) because BFO as the photocatalyst generated e⁻-h⁺ pairs under the UV light (Eq. (1)) (Li et al., 2018). And then, the h⁺ could degrade and mineralize TC (Eq. (2)), and the e⁻ could react with oxygen (O₂) to form ·O₂ radicals (Eq. (7)), which could break the structure of TC (Eq. (8)), facilitating the TC degradation and mineralization.

Compared with other systems, in the UV + BFO + H₂O₂ system, namely, the UV-heterogeneous Fenton-like system, the TC and TOC removal efficiencies were highly enhanced to 100% and 74.92%, respectively. In this system, besides the h⁺ and ·O₂ radicals, ·OH radicals, which were produced from the heterogeneous Fenton-like system and the photolysis of H₂O₂ (Eqs. (5) and (11)), could degrade and mineralize TC. Additionally, the e⁻ from BFO could react with H₂O₂ to form ·OH radicals (Eq. (9)), and e⁻ could promote the reduction of Fe (III) to Fe (II) (Eq. (4)), further boosting the generation of ·OH radicals, and ultimately highly improving the removal of TC and TOC. Therefore, the UV-heterogeneous Fenton-like system could achieve excellent performances in TC degradation and mineralization.

243 The reactions involved in the UV-heterogeneous Fenton-like system with BFO

244 were illustrated as following equations (1-11).

Fig. 1. Variation of (a) TC and (b) TOC removal efficiencies under different oxidation systems.

Table. 1 displayed the removal efficiencies of TC and TOC by various bismuth-based photocatalysts, also indicating that this system with the prepared BFO could achieve excellent performances in TC degradation and mineralization.

Table 1

Photocatalysts	System conditions	TC removal	TOC removal	Reference
		efficiency (%)	efficiency (%)	
BiVO ₄	TC (10 mg/L); BiVO ₄ (1.0 g/L); xenon light (500 W, $\lambda > 420$ nm filter)	45.32	10.32	(Wang et al., 2018a)
g-C ₃ N ₄ /BiOBr	TC (20 mg/L); g-C ₃ N ₄ /BiOBr (3.0 g/L); xenon light (300 W, $\lambda > 400$ nm filter)	86.10	57.40	(Shi et al., 2020)
Ag@AgI/BiOI	TC (20 mg/L); Ag@AgI/BiOI (0.3 g/L); xenon light (300 W, $\lambda > 420$ nm filter)	86.40	47.78	(Yang et al., 2018a)
Bi ₂ MoO ₆	TC (10 mg/L); Bi ₂ MoO ₆ (1.0 g/L); mercury light (300 W)	92.00	72.80	(Bai et al., 2017)
BiOCl/TiO ₂	TC (200 mg/L); BiOCl/TiO ₂ (1.5 g/L); metal halide light (250 W)	91.00	90.00	(Wang et al., 2019)
BiOI	TC (40 mg/L); BiOI (1.0 g/L); xenon light (1000 W, $\lambda > 420$ nm filter)	94.00	72.58	(Hao et al., 2012)
Bi ₂ WO ₆	TC (20 mg/L); Bi ₂ WO ₆ (0.5 g/L); xenon light (350 W, $\lambda > 420$ nm filter)	100.00	31.00	(Chu et al., 2016)
BiFeO ₃	TC (40 mg/L); BiFeO ₃ (2.0 g/L); mercury light (300 W, $\lambda \approx 365$ nm filter); H ₂ O ₂ (9.8 mM)	100.00	74.92	This work

degradation efficiency of TC by the prepared BFO in the UV-heterogeneous Fenton-like system (Fig. S9). The kinetic equation was expressed as

$$\ln(C_t / C_0) = -kt \quad (12)$$

where C_0 and C_t represented the concentration of TC at initial and sampling time intervals, respectively, and k is the apparent rate constant. Table. 2 showed apparent rate constants under different photocatalytic Fenton systems, demonstrating that the reaction rate in this system was relatively high due to the multifunction catalysis of the prepared BFO.

Table 2

The apparent rate constants under different photocatalytic Fenton systems.

