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# Parameters affecting sulfonamide photo-Fenton degradation – Iron complexation and substituent group

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ABSTRACT

The photo-Fenton degradation of the sulfonamide antibiotics sulfadiazine (SDZ) and sulfathiazole (STZ) mediated by Fe(III)-oxalate was studied in this work. The influence of iron complexation, $H_2O_2$ concentration and pH on the initial SDZ and STZ degradation rate was evaluated. Degradation of both antibiotics is drastically improved in the presence of Fe(III)-oxalate in comparison to free iron, achieving complete degradation after 8 min irradiation at pH 2.5 in the presence of 5 mM $H_2O_2$ (equivalent to $H_2O_2$/antibiotic = 50). It was also possible to extend pH range of the photo-Fenton reaction by the use of Fe(III)-oxalate reaching more the 70% degradation at pH 6, however without significant mineralization. Comparison of the degradation kinetics of both sulfonamides indicated higher recalcitrance of STZ due to the lower electron density of its thiazol ring in relation to pyrimidine ring in SDZ.



## 1. Introduction

The importance of iron in the degradation of organic pollutants in water has been recognized for long time [1]. Iron complexes redox reaction promoted by ligand to metal charge transfer (LMCT) is an important source of $Fe^{2+}$ and reactive oxygen species (ROS) in atmospheric water drops and surface waters [2]. Due to the formation of radicals, carboxylate iron complexes have been extensively used in photo-Fenton degradation of pollutants showing in most cases higher efficiency when compared to free iron, especially under solar irradiation [3–5]. The improved degradation is a result of mainly three points: (a) higher absorption coefficient of these organic complexes than free iron ions; (b) high quantum yield of $Fe^{2+}$ generation; (c) generation of $CO_2^{\bullet-}$ radicals after photochemical reduction to $Fe^{2+}$, which contributes to the formation of $H_2O_2$ and consequently $HO^{\bullet}$ [3,6]. With addition of $H_2O_2$ very high pollutant degradation efficiency may be obtained providing an increased $HO^{\bullet}$ radical production and fast $Fe^{2+}/Fe^{3+}$ interconversion [7]. Moreover, carboxylate ion competes favorably with hydroxide ion for iron coordination extending the pH range in which iron maintains soluble.

The occurrence of pharmaceutical residues has been reported in several studies especially in the last two decades [8–10]. Although in the range of ng $L^{-1}$ to μg $L^{-1}$, this contamination has been considered a great threat to the environment. The main source of such compounds is the excretion, due to the incomplete absorption of medicaments by organisms in human and veterinary medicine. These substances (either original or as metabolites) are continuously introduced into the environment and are not satisfactorily removed in sewage treatment plants achieving surface and ground waters [11,12]. Therefore, the degradation of residual pharmaceuticals such as antibiotics is very important to avoid the risks of direct input to soil or surface waters [8].

Sulfadiazine (4-amino-N-(2-pyrimidyl)benzenesulfonamide) and sulfathiazole (4-amino-N-(2-thiazolyl)benzenesulfonamide) are sulfonamide antibiotics derived from sulfanilamide (SNA; p-amino benzenosulfonamide) (Fig. 1). They are frequently used in the treatment of urinary tract infection, especially in livestock and can contaminate surface water via different routes, particularly by leaching from contaminated soil [13]. Sulfadiazine has been detected in water bodies and sewage treatment plants at concentrations ranging from 0.04 ng $L^{-1}$ to 5.15 μg $L^{-1}$ while the detected concentration of sulfathiazole varies from 0.08 to 9.6 ng $L^{-1}$ [14–18].

The photo-Fenton process has attracted considerable interest for the degradation of nonbiodegradable compounds, including antibiotics [19–21]. However, no studies on the correlation between structure and efficiency of photo-Fenton degradation of sulfonamides in aqueous solutions have been reported.

In this work, the influence of some parameters in the photo-Fenton degradation of two sulfonamides, sulfadiazine and sulfathiazole was studied. Comparison of the degradation kinetics under different conditions of pH, iron complexation and peroxide concentration, as well as the influence of pyrimidine and thiazol rings present on sulfadiazine and sulfathiazole antibiotics were carried out.

