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RESEARCH ARTICLE

Effect of Chlorine Dioxide on the Removal of Sulfadimethoxine and Sulfamethoxazole in Freshwater and Seawater

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Abstract

This study aimed to understand the fate of sulfonamides (SAs) under dark condition in a laboratory-scale aquatic system, and evaluate the removal of SAs by using Chlorine dioxide. Based on the mass spectrometry quantification, our results have shown that two sulfonamides were transformed at very slow rate in the dark. The 180 day degradation efficiencies (%) of sulfadimethoxine (SDM) in freshwater and seawater were 6.37 ± 2.56 and 4.38 ± 3.43 , respectively, while those of sulfamethoxazole (SMX) in freshwater and seawater were 7.81 ± 2.15 and 6.60 ± 2.69 , respectively. In the treatment of Chlorine dioxide for the removal of SAs in freshwater and seawater, it was found that the complete removals can be achieved within 7 day at the 1:1 ratio. The removal efficiencies increased significantly as the concentration ratio of treatment increasing to 5:1 and 10:1. SDM (0.1 mg/L) in freshwater was removed completely at 7.0, 2.0 and 0.5 day by treating Chlorine dioxide of 0.1, 0.5, and 1.0 mg/L, respectively. It was noted that the removals of SDM in seawater were improved to 0.25 day in both treatments of 0.5 and 1.0 mg/L. Similar improvements were also observed in the removal of SMX (0.1 mg/L) under the same treatment. The complete removal of SMX in freshwater was done at 7.0, 2.0 and 0.5 day, respectively, whereas that of SMX in seawater was done at 4.0, 0.25 and 0.25 day, respectively.

Keywords: Chlorine dioxide, Sulfadimethoxine, Sulfamethoxazole

1. Introduction

Antibiotics are widely used to treat disease and protect the animal health. The growth rate and feed efficiency can be improved by incorporation of antibiotics into animal feed [1]. The worldwide consumption of antibiotic was estimated around 200,000 tons annually [2,3]. The over-use and misuse of antibiotics became a worldwide issue including (1) the increase of antibiotic-resistant

bacteria which may transfer to human pathogens, (2) the emission of antibiotics into the environment and (3) drug residues in food chain [4,5]. Therefore, WHO aim to decrease the demand of antibiotics in veterinary fields since the year 2000.

Recent findings have shown that the ubiquitous occurrence of antibiotics in aqueous matrices, including groundwater, wastewater treatment plants, surface water and sediment [6–9]. Most pharmaceuticals are not completely metabolized in

Abbreviations: MRM, Multiple reaction monitoring; SAs, Sulfonamides; SDM, Sulfadimethoxine; SMX, Sulfamethoxazole; TFDA, Taiwan Food and Drug Administration; WHO, World Health Organization,



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animals result in both unmodified parent compound and metabolites are excreted and enter the water cycle through wastewater. Moreover, the use of antibiotics impact the food safety because of their residues in aquaculture [10]. To solve this issue, removal and elimination of the parent antibiotics and its metabolites is the primary task [11,12].

Sulfonamides (SAs) comprise a class of synthetic sulfanilamide derivatives [1]. Since a case of treating furunculosis of trout (*Salvelinus fontinalis*) with sulfamerazine in the early 1949, SAs have been considered one of the most widely used synthetic antibiotics in aquaculture [13]. The SAs are bacteriostatic against most gram-positive and many gram-negative bacterial by acting as competitive inhibitors of *p*-aminobenzoic acid in the folic acid metabolism [1]. A variety of strategies, including oxidation, membrane filtration, biodegradation, photocatalysis and adsorption, were developed for SAs removal in water [14–16]. However, little is known about the comparison of fate, removal effects and risks of SAs under different aquatic environment. The two main SAs, sulfadimethoxine (SDM) and sulfamethoxazole (SMX) were addressed in this study. The degradations of SAs under both freshwater and seawater were quantified by using mass spectrometry. Moreover, the efficiencies of Chlorine dioxide for oxidative degradations of SAs were evaluated.

