



## Degradation of sulfamethoxazole by UV/persulfate in different water samples: Influential factors, transformation products and toxicity

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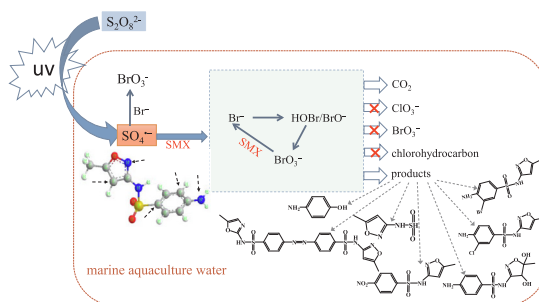
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### HIGHLIGHTS

- SMX was degraded by UV/PS system in sea water.
- The active sites of SMX were calculated by density functional theory.
- Neither trichloromethane nor halate was formed during the reaction.
- UV/PS is relatively safer than the traditional UV/NaClO disinfection.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Sulfate radical ( $\text{SO}_4^{\cdot-}$ ) based advanced oxidation processes are effective for the removal of antibiotics including sulfonamides from freshwater. However, few studies were focused on the degradation of sulfonamides in marine aquaculture water and seawater, as well as the impact of transformation products on seafood such as fishes. In this work, sulfamethoxazole (SMX) was treated with UV/persulfate (UV/PS) system in different water samples. Chloride ions ( $\text{Cl}^-$ ) had an inhibitory effect possibly due to the consumption and mutual quenching of reactive radicals. A slight promotion by bromide ions ( $\text{Br}^-$ ) was observed and should be related not only to the transformation of  $\text{Br}^-$ , but also to the properties of the SMX itself. Bicarbonate ions ( $\text{HCO}_3^-$ ) significantly inhibited degradation as it is a scavenger of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}\cdot$  in UV/PS. Sulfate ions ( $\text{SO}_4^{2-}$ ) showed a negligible impact on SMX degradation. The active sites of SMX were calculated to be the N1 and C7 atoms of the isoxazole ring, as well as the C9, C13 and N3 atoms of the benzene ring. Seven organic transformation products were identified by LC-MS/MS. Bromate ( $\text{BrO}_3^-$ ) and chloromethane as the potential human carcinogens were not detected from the reaction system of UV/PS with SMX in marine aquaculture water and seawater. Preliminary analysis of toxicity by the EPI Suite model, absorbable organic halogen (AOX) analysis and growth inhibition of *Chlorella vulgaris* proved that the UV/PS process could be used as a new disinfection method and it is relatively safer than traditional UV/NaClO disinfection.

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## 1. Introduction

Currently, antibiotics are extensively used to clear infections in both humans and animals [1,2]. However, the overuse and uncontrolled release of these compounds have direct ecological risks impacts [3,4]. For example, the development of antibiotic-resistant bacteria and antibiotic resistance genes have aroused great alarm around the world [5,6]. Due to their stability and biological resistance, the majority of antibiotics cannot be efficiently removed by conventional biological water treatment processes [7,8]. Sulfonamides are important classes of broad-spectrum antibiotics [9,10], and the degradations of sulfonamides by different physical and chemical methods has been investigated in the past few years [11,12].

Sulfate radical ( $\text{SO}_4^{\cdot-}$ ,  $E_0 = 2.5\text{--}3.1\text{ V}$ ) based advanced oxidation processes have been proven to be effective for the removal of antibiotics including sulfonamides [13,14]. Peroxymonosulfate (PMS) and persulfate (PS) have been used as radical precursors to generate  $\text{SO}_4^{\cdot-}$  by various activation methods [15,16]. As reported by Ismail et al. activating PS ions with UV light, solar irradiation, Fe(II) and UV/TiO<sub>2</sub> systems to generate  $\text{SO}_4^{\cdot-}$  were efficient for the removal of sulfaclozine [17,18]. UV irradiation is a strategy for activating peroxides and UV/PMS (PS) processes are effective for degrading sulfonamides. For instance, Ao et al. [19] investigated the degradation of sulfamethoxazole (SMX) by both UV/ PMS and UV/ PS processes. The results showed that SMX could be removed by direct UV photolysis, and the addition of PMS and PS obviously accelerated the degradation process. Sulfamethoxypyridazine (SMP) was also effectively removed by the UV/PS process and the removal rate was obviously increased compared with that of direct UV photolysis due to the formation of  $\text{SO}_4^{\cdot-}$  and hydroxyl radicals ( $\text{HO}\cdot$ ) [20].

Studies on the degradation of sulfonamides by UV/PMS (PS) have often been conducted in freshwater samples. The processes and results may be different in seawater because of the presence of the inorganic anions including chloride ions ( $\text{Cl}^-$ ), bromide ions ( $\text{Br}^-$ ), sulfate ions ( $\text{SO}_4^{2-}$ ) and bicarbonate ions ( $\text{HCO}_3^-$ ). As reported,  $\text{SO}_4^{\cdot-}$  can cause chain reactions including the generation of other active species [21]. Many studies have confirmed the formation of  $\text{HO}\cdot$  in UV/PMS (PS) processes under neutral and alkaline pH conditions [22]. In addition to  $\text{SO}_4^{\cdot-}$  and  $\text{HO}\cdot$ , halogen radicals and carbonate radicals can be generated in UV/PMS (PS) processes, and these species may also be responsible for the degradation of antibiotics [14,23]. Moreover, halates such as chlorate ( $\text{ClO}_3^-$ ) and bromate ( $\text{BrO}_3^-$ ) can be formed as a result of the reaction of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}\cdot$  with halide ions. Lutze et al. [24] investigated  $\text{SO}_4^{\cdot-}$  based water treatment processes in the presence of  $\text{Cl}^-$ , and the results indicated that chlorine atoms ( $\text{Cl}\cdot$ ) were the primary products which induced a sequence of reactions dependent on pH values.  $\text{ClO}_3^-$  and  $\text{HO}\cdot$  were generated under low pH ( $< 5$ ) and neutral pH conditions, respectively.  $\text{Br}^-$  was transformed to several reactive bromine species such as bromine atoms ( $\text{Br}\cdot$ ), dibromide radical ( $\text{Br}_2^{\cdot-}$ ) and hypobromous radical ( $\text{HBrO}^{\cdot-}$ ) upon oxidation by  $\text{SO}_4^{\cdot-}$  [25]. The reactive bromine species then reacted with humic substance to form bromide byproducts which could be further degraded by  $\text{SO}_4^{\cdot-}$ .  $\text{Br}^-$  was eventually transformed into  $\text{BrO}_3^-$  which is regarded as a potential 2B-level carcinogen by the International Agency for Research on Cancer.  $\text{BrO}_3^-$  was also confirmed by Fang et al. to be the final product of  $\text{Br}^-$  oxidation in the UV/PS process [26]. Hypobromous acid/hypobromite ( $\text{HOBr/OBr}^-$ ) were formed as intermediates. Notably, the presence of natural organic matter in real water samples decreased the amount of  $\text{BrO}_3^-$  formed due to the consumption of oxide species [27].

However, the reported studies did not provide information regarding the impacts of inorganic anions on the degradation of sulfonamides by UV/PMS (PS) in seawater or the formation of  $\text{ClO}_3^-/\text{BrO}_3^-$  in this process. The toxicities of the products to humans and other species should also be investigated.  $\text{SO}_4^{\cdot-}$  has been used for the disinfection of *Escherichia coli* in swimming pools [28]. Our previous

studies identified several unique chlorinated and brominated disinfection byproducts (DBPs) using various antibiotics and estrogen as precursors during a traditional NaClO disinfection of marine aquaculture water (a mixture of seawater and freshwater at a ratio of approximately 1:2). The bioaccumulative properties and toxicities of the DBPs were found to be more substantial than those of the precursors [12,29]. To ensure safety, UV/PMS (PS) processes may be used as an alternative disinfection method for marine aquaculture water.