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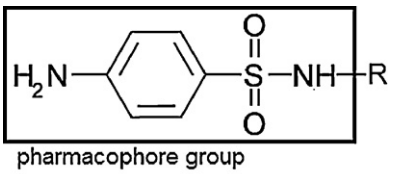


(A) SDZ

R:

MM = 250.28 g mol$^{-1}$

$pK_1$ = 1.94 and $pK_2$ = 6.33

(B) STZ

R:

MM = 255.32 g mol$^{-1}$

$pK_1$ = 1.89 and $pK_2$ = 7.12

**Fig. 1.** Molecular structure of the sulfonamides studied.

## 2. Experimental

### 2.1. Chemicals

All solutions were prepared using ultrapure water (Millipore Milli-Q). Potassium ferrioxalate ($K_3Fe(C_2O_4)_3{\cdot}3H_2O$) was prepared and purified as described previously [22] using iron nitrate and potassium oxalate (Mallinckrodt). A 0.250 M Fe(III)-oxalate stock solution was prepared and stored in the dark at room temperature for within a week. A 30% (w/w) $H_2O_2$ solution (Merck) was used. Ammonium metavanadate (Vetec) at the concentration of 0.06 M was prepared in $H_2SO_4$ 0.56 M (Merck) and used for hydrogen peroxide determination. Sulfadiazine (SDZ) and sulfathiazole (STZ) (Sigma–Aldrich 99.99%) were used as standard in high performance liquid chromatography (HPLC) analysis and in degradation experiments. HPLC-grade methanol (Mallinkrodt) and acetic acid (Merck) were used in HPLC analysis.

### 2.2. Photodegradation procedure

Photodegradation experiments were performed using a 15 W blacklight lamp as source of radiation in a previously described upflow photoreactor [23]. The lamp irradiance, measured using a radiometer (PMA 2100 Solar Light Co.) in the UVA region (320–400 nm) was 19 W m$^{-2}$. Unless otherwise stated, the concentration of the antibiotics was 25.0 mg L$^{-1}$ of SDZ (TOC = 12.0 mg L$^{-1}$) and STZ (TOC = 10.6 mg L$^{-1}$). Adequate volumes of iron stock solution were added to antibiotic solution before irradiation to achieve 0.20 mM iron concentration in the photo-Fenton experiments. The initial pH of solutions was adjusted using either $H_2SO_4$ or NaOH.The irradiation time ($t_{irrad}$) was calculated according to $t_{irrad} = (t_{total} \times V_{reactor})/V_{total}$, where $t_{total}$ represents total time, $V_{reactor}$ is the reactor volume and $V_{total}$ is the total volume of SDZ and STZ solutions. The total and irradiated volume of SDZ or STZ solutions were 500 mL and 280 mL, respectively, recirculated at 80 mL min$^{-1}$ flow rate using a peristaltic pump (Masterflex 7518-12). The lamp was switched on when the reactor was completely filled and the time started to be monitored. Three replicates of each experimental condition were carried out and the corresponding calculated standard deviations are shown on the figures. Tukey's multiple comparison significance test ($P = 0.05$) was applied to assess the significant difference between the results obtained.

### 2.3. Chemical analysis

The concentration of SDZ and STZ during irradiation was determined using HPLC analysis in a Shimadzu LC-20AT chromatograph with diode array detector (SPD-M20A) and a C-18 column (Luna, 5 μm, 250 mm × 4.6 mm from Phenomenex). The wavelength detection of SDZ and STZ was 266 nm and 284 nm, respectively. The injection volume of the samples was 50 μL. Methanol/acetic acid 0.1% 13:87 and 15:85 ratios were used as eluent at a 1 mL min$^{-1}$ flow rate for SDZ and STZ determinations, respectively. Under these conditions, SDZ and STZ detection limits were 0.11 mg L$^{-1}$ and 0.55 mg L$^{-1}$, respectively. The enzyme catalase was used to interrupt the Fenton reaction by decomposition of residual $H_2O_2$ to allow later HPLC analysis [24]. This procedure permits the storage of the samples for at least 2 weeks. Residual $H_2O_2$ concentration during experiments was determined spectrophotometrically measuring the solution absorption at 450 nm after reaction with ammonium metavanadate [25]. The mineralization of the antibiotics during the experiments was measured by the decay of the TOC concentration using a carbon analyzer (TOC 5000A from Shimadzu). TOC determination was always performed immediately after the sample withdrawal to avoid further thermal reaction, without any previous treatment. The TOC concentration includes the carbon content from the antibiotics, intermediates generated during its degradation and oxalate when Fe(III)-oxalate was used. The $Fe^{2+}$ concentration was determined spectrophotometrically after complexation with 1,10-phenanthroline [26,27].

