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Degradation of ofloxacin in water by combination of simulated solar light and persulfate

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ABSTRACT

The utilization of solar energy is an environmentally friendly and cost-effective way of removing pharmaceuticals in water. In this work, the influence of solution pH and water matrix on ofloxacin (OFX) degradation with stimulated solar/persulfate (PS) was studied, and the mechanism of OFX degradation was also explored. The result showed that the combination of PS and solar led to a significant synergistic effect for OFX degradation. The degradation curves can be well fitted by the pseudo-first-order model, and the calculated reaction rate constants decreased from 0.9704 to 0.0909 min^{-1} with increasing solution pH from 4 to 10. The rate constants at pH 4–8 (0.6916–0.9704 min^{-1}) are much higher than those of many reported PS activation processes. Moreover, ubiquitous inorganic ions had little effect on OFX degradation, indicating the potential application of this process. The degradation of OFX did not follow a radical mechanism because PS was hardly activated by solar irradiation and the formed radicals were very limited. In comparison with PS, OFX can be activated by solar irradiation more readily. Although PS can hardly react with OFX, it can oxidize the photoactivated OFX readily. Therefore, OFX could be effectively degraded by the combination of PS and solar.

Keywords: Ofloxacin; Persulfate; Solar; Photoexcited; Degradation

1. Introduction

Water pollution with pharmaceuticals has received increasing attention in recent years due to their detrimental effect on the environment and human health. Ofloxacin (OFX) is a widely used fluoroquinolone antimicrobial for treating respiratory diseases and bacterial infections [1,2]. Because it cannot be effectively removed by traditional wastewater treatment technologies, it is frequently detected in wastewater and surface water [3–5]. Therefore, it is highly desired to develop effective technology for removing OFX in wastewater.

Up to now, various advanced oxidation processes (AOPs) have been explored in the treatment of refractory pharmaceuticals pollutants in water [6–10]. Among them, persulfate (PS) based AOPs showed superior performance for removing pharmaceuticals due to their wide pH wording range and high selectivity towards pharmaceuticals. PS is a strong oxidant with a redox potential of 2.01 V. It can be activated by various methods, such as base, heat, electrochemistry, UV irradiation, transition metal ion, and solid catalyst [10–12]. It has been reported that various reactive oxygen species including sulfate radical ($^{\bullet}SO_4^{-}$), hydroxyl radical ($^{\bullet}OH$), superoxide radicals ($^{\bullet}O_2^{-}$), singlet oxygen ($^1O_2$) and activated PS can be produced in the PS activation process, leading to the high removal efficiency of organic pollutants. Since pharmaceuticals usually have strong absorption in the UV region and PS can be

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decomposed into $^{\bullet}SO_4^-$ by UV irradiation, UV/PS may lead to a combination of photolysis and radical oxidation, which can remove organic pollutants more efficiently. Moreover, this process does not require the addition of chemical reagents except for PS. However, the operation of the UV/PS process requires UV light devices and has high energy consumption and operational costs, which limits its practical application in water treatment.

Solar energy is a low cost and readily available renewable energy source. The utilization of solar for PS activation could significantly reduce the operational costs. Although PS shows the strongest absorption band below 250 nm, it can also be excited by light with a wavelength of 248–351 nm [13]. Thus PS can be activated by solar irradiation. In addition, solar irradiation can directly lead to the degradation of some organic pollutants to CO_2, H_2O and other intermediates. Photolysis has been demonstrated to be one of the most important pathways for the elimination of pharmaceuticals in natural water [14–16]. Solar activated PS was found to be effective for the inactivation of *E. coli* and *E. faecalis* in both isotonic water and synthetic urban wastewater [17]. Lin et al. [18] reported that the addition of PS could promote the degradation of sulfamethoxazole by a sunlight-focusing and solar tracking system. The results suggest that solar/PS might be a promising technology for removing pharmaceuticals in water. However, previous studies focused on the solar/PS process with the assistance of homogeneous or heterogeneous catalysts [19–23]. To the best of our knowledge, the performance of solar/PS without catalyst has been rarely investigated.

In this work, solar/PS was found to be superior to many PS activation processes for removing OFX in water. Moreover, the reactive species generated from PS activation were not responsible for OFX degradation. The result is quite different from the previously reported PS processes. Hence, the influence of solution pH, PS concentration and water matrix on OFX degradation was further studied. The main active species in this process and the degradation products of OFX were identified. Accordingly, the possible mechanism for OFX degradation with solar/PS can be revealed, which can provide useful information for treating this pollutant.

2. Experimental setup

2.1. Degradation of OFX by simulated solar light and PS

OFX (10 mg L^{-1}) and PS were dissolved in 100 mL deionized water in a 200 mL glass beaker (internal diameter 5.3 cm) covered with foil. The solution pH was adjusted by diluted H_2SO_4 and NaOH solutions. A 300 W Xe lamp (PLS-SXE300c, Perfect light) equipped with an AM 1.5 G filter (200 W cm^{-2}) was used as a simulated solar source and placed above the glass beaker. The emission spectrum of the Xe lamp equipped with the filter was presented in Fig. S1. The reaction was started by turning on the lamp. This solution was magnetically stirred and maintained at room temperature (22°C ± 2°C) by circulating water throughout this reaction. Samples were withdrawn at a different time and the reaction was quenched by adding a drop of 0.1 M sodium thiosulfate solution.

