Removal of sulfonamides from wastewater in the UV/TiO$_2$ system: effects of pH and salinity on photodegradation and mineralization

C. H. Wu, C. Y. Kuo, C. D. Dong, C. W. Chen and Y. L. Lin

ABSTRACT

The effects of salinity on the photodegradation and mineralization of sulfonamides in the UV/TiO$_2$ system were investigated. The goals of this study were to analyze the effects of pH and salinity on the sulfonamide concentration and total organic carbon (TOC) during the removal of sulfonamides in a UV/TiO$_2$ system. Four sulfonamides – sulfadiazine (SDZ), sulfamethizole (SFZ), sulfamethoxazole (SMX) and sulfathiazole (STZ) - were selected as parent compounds. The photodegradation and mineralization rates of sulfonamides in the UV/TiO$_2$ system satisfy pseudo-first-order kinetics. Direct photolysis degraded sulfonamides but sulfonamides cannot be mineralized. The photodegradation and mineralization rate constants in all experiments followed the order pH 5 > pH 7 > pH 9. At pH 5, the mineralization rate constants of SMX, SFZ, SDZ and STZ were 0.015, 0.009, 0.012 and 0.011 min^{-1}, respectively. The addition of NaCl inhibited the mineralization of the four tested sulfonamides more than it inhibited their photodegradation. The inhibitory effect of chloride ions on the removal of sulfonamides in the UV/TiO$_2$ system was attributed to the scavenging by chloride ions of hydroxyl radicals (HO•) and holes and the much lower reactivity of chlorine radicals thus formed, even though the chlorine radicals were more abundant than HO•.

Key words | mineralization, photodegradation, salinity, sulfonamides, TiO$_2$

C. H. Wu (corresponding author)
C. D. Dong
C. W. Chen
Y. L. Lin
Department of Chemical and Materials
    Engineering,
National Kaohsiung University of Science and
    Technology,
Kaohsiung,
Taiwan
E-mail: wuch@nkust.edu.tw

C. Y. Kuo
Department of Environmental and Safety
    Engineering,
National Yunlin University of Science and
    Technology,
Yunlin,
Taiwan

INTRODUCTION

Advanced oxidation processes (AOPs) are becoming increasingly important in the detoxification of wastewaters. Heterogeneous photocatalysis by TiO$_2$ based on hydroxyl radicals (HO•) (2.8 eV) has been proved to be an attractive method for effectively degrading various organic pollutants. The effects of chloride ions on HO•-based AOPs, such as Fenton, ozone, UV/H$_2$O$_2$, UV/Fenton and UV/TiO$_2$, have attracted substantial attention from researchers. Previous studies have proved that the presence of chloride ions can make the treatment of saline water by AOPs inefficient (Adams & Impellitteri 2009; Yuan et al. 2012a, 2012b; Wang et al. 2015; Amasha et al. 2018). Chloride ions greatly reduce the extent of photooxidative decoloration and mineralization of Acid Orange 7 (AO7) in the UV/H$_2$O$_2$ process because chloride ions scavenge HO• and chlorine radicals have a much lower reactivity than HO• (Yuan et al. 2012a). Yuan et al. (2011) found that appreciable concentrations of salts in wastewater from the textile

industry may reduce the degree of dye mineralization in treatment by AOPs and may even lead to the formation of more toxic chlorinated compounds. HO• (2.8 V) can oxidize Cl$^-$ to form the less reactive chlorine species, Cl$_2$/2Cl$^-$ (1.36 V) and HOCl/Cl$^-$ (1.48 V). Furthermore, Cl$^-$ in industrial wastewater can rapidly scavenge HO• to form less reactive chlorine radicals (Cl$_2^-$•, Cl• and HOCl$^-$•), significantly affecting the degradation kinetics of organic contaminants during AOPs (Yuan et al. 2012b). Accordingly, the involvement of Cl$^-$ can inhibit the HO•-based radical chain reactions, significantly reducing the overall efficiency of the AOPs.

Salt in water has been reported to reduce the biodegradation and photodegradation of antibiotics in that water (Trovo et al. 2009; Li & Zhang 2010; Yang et al. 2015). Some investigations have found that inorganic ions can significantly reduce photocatalytic efficiency (Guillard et al. 2005; Chong et al. 2010); this effect is primarily attributed

to the adsorption of ions onto the TiO₂ surface (Guillard *et al.* 2005). In the UV/TiO₂ system, Cl⁻ ions (0–200 mM) significantly promote dye decolorization, but adding too much Cl⁻ apparently inhibits dye degradation (Yuan *et al.* 2012b). The decline in efficiency has been widely attributed to the quenching of radicals by salts (Adams & Impellitteri 2009). NaCl has a detrimental effect on the degradation of Rhodamine B (RhB) in a UV/P25-reduced graphene oxide system. The degradation rate decreases as the amount of NaCl increases in the experimental range (Wang *et al.* 2015). The addition of 1 mM Cl⁻ slightly reduces the degradation of carbamazepine from 90.6% to 84.5% at 3,600 mJ cm⁻² UV fluence (Ali *et al.* 2018). Although this inhibition is not great, the scavenging of HO• by Cl⁻ may be responsible for it (Yu & Barker 2003).

