

Degradation of 17 β -estradiol by UV/persulfate in different water samples

Yunjie Zhu^a, Yanan Shao^{a,b}, Min Wei^a, Kefu Yu^{a,c,d}, Yuanyuan Zhang^{a,c,d,*}, Jianping Huang^a and Xinyue Yin^a

^a School of Marine Sciences, Guangxi University, Nanning 530004, China

^b College of Environmental Science and Engineering, Hunan University, Changsha 410082, China

^c Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, China

^d Guangxi Key Laboratory on the Study of Coral Reefs in the South China Sea, Nanning, 530004, China

*Corresponding author. E-mail: jiedeng05@sina.com

ABSTRACT

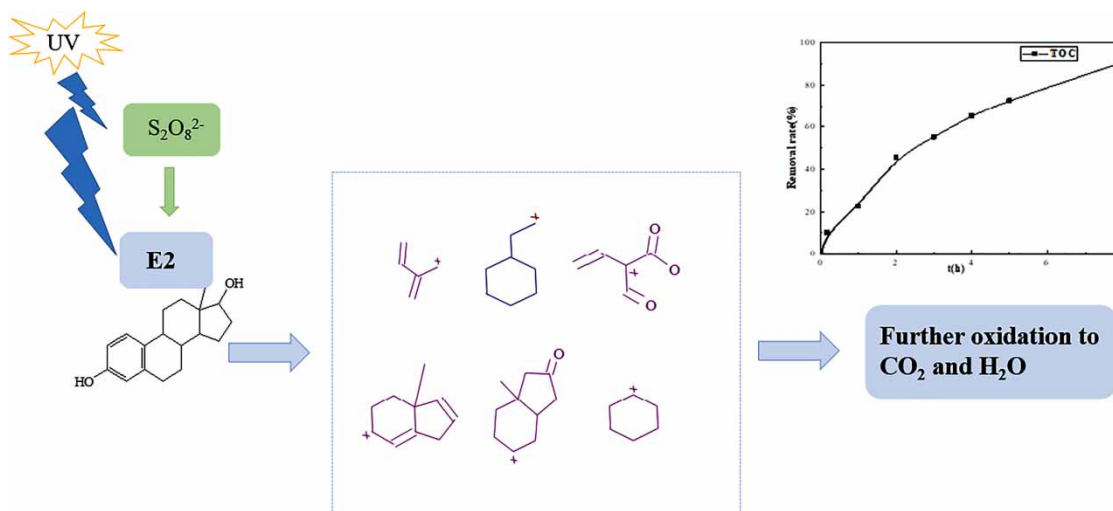
Sulfate radical ($\bullet\text{SO}_4^-$)-based advanced oxidation processes are widely used for wastewater treatment. This study explored the potential use of UV/persulfate (UV/PS) system for the degradation of 17 β -estradiol (E2). The pH of the reaction system can affect the degradation rate of E2 by UV/PS and the optimum pH was 7.0; Br^- and Cl^- in water can promote the degradation rate, HCO_3^- has an inhibitory effect on the reaction, SO_4^{2-} and cations (Na^+ , Mg^{2+} , K^+) have no effect on the degradation rate. The degradation of E2 by UV/PS was a mineralization process, with the mineralization rate reaching 90.97% at 8 h. E2 in the UV/PS system was mainly degraded by hydroxylation, deoxygenation, and hydrogenation. E2 reaction sites were mainly located on benzene rings, mainly carbonylation on quinary rings, and bond breakage between C10 and C5 resulted in the removal of benzene rings and carboxyl at C2 and C3 sites. In the presence of halogen ions, halogenated disinfection by-products were not formed in the degradation process of E2 by UV/PS. E2 in the UV/PS system could inhibit the formation of bromate. The results of this study suggest that UV/PS is a safe and reliable method to degrade E2.

Key words: 17 β -estradiol, bromate, sulfate free radical, UV/persulfate

HIGHLIGHTS

- The reaction kinetics, mechanisms and degradation pathways of the UV/PS process in degrading E2 in marine aquaculture water were elucidated.
- The fates of E2 in marine aquaculture water were analyzed in the presence of potential interfering factors such as anions (Br^- , Cl^- , HCO_3^- , SO_4^{2-}), cation (Na^+ , Mg^{2+} , K^+) and pH value.
- The inorganic disinfection by-products namely bromate of E2 treated by UV/PS was also explored.

GRAPHICAL ABSTRACT



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INTRODUCTION

Endocrine disrupting chemicals (EDCs) are a diverse group of natural and synthetic organic substances which cause risk to human beings and animals via influencing the processes and functions of the endocrine system (Geyer *et al.* 2000; Mai *et al.* 2008; Mazellier *et al.* 2008; Zhao *et al.* 2008; Zhang *et al.* 2013; Ahmad *et al.* 2015; Bajard *et al.* 2021). Among the EDCs, the main synthetic chemicals include pesticides, plastics, and other industry-related materials (such as bisphenol A) produced by humans, natural compounds such as estrone (E1), 17 β -estradiol (E2) released by humans and animals (Irmak *et al.* 2005; Yoon *et al.* 2020). Over the past few years, EDCs have been frequently detected at a level from picograms per liter to nanograms per liter in surface waters and sewage effluent (Zhao *et al.* 2008; Brienza *et al.* 2014; Park *et al.* 2018). Furthermore, recent studies have demonstrated that EDCs have been identified as having the highest endocrine disrupting activity, even at very low concentrations (ng/L) in the aquatic environment and are not commonly regulated (Zhang *et al.* 2013). For example, a Canadian field study showed that long-term exposure to EDCs at ambient concentrations (5–6 ng/L) can lead to feminization of wild fish in lake waters and eventually cause fish population decline (Kidd *et al.* 2007).