Photocatalysts	System conditions	The apparent rate constant (min^{-1})	Reference
Polyhedral Fe_3O_4	TC (50 mg/L); Polyhedral Fe_3O_4 (0.30 g/L); H_2O_2 (10.00 mM); UVC light (10 W)	0.00450	(Zhu et al., 2019)
$\alpha\text{-Fe}_2\text{O}_3$	TC (40 mg/L); $\alpha\text{-Fe}_2\text{O}_3$ (0.50 g/L); H_2O_2 (10.00 mM); LED light (100 W)	0.00600	(Guo et al., 2018)
Fe-rectorite	TC (100 mg/L); Fe-rectorite (0.40 g/L); H_2O_2 (10.00 mM); LED light (500 W)	0.01000	(Guo et al., 2020)
CeO_2/Fh	TC (10 mg/L); CeO_2/Fh (1.00 g/L); H_2O_2 (50.00 Mm); LED light (5 W)	0.01093	(Huang et al., 2019)
Schwertmannite	TC (15 mg/L); Schwertmannite (0.25 g/L); H_2O_2 (1.00 mM); xenon light (350 W)	0.02425	(Ma et al., 2020)

ZIF-8/MnFe ₂ O ₄	TC (20 mg/L); ZIF-8/MnFe ₂ O ₄ (0.3 g/L); H ₂ O ₂ (50.00 mM); xenon light (300 W)	0.03000	(Wang et al., 2020)
BFO	TC (40 mg/L); BFO (2.00 g/L); H ₂ O ₂ (9.80 mM); mercury light (300 W)	0.02650	This work

275 3.3. Influencing factors

276 3.3.1. Initial solution pH

277 Photocatalytic experiments were conducted at pH 4, 7, and 10 to investigate the
278 effect of initial solution pH value for the TC degradation. Fig. S10a illustrated that TC
279 removal efficiency dropped from 100% to 89% when the initial pH value increased
280 from 4 to 10, possibly because the lower pH could improve the generation of ·OH
281 radicals to oxidize TC (Jawale and Gogate, 2017). Besides, with the increase of pH
282 values, the affinity of Fe (III) for hydroxide ions (OH⁻) enhanced, which reduced the
283 reaction between Fe (III) and e⁻ (Eq. (4)), and this further restricted the generation
284 of ·OH radicals. Before 45 min, TC removal efficiencies at pH 10 were higher than
285 those at pH 4 and 7, possibly because TC was mainly in the forms of TCH⁻ and TC²⁻ at
286 pH 10 (Fig. S11), and TCH⁻ and TC²⁻, with a high electron density, were more accessible
287 to be attacked by radical species (López-Peñalver et al., 2010). But as the reaction
288 progressed, iron hydroxide complexes would be produced (Hussain et al., 2018), which
289 reduced the active catalytic sites of BFO, hindering the generation of ·OH radicals.
290 Additionally, in the alkalinity conditions, H₂O₂ could be decomposed into H₂O and O₂
291 rather than ·OH radicals (Eqs. (13) and (14)). Moreover, hydroperoxy anion (HO₂⁻),
292 which was the conjugated base of H₂O₂, reacted with ·OH radicals and H₂O₂, lessening

the TC removal efficiency (Eqs. (15) and (16)) (Galindo and Kalt, 1999; Muruganandham and Swaminathan, 2004). As displayed in Fig. S10b, TOC removal efficiency also decreased with the increase of pH values, due to the more generation of effective oxidation radicals at the lower pH. Therefore, the preferable initial solution pH value was 4.

3.3.2. H₂O₂ dosages

Photocatalytic experiments were conducted with various H₂O₂ dosages fixed at 4.9, 9.8, 19.6, and 49.0 mmol/L, respectively. Fig. S12a presented that TC removal efficiency increased from 90% to 99% as the H₂O₂ dosage raised from 4.9 to 9.8 mmol/L at 210 min. This because more $\cdot\text{OH}$ radicals were produced through some pathways, like the reaction between Fe (II) and H₂O₂ (Eq. (5)); the reaction between e^- and H₂O₂ (Eq. (9)); the reaction between $\cdot\text{O}_2^-$ and H₂O₂ (Eq. (10)); and the photolysis of H₂O₂ under UV light (Eq. (11)). However, when the H₂O₂ dosage raised to 19.6 or 49.0 mmol/L, TC removal efficiencies showed few differences, or even declined, possibly because catalytic sites of BFO were saturated and the excessive H₂O₂ caused the scavenging effect. $\cdot\text{OH}$ radicals could be eliminated by reacting with the excessive H₂O₂ (Eq. (17)), and $\cdot\text{OH}$ radicals tended to react with the positive h^+ to form hydroperoxyl radicals ($\text{HO}_2\cdot$) (Eq. (18)) (Liu et al., 2017), which was less reactive

versus $\cdot\text{OH}$ radicals. In addition, $\text{HO}_2\cdot$ radicals could also react with $\cdot\text{OH}$ radicals to form O_2 and H_2O (Eq. (19)), lessening reactive radicals. Moreover, $\cdot\text{OH}$ radicals with high concentration could dimerize to form H_2O_2 (Eq. (20)) (Ghodbane and Hamdaoui, 2010), also decreasing reactive radicals, and ultimately lowering TC removal efficiency. As illustrated in Fig. S12b, with the increase of H_2O_2 dosages, TOC removal efficiency firstly raised and then decreased, but TOC removal efficiencies with different H_2O_2 dosages showed few differences at 10 h. Therefore, considering the efficiency and cost, 9.8 mmol/L was set as the preferable H_2O_2 dosage.