García-Munoz *et al.* (2017) photodegraded sulfadimethoxine (SFX) and sulfamethizole (SFZ) in UV/ilmenite and UV/ilmenite/H₂O₂ systems. They suggested that the removal of sulfonamides can be described using a pseudo-first-order kinetic model. The removal of TOC fitted a zero-order kinetic model. The removal rate constants of SFX and SFZ in the UV/ilmenite system were 0.13 and 0.12 min⁻¹, respectively, and those of SFX and SFZ in the UV/ilmenite/H₂O₂ system were 0.42 and 0.24 min⁻¹, respectively. The mineralization rate constants of SFX and SFZ in the UV/ilmenite system were 0.016 and 0.013 mg.L⁻¹.min⁻¹, respectively, while those of SFX and SFZ in the UV/ilmenite/H₂O₂ system were 0.038 and 0.025 mg.L⁻¹.min⁻¹, respectively. Ji *et al.* (2017) used thermally activated persulfate oxidation to degrade sulfonamides with six-membered heterocyclic rings. Sulfamethazine (SMZ), sulfapyridine (SPD), sulfadiazine (SDZ), sulfadimethoxine (SDM), and sulfachloropyridazine (SCP) exhibited pseudo-first-order degradation with rate constants of 0.0127, 0.0110, 0.0100, 0.0098 and 0.0126 min⁻¹, respectively. Liu *et al.* (2018) used electron beam irradiation to decompose sulfonamides and the radiolysis efficiencies followed the order STZ > SMX > SMZ.
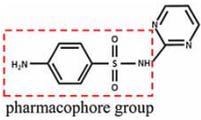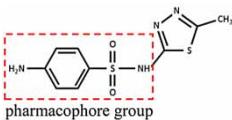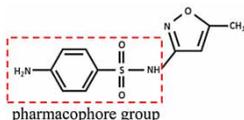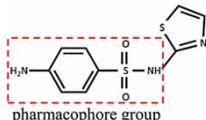
Despite several investigations having introduced the degradation of sulfonamides by AOPs, the further development of AOPs regarding how high salinity affected photocatalysis was required. Sulfonamides are one of the largest classes of globally used antibiotics. The eight commonly used sulfonamides are SFZ, sulfamethoxazole (SMX), SDZ, sulfacetamide, sulfadoxine, sulfanilamide, sulfasalazine, and sulfisoxazole (Garoma *et al.* 2010). Accordingly, in this investigation, a UV/TiO₂ system is used to elucidate the effects of high salinity on the photodegradation and mineralization of SDZ, SFZ, SMX and sulfathiazole (STZ). The objectives of this study are (i) to determine the effects of pH and chloride ions on the photodegradation and mineralization of sulfonamides in a UV/TiO₂ system and (ii) to compare the efficiencies of the photodegradation and mineralization of sulfonamides that are achieved by direct photolysis and by photocatalytic reactions.

MATERIALS AND METHODS

Materials

The photocatalyst herein was TiO₂ P25 (Degussa, Germany), which consists mainly of anatase (80%), with a specific surface area of 50 m²/g and a mean particle size of 30 nm. The Na₂S₂O₈, SDZ, SMX and STZ were obtained from Sigma-Aldrich, and SFZ was purchased from Alfa Aesar. The molecular structure, formula and weight of the sulfonamides studied are summarized in Table 1. NaCl was the source of salinity and this was obtained from Taiyen (Taiwan). The pH of the solution was adjusted by adding 0.1 M HNO₃ or NaOH during the reaction, both of which were purchased from Merck (Germany). All chemicals were used as received. The Milli-Q water purification system was used to obtained ultrapure water (resistivity > 18 MΩ.cm).

Table 1 | The molecular structure, formula and weight of sulfonamides (Wu *et al.* 2015)

Compounds	SDZ	SFZ	SMX	STZ
Molecular structure				
Molecular formula	$C_{10}H_{10}N_4O_2S$	$C_9H_{10}N_4O_2S_2$	$C_{10}H_{11}N_3O_3S$	$C_9H_9N_3O_2S_2$
Molecular weight	250 g/mol	270 g/mol	253 g/mol	255 g/mol

Experimental methods

Since the salinity of seawater is approximately 3.5%, this study examines the effects of high salinity on the removal of sulfonamides from wastewater. The most abundant ions that are dissolved in seawater are sodium and chloride. NaCl was added to the solutions herein to provide the same salinity as that of seawater.