2. Materials and methods

2.1. Materials

Samples of freshwater was double-distilled water (Ultrapure Water System: Ultra Analytic; ELGA) and seawater was collected from aquatic animal culture room of Department of Aquaculture, National Taiwan Ocean University. Seawater quality was maintained at pH 8.0 ± 1 and salinity $34 \pm 1\text{‰}$ and was sterilized prior to experiment. Stock solutions of SDM and SMX (Sigma–Aldrich) for treatments and analytic standard solutions were prepared by dissolving in acetonitrile (HPLC grade, Spectrum) to 1000 mg/L. Chlorine dioxide (3000 mg/L) (Taiwan Pulp & Paper Co., Ltd) was prepared by the combination of component A (7.5% sodium chlorite), double-distilled water and component B (hydrochloric acid) at the volume ratio of 1:10:1 and kept in the dark for at least 30 min.

2.2. Experimental procedure

In viewing of the stabilities of SAs, SAs were spiked into 20 mL of both water samples with the

final concentration of 100 µg/L. Samples were collected after 0, 1, 2, 4, 7, 14, 30, 60, 90, 120, 150 and 180 days for the detection of SAs. In examining the removal of SAs, chlorine dioxide was added into SA solutions with three concentrations (0.1, 0.5, and 1.0 mg/L). The removal of SAs was measured in 0.25, 0.5, 1, 2, 4, and 7 days. All experiments were performed at room temperature under dark environment. The removal or degradation efficiency (%) of SAs was fitted into the following equation [17]: Removal (%) = $(C_{\text{initial}} - C_{\text{final}}) / C_{\text{initial}} \times 100\%$, where C_{initial} and C_{final} are the concentrations of SAs in the control and experimental group, respectively. For the extraction of SAs in solutions, 5 mL was sampled into 50 mL centrifuge tube followed by the addition of 20 mL of 100% acetonitrile and 10 g of anhydrous sodium sulfate. Mixture was blended well for 1 min and then centrifuged under 3750 rpm for 20 min. The supernatant was moved to the round bottom flask. The remnant was resuspended with 20 mL of 100% acetonitrile and underwent centrifugation again. Supernatants were combined and the solvent was removed using rotary vacuum evaporation at 40 °C. The residue was restored with 2 mL of 40% acetonitrile. The final analytes was kept in a dark brown vial bottle after filtration with 0.22 µm filter.

2.3. HPLC-MS/MS analysis

SAs were analyzed by high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS). The system consisted of an Agilent 1100 Series HPLC (Agilent, Germany) and an API 4000 Q-Trap mass spectrometry (Applied Biosystems, Canada) with electrospray ionization (ESI). The compounds were separated by a 4.6×150 nm Agilent Zorbax XDB-C18 column (Agilent Technologies, USA) at 35 °C with a flow rate of 0.8 mL/min. The injection volume was 20 µL and the separations were carried out with an eluent mixture of A (purified water with 0.1% formic acid (v/v)) and B (acetonitrile with 0.1% formic acid (v/v)) as the following linear gradient: A decrease from 95% to 5% over 9 min and hold for 1 min. Then A increase to 95% over 2 min and hold for 3 min. Post-run was maintained for 1 min until the next injection. Quantitative analysis of each compound was performed in the MRM mode using the highest characteristic precursor ion/product ion transitions: SDM (311 → 156), SMX (254 → 156). The parameters for the MS analysis were as following: ionization mode, ES⁺; capillary voltage, 3.3 kV; source temperature, 120 °C; desolvation temperature, 450 °C; desolvation gas flow, 800 L/h. Detailed parameters were documented in supplementary file

(https://jmstt.ntou.edu.tw/cgi/viewcontent.cgi?filename=1&article=1588&context=journal&type=additional&preview_mode=1). All data were acquired using Analyte 1.4.1 software (Applied Biosystems, USA).

