Removal of sulfamethizole from aqueous solution using advanced oxidation processes: effects of pH and salinity

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ABSTRACT

This study investigates the removal of sulfamethizole (SFZ) in ozone (O_3), $O_3/Na_2S_2O_8$ (sodium persulfate), $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ systems. The effects of pH and salinity on SFZ mineralization were evaluated. The mineralization of SFZ followed pseudo-first-order kinetics. At pH 5, the rate constants of SFZ mineralization in O_3, $O_3/Na_2S_2O_8$, $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ systems were 0.576, 0.924, 0.702, 1.26, and 5.21 h^{-1}, respectively. The SFZ mineralization rate followed the order pH 5 > pH 7 > pH 9 in all tested advanced oxidation processes. Salinity increased the rate of SFZ mineralization in O_3 and $O_3/Na_2S_2O_8$ systems and decelerated it in $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ systems. $UV/O_3/Na_2S_2O_8$ was the best system for mineralizing SFZ, and sulfate radicals were the predominant species in $UV/O_3/Na_2S_2O_8$.

Key words | mineralization, ozone, persulfate, sulfonamide

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HIGHLIGHTS

- This study compared the efficiencies of SFZ mineralization in O_3, $O3/Na_2S_2O_8$, $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ processes.
- This study determined the influences of pH and salinity on SFZ mineralization in these AOPs.

INTRODUCTION

Sulfonamides are extensively used as antibiotics in human and veterinary medicine due to their strong antimicrobial activity, stable chemical properties, and low cost (Magureanu et al. 2015; Wang & Wang 2016). The chemical structure of sulfonamides is characterized by a common sulfanilamide group and a distinct five- or six-membered heterocyclic ring. Sulfonamides have frequently been detected in aquatic environments and are of increasing concern due to their detrimental bio-effects and their potential to induce antibiotic resistance (Anjali & Shanthakumar 2019). The detection of sulfonamides in treated drinking water and wastewater treatment plant effluent demonstrates that they are not effectively removed by conventional water and wastewater treatment (Garoma et al. 2010). Therefore, effective advanced treatment processes are required to prevent the entry of sulfonamides into the natural environment.

Radical-based advanced oxidation processes (AOPs), and especially those that involve hydroxyl radicals

($HO^{\bullet}$) and sulfate radicals ($SO_4^{-\bullet}$), have been successfully used to destroy organic pollutants in various water matrices, such as wastewater, surface water, and groundwater. Zhang et al. (2015) and Acosta-Rangel et al. (2018) 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. Gao et al. (2019) used $UV/Na_2S_2O_8$ (sodium persulfate) to degrade sulfamethoxypyridazine (SMP) and found that the rate of SMP degradation increased as the $Na_2S_2O_8$ dose was increased or the pH was decreased. Zhou et al. (2019) showed that sulfate radical-based AOPs were promising for the removal of sulfonamides from the environment. However, Zhang et al. (2020) showed the mineralization efficiency was only approximately 70.7% after a reaction for 8 h in seawater, revealing that $UV/Na_2S_2O_8$ oxidation incompletely degraded sulfamethoxazole (SMX).
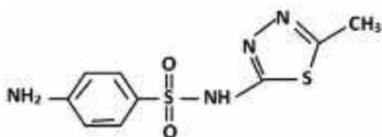
Ozone (O_3) has been proven to be effective in degrading organic pollutants in water due to its high oxidation potential. Ozone can also degrade sulfonamides in water (Urbano et al. 2017). Ozone and persulfate are oxidants that are frequently used to treat water or wastewater. The combination of solar and UV AOPs with compounds such as ozone, hydrogen peroxide, and persulfate increases the efficiency of removal of pollutants. Zhou et al. (2019) showed that sulfamethizole (SFZ) was less amenable to persulfate oxidation than sulfisoxazole (SIX), sulfathiazole (STZ) and SMX, suggesting that the thiadiazole ring is more resistant than other heterocyclic rings to attack by persulfate radicals. Therefore, in this study, SFZ was the target compound. No systematic comparison of the combined homogeneous oxidation treatments of hydroxyl and sulfate radicals using SFZ has been published. Therefore, in this work, O_3, $O_3/Na_2S_2O_8$, $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ processes are used to mineralize SFZ. The objectives of this investigation are (1) to compare the efficiencies of SFZ mineralization using these AOPs; (2) to evaluate the effects of pH on SFZ mineralization, and (3) to determine the influences of salinity on SFZ mineralization in these AOPs.