3.3.3. Photocatalyst dosages

Photocatalytic experiments were conducted with BFO dosages of 0.5, 1.0, and 2.0 g/L, respectively. As exhibited in Fig. S13, TC removal efficiency raised from 93% to 100% at 210 min when the BFO dosage increased from 0.5 g/L to 2.0 g/L, possibly because ascending dosage provided more reactive sites for producing reactive species. Additionally, the variation of TOC removal efficiency with BFO dosages was similar to that of TC removal efficiency, but there were few differences between various dosages for TOC removal at 10 h. Therefore, the preferable BFO dosage was 2.0 g/L.

3.4. Stability of BFO in successive TC treatment process

As shown in Fig. S14, after five cycles, TC and TOC removal efficiencies

remained at about 91% and 40%, respectively. Furthermore, the leaking bismuth and iron were less than 0.43 mg/L and 0.18 mg/L, respectively. It concluded that the prepared catalyst could be recycled and reused with no secondary pollution.

3.5. Possible mechanisms of TC Degradation

Scavengers were added into the system to determine possible reactive species in the UV-heterogeneous Fenton-like system (Fig. S15). Obviously, after adding various scavengers, TC removal efficiencies all decreased, which suggested that e^- , h^+ , $\cdot OH$, and $\cdot O_2^-$ all contributed to the TC removal. Moreover, the ESR technique was used to further confirm $\cdot O_2^-$ and $\cdot OH$ radicals. ESR spectra (Fig. 2a) presented four strong groups of signals of DMPO- $\cdot O_2^-$. Also, four strong groups of signals of DMPO- $\cdot OH$ were observed (Fig. 2b). These results stated that $\cdot O_2^-$ and $\cdot OH$ radicals were generated in this system (Li et al., 2018).

According to the above results, the possible mechanisms of TC degradation in the UV-heterogeneous Fenton-like system were illustrated in Fig. 2c. In summary, under the excitation of UV light, the e^- transferred from the valance band (VB) to the conduction band (CB) in BFO, and BFO produced photogenerated e^- - h^+ pairs (Eq. (1)). On the one hand, the h^+ could directly degrade TC absorbed on the surface of BFO (Eq. (2)), and h^+ could also react with H_2O to form $\cdot OH$ radicals (Eq. (3)). On the other hand, e^- could facilitate the reduction of Fe (III) to Fe (II) (Eq. (4)), promoting the heterogeneous Fenton process to generate $\cdot OH$ radicals (Eq. (5)), and e^- could react with O_2 to form $\cdot O_2^-$ radicals (Eq. (7)). Besides, H_2O_2 added in the system can react with e^- or $\cdot O_2^-$ radicals to form $\cdot OH$ radicals, and meantime, e^- could be captured by

H_2O_2 (Eqs. (9) and (10)), depressing the recombination of photogenerated charges.

Additionally, H_2O_2 could produce $\cdot\text{OH}$ radicals under the photolysis of the UV light

(Eq. (11)). All the above reactive species could degrade and mineralize TC (Eqs. (2),

(6) and (8)).

Fig. 2. ESR spectra of (a) $\text{DMPO}\cdot\text{O}_2^-$ and (b) $\text{DMPO}\cdot\text{OH}$, and (c) Schematic diagram of mechanisms for TC degradation.

3.6. Possible intermediate products

LC-MS/MS was employed to investigate possible intermediate products. The results (Fig. S16) suggested that the main intermediate products were compounds at $m/z=459$, $m/z=445$, and $m/z=134$. Possible intermediate products were displayed in Fig.

3 and Table 3, based on analyses by Mass Hunter software and related reports. Moreover, possible TC degradation schemes were exhibited in Fig. 4.