As a representative EDC, E2, an extremely potent estrogen receptor modulator, is widely used to treat advanced prostate cancer and estrogen deficiency (Lee & Peart 1998; Servos *et al.* 2005; Weber *et al.* 2005; Mispagel *et al.* 2009). As well, E2 has also been used as a feed supplement to aquaculture, with great success (Pechsiri & Yakupitiyage 2005; Flynn & Benfey 2007). Due to its extensive use, many studies have reported that E2 with heavy concentrations has been detected in marine and freshwater systems or drinking water in various countries (Mai *et al.* 2008; Sun *et al.* 2017; Jiang *et al.* 2018; Ma & Yates 2018; Mauricio *et al.* 2018). For example, Duong's research shows that an average concentration of 9.1 ng/L for E2 has been detected in the surface water of China (Duong *et al.* 2010).

Furthermore, the potentially detrimental effects of E2 on human health have caused increasing concern, with some studies suggesting that the toxicity of E2 may transfer from the parental generation to subsequent generations (Pedram *et al.* 2006; Bradley *et al.* 2009; Cajthaml 2015). Due to its impact both on public and ecological health concerns, research on water treatment methods regarding the removal of E2 is a critically important issue (Bila *et al.* 2007; Maniero *et al.* 2008; Jiang *et al.* 2012; Ting *et al.* 2017). However, E2 can resist the degradation of conventional sewage treatment operation, with typical chemical and biological treatment methods not adequately achieving removal of its biological activity (Bradley *et al.* 2009; Jiang *et al.* 2010; Mashtare *et al.* 2013). As reported, the concentration of E2 in effluent of wastewater treatment plants (WWTP) is 0.1–88 ng/L which is much higher than its typical detection (Li *et al.* 2016).

In the past few years, advanced oxidation processes (AOPs) have been investigated to attenuate EDCs from various types of water because these techniques are considered to be an efficient method to destroy the biological activity of EDCs (Wu *et al.* 2014; Ahmad *et al.* 2015; Lian *et al.* 2017; Joao *et al.* 2021). EDCs' degradation by AOPs, such as ozonation, photo-Fenton reaction, and UV/hydrogen peroxide (UV/H₂O₂) has been well investigated (Gibson *et al.* 2005; Zhao *et al.* 2008; Zhang *et al.* 2010; Nakrst *et al.* 2011). Among the AOPs, persulfate (PS), which generates the highly reactive sulfate free radical ($\bullet\text{SO}_4^-$) that can rapidly degrade the wide variety of compounds to nontoxic CO₂ and H₂O, has gained considerable attention (Ahmad *et al.* 2015; Lin & Tsai 2019; Xiong & Pei 2021). PS can completely decompose EDCs due to its strong redox potential (2.5–3.1 V) which is stronger than that of $\bullet\text{OH}$ (1.9–2.7 V) (Lian *et al.* 2017). Moreover, PS can be activated by a series of methods, including heat, UV irradiation or transition metal to catalysis (Fu *et al.* 2019). As typical UV-based AOPs, UV/Na₂S₂O₈ (UV/PS) processes not only exhibit great potential removal of refractory organics with less energy consumption, but also do not cause secondary pollution (Zhang *et al.* 2018). For instance, Ye *et al.* (2016) found that UV/PS treatment was an effective method to degrade ciprofloxacin (CIP). The time of UV/PS complete degradation of CIP was no longer than 20 minutes and the apparent rate constants 0.2413 min⁻¹.

Degradation of other man-made organic compounds by UV/PS have been studied previously and the results show that the reaction process is capable of oxidizing the vast majority of organic contaminants (Mai *et al.* 2008). Nonetheless, to the best of our knowledge, few studies have been done with the focus on the degradation of E2 by UV/PS, and using the UV/PS process in marine aquaculture water treatment has yet to be performed. Accordingly, the aim of this investigation is to elucidate the reaction kinetics, mechanisms, and degradation pathways of the UV/PS process in degrading E2 in marine aquaculture water. The fate of E2 in marine aquaculture water was analyzed in the presence of potential interfering factors such as anions (Br⁻, Cl⁻, HCO₃⁻, SO₄²⁻), cation (Na⁺, Mg²⁺, K⁺), and pH value. Furthermore, the degradation pathways of E2 were explored based on the main intermediates identified by LC/MS/MS. As well, the degradation pathways of E2 were investigated based on the

main intermediates identified by LC/MS/MS. The inorganic disinfection by-product, namely, bromate (BrO_3^-) of E2 treated by UV/PS was also explored.

MATERIALS AND METHODS

Chemicals

E2 (>98% purity) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification in the experiments. Both sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium sulfite (Na_2SO_3) were analytical grade and obtained from Tianjin Komeo Chemical Reagent Company (Tianjin, China). High performance liquid chromatography (HPLC) grade methanol was supplied by Anhui Fulltime Specialized Solvents & Reagents Co., Ltd (China). Other chemicals were analytical grade without further purification and purchased from China Pharmaceutical Group Chemical Reagents Co., Ltd (China). Deionized water was obtained from a Millipore Milli-Q Ultrapure Gradient A10 purification system. Water samples used in the experiment containing 0.1 mmol/L E2 were prepared by spiking 100 mL E2 stock solution (1 mmol/L in methanol) into 1 L deionized water. According to the components of actual water samples, the synthetic sea water was prepared by adding essential anions into ultrapure water including Cl^- (6.6 g/L), Br^- (22 mg/L), HCO_3^- (0.047 g/L), and SO_4^{2-} (0.903 g/L). In the actual marine aquaculture, the water was a mixture of freshwater and seawater at a ratio of 2:1. Therefore, the salinity and various ion concentrations of marine aquaculture water were one-third of seawater. The pH of all water samples was adjusted to 7 with phosphate buffer.

UV/PS experiment procedures

E2 degradation experiments were carried out in a photoreactor (BL-GHX-V, Shanghai Bilang Instruments Co., Ltd, China). The UV light source was a high-pressure mercury lamp (254 nm) equipped with a quartz cover which was vertically fixed in the center of the reactor. Eight quartz tubes with a height of 18.5 cm and an internal diameter of 2.0 cm were evenly placed around the high-pressure mercury lamp. An agitator was placed inside each quartz tube ensuring complete mixing of the reaction solution. A steady flow of cooling system was applied to maintain the temperature of reaction solutions at about 25 °C during the irradiation process.

