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**Photodegradation of sulfadiazine in different aquatic environments –
evaluation of influencing factors**

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Abstract

The presence of antibiotics, such as sulfadiazine (SDZ), in the aquatic environment contributes to the generation of antimicrobial resistance, which is a matter of great concern. Photolysis is known to be a major degradation pathway for SDZ in surface waters. Therefore, influencing factors affecting SDZ photodegradation in different aquatic environments were here evaluated in order to have a better knowledge about its persistence in the environment. Photodegradation of SDZ was found to be more efficient at higher pH ($t_{1/2} = 6.76$ h, at pH = 7.3; $t_{1/2} = 12.2$ h, at pH = 6.3), in the presence of humic substances (HS) (with $t_{1/2}$ between 1.76 and 2.42 h), as well as in the presence of NaCl ($t_{1/2} = 1.00$ h) or synthetic sea salts ($t_{1/2} = 0.78$ h). Using $\cdot\text{OH}$ and $^1\text{O}_2$ scavengers, it was possible to infer that direct photolysis was the main path for SDZ photodegradation in ultrapure water. Furthermore, results under N_2 purging confirmed that $^1\text{O}_2$ was not relevant in the phototransformation of SDZ. Then, the referred observations were used for the interpretation of results obtained in environmental matrices, namely the final effluent of a sewage treatment plant (STPF), fresh and brackish water (with $t_{1/2}$ between 2.3 and 3.48 h), in which SDZ photodegradation was found to be much faster than in ultrapure water ($t_{1/2} = 6.76$ h).

Keywords: *Phototransformation; Sulfonamides; Dissolved organic matter (DOM); Excited triplet states; Reactive oxygen species (ROS); Reactive halogen species (RHS)*

1. INTRODUCTION

Antibiotics are organic compounds capable of selectively weaken or affect functions of other organisms, being widely used, with both prophylactic and therapeutic purposes, in humans and livestock (Bian and Zhang, 2016). Their incomplete removal in sewage treatment plants (STPs) accounts for the occurrence of these compounds in effluents from STPs and receiving waters (Oliveira et al., 2019). Even at relative low concentrations, their presence in the aquatic environment is of severe concern because of the induction of bacterial resistance (Zhao et al., 2019), which is actually considered a major threat to global health by the World Health Organization (WHO, 2019).

In surface waters, the fate of pharmaceuticals is largely influenced by naturally occurring removal processes as biodegradation, sorption, and photodegradation. Some pharmaceuticals are designed to be resistant to biodegradation while sorption removal cannot be globally generalised since it is significantly affected by the sediment type (Yan and Song, 2014). Therefore, photochemical transformation is a pivotal process governing the fate of pharmaceuticals, including antibiotics, in the aquatic environment (Oliveira et al., 2016; Oliveira et al., 2019; Silva et al., 2016a; Silva et al., 2016b; Silva et al., 2020).

Sulfonamides (SAs) constitute a class of antibiotics that has been extensively applied around the world, presenting low price and stable properties, and therefore have a wide occurrence in the aquatic environment (Cui et al., 2020). Furthermore, SAs are quite resistant to conventional treatments in STPs, being reported to be more resistant to degradation than the recalcitrant pentachlorophenol (Batista et al., 2014a). Among most consumed SAs, sulfadiazine (SDZ) (Figure 1) is used in the therapy of mild-to-moderate infections not only in human, but also in veterinary treatments. As for its high consumption, Cui et al. (2020) recently found that, comparatively with other SAs, SDZ

presented a very high detection frequency (100%) and concentration (up to 216 ng L⁻¹) in STP influents and effluents (Cui et al., 2020), having been detected in different aquatic environments. For example, Su et al. (2020) detected SDZ in river water with a mean concentration of 15 ng L⁻¹ and with a frequency of detection of 41%, while Guo et al. (2020) detected concentrations up to 4.5 ng L⁻¹ in estuarine water with a detection rate of 83%. Moreover, SDZ was also detected in ground water in concentrations up to 3.10 ng L⁻¹ (Qin et al., 2020). Apart from the associated bacterial resistance spreading, the wide occurrence of SDZ, may have associated toxicity risks since, on the basis of criterion issued by the Globally Harmonized System of Classification and Labelling of Chemicals, it can be sorted as a very toxic organic contaminant (Duan et al., 2020).

SDZ is a weak acid that may occur in two main forms - HSDZ (undissociated form) and SDZ⁻ (deprotonated form) - and, due to its chemical structure, exhibits limited biodegradation (Biošić et al., 2017; Pan et al., 2014). However, photolysis has been shown to be a significant process for decreasing its concentration in the aquatic environment (Biošić et al., 2017; Ge et al., 2019).

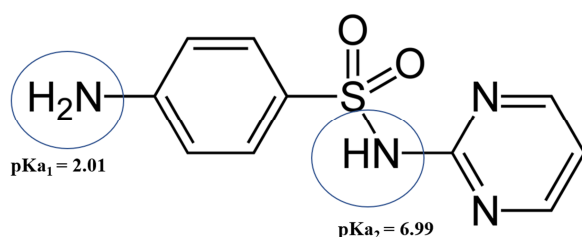


Figure 1: Sulfadiazine (SDZ) molecular structure, with indication of pKa values. Note: In natural waters, pH values are usually comprised between 6 and 8.7.