## 3. Results and discussion

Before evaluating the photo-Fenton degradation of the antibiotics, control experiments were carried out. Irradiation of SDZ and STZ in the absence of iron ion and hydrogen peroxide resulted in negligible photolysis given the low absorption of these compounds in the UVA region. The maximum absorption of SDZ and STZ is at 266 nm and 284 nm, respectively, while the maximum emission of the blacklight lamp is at the 360–410 nm range. Furthermore, no degradation was observed during irradiation of either SDZ or STZ in the presence of only $H_2O_2$, due to the negligible absorbance of $H_2O_2$ in the UVA range. Furthermore, no degradation in the dark in presence of both $Fe(NO_3)_3$ and hydrogen peroxide was observed.

### 3.1. Effect of initial $H_2O_2$ concentration

The influence of $H_2O_2$ concentration (2.5, 5.0, 7.5 and 10 mmol L$^{-1}$) on SDZ and STZ photodegradation using Fe(III)-oxalate/$H_2O_2$/UV was studied at pH 2.5 (Fig. 2). These $H_2O_2$ concentrations correspond to [$H_2O_2$]/[antibiotics] molar ratio of approximately 25, 50, 75 and 100, respectively.

The degradation rate of both antibiotics increased when increasing the $H_2O_2$ concentration from 2.5 to 5.0 mM due to the higher production of hydroxyl radical from $H_2O_2$ decomposition in Fenton reaction. The antibiotics concentrations were bellow detection limits after 8 min (SDZ) and 11 min (STZ) of irradiation. However, a further increase of $H_2O_2$ concentration to 10 mM hindered significantly the degradation rate of both antibiotics achieving

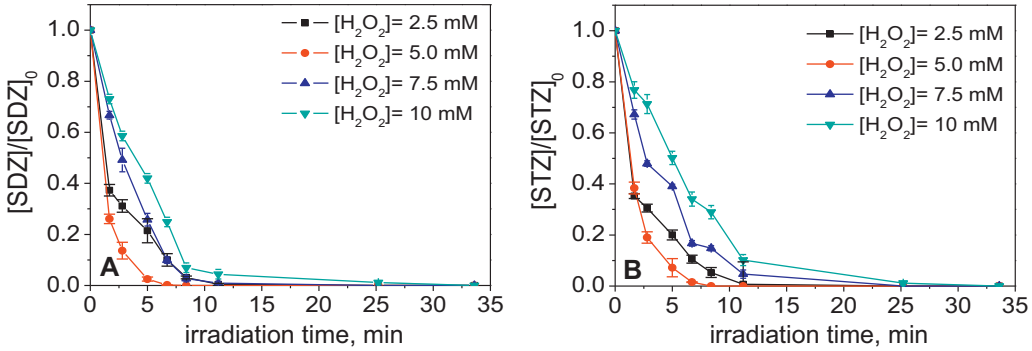


**Fig. 2.** Influence of the hydrogen peroxide concentration on SDZ (A) and STZ (B) degradation during irradiation at pH 2.5 in the presence of 0.20 mM Fe(III)-oxalate. Initial concentration: SDZ = STZ = 25 mg $L^{-1}$.

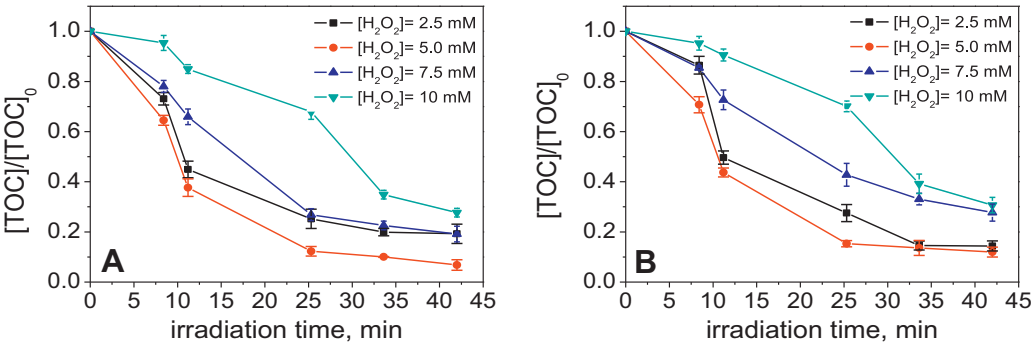


**Fig. 3.** TOC removal during irradiation of solution containing (A) SDZ and (B) STZ at pH 2.5 and 0.20 mM Fe(III)-oxalate. Initial concentration: [SDZ] = [STZ] = 25 mg $L^{-1}$.