The initial concentrations of sulfonamide, NaCl and TiO_2 in experiments were 20 mg/L, 36.27 g/L and 1 g/L, respectively. Photocatalysis experiments were conducted in a 3 L glass reactor. A 400 W Xe lamp (200 nm < wavelength < 700 nm, UniVex BT-580, Taiwan) was used to provide UV radiation. The reaction medium was stirred continuously at 300 rpm and aerated with air to maintain a suspension. Twenty milliliter aliquots were withdrawn from the photoreactor at pre-specified intervals, and solids were separated by filtration using a 0.22 μm filter (Millipore, USA) before the sulfonamide concentration and total organic carbon (TOC) measurements were made. The concentrations of SMX, SFZ, SDZ and STZ were measured using a spectrophotometer (Hitachi U-5100, Japan) at 266, 274, 265 and 283 nm, respectively. Since the addition of NaCl affects the dissociation of sulfonamides, it also influences their absorption wavelengths. In the experiments that involved the addition of NaCl, the concentrations of SMX, SFZ, SDZ and STZ were measured at 260, 270, 262 and 283 nm, respectively. The photodegradation efficiency was obtained from the difference between sulfonamide concentrations before and after each experiment. The decrease in TOC, measured using an O.I. 1010 TOC analyzer (USA), yielded the degree of sulfonamide mineralization. The

catalytic system of TOC was wet oxidation. The oxidant and detector that were used in TOC were $Na_2S_2O_8$ and a nondispersive infrared sensor, respectively.

RESULTS AND DISCUSSION

Effects of pHs

The theoretical TOC values of 20 mg/L SMX, SFZ, SDZ and STZ are 9.5, 8.0, 9.6 and 8.5 mg/L, respectively, and the experimental TOC values that were obtained by the TOC analyzer were 9.4, 7.9, 9.5 and 8.5 mg/L, respectively. Figures 1–4 display the efficiency of removal of SMX, SFZ, SDZ and STZ, respectively. After 180 min of the direct photolysis reaction at pH 5, 46%, 56%, 18% and 60% of SMX (Figure 1(a)), SFZ (Figure 2(a)), SDZ (Figure 3(a)) and STZ (Figure 4(a)) had photodegraded, respectively; however, no SMX (Figure 1(b)), SFZ (Figure 2(b)), SDZ (Figure 3(b)) and STZ (Figure 4(b)) was mineralized. Direct photolysis by UV irradiation photodegraded sulfonamides to intermediates but did not mineralize them.

The photodegradation and mineralization of these four sulfonamides approximately followed pseudo-first-order kinetics, expressed as Equation (1):

$$\ln(C_t/C_0) = -kt \tag{1}$$

where t is reaction time, k is the pseudo-first-order rate constant, and C_0 and C_t are the concentrations of sulfonamide at times t = 0 and t = t, respectively. Wu *et al.* (2015; 2016) also found that the photodegradation and mineralization