Photolysis of organic compounds, such as SDZ, may occur by direct, self-sensitized or indirect photodegradation. In direct photodegradation, photon absorption by SDZ promotes electrons from its initial ground-state to produce electronically excited species in the singlet state (SDZ^{*}) or triplet state (³SDZ^{*}) that then decompose

into photoproducts. On the other hand, $^3\text{SDZ}^*$ can transfer the energy to dissolved oxygen (DO) or H_2O to form reactive oxygen species (ROS, such as hydroxyl radicals ($\cdot\text{OH}$) or singlet oxygen ($^1\text{O}_2$)), which subsequently cause the self-sensitized photooxidation of SDZ (Figure 2). In indirect photodegradation, other substances present in the medium (photosensitizers) absorb the radiation and generate species (e.g., $\text{OH}\cdot$, $^1\text{O}_2$, peroxy radicals ($\text{ROO}\cdot$), excited triplet states of dissolved organic matter ($^3\text{DOM}^*$)) (Carlos et al., 2012; Silva et al., 2016a; Yi et al., 2018; Zhao et al., 2019) capable of causing the phototransformation of SDZ. In any case, these processes can be noticeably impacted by the characteristics of the aquatic medium and, therefore, for an appropriate assessment of the environmental fate and risks of SDZ, it is necessary to understand matrix effects on its photodegradation.

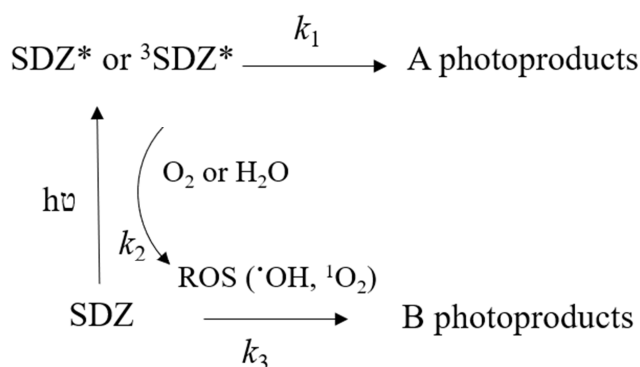


Figure 2. Pathway for direct and self-sensitized SDZ photolysis (adapted from Li et al., 2015).

For example, direct photolysis is more important for SDZ^- than for HSDZ, whilst in the indirect process, both species are oxidised fast by $^3\text{DOM}^*$ and their reaction with $^1\text{O}_2$ is barely meaningful (Vione and Koehler, 2018). On the other hand, SDZ is the only compound that is known to undergo the back-reduction process and both SDZ^- and HSDZ may be reduced back to the initial compounds by the phenolic moieties contained in DOM (Vione and Koehler, 2018). Yet, the type and concentration

of DOM has been shown to largely affect the phototransformation of SDZ (Bahn Müller et al., 2014). Still, most of the studies about the effect of DOM on SDZ photodegradation have been carried out using freshwater and effluent DOM (Bahn Müller et al., 2014; Sukul et al., 2008; Wang et al., 2018). However, populations usually concentrate along the coasts and, therefore, the discharge of antibiotics in coastal waters and the effects of seawater DOM on their photodegradation cannot be disregarded (Zhou et al., 2020). Indeed, seawater DOM has already shown to have higher reactivity than freshwater DOM on the photodegradation of sulfonamides (Wang et al., 2018). Along with DOM, halide ions were found responsible for the larger SDZ photodegradation in estuarine than in freshwaters by Zhao et al. (2019), who highlighted that antibiotics photodegradation from freshwaters downstream into seawater is largely unknown. Contrarily, Conde-Cid et al. (2018) did not find a significant influence of ionic species (including the halide Cl^-) on the photodegradation of SDZ. These authors (Conde-Cid et al., 2018) highlighted the increase of SDZ photodegradation with pH (between 4 and 7.2), which they related with the increase in the anionic form (SDZ⁻). DO is another factor that may affect antibiotics photodegradation, since the generation rate of ROS increases with increasing DO concentration (Saadati et al., 2016). Among ROS, Ge et al. (2019) indicated that $^1\text{O}_2$ oxidation can be a central factor in determining the fate of sulfonamides (especially in waters with a pH > 7), with oxidation by $\cdot\text{OH}$ also contributing to phototransformation relative to direct photolysis.

Overall, photodegradation of SDZ in the aquatic environment is affected by a complex interplay of different matrix effects. Therefore, in order to contribute to a better understanding of the fate and persistence of SDZ in natural waters, this work aimed: (i) to determine the effects of influencing factors such as the presence of the

several fractions of estuarine humic substances (HS) (humic acids (HA), fulvic acids (FA), and XAD-4 fraction), pH, salinity, DO and the presence of $^1\text{O}_2$ and $\cdot\text{OH}$ scavengers on the photodegradation of SDZ; and (ii) to find out if these effects (or their absence) can be related with the photodegradation behaviour of SDZ in real matrices, namely fresh, brackish and wastewater. Apart from this approach, another main novelty of this work was studying the effect of HS fractions extracted from estuarine waters, including for the very first time the XAD-4 fraction, on the photodegradation of SDZ. Since the extraction of HS from estuarine waters is especially challenging due to the highly diluted and saline aqueous medium, the obtained results constitute a relevant contribution.

2. MATERIALS AND METHODS

2.1. Chemicals

SDZ (> 99%) was provided by TCI Europe. Methanol (HPLC grade) and formic acid (> 98%) used for high-performance liquid chromatography with a UV-visible detector (HPLC-UV) analysis, were obtained from Fisher Scientific and Sigma-Aldrich, respectively. Sodium dihydrogen phosphate dihydrate (Fluka, Biochemika, $\geq 99.5\%$) and di-sodium hydrogen phosphate dihydrate (Fluka, Biochemika, $\geq 99\%$) were used to prepare a stock solution of phosphate buffer 0.1 mol L^{-1} , which was diluted to 0.001 mol L^{-1} . The pH of this solution was adjusted using hydrochloric acid (NormaPur, 37%) to both 6.3 and 7.3. SDZ stock solution was prepared using 0.001 mol L^{-1} phosphate buffer at pH 6.3 and 7.3. HS (HA, FA, and XAD-4) used in the photodegradation experiments were extracted and isolated from estuarine water (Ria de Aveiro, Aveiro, Portugal) as described by Santos et al. (1994) and Esteves (1995). Synthetic sea salt solution (21‰) was prepared using Red Sea Salt (Red Sea Europe) in phosphate buffer

solution (0.001 mol L^{-1}) with pH adjusted to 7.3. Sodium chloride (99.5%) was obtained from Fluka.