The objectives of this study are (1) to investigate the degradation of sulfonamides by  $\text{SO}_4^{\cdot-}$  in the presence of the inorganic anions in seawater; (2) to identify the reaction products including the organic chlorinated products, brominated products and the inorganic products such as  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$ ; and (3) to preliminarily evaluate the toxicity of the reaction solution. The UV/PS process was used to produce  $\text{SO}_4^{\cdot-}$ , and SMX (a representative sulfonamide antibiotic which has been frequently detected in aquatic environment) was selected as the model material.

## 2. Materials and methods

### 2.1. Materials

SMX was obtained from Shanghai Yuanye Biological Co. Ltd., and the reference material was purchased from Aladdin. Sodium chloride (NaCl) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) of analytical-reagent grade were obtained from Sinopharm Chemical Reagent Company. Sodium bicarbonate ( $\text{NaHCO}_3$ ) of analytical-reagent grade was purchased from Tianjin Damao Chemical Reagent Factory. Sodium bromide (NaBr) of analytical-reagent grade was purchased from Chengdu Jinshan Chemical Reagent Company. Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) was of analytical-reagent grade and purchased from Chengdu Jinshan Chemical Reagent Company. In the preparation of mobile phases, analytical grade formic acid (HCOOH) was purchased from Chengdu Jinshan Chemical reagent Company. HPLC grade acetonitrile ( $\text{CH}_3\text{CN}$ ) and methanol ( $\text{CH}_3\text{OH}$ ) were received from Thermo Fisher Scientific. HCOOH was filtered through 0.45  $\mu\text{m}$  microporous filter membranes prior to use. Ultrapure water from a Milli-Q purification system (Millipore, Billerica, MA) was used to prepare all solutions.

### 2.2. Experimental procedures

The photo-reactor was designed by Shanghai Bilang Instruments and Equipment Co., Ltd. A high pressure mercury lamp was used to conduct photochemical experiments in a quasi-collimated beam apparatus. A quartz reaction tube (2.5 cm diameter, 18 cm length) was used in the photolysis experiments. 0.5 mL of methanol was added to the quartz tube to terminate the reaction, and the reaction solutions were putted in 10 mL colorimetric tube, followed by filtration and quantitative detection. Ultra performance liquid chromatography (UPLC) was used to determine the concentrations of SMX after reaction. The degradation kinetic of SMX in UV/PS system was assessed by a pseudo-first-order kinetic model. As shown in Eq. (1),  $K_{obs}$  is the pseudo-first-order rate constant ( $\text{min}^{-1}$ ),  $C_0$  and  $C$  is the initial concentration and the residual concentration of SMX, respectively.

$$\ln\left(\frac{C_0}{C}\right) = k_{obs}t \quad (1)$$

The purification and cultivation of *Chlorella vulgaris* were carried out under aseptic conditions. *Chlorella vulgaris* was cultivated to the logarithmic growth phase in an incubator. The initial pH of the *Chlorella vulgaris* was adjusted to 8, and the treated water samples that had been sterilized in an autoclave were inoculated into 100 mL conical flasks containing 50 mL of the algae. A blank sample with only algae was used as a control. All of the flasks were placed in an incubator. The aquacultures were maintained at 28 °C in a light/dark cycle of 12 h–12 h. The light intensity was set at approximately 3000 Lx. The flasks were

shaken twice per day to keep the algae suspended.

### 2.3. Analytical methods

Waters AcQuity UPLC system equipped with a Zorbax RX-C18 column (2.1 × 50 mm, 1.7 μM) and dual λ absorbance detector (Waters, USA) was used to analyze SMX and structurally related compounds. The concentrations of SMX were quantified at λ = 275 nm, the eluent water (0.3% formic acid) and acetonitrile at a ratio of 85:15 (v/v %) and a flow rate of 0.35 mL/min was used in this system. The concentrations of bromate and chlorate were determined by ion chromatography (ICS-900, Thermo Fisher Scientific), and volatile transformation products were analyzed by gas chromatography-mass spectrometry (GC-MS) (59575C, Agilent).

### 2.4. Identification of the transformation products

ESI-high resolution mass spectrometry couple using a Zorbax SB-C18 column (2.4 mm × 150 mm, 5 mm), a mass spectrometer and a diode-array UV/vis detector was used to identify the reaction products. The gradient elution system consisted of acetonitrile and 0.2% formic acid at a flow rate of 0.30 mL/min. The products were analyzed in a positive electrospray ionization mode (ESI+) with a mass scan range of *m/z* 50–1000. The XCalibur™ and ChemSpider databases were employed to deduce the structures and molecular formula of the compounds. Mass Frontier 7.0 was used to analyze the MS/MS fragments of the products. The concentration of TOC was measured with a TOC analyzer (TOC-VSH, Shimadzu).

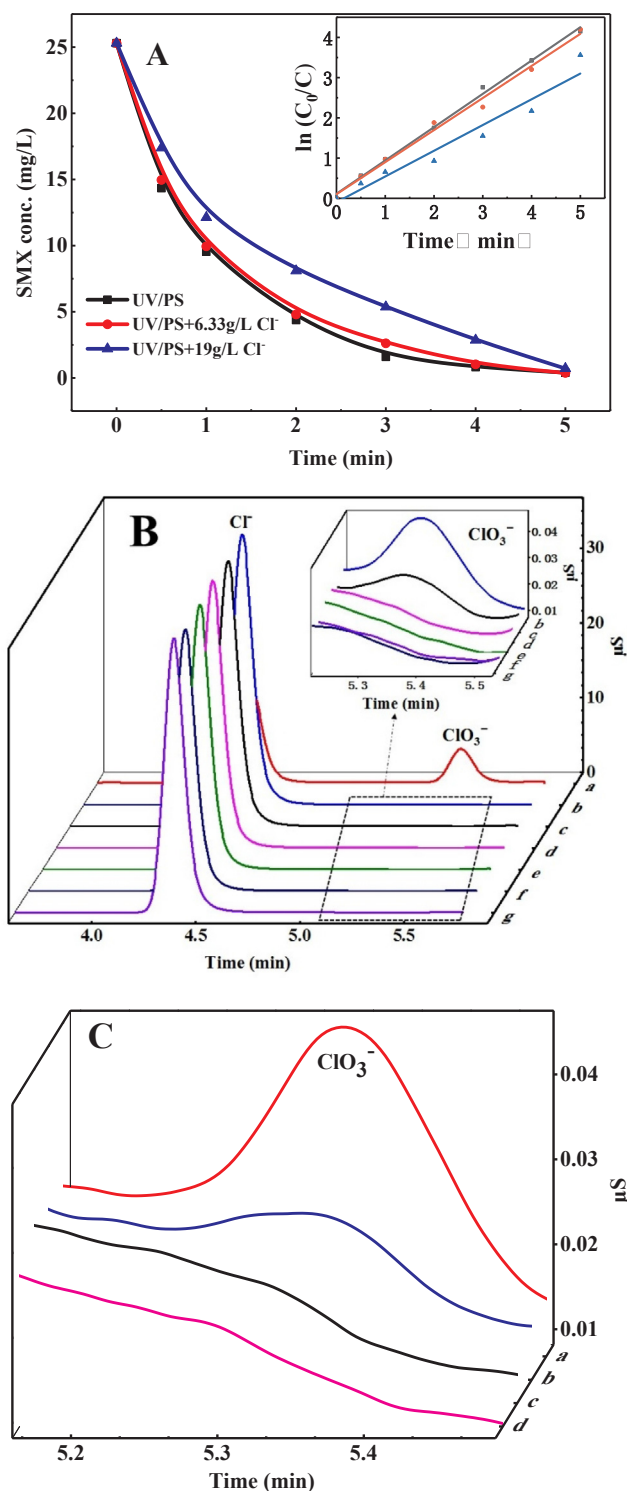
### 2.5. Toxicity analysis

EPI Suite was used to provide models for US-EPA risk assessment. Octanol–water partition coefficients (Kow values) and bioconcentration factors (BCF) as the accumulation parameters were calculated by EPI Suite. Meanwhile, absorbed organic halogen (AOX) which was measured by a total organic halogen analyzer (XPLOERER, TE instruments) and the growth inhibition effect against *Chlorella vulgaris* were chosen to provide preliminary toxicity analysis of the products. The densities of *Chlorella vulgaris* from different samples were measured using a visible spectrophotometer.

