

Contents lists available at ScienceDirect

Science of the Total Environment



journal homepage: www.elsevier.com/locate/scitotenv

Efficient degradation and detoxification of antibiotic Fosfomycin by UV irradiation in the presence of persulfate

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- UV/persulfate oxidation can significantly degrade fosfomycin.
- OH played the dominant role in fosfomycin degradation.
- Hydroxylation, C—P bond cleavage, and coupling reactions are involved in fosfomycin degradation.
- Toxicity of fosfomycin solution by UV/ persulfate is completely detoxified.



ARTICLE INFO

Editor: Deyi Hou

Keywords: Fosfomycin Advanced oxidation processes Degradation mechanisms Theoretical calculations Toxicity evaluation

ABSTRACT

Fosfomycin (FOS) as a widely used antibiotic has been found in abundance throughout the environment, but little effort has been devoted to its treatment. In this study, we systemically looked into the degradation of FOS by ultraviolet-activated persulfate (UV/PS) in aqueous solutions. Our findings demonstrated that FOS can be degraded efficiently under the UV/PS, e.g., >90 % of FOS was degraded with 19,200 mJ cm⁻² of UV irradiance and 20 μ M of PS. HO' was the dominant radical responsible for FOS degradation. FOS degradation increased as PS dosage increased, and higher degradation efficiency was observed at neutral pH. Natural water constitutes either promoted (e.g., Cu²⁺, Fe³⁺, and SO²₄⁻) or inhibited (e.g., humic acid, HCO³₃, and CO³₃⁻) FOS degradation pathways for FOS degradation. Finally, the toxicity evaluation revealed that FOS was toxic to *E. coli* and *S. aureus*, but the toxicity of the intermediate products of FOS to *E. coli* and *S. aureus* rapidly decreased over time after UV/PS treatment. Therefore, these findings provided a fundamental understanding of the transformation

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https://doi.org/10.1016/j.scitotenv.2023.167249

Received 30 April 2023; Received in revised form 18 September 2023; Accepted 20 September 2023 Available online 21 September 2023 0048-9697/© 2023 Elsevier B.V. All rights reserved. process of FOS and supplied useful information for the environmental elimination of FOS contamination and its toxicity.

1. Introduction

Fosfomycin (1R-2S-epoxypropyl phosphonic acid, FOS) is a widely used antibiotic that has been discovered more than five decades ago. Recently, it has regained interest as a potential therapy option against extensively drug-resistant and multidrug-resistant pathogens (Sastry and Doi, 2016). It is primarily used to treat sensitive gram-negative bacteria-related digestive tract infections, skin and soft tissue infections, and urinary tract infections (Zurfluh et al., 2020). Like other antibiotics, during the production and application processes, FOS wastewater will be produced and eventually excreted into the aquatic environment in its raw or metabolized form (Oiu et al., 2011), posing potential threats like disrupting microbial communities and causing the evolution of antibiotic resistance to both humanity and the environment (Gothwal and Shashidhar, 2015). Moreover, the mobile fosfomycinresistant genes (fosA3 and fosL1) have been widely detected in isolates from humans, animals, food, and the environmental medium, which raises concerns about the potential risk of such bacteria, particularly Escherichia coli (E. coli) and Salmonella (Zurfluh et al., 2020). As a result, it is crucially important to explore efficient methods for the removal of FOS from water. Aside from FOS treatment, the elimination of its bacterial toxicity is also needed to avoid inducing FOS-resistant genes.

At present, exploration of the potential treatment methods of FOS is still in the initial stage. The methods including adsorption, biodegradation, and chemical oxidation have been tried to treat FOS wastewater (Abdelmigeed et al., 2022; McGrath et al., 1998; Shi et al., 2016; Yang et al., 2019a). Abdelmigeed et al. (Abdelmigeed et al., 2022) have prepared a core-shell Fe₃O₄/PVP/ZIF-8 nanostructure adsorbent with an impressive adsorption capacity of 126.58 mg g⁻¹ toward FOS. Additionally, it has been reported that a bacterium (Rhizobium huakuii PMY1) can use FOS as the sole phosphorus and carbon source causing the cleavage of the C-P bond after 30 days of treatment (McGrath et al., 2009; McGrath et al., 1998; Pallitsch et al., 2017). Recently, it has been demonstrated that chemical oxidation is efficient to treat FOS. It has been confirmed that FOS can be efficiently removed by schorl/H₂O₂ treatment (a tourmaline mineral-catalyzed Fenton-like system) with phosphorus crystallization into dicalcium phosphate anhydrous (Shi et al., 2016; Yang et al., 2019a). Nevertheless, little effort has been devoted to the chemical oxidation process of FOS, including the degradation kinetics, degradation products, and mechanisms. Moreover, the toxicity evolution of FOS degradation products has not been addressed in previous studies, which is important information for the optimization of the treatment process.

