



Removal kinetics and pathways of oxytetracycline by UV/PDS

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Received 3 March 2020; Accepted 10 July 2020

ABSTRACT

The large influx of antibiotics in the environment may pose a threat to humans. Therefore, the fate of antibiotics in the environment has attracted a great deal of attention. In this work, the degradation of oxytetracycline (OTC), a type of tetracycline antibiotic, by UV-activated peroxydisulfate (PDS) advanced oxidation process was investigated. The results showed that OTC could be efficiently degraded by UV/PDS, with the degradation process following the pseudo-first-order kinetics equation. The degradation rate was dependent on the initial concentration of PDS. Neither acidic nor alkaline conditions facilitated the degradation of OTC. The existence of Cl⁻ promoted the degradation of OTC, whereas other inorganic ions (NO₃⁻, CO₃²⁻, and HCO₃⁻) slightly inhibited the degradation of OTC. Meanwhile, humic acid and fulvic acid strongly inhibited the removal of OTC. In a natural water matrix, OTC degradation was slowed down compared with that in ultrapure water. Ultra-high-performance liquid chromatography time-of-flight mass spectrometry yielded five products of OTC degradation. The degradation pathways were primarily decarbonylation, dehydration, hydroxylation, and secondary alcohol oxidation.

Keywords: Degradation; Kinetics; Mechanism; Oxytetracycline; UV/peroxydisulfate

1. Introduction

Over the past few decades, oxytetracycline (OTC), a type of tetracycline antibiotic, has been widely used in aquaculture and livestock breeding owing to its effect on growth promoters and bactericides for the prevention and treatment of diseases [1]. In fact, it was reported that high levels of OTC were commonly detected in different waters around the world [2], which may cause resistance in bacterial populations, promote the production of antibiotic-resistant genes, and, ultimately, pose a threat to human health [3].

Up to now, an increasing amount of attention has been paid to the removal of OTC from the water environment. OTC can undergo photodegradation, hydrolysis, and microbial degradation. In previous studies, several technologies were used to remove OTC, such as adsorption [4], photo-Fenton oxidation [5], O₃ oxidation [6], UV/H₂O₂ [7], and photocatalysis [8].

UV-activated peroxydisulfate (PDS) has emerged as a promising technology for the degradation of various organic pollutants in the water environment [9]. A series of studies have shown that UV/PDS was superior to UV/

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H_2O_2 in the degradation of several antibiotics, for example, sulfonamide antibiotics [10] and cylindrospermopsin [11]. Although significant progress had been made in the degradation of antibiotics by UV/PDS [12], a full understanding of the degradation of OTC by UV/PDS has remained lacking. Recently, Liu et al. [13] reported the degradation of OTC by UV/PDS; however, high concentrations of both OTC and PDS were used. Thus, the experiment was neither quite environmentally relevant nor cost-effective.

In this study, the degradation kinetics of OTC by UV/PDS was reported, and the effects of PDS dosage, pH value, and the existence of humic acid, fulvic acid, and major inorganic ions (NO_3^- , Cl^- , CO_3^{2-} and HCO_3^-) were inspected. Furthermore, the photoproducts of OTC were determined, and possible removal schemes were proposed. The results can provide fundamental information on the practical application of the removal of OTC by UV/PDS technology.

2. Experimental setup

2.1. Reagents

Oxytetracycline hydrochloride was purchased from Hefei Bomei Biotechnology Co., Ltd., China. Acetic acid and sodium chloride (analytical grade) were supplied by Beijing Chemical Plant, China. Humic acid (HA) and fulvic acid (FA) were separately obtained from Aldrich, US and Shanghai Future Industrial Co., Ltd., China. Acetonitrile and methanol of a suitable grade for high-performance liquid chromatography (HPLC) were obtained from Tedia Chemicals, US. Ultra-pure water ($>18.2 \text{ M}\Omega \text{ cm}$) was obtained by a 1820A Ultra-pure Water System (Molecular Water System Co., Chongqing, China).

