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Photodegradation of sulfonamides in UV/ozone, UV/oxidant, and UV/ozone/oxidant systems: comparison in terms of mineralization efficiency and power consumption

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ABSTRACT

UV/O_3, UV/H_2O_2, $UV/Na_2S_2O_8$, $UV/O_3/H_2O_2$, and $UV/O_3/Na_2S_2O_8$ systems were used to mineralize sulfamethoxazole (SMX) and sulfathiazole (STZ). The effects of pH and salinity on sulfonamide mineralization were determined. The mineralization of sulfonamides exhibited pseudo-first-order kinetics. At pH 5, the pseudo-first-order rate constants (k) of SMX in the UV/O_3, UV/H_2O_2, $UV/Na_2S_2O_8$, $UV/O_3/H_2O_2$, and $UV/O_3/Na_2S_2O_8$ systems were 0.0193, 0.0011, 0.0022, 0.0172, and 0.0925 min^{-1}, respectively, and those of STZ were 0.0238, 0.0011, 0.0031, 0.0201, and 0.0536 min^{-1}, respectively. At pH 5, adding $Na_2S_2O_8$ to the UV/O_3 system promoted sulfonamide mineralization, whereas adding H_2O_2 to the UV/O_3 system inhibited it. At pH 9, adding $Na_2S_2O_8$ or H_2O_2 to the UV/O_3 system promoted sulfonamide mineralization. The highest efficiency of mineralization for both SMX and STZ was achieved using the $UV/O_3/Na_2S_2O_8$ system and the efficiency followed the order pH 5 > pH 7 > pH 9. In the $UV/O_3/Na_2S_2O_8$ system at pH 9, adding 0.62 mM salinity reduced the k value of SMX from 0.0224 to 0.0181 min^{-1} and that of STZ from 0.0322 to 0.0233 min^{-1}. In the $UV/O_3/H_2O_2$ system at pH 9, adding 0.62 mM salinity reduced the k value of SMX from 0.0137 to 0.0065 min^{-1} and that of STZ from 0.0159 to 0.0072 min^{-1}. The figure-of-merit electrical energy per order was used to estimate the electrical energy efficiencies of the systems. At pH 5, the $UV/O_3/Na_2S_2O_8$ system exhibited the highest energy efficiency for SMX mineralization whereas the $UV/Na_2S_2O_8$ system did so for STZ mineralization. The highest energy efficiency system varied with the parent compound.

Keywords: Sulfamethoxazole; Sulfathiazole; Ozone; Hydrogen peroxide; Persulfate; Mineralization

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1. Introduction

Advanced oxidation processes (AOPs) have emerged as promising alternatives for removing non-biodegradable compounds from wastewater due to their efficient generation of reactive oxygen species, such as sulfate radicals ($SO_4^{-\bullet}$), hydroxyl radicals ($HO^\bullet$), and superoxide radicals ($O_2^{-\bullet}$) [1]. In recent years, ultraviolet (UV)-based AOPs have been widely studied and used to degrade recalcitrant organic compounds. Klauson et al. [2] and Wang and Zhuan [3] indicated that AOPs had greater potential than conventional treatment processes to degrade and mineralize recalcitrant and toxic organic pollutants in water matrices.

Ozonation has excellent potential as a means of photodegradation for the following reasons; (i) it poses minimal danger to humans; (ii) it generates no sludge; (iii) all residual ozone can be decomposed easily into oxygen and water; (iv) it requires little space; and (v) the process is easily conducted [4]. Ozone has an oxidation potential of 2.07 V whereas $HO^\bullet$ has an oxidation potential of 2.80 V, so direct oxidation is slower than radical oxidation. Ozonation under UV radiation removes organics more effectively than ozonation alone. The combined process is more effective because UV radiation accelerates the decomposition of ozone, yielding freer $HO^\bullet$, and therefore producing a higher ozonation rate. A disadvantage of ozonation alone for treating wastewater is the large amount of energy that is required; accordingly, any improvement that reduces the required reaction time would be welcomed.

UV/H_2O_2 can generate $HO^\bullet$ [5,6] and UV/$Na_2S_2O_8$ can be activated to form $HO^\bullet$ and $SO_4^{-\bullet}$ [6,7]. $SO_4^{-\bullet}$ has a lower reaction rate than $HO^\bullet$, but higher selectivity toward organic compounds and it is less influenced by impurities in water [7,8]. Zhang et al. [9] and Acosta-Rangel et al. [10] degraded sulfamethazine (SMZ) and sulfadiazine (SDZ) using UV, UV/H_2O_2, and UV/$K_2S_2O_8$ systems, which have been proved to exhibit low selectivity toward various sulfonamides. Wang et al. [11] indicated that sulfamethoxazole (SMX) can be degraded effectively by $HO^\bullet$ and $SO_4^{-\bullet}$. Gao et al. [12] used UV/$Na_2S_2O_8$ to degrade sulfamethoxypyridazine (SMP) and found that rate of SMP degradation increased as the $Na_2S_2O_8$ dose was increased or the pH was decreased. The mineralization of sulfonamides was less effective than their degradation using either individual or simultaneous systems in ozone-based AOPs [13]. Zhou et al. [14] showed that sulfate radical-based AOPs had potential for removing sulfonamides from the environment. Combining various AOPs commonly produces interesting synergistic effects that can significantly reduce the reaction time. Accordingly, H_2O_2 or $Na_2S_2O_8$ was added to UV/O_3 systems herein, to yield UV/O_3/H_2O_2 and UV/O_3/$Na_2S_2O_8$ systems that were used to mineralize pharmaceuticals. Antibiotic pharmaceuticals have been widely detected in the aquatic environment, raising increased concerns about the aquatic ecological system and potential risks to human health. Sulfonamide is one of the largest classes of antibiotics used globally. The eight currently used, common sulfonamides are sulfacetamide, sulfadiazine, sulfadoxine, sulfamethizole, SMX, sulfanilamide, sulfasalazine, and sulfisoxazole [15]. In tropical Asian waters, the most abundant antibiotic sulfonamide is SMX, followed by lincomycin and sulfathiazole (STZ) [16]. Additionally, SMX, STZ, and SMZ are typical sulfonamides, which are widespread in aqueous environments and have aroused great concern in recent years [17]. Therefore, SMX and STZ were selected as the parent compounds in this study.