concentrations below the detection limit after 34 min of irradiation (Fig. 2). The same behavior was observed for TOC removal (Fig. 3), with higher degradation rates when 5.0 mM $H_2O_2$ was used. Under this condition, a plateau with no further mineralization was observed after 42 min irradiation achieving 92% and 90% mineralization of SDZ and STZ, respectively. This corresponds to a residual TOC concentration of $2.0 \pm 0.6$ mg $L^{-1}$ for SDZ and $4.2 \pm 0.7$ mg $L^{-1}$ for STZ.

Monitoring of $H_2O_2$ concentration indicated that degradation was not limited due to insufficient $H_2O_2$ since total consumption was not achieved in any case (Fig. 4). However, the $H_2O_2$ concentrations of 2.5 mM and 5 mM have led to an incomplete TOC removal, probably due to the formation of more recalcitrant compounds.

The low TOC removal at increased $H_2O_2$ concentrations was also reported previously [5]. Deleterious effect of high $H_2O_2$ concentrations can be attributed to $HO^\bullet$ scavenging by the excess of $H_2O_2$ and/or $HO^\bullet$ recombination (Eqs. (1) and (2)) [28]:

$$HO^\bullet + H_2O_2 \rightarrow H_2O + HO^\bullet{}_2 \quad (1)$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \quad (2)$$

Further experiments were carried out with an initial $H_2O_2$ concentration of 5.0 mM.

### 3.2. Effect of iron complexation

The pH controls Fe(III) speciation in solution [29]. Ferric ion at very low pH occurs as the aquacomplex $[Fe(H_2O)_6]^{3+}$. As pH increases to values between 2 and 3, hydrolysis of iron complex occurs leading to hydroxylated species such as $[Fe(OH)(H_2O)_5]^{2+}$ and $[Fe(OH)_2(H_2O)_4]^{+}$ which show absorption in the UV region. Irradiation of such species generate Fe(II) which reacts with $H_2O_2$ in a Fenton reaction and produces additional hydroxyl radicals. Further pH increase results in iron precipitation hindering significantly the Fenton degradation. So the pH value influences drastically the generation of hydroxyl radicals and hence the degradation efficiency. Therefore, the optimum pH for the Fenton reaction is around 3. As pH values above 3–4 limits the application of Fenton process to wastewater treatment process, the iron complexation with organic ligands is a possibility for extending the optimum pH range for degradation by increasing its solubility at neutral pH, what was also evaluated in this work. Furthermore, the iron complexes as oxalates show higher absorption in the UV–vis region taking better advantage of lamp or solar radiation.

When comparing the degradation of the antibiotics mediated by Fe(III)-oxalate with free iron ($Fe(NO_3)_3$) at pH 2.5, a very marked positive effect was observed when Fe(III)-oxalate was used, achieving concentrations of both SDZ and STZ bellow the detection limit after 8 min irradiation while when free iron was used, only 38% and 35% removal of SDZ and STZ was achieved, respectively (Fig. 5). This significant improvement on the degradation rate in the presence of Fe(III)-oxalate was previously reported for the herbicide tebuthiuron [5]. Further studies demonstrated the complexation of tebuthiuron with iron ions, probably through unpaired electron pairs in N atoms present in its structure, hindering the Fenton reaction [30]. Such a complexation is also possible to occur with the sulfonamides studied in this work. It is also interesting to note that with free iron, the reaction rate is very low in the first 8 minutes, increasing significantly after this time. This is probably due to the slow reduction of Fe(III) to Fe(II) in the absence of oxalate (data not shown), for subsequent reaction with hydrogen peroxide in the presence of sulfonamides. On the other hand, when the concentration of sulfonamides decreases, decreases iron complexation and reaction rate increases.