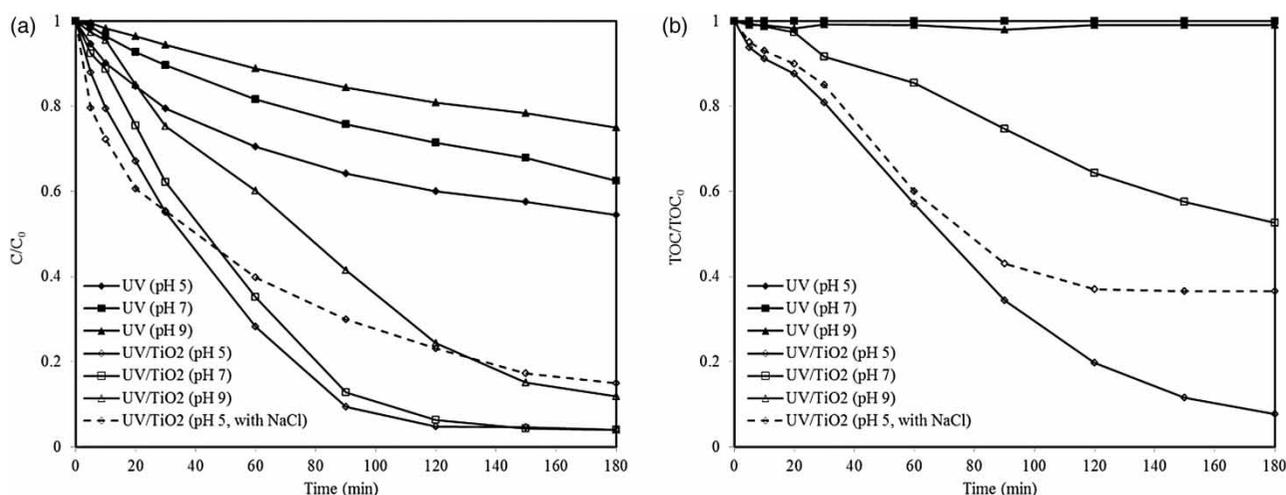**Figure 1** | Removal of SMX in UV/TiO₂ system (a) photodegradation, (b) mineralization.
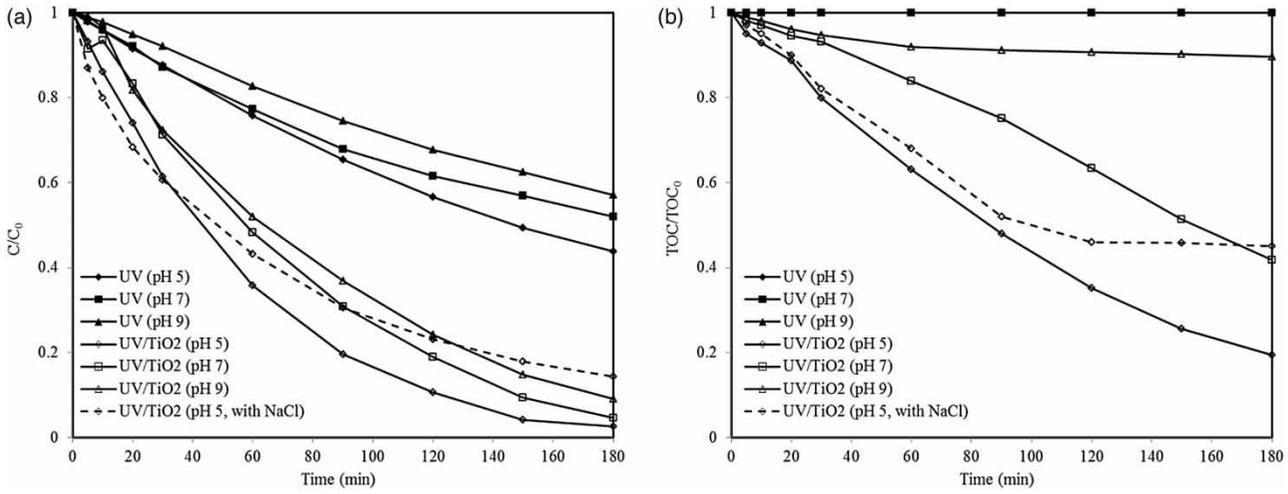
Figure 2 | Removal of SFZ in UV/TiO₂ system (a) photodegradation, (b) mineralization.
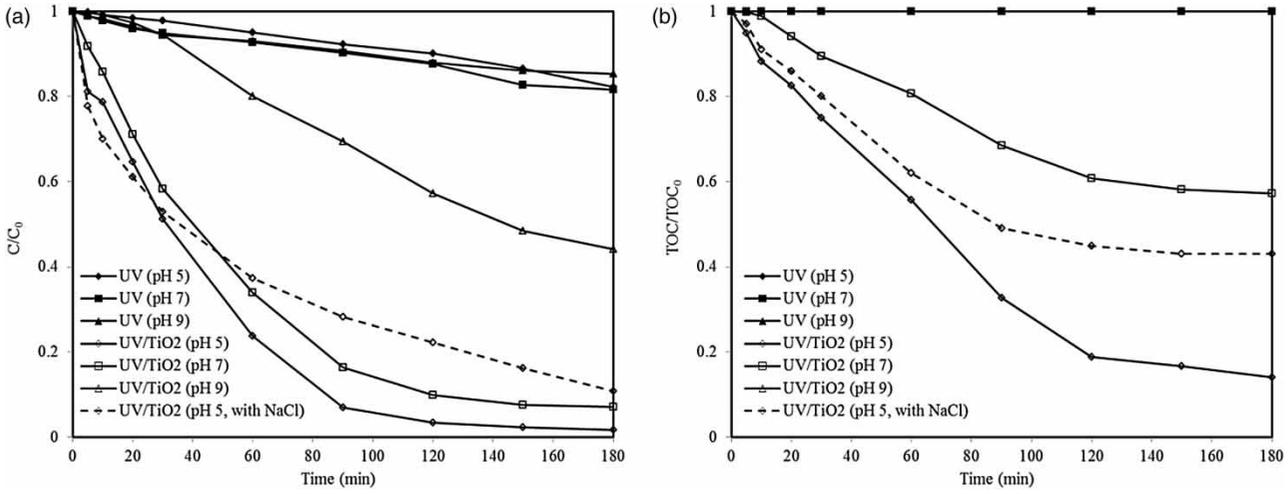