## 3. Results and discussion

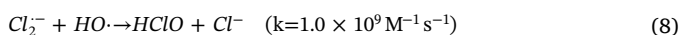
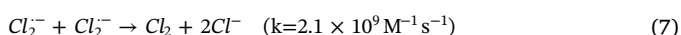
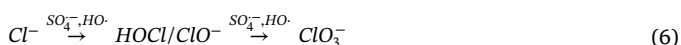
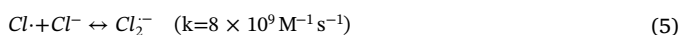
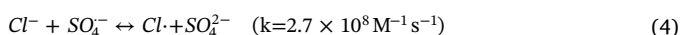
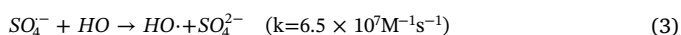
### 3.1. Effects of coexisting inorganic anions on the degradation of SMX by UV/PS

The degradations of SMX by UV/PS were primarily investigated in water samples containing different amounts of inorganic anions including Cl<sup>-</sup>, Br<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The concentrations of these inorganic anions were set according to their actual concentrations in fresh water, marine aquaculture water and seawater. As shown in Fig. 1(A), SMX degradation generally followed pseudo-first-order rate kinetics and the degradation rate constant of SMX decreased from 0.827 min<sup>-1</sup> to 0.797 min<sup>-1</sup> when the concentration of Cl<sup>-</sup> content increased from 0 g/L (freshwater) to 6.33 g/L (marine aquaculture water). Moreover, the rate constant obviously decreased to 0.640 min<sup>-1</sup> when the Cl<sup>-</sup> content increased to 19 g/L (seawater). This phenomenon was similar to the degradation of chloramphenicol by the UV/PS system [2] which could be attributed to the behavior of Cl<sup>-</sup> in the UV/PS system as shown in Eqs. 2–8 on the basis of reported studies [24]. Under the experimental conditions of Fig. 1, SO<sub>4</sub><sup>2-</sup> was limited compared with the relatively high amounts of Cl<sup>-</sup> in both marine aquaculture water and seawater. Cl· (E<sup>0</sup> = 2.4 V) would be initially generated by the reaction of SO<sub>4</sub><sup>2-</sup> with Cl<sup>-</sup> (Eq. (4)). Then, Cl· would also react with the excess Cl<sup>-</sup> resulting of the Cl<sub>2</sub><sup>-</sup> (E<sup>0</sup> = 2.0 V) formation (Eq. (5)). Finally, ClO<sub>3</sub><sup>-</sup> (E<sup>0</sup> = 1.45 V) would be formed as the stable product of the

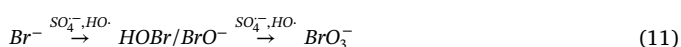
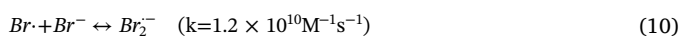
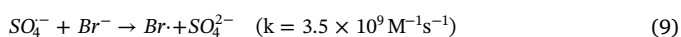


**Fig. 1.** Effect of Cl<sup>-</sup> on degradation of SMX and formation of ClO<sub>3</sub><sup>-</sup> in UV/PS system. A: Effect of Cl<sup>-</sup> concentration on degradation of SMX in UV/PS systems. B: Formation of ClO<sub>3</sub><sup>-</sup> in UV/PS system at the presence and absence of SMX. a: reference materials of Cl<sup>-</sup> and ClO<sub>3</sub><sup>-</sup>; b: UV/PS, 3 h; c: UV/PS, 1 h; d: UV/PS, 30 min; e: UV/PS, 10 min; f: UV/PS, 5 min; g: UV/PS + 0.1 mmol/L SMX, 3 h. C: effect of SMX concentration on the formation of ClO<sub>3</sub><sup>-</sup> after 3 h reaction. a: 0 mmol/L SMX; b: 0.02 mmol/L SMX; c: 0.05 mmol/L SMX; d: 0.1 mmol/L SMX. Initial concentration of SMX in Fig. A: 0.1 mmol/L; [PS]<sub>0</sub> = 2 mmol/L; Puv = 240 W; pH = 7.

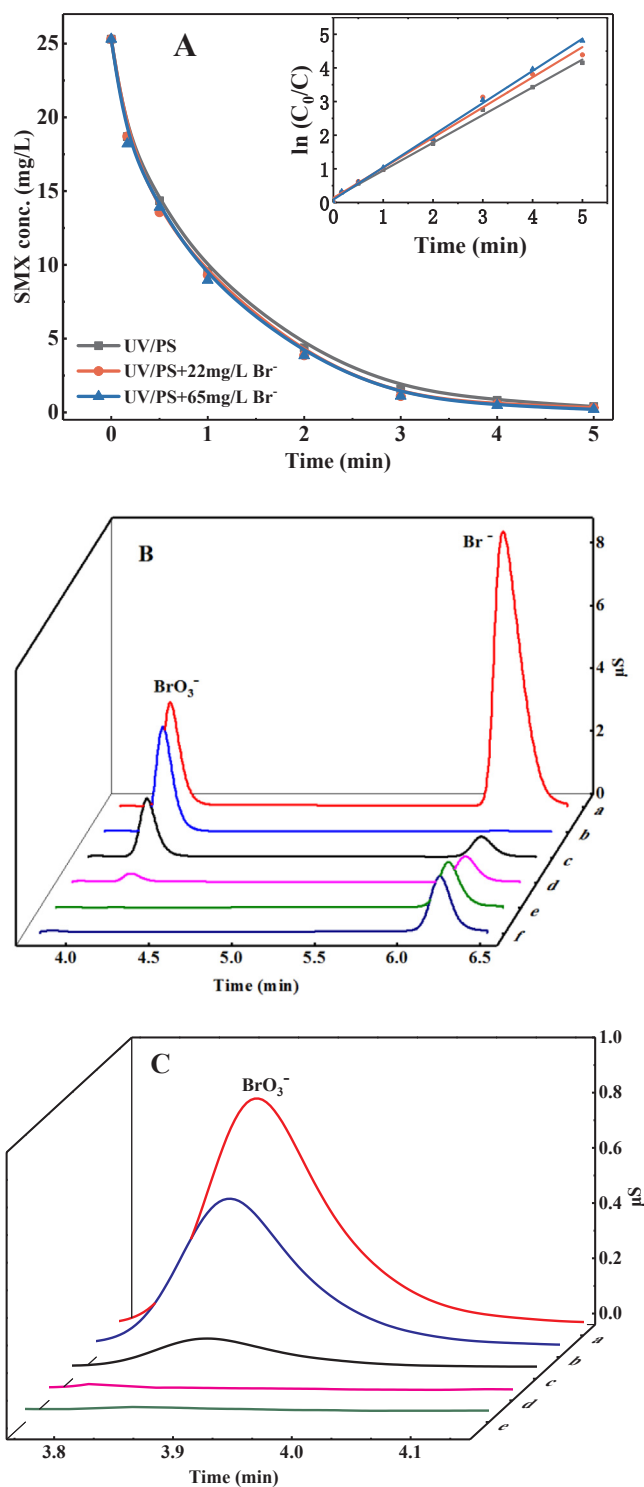
reactive chlorine radicals (RCs) oxidized by  $\text{SO}_4^{\cdot-}$  and  $\text{HO}\cdot$  (Eq. (6)). As shown in Fig. 1(B), in the absence of SMX,  $\text{ClO}_3^-$  was formed during the UV/PS process from  $\text{Cl}^-$  and was determined to be 232.2 mg/L after 3 h of reaction. However, the concentration of  $\text{ClO}_3^-$  decreased gradually with the addition of SMX into the reaction system as shown in Fig. 1(C). When the concentration of SMX was greater than 0.1 mmol/L,  $\text{ClO}_3^-$  was undetectable after 3 h of reaction. The data indicated that SMX could react with the RCs and impede the generation of  $\text{ClO}_3^-$ . Therefore, the inhibitory effect of  $\text{Cl}^-$  on the degradation efficiency of SMX could be attributed to: (1) the consumption of  $\text{SO}_4^{\cdot-}$  by the substantial amount of  $\text{Cl}^-$  present; (2) the formations of RCs, which have oxidation capacities that are relatively weaker than that of  $\text{SO}_4^{\cdot-}$ ; (3) the mutual quenching of the generated RCs and  $\text{HO}\cdot$  as in Eqs. (7–8) which were faster than the degradation of SMX [24].