2.2. Analytical methods

The concentration of OFX was determined by high-performance liquid chromatography (HPLC, Agilent 1200, USA) equipped with a ZORBAX Eclipse XDB-C18 column (150 mm × 4.6 mm). The wavelength, flow rate and column temperature were 30°C, 1 mL min^{-1} and 294 nm, respectively. Formic acid aqueous solution and acetonitrile with a volume ratio of 75:25 were used as the mobile phase. The degradation products of OFX after reaction for 1, 3 and 15 min were analyzed by a 3200 Q TRAP liquid chromatography–mass spectrometer (LC-MS, AB SCIEX, USA). Formic acid aqueous solution and acetonitrile with a volume ratio of 65:35 were used as the mobile phase. The flow rate was 0.3 mL min^{-1}. MS analysis was performed from 50 to 500 m/z in the positive and negative ion modes. The mineralization efficiency of OFX was determined by a Phoenix 8000 (Tekmar-Dohrmann, USA) total organic carbon (TOC) analyzer. The concentration of PS was determined by the reported iodometric titration method through the reaction of PS with KI [24]. This experiment was carried out with a UV-vis spectrophotometer (UV-7504). The toxicity assessment was performed by the luminescent bacteria test using *Vibrio qinghaiensis*. The freeze-dried powder of *Vibrio qinghaiensis* was incubated and dispersed in the culture solution. The resultant solution was mixed with the OFX solution treated by solar/PS for different reaction times and then was determined by an ET1500 toxicity analyzer (Euro-Tech, China).

Electron paramagnetic resonance (EPR) measurements were carried out with a MS-5000 spectrometer (Magnettech, Germany). The generated $^{\bullet}SO_4^-$, $^{\bullet}OH$ and $^{\bullet}O_2^-$ were identified using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the probe. Different from SO_4^- and $^{\bullet}OH$ in aqueous solution, the determination of $^{\bullet}O_2^-$ was carried out in a methanol/water (9:1) mixed solution so that the generated SO_4^- and $^{\bullet}OH$ can be quenched and their interference can be eliminated. While $^1O_2$ was determined in aqueous solution using 2,2,6,6-tetramethyl-4-piperidone (TEMP) as the probe.

3. Results and discussion

3.1. Degradation of OFX by simulated solar light and PS

Fig. 1 shows the degradation of OFX with different concentrations of PS under-simulated solar irradiation. The photolysis of OFX in the absence of PS was very slow, and the degradation efficiency at 15 min was only 6.1%. The addition of PS significantly accelerated the degradation of OFX. About 98.1% of OFX was degraded by 0.1 mmol L^{-1} PS at 10 min, and the degradation efficiency increased with increasing PS concentration. This can be ascribed to that a higher PS concentration might lead to the formation of more active species for OFX degradation. The photolysis of OFX should be attributed to the UV irradiation. The degradation of OFX by the Xe lamp equipped with a UV cutoff filter ($\lambda \geq 420$ nm) was also examined, and no degradation was observed. The UV-Vis absorption spectrum of the OFX solution was measured and presented in Fig. 2. The adsorption band was below 400 nm and the peak centered at about 294 nm, indicating that OFX cannot adsorb visible light. The result further demonstrates that the photolysis of OFX was caused by UV irradiation. In addition, although PS is a

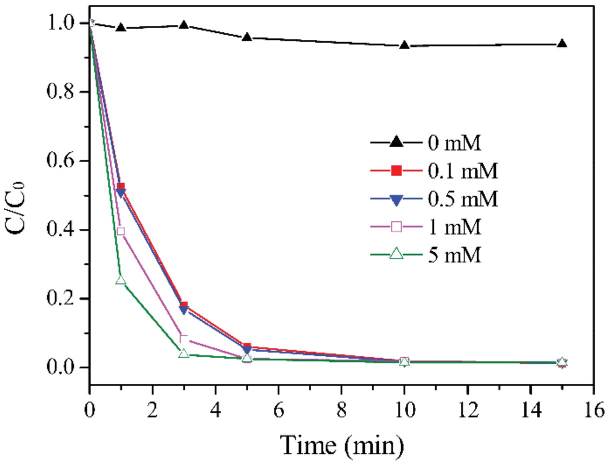

Fig. 1. Effect of PS concentration on OFX degradation in the solar/PS system (OFX 10 mg L^{-1}; pH 8).