Figure 3 | Removal of SDZ in UV/TiO₂ system (a) photodegradation, (b) mineralization.
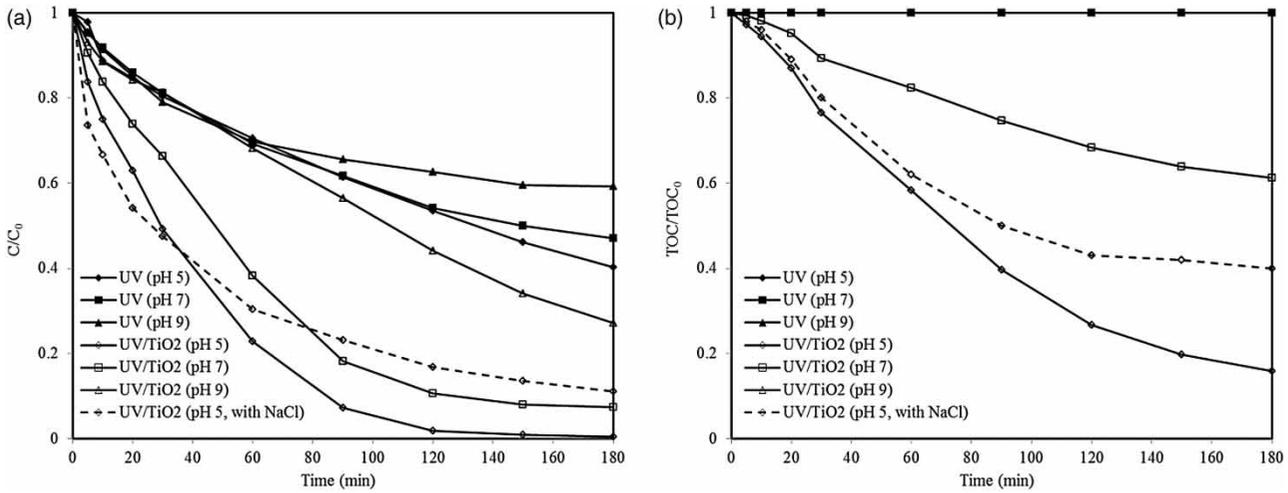

Figure 4 | Removal of STZ in UV/TiO₂ system (a) photodegradation, (b) mineralization

of sulfonamides in AOPs followed pseudo-first-order kinetics. Table 2 summarizes the pseudo-first-order reaction rate constants and correlation coefficients of four sulfonamides in the UV/TiO₂ system. The rate of mineralization was lower than that of photodegradation, and mineralization was not observed at pH 9. The rates of photodegradation and mineralization of the tested sulfonamides in the UV/TiO₂ system all followed the order pH 5 > pH 7 > pH 9 (Table 2). At the pH of zero charge (pH$_{pzc}$) of TiO₂, the interaction between TiO₂ particles and sulfonamides was minimal owing to the absence of any electrostatic force. At pH < pH$_{pzc}$, the surface charge of TiO₂ became positively charged and exerted an electrostatic attraction force on the negatively charged compounds. Such polar attractions between TiO₂ and charged anionic organic compounds can promote adsorption onto a photon-activated TiO₂ surface, favoring subsequent photocatalytic reactions. At pH > pH$_{pzc}$, the TiO₂ surface was negatively charged and repelled anionic compounds in water. At acidic pH, the adsorption of anions on the surface of the photocatalyst reduces the availability of surface sites for the adsorption of intermediates, such as carboxylic acids, which are degraded by the direct oxidation of holes (Chen *et al.* 2005). In this study, the photodegradation and mineralization rates increased as the pH decreased; this result is consistent with that of Piscopo *et al.* (2001). This study revealed that mineralization did not occur at pH 9, and that the rate of mineralization was lower than that of photodegradation. Kang *et al.* (2018) indicated that the rate of the direct degradation of SCP by peroxymonosulfate was high, but that the overall mineralization efficiency was rather low because SCP was just

transformed to smaller organic compounds without further mineralization. The findings of this study are similar to those of Kang *et al.* (2018). A comparison of the four sulfonamides reveals that SDZ was the most difficult to mineralize in every tested UV/oxidant system. This experimental result probably arose from the fact that SDZ is connected to the pharmacophore group and has a six-member heterocyclic ring, which is more resistant to mineralization than is the five-member heterocyclic ring (SFZ, SMX and STZ) (Wu *et al.* 2015). However, García-Munoz *et al.* (2017) demonstrated that SFX with a six-member heterocyclic ring was more resistant to mineralization than was SFZ with a five-member heterocyclic ring. Hence, this study concluded that the mineralization rate varied with the molecular structure of the sulfonamide, the pH and the photocatalytic system used.