The influence of  $\text{Br}^-$  on the degradation efficiency of SMX by UV/PS was also investigated. Fig. 2(A) showed the degradation rates at different  $\text{Br}^-$  concentrations (0–65 mg/L) under UV intensity of 240 W at pH 7. The degradation of SMX in 5 min was slightly promoted by  $\text{Br}^-$ , and pseudo-first-order degradation rate constants of approximately  $0.827 \text{min}^{-1}$ ,  $0.898 \text{min}^{-1}$  and  $0.964 \text{min}^{-1}$  were recorded at  $\text{Br}^-$  concentrations of 0 mg/L (freshwater), 22 mg/L (marine aquaculture water), and 65 mg/L (seawater), respectively. The slight promotion was also found in the degradation of benzophenone-4 by UV and  $\text{Fe}^{2+}$  activated PS at a  $\text{Br}^-$  concentration of 400 mg/L as reported by Luca et al. Moreover, the presence of  $\text{Br}^-$  significantly enhanced the degradation of nitrobenzene and inhibited the degradation of atrazine, ampicillin and nitrobenzoic acid conversely under the same reaction conditions [27]. The results indicated that the effect of  $\text{Br}^-$  on the degradation of organic matter by UV/PS is related not only to the transformation of  $\text{Br}^-$ , but also to the properties of the organic matter itself. In general, similar to the reaction of  $\text{Cl}^-$  with  $\text{SO}_4^{\cdot-}$ , reactive bromine radicals including  $\text{Br}\cdot$  ( $E_0 = 2.00 \text{V}$ ) and  $\text{Br}_2^{\cdot-}$  would be formed via Eqs. (9) and (10) [25]. Then,  $\text{BrO}_3^-$  would be formed upon exposure to sufficient  $\text{SO}_4^{\cdot-}$  as Eq. (11) [26]. As shown in Fig. 2(B), in the absence of SMX,  $\text{BrO}_3^-$  was formed during the reaction of UV/PS with  $\text{Br}^-$  and was determined to be 29.76 mg/L after 3 h of reaction. However, the concentration of  $\text{BrO}_3^-$  also decreased gradually with the addition of SMX as shown in Fig. 2(C). When the concentration of SMX was greater than 0.1 mmol/L,  $\text{BrO}_3^-$  was undetectable after 3 h of reaction. The formation of  $\text{BrO}_3^-$  indicated that the reactive bromine radicals could react with SMX with a slower rate than  $\text{SO}_4^{\cdot-}$ . Under the experimental conditions, 92% of the  $\text{Br}^-$  was converted to  $\text{BrO}_3^-$  in the absence of  $\text{Br}^-$  while the addition of SMX inhibited the formation of this carcinogen. Nevertheless, more research is still needed to better understand the effect of  $\text{Br}^-$  on the degradation of SMX and other organic matter.



The influence of the  $\text{HCO}_3^-$  concentration on SMX degradation by



**Fig. 2.** Effect of  $\text{Br}^-$  on degradation of SMX and formation of  $\text{BrO}_3^-$  in UV/PS system. A: Effect of  $\text{Br}^-$  concentration on degradation of SMX in UV/PS systems. B: Formation of  $\text{BrO}_3^-$  in UV/PS system at the presence and absence of SMX. a: reference materials of  $\text{Br}^-$  and  $\text{BrO}_3^-$ ; b: UV/PS, 3 h; c: UV/PS, 30 min; d: UV/PS, 10 min; e: UV/PS, 5 min; f: UV/PS + 0.1 mmol/L SMX, 3 h. C: effect of SMX concentration on the formation of  $\text{BrO}_3^-$  after 3 h reaction. a: 0 mmol/L SMX; b: 0.01 mmol/L SMX; c: 0.02 mmol/L SMX; d: 0.05 mmol/L SMX; e: 0.1 mmol/L SMX. Initial concentration of SMX in Fig. A: 0.1 mmol/L;  $[\text{PS}]_0 = 2 \text{mmol/L}$ ;  $P_{\text{UV}} = 240 \text{W}$ ;  $\text{pH} = 7$ .

UV/PS is shown in Fig. 3(A). The addition of  $\text{HCO}_3^-$  significantly inhibited the degradation of SMX. The degradation rate constant decreased from  $0.735 \text{min}^{-1}$  to  $0.404 \text{min}^{-1}$  and  $0.282 \text{min}^{-1}$  when the



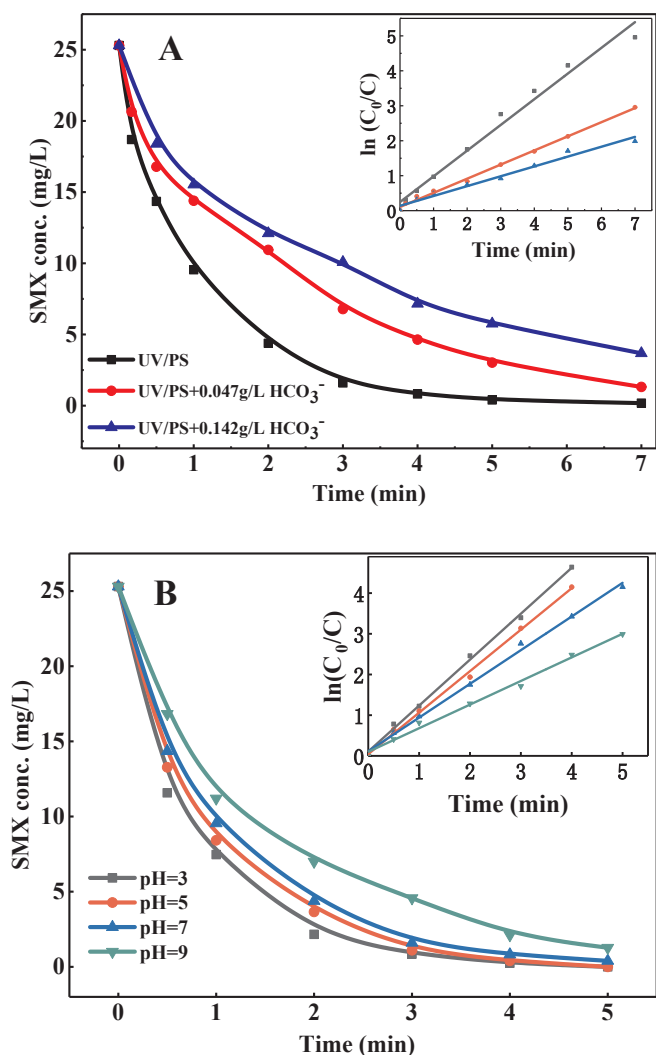
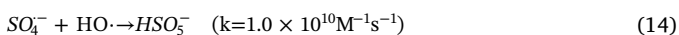
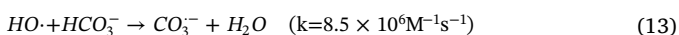
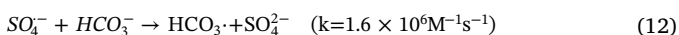


