Removal of sulfonamides from wastewater in the UV/TiO₂ 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/TiO₂ 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/TiO₂ 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/TiO₂ 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/TiO₂ 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, TiO₂

INTRODUCTION

Advanced oxidation processes (AOPs) are becoming increasingly important in the detoxification of wastewaters. Heterogeneous photocatalysis by TiO₂ 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/H₂O₂, UV/Fenton and UV/TiO₂, 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/H₂O₂ 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, Cl₂/2Cl⁻ (1.36 V) and HOCl/Cl⁻ (1.48 V). Furthermore, Cl⁻ in industrial wastewater can rapidly scavenge HO· to form less reactive chlorine radicals (Cl₂•, 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 TiO\textsubscript{2} surface (Guillard et al. 2005). In the UV/TiO\textsubscript{2} system, Cl\textsuperscript{−} ions (0–200 mM) significantly promote dye decolorization, but adding too much Cl\textsuperscript{−} apparently inhibits dye degradation (Yuan et al. 2022b). The decline in efficiency has been widely attributed to the quenching of radicals by salts (Adams & Impellitteri 2013). 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. 2018). The addition of 1 mM Cl\textsuperscript{−} slightly reduces the degradation of carbamazepine from 90.6% to 84.5% at 3,600 mJ cm\textsuperscript{−2} UV fluence (Ali et al. 2012). Although this inhibition is not great, the scavenging of HO\textsuperscript{•} by Cl\textsuperscript{−} may be responsible for it (Yu & Barker 2005).

García-Munoz et al. (2017) photodegraded sulfadimethoxine (SFX) and sulfamethizole (SFZ) in UV/ilmenite and UV/ilmenite/H\textsubscript{2}O\textsubscript{2} 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\textsuperscript{−1}, respectively, and those of SFX and SFZ in the UV/ilmenite/H\textsubscript{2}O\textsubscript{2} system were 0.42 and 0.24 min\textsuperscript{−1}, respectively. The mineralization rate constants of SFX and SFZ in the UV/ilmenite system were 0.016 and 0.013 mg.L\textsuperscript{−1}.min\textsuperscript{−1}, respectively, while those of SFX and SFZ in the UV/ilmenite/H\textsubscript{2}O\textsubscript{2} system were 0.038 and 0.025 mg.L\textsuperscript{−1}.min\textsuperscript{−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\textsuperscript{−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/TiO\textsubscript{2} 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/TiO\textsubscript{2} 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 TiO\textsubscript{2} P25 (Degussa, Germany), which consists mainly of anatase (80%), with a specific surface area of 50 m\textsuperscript{2}/g and a mean particle size of 30 nm. The Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, 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 HNO\textsubscript{3} 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 obtain ultrapure water (resistivity > 18 M\textomega.cm).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>SDZ</th>
<th>SFZ</th>
<th>SMX</th>
<th>STZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular structure</td>
<td><img src="image1" alt="SDZ" /></td>
<td><img src="image2" alt="SFZ" /></td>
<td><img src="image3" alt="SMX" /></td>
<td><img src="image4" alt="STZ" /></td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C\textsubscript{10}H\textsubscript{10}N\textsubscript{4}O\textsubscript{2}S</td>
<td>C\textsubscript{9}H\textsubscript{10}N\textsubscript{4}O\textsubscript{2}S\textsubscript{2}</td>
<td>C\textsubscript{10}H\textsubscript{11}N\textsubscript{3}O\textsubscript{3}S</td>
<td>C\textsubscript{9}H\textsubscript{9}N\textsubscript{4}O\textsubscript{2}S\textsubscript{2}</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>250 g/mol</td>
<td>270 g/mol</td>
<td>253 g/mol</td>
<td>255 g/mol</td>
</tr>
</tbody>
</table>

Table 1 | The molecular structure, formula and weight of sulfonamides (Wu et al. 2015)
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 TiO₂ 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 photo-reactor 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. 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. 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. 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 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 Na₂S₂O₈ 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):

\[ \ln\left(\frac{C_t}{C_0}\right) = -kt \]

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 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. (2008) 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. (2008). 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 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

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

* 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).

$$\text{HO}^• + \text{Cl}^- \rightarrow \text{HOCl}^-$$  \hspace{1cm} (2)

$$\text{HOCl}^- + \text{H}^+ \rightarrow \text{Cl}^- + \text{H}_2\text{O} \quad \text{pK} \approx 7.2$$  \hspace{1cm} (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.

$$\text{h}^+ + \text{Cl}^- \rightarrow \text{Cl}^-$$  \hspace{1cm} (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**

The authors would like to thank the National Kaohsiung University of Science and Technology, Taiwan, for financially supporting this research under Contract No. 107M01-1.

**REFERENCES**


First received 9 September 2018; accepted in revised form 28 January 2019. Available online 11 February 2019