Effects of salinity

After 180 min of reaction at pH 5, the extents of photodegradation of SMX (Figure 1(a)), SFZ (Figure 2(a)), SDZ (Figure 3(a)) and STZ (Figure 4(a)) in the UV/TiO₂ system were 96%, 97%, 98% and 100%, respectively, and those in the UV/TiO₂/NaCl system were 85%, 86%, 89% and 89%, respectively. The degrees of mineralization of SMX (Figure 1(b)), SFZ (Figure 2(b)), SDZ (Figure 3(b)) and STZ (Figure 4(b)) in the UV/TiO₂ system were 92%, 81%, 86% and 84% respectively, and those in the UV/TiO₂/NaCl system were 63%, 53%, 56% and 56%, respectively. It should be noticed that the mineralization of all tested sulfonamides in UV/TiO₂/NaCl system was almost terminated after 90 min reaction (Figures 1–4). The experimental results

Table 2 | The pseudo first-order removal rate constant (k) and linear coefficient (R²) of sulfonamides in the UV/TiO₂ system

Conc.	pH 5		pH 7		pH 9	
	k (min⁻¹)	R²	k (min⁻¹)	R²	k (min⁻¹)	R²
SMX	0.026 (0.011)[a]	0.990 (0.990)[a]	0.024	0.988	0.012	0.979
SFZ	0.021 (0.010)[a]	0.994 (0.991)[a]	0.017	0.983	0.013	0.995
SDZ	0.029 (0.011)[a]	0.977 (0.995)[a]	0.020	0.996	0.005	0.991
STZ	0.028 (0.011)[a]	0.985 (0.978)[a]	0.019	0.983	0.007	0.992
TOC						
SMX	0.015 (0.009)[a]	0.988 (0.983)[a]	0.004	0.994	–	–
SFZ	0.009 (0.007)[a]	0.997 (0.992)[a]	0.005	0.969	–	–
SDZ	0.012 (0.007)[a]	0.976 (0.983)[a]	0.004	0.962	–	–
STZ	0.011 (0.008)[a]	0.996 (0.992)[a]	0.003	0.986	–	–

[a]: with 3.5% NaCl.

implied that the remaining radicals after 90 min reaction in UV/TiO$_2$/NaCl system could only photodegrade sulfonamides; however, they could not mineralize sulfonamides and byproducts. Increasing salinity inhibited mineralization in the UV/TiO$_2$ system more than it inhibited photodegradation. For Degussa P25, the pH$_{pzc}$ was 6.3, which was determined by titration (Jaffrezic-Renault *et al.* 1986). Chloride ions inhibited both adsorption and photodegradation at pH < pH$_{pzc}$ when the TiO$_2$ surface was positively charged (Piscopo *et al.* 2001). In this study, the final pH was 4.7–5.2, which was slightly below the pH$_{pzc}$ of TiO$_2$, and the addition of a high concentration of sodium chloride was expected to reduce the reaction rate.

Trovo *et al.* (2009) evaluated the solar photo-Fenton reaction of SMX, and found that the photodegradation and mineralization of SMX were significantly slower in seawater than in freshwater. The photocatalytic degradation of antibiotic trimethoprim was slower in seawater than in demineralized water (Sirtori *et al.* 2010) and Yang *et al.* (2015) made a similar observation regarding SMX, sulfamonomethoxine (SMM), and SDM in a UV/TiO$_2$ system. The mineralization of AO7 has been found to be inhibited by Cl$^-$, especially under acidic conditions (Yuan *et al.* 2014). Ketoprofen degradation is inhibited in seawater by the presence of a high Cl$^-$ load, because Cl$^-$ participates in persulfate quenching reactions (Amasha *et al.* 2018). Cl$^-$ inhibits TiO$_2$ photocatalysis by preferential adsorption displacement over that of the surface-bound OH$^-$ ions. This mechanism reduces the number of OH$^-$ ions that are available on the TiO$_2$ surface, and the substituted Cl$^-$ further increases the rate of recombination of electron-hole pairs (Chong *et al.* 2010).