Total organic carbon (TOC) analyses and ion chromatography

The TOC was measured using a Liquid TOC analyzer (TOC-VSH, Shimadzu), and the determination of bromate (BrO_3^-) was performed using an ion chromatography system (Dionex ICS-5000, Thermo USA).

Analytical methods

The concentration of E2 was determined by using an ultra-performance liquid chromatography (UPLC) system equipped with an Acquity UPLC QSM (Waters, USA) and Waters C18 reversed phase column (2.1 mm × 50 mm, 1.7 μm particle) was adopted. The injection volume for UPLC was 10 μL and the analytic samples were degassed by sonication for more than 30 min. The mobile phase was 30:70 v/v of ultrapure water and methanol, the flow rate was 0.35 mL min⁻¹, and the column temperature was set at 35 °C. The degradation kinetic of E2 in the UV/PS system was assessed by a pseudo first-order kinetic model. As shown in Equation (1), k is the pseudo-first order rate constant (min⁻¹), $[\text{E2}]_0$ and $[\text{E2}]_t$ is the initial concentration and the residual concentration of E2 at time t , respectively.

$$\ln\left(\frac{[\text{E2}]_0}{[\text{E2}]_t}\right) = kt \quad (1)$$

RESULTS AND DISCUSSION

Degradation kinetics of E2 by the UV/persulfate process

Effect of pH value

Figure 1 presents the degradation of E2 in synthetic brackish marine culture water at different pH values. The observed degradation rate was highest at pH 7 and decreased with either an increase or a decrease in pH value. At pH values of 7, 4, 5, 9, and 10, the rate constants were 0.148 min⁻¹, 0.0418 min⁻¹, 0.0798 min⁻¹, 0.0464 min⁻¹, and 0.0308 min⁻¹, respectively. As is well known, the solution pH value can influence the oxidation kinetics through affecting the active oxidation species. For

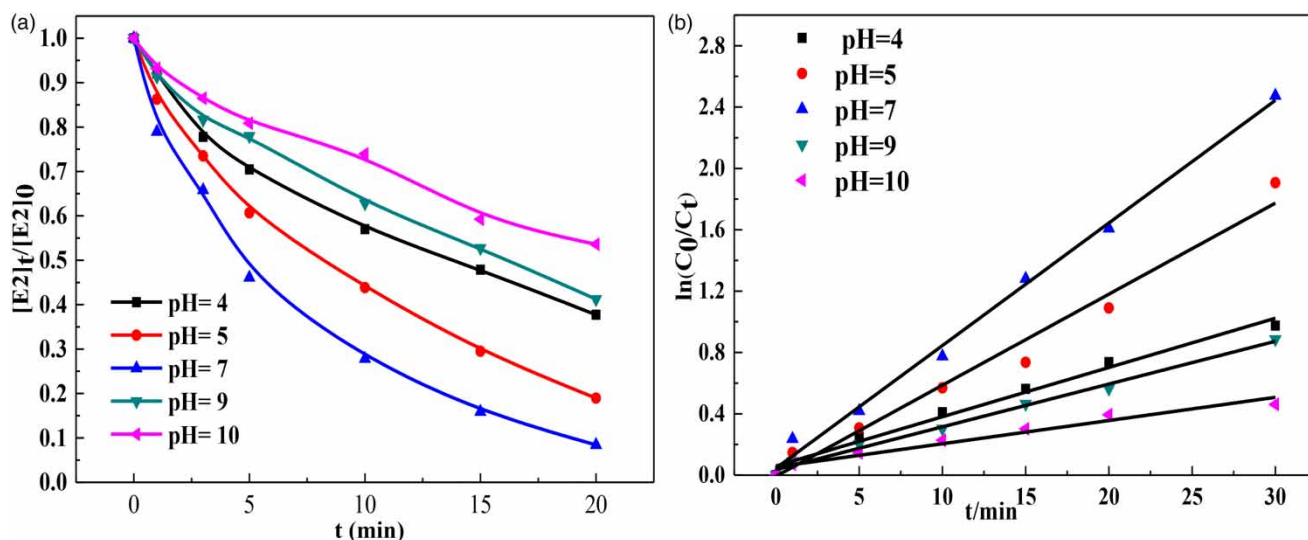


Figure 1 | Oxidation of E2 by UV/PS at different pH values and the linear fit of the kinetic data ($[E2]_0 = 0.1$ mM, 20 mL, $[Na_2S_2O_8]_0 = 0.1$ mM, 1 mL, $[Cl^-]_0 = 6.6$ g L⁻¹, $[Br^-]_0 = 22$ mg L⁻¹, SO_4^{2-} : 0.9 g/L, HCO_3^- : 0.047 g/L T = 298.15 K).

this study, under neutral pH conditions, $\bullet SO_4^-$ was the main active oxidation species, but under acidic pH conditions, the reaction between H^+ and $\bullet SO_4^-$ would be enhanced through Equation (2) (Liang *et al.* 2007). Moreover, under high pH, OH^- in solution may undergo reactions with $\bullet SO_4^-$ to generate $\bullet OH$ in accordance with Equation (3) (Liang *et al.* 2007).



Under acidic conditions, the generation of $\bullet S_2O_8^-$ in water samples may result in decrease of $\bullet SO_4^-$ contents in accordance with Equation (2). However, the higher $\bullet S_2O_8^-$ generation rate may cause radical with radical scavenger reactions, which could result in inhibition of the reactivity of $\bullet SO_4^-$. A similar inhibition mechanism was observed at an alkaline solution as shown in Equation (3). As reported, $\bullet SO_4^-$ has a longer oxidation time than $\bullet OH$; $\bullet SO_4^-$ has a longer oxidation time on pollution and can improve the degradation effect. Under the same reaction conditions, $\bullet SO_4^-$ has a higher degradation degree on compounds than $\bullet OH$. With the reaction in alkaline solution, $\bullet OH$ gradually increases in the reaction system, and the content of $\bullet SO_4^-$ decreases gradually. Compared with $\bullet OH$, it was easier for $\bullet SO_4^-$ to cause electron transfer on E2 and it selectively oxidized E2. The above oxidation mechanism leads to $\bullet SO_4^-$ degrading E2 faster than $\bullet OH$. On the other hand, when the system was under alkaline conditions, it resulted in an increase in the production of $\bullet OH$ which affects the content of $\bullet SO_4^-$. Therefore, the degradation of E2 is slowed down by the mass production of $\bullet OH$ under strong alkali conditions.