2.2. UV/PDS degradation experiments

A typical experiment could be described as follows: 500 mL of a mixed solution of OTC and PDS was transferred into a self-made cylinder reactor. In the center of the reactor, an 11 W low-pressure mercury lamp (Institution of Light Source, Beijing, China) was set as the UV source (main emitting wavelength was 254 nm). At the bottom of the reactor, a magnetic stirring device was equipped to ensure that the solution was mixed well. As reported in our previous study [14], the UV-fluence was 2.12 mW cm^{-2} , and the effective path length of the reactor was 1.9 cm.

All experiments were carried out at room temperature (20°C). For degradation experiments, the initial concentration of OTC and PDS were 5 and $100 \mu\text{M}$, respectively, unless noted otherwise. The degradation reaction of OTC last for 5 min, and at every minute, the irradiated solution (0.5 mL) was taken immediately for concentration analysis.

2.3. Analysis of OTC and its degradation intermediates

The concentration of OTC was quantified by an Agilent 1200 Series HPLC system equipped with a variable wavelength detector. A C18 symmetry column ($4.6 \times 150 \text{ mm}$, $5 \mu\text{m}$, Waters, US) was utilized as a stationary phase, while the mobile phase was acetonitrile and 0.01 M oxalic acid solution (10/90). The analysis was performed at a flow rate

of 1.0 mL min^{-1} , with a detection wavelength of 357 nm, a column temperature of 30°C , and a sample injection volume of $20 \mu\text{L}$.

For the reaction products, an investigation by ultra-high-performance liquid chromatography time-of-flight mass spectrometry (UPLC/TOF-MS) was performed in which a mixture of $50 \mu\text{M}$ OTC and 0.5 mM PDS was irradiated for 10 min. Detailed analytical methods used were the same as found in the literature [15].

For the mineralization experiments, the mixed solution of OTC and PDS was irradiated for a certain time, and total organic carbon (TOC) was immediately analyzed by a TOC-VCPH analyzer (Shimadzu, Japan). To determine the pH, a PHSJ-5 pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., China) was used. All experiments were carried out in triplicate, and the mean value was reported.

3. Results and discussion

3.1. Effect of PDS dosage

Fig. 1 shows the degradation of OTC with different PDS dosages. It should be mentioned that before UV irradiation, when PDS ($5\text{--}100 \mu\text{M}$) was added into the OTC solution, the loss of OTC was $0.89\%\text{--}4.24\%$, which was subtracted from the initial concentration of OTC. As shown in Fig. 1, the degradation of OTC was promoted with the presence of PDS, and the promotion effect was enhanced with increasing concentration of PDS from 5 to $100 \mu\text{M}$. This was because $\text{SO}_4^{\bullet-}$ can be formed during the activation of PDS by UV irradiation. With the increase in PDS dosage, the amount of $\text{SO}_4^{\bullet-}$ increased; thus, the promotion effect on OTC degradation was more pronounced.

Table 1 shows the kinetics parameters of the degradation of OTC by UV/PDS. All the degradation processes of OTC by UV/PDS are shown to follow the pseudo-first-order kinetics law. Evidently, the higher the dosage of PDS is, the faster the degradation of OTC is. When OTC was $5 \mu\text{M}$ and PDS was $100 \mu\text{M}$, the pseudo-first-order rate constant (k) was 0.6017 min^{-1} ($0.0049 \text{ cm}^2 \text{ mJ}^{-1}$), a value lower than that found in previous studies. Liu et al. [13] found a value for k of $0.0273 \text{ cm}^2 \text{ mJ}^{-1}$ for the UV/PDS degradation of OTC,

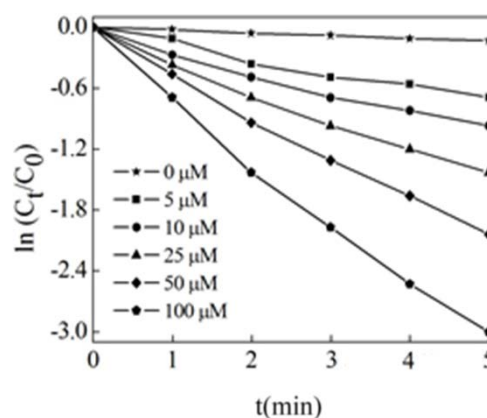


Fig. 1. Effect of the initial concentration of PDS on the degradation of OTC by UV/PDS, $[\text{OTC}]_0 = 5 \mu\text{M}$.