The photodegradation of aqueous organic pollutants is an electrical-energy-intensive process, and electrical energy typically represents a major fraction of its costs. Simple figures-of-merit that are based on electric energy consumption can therefore be very useful. Most relevant studies compare efficiencies using reaction rate constants. Few investigations have considered the effects of power consumption on photodegradation. Notably, the literature on simultaneously evaluating the photodegradation efficiency and power consumption of sulfonamide oxidation in various AOPs is scarce. Accordingly, the value of electrical energy per order of pollutant removal (EEO) is used herein to compare the energy efficiencies of tested systems. Identifying the optimal operational parameters is critical for the successful application of AOPs. The objectives of this study are as follows; (i) to compare the mineralization efficiencies of SMX and STZ in UV/O_3, UV/H_2O_2, UV/$Na_2S_2O_8$, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems; (ii) to determine the synergistic effects of adding H_2O_2 or $Na_2S_2O_8$ to UV/O_3 at different pHs; (iii) to evaluate the effects of salinity on SMX and STZ mineralization; and (iv) to calculate the values of EEO and mineralization rates of all tested systems.

2. Materials and methods

2.1. Materials

SMX, STZ, sodium persulfate ($Na_2S_2O_8$), and phosphoric acid (H_3PO_4) were purchased from Sigma-Aldrich (USA). Table 1 presents the physiochemical properties of SMX and STZ. The hydrogen peroxide solution (H_2O_2, 30% w/w) was obtained from Merck (USA). Salinity was provided by NaCl, which was obtained from Taiyen. The pH of the solution was controlled by adding HNO_3 and NaOH via an automatic titrator. All solutions were prepared using deionized water (D.I. water). All experimental chemicals were analytical grade and used as purchased.

2.2. Mineralization experiments

Ozone was produced using a corona discharge ozone generator (250 W, ozone solutions TG-20) with oxygen as the feed gas. Before the experiment, 1,500 mL of D.I. water was added to the reactor and then ozonized for 30 min, in which time a constant ozone concentration in an aqueous solution was reached. Then, 500 mL sulfonamide solution was added to the reactor. Ozone gas was continuously fed in with a constant flow rate of 3.353 L/min at 298 K. The residual ozone concentration in the solution was measured using the indigo colorimetric method (Method 4500) [18]. In this study potassium titanium(IV) oxalate spectrophotometric determination was used to obtain the concentration of residual hydrogen peroxide in the solution [19]. The initial concentrations of sulfonamide and NaCl were 0.08 and 0.62 mM, respectively, and the temperature was 298 K. Photodegradation experiments were conducted in a 3 L glass reactor. The radius and height of the ozonation reactor were 14.5 and 23 cm, respectively. An 8 W UV lamp (254 nm, 1.12 W/m^2, Philips, China) was placed inside a quartz tube as a light source. The effects of H_2O_2 and $Na_2S_2O_8$ concentration on sulfonamide mineralization at pH 5 were evaluated. The effect of salinity on sulfonamide mineralization at pH 9 was determined. Twenty-milliliter aliquots were withdrawn from the reactor at pre-specified intervals. $Na_2S_2O_8$ and H_3PO_4 were utilized as the oxidant and the acidifier, respectively, in the total organic carbon (TOC) analyzer. The TOC values were measured by the thermal persulfate oxidation method. The decrease in TOC, measured using an O.I. 1010 TOC analyzer (O.I., College Station), revealed sulfonamide mineralization. The reported data are averages from triplicate samples.

3. Results and discussion

3.1. Effects of pH on sulfonamide mineralization

SMX and STZ have two pKa values; therefore, they can exist in cationic, neutral, and anionic forms. Under environmental conditions, only the latter two forms are relevant. pH is an important factor that affects the photodegradation of sulfonamides; therefore, the effects of pH on sulfonamide mineralization in UV/O_3, UV/H_2O_2, UV/$Na_2S_2O_8$, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems were investigated herein. Fig. 1 displays the results of SMX and STZ mineralization by UV photolysis, ozonation, persulfate, and hydrogen oxidation at pH 5. After 180 min of reaction, the SMX mineralization efficiencies by UV photolysis, O_3, persulfate, and hydrogen oxidation were 9%, 55%, 13%, and 16%, respectively (Fig. 1a); the STZ mineralization efficiencies were 7%, 68%, 13%, and 17%, respectively (Fig. 1b). Only O_3 significantly mineralized sulfonamide but the mineralization efficiency should be improved. Fig. 2 plots the SMX mineralization efficiency of various systems at different pHs. After 60 min of reaction, the SMX mineralization ratios in UV/O_3, UV/H_2O_2, UV/$Na_2S_2O_8$, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems at pH 5 were 73%, 5%, 11%, 64%, and 96%, respectively; those at pH 7 were 64%, 6%, 17%, 68%, and 94%, respectively; and those at pH 9 were 54%, 6%, 14%, 60%, and 77%, respectively. Fig. 3 plots the STZ mineralization efficiency of various systems at different pHs. After a 60 min reaction, the STZ mineralization ratios in UV/O_3, UV/H_2O_2, UV/$Na_2S_2O_8$, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems at pH 5 were 76%, 9%, 27%, 71%, and 95%, respectively; those at pH 7 were 73%, 7%, 15%, 66%, and 92%, respectively; and those at pH 9 were 50%, 14%, 28%, 65%, and 87%, respectively.