2.4. Statistical analyses

Each experiment was repeated in triplicate and data was shown as mean ± SD (standard deviation). All data were analyzed by using Statistical Analysis System (SAS-PC) software. Statistical significance was set at α = 0.05 for the One-way ANOVA with a subsequent Scheffe's test.

3. Results

3.1. SAs degradation

Extraction and detection methods in this study were modified from the Method of Test for Veterinary Drug Residues in Foods-Method for Multi-residue Analysis Part 2, TFDA. The method verification for the analysis of SAs was documented in supplementary file (https://jmstt.ntou.edu.tw/cgi/viewcontent.cgi?filename=1&article=1588&context=journal&type=additional&preview_mode=1), including Linearity, Specificity, Accuracy, Precision and Limit of Quantification (LOQ). The self-degradations of SAs in freshwater and seawater were observed in a slow rate under dark condition. As shown in Fig. 1 and Table 1, the concentrations of SDM showed below 7% loss in both water systems during the 180 day experimental period, while those of SMX showed the similarity with 8% loss below (Fig. 2 and Table 1).

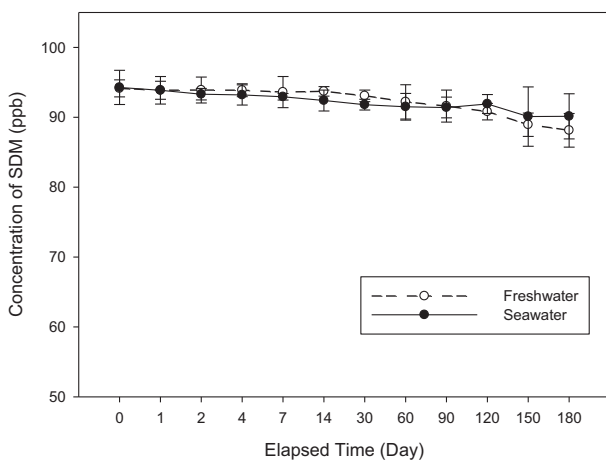


Fig. 1. The variation of SDM concentration in freshwater and seawater during 180 days.

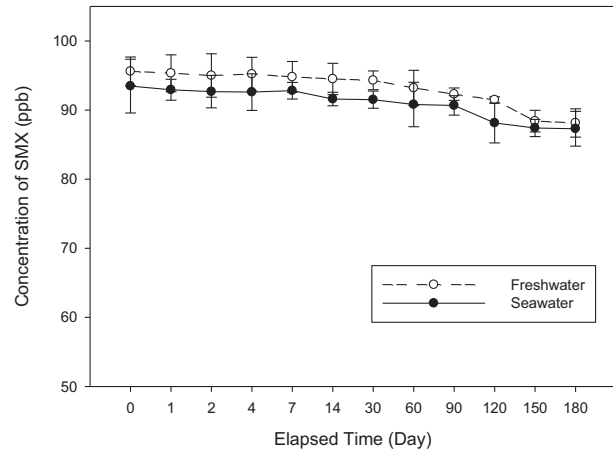


Fig. 2. The variation of SMX concentration in freshwater and seawater during 180 days.

3.2. Effect of chlorine dioxide on the removal of SAs

It was shown that SAs were efficiently degraded within 7 days by Chlorine dioxide treatment and the efficiency increased significantly as the concentration of Chlorine dioxide increasing. As shown in Table 2 and Table 3, Chlorine dioxide of 0.1, 0.5, and 1.0 mg/L were effective to completely remove SDM in freshwater at 7.0, 2.0 and 0.5 day, respectively. It was noted that the removals of SDM were more efficient in seawater, while the complete removals were achieved at 0.25 day for the treatment of 0.5 and 1.0 mg/L (Table 4 and Table 5). Similar improvements were also found in removal of SMX. Using the same concentration of Chlorine dioxide, the complete removal of SMX in freshwater was done at 7.0, 2.0 and 0.5 day, respectively (Table 6 and Table 7), whereas that of SMX in seawater was done at 4.0, 0.25 and 0.25 day, respectively (Table 8 and Table 9).