Fig. 3. Effect of  $\text{HCO}_3^-$  (A) and pH value (B) on degradation of SMX.  $[\text{SMX}]_0 = 0.1 \text{ mmol/L}$ ;  $[\text{PS}]_0 = 2 \text{ mmol/L}$ ;  $P_{\text{uv}} = 240 \text{ W}$ .

concentration of  $\text{HCO}_3^-$  increased from 0 g/L (freshwater) to 0.047 g/L (marine aquaculture water) and 0.142 g/L (seawater), respectively. A similar inhibition by  $\text{CO}_3^{2-}$  on SMX degradation in UV/PS treatment was reported by Liu et al., as the addition of  $\text{CO}_3^{2-}$  would result in the equilibration of  $\text{CO}_3^{2-}$ - $\text{HCO}_3^-$  [30]. This phenomenon can be attributed to two factors: (1) It was noted that the pH values of the SMX solutions were 6.0, 7.6 and 8.9 at the above three different concentrations of  $\text{HCO}_3^-$ . As shown in Fig. 3(B), the SMX degradation rate decreased from  $1.112 \text{ min}^{-1}$  to  $0.525 \text{ min}^{-1}$  with pH value increase from 3 to 9. The results were consistent with the literature reports. The quantity and composition of the active species depended largely on the pH of the reaction solution [19]. Under alkaline conditions, reactive radical  $\text{HO}\cdot$ ,  $\text{HCO}_3\cdot$  and  $\text{CO}_3^{\cdot-}$  with a lower redox potentials would be formed (Eqs. (3), (12) and (13)). Moreover, the coexistence of  $\text{HO}\cdot$  and  $\text{SO}_4^{\cdot-}$  would lead to mutual quenching which inhibited SMX degradation (Eq. (14)) [19,31].



In addition, the pH of the solution also affected the speciation of SMX (cationic, neutral, and anionic) which would then affect the degradation rate. As reported, one basic amine group ( $-\text{NH}_2$ ) with  $\text{pKa}_1$  of

1.85 and one acidic amide group ( $-\text{NH}-$ ) with  $\text{pKa}_2$  of 5.60 were included in the ionizable group of SMX [32]. An increase in pH decreased the proportion of amide groups that were able to release a proton. Therefore, acidic conditions favored the degradation of SMX in the UV/PS system. (2)  $\text{HCO}_3^-$  is a scavenger of reactive radicals including  $\text{SO}_4^{\cdot-}$  and  $\text{HO}\cdot$  in the UV/PS system. The generated reactive radicals such as  $\text{CO}_3^{\cdot-}$  and  $\text{HCO}_3\cdot$  were less reactive than  $\text{SO}_4^{\cdot-}$  and  $\text{HO}\cdot$ .

Sulfate ( $\text{SO}_4^{2-}$ ) is another abundant inorganic anion in seawater, therefore, the effect of  $\text{SO}_4^{2-}$  on the degradation of SMX in UV/PS was also investigated. The degradation rate constant of SMX with  $\text{SO}_4^{2-}$  concentrations of 0 g/L (freshwater), 0.09 g/L (marine aquaculture water) and 2.71 g/L (seawater) was  $0.827 \text{ min}^{-1}$ ,  $0.833 \text{ min}^{-1}$  and  $0.825 \text{ min}^{-1}$ , respectively. This result was consistent with the literature [19]. The reactions of  $\text{SO}_4^{2-}$  with reactive radicals such as  $\text{SO}_4^{\cdot-}$  and  $\text{HO}\cdot$  was much slower than those of the other inorganic anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{HCO}_3^-$  [33]. Therefore, the neglectable impact of  $\text{SO}_4^{2-}$  on the degradation of SMX can be attributed to the fact that  $\text{SO}_4^{2-}$  neither changed the pH of the solution nor participated in the UV/PS reaction as a robust scavenger for reactive radicals.

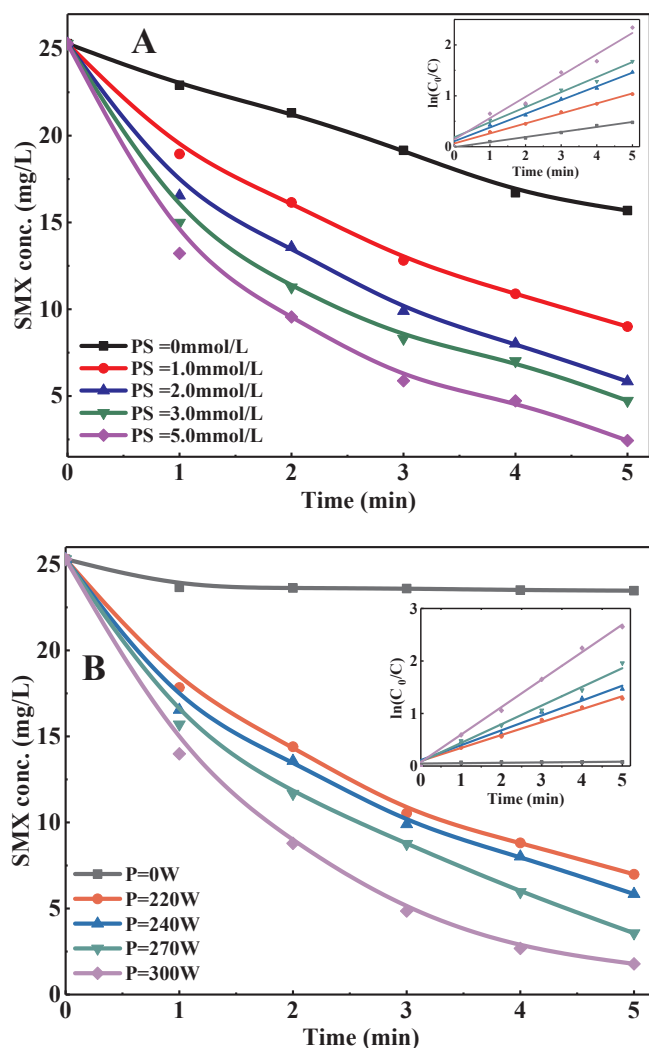
### 3.2. Effects of PS concentration and UV-light intensity on the degradation of SMX