In order to verify if the sulfonamides could interfere in $Fe^{2+}$ generation due to a possible complexation with iron ions, $Fe^{2+}$ concentration was measured during the irradiation of free $Fe^{3+}$ ($Fe(NO_3)_3$) and Fe(III)-oxalate in the presence or absence of SDZ and

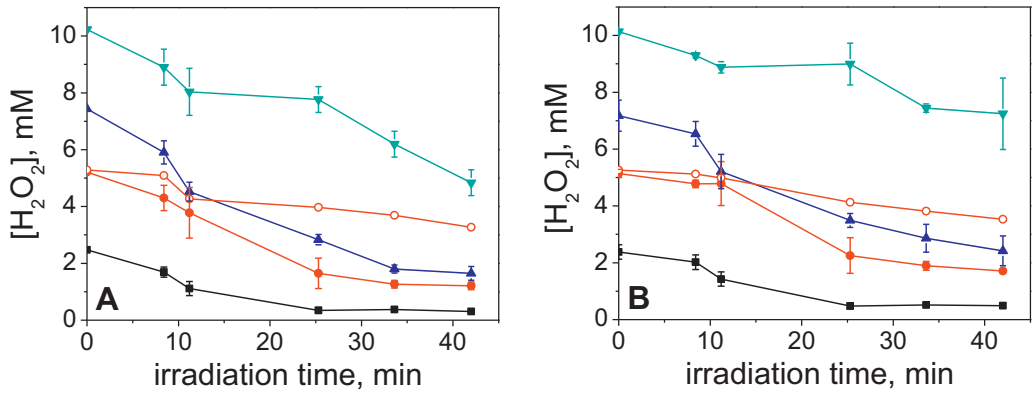


**Fig. 4.** Hydrogen peroxide consumption during irradiation of solution containing (A) SDZ and (B) STZ at pH 2.5. Initial concentrations: SDZ = STZ = 25 mg $L^{-1}$; Fe(III)-oxalate (solid symbols) or $Fe(NO_3)_3$ (open symbol) = 0.2 mM; $H_2O_2$: ■ 2.5 mM; ● 5.0 mM; ▲ 7.5 mM; ▼ 10 mM; ○ 5.0 mM.

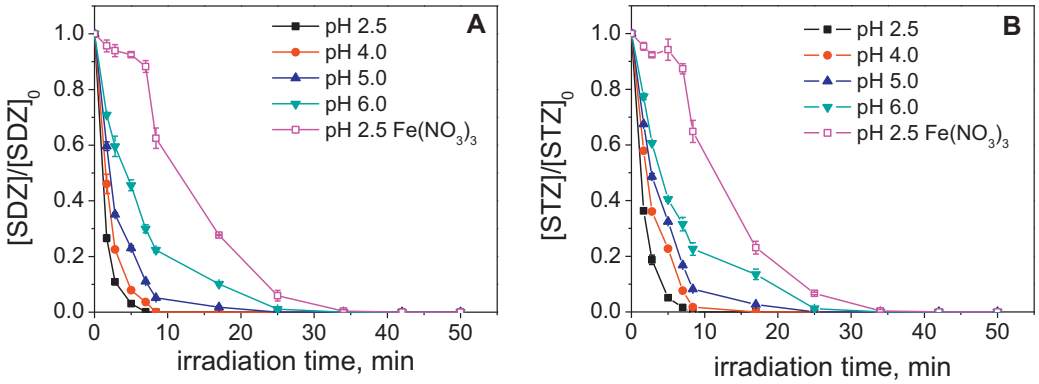


**Fig. 5.** Influence of pH on (A) SDZ and (B) STZ degradation. Initial concentrations: SDZ = STZ = 25 mg $L^{-1}$; Fe(III)-oxalate or $Fe(NO_3)_3$ = 0.20 mM; $H_2O_2$ = 5.0 mM.