Table 1. The degradation of SAs in freshwater and seawater during 180 days.

Elapsed Time (Day)	Degradation percentage of SDM (%)		Degradation percentage of SMX (%)	
	Freshwater	Seawater	Freshwater	Seawater
1	0.28 ± 1.37 ^a	0.42 ± 2.09 ^a	0.28 ± 2.79 ^a	0.57 ± 1.62 ^a
2	0.25 ± 1.97 ^a	1.03 ± 0.87 ^a	0.63 ± 3.29 ^a	0.86 ± 2.51 ^a
4	0.28 ± 0.98 ^a	1.13 ± 1.53 ^a	0.42 ± 2.55 ^a	0.93 ± 2.83 ^a
7	0.57 ± 2.37 ^a	1.41 ± 0.49 ^a	0.84 ± 2.33 ^a	0.71 ± 1.28 ^a
14	0.46 ± 0.73 ^a	1.98 ± 1.59 ^a	1.15 ± 2.38 ^a	2.00 ± 1.05 ^a
30	1.13 ± 0.88 ^a	2.62 ± 0.81 ^a	1.36 ± 1.42 ^a	2.10 ± 1.32 ^a
60	2.05 ± 2.61 ^a	2.93 ± 2.03 ^a	2.51 ± 2.67 ^a	2.85 ± 3.44 ^a
90	2.69 ± 2.43 ^a	3.04 ± 1.57 ^a	3.45 ± 0.93 ^a	3.00 ± 1.50 ^a
120	3.54 ± 1.25 ^a	2.51 ± 1.44 ^a	4.32 ± 0.48 ^a	5.71 ± 3.10 ^a
150	5.52 ± 1.77 ^a	4.42 ± 4.51 ^a	7.53 ± 1.64 ^a	6.49 ± 1.32 ^a
180	6.37 ± 2.56 ^a	4.38 ± 3.43 ^a	7.81 ± 2.15 ^a	6.60 ± 2.69 ^a

(1) Values are presented as mean ± SD.
 (2) The values with different letters are significant different (p < 0.05).

Table 2. The variation of SDM concentration (100 µg/L) in freshwater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)						
	0	0.25	0.5	1	2	4	7
Control	103.20 ± 2.43 ^A	102.50 ± 1.51 ^A	101.73 ± 3.23 ^A	101.47 ± 2.66 ^A	100.27 ± 1.62 ^A	99.73 ± 2.81 ^A	84.90 ± 3.32 ^B
0.1 ppm		73.60 ± 2.09 ^B	52.80 ± 1.03 ^C	45.30 ± 1.10 ^D	30.31 ± 0.46 ^E	9.43 ± 0.44 ^F	N.D.
0.5 ppm		43.50 ± 1.10 ^B	10.91 ± 0.72 ^C	6.72 ± 0.53 ^D	N.D.	N.D.	N.D.
1 ppm		14.45 ± 1.96 ^B	N.D.	N.D.	N.D.	N.D.	N.D.

(1) Data are means ± SD.

(2) N.D. means not detectable (below the limit of quantification).

(3) Means in the same row with different letters (A, B, C) are significantly different ($p < 0.05$).

(4) Means in the same column with different letters (a, b, c) are significantly different ($p < 0.05$).

Table 3. The removal efficiency (%) of SDM in freshwater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)						
	0.25	0.5	1	2	4	7	
0.1 ppm	28.20 ± 2.04 ^E	48.10 ± 1.02 ^D	55.35 ± 1.09 ^C	69.77 ± 0.46 ^B	92.91 ± 4.74 ^A	100.00 ± 0.00 ^A	
0.5 ppm	57.56 ± 1.07 ^D	89.27 ± 0.71 ^C	93.38 ± 0.52 ^B	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	
1 ppm	85.90 ± 1.91 ^B	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	

(1) Data are means ± SD.