Due to the harmful effects on microorganisms (Loos et al., 2013), many antibiotics, including FOS, cannot be removed from wastewater by conventional wastewater treatment plants (WWTPs). Therefore, advanced oxidation processes (AOPs) have been developed and widely used to remove antibiotics from wastewater (Wang and Zhuan, 2020). AOPs with highly reactive hydroxyl (HO') or sulfate (SO_4^-) radicals as the primary reaction species are prospective for the removal of pharmaceutical pollutants from aquatic environment (Feng et al., 2017; Huber et al., 2003; Klavarioti et al., 2009). In the past few years, SO₄based AOPs have drawn the interest of researchers due to their high removal efficiency toward recalcitrant pollutants that cannot be eliminated by conventional treatment methods (Parida et al., 2021). Therefore, SO₄-based AOPs have been created and considered as a potential alternative method to degrade toxic, bio-refractory, and highly concentrated organic substances (Feng et al., 2017; Fu et al., 2019c). HO' and SO_4^{-} , which are powerful oxidants with a high redox potential (i.e., 1.8-2.7 V for HO', and 2.5-3.1 V for SO4'), are effective and promising in eliminating most organic pollutants from water (Yang

et al., 2019b).

Recently, persulfate (PS), a popular ISCO oxidant with the characteristics of green, good water solubility, a wide range of use, and easy storage and transportation, has gained attention in environmental applications (Yang et al., 2021). With a standard oxidation potential (E_0) of 2.01 V, $S_2O_8^{2-}$ itself is a vigorous oxidant in and of itself (Deng and Zhao, 2015). It can be activated to produce SO_4^{-1} ($E_0 = 2.6$ V) in many ways, including UV (Fu et al., 2019b), ultrasonic (Wei et al., 2017), heat (Feng et al., 2017), transition metals, or carbon nanomaterials (Xiao et al., 2018). Among the above activation methods, UV irradiation has a good prospect in the practical application for persulfate activation due to its simple system and operational feasibility (Liu et al., 2021). It has been demonstrated that medium-pressure UV lamp (MPUV) has a significant potential for photodegrading organic micropollutants (Lekkerkerker-Teunissen et al., 2012). Moreover, due to the significantly higher installed power of a single MPUV lamp, fewer and smaller reactors are needed. Therefore, the MPUV-activated persulfate/peroxymonosulfate processes have been widely used for the degradation of emerging micropollutants, e.g., antibiotics tetracycline, sulfamethoxazole, and ciprofloxacin (Ao and Liu, 2017; Ao et al., 2018a; Ao et al., 2018b; Ao et al., 2019). In UV/PS process, $S_2O_8^{2-}$ can be activated to produce SO_4^{--} (Eq. (1)), and the SO_4^{-1} subsequently reacts with H_2O or OH^- to produce HO' through Eqs. (2) and (3). In addition, the application of UVactivated peroxides for the treatment of pollutants has become an important research hotspot. UV/PS-based AOPs are a promising replacement to traditional treatment methods applied in wastewater treatment plants, including coagulation, membrane bioreactors, and conventional activated sludge because of their capacity to produce highly reactive free radicals, such as HO' and SO₄. (Tan et al., 2013). Therefore, the application of UV/PS for FOS degradation has great potential and excellent prospects.

$$S_2 O_8^{2-} + h v \rightarrow 2S O_4^{\pm} \tag{1}$$

$$SO_4^- + H_2 O \rightarrow HO + H^+ + SO_4^{2-} \tag{2}$$

$$SO_4^{-} + OH^{-} \rightarrow HO^{+}SO_4^{2-} \tag{3}$$

In this study, the kinetics, products, and degradation pathways of FOS by the UV/PS reaction were all thoroughly examined, along with the toxicity evaluation. The possible active species that contributed to FOS degradation in the UV/PS process were identified. The influence of initial PS concentration, pH, humic acid (HA), and the presence of anions and cations on FOS degradation by UV/PS were investigated. The specific degradation processes and transformation pathways were postulated from degradation products identified by LC-MS/MS analysis and theoretical calculations. In particular, the effectiveness of FOS degradation in various natural water matrices was tested to assess the feasibility of the UV/PS process. Finally, we evaluated the potential toxicity of FOS to *E. coli* and *Staphylococcus aureus* (*S. aureus*) before and after UV/PS treatment.

2. Materials and methods

2.1. Chemicals and reagents

Detailed information on the chemicals and reagents are provided in Text S1 of the Supplementary material.

2.2. Degradation experiments

All photochemical experiments were conducted in a photocatalytic

reactor (XPA-7, Nanjing Xujiang Motor Factory, China), which employed a 1000 W medium-pressure ultraviolet mercury lamp (254–400 nm) as the sole source of UV irradiation. To control the reaction temperature, a circulating water-cooling system was employed to maintain a steady temperature of 25.0 \pm 0.2 °C, and light intensity within 50 mL quartz tubes was measured to be 5.7 \times 10⁻⁵ Einstein cm⁻² s⁻¹. An appropriate amount of FOS stock solution was mixed with DI water containing 0–100 μ M of persulfate (PS) to make sure that the reaction solution would have a final volume of 50.0 mL. During the ultraviolet radiation, a magnetic stirrer was used for mixing the samples. The initial concentration of FOS was set at 10.0 μ M. The reaction solution was quenched with 100 μ L of methanol after a preset reaction time. All experiments were performed in triplicate and the error bar represented the calculated standard deviation.