To evaluate the influence of the operating parameters on SMX removal, different concentrations of PS and intensities of UV-light were employed. As shown in Fig. 4(A), the reaction rate constant increased from  $0.099 \text{ min}^{-1}$  to  $0.418 \text{ min}^{-1}$  when the concentration of  $\text{Na}_2\text{S}_2\text{O}_8$  was increased from 0 mmol/L to 5 mmol/L. SMX could be degraded by UV-light directly, but the addition of oxidants could significantly enhance the degradation rate. The results were consistent with literature reports on the degradation of tetrabromobisphenol A and 2,2,3,3-tetrafluoro-1-propanol by UV/PS [21]. The degradation of SMX was influenced by  $\text{SO}_4^{\cdot-}$  which is the dominant reactive species in the UV/PS system. As  $\text{SO}_4^{\cdot-}$  was formed upon UV light activation, the addition of PS increased the concentration of  $\text{SO}_4^{\cdot-}$  in the system, meaning that the higher PS dosage resulted in higher  $\text{SO}_4^{\cdot-}$  contents and faster SMX degradation. However, some studies suggested that the degradation efficiency of contaminants decreased at high PS contents due to the quenching of free radicals [34]. Obviously, the oxidant content was below the inhibition point in this study. In contrast, almost no degradation of SMX was observed in the absence of UV light. The rate constant increased from  $0.246 \text{ min}^{-1}$  to  $0.524 \text{ min}^{-1}$  when the UV light intensity was increased from 220 W to 300 W because UV light activated the PS to produce  $\text{SO}_4^{\cdot-}$  as shown in Fig. 4(B).

### 3.3. Identification of organic transformation products

As shown in Fig. 5, the TOC removal efficiencies by UV/PS were 4.6%, 32.4% and 54.6% in seawater samples after 5 min, 2 h and 3 h of reaction, respectively. When the reaction time was extended to 8 h, the TOC removal efficiency only increased to approximately 70.7% indicating that UV/PS oxidation induced incomplete degradation of SMX. In fact, it is difficult to completely degrade organic pollutants to  $\text{CO}_2$  by advanced oxidation processes including UV/PS. For example, during the oxidation of ciprofloxacin (CIP) by UV/PS, only a slight variation of TOC was observed after a reaction time of 60 min. Various oxidized intermediates were identified and the C-N bonds in CIP remained [35]. Therefore, the organic transformation products were analyzed based on the structure of SMX.

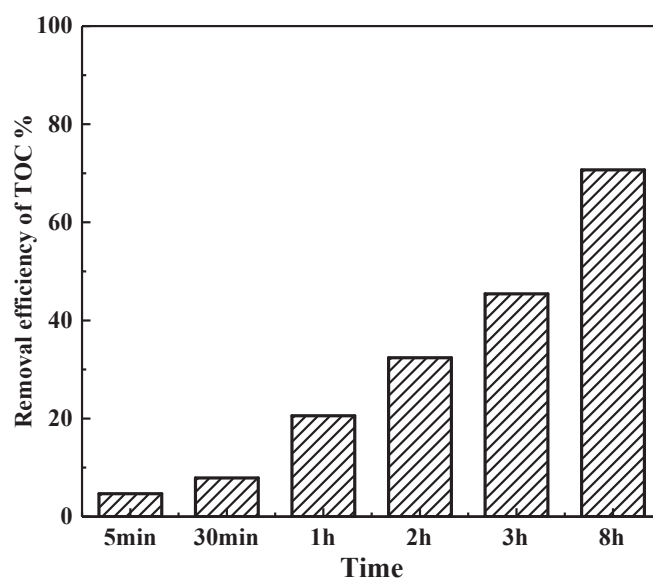
First, the SMX molecule was calculated by Gaussian09 program and investigated with density functional theory (DFT) to deduce the characteristic of structure and its charge distribution. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the associated gap energy of SMX were calculated by the B3LYP level with the 6-311 + G (2d, 2p) basis set by using the Gaussian09 program. All geometry optimizations and natural bond



**Fig. 4.** Effect of PS concentration (A) and UV intensity (B) on degradation of SMX. UV intensity in Fig. A: 240 W; initial concentration of PS in Fig. B: 2 mmol/L;  $[SMX]_0 = 0.1$  mmol/L;  $[Cl^-]_0 = 6.33$  g/L;  $[Br^-]_0 = 22$  mg/L;  $[HCO_3^-]_0 = 0.047$  g/L;  $[SO_4^{2-}]_0 = 0.903$  g/L; pH = 7.

orbital (NBO) analyses were performed using Gaussian09 program. The HOMO - LUMO energy separation was used as a simple indicator and conventional measure of kinetic stability with respect to the activated complex for further chemical reaction [36]. A large HOMO-LUMO gap ( $\Delta E$ ) correspond to high kinetic stability and low chemical reactivity because it is not conducive to extracting electrons from a low-lying HOMO and adding electrons to a high-lying LUMO [37]. The HOMO and LUMO of SMX was shown in Fig. 6. The  $\Delta E$  was calculated to be as high as 5.259 eV indicating that SMX is very stable [38].

The HOMO and LUMO of SMX showed that the electrons were locally distributed. The electrons of the HOMO was mainly distributed on the benzene ring and the double-bond between carbon and nitrogen in isoxazole ring which were the main electron donor of SMX. The data calculated by Gaussian09 indicated that the charge distribution on the N1, C5 and C7 atoms were  $-0.189$  eV,  $-0.622$  eV and  $-0.361$  eV, respectively. The high electronegativities caused these atoms more vulnerable to attack by free radicals through electrophilic reactions. In addition, the electrons of the LUMO were mainly distributed on the benzene ring and the charge distribution on the C9 atom, C13 atom and N3 atom were calculated to be  $-0.332$  eV,  $-0.254$  eV and  $-0.778$  eV, respectively. The C9 atom may also be attacked by radicals leading to the cleavage of the S-C bond. The potential destruction of the aniline groups was attributed to the electrophilic reaction of  $SO_4^{\cdot-}$  with the



**Fig. 5.** Removal efficiency of TOC by UV/PS system.  $[SMX]_0 = 0.1$  mmol/L;  $[PS]_0 = 2$  mmol/L;  $P_{uv} = 240$  W;  $[Cl^-]_0 = 19$  g/L;  $[Br^-]_0 = 65$  mg/L;  $[HCO_3^-]_0 = 0.142$  g/L;  $[SO_4^{2-}]_0 = 2.71$  g/L; pH = 7.

N3 atom.

The transformation products were then analyzed based on the structure of the parent compound SMX. In terms of the electron distribution on the HOMO and LUMO,  $SO_4^{\cdot-}$ , an electrophile, tends to attack the groups with dense electrons. Seven organic transformation products in marine aquaculture water and seawater were identified by LC-MS/MS, simultaneously. Combined with the isotope peak clusters and the accurate masses obtain from their mass spectra, the products have been identified (Fig. S1-S2). The identified products were formed by cleavage reactions such as photolysis and oxidation by reactive species. As shown in Scheme 1, the formation of the P287-1 occurred via the oxidation of the oxazole ring by  $SO_4^{\cdot-}$ . An electrophilic attack of  $SO_4^{\cdot-}$  occurred on the olefinic double bond between the C6 atom and the C7 atom to generate the olefinic radical, and subsequent hydrolysis of the olefinic radical led to the formation P287-1. The N3 atom of the  $-NH_2$  group was attacked by  $SO_4^{\cdot-}$  electronically, resulting in the formation of an N-centered radical. And P502, a dimeric product was then formed by the coupling of the N-centered radical. P283 was also generated from the reaction of the N-centered radical with water to form aniline radicals, and then aniline nitrogen was then oxidized to form P283 [39]. The S-C bond was also attacked resulting in bond cleavage and the formation of P162. P109 was then formed following the oxidation of aniline. Two halogenated organic DBPs were identified in marine aquaculture water and seawater. Chlorine substitution and bromine substitution occurred at C13 and formed a mono-chlorinated compound P287-2 and mono-bromated compound P330. Substitution occurred on the *ortho*-position to  $-NH_2$  group, it was described as an ring-chlorinated [40]. For comparison with products in seawater, the degradation products obtained in freshwater were identified by LC-MS/MS. The results showed that except for the two halogenated organic products, all of the other products (including P109, P162, P283, P287-1 and P502) could be found in freshwater. No halogenated organic DBPs were found in freshwater due to the absence of  $Cl^-$  and  $Br^-$ . The volatile transformation products were detected by GC-MS. As shown in Fig. S3, after comparison with the peak of mass spectrogram in the National Institute of Standards and Technology (NIST) library, characteristic peaks of  $CO_2$  were detected during the reaction of UV/PS with SMX in marine aquaculture water and seawater. The results of chromatograms and mass spectrograms at different reaction times (1 min, 5 min, 3 h) proved that haloalkanes were not generated.