(2) Means in the same row with different letters (A, B, C) are significantly different ($p < 0.05$).

(3) Means in the same column with different letters (a, b, c) are significantly different ($p < 0.05$).

Table 4. The variation of SDM concentration (100 µg/L) in seawater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)						
	0	0.25	0.5	1	2	4	7
Control	102.93 ± 0.61 ^A	102.67 ± 1.22 ^A	101.33 ± 3.11 ^{AB}	101.07 ± 1.15 ^{AB}	96.40 ± 1.57 ^{BC}	95.87 ± 3.00 ^{BC}	92.13 ± 1.15 ^C
0.1 ppm		82.90 ± 3.54 ^B	77.10 ± 1.05 ^C	67.60 ± 0.57 ^D	41.90 ± 1.91 ^E	5.33 ± 0.54 ^F	N.D.
0.5 ppm		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 ppm		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

(1) Data are means ± SD.

(2) N.D. means not detectable (below the limit of quantification).

(3) Means in the same row with different letters (A, B, C) are significantly different ($p < 0.05$).

(4) Means in the same column with different letters (a, b, c) are significantly different ($p < 0.05$).

Table 5. The removal efficiency (%) of SDM in seawater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)						
	0.25	0.5	1	2	4	7	
0.1 ppm	19.25 ± 3.45 ^D	23.91 ± 1.04 ^D	33.11 ± 0.56 ^C	56.54 ± 1.99 ^B	95.83 ± 2.82 ^A	100.00 ± 0.00 ^A	
0.5 ppm	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	
1 ppm	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	

(1) Data are means ± SD.

(2) Means in the same row with different letters (A, B, C) are significantly different ($p < 0.05$).

(3) Means in the same column with different letters (a, b, c) are significantly different ($p < 0.05$).

Table 6. The variation of SMX concentration (100 µg/L) in freshwater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)						
	0	0.25	0.5	1	2	4	7
Control	102.40 ± 1.06 ^A	102.27 ± 0.83 ^A	100.80 ± 2.12 ^{AB}	98.80 ± 2.71 ^{AB}	97.20 ± 0.40 ^{AB}	93.00 ± 2.37 ^B	92.80 ± 4.54 ^B
0.1 ppm		74.10 ± 2.05 ^B	66.10 ± 2.50 ^B	51.20 ± 1.46 ^C	32.88 ± 2.10 ^D	16.80 ± 2.24 ^E	N.D.
0.5 ppm		26.81 ± 1.39 ^C	17.54 ± 1.14 ^C	15.24 ± 0.27 ^C	N.D.	N.D.	N.D.
1 ppm		7.60 ± 0.77 ^D	N.D.	N.D.	N.D.	N.D.	N.D.

- (1) Data are means ± SD.
- (2) N.D. means not detectable (below the limit of quantification).
- (3) Means in the same row with different letters (A, B, C) are significantly different (p < 0.05).
- (4) Means in the same column with different letters (a, b, c) are significantly different (p < 0.05).

Table 7. The removal efficiency (%) of SMX in freshwater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)					
	0.25	0.5	1	2	4	7
0.1 ppm	27.54 ± 2.00 ^F	34.42 ± 2.48 ^E	48.18 ± 1.48 ^D	66.17 ± 2.16 ^C	81.94 ± 2.41 ^B	100.00 ± 0.00 ^A
0.5 ppm	73.78 ± 1.36 ^D	82.60 ± 1.13 ^C	84.57 ± 0.27 ^B	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A
1 ppm	92.57 ± 0.75 ^B	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A

- (1) Data are means ± SD.
- (2) Means in the same row with different letters (A, B, C) are significantly different (p < 0.05).
- (3) Means in the same column with different letters (a, b, c) are significantly different (p < 0.05).