MATERIALS AND METHODS

Materials

SFZ, sodium persulfate ($Na_2S_2O_8$), and phosphoric acid (H_3PO_4) were purchased from Sigma-Aldrich. Table 1 provides the physicochemical properties of SFZ. The pH of the solution was adjusted by adding 0.1 M nitric acid (HNO_3) or sodium hydroxide (NaOH) during the reaction, both of which were purchased from Merck. Sodium chloride (NaCl) was the source of salinity and was obtained from Taiyen. Tert-butyl alcohol (TBA) and isopropyl alcohol (IPA), which were used as radical scavengers, were obtained from J. T. Baker. All reagents were of analytical grade and used without further purification. Deionized water (D.I. water) was used throughout this study.

Experimental methods

Ozone was generated using a corona discharge ozone generator (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 period a constant ozone concentration in aqueous solution was reached. Ozone gas was fed in continuously at a constant flow rate of 3.353 L/min and 298 K. The residual ozone concentration in the solution was measured using the indigo colorimetric method (Method 4500) (APHA 1992). Since the average salinity of seawater is approximately 3.5%, the effects of salinity on the removal of SFZ from aqueous solution were investigated. The initial concentrations of SFZ, $Na_2S_2O_8$, and NaCl were 20 mg/L, 10 mM, and 36.27 g/L, respectively, and the temperature was 298 K. Photodegradation experiments were conducted in a 3-L glass reactor. A UV lamp (8 W, 254 nm, 1.12 W/m²,

Table 1 | Physicochemical properties of SFZ

Chemical formula	$C_9H_{10}N_4O_2S_2$
Molecular weight (g/mol)	270
CAS no.	144-82-1
Vapor pressure (mmHg) at 298 K	2.06×10^{-9} Anjali & Shanthakumar (2019)
log K_{ow}	0.54 Anjali & Shanthakumar (2019)
Dissociation constants	$pK_{a1} = 1.9$ and $pK_{a2} = 5.3$ Garoma et al. (2010)
Melting point (K)	483 Klauson et al. (2019)
Solubility in water (mg/L) at 298 K	105 Klauson et al. (2019)
λ_{max} (nm)	274 Wu et al. (2019)
Molecular structure	

log K_{ow}: partition coefficient between water and octanol.
λ_{max}: maximum absorption wavelength.

Philips) was placed inside a quartz tube as an irradiation source. The concentration of TBA and IPA used in the radical scavenging experiments was 250 mM. Aliquots (20 mL) were extracted from the photoreactor at predetermined intervals. In the total organic carbon (TOC) analyzer, the oxidant and the acidifier were $Na_2S_2O_8$ and H_3PO_4, respectively. The decrease in TOC, measured using an O.I. 1010 TOC analyzer, yielded the degree of SFZ mineralization. All experiments were conducted in duplicate, and mean values were reported.

RESULTS AND DISCUSSION

Reaction species in AOPs

Solution pH is an important factor that affects the predominant radical species and the speciation of the parent compound. Figure 1(a)–1(c) provide the efficiency of SFZ mineralization in O_3, $O_3/Na_2S_2O_8$, $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ systems at pH 5, pH 7, and pH 9. After 60 min of reaction at pH 5, the percentages of SFZ mineralization in the O_3, $O_3/Na_2S_2O_8$, $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ systems were 54, 64, 45, 81, and 91%, respectively (Figure 1(a)). At all tested pHs, $UV/O_3/Na_2S_2O_8$ was the tested AOPs with the highest SFZ mineralization efficiency. The experimental results revealed that as the reaction time increased, the SFZ concentration decreased. In the $UV/O_3/Na_2S_2O_8$ system, a plateau without further mineralization was reached after 60 min of reaction, corresponding to 91%, 85% and 58% mineralization at pH 5, pH 7, and pH 9, respectively (Figure 1(a)–1(c)). No system achieved complete mineralization in 180 min.

Figure 2(a) and 2(b) plot the ozone concentration during the reactions in the O_3 and UV/O_3 systems, respectively. After the first 30 min of aeration of D.I. water with ozone, the dissolved ozone concentration at pH 5, pH 7, and pH 9 was 6.2, 4.1, and 1.7 mg/L, respectively. After SFZ was added for 60 min, the dissolved ozone concentration in the O_3 system at pH 5, pH 7, and pH 9 was 5.4, 4.3, and 2.5 mg/L (Figure 2(a)), respectively; and the concentration in the UV/O_3 system was 0.81, 0.90, and 0.81 mg/L, respectively (Figure 2(b)).