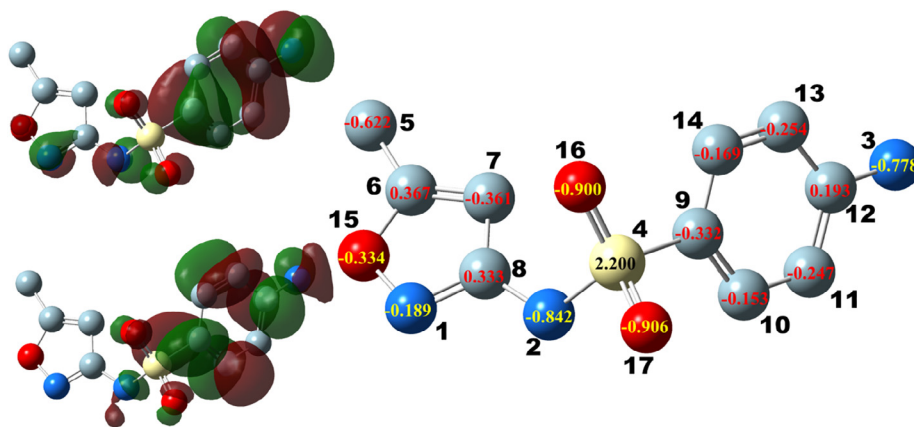


Fig. 6. The HOMO, LUMO and net charge distribution of SMX.

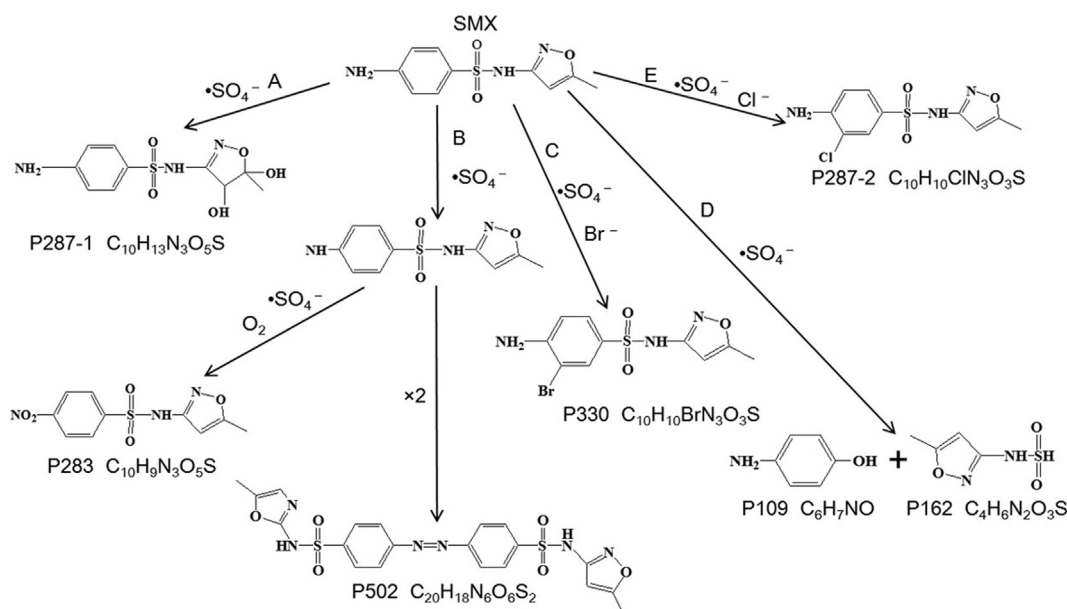
Considering the possibility of UV/PS being used as a disinfectant for marine aquaculture water, the transformation products were compared with the disinfection byproducts (DBPs) formed in the traditional UV/NaClO disinfection process (Fig. S3). Our previous study reported four Br-DBPs based on SMX in marine aquaculture water and seawater samples [12]. Moreover, the dichloromethane (a 2A-level carcinogenic organic matter) and ethyl acetate (common DBPs) were detected in the reaction system of UV/NaClO with SMX. The comparison indicated that UV/PS is a safer disinfection method for marine aquaculture water based on the formation of DBPs.

### 3.4. Preliminary analysis of the toxicity

The bioaccumulation of transformation products were estimated by the EPI Suite model and two predictors log Kow and log BCF were chosen to demonstrate the different responses on fish (normalized to 10 g fish) [41,42]. The compound with greater value of log Kow and log BCF will readily soluble in nonpolar media and be more easily absorbed by cellular organisms. As shown in Table 1, the log Kow and log BCF values for P287-1, P163 and P109 were smaller than SMX indicating that they were less likely to accumulate in fish than those of SMX. In addition, the values of P283 were slightly higher than those of SMX,

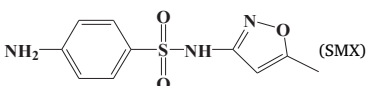
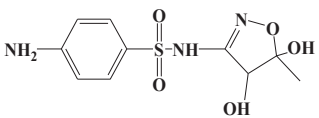
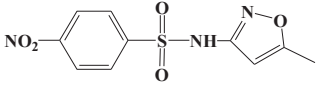
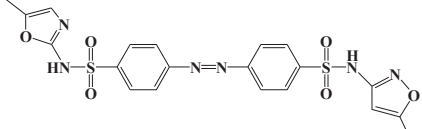
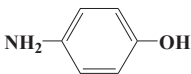
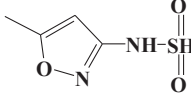
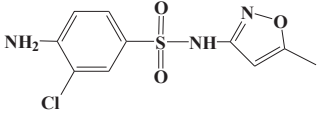
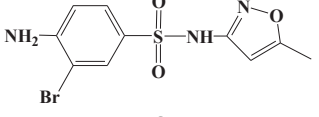
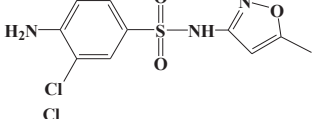
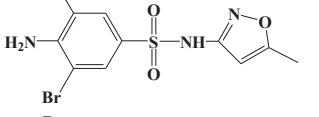
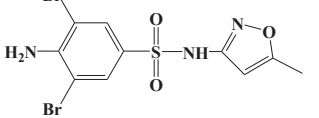
and the log Kow and log BCF were 1.88 and 2.93, respectively. P502 exhibited higher bioaccumulation in fish as a dimeric product. Nevertheless, P502 was also a product of the UV/NaClO disinfection process. In addition to P502, the halogenated DBPs with higher log Kow and log BCF were more likely to accumulate biologically, the log Kow and log BCF values of P287-2 were 0.289 and 1.13, respectively. The values of P330 rose slightly as Br-DBPs, the log Kow and log BCF values were 0.428 and 1.37, respectively. However, the log Kow and log BCF values of the Br-DBPs in the UV/NaClO disinfection process were larger than those of the products in the UV/PS system.