Table 8. The variation of SMX concentration (100 µg/L) in seawater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)						
	0	0.25	0.5	1	2	4	7
Control	97.33 ± 2.89 ^A	92.50 ± 4.08 ^{AB}	95.70 ± 3.74 ^{AB}	90.80 ± 1.60 ^{AB}	91.87 ± 3.26 ^{AB}	91.70 ± 3.12 ^{AB}	86.70 ± 2.96 ^B
0.1 ppm		53.50 ± 1.51 ^B	50.50 ± 1.32 ^B	46.40 ± 1.73 ^B	18.79 ± 0.73 ^C	N.D.	N.D.
0.5 ppm		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1 ppm		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

- (1) Data are means ± SD.
- (2) N.D. means not detectable (below the limit of quantification).
- (3) Means in the same row with different letters (A, B, C) are significantly different (p < 0.05).
- (4) Means in the same column with different letters (a, b, c) are significantly different (p < 0.05).

Table 9. The removal efficiency (%) of SMX in seawater treated with different concentrations of Chlorine dioxide during 7 days.

Chlorine dioxide	Elapsed Time (day)					
	0.25	0.5	1	2	4	7
0.1 ppm	42.38 ± 1.63 ^D	47.23 ± 1.38 ^C	48.90 ± 1.90 ^C	79.55 ± 0.80 ^B	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A
0.5 ppm	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A
1 ppm	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A	100.00 ± 0.00 ^A

- (1) Data are means ± SD.
- (2) Means in the same row with different letters (A, B, C) are significantly different (p < 0.05).
- (3) Means in the same column with different letters (a, b, c) are significantly different (p < 0.05).

4. Discussion

The degradation of aqueous antibiotics have been carried out under irradiation [18,19], photolysis [20] and microbial environment [21–23]. The synergic effects on the transformation of the SA occurred with the contribution of light and microbial activity [24,25]. Under sterile and dark condition over a period of 180 days, the degradation efficiencies of SDM and SMX (ranging from 4.38 to 7.81%) were anticipated low in both freshwater and seawater (Table 1). Moreover, our data were in agreement with previous studies that SAs are hydrolytically stable with a long half-life under neutral water (pH 6.0–8.5) [26–28].

Recent studies have shown that SAs are susceptible to chemical-oxidation processes such as chlorination and ozonation [29–31]. Chlorine dioxide, a stable free radical and powerful oxidant has been used as free available chlorine for the removal of SAs. The breakage of S–N and C–S bonds and the hydroxylation of aniline moiety in the SMX molecule constituted the major degradation pathways [32]. As shown in Table 2 to Table 9, the removal activities of Chlorine dioxide toward SDM and SMX in both freshwater and seawater were highly effective even at low concentrations (0.1 ppm). ClO_2 is highly reactive to specific functional groups of organic compounds such as phenolic moieties and tertiary amino groups in a pH-dependent manner [33]. The strongly pH-dependent was presented in reaction of SMX which exhibiting relative high reactivity to ClO_2 at $\text{pH} \geq 7$ [34]. Moreover, the oxidation of aniline by Chlorine dioxide has been demonstrated that the reaction rate constant increases with increasing pH [35]. Thus, regarding the treatment of Chlorine dioxide in our studies, the removal of SAs in seawater ($\text{pH} = 8$) is reasonably faster than in freshwater ($\text{pH} \leq 7$). Overall, the present study could provide useful information on the practical use of Chlorine dioxide for removing SA antibiotics in aquaculture waste water. Rapid removal of SAs in freshwater and seawater can be achieved with dosage of 1.0 ppm and 0.5 ppm, respectively.

Declaration of competing interest

None of the authors has a financial relationship with a commercial entity that has an interest in the subject of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://jmsst.ntou.edu.tw/cgi/viewcontent.cgi?filename=1&article=1588&context=journal&type=additional&preview_mode=1.

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