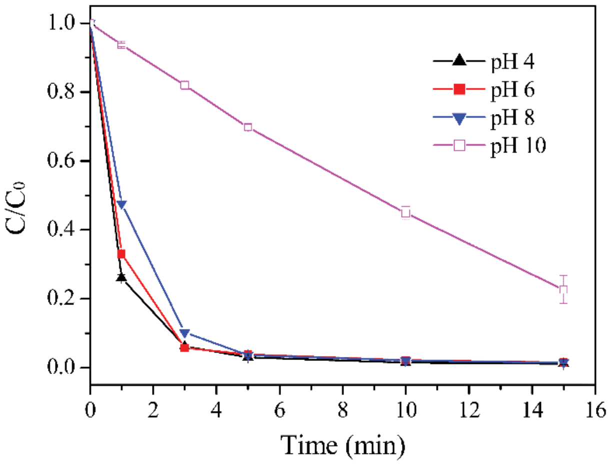

Fig. 3. Degradation of OFX by stimulated solar/PS at different initial pH (OFX 10 mg L^{-1}; PS 1 mmol L^{-1}).

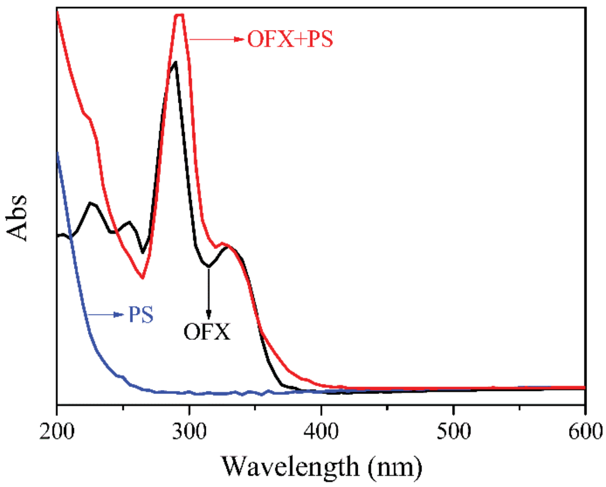

Fig. 2. UV-Vis spectrum of OFX, PS and OFX + PS solution.

strong oxidant, it hardly oxidized OFX. Only 2.2% of OFX was degraded at 15 min by PS without irradiation. It can be seen that the combination of PS and solar led to a significant synergistic effect for OFX degradation.

The solution pH is an important parameter affecting the degradation of organic pollutants in water. As shown in Fig. 3, the degradation efficiency of OFX decreased with increasing solution pH. Especially at pH 10, the degradation efficiency significantly decreased to 77.3% after a reaction time of 15 min. The degradation curves at different pH can be fitted by the pseudo-first-order model with the correlation coefficients of 0.9593–0.9952. The reaction rate constant at pH 10 was calculated to be 0.0909 min^{-1}, much lower than those at pH 4–8 (0.6916–0.9704 min^{-1}). The result indicates that stimulated solar/PS is effective for OFX degradation at acidic and neutral conditions. The reaction rate constants at pH 4–8 are far higher than many reported processes for OFX degradation, such as Fe_3O_4/MMT/PS (0.038 min^{-1}), UV/PS (0.1089 min^{-1}) $LaNiO_3$/PMS (0.239 min^{-1}), $LaMnO_3$/PMS (0.088 min^{-1}), bio-$FeMnO_x$/photo-Fenton (0.0341 min^{-1}), Cu-Ce-TC/PS/heat (0.0757 min^{-1}), Fe_3O_4@FeOOH/PS (9.04 h^{-1}) and CuFe/PS (0.140 min^{-1}) [25–32].

The different degradation efficiencies of OFX at different pH might be associated with the state of OFX and PS. According to the literature [33], OFX is an amphoteric antibacterial compound that has three forms at different pH due to its zwitterionic functional group. At pH < 6, it is cationic due to the protonation of its piperazine ring. At pH > 8, it is anionic due to the deprotonation of its carboxyl group. At neutral pH, it exists in the zwitterionic form. Therefore, the pH of the solution could affect the speciation of OFX. As reported in the literature [34], the apparent second-order rate constant of sulfamethoxazole with $^{\bullet}SO_4^-$ increased with increasing pH, which can be ascribed to that $^{\bullet}SO_4^-$ has high reactivity towards the anionic form of sulfamethoxazole because of its electrophilic nature. The result obtained in our work is quite different from the above literature, suggesting that $^{\bullet}SO_4^-$ might not be the dominant reactive species for OFX degradation. A previous study reported that the highest degradation efficiency of OFX was achieved at pH 7 by UV/PS [35]. The reason is that the piperazine ring of OFX has a relatively higher electron cloud density at this pH and was susceptible to electrophilic attack. In this work, the degradation efficiencies of OFX increased with decreasing pH, indicating that the cationic form of OFX might be readily oxidized by the reactive species.

It is well-known $^{\bullet}SO_4^-$ could react with OH^- to form $^{\bullet}OH$. The increasing pH would promote this reaction. It was reported that that the conversion of $^{\bullet}SO_4^-$ to $^{\bullet}OH$ occurred at pH > 9 and $^{\bullet}OH$ would become the predominant radical at pH 11 [36]. In addition, the redox potential of oxidants including radicals and PS will decrease with the increase of pH. Therefore, the degradation efficiency of OFX decreased with increasing solution pH.