The equations for the reaction of chloride ions with HO• are as follows (Liao *et al.* 2001).

$$HO\bullet + Cl^- \rightarrow HOCl\bar{\bullet} \tag{2}$$

$$HOCl\bar{\bullet} + H^+ \rightarrow Cl\bullet + H_2O \quad pK = 7.2 \tag{3}$$
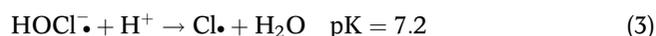
The first reaction is fast and the second reaction is five times as rapid as the first. At pH < 7.2, Cl• is the dominant species (Liao *et al.* 2001). Chloride ions can also scavenge holes (h$^+$) via the following reaction (Equation (4)) (Yap & Lim 2011). Therefore, chloride ions reduce the availability of holes and HO•. Alvarez *et al.* (2018) showed that the presence of Cl$^-$ ions reduced the amitrole degradation rate, because Cl$^-$ ions behave as h$^+$ and HO• scavengers.

$$h^+ + Cl^- \rightarrow Cl\bullet \tag{4}$$

CONCLUSIONS

This study compared the photodegradation and mineralization efficiencies of SMX, SFZ, SDZ and STZ in UV and UV/TiO$_2$ systems. Direct photolysis by UV irradiation could only photodegrade sulfonamides to intermediates but could not mineralize them. In the UV/TiO$_2$ system, the rate of mineralization was lower than that of photodegradation, and the rates of photodegradation and mineralization of the tested sulfonamides followed the order pH 5 > pH 7 > pH 9. The addition of salinity inhibited mineralization in a UV/TiO$_2$ system more than it did photodegradation. Chloride ions scavenged HO• and h$^+$ to form less reactive chlorine radicals and they blocked the active sites of TiO$_2$. Accordingly, the removal rate of sulfonamides in the UV/TiO$_2$ system decreased as salinity increased.

ACKNOWLEDGEMENT

REFERENCES

Adams, W. A. & Impellitteri, C. A. 2009 The photocatalysis of *N,N*-diethyl-*m*-toluamide (DEET) using dispersions of Degussa P-25 TiO₂ particles. *Journal of Photochemistry and Photobiology A: Chemistry* **202** (1), 28–32.

Ali, F., Khan, J. A., Shah, N. S., Sayed, M. & Khan, H. M. 2018 Carbamazepine degradation by UV and UV-assisted AOPs: kinetics, mechanism and toxicity investigations. *Process Safety and Environmental Protection* **117**, 307–314.

Alvarez, M. A., Orellana-Garcia, F., Lopez-Ramon, M. V., Rivera-Utrilla, J. & Sanchez-Polo, M. 2018 Influence of operational parameters on photocatalytic amitrole degradation using nickel organic xerogel under UV irradiation. *Arabian Journal of Chemistry* **11** (4), 564–572.

Amasha, M., Baalbaki, A. & Ghauch, A. 2018 A comparative study of the common persulfate activation techniques for the complete degradation of an NSAID: the case of ketoprofen. *Chemical Engineering Journal* **350**, 395–410.

Chen, Y., Yang, S., Wang, K. & Lou, L. 2005 Role of primary active species and TiO₂ surface characteristic in UV-illuminated photodegradation of Acid Orange 7. *Journal of Photochemistry and Photobiology A: Chemistry* **172** (1), 47–54.

Chong, M. N., Jin, B., Chow, C. W. K. & Saint, C. 2010 Recent developments in photocatalytic water treatment technology: a review. *Water Research* **44** (10), 2997–3027.

García-Munoz, P., Pliego, G., Zazo, J. A., Bahamonde, A. & Casas, J. A. 2017 Sulfonamides photoassisted oxidation treatments catalyzed by Ilmenite. *Chemosphere* **180**, 523–530.

Garoma, T., Umamaheshwar, S. K. & Mumper, A. 2010 Removal of sulfadiazine, sulfamethizole, sulfamethoxazole, and sulfathiazole from aqueous solution by ozonation. *Chemosphere* **79** (8), 814–820.

Guillard, C., Puzenat, E., Lachheb, H., Houas, A. & Herrmann, J. M. 2005 Why inorganic salts decrease the TiO₂ photocatalytic efficiency. *International Journal of Photoenergy* **7** (1), 1–9.

Jaffrezic-Renault, N., Pichat, P., Foissy, A. & Mercier, R. 1986 Study of the effect of deposited platinum particles on the surface charge of titania aqueous suspensions by potentiometry, electrophoresis, and labeled-ion adsorption. *The Journal of Physical Chemistry* **90** (12), 2733–2738.

Ji, Y., Shi, Y., Wang, L., Lu, J., Ferronato, C. & Chovelon, J. M. 2017 Sulfate radical-based oxidation of antibiotics sulfamethazine, sulfapyridine, sulfadiazine, sulfadimethoxine, and sulfachloropyridazine: formation of SO₂ extrusion products and effects of natural organic matter. *Science of the Total Environment* **593–594** (1), 704–712.