Table 1
Kinetics parameters of degradation of OTC by UV/PDS

Concentration of PDS (μM)	k ($\text{cm}^2 \text{mJ}^{-1}$)	k (min^{-1})	R^2
0	0.0002	0.0269	0.9913
5	0.0011	0.1409	0.9713
10	0.0015	0.1914	0.9824
25	0.0022	0.2834	0.9903
50	0.0032	0.4049	0.9958
100	0.0049	0.6017	0.9933

owing to the high ratio of PDS to OTC (100:1), whereas our ratio was only 20:1. To obtain better treatment efficiency, we chose 100 μM PDS and 5 μM OTC for the following experiments.

3.2. Influence of pH value

Fig. 2 shows the effect of the pH value on the degradation of OTC. The initial pH value of a mixed solution of OTC (5 μM) and PDS (100 μM) was 6.30, and the pH value of the reaction solution was adjusted by sulfuric acid and sodium hydroxide. In comparison with the degradation of OTC under near-neutral conditions (pH = 6.30), the OTC degradation under both acidic (pH = 3.98) and alkaline (pH = 10.13) conditions was inhibited, with a stronger inhibition effect under alkaline conditions. Liu et al. [13] also reported that the pseudo-first-order rate constant of OTC degradation by UV/PDS was the highest under near-neutral conditions (pH 5.5–8.5) and decreased with either a decrease or increase in pH in the range of pH values (~3–11), which was in accordance with our results.

Previous studies also indicated that under acidic conditions, $\text{SO}_4^{\cdot-}$ was the main oxidizer [9]. However, under acidic conditions, $\text{SO}_4^{\cdot-}$ can undergo self-quenching to form a weakly oxidizing species $\text{S}_2\text{O}_8^{2-}$ (Eq. (1)) [13], thereby inhibiting the degradation of OTC. Under alkaline conditions, $\cdot\text{OH}$ was the main oxidizing species; however, it may have been scavenged by $\text{SO}_4^{\cdot-}$, forming a weakly oxidizing species HSO_4^- (Eq. (2)) [13] and, thus, inhibiting the degradation of OTC as well.

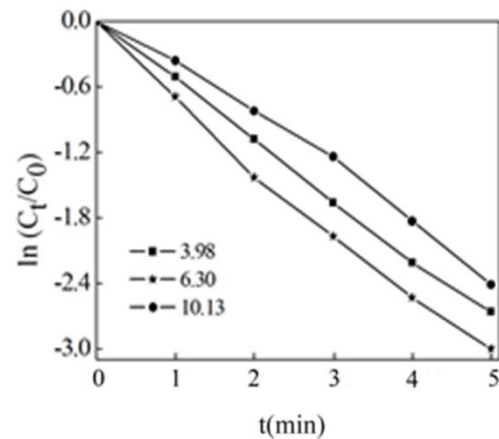
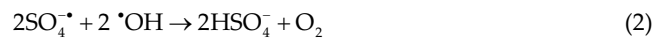


Fig. 2. Effect of pH on the degradation of OTC by UV/PDS, $[\text{OTC}]_0 = 5 \mu\text{M}$, $[\text{PDS}]_0 = 100 \mu\text{M}$.



3.3. Effect of humic acid and fulvic acid

Dissolved organic matter (DOM) was ubiquitously present in the natural aquatic environment and may affect the effectiveness of UV/PDS technology through radical-scavenging and UV-filtering [16]. Fig. 3 shows the effects of HA and FA on the degradation of OTC by UV/PDS. Both HA and FA inhibited the degradation of OTC, and with increasing concentrations of both HA and FA, the reduction effect was enhanced. This could be explained by the fact that both HA and FA could absorb UV light, decreasing the UV irradiation available for OTC. This further reduces the generation of reactive $\text{SO}_4^{\cdot-}$ and inhibits the degradation of OTC. In addition, OTC could also compete for reactive radicals ($\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$) with HA and FA, decreasing the degradation rate of OTC. Liu et al. [13] also observed the inhibition effect of HA and FA (3 mg DOC L^{-1}) on the UV/PDS degradation of OTC.