3.2. Mechanism for OFX degradation by simulated solar light and PS

It is generally believed that $^{\bullet}SO_4^-$ is the dominant reactive species in UV/PS process because PS can be effectively decomposed into $^{\bullet}SO_4^-$ by UV irradiation. $^{\bullet}OH$ can be generated via the reaction of $^{\bullet}SO_4^-$ with H_2O/OH^-. In addition, $^{\bullet}O_2^-$ and $^1O_2$ are frequently detected in the photoreactions for organic pollutants removal. Therefore, the reactive species in this solar/PS process was studied using scavenging experiments. Ethanol (EtOH), *tert*-butanol (TBA), benzoquinone (BQ) and furfuryl alcohol (FFA) were used as the scavengers for $^{\bullet}SO_4^-$, $^{\bullet}OH$, $^{\bullet}O_2^-$ and $^1O_2$, respectively. However, the addition of them with much higher concentrations than OFX had a very limited effect on OFX degradation (Fig. 4). The interesting result implies that these reactive oxygen species should not be the dominant species for OFX degradation.

Fig. 5 depicts the generated active species at different pH. The signals assigned to $^{\bullet}SO_4^-$, $^{\bullet}OH$, $^{\bullet}O_2^-$ and $^1O_2$ can be observed in the solar/PS process. However, the highest intensities of $^{\bullet}SO_4^-$ and $^{\bullet}OH$ signals were observed at pH 10, implying that high pH value facilitates the activation of PS. The intensities of $^{\bullet}O_2^-$ and $^1O_2$ signals were similar at different pH, which is also independent of the degradation efficiency of OFX. The EPR result further demonstrates that the identified reactive oxygen species are not the dominant species for OFX degradation. In addition, the signals of $^{\bullet}SO_4^-$, $^{\bullet}OH$ and $^{\bullet}O_2^-$ were very weak, indicating the poor efficiency of PS activation by simulated solar irradiation.

The result in Fig. 1 has shown that OFX was hardly degraded by direct photolysis, while its degradation was dramatically accelerated with the addition of PS. Hence, PS should play a key role in the oxidization of OFX. Subsequently, the consumption of PS in the solar/PS/OFX process at different pH was determined and presented in Fig. 6. It is interesting that the amount of consumed PS did not occur in parallel with the degradation efficiency of OFX at pH 4–8. In general, PS can be activated by alkali and high pH value facilitates the decomposition of PS. However, the lowest amount of consumed PS was observed at pH 10, agreeing well with the lowest OFX degradation efficiency. This means that the gradation of OFX was independent on PS decomposition as well as on the corresponding generated radicals, in accordance with the result in Figs. 4 and 5. The decomposition of PS in the absence of OFX was also investigated. As shown in Fig. 7, PS was hardly decomposed by simulated solar irradiation at pH 4, which is contrary to the highest degradation efficiency of OFX. It can be understood that the ionization degree of PS will decrease and its stability will increase with decreasing solution pH. The low decomposition efficiency of PS suggests that the ability of solar irradiation for PS activation is very limited. This can be attributed to that only 3%–4% of the solar spectrum falls within the UV range. Furthermore, solar UV contains mainly UV-A and UV-B (280–400 nm). Therefore, the mechanism of this solar/PS process should be different from that of reported UV/PS processes using a UV lamp with $\lambda \leq 280$ nm [19,26,34,35,37]. In these previous processes, the degradation of pollutants followed a radical mechanism because PS can be effectively decomposed into radicals by UV irradiation. In this work, the emission spectrum of the Xe lamp below 300 nm is very weak and PS almost had no absorption above 300 nm (Fig. 2 and S1). Therefore, PS can hardly be activated by simulated solar irradiation. While OFX still had strong absorption from 300 to 370 nm, thus it could be activated by simulated solar irradiation. The activated OFX might react with PS more readily, leading to a significant synergistic effect of solar/PS for OFX degradation. After comparing the PS consumption with and without OFX, it was found that the amount of consumed PS was significantly increased by the addition of OFX. The increased amounts of consumed PS at pH 4–8 were almost the same but much higher than that at pH 10. OFX was almost completely degraded after 5 min at pH 4–8, while the degradation efficiency at pH 10 was only about 30%. According to the results, OFX might react with PS directly, leading to the increased consumption of PS. However, the previous experiment revealed that OFX was hardly degraded by PS without irradiation. OFX had strong absorption in the UV region Therefore, it can be deduced that OFX was activated by solar irradiation. The activated OFX was more active than unexcited one, and so can be oxidized by PS more readily. The trend of OFX degradation at different pH can also be well explained by this mechanism. The redox potential of PS will increase with decreasing solution pH, thus it can oxidize OFX more readily at lower pH. Hence, the degradation efficiency of OFX increased with decreasing solution pH.