Effect of water composition

Besides the initial pH value of water samples, the ions present in the solution may also have an effect on the degradation of E2 in the UV/PS system. The salinity of marine aquaculture water samples is different according to different seafood. For example, the salinity of some shrimp water bodies is one-third of seawater, the salinity of some fish water bodies is very low (close to fresh water) and some are close to the salinity of seawater. Considering the difference of salinity in actual marine aquaculture water bodies, we studied the degradation of E2 in the concentration gradient range from fresh water to seawater. In order to investigate the effect of Cl^- on the degradation rate of the UV/PS system in the presence of Cl^- in water, this paper carried out a comparative study on UV/PS degradation of E2 in different concentrations of Cl^- . As shown in Figure 2(a), when, in the absence of Cl^- , the reaction is carried out for 10 min in the UV/PS system, the degradation rate of E2 is only about 40%. However, in the presence of Cl^- with concentrations greater than 19 g/L, the degradation rate of E2 is up to about 70%. The results show that in the UV/PS system, Cl^- promotes the degradation reaction of E2. Studies have shown that the following series of reactions occur mainly when a large amount of Cl^- is present in the solution (Wicktor *et al.* 2003). In addition, the reaction between $\bullet SO_4^-$ and Cl^- would generate $\bullet Cl$ through Equation (4). In the next series of

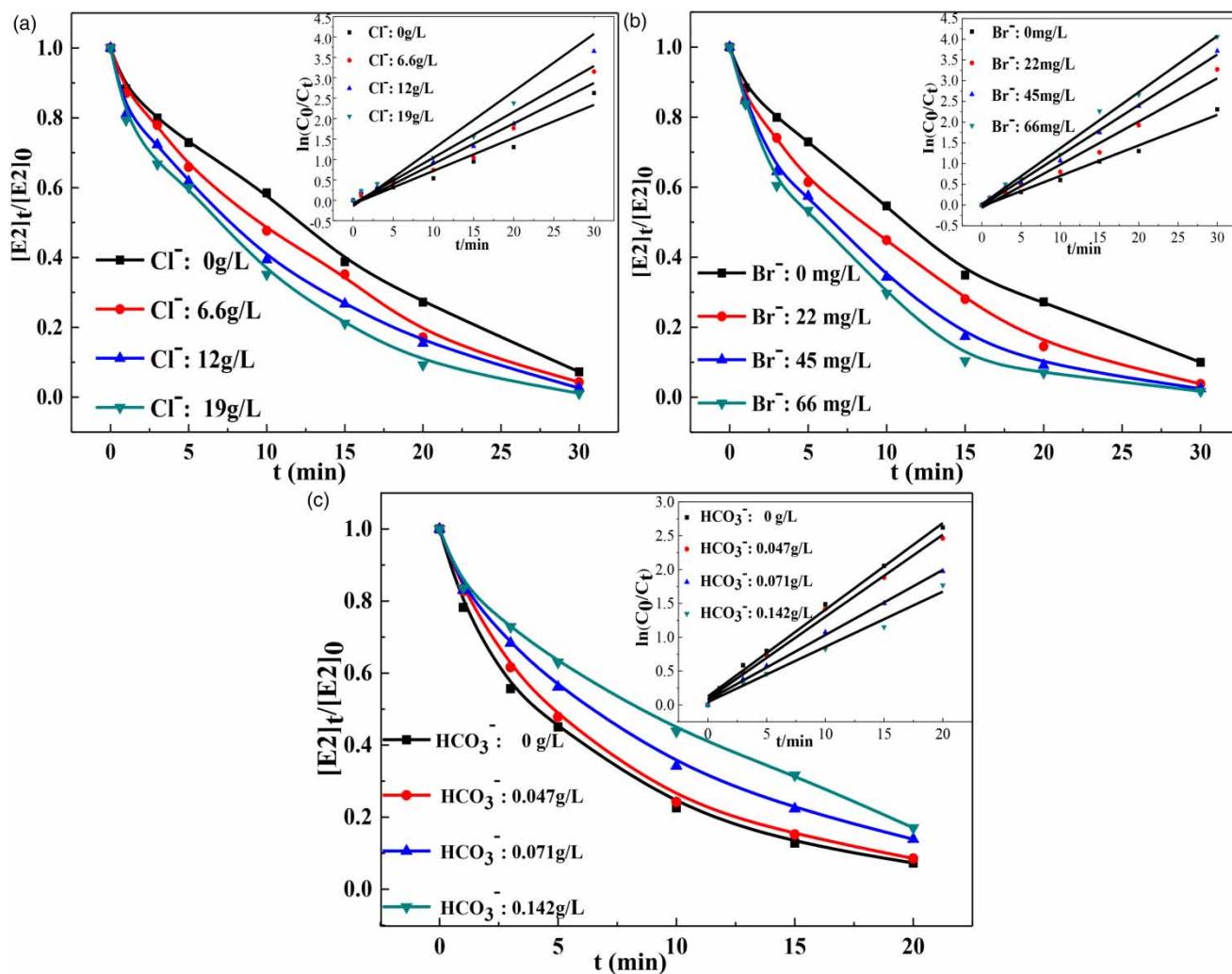


Figure 2 | Oxidation of E2 by UV/PS and the linear fit of the kinetic data at different concentrations of Cl⁻ (a), Br⁻ (b), and HCO₃⁻ (c). ([E2]₀ = 0.1 mM, 20 mL, [Na₂S₂O₈]₀ = 0.1 mM, 1 mL, pH = 7, T = 298.15 K).

reactions, $\bullet\text{Cl}$ is transformed into $\bullet\text{Cl}_2^-$ and Cl_2 through Equations (5) and (6), then finally transformed to HClO through Equation (7) which has strong oxidizing property and accelerates the reaction rate of the reaction system.