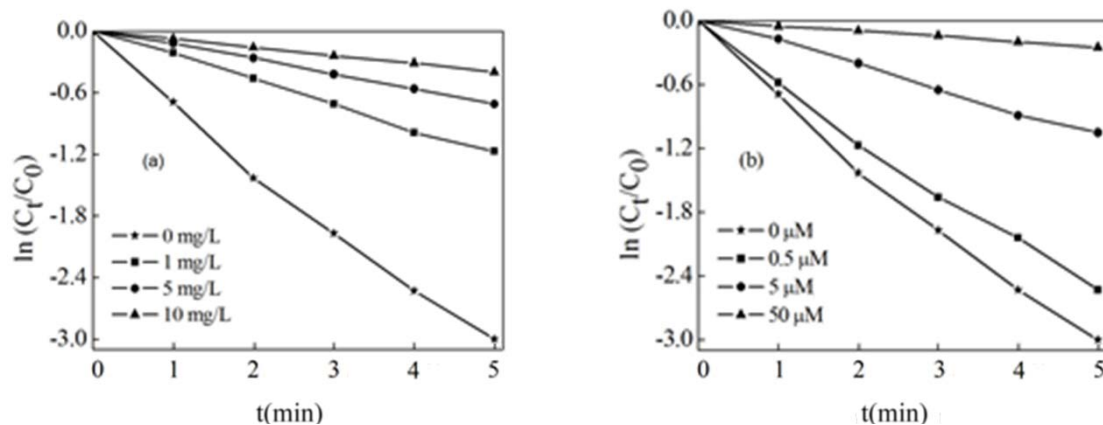


Fig. 3. (a) Effect of HA and (b) FA on the degradation of OTC by UV/PDS, $[\text{OTC}]_0 = 5 \mu\text{M}$, $[\text{PDS}]_0 = 100 \mu\text{M}$.

3.4. Effect of inorganic ions

NO_3^- , Cl^- , CO_3^{2-} and HCO_3^- were common components of the natural aquatic environment, as they can scavenge either $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ to form new radicals [17] or alter the pH value of the solution. Fig. 4 shows the effect of these anions on the degradation of OTC. It was evident that Cl^- promoted the degradation of OTC, whereas other anions (NO_3^- , CO_3^{2-} and HCO_3^-) weakly inhibited the degradation of OTC. However, neither the promotion nor inhibition effects were significant. After irradiation for 5 min, more than 90% OTC was removed, both with and without the presence of anions.

3.5. Effect of natural waters

The practical application of UV/PDS in the degradation of OTC was tested by using surface water (SW) sampled from the Nierji Reservoir, which is located in Nierji Town, an autonomous county of Molidawa Daur Nationality in Inner Mongolia Autonomous Region, China. As shown in Fig. 5, the performance of UV/PDS was significantly inhibited by using natural water as compared with using ultrapure water. This was because the reaction solution prepared with SW was slightly alkaline (pH = 7.55), whereas the alkaline condition does not facilitate the degradation of OTC (Fig. 2). Furthermore, SW exhibited strong radical scavenging effects owing to the existence of DOM and inorganic ions; thus, the degradation of OTC was slowed down. In contrast, the comparable or promising removal efficiency was observed in several river or lake waters during the degradation of OTC by UV/PDS, and the significant contribution of carbonate radical was proposed [18].

3.6. Degradation mechanism

In the UV/PDS system, 5 μM OTC and 100 μM PDS solution were irradiated for 5 min, and the pH decreased from 6.30 to 4.67 ($\Delta\text{pH} = -1.63$). The TOC removal rate was 4.38% after 5 min irradiation. Meanwhile, the OTC degradation rate reached 95.10% after 5 min degradation by UV/PDS, which means that only a small portion of OTC was decomposed

into inorganic carbon, and intermediates were produced. Liu et al. [13] also observed a rather low TOC removal rate (6.5%) after 3 h degradation of OTC (10 μM) by UV/PDS (1 mM). Similarly, a relatively low TOC removal rate (9.5%) after 10 h degradation of OTC (10 μM) by UV/ H_2O_2 (500 μM) was observed [6], which suggests that OTC is difficult to mineralize.