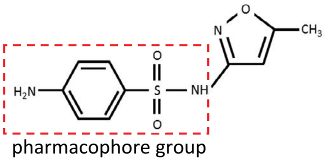
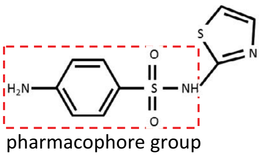
The mineralization follows pseudo-first-order kinetics as in Eq. (1):

$$\ln\left(\frac{C_t}{C_0}\right) = -kt \tag{1}$$

where C_t and C_0 (mg/L) are the concentrations of sulfonamides at reaction time t and the beginning of the reaction, respectively, and k (min^{-1}) is the pseudo-first-order rate constant of sulfonamide mineralization. Several researchers have indicated that the photodegradation of sulfonamides follows pseudo-first-order kinetics [6,12,21]. Table 2 presents the k values and correlation coefficients of sulfonamide mineralization in various oxidation systems. At pH 5, the k values of both SMX and STZ followed the order UV/O_3/$Na_2S_2O_8$ > UV/O_3 > UV/O_3/H_2O_2 > UV/$Na_2S_2O_8$ > UV/H_2O_2. In UV/O_3/$Na_2S_2O_8$, UV/O_3, and UV/O_3/H_2O_2 systems, the k values of SMX and STZ followed the order pH 5 > pH 7 > pH 9.

Ozone reacts with organics either by electrophilic attack or indirectly by a radical chain reaction, depending on the pH. Under alkaline conditions, ozone in solution rapidly decomposes to yield HO$^\bullet$ and other radicals in solution (Eqs. (2)–(4)); under acidic conditions, ozone remains stable, and reacts directly with organic substrates [22]. Since

Table 1
Physiochemical properties of SMX and STZ

	SMX	STZ
Chemical formula	$C_{10}H_{11}N_3O_3S$	$C_9H_9N_3O_2S_2$
Molecular weight (g mol^{-1})	253	255
CAS no.	723-46-6	72-14-0
logK_{ow}	0.89	0.05
Dissociation constants[a]	pK_{a1} = 1.6 and pK_{a2} = 5.7	pK_{a1} = 2.2 and pK_{a2} = 7.2
Melting point (K)	440	462
Solubility in water (mg L^{-1})	610 at 310 K	373 at 298 K
λ_{max} (nm)	266	283
Molecular structure		

[a] Boreen et al. [20].
logK_{ow}: partition coefficient between water and octanol.
λ_{max}: maximum absorption wavelength.

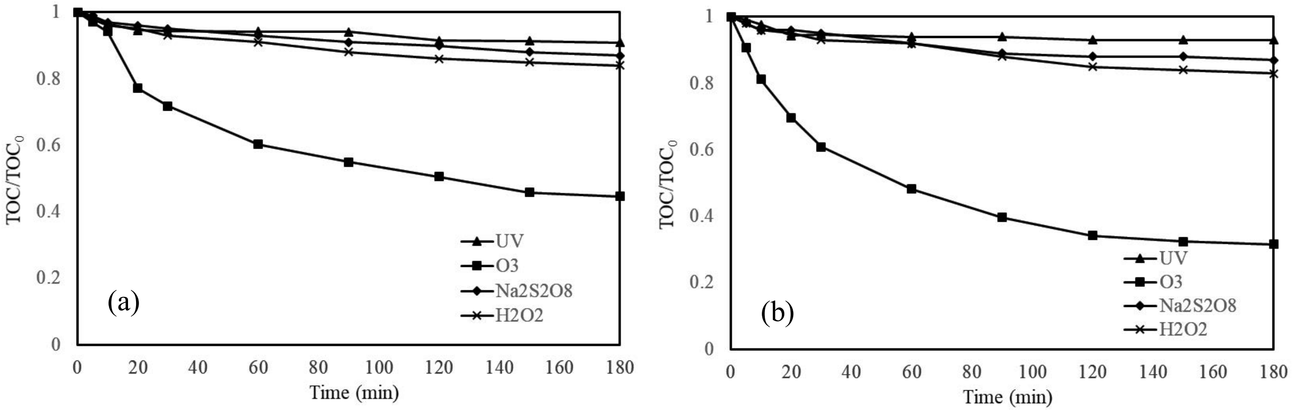


Fig. 1. SMX and STZ mineralization by UV photolysis, ozonation, persulfate, and hydrogen oxidation: (a) SMX and (b) STZ ([sulfonamide] = 0.08 mM; [oxidant] = 2.5 mM; pH 5; [O_3] = 0.14 mM).