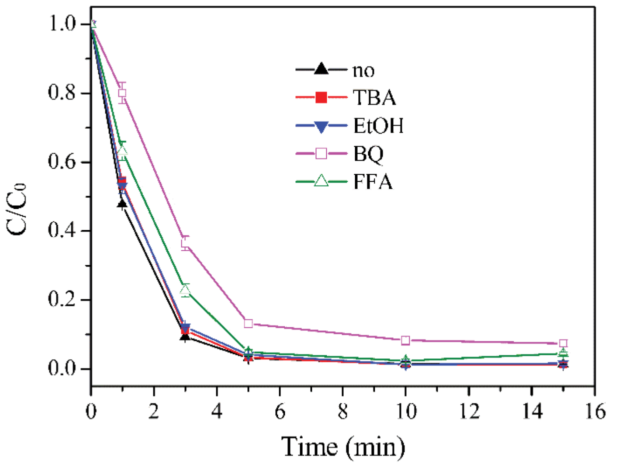

Fig. 4. Effect of scavengers on the degradation of OFX with stimulated solar/PS (pH 8; OFX 10 mg L^{-1}; PS 1 mmol L^{-1}; TBA and EtOH 500 mmol L^{-1}; BQ 10 mmol L^{-1}; FFA 5 mmol L^{-1}).

3.3. *Influence of water matrix on OFX degradation*

There are many coexisting ions in real water that can affect the degradation of organic pollutants. Fig. 8 shows the influence of common ions on the degradation of OFX with stimulated solar/PS. The degradation of OFX was slightly inhibited by these ions, and the inhibitory effect was very limited. It is well known that chloridion and bicarbonate are effective scavengers of active radicals. However, the addition of chloridion had little effect on this process. The inhibitory effect of bicarbonate was slightly higher than that of chloridion, which might be due to its buffer capacity. The result in Fig. 3 has revealed that the higher pH could suppress the degradation of OFX. The solution pH in the absence of bicarbonate decreased from 8 to 6.9 after reaction for 15 min, while that in the presence of bicarbonate remained constant.

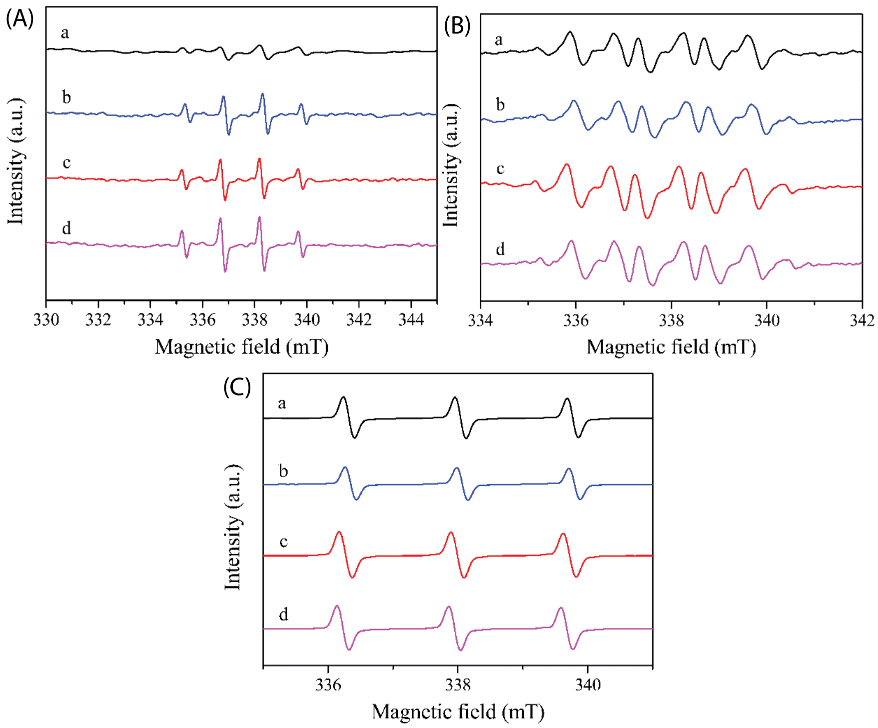

Fig. 5. EPR spectra of DMPO trapped (A) $^{\bullet}OH$ and (B) $^{\bullet}O_2^-$ and (C) TEMP trapped $^1O_2$ at different pH: (a) pH 4, (b) pH 6, (c) pH 8 and (d) pH 10.

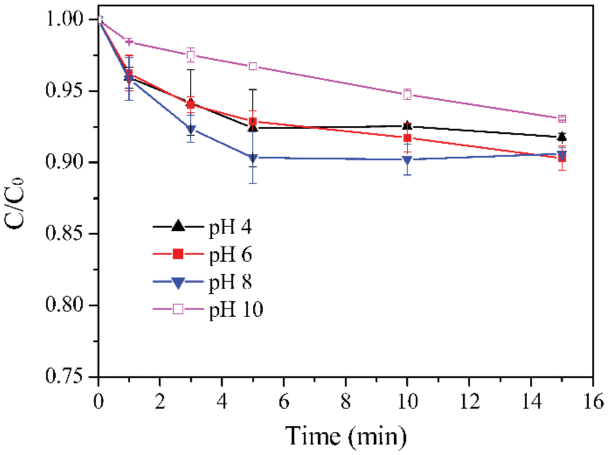

Fig. 6. PS decomposition at different pH in the degradation of OFX with solar/PS (OFX 10 mg L^{-1}; PS 1 mmol L^{-1}).