Ozone oxidizes organics by two possible degradation routes: (1) at basic pH, it rapidly decomposes to yield hydroxyl and other radicals in solution, according to Equations (1), and (2) at acidic pH, ozone is stable and can react directly with organics. UV radiation can decompose
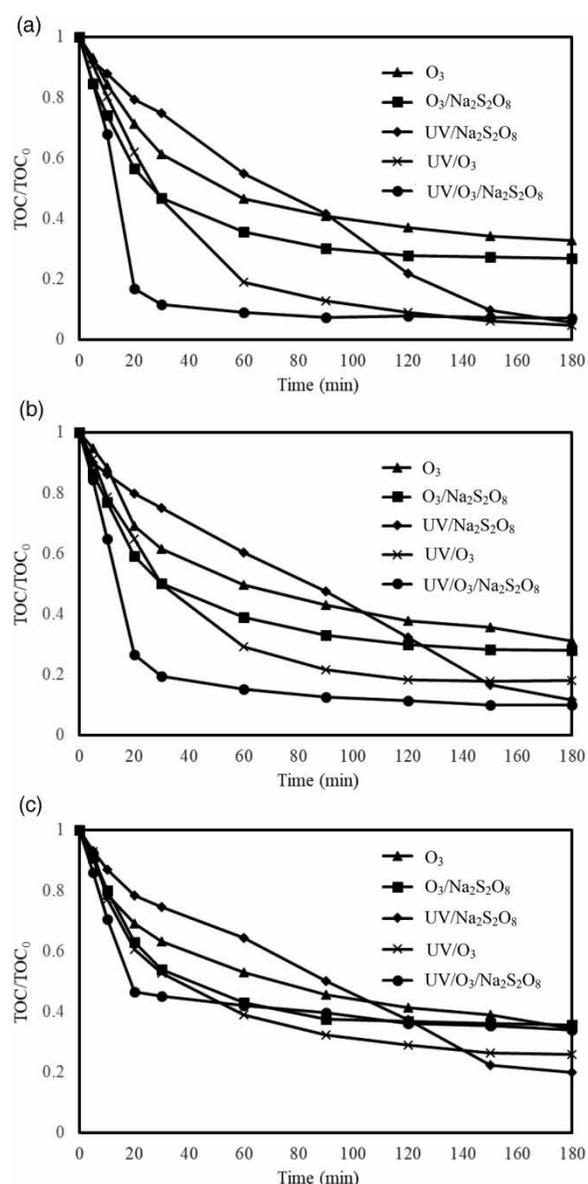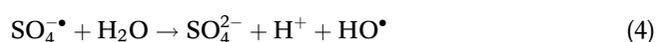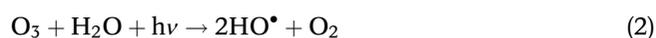

Figure 1 │ The SFZ mineralization efficiency in different AOPs (a) pH 5 (b) pH 7 (c) pH 9 ([SFZ] = 20 mg/L and [$Na_2S_2O_8$] = 10 mM).

ozone in water, yielding hydroxyl radicals (Equation (2)) (Glaze *et al.* 1987). Accordingly, the residual ozone concentration in aqueous solution in the O_3 system (Figure 2(a)) exceeded that in the UV/O_3 system (Figure 2(b)). Ozonation at neutral pH is known to involve both direct and indirect mechanisms. As hydroxyl radical-based oxidation is ruled out, the electrophilic reactions of molecular ozone are considered to be responsible for the observed mineralization of sulfonamides during ozonation (Klauson *et al.* 2019). Gao *et al.* (2019) suggested that persulfate ions undergo photolysis under UV irradiation, generating sulfate radicals
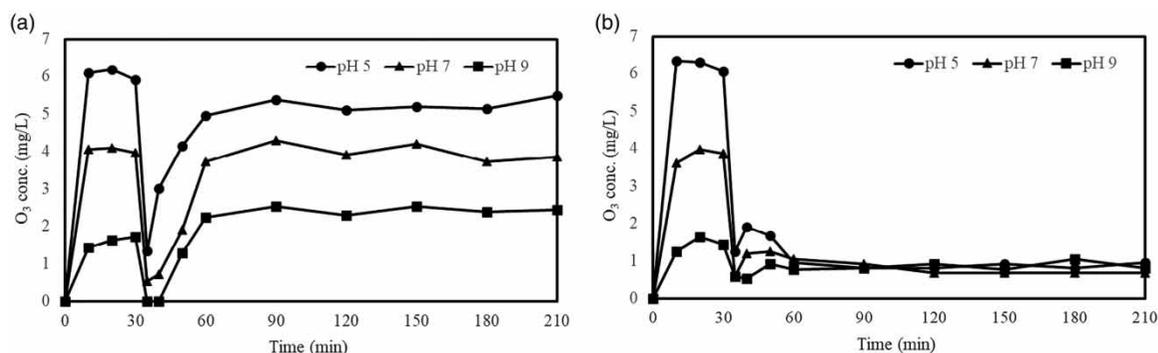
Figure 2 | The residual ozone concentration in aqueous solution (a) O_3 (b) UV/O_3.