In the UV-heterogeneous Fenton-like system, the double bands of C₂-C₃ and C_{11a}-C₁₂ in TC were attacked by oxidative species ($\cdot\text{O}_2^-$, h^+ , and $\cdot\text{OH}$) (scheme (1) and (2)) (Liu et al., 2016b). And subsequently, the hydroxyl group at position C₆ broke and water molecules lost to form product A1 (Yang et al., 2018b); or the loss of the amino group at position C₂ as well as the hydroxyl group at position C₆, and the attack at the double band of C_{11a}-C₁₂ by oxidative species led to the generation of product C1 (Wu et al., 2020). Product C2 was directly produced by the deamination and cyclization of TC (Fu et al., 2017). When the cyclization and deamination occurred at position C₂ in product A1 (scheme (6)), and the cyclization and dehydration occurred between C₆ and C_{11a}, product B was produced (Wang et al., 2012). Product A2 was obtained from the TC via the H-atom abstraction at position C_{5a} and the double band of C_{11a}-C₁₂ attacked by oxidative species (scheme (1) and (3)) (Li and Hu, 2016; Song et al., 2020). When the phenolic moiety (D ring) was attacked by oxidation species, the addition of the hydroxyl group could occur at position C₇ or C₉, and a para-substituted or an ortho-substituted product were produced. Then these substituted products transformed into corresponding quinoid-type products (product A3 and A4) by a two-transfer-oxidation process (scheme (4) and (5)) (Zhang et al., 2019a). Furthermore, these intermediate products could be further oxidized by oxidation species to form some smaller organic molecules, like compound D1 and D2, ultimately achieving TC degradation and mineralization (Wang et al., 2018b; Zhang et al., 2019b).

Fig. 3. Proposed degradation pathways of TC.

Table 3

Degradation intermediates of TC.

Products	m/z	Molecular formula	Molecular mass	Error (ppm)	Molecular structure
A1	459	C ₂₂ H ₂₂ N ₂ O ₉	458	-0.25	
A2		C ₂₂ H ₂₂ N ₂ O ₉	458	-0.25	

A3		$C_{22}H_{22}N_2O_9$	458	-0.25
A4		$C_{22}H_{22}N_2O_9$	458	-0.25
B		$C_{22}H_{19}NO_9$	441	-0.26
C1	445	$C_{22}H_{21}NO_8$	427	0.17
C2		$C_{22}H_{21}NO_8$	427	0.17
D1	134	$C_6H_{12}O_2$	116	0.62
D2		$C_6H_{12}O_2$	116	0.62

Scheme.1

Scheme.2

Scheme.3

Scheme.4

Scheme.5

Scheme.6

Fig. 4. Proposed degradation schemes of TC.

4. Conclusions

In this study, BFO as the catalyst in the UV-heterogeneous Fenton-like system was successfully prepared. The catalytic of BFO was stable with no secondary pollution, and BFO could be recovered by an extra magnet to reuse. Compared with other advanced oxidation systems, this system showed an outstanding performance in the treatment of TC. When the concentrations of TC, BFO, and H_2O_2 were 40 mg/L, 2g/L,

and 9.8 mmol/L, respectively, with 300 W mercury lamp, TC and TOC removal efficiencies reached 100% and 74.92%, respectively. Moreover, the mechanism of TC degradation involved that TC was degraded by reactive species generated in this system, such as $\cdot\text{O}_2^-$, $\cdot\text{OH}$, h^+ , and e^- . Besides, Intermediate products in the TC degradation process mainly were products at $m/z=459$, $m/z=445$, and $m/z=134$. This work successfully integrated the photocatalytic oxidation system with the heterogeneous Fenton-like system, cooperating with the photolysis of H_2O_2 . And these coupled effects could boost the reduction of (III) to Fe (II) and depress the recombination of photogenerated charges, which further promoted the generation of reactive species, and ultimately facilitated the TC degradation and mineralization. Therefore, this work provides an efficient strategy for the treatment of TC pollution.

Authors' contributions Yongwei Jiang: Funding acquisition, Writing - Review & Editing. Chao Xing: Formal analysis, Writing - Original Draft, Writing - Review & Editing. Yue Chen: Investigation, Formal analysis, Writing - Original Draft. Jing Shi: Conceptualization, Resources, Writing - Review & Editing, Supervision, Funding acquisition. Sheng Wang: Investigation, Formal analysis.

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Data availability All data generated or analysed during this study are included in this published article and its supplementary information files.

Declarations

Ethics approval and consent to participate Not applicable.

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Figures

Figure 1

Variation of (a) TC and (b) TOC removal efficiencies under different oxidation systems.

Figure 2

ESR spectra of (a) DMPO- $\cdot O_2^-$ and (b) DMPO- $\cdot OH$, and (c) Schematic diagram of mechanisms for TC degradation.

Figure 3

Proposed degradation pathways of TC.

Scheme.1

Scheme.2

Scheme.3

Scheme.4

Scheme.5

Scheme.6

Figure 4

Proposed degradation schemes of TC.

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