2.3. Analysis methods

The detection of the residue FOS was achieved through analysis with liquid chromatography-triple quadrupole mass spectrometry (LC-MS/MS, TSQ Quantiva, Thermo Scientific) (Text. S2). The level of the released phosphate ions (PO_4^{3-}) in the reaction solutions was determined using a Mo-Sb Anti-spectrophotometer method (Song et al., 2019). The quantity of total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, TOC-L CPH, Japan). In order to identify the transformation products of FOS degradation, a sample of the reaction solution following a 40-min UV/PS treatment was taken, which allowed for the gathering of the largest variety of transformation products. Product characterizations were performed on an HPLC system coupled with hybrid quadrupole-orbitrap mass spectrometry (UPLC-Q-Exactive Orbitrap-MS, Thermo, Bremen, Germany) (Text S3).

2.4. Theoretical calculations

In this study, we used the B3LYP/6-31(d) approach to optimize the geometries of the reactants, transition states, and products while simultaneously computing their vibrational frequencies to identify that the optimized geometries were the real minima (Xiao et al., 2020). In addition, single-point energy calculations using Grimme's dispersion-correction D3 at the M06-2X/6-311+G (d, p) level of theory were performed (Grimme et al., 2010; Grimme et al., 2011). The Gaussian 16 software package (Gaussian 16, Revision, C.01) was employed for all calculations. Detailed information is provided in Text S4.

2.5. Toxicity assessment

In this study, we used *E. coli* and *S. aureus* to evaluate the toxicity of FOS and its transformation products. Before the tests, the bacterial suspension $(1.0 \times 10^8 \text{ CFU mL}^{-1})$ was prepared according to the method described in Text S5 of the Supplementary material. The toxicity tests were conducted for 8 h at 37 °C in a shaker incubator (150 rpm) (Li et al., 2011). Cell density was used interchangeably with optical absorbance at 600 nm to express bacterial survival. The growth inhibition assay was monitored throughout exposure periods (0, 1, 2, 3, 4, 5, and 8 h). All treatments were prepared in triplicate.

3. Results and discussion

3.1. Degradation of FOS in UV/PS process

Firstly, we examined the degradation of FOS in four reaction systems, i.e., sole PS, UV, UV/PS, and UV/H₂O₂, to study the degradation of FOS in DI water (Fig. 1a). It shows that FOS underwent a rapid decay in binary systems, resulting in a removal rate of 76.8 % and 91.8 % within 40-min reaction in UV/H₂O₂ and UV/PS processes, respectively, whereas PS alone led to negligible removal of FOS and sluggish degradation was observed in UV system (<30.00 %), which manifested the synergistic interaction of UV and the peroxides. The degradation of FOS in UV, UV/PS, and UV/H₂O₂ systems could be well-described by the pseudo-first-order kinetics model (Fig. 1b). The pseudo-first-order rate constant of the UV/PS system was calculated to be 0.2031 min⁻¹, which is approximately 18.0 and 2.0 times greater than that observed in UV and UV/H₂O₂ systems, respectively.

The superior performance of the UV/PS technique may stem from the following factors: 1). PS may be a stronger UV absorber than H_2O_2 . PS and H_2O_2 have absorption coefficients of approximately 20–22 and 18.6 $M^{-1} \bullet cm^{-1}$ at 254 nm, respectively (Morgan et al., 1988; Xu et al., 2017). 2). For Eqs. (2) and (3), quantum yields of SO₄⁻⁻ were reported to span the range of 1.4–1.8 mol•E⁻¹ (Rachel H. Waldemer et al., 2007), substantially higher than that of HO⁻ (1.0 mol•E⁻¹). 3). The distinct reactivity of SO₄⁻⁻ and HO⁻ may further discriminate the effectiveness of UV/PS and UV/H₂O₂ processes, which will be discussed below.

It is known that one of the major contributors determining the degradation mechanism of contaminants is the distribution of reactive oxygen species (ROS) (Wang et al., 2021c). Here, the quenching experiments demonstrated the contributions of each ROS. Methanol (MeOH) was able to efficiently scavenge both SO_4^- and HO', with the second-order rate constants of $2.5 \times 10^7 \, \text{M}^{-1} \, \text{es}^{-1}$ and $9.7 \times 10^8 \, \text{M}^{-1} \, \text{es}^{-1}$ (Neta et al., 1988), respectively, while tert-butanol (TBA) was used to



Fig. 1. (a) Degradation kinetics of FOS by persulfate (PS), UV, UV/H₂O₂, and UV/PS treatment, and (b) the obtained pseudo-first-order rate constants (k_{obs}). Experimental conditions: $[FOS]_0 = 10 \ \mu\text{M}$, $[PS]_0 = [H_2O_2]_0 = 20 \ \mu\text{M}$, initial pH = 7.0, and temperature = 25 °C. Data points with different letter have significant difference from each other, p < 0.5.

exclusively capture HO' because of its relatively low reactivity toward SO_4^- ($k = 4.0-9.1 \times 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$) (Wang et al., 2021a). As Fig. 2a depicts, MeOH and TBA both significantly slow down the degradation of FOS, indicating the crucial participation of HO' and SO_4^- in the process. Furthermore, the relative contributions of UV photolysis, HO', and SO_4^- were modeled with Eq. (4) (Fu et al., 2019a).

$$ln \frac{C_t}{C_0} = -k_{obs}t = -\left(k_{H\sigma} + k_{S\sigma_4^-} + k_{UV}\right)t$$
(4)

It was found that the relative contribution to FOS degradation followed the order of HO' > SO_4^- > UV photolysis (Fig. 2b). The results showed that the production of HO' was the most important factor for effective FOS degradation. It can be seen that HO' plays a major role in the UV/PS system, while PS was more effective than H₂O₂ at degrading FOS in the presence of the oxidant at the same concentration (Fig. 1a).