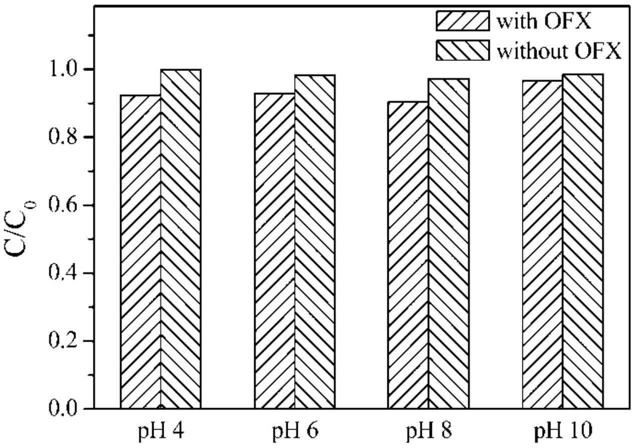

Fig. 7. Effects of solution pH on PS decomposition in the absence and presence of OFX (OFX 10 mg L^{-1}; PS 1 mmol L^{-1}; reaction time 5 min).

And so the lower degradation efficiency of OFX with bicarbonate could be ascribed to the higher solution pH. Fulvic acid, a common organic matter in natural waters, showed a slightly higher inhibitory effect than chloridion and metal cations. This might be attributed to its shading effect and/or competition for active species. The result in Fig. 8 further demonstrates that the degradation of OFX did not follow the radical mechanism. Therefore, these ions that can capture radicals had little effect on OFX degradation. In addition, these ions can be removed by ion exchange resin after removing organic pollutants.

In order to assess the practicability of this process for treating OFX, the degradation of OFX in real water or under real solar irradiation was also investigated. As shown in Fig. 9, the degradation efficiency of OFX in river water was only slightly lower than that in deionized water. The experiment under real solar irradiation was performed without stirring in the outdoor environment (Shijiazhuang, 2:00 PM, November 13, 2019). The condition is listed as follows temperature 13°C, solar light intensity 34 W cm^{-2}. It can be seen that degradation efficiency was still high at a low temperature

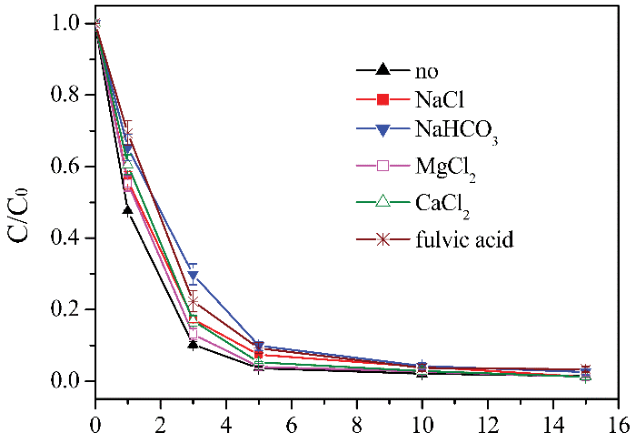

Fig. 8. Effect of coexisting substances on the degradation of OFX with stimulated solar/PS (pH 8; OFX 10 mg L^{-1}; PS 1 mmol L^{-1}; inorganic ions 10 mmol L^{-1}; FFA 10 mg L^{-1}).

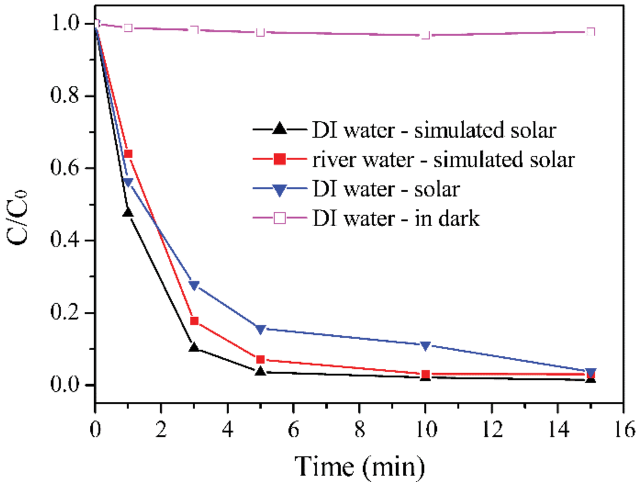

Fig. 9. Degradation of OFX in real water or under real solar irradiation (pH 8; OFX 10 mg L^{-1}; PS 1 mmol L^{-1}).

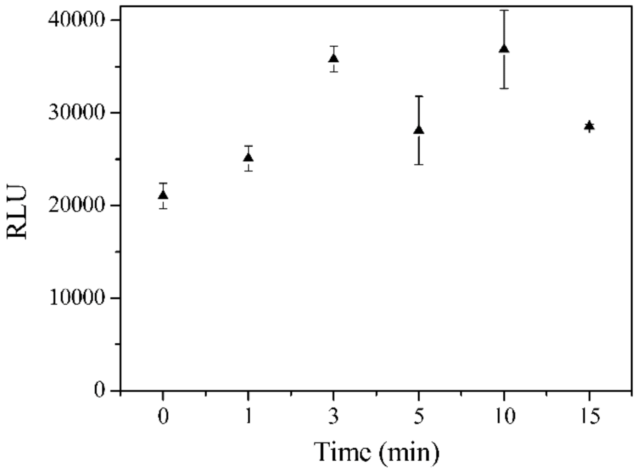

Fig. 10. Toxicity of the OFX solution treated by stimulated solar/PS for different times.

in winter, suggesting the potential application of this process for removing OFX in the environment.