A stock solution of sodium azide (Riedel-de Haën, 99%) was prepared at a concentration of 0.023 mol L^{-1} in ultrapure water, while isopropanol (Sigma-Aldrich, 99.8%) stock solution was prepared at a concentration of 1 mol L^{-1} in ultrapure water. Ultrapure water was obtained from a Millipore system (Milli-Q plus 185).

2.2. Chromatographic and dissolved organic carbon (DOC) analysis

Quantitative analysis was performed using HPLC-UV. The device consisted in a Waters Alliance 2695 Separations Module equipped with a Waters 2487 Dual Absorbance detector. Separation was carried out using a $150 \text{ mm} \times 4.6 \text{ mm}$ i.d. ACE[®] C18 column-PFP ($5 \mu\text{m}$ particle size) connected to a 4.6 mm i.d. ACE[®] 5 C18 guard column at 25°C . The mobile phase consisted of methanol:0.1% formic acid, 20:80 (v/v), at a flow rate of 0.9 mL min^{-1} . An injection volume of $20 \mu\text{L}$ was used and detection was performed at 270 nm . Before use as mobile phase, methanol and 0.1% formic acid aqueous solutions were filtered through a $0.2 \mu\text{m}$ polyamide membrane filter (Whatman).

Dissolved organic carbon (DOC) was measured using a Total Organic Carbon analyser, TOC-VCPH, from Shimadzu. Samples were acidified with 2% (v/v) of HCl 2 mol L^{-1} , previously to the analysis. A stock solution of 1000 mg L^{-1} potassium hydrogen phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$) was prepared in ultrapure water. The calibration curve was performed using standard solutions of $\text{KHC}_8\text{H}_4\text{O}_4$ in ultrapure water ($0.0\text{-}10.0 \text{ mg L}^{-1}$), by dilution of proper amounts of the stock solution. The coefficient of determination (R^2) and limit of detection (LOD) for the obtained calibration curve were 0.9984 and 0.613 mg L^{-1} , respectively. To confirm the stability of the calibration curve, a newly

prepared standard solution of 5.0 mg L^{-1} of $\text{KHC}_8\text{H}_4\text{O}_4$ was analysed daily prior to the samples.

2.3. Photodegradation experiments

2.3.1. Apparatus

A solar radiation simulator Solarbox 1500 (Co.fo.me.gra, Italy) was used for irradiation experiments. This instrument is equipped with a xenon arc lamp (1500 W) and UV filters that limit the transmission of light below 290 nm. All experiments were performed with a constant irradiation of 55 W m^{-2} (290–400 nm), which corresponds to 550 W m^{-2} in the spectral range, according to the manufacturer. The level of irradiance and temperature was monitored by a multimeter (Co.fo.me.gra, Italy) equipped with a UV 290–400 nm band sensor and a black standard temperature sensor. A parabolic reflection system was used to ensure irradiation uniformity in the chamber, which was kept refrigerated by an air-cooling system.

SDZ aqueous solutions (20 mL) were irradiated, in triplicate, in quartz tubes (internal diameter \times height = 1.8×20 cm), until no SDZ was detected. Each set of experiments was accompanied by dark controls under identical conditions except for irradiation (quartz tubes covered by aluminium foil), maintained inside the solar simulator during the same time as the irradiated solutions. Aliquots (500 μL) of replicates and dark controls were stored in the dark at $4 \text{ }^\circ\text{C}$ and analysed within 24 h. The remaining concentration of SDZ in irradiated solutions (C) was compared with that in the respective dark control (C_0) for determining the percentage of degradation at each irradiation time (t , h). GraphPad Prism 5 was used to determine the fittings of experimental data to the pseudo first-order kinetic equation $C/C_0 = e^{-kt}$, where k is the

pseudo first-order degradation rate constant (h^{-1}). Also, SDZ half-life times ($t_{1/2}$) were calculated as $\ln 2/k$.

2.3.2. Effect of pH, humic substances and salinity

Photodegradation was studied using an initial SDZ concentration (C_i) of $500 \mu\text{g L}^{-1}$. The concentration of SDZ used was chosen according to the LOD of the HPLC-UV and in order to follow more than 95% of SDZ photodegradation.

Since SDZ presents two pK_a values (2.01 and 6.99), pH greatly affects the antibiotic speciation in solution, and thus its photodegradation behavior. On the other hand, the pH of most natural waters is between 6 and 8.7, which comprises the pK_{a2} of SDZ. Therefore, the effect of pH at two different values, namely below and above pK_{a2} , was here assessed. For this purpose, the working SDZ solution was prepared using a 0.001 mol L^{-1} phosphate buffer, adjusting pH to 6.3 or 7.3.

To evaluate the influence of DOM in SDZ photodegradation behaviour, HS (HA, FA, and XAD-4 fraction) were used. SDZ solutions in HS fractions (20 mg L^{-1}) were prepared in 0.001 mol L^{-1} phosphate buffer with pH adjusted to 7.3. HS concentration used was chosen taking into account that the mean DOC concentration of lakes, streams and rivers has been referred to be between 2.0 and 10 mg L^{-1} (Leech et al., 2009). HS used in this work were extracted and isolated from coastal estuarine water (collected at Ria de Aveiro (Aveiro, Portugal)) as described by Santos et al. (1994) and Esteves et al. (1995). Characterization of the purified fractions by elemental analysis, solid-state ^{13}C cross polarization magic angle spinning nuclear magnetic resonance (CPMAS-NMR) and UV-visible spectrophotometry was performed and deeply discussed in Esteves et al. (2009).