Fig. 2. (a) Degradation kinetics of FOS by UV/PS with different scavengers, and (b) the first-order degradation rate constants of FOS by reactive species in the UV/PS process. Experimental conditions: $[FOS]_0 = 10 \ \mu\text{M}$, $[PS]_0 = 20 \ \mu\text{M}$, $[TBA] = [MeOH] = 1 \ \text{mM}$, initial pH = 7.0, and temperature = 25 °C. Data points with different letter have significant difference from each other, p < 0.5.

The possible reason is the synergistic effect of SO_4^- and HO' produced by UV-activated PS is more efficient than that of H_2O_2 producing only HO'. Fu et al. (Fu et al., 2019c) also discovered that HO' primarily contributes to the degradation of sucralose in the UV/PS system.

3.2. Effects of water matrix

Natural organic matter (NOMs) and inorganic anions, cations, are abundant in natural waterways and may have an impact on advanced oxidation processes by consuming radicals, shading light, or interfering with electron transfer (Sezonov et al., 2007). Hence, to examine the practicability of the UV/PS system in treating FOS-laden wastewaters, degradation experiments were conducted under various operational conditions and water matrices. We first investigated the influence of the initial PS concentration. In Fig. 3a, the degradation of FOS monotonously improved as the PS initial concentration increased from 5 to 100 μ M, which was attributed to the stronger UV absorption and thus a higher yield of ROS at high PS dosage (Wang et al., 2021b). As expressed in Eqs. (5) and (6), an overdose of PS would scavenge SO₄⁻, and hence reduced the degradation of the target pollutant (Liu et al., 2020).

The effect of initial solution pH (5.0–9.0) on FOS degradation was examined and the results are given in Fig. 3b. The observed degradation efficiency of FOS is slightly higher in the neural condition than in the acidic and alkaline pHs. Under alkaline pH, SO_4^- can react with OH⁻ to generate HO' (k = $6.5 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$) (Eqs. (2) and (3)), while the generated HO' will be further scavenged by OH⁻ through Eq. (7), thus decreased the degradation rate of FOS. In addition, it has been reported that the activation energy of sulfate radicals is minimal at neutral pH, resulting in the better performance of UV/PS systems under neutral conditions (Dhaka et al., 2017; Liang et al., 2007).

$$SO_4^{\perp} + SO_4^{\perp} \rightarrow S_2O_8^{2-} \tag{5}$$

$$SO_4^{-} + S_2O_8^{2-} \leftrightarrow S_2O_8^{-} + SO_4^{2-} \tag{6}$$

$$HO \dot{+}OH^{-} \rightarrow O^{-} + H_2O \tag{7}$$

Previous literature has demonstrated the complicated chemistry of natural humic acid (HA) in environmental processes (Feng et al., 2017). It has been postulated that HA may be a double-edged sword with respect to the degradation of target pollutants. On the one hand, HA could function as a competitor to absorb UV light, thus limiting the oxidative destruction of target pollutants, it also competes with pollutants for HO' and SO₄⁻ radicals (Nie et al., 2014), thus halting their degradation. Moreover, UV irradiation can transform HA to a transient excited state (e.g., triplet states, ³HA*), which could react with oxygen to generate more reactive species like singlet oxygen, or directly react with the target pollutants, thus promoting the degradation of pollutants (Canonica et al., 1995; Zepp et al., 1985). According to Fig. 3c, the addition of HA remarkably raised the residual concentration of FOS, it is thus concluded that the downside of HA dominated the process in the present study. We then examined the second reaction rate constant, k $(SO_4^- + HA)$, as detailed in Text S6 and Fig. S1. As scavengers of SO_4^- , the $k(SO_4^- + HA)$ was calculated to be 3.48–4.65 $\times 10^6$ mgC⁻¹ s⁻¹ within the range of the previously stated values (e.g., 6.8×10^3 – $2.5 \times$ $10^7 \text{ mgC}^{-1} \text{ s}^{-1}$) (Lee et al., 2020; Lutze et al., 2015). Therefore, UV/PS system favors the treatment of FOS-bearing wastewater with low HA content.