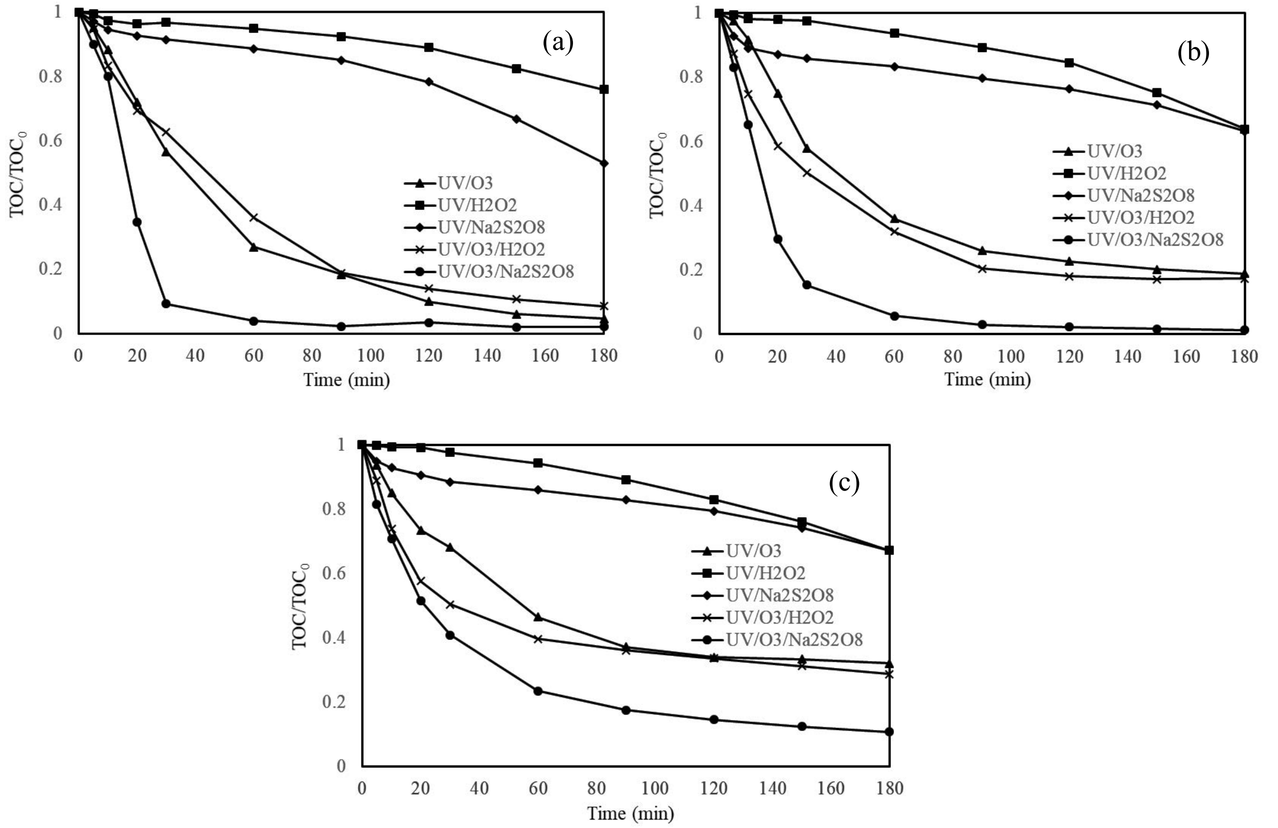


Fig. 2. Mineralization of SMX in different oxidation systems: (a) pH 5, (b) pH 7, and (c) pH 9 ([SMX] = 0.08 mM; [oxidant] = 2.5 mM; [O_3] = 0.14 mM).

the oxidation potential of $HO^\bullet$ considerably exceeds that of ozone molecules, direct oxidation is slower than radical oxidation. Typically, at pH < 4, direct ozonation dominates; at pH 4–9, both direct and radical oxidation are important; and at pH > 9, the indirect pathway dominates [1]. UV radiation can decompose ozone in water, yielding $HO^\bullet$ (Eq. (5)) [23]. The combined process is more effective than the process without UV because UV radiation promotes ozone decomposition, yielding additional $HO^\bullet$, increasing ozonation. Liu et al. [24] demonstrated that the removal of SMX by ozone was dominated by direct attack by molecular ozone rather than by free radicals; therefore, the removal rate of SMX increased as the pH decreased:

$$O_3 + OH^- \rightarrow 2HO^\bullet + O_3^{-\bullet} \tag{2}$$

$$O_3^{-\bullet} \rightarrow O_2 + O^{-\bullet} \tag{3}$$

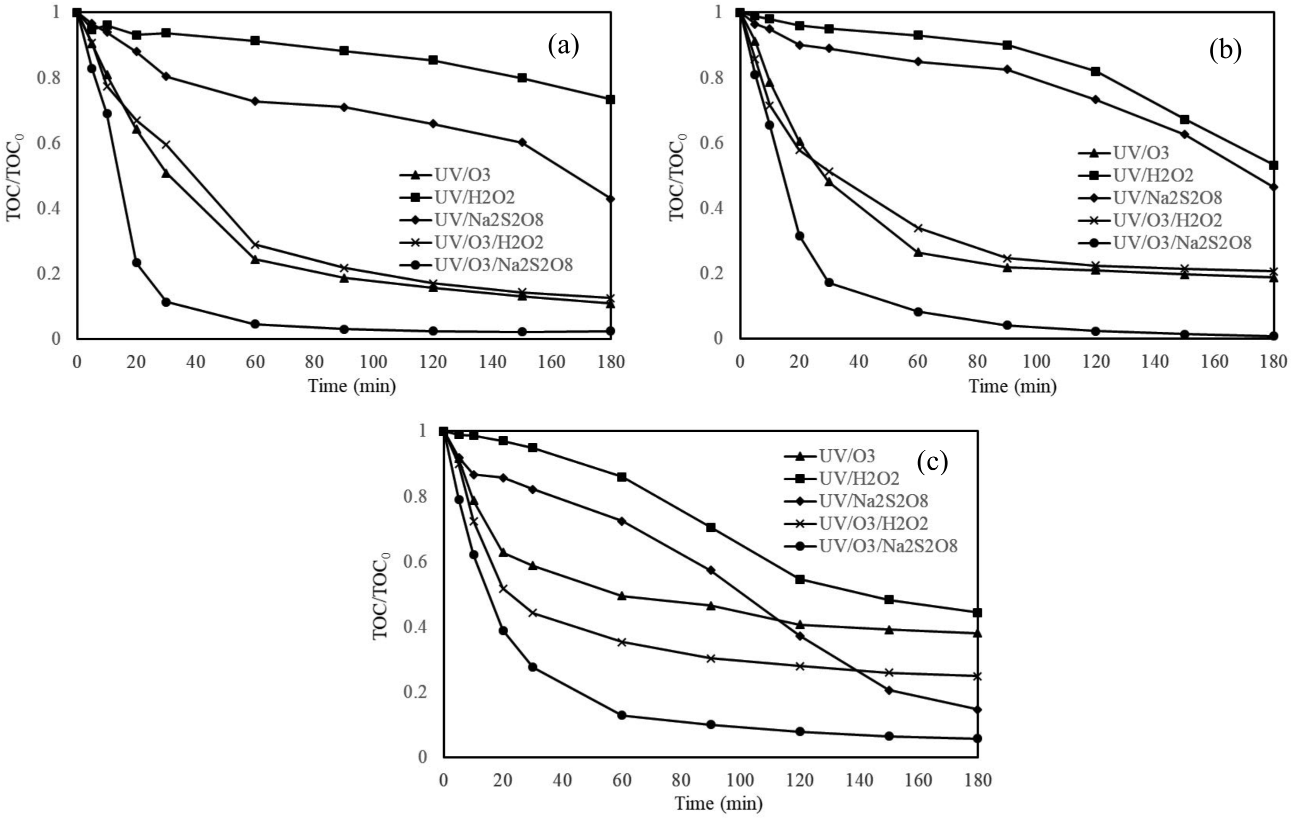


Fig. 3. Mineralization of STZ in different oxidation systems: (a) pH 5, (b) pH 7, and (c) pH 9 ([STZ] = 0.08 mM; [oxidant] = 2.5 mM; [O_3] = 0.14 mM).