It can be seen from Figure 2(b) that within half an hour in the UV/PS system, the degradation of E2 was less than 90% in the absence of Br⁻; however, the degradation of E2 reached over 99% when the concentration of Br⁻ increased to 66 mg/L. This suggests that the presence of Br⁻ can accelerate the rate of UV/PS degradation of E2. It can also be seen from Figure 2(b) that when a high concentration of Br⁻ is present in the reaction system, the reaction rate is greater than that of the reaction system containing no Br⁻, and the reaction rate increases as Br⁻ increases. The acceleration mechanism for this phenomenon is similar to that of Cl⁻. When the UV/PS reaction system contains a higher concentration of Br⁻, HBrO is formed in the system, thereby accelerating the degradation of E2.

In addition to the Br^- and Cl^- , there are other matters such as HCO_3^- with high concentration in seawater which may also affect the rate at which the UV/PS system degrades E2. As shown in Figure 2(c), when 142 mg/L of HCO_3^- is present in the reaction system, the degradation rate of E2 has reached about 55% at 15 min in the experiment. At the same time, when in the reaction system 47 mg/L of HCO_3^- is present, the degradation rate of E2 is about 78%. Correspondingly, in the system without HCO_3^- , the degradation rate of E2 is about 80% when the reaction is carried out for 15 min. Figure 2(c) also shows that as the corresponding concentration of HCO_3^- in the reaction system increases, the degradation rate of E2 in the UV/PS system decreases. It is possible that the pH of the system changed due to the addition of HCO_3^- . As HCO_3^- in the reaction system increased, the pH gradually increased. As shown in Equation (3), the conversion of $\cdot\text{SO}_4^-$ to $\cdot\text{OH}$ led to lower reaction rate in the reaction system when in the alkaline condition. The presence of higher levels of SO_4^{2-} in seawater may influence the reactions. As shown in Figure 3(a), SO_4^{2-} did not exhibit an obvious effect on the degradation of E2 in the UV/PS system. On the other hand, the effect of cations present in seawater on the degradation of E2 in UV/PS systems is also discussed in this paper, and similar to the effect of SO_4^{2-} , cations such as Na^+ , Ca^{2+} , Mg^{2+} , and K^+ have almost no effect on the reaction rate (Figure 3(b)).

Determination of TOC

The process of oxidative degradation of E2 by UV/PS system also is a mineralization process. In order to determine the degree of mineralization of E2, the ability of UV/PS to degrade E2 was explored. In this study, TOC removal rate of UV/PS degradation of E2 was studied in brackish water. As shown in Figure 4, when the reaction time increases, the TOC removal rate increases gradually. The mineralization rate of E2 reaches 22.16% at 1 h. Then, the reaction proceeds for 2 h, 4 h, 5 h, and 8 h, and the mineralization rates were 45.47%, 65.31%, 72.76%, and 90.97%, respectively.

Identification of the by-products and reaction centers

Reaction centers recognition of E2

Since the most important oxidants in the UV/PS system are $\cdot\text{SO}_4^-$ and $\cdot\text{OH}$, which have strong oxidizing properties, the results show that although the reaction rate of UV/PS degrading E2 is affected by the anions, the reaction pathways were substantially the same. On the other hand, computational chemistry based on quantum theory has become an important analytical method in this paper. According to the frontier orbital theory, the highest energy level (HOMO) of the E2 molecule and the lowest energy level (LUMO) of the non-occupied electron are the keys to determining the chemical reaction (Aihara 1999). The position of the material having a large charge density is most susceptible to attack by electrophiles, causing the chemical bonds associated with it to break (Zhan *et al.* 2003).

The HOMO, LUMO, and net charge distribution of E2 are shown in Figure 5. The HOMO of the E2 molecule and the electron cloud on the LUMO are concentrated in the benzene ring. It can be inferred that the benzene ring structure is

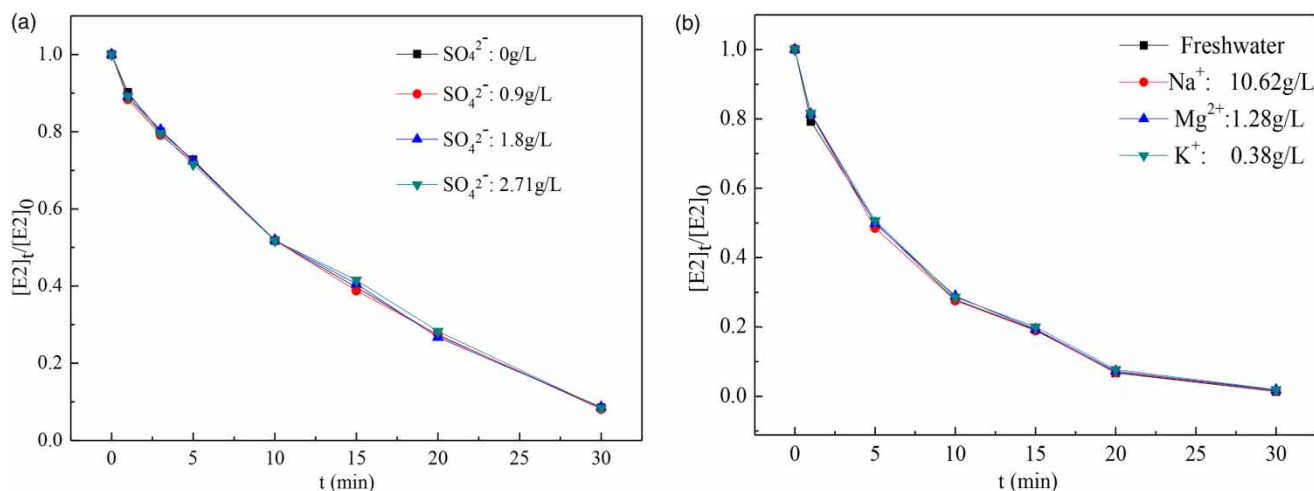


Figure 3 | Oxidation of E2 by UV/PS at different concentrations of SO_4^{2-} (a) and cations (b) ($[\text{E2}]_0 = 0.1 \text{ mM}$, 20 mL , $[\text{Na}_2\text{S}_2\text{O}_8]_0 = 0.1 \text{ M}$, 1 mL , $\text{pH} = 7$, $T = 298.15 \text{ K}$).