The numerous processes that take place in the water are significantly impacted by the abundance of anions and cations in the natural water environment. In this work, we also investigated the potential effect of anions (Cl⁻, SO₄²⁻, NO₃⁻, CO₃²⁻, and HCO₃⁻, in the form of sodium salts) and cations (Cu²⁺, Fe³⁺, NH₄⁺, Ca²⁺, Mg²⁺, and K⁺, in the form of chloride), which are pervasive in the environment. The concentration of anions or cations was set at 10 mM. Fig. 3d and e displayed the influence of anions and cations on the degradation of FOS by UV/PS process. All

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Fig. 3. Influence of (a) initial PS concentration, (b) initial pH, (c) humic acid (HA), (d) different anions (Cl⁻, SO₄²⁻, NO₃⁻, CO₃⁻) and cations (Cu²⁺, Fe²⁺, NH₄⁺, Ca²⁺, Mg²⁺, K⁺) on the degradation of FOS by UV/PS; (f) degradation of FOS by UV/PS in different water matrices. Experimental conditions: [FOS]₀ = 10 μ M, [PS]₀ = 20 μ M, [ions] = 10 mM, [HA]₀ = 0–40 mg L⁻¹, initial pH = 7.0, temperature = 25 °C, reaction time = 5 min. Data points with different letter have significant difference from each other, p < 0.5.

inorganic anions and cations examined affected the degradation of FOS to varying degrees.

 CO_3^{2-} and HCO_3^- significantly inhibited the degradation of FOS by UV/PS system as HCO_3^- and CO_3^{2-} react with free radicals thereby producing the secondary radical CO3- with lower activity than SO4 and HO', according to Eqs. (1)-(4) in Scheme S1 in the Supplementary material. Besides, the addition of HCO_3^- and CO_3^{2-} increased the solution pH to 11.15 and 9.43 respectively (Table S2). However, the degradation of FOS slightly promoted from 58.5 % to 66.2 % with the addition of 10 mM Cl⁻ following 5-min treatment. A similar discovery was reported by Yuan et al. (Yuan et al., 2011), who used the activated peroxymonosulfate (PMS) system to demonstrate a dual effect of Cl- on the degradation of azo dye acid orange 7 (AO7). An inhibitory impact at low chloride concentrations (5 mM) may result from the one-electron mechanism in which Cl⁻ consumes SO₄⁻⁻ to produce the less reactive chloride radicals (Eqs. (5) and (6) in Scheme S1). However, the beneficial effect of higher Cl⁻ concentrations was triggered by the production of HOCl and Cl₂ (Eqs. (7)-(9) in Scheme S1). In general, the presence of Cl⁻ results in a dual impact with relatively low reactivity toward contaminants and a slight quenching effect on HO' and SO'- radicals (Yang et al., 2014).

In the current study, the effect of NO₃⁻ addition on the UV/PS process was negligible, which has been previously reported due to the relatively low reaction rates that these species with SO₄⁻⁻ (Nie et al., 2014). The addition of NO₃⁻⁻ also played a certain photosensitizing effect on the degradation of FOS. It is known that NO₃⁻⁻ can undergo a series of photochemical reactions under the irradiation of UV light (Eqs. (8)–(9)) to form HO⁻, which has a strong oxidizing ability to accelerate the degradation of pollutants (Keen et al., 2012). Nonetheless, the promotion effect of NO₃⁻⁻ on the degradation of FOS was not significant in this study, which was presumably due to the limited radiation energy received by NO₃⁻⁻ under the experimental light conditions. However, with the addition of SO₄²⁻⁻, the degradation rate of FOS in the UV/PS system did increase by about 26.77 % within 5 min, indicating the positive effect of SO_4^{2-} on the process. This phenomenon has been seen in UV-activated PS systems, where the presence of sulfate exhibited a beneficial effect on the degradation of ofloxacin and levofloxacin (Liu et al., 2020). According to Eq. (10) in Scheme S1, SO_4^{-} reacts with $S_2O_8^{2-}$ to produce $S_2O_8^{-}$ and SO_4^{2-} causing the quenching of SO_4^{--} (Ghauch et al., 2017; Liu et al., 2020). Therefore, the increase of sulfate anion alleviated the quenching of SO_4^{--} , thus making more FOS degradation (Deng et al., 2014).

$$NO_3^- \xrightarrow{\text{NV}} NO_2^- + O^-$$
 (8)

$$O^- + H_2 O \rightarrow HO \dot{+}OH^- \tag{9}$$

Furthermore, the presence of cations also affected the degradation of FOS to different degrees. It has been reported that transition metals and their ionic forms can synergistically activate persulfates to accelerate their degradation of organic pollutants (Yan et al., 2019). The metal element involved in the persulfate system has a significant catalytic effect on the reaction of the persulfate ion as a catalyst, which can greatly accelerate the rate of the reaction (Fu et al., 2020). As we can see, Cu^{2+} and Fe^{3+} obviously enhanced the degradation of FOS in a short time. This may be due to the catalytic role of metal ions in the system, leading to the degradation of organic pollutants. This may indicate that metal ions can activate persulfate and form sulfate radicals, as shown by the equation follows:

$$Cu^{2+} + S_2 O_8^{2-} \rightarrow Cu^{3+} + SO_4^{-} + SO_4^{2-}$$
(10)

$$Fe^{3+} + S_2 O_8^{2-} \to Fe^{2+} + S_2 O_8^{-} \tag{11}$$

$$Fe^{2+} + S_2 O_8^{2-} \to Fe^{3+} + SO_4^{-} + SO_4^{2-}$$
(12)

$$Cu^{3+} + S_2 O_8^{2-} \to Cu^{2+} + SO_4^{-} + SO_4^{2-}$$
(13)

The formation of Cu³⁺ is unstable but may oxidize and degrade

organic pollutants (McCann et al., 2018), which may be another potential mechanism to accelerate the degradation of FOS. Additionally, the formation of metal complexes containing persulfate might benefit the electrons transfer between each other, and hence enhance the photolyzed efficiency of persulfate (Li et al., 2020). However, the weak inhibition of Ca²⁺, Mg²⁺, and K⁺ to the degradation of FOS may be because the presence of these cations attracts UV light-generating electrons to some extent, thus hindering the reaction system from producing free radicals like SO₄⁻ and HO' (Selvam et al., 2007).