To obtain more information on the products, high concentrations of OTC (50 μM) and PDS (0.5 mM) were used, and the irradiation time was prolonged to 10 min. Finally, five products were detected by UPLC/TOF-MS, and the specific information regarding intermediates is displayed in Table 2.

Based on the molecular structure of OTC and the properties of the UV/PDS system, the possible degradation pathways of OTC in the UV/PDS system were proposed (Fig. 6).

As seen in Fig. 6, the degradation of OTC in the UV/PDS system formed intermediate m/z 433 by decarbonylation reaction. Further dehydration of m/z 433 formed product m/z 415. Finally, through the secondary oxidation reaction, product m/z 413 was produced, while the hydroxylation of intermediate m/z 433 formed m/z 449. Meanwhile, OTC underwent secondary alcohol oxidation forming intermediate m/z 459, and the hydroxylation of m/z 459 led to the formation of product m/z 475.

During the UV/ H_2O_2 degradation of OTC, these four products (m/z 413, m/z 415, m/z 449, and m/z 475) were also obtained [7], which was in accordance with our results. Products m/z 415 and m/z 449 were also reported during the degradation of OTC by UV/PDS [13]. Meanwhile, in addition to m/z 415 and m/z 449, the formation of m/z 475 was also reported during the degradation of OTC by UV/ H_2O_2 and UV/PDS system with the presence of carbonate, owing to the reaction with carbonate radical [18]. Li et al. [8] also observed the formation of m/z 415 during the photocatalytic degradation of OTC by $\text{Fe}_2\text{O}_3\text{-TiO}_2$. Product m/z 449 was also reported as the microbial degradation product of OTC by *Pseudomonas* [19], and both m/z 415 and m/z 449 were found during the photocatalytic degradation of OTC by multi-walled carbon nanotube/ BiVO_4 [20].

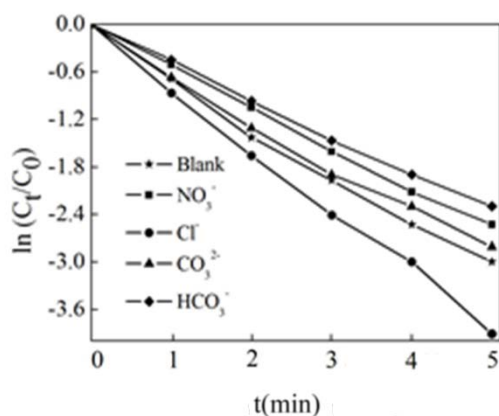


Fig. 4. Effect of inorganic anions on the degradation of OTC by UV/PDS, $[\text{OTC}]_0 = 5 \mu\text{M}$, $[\text{PDS}]_0 = 100 \mu\text{M}$, $[\text{NO}_3^-]_0 = [\text{Cl}^-]_0 = [\text{CO}_3^{2-}]_0 = [\text{HCO}_3^-]_0 = 5 \mu\text{M}$.

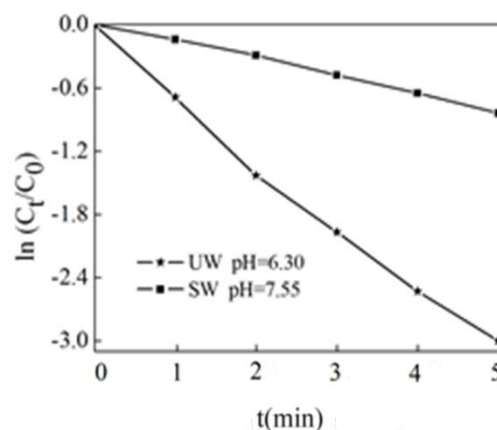


Fig. 5. Effect of water quality on the degradation of OTC by UV/PDS, $[\text{OTC}]_0 = 5 \mu\text{M}$, $[\text{PDS}]_0 = 100 \mu\text{M}$.