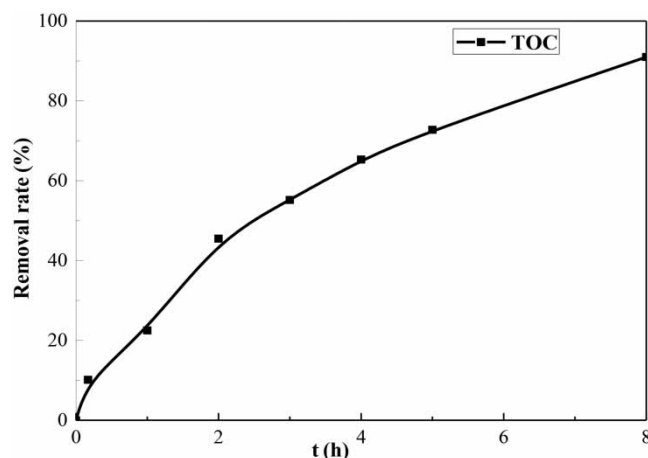


Figure 4 | TOC removal rate of E2 ($[E2]_0 = 0.01$ mM, 20 mL, $[Na_2S_2O_8]_0 = 0.01$ mM, 1 mL, pH = 7, T = 298.15 K, Cl^- : 6.6 g L⁻¹, Br^- : 22 mg L⁻¹, HCO_3^- : 0.047 g L⁻¹, SO_4^{2-} : 0.9 g/L).

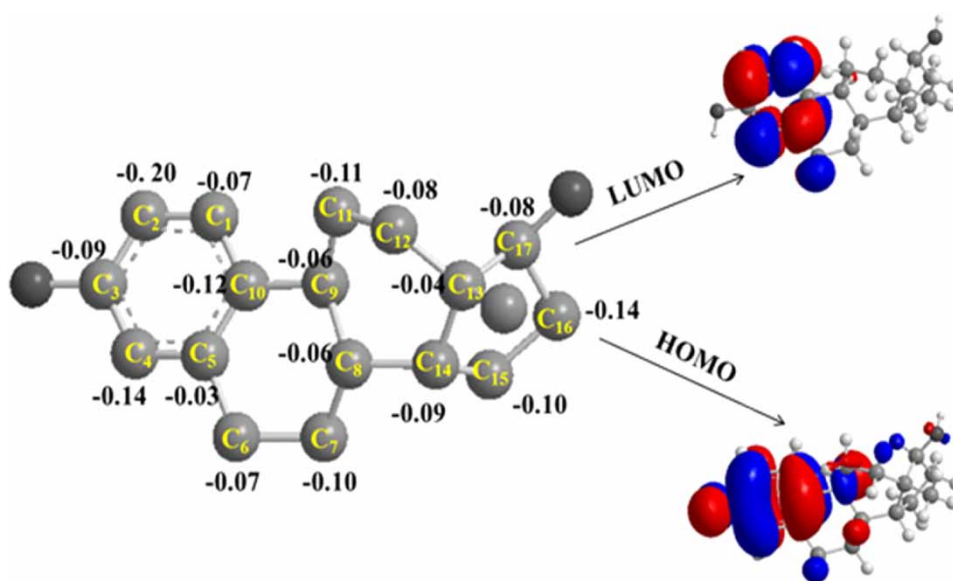


Figure 5 | HOMO, LUMO, and net charge distribution of E2.

both the electron donor of the E2 molecule and the main acceptor part of the electron (Hu *et al.* 2002). The HOMO of a molecule is more susceptible to attack by electrophiles to generate an electrophilic reaction, and the nucleophile is more likely to attack the atom with a higher charge density on the LUMO (Serna-Galvis *et al.* 2017). This paper calculates the atomic net charge distribution in the E2 molecular structure, and the main reactive sites on E2 are inferred. From the microscopic level, the mode of action of $\bullet SO_4^-$ and E2 is combined with the high-resolution LC/MS/MS first-order mass spectrum display. The intermediate product has an accurate molecular mass that is inferred from the possible pathways of the E2 degradation process.

Identification of the by-products

The UV/PS degradation of E2 in fresh and brackish water was carried out for 10 min, 30 min, and 2 h, and the mixture was analyzed by full sweep in positive ion mode via LC/MS/MS. Three more obvious product peaks were found in the two

solutions for 2 h, named P1, P2, and P3. In addition, a total of six distinct peaks were found to be named Pm1–Pm6 in the solution in which the reaction was carried out for 10 and 30 min, respectively. Information about these intermediate products of the mass spectrum is shown in Supplementary Material, Figure S1(a)–(j).