STZ (same concentrations as in degradation experiments). In the absence of the antibiotics, the concentration of $Fe^{2+}$ generated during irradiation of Fe(III)-oxalate was 158 ± 5 μM after 8 min while during irradiation of $Fe(NO_3)_3$ only 65 ± 5 μM were generated after the same time (Fig. 6). The higher concentration of $Fe^{2+}$ generated from Fe(III)-oxalate in relation to $Fe(NO_3)_3$ was already expected due to its reported higher quantum yield of $Fe^{2+}$ generation [22]. In the presence of SDZ or STZ, however, the concentration of $Fe^{2+}$ generated from irradiation of $Fe(NO_3)_3$ was considerably lower

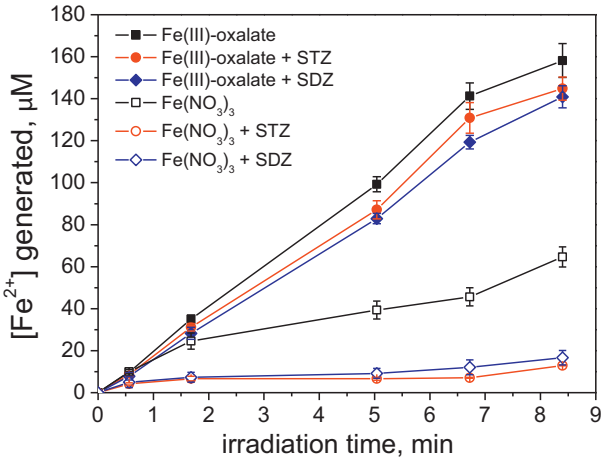


**Fig. 6.** Concentration of $Fe^{2+}$ generated during irradiation of SDZ and STZ at pH 2.5. Initial concentrations: SDZ = STZ = 25 mg $L^{-1}$; Fe(III)-oxalate or $Fe(NO_3)_3$ = 0.2 mM; $H_2O_2$ = 5.0 mM.

with either of the antibiotics reaching a maximum of 17 ± 3 μM and 13 ± 1 μM respectively, about 25% of the concentration generated in the absence of the antibiotics (Fig. 6). This lower $Fe^{2+}$ concentration in the presence of SDZ and STZ indicates that the photoreduction of $Fe^{3+}$ was hindered probably due to complexation of Fe(III) or Fe(II) ions with the antibiotics, decreasing the decomposition of $H_2O_2$ in Fenton reaction and the overall efficiency of the photo-Fenton process. It is important to mention that by comparing the absorbance of a Fe(II)-1,10-phenanthroline solution with and without addition of the antibiotics, it was verified that no interference due to neither SDZ or STZ occurs since no change in the absorption at 510 nm was observed.

On the other hand, when irradiating Fe(III)-oxalate in the presence of SDZ or STZ, no significant difference in concentration of $Fe^{2+}$ was observed ($F$ = 0.08363; $P$ = 0.77834 for SDZ and $F$ = 0.03234; $P$ = 0.86074 for STZ), achieving 141 ± 5 μM in the presence of SDZ and 145 ± 5 μM in the presence of STZ. No interference on $Fe^{2+}$ generation during irradiation of Fe(III)-oxalate was also previously reported in the presence of the herbicide tebuthiuron [30]. These results illustrate the importance of iron complexation in photo-Fenton process.

Consequently, the high efficiency of SDZ and STZ degradation in UV/$H_2O_2$/Fe(III)-oxalate system can be explained by its effective generation of $Fe^{2+}$ available for the Fenton reaction. Previous studies by Nogueira et al. [5] and Jeong and Yoon [6] revealed that hydrogen peroxide reacts faster with Fe(III)-oxalate than with Fe(III)-aquacomplexes accelerating the efficiency of pollutant degradation. Our results (Fig. 4) also show higher consumption of $H_2O_2$ in presence of Fe(III)-oxalate in relation to free $Fe^{3+}$ (Fe(III)-aquacomplexes).

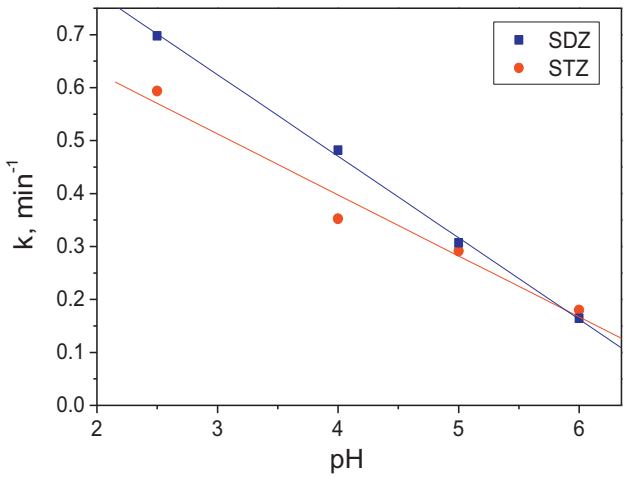


**Fig. 7.** Pseudo first-order rate constants for SDZ and STZ degradation at different initial pH values. Initial concentrations: SDZ = STZ = 25 mg $L^{-1}$; Fe(III)-oxalate = 0.20 mM; $H_2O_2$ = 5.0 mM.