(Equation (3)). These sulfate radicals then react with water molecules to form hydroxyl radicals (Equation (4)). Gao et al. (2019) suggested that both hydroxyl and sulfate radicals contributed to SMP degradation in UV/$Na_2S_2O_8$, and sulfate radicals played the more important role. Cui et al. (2016) also found that sulfate radicals were the predominant species in the degradation of sulfonamides by UV/peroxymonosulfate. Li et al. (2016) showed that persulfate ions also react with water to generate sulfate and superoxide radicals (Equation (5)). In the UV/O_3/$Na_2S_2O_8$ system, the reactions described by Equations (1)–(5) proceeded simultaneously in aqueous solution:

$$O_3 + OH^- \rightarrow 2HO^\bullet + O_3^{-\bullet} \tag{1}$$

$$O_3 + H_2O + h\nu \rightarrow 2HO^\bullet + O_2 \tag{2}$$

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\bullet} \tag{3}$$

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + H^+ + HO^\bullet \tag{4}$$

$$S_2O_8^{2-} + 2H_2O \rightarrow 3SO_4^{2-} + 4H^+ + SO_4^{-\bullet} + O_2^{-\bullet} \tag{5}$$

The mineralization of SFZ approximately followed pseudo-first-order kinetics, described by Equation (6):

$$\ln(C_t/C_0) = -kt \tag{6}$$

where t is reaction time; k is the pseudo-first-order rate constant, and C_0 and C_t are the concentrations of TOC at times $t = 0$ and $t = t$, respectively. Several researchers have also found that the photodegradation of sulfonamides in AOPs follows pseudo-first-order kinetics (Lin et al. 2009; Urbano et al. 2017; Gao et al. 2019). Table 2 shows the pseudo-first-order reaction rate constants and correlation coefficients of SFZ mineralization. The k value for SFZ mineralization decreased as pH increased from 5 to 9 in all

tested AOPs. At pH 5, the k values followed the order UV/O_3/$Na_2S_2O_8$ > UV/O_3 > O_3/$Na_2S_2O_8$ > UV/$Na_2S_2O_8$ > O_3. Combining UV or/and persulfate with ozone improved the SFZ mineralization rate because hydroxyl and sulfate radicals were generated simultaneously.

pH effects of O_3 and UV/O_3 systems on SFZ mineralization

The residual ozone concentration in aqueous solution in O_3 and UV/O_3 systems followed the order pH 5 > pH 7 > pH 9 (Figure 2(a) and 2(b)), and so the k values in the O_3 and UV/O_3 systems followed the same order as the residual ozone concentration. Gao et al. (2014) showed that a higher pH favored the oxidative removal of SMX, perhaps because deprotonation at higher pH made the SMX more reactive toward molecular ozone than neutral SMX. The rate of ozonation of SMX, sulfadimethoxine (SDM), and SMZ decreased in the order pH 3 > pH 7 > pH 11 (Lin et al. 2009), which is consistent with the fact that the principle of dissolution, O_3, had a higher concentration at a lower pH. When OH^- is scarce (at low pH), the depletion reaction is slow, allowing the accumulation of much dissolved O_3, whereas when OH^- is abundant (at high pH), the depletion reaction is rapid, preventing the accumulation of dissolved O_3. The mineralization of SFZ, which is susceptible to electrophilic attack by O_3, is more rapid at lower pH, at which the aqueous O_3 concentration is higher. During ozonation, the degradation of target chemicals can be initiated by a direct reaction with aqueous ozone and hydroxyl radicals, which are generated by the decomposition of aqueous ozone (Garoma et al. 2010). Liu et al. (2012) and Klauson et al. (2019) showed that the removal of sulfonamides by ozone primarily involved direct attack by molecular ozone rather than by free radicals. Despite the high reduction