Proposed reaction pathways

The intermediate by-products of E2 were estimated by the molecule mass difference and isotope patterns in the mass spectra. The mass spectral characterized data for these organic products were confirmed by LC/MS which is shown in Supplementary Material, Figure S1. Based on the organic intermediates, two pathways (A and B) are extrapolated as shown in Figure 6. In pathway A, the hydroxyl group of the E2 five-membered ring is oxidized to form E1 ($m/z = 270$), and in the process of oxidation of E1, the two paths of A1 and A2 are, respectively, formed to produce two products of P1 ($m/z = 252$) and P2 ($m/z = 196$). In the pathway A1, the C6 position on E1 is oxidized to a hydroxyl group to form Pm3 ($m/z = 286$), and Pm3 continues to be oxidized by oxygenation to dehydrogenate to P1. It is presumed that the chemical bond between C10 and C5 of the benzene ring of E2 is broken by oxidation. The chemical bond between C2 and C4 also ruptures, and the chemical bond between C5 and C6 on the six-membered ring also breaks, resulting in the formation of a five-membered ring by C6 and C10, and the oxygenation reaction at the C1 position to forming P1. In the pathway A2, on the basis of the structural characteristics of E1, the chemical bond between C1 and C10, C4 and C5 is broken to remove the benzene ring, thereby forming Pm4 ($m/z = 206$), and the alkyl group on Pm4 undergoes oxygenation and dehydrogenation to form Pm6 ($m/z = 222$). Pm6 continues to oxidize and dehydrogenate to oxidize the alkyl group on the original five-membered ring to a carboxyl group to form Pm7 ($m/z = 236$). The decarboxylation reaction that occurred at the C13 position on the five-membered ring and the five-membered ring was cleaved at the C17 and C14 positions, and the hydroxyl group linked to C17 was oxidized to the carboxyl group, resulting in the production of P2.

In pathway B, P3 ($m/z = 334$) with a retention time of 5.20 min, the spectrum is shown in Supplementary Material, Figure S1(c). First, the C2 site on the E2 benzene ring is electrophilically attacked to form a hydroxyl group to form Pm2 ($m/z = 288$). Then, the site connecting the hydroxyl group at the benzene ring site of Pm2 is oxidized to form a carboxyl group and simultaneously causes a chemical bond between C2 and C3. Moreover, E2 electron cloud distribution characteristics are also known to be susceptible to electro-electrical attack at the C6 site (Hu *et al.* 2003). A hydroxyl group formed at the C6 site during the subsequent oxidative degradation process which led to forming Pm5. The hydroxyl group in Pm5 undergoes a dehydrogenation reaction to become a carbonyl group to form P3. The analysis of the reaction sites of E2 in the degradation process, combined with mass frontier software led to speculating the possible degradation pathways. The study found that the above intermediate products were gradually broken during the degradation reaction, and the fragments with smaller mass fractions (Supplementary Material, Figure S1(k)–(q)) were broken. The mass spectrum of each product's fragment is shown in Figure 5, and E2 eventually mineralized into H₂O and CO₂.

Formation and control of bromate

As reported, when Br⁻ is present in the solution, UV/PS will produce BrO₃⁻ while degrading the contaminants (Li *et al.* 2014). This paper preliminarily explores the general rule of BrO₃⁻ generation during the degradation of E2 by UV/PS technology in a brackish water system. This study found that BrO₃⁻ was not detected after 2 h of degradation of E2 by UV/PS in a brackish water system. It has been reported that the formation of BrO₃⁻ during UV/PS oxidation is inhibited in the presence of humic acid. Thus, this paper explores the formation of BrO₃⁻ in a brackish water system without E2. As shown in Figure 7(a), the experiment times were set at 5 min, 10 min, 30 min, and 2 h, respectively. With the increase of time, the BrO₃⁻ formed in the brackish water system showed an increasing trend, while the Br⁻ content showed a downward trend. When the reaction was set as 10 min, BrO₃⁻ with a content of 1.08 mg/L was detected in the system. After 2 h, the BrO₃⁻ production amount reached 14.88 mg/L. At the same time, Br⁻ in the reaction system was almost completely consumed. The experimental results show that the •SO₄⁻ formed in the system can oxidize Br⁻ to BrO₃⁻ when UV/PS is used to treat the water containing Br⁻.

The above experiment proves that in the absence of E2 in the reaction system, BrO₃⁻ is formed. This paper investigated the effect of E2 on the formation of BrO₃⁻ in the UV/PS system under the background value of brackish water. During the experiments, the reaction time was fixed and the concentration of E2 increased from 0 to 0.1 mmol/L. As shown in Figure 7(b), when the experiment was carried out for 30 min, the content of BrO₃⁻ decreased with the increase of E2 concentration in the brackish water. In the absence of E2, 7.38 mg/L of BrO₃⁻ was formed in the reaction system. When the concentration of E2 was set as 0.01 mmol/L, the amount of BrO₃⁻ in the reaction system was 5.934 mg/L. When the concentration of E2