Table 2
Pseudo-first-order reaction rate constants (k) and correlation coefficients (R^2) of sulfonamide mineralization in different oxidation systems ([sulfonamide] = 0.08 mM; [oxidant] = 2.5 mM; [O_3] = 0.14 mM)

	pH 5		pH 7		pH 9	
SMX	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
UV/O_3	0.0193	0.995	0.0160	0.983	0.0108 (0.0091)^a	0.987 (0.991)^a
UV/H_2O_2	0.0011	0.920	0.0014	0.978	0.0013	0.969
UV/$Na_2S_2O_8$	0.0022	0.920	0.0016	0.975	0.0015	0.981
UV/O_3/H_2O_2	0.0172	0.992	0.0165	0.989	0.0137 (0.0065)^a	0.897 (0.929)^a
UV/O_3/$Na_2S_2O_8$	0.0925	0.957	0.0692	0.996	0.0224 (0.0181)^a	0.984 (0.985)^a
STZ	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
UV/O_3	0.0238	0.999	0.0222	0.994	0.0103 (0.0090)^a	0.856 (0.986)^a
UV/H_2O_2	0.0011	0.955	0.0014	0.934	0.0039	0.942
UV/$Na_2S_2O_8$	0.0031	0.942	0.0026	0.937	0.0052	0.970
UV/O_3/H_2O_2	0.0201	0.986	0.0159	0.970	0.0159 (0.0072)^a	0.854 (0.944)^a
UV/O_3/$Na_2S_2O_8$	0.0536	0.924	0.0418	0.937	0.0322 (0.0233)^a	0.975 (0.977)^a

()^a: at 0.62 mM NaCl.

$$O^{-\bullet} + H^+ \rightarrow HO^\bullet \quad (4)$$

$$O_3 + H_2O + h\nu \rightarrow 2\ HO^\bullet + O_2 \quad (5)$$

The efficiency of ozonation depends strongly on the rate of ozone decay. After the first 30 min of aeration of D.I. water with ozone, the dissolved ozone concentrations at pH 5, pH 7, and pH 9 were 0.14, 0.09, and 0.04 mM, respectively. The residual ozone concentrations in solution followed the order pH 5 > pH 7 > pH 9, so the k values in the UV/O_3/$Na_2S_2O_8$, UV/O_3, and UV/O_3/H_2O_2 systems followed the same order as the residual ozone concentration. When the reaction at pH 5 began, molecular ozone might have primarily attacked sulfonamide molecules, while at pH 9, the $HO^\bullet$ attacked both sulfonamides and their degradation products. Klauson et al. [2] and Liu et al. [24] demonstrated that the removal of sulfonamides by ozone primarily involved direct attack by molecular ozone rather than by free radicals. Sulfonamides are aromatic compounds that are susceptible to electrophilic attack by ozone at low pH, at which the molecular ozone concentration is relatively high [25,26]. Urbano et al. [21] and Lin et al. [25] also reported that the degradation of sulfonamides by ozone decreased as pH increased.

Under alkaline conditions, H_2O_2 can react with O_3 in the $UV/O_3/H_2O_2$ system, yielding $HO^\bullet$, and hydroperoxyl radicals ($HO_2^\bullet$) (Eq. (6)) [27]. However, since Eq. (6) does not apply under acidic and neutral conditions, adding H_2O_2 to the UV/O_3 system did not increase the sulfonamide mineralization efficiency at pH 5 and 7. H_2O_2 scavenged $HO^\bullet$ from the solution to form $HO_2^\bullet$ (Eq. (7)). Eq. (8) describes the reaction in the UV/H_2O_2 system. Adding H_2O_2 to the UV/O_3 system at pH 5 or pH 7 suppressed the sulfonamide mineralization reactions (Table 2). In the $UV/O_3/H_2O_2$ system, the reactions are described by Eqs. (5)–(8), and the hybrid system at pH 9 provided a higher mineralization rate than the UV/O_3 and UV/H_2O_2 systems. The concentration of residual H_2O_2 in H_2O_2, UV/H_2O_2, and $UV/O_3/H_2O_2$ systems was measured herein. After 50 min of SMX mineralization at pH 5, the concentrations of residual H_2O_2 in H_2O_2, UV/H_2O_2, and $UV/O_3/H_2O_2$ system was 2.2, 1.7, and 0 mM, respectively (Fig. 4a); STZ mineralization yielded the same concentrations (Fig. 4b). UV decomposed H_2O_2 to $HO^\bullet$ (Eq. (8)); H_2O_2 reacted with O_3 in the $UV/O_3/H_2O_2$ system, yielding $HO^\bullet$, and hydroperoxyl radicals ($HO_2^\bullet$) (Eq. (6)) [27]. Accordingly, the residual concentrations of H_2O_2 in the tested H_2O_2-base systems followed the order $H_2O_2 > UV/H_2O_2 > UV/O_3/H_2O_2$:

$$O_3 + H_2O_2 \rightarrow O_2 + HO^\bullet + HO_2^\bullet \tag{6}$$

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{7}$$

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \tag{8}$$

Gao et al. [12] suggested that persulfate ions undergo photolysis under UV irradiation, generating $SO_4^{-\bullet}$ (Eq. (9)). These $SO_4^{-\bullet}$ radicals then react with water molecules to generate $HO^\bullet$ (Eq. (10)). Li et al. [28] revealed that persulfate ions also reacted with water to yield $SO_4^{-\bullet}$ and superoxide radicals ($O_2^{-\bullet}$) (Eq. (11)). In the $UV/O_3/Na_2S_2O_8$ system, reactions that are described by Eqs. (5) and (9)–(11) proceeded simultaneously in solution. $SO_4^{-\bullet}$, $HO^\bullet$, and $O_2^{-\bullet}$ were the main oxidizing radicals in the $UV/O_3/Na_2S_2O_8$ system herein. Hu et al. [6] showed that $SO_4^{-\bullet}$ and $HO^\bullet$ contributed to the degradation of iohexol in $UV/S_2O_8^{2-}$ system. The k value of iohexol degradation in the $UV/S_2O_8^{2-}$ system decreased as pH increased from 5 to 7, as did the k values of SMX and STZ herein. This result can be explained by the possibility that H^+ accelerated persulfate decomposition to produce $SO_4^{-\bullet}$ and reduced the generation of $HO^\bullet$ [6]. Under alkaline conditions (pH 7–9), the reactions between $SO_4^{-\bullet}$ and OH^- were accompanied by the generation of $HO^\bullet$ (Eq. (10)); hence, the k value of sulfonamide mineralization in the $UV/Na_2S_2O_8$ system increased with pH from 7 to 9 (Table 2).