Moreover, we also studied the degradation effect of FOS in various real natural water environments, including DI water, Tap water, WWTP effluent, Sea water, and River water. The primary chemical components of these waters are summarized in Table S3. Fig. 3f shows the degradation of FOS in various water matrices. Compared to DI water, the efficiency of FOS degradation by UV/PS was reduced in water from river, tap, and WWTP effluent, while it was greatly increased in seawater. Fig. 3c and e presents the inhibitory effect of co-existing cations and HA on FOS degradation. The low degradation efficiency of FOS in these natural water samples could be attributed to the TOC contents, which ranged from 0.36 to 4.17 mg L^{-1} in three samples analyzed (Table S3) (Feng et al., 2017; Xiao et al., 2016). However, the degradation efficiency of FOS was greatly improved in the Sea water sample at 20 μ M PS dosage, which may be due to the high presence of SO₄²⁻ in the seawater that greatly contributed to the degradation of FOS. Overall, these results indicated that applying UV/PS system to FOScontaminated natural surface water or WWTP effluent is feasible from a technical standpoint. Nonetheless, a higher PS dosage and longer reaction time may be required to achieve complete FOS removal from natural waters (Ghauch et al., 2015).

3.3. Proposed reaction pathways

The degradation products of FOS via UV/PS oxidation have been identified by using LC-MS/MS analysis in positive ionization mode ($[M + H]^+$). The total ion chromatograms and MS spectra of FOS and the products of its UV/PS oxidation degradation were displayed in Figs. S2 and S3, respectively. No product was detected in the control group without oxidation treatment. The MS/MS spectra of the possible degradation products were given in Fig. S4, from which the possible formulas and structures of intermediates and products were proposed. A hypothetical degradation pathway of FOS was provided in Fig. 4 based

on the identified intermediates and the reaction characteristics of each ROS.

Two detailed pathways and bond cleavages are proposed (Fig. 4). First, HO' attacks the C atom of the epoxy groups, forming a carboncentered radical and releasing phosphate (Barrett and McBride, 2005; Sun et al., 2019). Afterward, HO' quickly attacked the carbon-centered radical, producing the hydroxylation intermediate P1. Then, after acidic hydrolysis of the epoxy groups on P1, P2 was generated. In addition, SO₄- and HO could abstract a hydrogen atom from three sites on the FOS molecule, forming carbon-centered radicals (R2). On the one hand, R2 will be transformed into P3 by acidic hydrolysis of the epoxy groups. On the other hand, R2 will be further attacked by HO' to form P4. Then, SO_4^- and HO' abstract the hydrogen atoms from the degradation intermediates P1 - P4, causing the production of many Ccentered and C-O radicals, as well as the release of phosphate, C-O and C-C cross-coupling reactions will occur between these radical intermediates and finally results in the formation of abundant dimerization products like P5 – P10. Meanwhile, further attack by SO₄⁻ and HO⁻ could also lead to the mineralization of FOS.

3.4. Theoretical analysis

3.4.1. Hydrogen abstraction from FOS

To gain a deep insight into the degradation pathway of FOS, DFT calculation was performed to understand the selectivity of HO' and SO₄. As strong electrophilic agents, SO₄⁻ and HO⁻ could abstract a hydrogen atom from the FOS molecule, and then, the carbon-centered radicals could be generated. Hence, we further calculated the reaction barriers (ΔG) of the hydrogen extraction reaction from FOS mediated by HO' and SO_4^- . According to Fig. 5a and b, the ΔG values of the hydrogen abstraction reactions for FOS mediated by SO₄⁻ and HO⁻ are 6.89 and 4.62 kJ mol⁻¹, respectively. The calculation results illustrated that the hydrogen abstraction reaction on FOS by HO' is easier than that of SO_4^- . It is the reason that the experimentally determined $k_{\rm HO}^{-1}$ is much larger than $k_{SQ_{i}}$ shown in Fig. 2b. The difference in energy profiles may be attributed to the different stability of the reaction intermediates (Yang et al., 2017). HO' and SO₄-' can abstract H atoms from three possible C-H sites, as indicated in Fig. 5a and b. Given the lowest energy barrier, HO' and SO₄⁻ tend to abstract the hydrogen atom in site 1 and lead to the generation of P4. The further hydrogen abstraction from the degradation products generated the C-centered radicals and C-O radicals, resulting



Fig. 4. Proposed degradation pathways of FOS by UV/PS (Barrett and McBride, 2005; Sun et al., 2019).