Table 2

Intermediates formed in UV/PDS degradation of OTC identified by UPLC/TOF-MS, [OTC]₀ = 50 μM, [PDS]₀ = 0.5 mM, irradiation for 10 min

m/z	Retention time (min)	Molecular formula	Difference with OTC	Reaction pathways
274	9.860	C ₁₈ H ₂₄ O ₂	-4C 2N 7O	Deep oxidation
413	20.399	C ₂₁ H ₂₀ N ₂ O ₇	-C 4H 2O	Dehydration
415	5.389	C ₂₁ H ₂₂ N ₂ O ₇	-C 2H 2O	Dehydration, decarbonylation
449	1.619	C ₂₁ H ₂₄ N ₂ O ₉	-3C	Decarbonylation
475	5.260	C ₂₂ H ₂₂ N ₂ O ₁₀	-2C 2H +O	Secondary alcohol oxidation

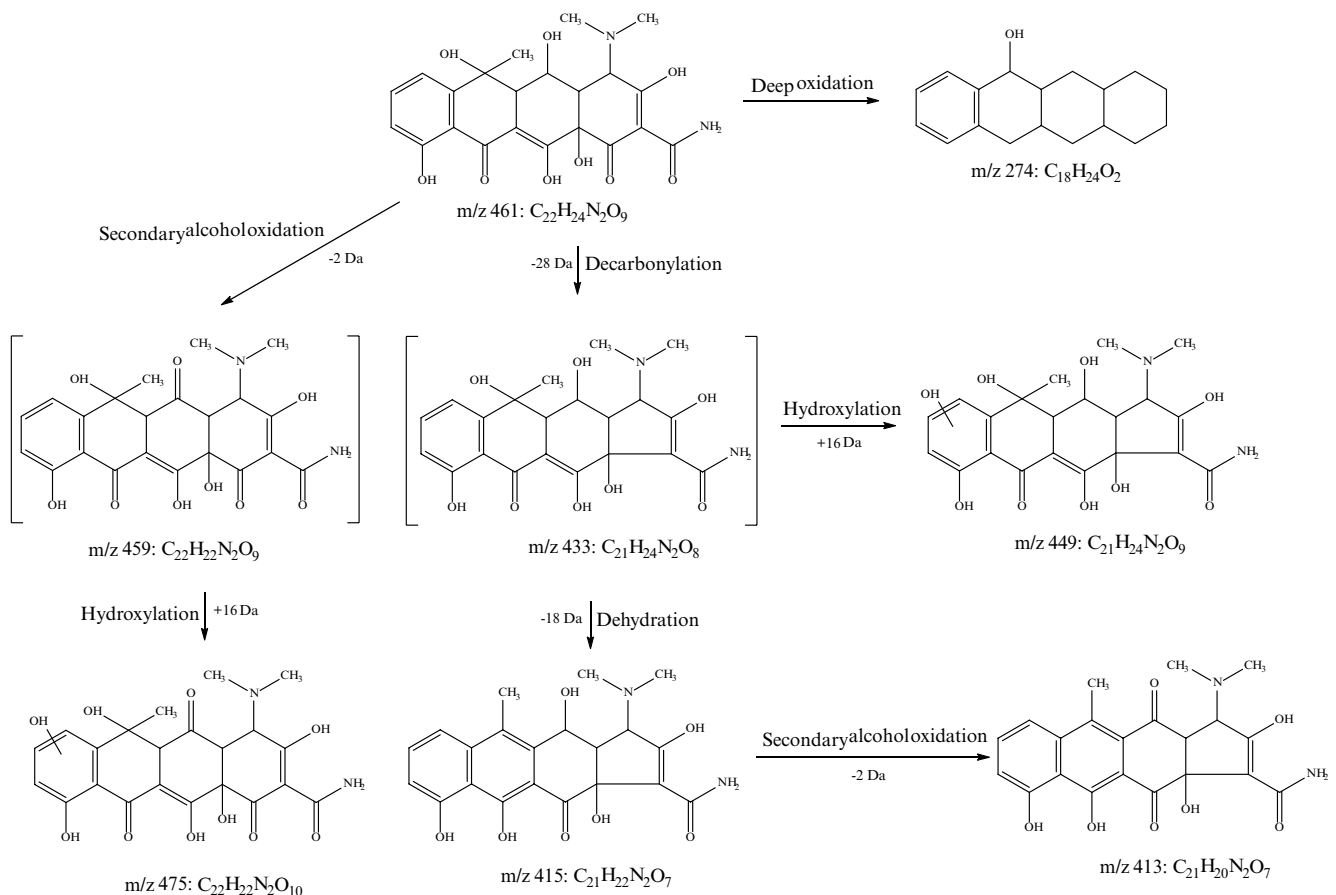


Fig. 6. Proposed degradation mechanisms for OTC in the UV/PDS system, [OTC]₀ = 50 μM, [PDS]₀ = 0.5 mM, irradiation for 10 min.

In addition, the product m/z 274 was formed from deep oxidation by UV/PDS, which was also observed during the photocatalytic degradation of OTC by Ti-MCM-41 [21].

4. Conclusions

OTC could be degraded by UV/PDS, and its degradation rate increased with an increase in PDS dosage. The degradation process of OTC was consistent with the quasi-first-order reaction kinetics model. Neither acidic nor basic pH conditions were conducive to the degradation of OTC, whereas alkaline conditions had a more pronounced inhibitory effect on the degradation of OTC. The existence of Cl⁻ promoted

the degradation of OTC, whereas other inorganic ions (NO₃⁻, CO₃²⁻ and HCO₃⁻) slightly inhibited the degradation of OTC. Meanwhile, HA and FA strongly inhibited the removal of OTC. The degradation of OTC in natural water was faster than that in ultrapure water. OTC underwent decarbonylation, dehydration, hydroxylation, and secondary alcohol oxidation, ultimately generating five products, namely, m/z 274, m/z 413, m/z 415, m/z 449, and m/z 475.

Acknowledgment

The work was funded by the Second Tibetan Plateau Scientific Expedition and Research Program (STEP,

2019QZKK0608), Department of Science and Technology of Jilin Province China (20190303092SF), and China Scholarship Council.