Table 2 | The pseudo-first-order reaction rate constants (k) and correlation coefficients (R^2) of SFZ mineralization in different AOPs

	pH 5		pH 7		pH 9	
	k (h^{-1})	R^2	k (h^{-1})	R^2	k (h^{-1})	R^2
O_3	0.576 (0.690)[a]	0.941 (0.918)[a]	0.540	0.915	0.444	0.932
$O_3/Na_2S_2O_8$	0.924 (0.960)[a]	0.929 (0.954)[a]	0.852	0.922	0.792	0.915
$UV/Na_2S_2O_8$	0.702 (0.480)[a]	0.966 (0.975)[a]	0.510	0.985	0.444	0.987
UV/O_3	1.26 (0.714)[a]	0.969 (0.994)[a]	0.858	0.952	0.576	0.906
$UV/O_3/Na_2S_2O_8$	5.21 (1.48)[a]	0.941 (0.962)[a]	3.71	0.961	1.62	0.889

[a]: At 3.5% NaCl.

potential of hydroxyl radicals, direct oxidation by ozone was more effective in degrading sulfaquinoxaline (SQX) (Urbano et al. 2017). The rate of SQX degradation declined as the pH value increased. The findings concerning SFZ herein are similar to those of Urbano et al. (2017) concerning SQX.

pH effects of $O_3/Na_2S_2O_8$, $UV/Na_2S_2O_8$, and $UV/O_3/Na_2S_2O_8$ systems on SFZ mineralization

The dependence of k on pH is attributable to the combined speciation effects of oxidant and SFZ. As revealed by the SFZ dissociation constant ($pK_{a1} = 1.9$ and $pK_{a2} = 5.3$), three major species of SFZ are present in the aqueous solution; they are the cationic form (SFZ^+), the neutral form (SFZ^0), and the anionic form (SFZ^-). Therefore, electrostatic repulsion is responsible for the inhibition of mineralization at high pH during SFZ oxidation by persulfate in $O_3/Na_2S_2O_8$ and $UV/O_3/Na_2S_2O_8$ systems. Sulfate radicals are generally accepted to react more selectively with organic compounds than hydroxyl radicals through the one-electron transfer mechanism (Ji et al. 2014). Moreover, the oxidative ability of hydroxyl radicals exceeds that of sulfate radicals, and so the k values of UV/O_3 exceeded those of $UV/Na_2S_2O_8$ (Table 2). Gao et al. (2019) revealed that the degradation rate of SMP in $UV/Na_2S_2O_8$ depends strongly on pH and decreased in the order pH 5.5 > pH 7.0 > pH 9.0. The effects of pH in $UV/Na_2S_2O_8$ herein were similar to those identified by them.
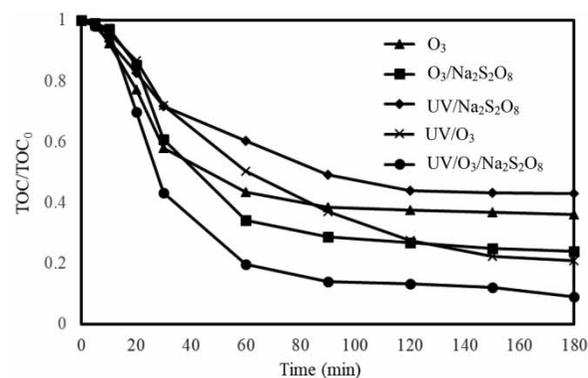
Effects of salinity on SFZ mineralization