Kang, J., Zhou, L., Duan, X., Sun, H. & Wang, S. 2018 Catalytic degradation of antibiotics by metal-free catalysis over nitrogen-doped graphene. *Catalysis Today* (in press).

Li, B. & Zhang, T. 2010 Biodegradation and adsorption of antibiotics in the activated sludge process. *Environmental Science & Technology* **44** (9), 3468–3473.

Liao, C. H., Kang, S. F. & Wu, F. A. 2001 Hydroxyl radical scavenging role of chloride and bicarbonate ions in the H₂O₂/UV process. *Chemosphere* **44** (5), 1193–1200.

Liu, N., Huang, W. Y., Li, Z. M., Shao, H. Y., Wu, M. H., Lei, J. Q. & Tang, L. 2018 Radiolytic decomposition of sulfonamide antibiotics: implications to the kinetics, mechanisms and toxicity. *Separation and Purification Technology* **202**, 259–265.

Piscopo, A., Robert, D. & Weber, J. V. 2001 Influence of pH and chloride anion on the photocatalytic degradation of organic compounds: Part I. Effect on the benzamide and para-hydroxybenzoic acid in TiO₂ aqueous solution. *Applied Catalysis B: Environmental* **35** (2), 117–124.

Sirtori, C., Agüera, A., Gernjak, W. & Malato, S. 2010 Effect of water-matrix composition on trimethoprim solar photodegradation kinetics and pathways. *Water Research* **44** (9), 2735–2744.

Trovo, A. G., Nogueira, R. F. P., Agüera, A., Fernandez-Alba, A. R., Sirtori, C. & Malato, S. 2009 Degradation of sulfamethoxazole in water by solar photo-Fenton. Chemical and toxicological evaluation. *Water Research* **43** (16), 3922–3931.

Wang, J., Zhu, H., Hurren, C., Zhao, J., Pakdel, E., Li, Z. & Wang, X. 2015 Degradation of organic dyes by P25-reduced graphene oxide: influence of inorganic salts and surfactants. *Journal of Environmental Chemical Engineering* **3** (3), 1437–1443.

Wu, J. T., Wu, C. H., Liu, C. Y. & Huang, W. J. 2015 Photodegradation of sulfonamide antimicrobial compounds (sulfadiazine; sulfamethizole; sulfamethoxazole and sulfathiazole) in various UV/oxidant systems. *Water Science & Technology* **71** (3), 412–417.

Wu, C. H., Wu, J. T. & Lin, Y. H. 2016 Mineralization of sulfamethizole (SFZ) in photo-Fenton and photo-Fenton-like systems. *Water Science & Technology* **73** (4), 746–750.

Yang, C. C., Huang, C. L., Cheng, T. C. & Lai, H. T. 2015 Inhibitory effect of salinity on the photocatalytic degradation of three sulfonamide antibiotics. *International Biodeterioration & Biodegradation* **102**, 116–125.

Yap, P. S. & Lim, T. T. 2011 Effect of aqueous matrix species on synergistic removal of bisphenol-A under solar irradiation using nitrogen-doped TiO₂/AC composite. *Applied Catalysis B: Environmental* **101** (3–4), 709–717.

Yu, X. Y. & Barker, J. R. 2003 Hydrogen peroxide photolysis in acidic aqueous solutions containing chloride ions. I. Chemical mechanism. *The Journal of Physical Chemistry A* **107** (9), 1313–1324.

Yuan, R., Ramjaun, S. N., Wang, Z. & Liu, J. 2011 Effects of chloride ion on degradation of Acid Orange 7 by sulfate radical-based advanced oxidation process: implications for formation of chlorinated aromatic compounds. *Journal of Hazardous Materials* **196**, 173–179.

Yuan, R., Ramjaun, S. N., Wang, Z. & Liu, J. 2012a Concentration profiles of chlorine radicals and their significances in ·OH-induced dye degradation: kinetic modeling and reaction pathways. *Chemical Engineering Journal* **209**, 38–45.

Yuan, R., Ramjaun, S. N., Wang, Z. & Liu, J. 2012b Photocatalytic degradation and chlorination of azo dye in saline wastewater: kinetics and AOX formation. *Chemical Engineering Journal* **192**, 171–178.

Yuan, R., Wang, Z., Hu, Y., Wang, B. & Gao, S. 2014 Probing the radical chemistry in UV/persulfate-based saline wastewater treatment: kinetics modeling and byproducts identification. *Chemosphere* **109**, 106–112.