In addition, experiments were carried out to determine the AOX of different water samples during UV/PS and UV/NaClO. AOX was analyzed because it positively correlates with the overall toxicity of a water sample containing halogens. As shown in Table 1, AOX was undetectable in freshwater and marine aquaculture water samples in the UV/PS process, but the concentration of AOX reached 1.17 mg/L in seawater. As expected, the concentration of AOX in UV/NaClO was obviously greater than that in UV/PS. The concentrations of AOX were 3.18 mg/L, 4.07 mg/L to 7.43 mg/L in freshwater, marine aquaculture water and seawater, respectively. The larger AOX contents in the UV/NaClO system should be attributed to the formation of halogenated DBPs.



Scheme 1. Possible degradation pathways of SMX in UV/PS system in seawater. [SMX]<sub>0</sub> = 0.1 mmol/L; [PS]<sub>0</sub> = 2 mmol/L; Puv = 240 W; [Cl<sup>-</sup>]<sub>0</sub> = 19 g/L; [Br<sup>-</sup>]<sub>0</sub> = 65 mg/L; [HCO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.142 g/L; [SO<sub>4</sub><sup>2-</sup>]<sub>0</sub> = 2.71 g/L; pH = 7.

**Table 1**  
Transformation products of SMX in different water samples by UV/PS process and relevant toxicity parameters.

Method	Product	Formula	Log BCF	Log Kow	AOX(mg/L)	Chlorella growth inhibition ratio within 48 h(%)	
		C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S	0.168	0.89	/	9.6	
UV/PS		C <sub>10</sub> H <sub>13</sub> N <sub>3</sub> O <sub>5</sub> S	< 0	< 0	freshwater	/	10.9
		C <sub>10</sub> H <sub>9</sub> N <sub>3</sub> O <sub>5</sub> S	0.366	1.22			
		C <sub>20</sub> H <sub>18</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub>	1.88	2.93	marine aquaculture water	/	13.28
		C <sub>6</sub> H <sub>7</sub> NO	< 0	0.04			
		C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub> S	< 0	< 0	seawater	1.17	22.31
		C <sub>10</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>3</sub> S	0.289	1.13			
		C <sub>10</sub> H <sub>10</sub> BrN <sub>3</sub> O <sub>3</sub> S	0.428	1.37			
UV/NaClO		C <sub>10</sub> H <sub>10</sub> ClN <sub>3</sub> O <sub>3</sub> S	0.289	1.13	fresh water	3.18	13.96
		C <sub>10</sub> H <sub>9</sub> BrClN <sub>3</sub> O <sub>3</sub> S	0.944	2.02	marine aquaculture water	4.07	17.95
		C <sub>10</sub> H <sub>9</sub> Br <sub>2</sub> N <sub>3</sub> O <sub>3</sub> S	1.119	2.26	sea water	7.43	25.38

[SMX]<sub>0</sub> = 0.1 mmol/L; [PS]<sub>0</sub> = 2 mmol/L; Puv = 240 W; pH = 7.

Marine aquaculture water: [Cl<sup>-</sup>]<sub>0</sub> = 6.33 g/L; [Br<sup>-</sup>]<sub>0</sub> = 22 mg/L; [HCO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.047 g/L; [SO<sub>4</sub><sup>2-</sup>]<sub>0</sub> = 0.903 g/L.

Seawater: [Cl<sup>-</sup>]<sub>0</sub> = 19 g/L; [Br<sup>-</sup>]<sub>0</sub> = 65 mg/L; [HCO<sub>3</sub><sup>-</sup>]<sub>0</sub> = 0.142 g/L; [SO<sub>4</sub><sup>2-</sup>]<sub>0</sub> = 2.71 g/L.

Finally, the toxicity of the reaction solution was evaluated by the growth inhibition of *Chlorella vulgaris*. As shown in Table 1, after a growth test of 48 h, the inhibition ratio was 9.6% when SMX (25.3 mg/L) alone was added to the aquaculture medium. The inhibition ratios gradually increased under the UV/PS/SMX oxidation system in the three different water samples, and the rates increased with increasing halogen ion content and reached 10.9%, 13.28% and 22.31% in freshwater, marine aquaculture water and seawater, respectively. Similar to the UV/PS system, the inhibition ratios also gradually increased in the three different water samples in UV/NaClO disinfection

process. The inhibition ratios were 13.96%, 17.95% and 25.38% in freshwater, marine aquaculture water and seawater, respectively. The slightly negative impact might be attributed to the greater toxicity of the products in UV/NaClO relative to those of UV/PS. These results further indicated that UV/PS is more suitable for the application of disinfection of marine aquaculture water.

#### 4. Conclusions

The UV/PS system was used to degrade SMX, an antibiotic in water



samples containing different amounts of inorganic anions. The concentrations of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  were set according to their actual concentrations in freshwater, marine aquaculture water and seawater. The results showed that the degradation rates of SMX decreased with increasing  $\text{Cl}^-$  and  $\text{HCO}_3^-$  concentrations. The inhibitory effect of  $\text{Cl}^-$  could be attributed to: (1) the consumption of  $\text{SO}_4^{\cdot-}$  in the presence of a large excess of  $\text{Cl}^-$ ; (2) the formation of RCs with oxidation capacities that are relatively weaker than that of  $\text{SO}_4^{\cdot-}$ ; and (3) the mutual quenching of the generated RCs and  $\text{HO}\cdot$ . Reactive bromine radicals including  $\text{Br}\cdot$  and  $\text{Br}_2\cdot$  would be formed by the oxidation of  $\text{Br}^-$  by  $\text{SO}_4^{\cdot-}$ . When 0.05 mmol/L SMX was added to the UV/PS system in seawater containing  $\text{Cl}^-$  and  $\text{Br}^-$ , neither  $\text{ClO}_3^-$  nor  $\text{BrO}_3^-$  were detected indicating that SMX could impede their generation. Except that the  $\text{HCO}_3^-$  is a scavenger of reactive radicals, the change in pH upon addition of  $\text{HCO}_3^-$  could account for the inhibition of SMX degradation because the degradation rate decreases with increasing pH.  $\text{SO}_4^{2-}$  had no significant influence on the degradation of SMX because  $\text{SO}_4^{2-}$  neither changed the pH of the solution nor participated in the UV/PS reaction as a robust scavenger of reactive radicals.

The TOC removal efficiency was only approximately 70.7% after a reaction of 8 h in seawater indicating that the UV/PS oxidation induced incomplete degradation of SMX. Seven transformation products were formed through the oxidation of the isoxazole ring, the coupling of the N-centered radical generated by the reaction of  $\text{SO}_4^{\cdot-}$  with the  $-\text{NH}_2$  group, the oxidation of aniline nitrogen and the cleavage of the S-C bond. The bioaccumulation of the transformation products was estimated by EPI Suite via their log K<sub>ow</sub> and log BCF values. The toxicity of the UV/PS/SMX reaction solution was then evaluated based on the concentrations of AOX and the growth inhibition effects on *Chlorella vulgaris*. Compared with traditional UV/NaClO disinfection, the transformation products of SMX formed in the UV/PS in seawater were less likely to accumulate in organisms such as fish. Moreover, the concentrations of AOX and the inhibition ratios of *Chlorella vulgaris* in the UV/NaClO system were obviously greater than those in the UV/PS system. All of these results confirm that UV/PS is more suitable for the disinfection of marine aquaculture water.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.122354>.

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