Salinity of brackish water can range between 0.5 and 35‰, varies between estuaries and can change from one day to the next depending on the tides, weather, or other factors (Levinton, 1995). Thus, the effect of salinity was evaluated using SDZ solutions prepared in 0.001 mol L⁻¹ phosphate buffer with pH adjusted to 7.3, containing 21‰ NaCl or 21‰ synthetic sea salts.

2.3.3. Effect of scavengers and dissolved oxygen (DO)

In order to qualitatively investigate the role of ROS, SDZ photodegradation was evaluated in the presence of two different scavengers: sodium azide (NaN₃, as ¹O₂ scavenger) and isopropanol (C₃H₈O, as [•]OH scavenger) (Batista et al., 2014b; Silva et al., 2014). SDZ standard solutions were prepared in 0.001 mol L⁻¹ phosphate buffer with pH adjusted to 7.3, containing 5 mmol L⁻¹ of NaN₃ or 20 mmol L⁻¹ of C₃H₈O and subjected to irradiation. Sodium azide concentration was chosen accordingly to Thermofisher online information (Thermofisher, 2020). For isopropanol, concentrations between 10 and 100 mM have been used in literature (Acero et al., 2019; Zhang et al., 2016), thus an intermediate concentration was chosen.

The role of DO on SDZ photodegradation was evaluated purging SDZ solution (in 0.001 mol L⁻¹ phosphate buffer; pH 7.3) with N₂ for 5 min. Deoxygenation of solutions was used to explore the role of triplet excited states, since oxygen (a ground state triplet because of its unpaired electrons) is a quencher of triplet excited states.

2.3.4. Effect of natural water matrix

In order to evaluate the influence of natural water matrices in SDZ photodegradation, fresh, brackish and wastewater samples were used. Freshwater was collected from a river located in Aveiro, while brackish water was collected from Ria de

Aveiro (Aveiro, Portugal). Wastewater was sampled from one of the Aveiro's STPs, after secondary treatment, corresponding to the final effluent (STPF). Immediately after collection, all samples were filtered through 0.45 μm nitrocellulose membrane filters (Millipore) and stored at 4 $^{\circ}\text{C}$ until use, within 7 days. Salinity, conductivity and pH of the samples used were measured using a Multi 3320 meter from WTW. DOC was measured as described previously (section 2.2.).

3. RESULTS AND DISCUSSION

3.1. Performance of the chromatographic analytical method

Under optimized conditions, the performance of the method was evaluated using the correlation coefficient (r), limit of detection (LOD) and linearity ($Lin (\%) = 100 - RSD_b$, where RSD_b is the relative standard deviation of the slope). LOD was calculated from the calibration curve as $a + 3s_{y/x}$, where a is the intercept of the regression line and $s_{y/x}$ is the statistical parameter that estimates the random errors in the y-axis (signal). The linear range was 25-500 $\mu\text{g L}^{-1}$, while LOD was 21.2 $\mu\text{g L}^{-1}$. SDZ calibration curve presented good correlation coefficient ($r = 0.9987$) and good linearity values ($Lin = 98.4\%$) for the concentration range used in this study.

3.2. Effect of pH, humic substances and salinity

Results on the effect of pH, HS, and salinity on the photodegradation of SDZ are depicted in Figure 3, which represents C/C_0 versus irradiation time under the different conditions described in section 2.3.2. Regarding photodegradation of SDZ at pH 6.3 and 7.3, results are shown in Figure 3(a).

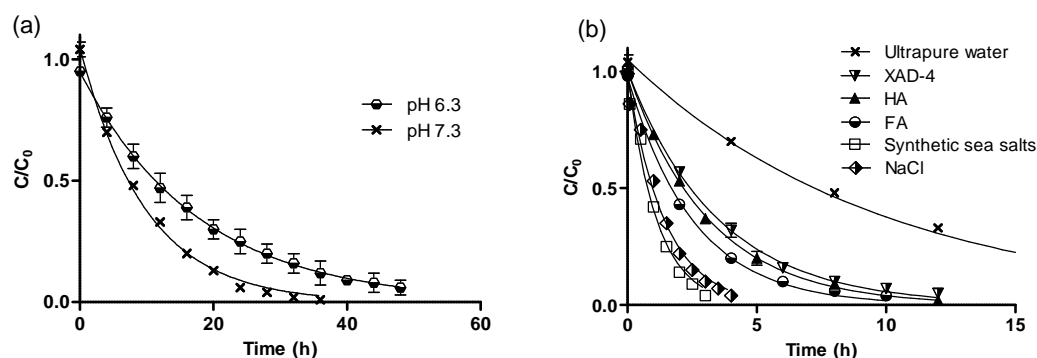


Figure 3. Experimental results on the kinetics of SDZ photodegradation ($C_i = 500 \mu\text{g L}^{-1}$) together with curves of pseudo first-order decay fitted to the data by nonlinear regression obtained for (a) different pH values; (b) different matrices (ultrapure water, HS fractions (20 mg L^{-1}), synthetic seawater (21‰) and NaCl (21‰); pH 7.3). (Note that, for most of the experimental points, error bars are so small that they are not visible in the figure).