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\bullet} \tag{9}$$

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + H^+ + HO^\bullet \tag{10}$$

$$S_2O_8^{2-} + 2H_2O \rightarrow 3SO_4^{2-} + 4H^+ + SO_4^{-\bullet} + O_2^{-\bullet} \tag{11}$$

The lengths of the O–O bonds in H_2O_2 and $S_2O_8^{2-}$ were 14.53 and 14.97 nm, respectively [29]. The molar extinction coefficient of $S_2O_8^{2-}$, which was in the range of 190–320 nm, exceeded that of H_2O_2, suggesting that $S_2O_8^{2-}$ is cleaved more easily than H_2O_2 and that the resulting $SO_4^{-\bullet}$ may be produced more readily than $HO^\bullet$ [30]. The experimental results of this study are consistent with the fact that the photodegradation efficiencies of 4-fluorophenol [31], C.I. Reactive Black 5 [32], 2,4-dichlorophenol [30], Cu(II)-EDTA [5], and iohexol [6] follow the order $UV/Na_2S_2O_8 > UV/H_2O_2$.

To understand better the enhancement of sulfonamide mineralization in the $UV/O_3/Na_2S_2O_8$ system, the enhancement ratio (α) was introduced. When $\alpha = 0$, the combined process is simply additive or cumulative; $\alpha > 1$ indicates an increase in the removal rate in the measured system, and $\alpha < 1$ indicates a reduction. The α values for SMX at pH 5, pH 7, and pH 9 were 4.3, 3.9, and 1.8, respectively, and those for STZ were 2.0, 1.7, and 2.1, respectively. The combination

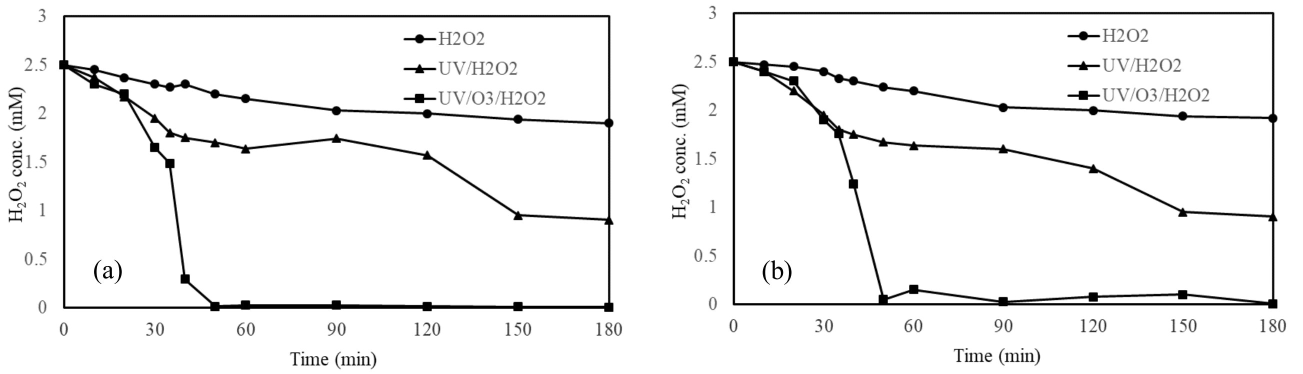


Fig. 4. Concentrations of residual H_2O_2 in H_2O_2, UV/H_2O_2, and $UV/O_3/H_2O_2$ systems: (a) SMX and (b) STZ ([sulfonamide] = 0.08 mM; pH 5; $[H_2O_2]$ = 2.5 mM; $[O_3]$ = 0.14 mM).

of $Na_2S_2O_8$ with UV/O_3 had significantly synergistic effects on sulfonamide mineralization. The UV/O_3/$Na_2S_2O_8$ system had the highest k values at all tested pHs and for both sulfonamides herein.

$$\alpha = [k\,(\mathrm{UV/O_3/Na_2S_2O_8})]/[k\,(\mathrm{UV/O_3}) + k\,(\mathrm{UV/Na_2S_2O_8})] \quad (12)$$

Since the mineralization efficiency of the UV/O_3/H_2O_2 system did not always exceed that of the UV/O_3 system, the effects of H_2O_2 concentration on mineralization efficiency in the UV/O_3/H_2O_2 system were determined. Fig. 5 plots the effects of H_2O_2 concentration on sulfonamide mineralization efficiency in the UV/O_3/H_2O_2 system. After a 60 min reaction, the SMX mineralization ratios in the UV/O_3/H_2O_2 system with the addition of 0, 2.5, 5, and 10 mM H_2O_2 were 73%, 64%, 47%, and 45%, respectively, and those for STZ were 76%, 71%, 51%, and 45%, respectively. Generally, the photodegradation rate of organic compounds increases with H_2O_2 concentration up to a threshold, beyond which photodegradation efficiency declines as H_2O_2 increasingly scavenges $HO^•$ [32]. H_2O_2 at high concentration acts as a scavenger of $HO^•$, generating $HO_2^•$, which has a much lower oxidation capacity than $HO^•$ (Eq. (7)). As the H_2O_2 concentration in the UV/O_3/H_2O_2 system was increased from 2.5 to 10 mM, no improvement could be observed. Accordingly, adding H_2O_2 to the UV/O_3 system had inhibitive effects at pH 5 and pH 7. Hence, the dose of H_2O_2 in the UV/O_3/H_2O_2 system must be carefully controlled.