Fig. 5. Calculated energy profiles (kcal/mol) for the oxidation of FOS via SO_4^- (a) and HO[•] (b) radical H-abstraction mechanism at the M06-2X/6-311+G (d, p) level; computed Mulliken charge (c) and FED (d) of FOS, where the green number represents the $FED_{HOMO}^2 + FED_{LUMO}^2$ data, and the blue number indicates the $2 FED_{HOMO}^2$ data of each atom in FOS.

in the formation of abundant polymerization products.

3.4.2. Electron transfer of FOS

According to the frontier molecular orbital theory, HOMO with high energy is prone to donate the electrons, whereas LUMO having low energy tends to accept electrons. As a result, the likelihood of the electron transfer reactions, including nucleophilic and electrophilic reactions, could be inferred based on the knowledge of frontier molecular orbits (Li et al., 2021). According to the calculated HOMO and LUMO (Fig. S5), the LUMO electron is likely to locate near the phosphate group, demonstrating that the nucleophilic radicals may favor the attack of the phosphate group. The distribution of charge, which showed that the P atom had the largest charge across the entire FOS molecule, served as extra proof for this conclusion (Fig. 5c).

After the optimization of molecular conformation, the calculated FED values of the C, P, and O atoms of FOS are shown in Fig. 5d. Theoretically, the higher the value of $\text{FED}_{\text{HOMO}}^2 + \text{FED}_{\text{LUMO}}^2$ is, the more vulnerable the molecule will be under the attack of ROS. Besides, structures with higher $2\text{FED}_{\text{HOMO}}^2$ values usually tend to trigger electrophilic reactions (Li et al., 2021). It can be seen that the double bond [P(4) = O(8)] possessed the largest $2\text{FED}_{\text{HOMO}}^2$ value, which is most likely attacked by HO', forming product P1 and leading to the release of HPO₄²⁻ in the UV/PS system. The HOMO orbital is mainly positioned on the epoxy group, making them more vulnerable to electron extraction.

3.5. Release of phosphate and mineralization

The release of phosphate and mineralization in the degradation of FOS were further examined. As displayed in Fig. S6a, phosphate accumulated in the solution with the degradation of FOS in all processes. The incremental concentration of phosphate was observed in the first 5 min, then reached a plateau where the accumulation of phosphate was retarded. The phosphate liberation of FOS by UV/PS treatment is higher compared to the UV treatment, which is consistent with FOS

degradation. The simulated maximum phosphate release was 7.03 and 1.41 μ M for the UV/PS and UV processes, respectively. Nevertheless, it was interesting to find that the stoichiometric ratio of $|\Delta C_{\text{phosphate}}/\Delta C_{\text{FOS}}|$ in each system was quite different from each other, and the ratio ranged from 0 to 0.55, and 0 to 0.79 in UV and UV/PS systems, respectively, implying that FOS degradation in these two systems may follow distinct pathways and mechanisms. Moreover, the higher mass stoichiometric ratio of $|\Delta C_{\text{phosphate}}/\Delta C_{\text{FOS}}|$ in the UV/PS system indicated that more organic phosphate can convert to inorganic phosphate, thus achieving better phosphate removal efficiency.

In addition, we also examined the TOC removal rate of FOS by UV/PS treatment. As illustrated in Fig. S7, gradual TOC reduction of FOS by UV/PS oxidation was observed, and the mineralization ratio was ca. 16.2 % after 60-min oxidation with 20 μM PS. It can be inferred from the obtained results that FOS and its degradation intermediates successively oxidized by SO₄- and HO', which ultimately resulted in the formation of CO₂ and H₂O (Drzewicz et al., 2012; Feng et al., 2020; Shen et al., 2022). Due to the release of H⁺, the solution pH will be greatly reduced for the PS-based oxidation treatment, which would affect the generation and consumption of radicals (Guan et al., 2011). Therefore, the pH change of the FOS reaction solution was also examined (Fig. S6b). We found that the pH value of the FOS reaction solution decreased gradually during 10 min and then reached an equilibrium pH of ca. 6.5. It should be noted that the pH change trend is consistent with the release of phosphate (Fig. S6b). As shown in Fig. 4, the species of released phosphate from FOS degradation is HPO_4^{2-} , which can be buffered by the H^+ released from the PS activation process (Eqs. (1) and (2)). We also compared the pH change of the degradation of phosphorus-free contaminant (represented by bisphenol AF) by UV/PS oxidation. Clearly, the pH of the bisphenol AF reaction solution gradually decreased from 7.0 to 4.5 in the 40-min reaction. Therefore, it can be concluded that the release of phosphate from FOS degradation contributes to the solution's pH stabilization, while a neural pH is beneficial to the formation of HO', as can be seen by Eq. (3) and Fig. 3b.