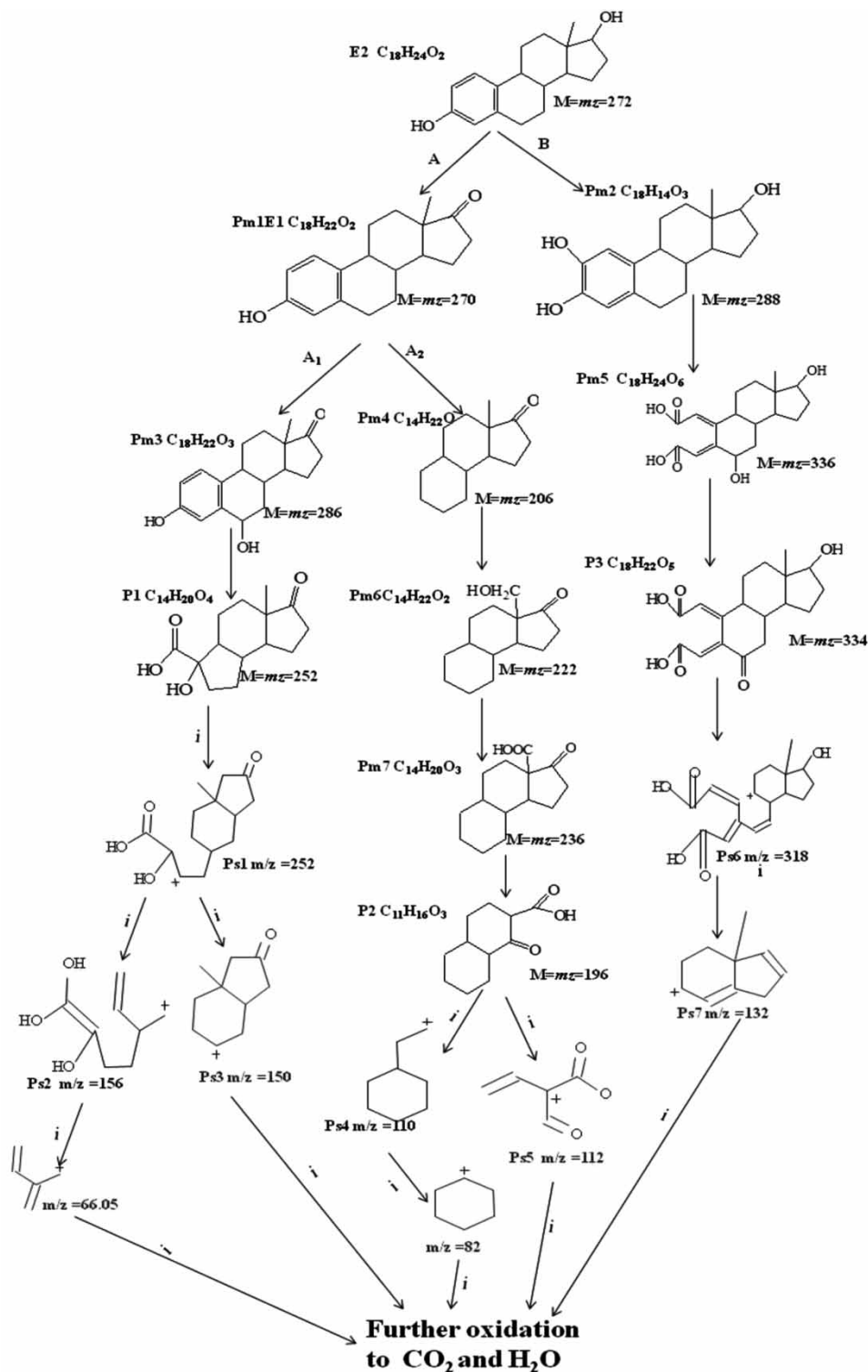


Figure 6 | The possible degradation pathways of E2 by UV/PS.

was further increased to 0.02 mmol/L, the concentration of BrO_3^- was reduced to 4.029 mg/L. The reason for this phenomenon may be that the oxidized BrO_3^- formed in the reaction system can react with E2 in the system. The presence of E2 can inhibit the formation of BrO_3^- in the reaction system.

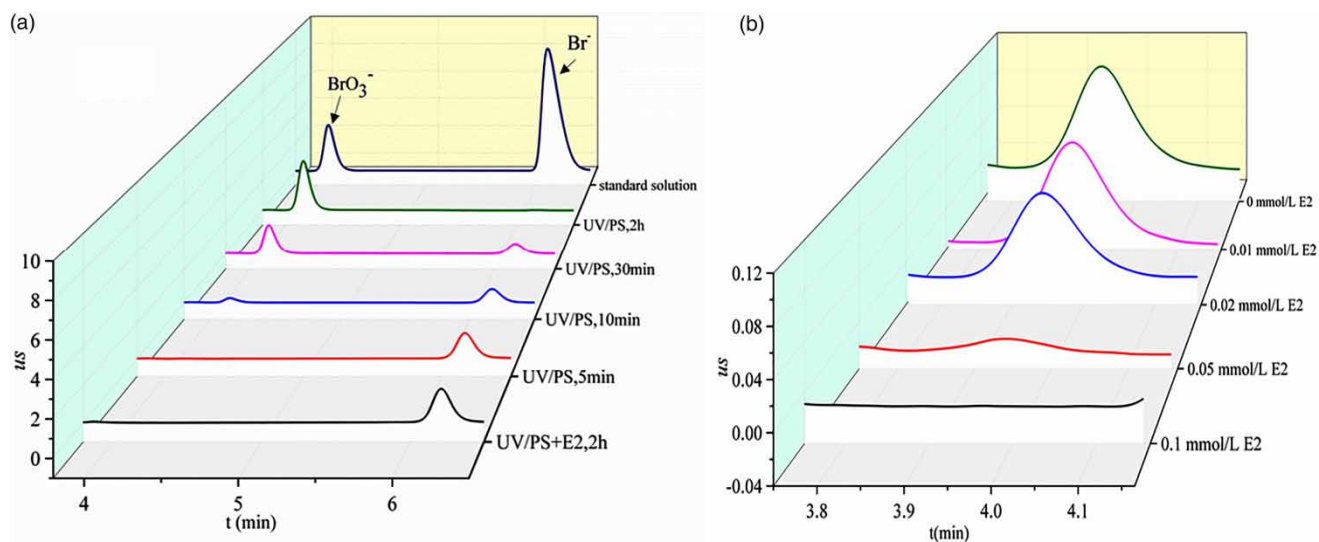


Figure 7 | Bromate production at different times (a) and different E2 concentrations (b) ($[\text{Na}_2\text{S}_2\text{O}_8]_0 = 0.01 \text{ mM}$, 1 mL , $\text{pH} = 7$, $T = 298.15 \text{ K}$).

CONCLUSION

The aim of our work was to investigate the fate of E2 in the UV/PS degradation process. The results show that the pH of the water will affect the rate of degradation of E2 by UV/PS. Under neutral conditions, the degradation rate is the fastest. Over-alkali or per-acid will inhibit the reaction. Anions such as Br^- and Cl^- in water will promote UV/PS degradation of E2. In the reaction process, HCO_3^- has an inhibitory effect on the reaction, while SO_4^{2-} and cation have no effect on the degradation rate. UV/PS degradation of E2 was also a mineralization process, with the mineralization rate reaching 90.97% at 8 h. In the UV/PS system, the same intermediate products were detected in both brackish water and fresh water. The reaction of hydroxyl, deoxygenation, and hydrogenation are the primary degradation reactions. The E2 reaction site is mainly located on the benzene ring. There is mainly carbonylation on the five-membered ring. The bond cleavage between C10 and C5 leads to the removal of the benzene ring and the carboxylation of the C2 and C3 sites. Otherwise, in the presence of halogen ions, halogenated DBPs are not produced during UV/PS degradation of E2. On the other hand, the presence of E2 in the UV/PS system inhibits the formation of bromate.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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