Figure 3 plots the effects of salinity at pH 5 on SFZ mineralization. The k values in O_3 and $O_3/Na_2S_2O_8$ systems were increased by adding salinity whereas those in $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ systems were reduced (Table 2). Increasing the ionic strength reduces the coalescence of O_3 bubbles, revealing that the interfacial surface area of the ozone bubbles and the mass transfer rate are increased (Gottschalk et al. 2010). Since the major oxidation species in the O_3 and $O_3/Na_2S_2O_8$ systems was molecular oxygen, the k values of O_3 and $O_3/Na_2S_2O_8$ in simulated seawater slightly exceeded those in D.I. water due to the high ionic strength of the former (Table 2). Chloride ions had an inhibitory effect possibly due to the consumption and mutual quenching of hydroxyl and sulfate radicals by chloride ions (Zhang et al. 2020). Yang et al. (2015) and Wu et al. (2019) revealed that the photocatalytic degradation and mineralization of sulfonamides decreased as the salinity in UV/TiO_2 increased. The slower mineralization of SFZ in simulated seawater was explained by the action of inorganic anions and cations therein as radical scavengers in $UV/Na_2S_2O_8$, UV/O_3, and $UV/O_3/Na_2S_2O_8$ systems, reducing SFZ mineralization efficiency.

Effects of radical scavenger addition on SFZ mineralization

TBA and IPA were used herein as scavengers to clarify the contributions of sulfate and hydroxyl radicals to SFZ degradation. Normally, IPA can rapidly react with both

Figure 3 | Effects of salinity on SFZ mineralization (pH = 5, [SFZ] = 20 mg/L, [$Na_2S_2O_8$] = 10 mM and [NaCl] = 36.27 g/L).
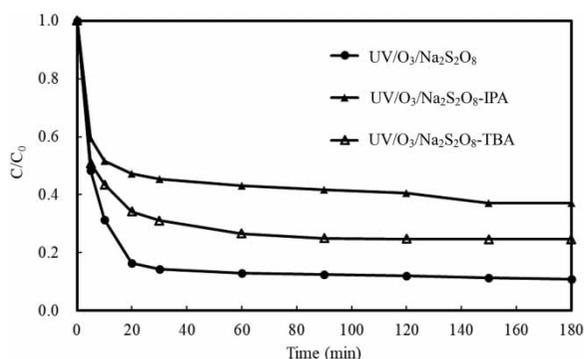
Figure 4 │ Removal efficiency of SFZ with radical scavenger addition in UV/O$_3$/Na$_2$S$_2$O$_8$ system (pH = 9, [SFZ] = 20 mg/L, [Na$_2$S$_2$O$_8$] = 10 mM, [NaCl] = 36.27 g/L and [radical scavenger] = 250 mM).

sulfate and hydroxyl radicals (Yu *et al.* 2016), whereas TBA reacts with hydroxyl radicals more rapidly than with sulfate radicals (Gao *et al.* 2019). The different reaction rates of the two scavengers of sulfate and hydroxyl radicals can help to identify their contributions to SFZ degradation in UV/O$_3$/Na$_2$S$_2$O$_8$. Figure 4 plots the efficiency of removal of SFZ with the addition of radical scavengers. After 180 min of reaction at pH 9, the SFZ removal percentage declined from 90% to 63% and 75% in the presence of 250 mM IPA and TBA, respectively, suggesting that both sulfate and hydroxyl radicals contributed to SFZ degradation. A weak inhibition effect was observed after TBA was added, indicating that sulfate radicals were more important than hydroxyl radicals in UV/O$_3$/Na$_2$S$_2$O$_8$.

CONCLUSIONS

The mineralization of SFZ in O$_3$, O$_3$/Na$_2$S$_2$O$_8$, UV/Na$_2$S$_2$O$_8$, UV/O$_3$, and UV/O$_3$/Na$_2$S$_2$O$_8$ systems at various pH values was studied. At pH 5, the k values followed the order UV/O$_3$/Na$_2$S$_2$O$_8$ > UV/O$_3$ > O$_3$/Na$_2$S$_2$O$_8$ > UV/Na$_2$S$_2$O$_8$ > O$_3$. In all tested systems, the SFZ mineralization rate followed the order pH 5 > pH 7 > pH 9. The major oxidation species were molecular oxygen in O$_3$ and O$_3$/Na$_2$S$_2$O$_8$ systems and sulfate radicals in UV/Na$_2$S$_2$O$_8$ and UV/O$_3$/Na$_2$S$_2$O$_8$ systems. Hydroxyl radicals played an important role in the UV/O$_3$ system. The decrease in the mineralization of SFZ upon the addition of salinity was attributed to the action of chloride ions in simulated seawater as hydroxyl or/and sulfate radical scavengers in UV/O$_3$/Na$_2$S$_2$O$_8$ system.

DATA AVAILABILITY STATEMENT

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

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