Complete photodegradation of SDZ at pH 7.3 occurred within 36 h, while at pH 6.3 it took more than 48 h to eliminate SDZ from aqueous solution. The constant k obtained at pH 7.3 was $0.103 \pm 0.003 \text{ h}^{-1}$, while at pH 6.3 was $0.0567 \pm 0.0005 \text{ h}^{-1}$ (Table 1).

At pH 6.3, 83% of SDZ is in the neutral form (HSDZ), while at pH 7.3, 67% of SDZ is in its anionic form (SDZ^-). As was already shown, SDZ k at pH 7.3 is almost twice the value obtained at pH 6.3 (Table 1). From these results it may be concluded that photodegradation is more efficient for SDZ^- than for HSDZ. Since natural water normally presents pH values higher than 7.3 (Oliveira et al., 2019), the SDZ photodegradation would be favored under the pH of most of environmental waters. However, Vione et al. (2018) observed that, in natural waters (with DOC contents between 6 and 13 mg C L^{-1}), both species were oxidised fast by the photogenerated $^3\text{DOM}^*$, but SDZ^- underwent back reactions at a larger extent than HSDZ, thus reducing the photodegradation efficiency.

Results of the photodegradation of SDZ in ultrapure water (pH 6.3) demonstrated that after 32 h, 84% of SDZ was eliminated from the aqueous solution. On the other hand, DOC results shown that 20% of SDZ was completely mineralized into CO₂ and H₂O.

Regarding the photodegradation of SDZ in the presence of different HS fractions (at pH 7.3), results are presented in Figure 3(b) and Table 1. The influence of organic matter will be a balance of opposite contributions: photosensitizing effect (through formation of reactive species) and inhibitory effects (inner filter effect, scavenging/quenching of reactive species and/or back-reductions) (Oliveira et al., 2019). A retardation of photodegradation by organic matter has been observed for some pharmaceuticals (Santoke and Cooper, 2017). Different effects by different fractions have also been described in the literature; for example, Batista et al. (2016) found that HA slightly increased photodegradation of sulfamerazine, while FA significantly decreased its photodegradation. However, in this work, the photodegradation of SDZ accelerated under the presence of the three HS fractions (Figure 3(b)). Indeed, the $t_{1/2}$ in ultrapure water was 6.76 ± 0.07 h, while in the presence of HS it was in the range 1.76-2.42 h. These results showed that photodegradation of SDZ is predominantly enhanced by ³DOM*, rather than inhibited by back-reductions, inner filter effect or scavenging/quenching of reactive species.

HS used in this study were extracted and isolated from coastal estuarine water (Esteves et al., 2009). These HS, compared with HS from freshwater, are known to have lower absorbance, due to a lesser influence from terrestrial organic matter (Esteves et al., 2009). Moreover, these HS generally present smaller adsorption coefficients (a_{λ} , m⁻¹) than those from terrestrial origin, thus lower a_{350} can be related to a lower aromatic carbon concentration, in agreement with the dominant role of aromatic chromophores in

coloured DOM. Esteves et al. (2009) also reported that FA and XAD-4 fraction from estuarine coastal water are generally more aliphatic fractions than fractions from terrestrial origin, with higher lignin-derived structures.

Comparing results obtained using different HS fractions, it was possible to observe that $t_{1/2}$ obtained for FA fraction was 1.76 ± 0.04 h. In fact, this fraction is known to be the most photochemically active fraction of DOM (Li and Sun, 2014). On the other hand, HA presented a higher $t_{1/2}$ (2.16 ± 0.02 h) and XAD-4 fraction the highest $t_{1/2}$ value (2.42 ± 0.04 h). Results demonstrated that FA are more efficient as natural photosensitizers than HA and XAD-4. This may be related to the fact that FA are less hydrophobic and less enriched in aromatic groups than HA (Oliveira et al., 2019) and thus, with less ability to act as light filter (inner filter effect). In fact, the spectra of the three fractions of HS (Oliveira et al., 2019) show that, within the studied wavelength range, the absorbance followed the order XAD-4 < FA < HA. Because of the structural heterogeneity of HS, they do not produce a resolved spectrum and the absorbance increases monotonously as the wavelength decreases. The fact that HA present a higher ability to absorb radiation may explain, at least partially, the lower SDZ photodegradation in their presence. As mentioned before, HS from estuarine coastal water present a lower aromatic carbon concentration, thus, a higher photodegradation rate of SDZ in this type of water samples is expected.

Also, a correlation between the aromatic degree of the DOM and the antioxidant activity has been mentioned, and therefore, HS with lower aromatic degree (as FA), have lower antioxidant activity (lower inhibition by back-reductions) (Vione et al. 2018). Moreover, DOM from aquatic origin (such as estuarine water), with low aromaticity, was shown to be a softer inhibitor than DOM from terrestrial origin, with high aromaticity, and thus, likely to act less as an antioxidant. Overall, the presence of

DOM, as simulated by HS, has an enhancement effect on the photodegradation of SDZ, which due to the characteristics of coastal estuarine samples will be favoured in this type of HS, rather than in terrestrial DOM.