3.6. Toxicity evaluation

Biological toxicity has become an increasingly significant indicator in assessing the performance of wastewater treatment (Epa, 1991). Herein, E. coli and S. aureus were employed as the model gram-negative and gram-positive bacteria to assess how toxicity changed following treatment. The survival curves of E. coli under exposure to various concentrations of FOS were exhibited in Fig. 6a. It was found that the presence of only 10 µM of FOS inactivated approximately 80 % of E. coli within 8 h, and the sterilization was promoted with the increase of FOS concentration, which reflected that the antibiotics are highly toxic to E. coli and can completely inhibit their growth. Meanwhile, the PS at 20 µM did not affect the bacterial activity compared with the control group. Then, we tested the toxicity of the UV/PS-treated FOS solution at different treatment times. Obviously, UV/PS process drastically alleviated the toxicity of FOS at either 10 or 100 µM (Fig. 6b and c). For example, after 2- and 5-min treatment, the survival rate of *E. coli* with 10 or 100 μ M FOS increased from 24.9 % and 20.8 % to 77.5 % and 51.2 %, 89.4 %, and 55.8 %, respectively. When the treatment was prolonged to >20 min, no negative influence of 10 µM FOS on *E. coli* was found. Even increasing the initial concentration of FOS to 100 µM, the toxicity was almost eliminated within 40 min treatment. Fig. S8 indicated that FOS also inhibited the growth of S. aureus, while the inhibition was greatly alleviated after UV/PS treatment. As discussed in the context, a great proportion of FOS was degraded within 40 min, and the treated solution was therefore mainly comprised of the degradation products of FOS. The negligible sterilization of the treated solution evidenced that the products formed in UV/PS system possess much lower toxicity compared to that of FOS. Overall, treatment with UV/PS technique led to rapid degradation of FOS, and associated toxicity was reduced to a large extent. This finding highlights the effects of antibiotic degradation products on the emergence of bacterial resistance and emphasizes the significance of taking these effects into account when evaluating the environmental risks associated with antibiotics.

3.7. Economic comparison

The energy efficiency comparison of UV, UV/H₂O₂, and UV/PS processes for the removal of FOS was conducted based on the total cost of electrical energy and the oxidants (Katsoyiannis et al., 2011; Xiao et al., 2016), as detailed in Text S7. As shown in Table S4, the cost_{total} for the UV/H₂O₂ and UV/PS processes in DI water are calculated to be 0.33 and 0.17 USD m⁻³ order⁻¹, respectively, for the molar fraction of oxidant/FOS = 2, which are 9 and 17 times lower than that by UV direct photolysis (2.96 USD m⁻³ order⁻¹). The results implied that the UV/PS

process is more economically advantageous for FOS removal and that the low dose of oxidant is enough for the complete degradation of FOS. In addition, previous studies have indicated the application feasibility of persulfate-based in situ chemical oxidation (ISCO) for field-scale remediation of contaminated soil, groundwater, and wastewater (Bolourani et al., 2023; Matzek and Carter, 2016; Tsitonaki et al., 2010; Wacławek et al., 2017). Therefore, we believed that UV/PS technology can be potentially used to treat the FOS-contaminated soil or water matrix.

4. Conclusions

The current work demonstrated that UV/PS technique efficiently eliminates FOS contamination in water. The degradation of FOS followed the pseudo-first-order kinetics and increasing PS concentrations significantly improved FOS degradation. The results of quenching experiments showed that HO' is the dominant active species involved in the oxidation of FOS. Nature water constituents, including HA, CO_3^{2-} , and HCO_3^- inhibited FOS degradation significantly, whereas Cu^{2+} , Fe^{3+} , and SO_4^{2-} promoted the reaction. Higher oxidant dosage and prolonged oxidation times were needed to remove FOS from natural waters with high removal efficiency and more completely mineralize it. The possible degradation pathway of FOS was proposed based on the discovered transformation products and DFT analysis. The toxicity of FOS to bacteria E. coli and S. aureus after treatment was greatly eliminated. The outcomes of this study will contribute to a better understanding of the fundamental reaction mechanisms. The kinetics and mechanisms of FOS degradation by SO₄⁻ based AOPs are influenced by natural water, as well as an assessment of changes in FOS toxicity in the aqueous environment. They will also provide a theoretical basis for estimating the removal of FOS from water.

CRediT authorship contribution statement

Jingyi Wu: Investigation, Methodology, Validation, Data curation, Writing – original draft. Zhe Xu: Formal analysis, Methodology, Data curation, Writing – review & editing. Kun Yao: Methodology, Validation, Data curation. Zhu Wang: Formal analysis, Methodology, Data curation, Writing – review & editing. Ruobai Li: Formal analysis, Methodology, Data curation, Writing – review & editing. Linzi Zuo: Methodology, Validation, Data curation. Guoguang Liu: Resources, Supervision. Yiping Feng: Conceptualization, Validation, Investigation, Writing – review & editing, Visualization, Project administration, Funding acquisition.



Fig. 6. The survival of *E. coli* under the exposure of FOS before and after UV/PS oxidation. (a) The survival curves of *E. coli* exposed to different concentrations of FOS (0–500 μM); the survival curves of *E. coli* of (b) 10 and (c) 100 μM of FOS reaction solutions after UV/PS oxidation by 0, 2, 5, 20, and 40 min.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (21707019 and 22176130), and the Natural Science Foundation of Guangdong Province (2021A1515010019). L. Z. acknowledges funding support from the Science and Technology Program of Guangzhou (202102021066).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.167249.

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