Fig. 6 presents the effects of $Na_2S_2O_8$ concentration on sulfonamide mineralization efficiency in the UV/O_3/$Na_2S_2O_8$ system. After a 60 min reaction, the SMX mineralization percentages in the UV/O_3/$Na_2S_2O_8$ system with the addition of 0, 2.5, 5, and 10 mM $Na_2S_2O_8$ were 73%, 89%, 95%, and 97%, respectively, while the corresponding STZ mineralization percentages were 76%, 93%, 94%, and 95%, respectively. The mineralization of sulfonamide in the UV/O_3/$Na_2S_2O_8$ system increased with the concentration of added $Na_2S_2O_8$; however, adding more than 5 mM $Na_2S_2O_8$ in the UV/O_3 system resulted in an insignificant improvement in mineralization.

3.2. Effects of salinity on sulfonamide mineralization

The most abundant dissolved ions in seawater are sodium and chloride. Therefore, NaCl was added to the solutions as part of a study of the photocatalysis of sulfonamide mineralization at the same salinity levels as in seawater, to elucidate the effects of Na^+ and Cl^- ions. Fig. 7 plots the effects of salinity on sulfonamide mineralization efficiency in UV/O_3, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$

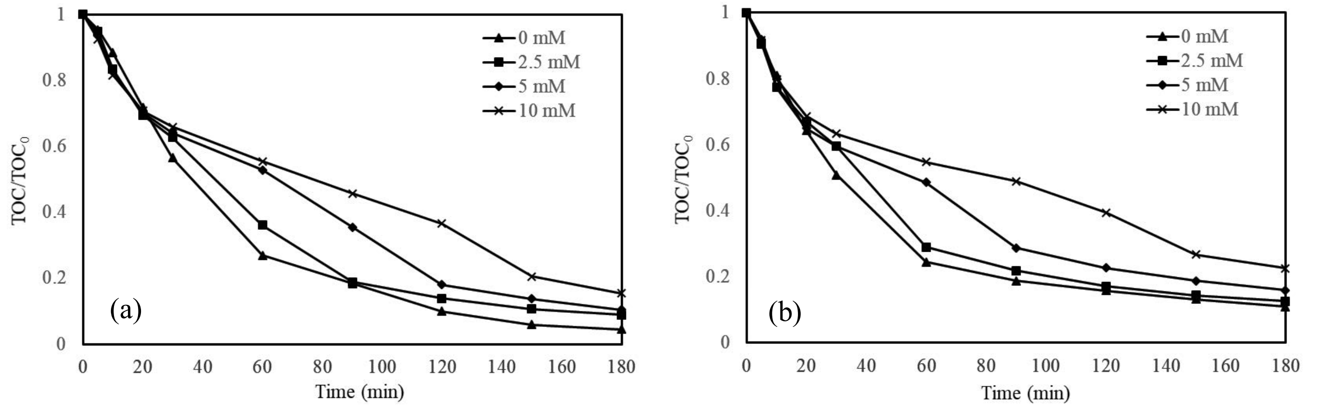


Fig. 5. Effects of H_2O_2 concentration on sulfonamide mineralization efficiency in UV/O_3/H_2O_2 system: (a) SMX and (b) STZ ([sulfonamide] = 0.08 mM; pH 5; [O_3] = 0.14 mM).

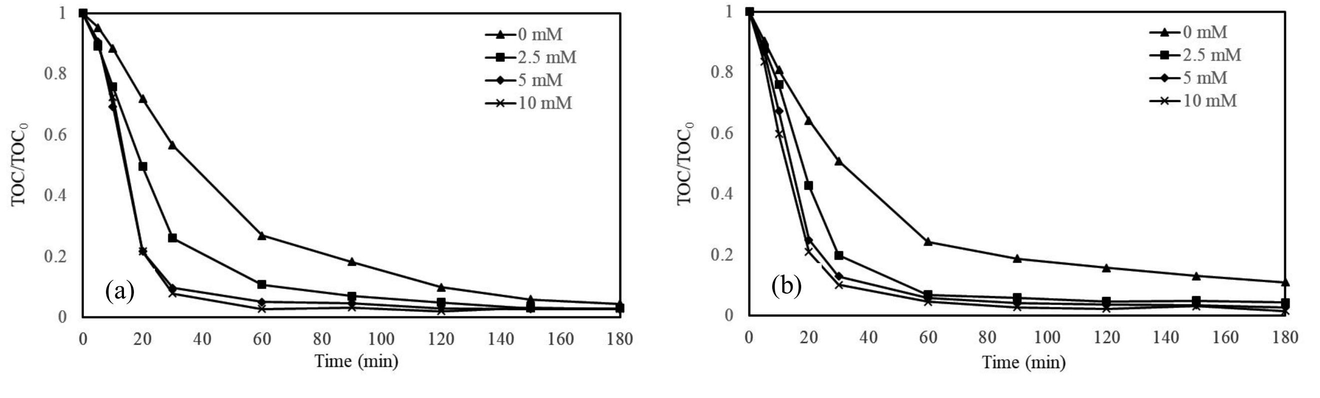


Fig. 6. Effects of $Na_2S_2O_8$ concentration on sulfonamide mineralization efficiency in UV/O_3/$Na_2S_2O_8$ system: (a) SMX and (b) STZ ([sulfonamide] = 0.08 mM; pH 5; [O_3] = 0.14 mM).