With respect to the effect of salinity, the obtained results (Figure 3(b)) demonstrated the photosensitizer effect that salinity has on the SDZ photodegradation. Fitted parameters of the pseudo first-order kinetic equation, which are depicted in Table 1, confirmed the higher k ($0.70 \pm 0.04 \text{ h}^{-1}$) in the presence of NaCl compared to that obtained in ultrapure water ($0.103 \pm 0.003 \text{ h}^{-1}$), resulting in a $t_{1/2}$ almost 7 times lower. The photosensitizing effect of NaCl can be attributed to the presence of chloride. Halides have been only considered as scavengers of $\cdot\text{OH}$ during advanced oxidation processes (AOP), especially in saline waters, where AOP would be anticipated to be ineffective. However, $\cdot\text{OH}$ scavenging by halides simply converts $\cdot\text{OH}$ to more selective oxidants, being AOP treatment in saline waters highly contaminant-specific (Grebel et al., 2010). Halides, such as chloride, can be converted into radical and non-radical reactive halogen species (RHS) by sensitized photolysis and by reactions with secondary reactive oxygen species (ROS) produced through sunlight-initiated reactions in water and atmospheric aerosols, such as $\cdot\text{OH}$, ozone, and nitrate radical (Yang and Pignatello, 2017). For the chloride concentration used, chloride atoms will quickly react with the anions to form $\text{Cl}_2^{\cdot-}$ radical anions (Pinto et al., 2018). According to Pinto et al. (2018), both direct and sensitized photolysis can be used to produce chloride atoms in aqueous solutions; these react rapidly with excess of chloride ion to produce the corresponding dihalide radical anions ($\text{Cl}_2^{\cdot-}$) as the dominant species. Chloride ions are also oxidized by hydroxyl radicals, with initial reversible formation of the $\text{ClOH}^{\cdot-}$ radical anion, which subsequently reacts with chloride ions to produce $\text{Cl}_2^{\cdot-}$ (Pinto et al., 2018). Halide scavenging may dramatically reduce the treatment efficiency of

electron-poor contaminants that react slowly with RHS, but the extent of the reduction with electron-rich contaminants may be less remarkable (Grebel et al., 2010). Zhao et al. (2019) demonstrated that RHS were largely responsible for the halide-specific enhancement in the SDZ photodegradation, rather than other reactive species, such as $^3\text{DOM}^*$ and $\cdot\text{OH}$. These findings are in agreement with those observed in this work but different from those obtained by other authors, which pointed out the absence of significant effects of ionic species (Conde-Cid et al., 2018) or the inhibitory effect of salinity on the photocatalytic degradation of sulfonamide antibiotics (Oliveira et al., 2019; Yang et al., 2015). When comparing the results that were obtained in this work using NaCl and synthetic sea salts at the same concentration, a higher k was determined in synthetic sea salts ($0.89 \pm 0.06 \text{ h}^{-1}$) than in NaCl ($0.70 \pm 0.04 \text{ h}^{-1}$). Sodium and chloride ions represent about 91% of all seawater ions, even though there are lower quantities of other ions in seawaters (e.g., K^+ , Mg^{2+} , or SO_4^{2-}) (Pinto et al., 2018). The synthetic sea salts from Red Sea Salt used in this study contain ions like calcium, magnesium, and carbonates, being free of synthetic additives, nitrates, phosphates or heavy metals (Red Sea, 2019). Therefore, in synthetic sea salts, carbonates, such as bicarbonate (HCO_3^-), may have favoured SDZ photodegradation since they can act as an $\cdot\text{OH}$ scavenger and produce selective carbonate radicals ($\text{CO}_3^{\cdot-}$) (Li et al., 2018), responsible for the degradation of electron-rich organic pollutants. Studies of pollutants' photodegradation behaviour using coastal waters are extremely important, since due to the global climate change, coastal lagoons are likely to experience high salinity in the coming decades (Pinto et al., 2018).

Table 1. Data on pseudo first-order rate constants (k (h^{-1})), determination coefficient (R^2), half-lives in simulated solar radiation ($t_{1/2}$ (h)).

Sample	k (h^{-1})	R^2	$t_{1/2}$ (h)
Ultrapure water, pH = 6.3	0.0567 ± 0.0005	0.9996	12.2 ± 0.03
Ultrapure water, pH = 7.3	0.103 ± 0.003	0.9973	6.76 ± 0.07
HA	0.321 ± 0.005	0.9995	2.16 ± 0.02
FA	0.39 ± 0.01	0.9984	1.76 ± 0.04
XAD-4	0.286 ± 0.007	0.9988	2.42 ± 0.04
Sea salts (21‰)	0.89 ± 0.06	0.9882	0.78 ± 0.06
NaCl (21‰)	0.70 ± 0.04	0.9897	1.00 ± 0.06
NaN ₃	0.157 ± 0.005	0.9963	4.41 ± 0.06
Isopropanol	0.090 ± 0.005	0.9874	7.7 ± 0.1
N ₂	0.21 ± 0.05	0.7979	3.3 ± 0.4
Freshwater	0.30 ± 0.01	0.9963	2.32 ± 0.05
Brackish water	0.29 ± 0.02	0.9919	2.3 ± 0.1
STPF	0.199 ± 0.007	0.9960	3.48 ± 0.07

3.3. Effect of scavengers and dissolved oxygen (DO)

Isopropanol and sodium azide were used to evaluate the influence of $\cdot\text{OH}$ and $^1\text{O}_2$, respectively, on SDZ photodegradation. The obtained results on the SDZ C/C_0 throughout irradiation time are represented in Figure 4 and the corresponding kinetic parameters are depicted in Table 1.

As may be seen in Table 1 and in Figure 4, in the presence of isopropanol, k presented no evident decline after adding this $\cdot\text{OH}$ scavenger (k decreased from $0.103 \pm 0.003 \text{ h}^{-1}$ (in ultrapure water) to $0.090 \pm 0.005 \text{ h}^{-1}$ (Table 1)), suggesting that direct photolysis was the main path for SDZ photodegradation behaviour in ultrapure water. Bahnmüller et al. (2014) also reported that, under the presence of isopropanol, a slight decrease in the SDZ k occurred in ultrapure water, which confirmed the importance of direct photodegradation in this matrix.