Although the non-radical process shows superior performance to radical process in terms of target pollutant degradation in real water, the mineralization efficiency of the pollutants might not be ideal and some more toxic intermediates might be formed. Therefore, the TOC removal efficiency and toxicity of the OFX solution treated with stimulated solar/PS were investigated. About 55% of TOC can be removed after reaction for 15 min. Fig. 10 shows that the relative light units of the treated OFX solutions were all higher than that of the fresh one, indicating that the toxicity of the OFX solution was significantly decreased by this stimulated solar/PS process. The results demonstrate that the solar/PS process is effective for the degradation and mineralization of OFX in water.

3.4. Degradation pathway for OFX

Since PS is the dominant active species for OFX degradation by solar/PS, it is necessary to investigate the degradation pathway of OFX. As shown in Fig. 11 and S2, the identified degradation products of OFX in this process are different from those in previous reported PS activation processes [27,29,35,37,38]. This can be ascribed to that OFX was mainly degraded by PS rather than radicals or $^1O_2$. P1 and P2 were generated through the cleavage of the piperazine ring, while P3 was generated through the cleavage of the oxazine ring. The demethylation of piperazinyl substituent led to the formation of P4 and P5, and the decarboxylation or cleavage of oxazinyl substituent also occurred. The decarboxylation of oxazinyl substituent in P2 gave rise to the formation of P6. P7 was formed due to the further oxidation of the piperazine side chain until it was reduced to an amino group [39].

According to the above results, the degradation process of OFX by solar/PS was summarized as follows. Solar irradiation could give rise to the activation of OFX, and meanwhile, a small amount of reactive oxygen species were formed. Then the excited OFX was readily attacked by PS, which led to the formation of the identified products. In addition, these intermediates might be further oxidized by PS and/or the generated reactive oxygen species, thus a high TOC removal efficiency and a decrease of toxicity of OFX solution were achieved.

4. Conclusion

Although single solar irradiation or PS oxidation can hardly degrade OFX, their combination could lead to a significant synergistic effect for OFX degradation. OFX could be effectively removed by solar-PS at acidic and neutral conditions, and its degradation efficiency decreased with increasing solution pH. The calculated reaction rate constants at pH 4–8 were much higher than those of many reported PS activation processes. Moreover, the water matrix had little effect on OFX degradation, indicating solar/PS is an efficient process for OFX removal. The active species for OFX degradation should be PS rather than radicals or $^1O_2$. The reason is that OFX can be activated by solar

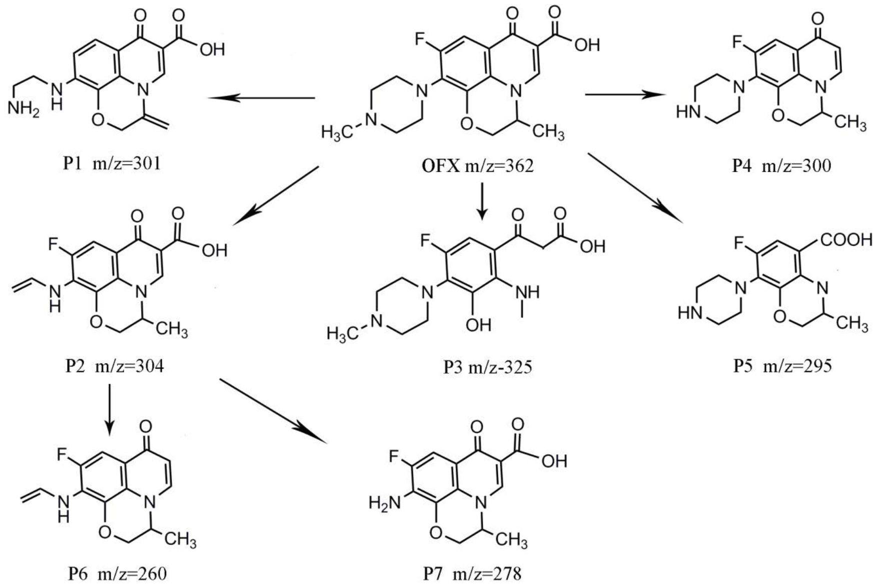

Fig. 11. Possible degradation pathway of OFX.

irradiation more readily than PS and the photoactivated OFX is prone to react with PS. Finally, the degradation products of OFX were identified by LC-MS. This study provides new insight into the mechanism for OFX degradation with solar/PS, which is useful for treating this pollutant.