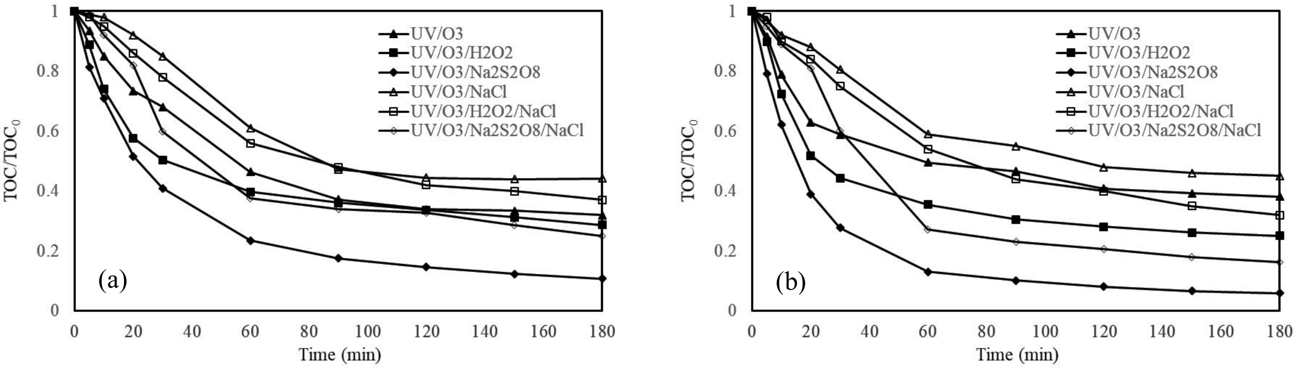


Fig. 7. Effects of salinity on sulfonamide mineralization efficiency in UV/O_3, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems: (a) SMX and (b) STZ ([sulfonamide] = 0.08 mM; [oxidant] = 2.5 mM; [NaCl] = 0.08 mM; pH 9; [O_3] = 0.14 mM).

systems. After a 60 min reaction at pH 9, the SMX mineralization percentages in the UV/O_3/NaCl, UV/O_3/H_2O_2/NaCl, and UV/O_3/$Na_2S_2O_8$/NaCl systems were 39%, 44%, and 62%, respectively; the corresponding STZ mineralization percentages were 41%, 46%, and 73%, respectively. Adding NaCl reduced the k values of SMX and STZ in the UV/O_3, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems. Inorganic salts influence ozonation as they are radical scavengers and affect the mass transfer rate [21]. The equations for the reaction of chloride ions with $HO^•$ (Eqs. (13) and (14)) [33] and $SO_4^{-•}$ (Eqs. (15)) [6] are as follows. The oxidizing ability of $Cl^•$ is weaker than that of $HO^•$ and that of $SO_4^{-•}$ [6,34], so the generation of $Cl^•$ reduced the rate of sulfonamide mineralization.

$$HO^• + Cl^- \rightarrow HOCl^{-•} \tag{13}$$

$$HOCl^{-•} + H^+ \rightarrow Cl^• + H_2O \tag{14}$$

$$SO_4^{-•} + Cl^- \rightarrow SO_4^{2-} + Cl^• \tag{15}$$

3.3. Analysis of electrical energy efficiency

The photodegradation of aqueous organic pollutant is an electrical-energy-intensive process, and electrical energy typically represents the largest part of the operating cost. Therefore, the energy efficiency must be evaluated. The figure-of-merit electrical energy per order (EEO) is appropriate for estimating the electrical energy efficiency [35]. It is a powerful scale-up parameter and measure of the rate of treatment in a fixed volume of contaminated water as a function of applied specific energy consumed [36]. The EEO value was used to compare the energy efficiencies of systems. For low pollutant concentrations, the EEO (kW h m^{-3} order^{-1}) value can be derived using Eq. (16).

$$EEO = \frac{(38.4 \times P)}{(V \times k)} \tag{16}$$

where P is the power (kW) of AOPs; V is the volume (L) of solution in the reactor; and k is the pseudo-first-order rate constant (min^{-1}) for mineralization [35,36]. A higher EEO value corresponds to a lower energy efficiency of the system. Table 3 summarizes the EEO value of various systems under different pHs. The EEO results at pH 5 revealed that the UV/O_3/$Na_2S_2O_8$ system consumed 79% and 56% less energy than the UV/O_3 system for SMX and STZ mineralization, respectively. For SMX, the UV/O_3/$Na_2S_2O_8$ system at pH 5 yielded the lowest EEO value; for STZ, the UV/$Na_2S_2O_8$ system at pH 9 did so. These results suggest that the optimal conditions (for both mineralization efficiency and energy consumption) varied with the sulfonamide, revealing that the development of a general mineralization method for a mixture of sulfonamides would be very difficult.

Table 3
EEO value (kW h m^{-3} order^{-1}) of various systems under different pHs ([sulfonamide] = 0.08 mm; [oxidant] = 2.5 mM; [O_3] = 0.14 mM)

	pH 5	pH 7	pH 9
SMX	EEO	EEO	EEO
UV/O_3	257	310	459
UV/H_2O_2	140	110	118
UV/$Na_2S_2O_8$	70	96	102
UV/O_3/H_2O_2	288	300	362
UV/O_3/$Na_2S_2O_8$	54	72	221
STZ	EEO	EEO	EEO
UV/O_3	208	223	481
UV/H_2O_2	140	110	39
UV/$Na_2S_2O_8$	50	59	30
UV/O_3/H_2O_2	246	312	312
UV/O_3/$Na_2S_2O_8$	92	119	154

4. Conclusions

UV/O_3, UV/H_2O_2, UV/$Na_2S_2O_8$, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems were used to mineralize SMX and STZ, and the mineralization rates and energy consumption efficiencies were compared. At pH 5, the k values of both SMX and STZ followed the order UV/O_3/$Na_2S_2O_8$ > UV/O_3 > UV/O_3/H_2O_2 > UV/$Na_2S_2O_8$ > UV/H_2O_2. For UV/O_3/$Na_2S_2O_8$, UV/O_3, and UV/O_3/H_2O_2 systems, the k values for both SMX and STZ followed the order pH 5 > pH 7 > pH 9. The combination of $Na_2S_2O_8$ with UV/O_3 had significantly synergistic effects on the mineralization of sulfonamides. Salinity inhibited the mineralization of sulfonamides in UV/O_3, UV/O_3/H_2O_2, and UV/O_3/$Na_2S_2O_8$ systems owing to the scavenging of radicals by chloride ions. At pH 5, the most energy-efficient system for SMX mineralization was UV/O_3/$Na_2S_2O_8$ and that for STZ mineralization was UV/$Na_2S_2O_8$.

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