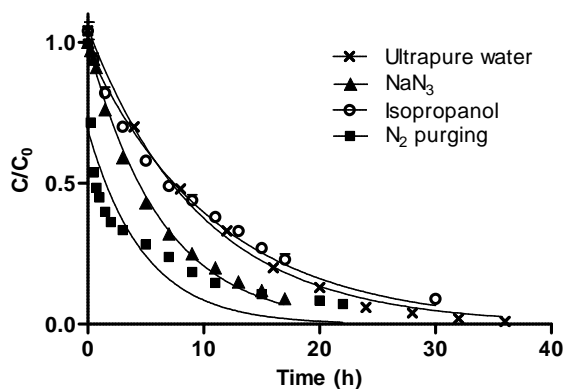


Figure 4. Experimental results on the kinetics of SDZ photodegradation ($C_1 = 500 \mu\text{g L}^{-1}$) together with curves of pseudo first-order decay fitted to the data by nonlinear regression obtained in ultrapure water, in the presence of isopropanol, NaN_3 and with nitrogen purging at pH 7.3). (Note that, for most of the experimental points, error bars are so small that they are not visible in the figure).

In presence of sodium azide (Figure 4), Table 1 evidences that k increased significantly from $0.103 \pm 0.003 \text{ h}^{-1}$ (in ultrapure water) to $0.157 \pm 0.005 \text{ h}^{-1}$. Sodium azide in presence of $^1\text{O}_2$ originates azidyl radical (N_3^\cdot) and $\text{O}_2^{\cdot-}$, thus the increase in k may be explained by the activity of the formed species during the scavenging process, especially N_3^\cdot , which are highly oxidative species (Trawiński and Skibiński, 2019).

In order to evaluate the influence of DO in SDZ photodegradation, solutions were purged with N_2 . Results (Figure 4 and Table 1) demonstrated a higher k under N_2 purging ($0.21 \pm 0.05 \text{ h}^{-1}$) than the obtained without purging ($0.103 \pm 0.003 \text{ h}^{-1}$), which evidences the involvement of triplet excited species in the direct photolysis (Table 1). DO is able to quench the excited states via energy/electron transfer, which leads to the formation of $^1\text{O}_2$. Quenching of the excited states may restrain the direct photodegradation process, whereas the formation of $^1\text{O}_2$ can promote the indirect process (Zhang et al., 2018). Therefore, the obtained results under N_2 purging further confirm that $^1\text{O}_2$ was not relevant in the transformation of SDZ observed in this work

and the importance of the triplet excited species in the direct photolysis of SDZ. If $^1\text{O}_2$ were the major reactive species responsible for the indirect photolysis, a significant decrease on the SDZ degradation rate would have occurred in the deoxygenated sample, which was not observed. These results are in agreement with those by Vione and Koehler (2018), who also reported that SDZ reaction with $^1\text{O}_2$ was barely meaningful and that the main SDZ⁻ phototransformation process was direct photolysis (predominant species at pH 7.3). Contrarily, $^1\text{O}_2$ oxidation was suggested by Ge et al. (2019) as a determinant process in determining the fate of sulfonamides in the aquatic medium, especially at pH higher than 7. Contradictory results may be related to the fact that oxygen can have opposite effects: the increased yields of ROS accelerates the self-sensitized photolysis of SDZ, while the greater quenching of excited SDZ inhibits its direct photodegradation. With the increase in DO level, the increase in self-sensitized photodegradation is outweighed by the reduction in direct photolysis.

3.4. Effect of natural water matrices

In order to understand the photodegradation behaviour of SDZ in different aquatic mediums, three water samples with different characteristics were used (Table 2). These experiments were conducted at the natural pH of each water sample.

Table 2. Physico-chemical characteristics of natural water samples.

Sample	pH	Conductivity (mS cm ⁻¹)	Salinity	DOC (mg C L ⁻¹)
STPF	8.7 ± 0.4	3.03	1.40	24.0 ± 0.1
Freshwater	7.3 ± 0.3	0.26	0.00	8.3 ± 0.4
Brackish water	8.6 ± 0.3	50.70	33.20	9.8 ± 0.3

The photodegradation rate of SDZ in natural water samples was found to be much higher than the obtained in ultrapure water (Figure 5).

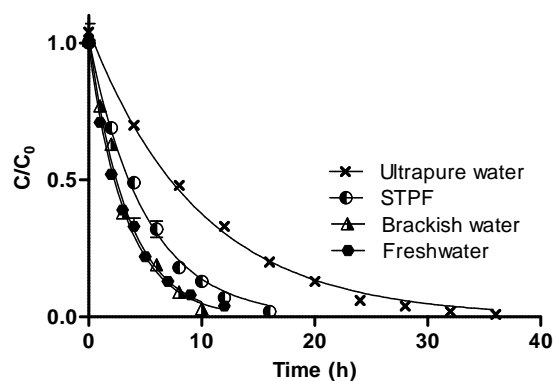


Figure 5. Experimental results on the kinetics of SDZ photodegradation ($C_i = 500 \mu\text{g L}^{-1}$) together with curves of pseudo first-order decay fitted to the data by nonlinear regression obtained in ultrapure water (pH = 7.3) and in three different environmental water matrices at natural pH values. (Note that, for most of the experimental points, error bars are so small that they are not visible in the figure).