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Supplementary information

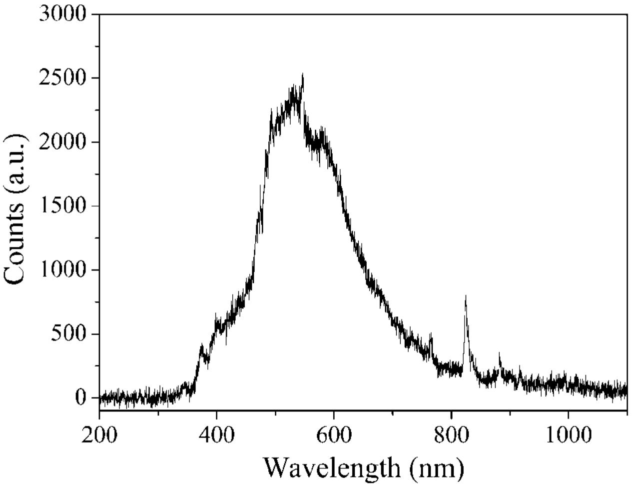

Fig. S1. The emission spectrum of the xenon lamp is equipped with an AM 1.5 G filter.

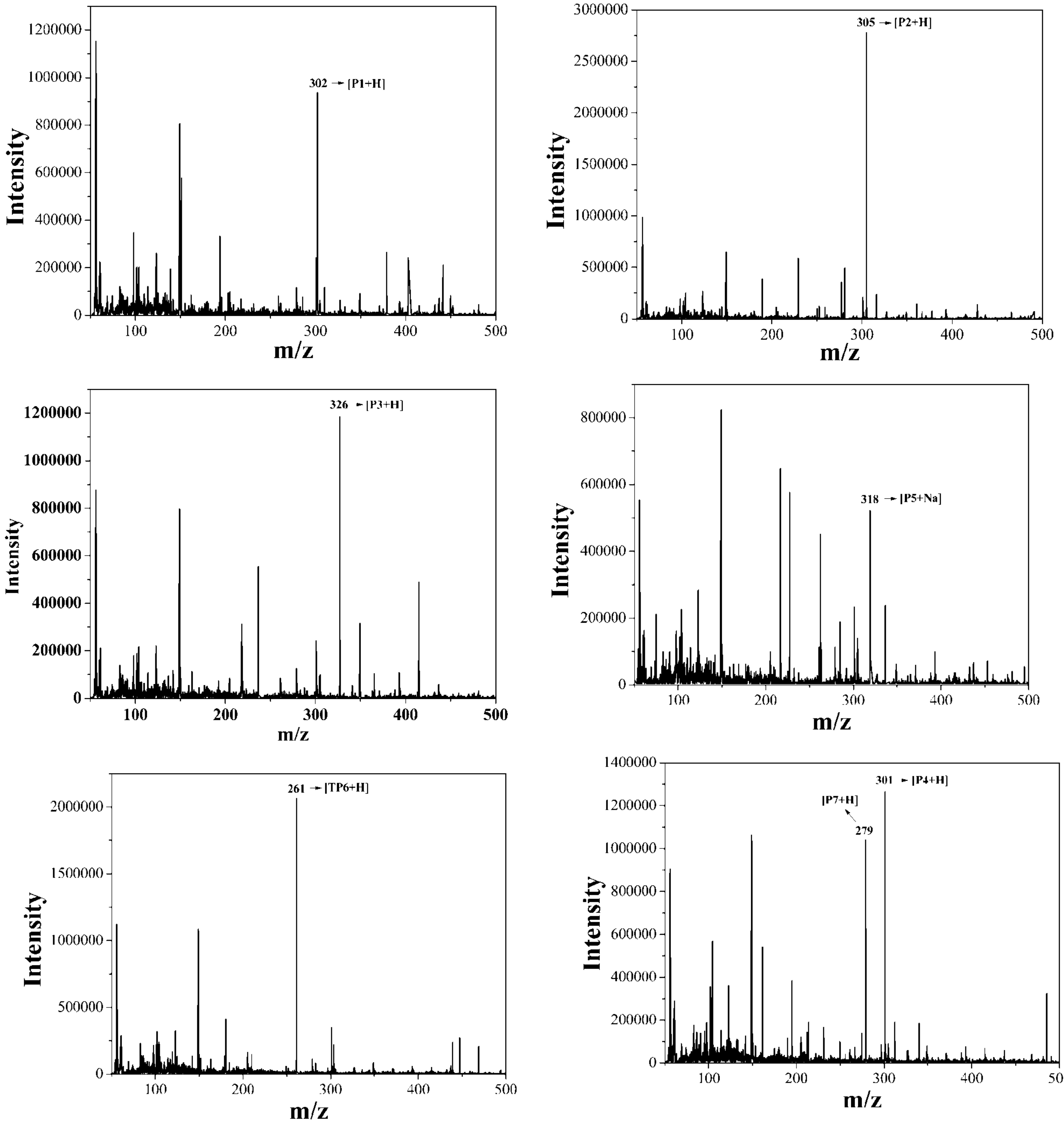

Fig. S2. HPLC-MS spectra in the positive ion mode (P1, RT (retention time) 2.48 min; P2, RT 3.67 min; P3, RT 5.03 min; P5, RT 10.04 min; P6, RT 1.58 min; P4 and P7, RT 1.96 min).