References

- [1] Z.-J. Li, W.-N. Qi, Y. Feng, Y.-W. Liu, E. Shehata, J. Long, Degradation mechanisms of oxytetracycline in the environment, *J. Integr. Agric.*, 18 (2019) 1953–1960.
- [2] E. Martínez-Carballo, C. González-Barreiro, S. Scharf, O. Gans, Environmental monitoring study of selected veterinary antibiotics in animal manure and soils in Austria, *Environ. Pollut.*, 148 (2007) 570–579.
- [3] Y. Xu, C.S. Guo, Y. Luo, J.P. Lv, Y. Zhang, H.X. Lin, L. Wang, J. Xu, Occurrence and distribution of antibiotics, antibiotic resistance genes in the urban rivers in Beijing, China, *Environ. Pollut.*, 213 (2016) 833–840.
- [4] P. Oleszczuk, B. Pan, B.S. Xing, Adsorption and desorption of oxytetracycline and carbamazepine by multiwalled carbon nanotubes, *Environ. Sci. Technol.*, 43 (2009) 9167–9173.
- [5] J.H.O.S. Pereira, D.B. Queirós, A.C. Reis, O.C. Nunes, M.T. Borges, R.A.R. Boaventura, V.J.P. Vilara, Process enhancement at near neutral pH of a homogeneous photo-Fenton reaction using ferric-carboxylate complexes: application to oxytetracycline degradation, *Chem. Eng. J.*, 253 (2014) 217–228.
- [6] N.B. Oncu, I.A. Balcioglu, Degradation of ciprofloxacin and oxytetracycline antibiotics in waste sewage sludge by ozonation, *J. Adv. Oxid. Technol.*, 16 (2013) 107–116.
- [7] Y.Q. Liu, X.X. He, Y.S. Fu, D.D. Dionysiou, Degradation kinetics and mechanism of oxytetracycline by hydroxyl radical-based advanced oxidation processes, *Chem. Eng. J.*, 284 (2016) 1317–1327.
- [8] R. Li, Y.F. Jia, J. Wu, Q. Zhen, Photocatalytic degradation and pathway of oxytetracycline in aqueous solution by Fe₂O₃-TiO₂ nanopowder, *RSC Adv.*, 5 (2015) 40764–40771.
- [9] L.W. Matzek, K.E. Carter, Activated persulfate for organic chemical degradation: a review, *Chemosphere*, 151 (2016) 178–188.
- [10] R.C. Zhang, Y.K. Yang, C.-H. Huang, L. Zhao, P.Z. Sun, Kinetics and modeling of sulfonamide antibiotic degradation in wastewater and human urine by UV/H₂O₂ and UV/PDS, *Water Res.*, 103 (2016) 283–292.
- [11] X.X. He, A.A. de la Cruz, K.E. O’Shea, D.D. Dionysiou, Kinetics and mechanisms of cytolindoperoxidase destruction by sulfate radical-based advanced oxidation processes, *Water Res.*, 63 (2014) 168–178.
- [12] S. Waclawek, H.V. Lutze, K. Gröbel, V.V.T. Padil, M. Černík, D.D. Dionysiou, Chemistry of persulfates in water and wastewater treatment: a review, *Chem. Eng. J.*, 330 (2017) 44–62.
- [13] Y.Q. Liu, X.X. He, Y.S. Fu, D.D. Dionysiou, Kinetics and mechanism investigation on the destruction of oxytetracycline by UV-254 nm activation of persulfate, *J. Hazard. Mater.*, 305 (2016) 229–239.
- [14] H. Xue, C. Hu, J. Peng, L. Wang, Y. Wang, N. Ji, X. Wen, Degradation of ofloxacin in aqueous solution with UV/H₂O₂, *Desal. Water Treat.*, 72 (2017) 386–393.
- [15] H.H. Xue, S.Y. Gao, N. Zheng, M. Li, X. Wen, X.D. Wei, Degradation of norfloxacin in aqueous solution with UV/peroxydisulfate, *Water Sci. Technol.*, 79 (2019) 2387–2394.
- [16] Q.F. Wang, Y.S. Shao, N.Y. Gao, W.H. Chu, X. Shen, X. Lu, J.X. Chen, Y.P. Zhu, Degradation kinetics and mechanism of 2,4-di-tert-butylphenol with UV/persulfate, *Chem. Eng. J.*, 304 (2016) 201–208.
- [17] Y.Y. Fu, G. Wu, J.J. Geng, J.C. Li, S.N. Li, H.Q. Ren, Kinetics and modeling of artificial sweeteners degradation in wastewater by the UV/persulfate process, *Water Res.*, 150 (2019) 12–20.
- [18] Y.Q. Liu, X.X. He, X.D. Duan, Y.S. Fu, D. Fatta-Kassinos, D.D. Dionysiou, Significant role of UV and carbonate radical on the degradation of oxytetracycline in UV-AOPs: kinetics and mechanism, *Water Res.*, 95 (2016) 195–204.
- [19] W.N. Qi, J. Long, C.Q. Feng, Y. Feng, D.M. Cheng, Y.W. Liu, J.M. Xue, Z.J. Li, Fe³⁺ enhanced degradation of oxytetracycline in water by *Pseudomonas*, *Water Res.*, 160 (2019) 361–370.
- [20] S.J. Ye, X. Zhou, Y.B. Xu, W.K. Lai, K. Yan, L. Huang, J.Y. Ling, L. Zheng, Photocatalytic performance of multi-walled carbon nanotube/BiVO₄ synthesized by electro-spinning process and its degradation mechanisms on oxytetracycline, *Chem. Eng. J.*, 373 (2019) 880–890.
- [21] H.L. Chen, Y.-P. Peng, K.-F. Chen, C.-H. Lai, Y.-C. Lin, Rapid synthesis of Ti-MCM-41 by microwave-assisted hydrothermal method towards photocatalytic degradation of oxytetracycline, *J. Environ. Sci.*, 44 (2016) 76–87.