Kinetic parameters from SDZ photodegradation are depicted in Table 1, which shows that k in ultrapure water ($0.103 \pm 0.003 \text{ h}^{-1}$) was quite lower than the values obtained in natural water samples (between 0.199 and 0.30 h^{-1}). Amongst the natural water samples here considered, the lowest k was obtained in the STP effluent. Meanwhile, SDZ photodegradation experiments in fresh and brackish water samples presented similar results. Since both ultrapure water and freshwater samples had the same pH value, differences in the photodegradation rate cannot be attributed to SDZ speciation. However, freshwater sample presented 8.3 mg C L^{-1} and, as was already shown in this work, enhancement of SDZ photodegradation by $^3\text{DOM}^*$ was dominant over other DOM effects such as back-reductions, inner filter effect or scavenging/quenching of reactive species. On the other hand, in the STPF sample, with a pH of 8.7, SDZ is present only in its anionic form, which is more susceptible to photodegradation (Vione et al., 2018). Nonetheless, STPF sample has a large DOC of 24 mg C L^{-1} and, therefore, the slower SDZ photodegradation could be related to the

inhibition of $^3\text{DOM}^*$ -mediated phototransformation by the back reactions (Vione and Koehler, 2018) and by inner filter effect.

In what concerns the brackish water, the pH 8.6 favours the presence of SDZ entirely in the negative form, which is more susceptible to photodegradation. The remarkably higher salinity of the brackish water (33.20), also help to justify the larger photodegradation rate compared to that observed in ultrapure water. Indeed, the formation of RHS is responsible for the halide-specific enhancement in the SDZ photodegradation in brackish water. However, other factors such as DOM content may affect the photodegradation of SDZ in brackish water. The DOC content of the brackish water sample is 9.8 mg C L^{-1} , which means that DOM will have both photosensitizing (through formation of reactive species) and inhibitory (inner filter effect, scavenging/quenching of reactive species and/or back-reductions) effects.

4. FINAL REMARKS AND FUTURE WORK

SDZ is a widely used antibiotic, which presence in the aquatic environment is especially concerning, as reflected by the large attention received by the scientific community. Photodegradation is a naturally occurring process that may largely affect the fate of antibiotics in surface waters, being the assessment of matrix effects essential for understanding SDZ behaviour. In this work, the effect of pH, HS and salinity on the photodegradation of SDZ were determined, which allowed to prove that: i) photodegradation of the anionic SDZ^- , which is the dominant species at the common pH values of natural waters, is favoured in relation to the neutral HSDZ; ii) SDZ photodegradation is notably enhanced under the presence of the three fractions of HS, namely HA, FA and XAD-4, which points to the predominance of the $^3\text{DOM}^*$ enhancing influence; and iii) salinity has a marked photosensitizing effect on the photodegradation of SDZ, which is not solely related to NaCl but also to other salts, such as bicarbonates. These effects were related with the

larger SDZ photodegradation observed in real matrices, namely in wastewater, brackish water and freshwater, as compared with that occurring in ultrapure water, where it was found that neither $^1\text{O}_2$ nor $\cdot\text{OH}$ are relevant in the phototransformation of SDZ, while the triplet excited species have an important role. These findings constitute a relevant contribution in the actual context and point to photodegradation as an important loss mechanism for SDZ in surface waters, where it is favoured due to pH effects and presence of DOM and photosensitizing inorganic ions. Such effects are extremely important and must be taken into account in the design of low-cost and low-energy alternatives to conventional tertiary wastewater treatments, such as constructed wetlands or stabilization lagoons. However, in order to gain a deeper understanding on SDZ photochemical fate, further research is to be carried out on the SDZ photodegradation pathways and products in the different matrices, assessing the toxicity of the resulting photoproducts. Also, the quantification of the concentration of the reactive species, namely ROS and $^3\text{DOM}^*$ in the different aqueous matrices, should be determined for ascertaining their relative importance in SDZ photodegradation. Such information, together with the degree of mineralization that occurs along photodegradation, is essential for the implementation of wastewater alternative treatments that allow for the removal of antibiotics. On the other hand, in view of the large influence of DOM in SDZ photochemical degradation, research is to be undertaken on the extraction, characterization and effects of the HS fractions (HA, FA and XAD-4) from waters of different origin. In this way, it will be possible to correlate the specific chemical and spectroscopic characteristics of HS fractions with the photodegradation of SDZ.

5. CONCLUSIONS

SDZ photodegradation was shown to be notably affected by pH, the presence of HS and salinity. Thus, in ultrapure water, the $t_{1/2}$ determined for SDZ was 6.8 h at pH = 7.3 and 12.2 h at pH = 6.3. Under the presence of HA, FA or XAD-4 fractions of estuarine HS, SDZ photodegradation was favoured, with $t_{1/2}$ of 2.2, 1.8 and 2.4 h, respectively. On the other hand, salinity exhibited a photosensitizing effect, with $t_{1/2}$ of 1.0 and 0.8 h in NaCl and sea salts (both 21‰), respectively. Studies in the presence of scavengers, namely isopropanol and sodium azide, and under N₂ purging, allowed to verify that ¹O₂ and [•]OH had not influence, but triplet excited states had a relevant role in SDZ direct photodegradation. All these effects were related with photodegradation results in real matrices, namely in wastewater (STPF), freshwater and brackish water, where the determined $t_{1/2}$ were 3.5, 2.3 and 2.3 h, respectively. In STPF, the relatively high pH (8.7) favoured SDZ photodegradation but the very high DOC concentration probably lessened it by back reactions inhibition of ³DOM*-mediated phototransformation, inner filter effects and/or scavenging/quenching of reactive species. Differently, ³DOM*-mediated phototransformation was probably dominant and had an important role in freshwater while halide-specific enhancement of SDZ photodegradation may have occurred in saline brackish water.

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Highlights

- Sulfadiazine (SDZ) photodegradation was found to be more efficient at higher pH
- Dissolved organic matter resulted in an increase of SDZ photodegradation
- Salinity and reactive halogen species caused an increase in SDZ photodegradation
- Direct photolysis was the main path for SDZ photodegradation in ultrapure water
- $t_{1/2}$ decreased from 6.76 h in ultrapure water to 2.3–3.48 h in environmental samples