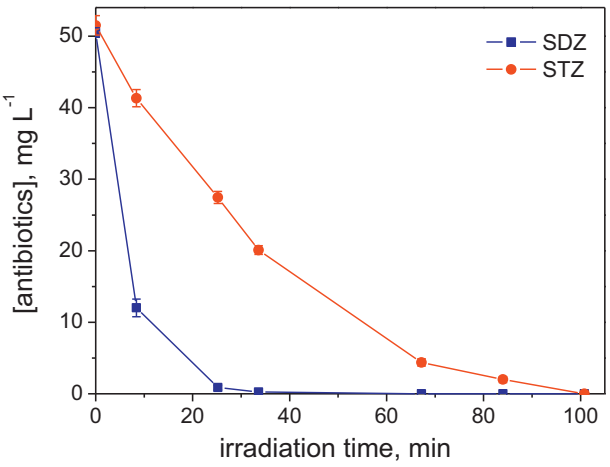


**Fig. 8.** Comparison of SDZ and STZ degradation at higher concentration (50 mg $L^{-1}$) pH 2.5. Initial concentrations: SDZ = STZ = $H_2O_2$ = 10 mM; Fe(III)-oxalate = 0.20 mM.

### 3.3. pH effect

In relation to pH effect, a linear decrease of the pseudo-first-order rate constants for the antibiotics degradation was observed with the increase of pH from 2.5 to 6.0 in the presence of Fe(III)-oxalate, more significant for SDZ (Fig. 7). Even so, after 25 min irradiation the concentration of both antibiotics were bellow detection limit at pH 6 (Fig. 5). This decrease of the antibiotic degradation rate constants with increasing the pH value may be explained by speciation of Fe(III)-oxalate ions. Different Fe(III)-oxalate species occurs at different pH values, such as $Fe(C_2O_4)^+$ at low pH values, $Fe(C_2O_4)_2^-$ between pH 2.0 and 3.0 and $Fe(C_2O_4)_3^{3-}$ between pH 4.0 and 5.0, with decreasing quantum yields of hydroxyl radicals generation [4].

Furthermore, the degradation efficiency in the presence of Fe(III)-oxalate at pH 6 was higher than that observed in the presence of free iron ions (Fe(III)-aquacomplexes) at pH 2.5 after the same irradiation time (Fig. 5). It is important to mention that although oxalate promotes higher degradation efficiency, it was also oxidized during irradiation and iron underwent precipitation, however only after total degradation of SDZ and STZ.

Considering that the acidic optimum pH is the major limitation of photo-Fenton process, iron complexation with organic ligands is a possibility for extending its application and avoids costs with pH adjustment.

### 3.4. Substituent effect

When comparing the chemical structure of SDZ and STZ, they can be distinguished by the –R group bonded to sulfonamide, pyrimidine ring in the case of SDZ and thiazol ring in the case of STZ. Although in previous experiments there were already indications about the recalcitrance of STZ in relation to SDZ, experiments were carried out at higher antibiotics concentration (50 mg $L^{-1}$), aiming a better distinction between SDZ and STZ degradation rate. In this case, concentrations of $H_2O_2$ and iron complex were 10 mM and 0.20 mM, respectively at pH 2.5.

Comparison between degradation kinetics of SDZ and STZ showed that at the initial concentration of 50 mg $L^{-1}$ the rate constant for SDZ ($k = 0.165 \pm 0.03\ min^{-1}$) is approximately five times higher than that for STZ ($k = 0.042 \pm 0.003\ min^{-1}$), revealing the higher recalcitrance of STZ in relation to SDZ (Fig. 8).

It has been observed before during the degradation of sulfametoxazol (a sulfonamide antibiotic), that benzenic ring is less susceptible to hydroxyl radical attack than isoxazol ring (containing nitrogen and oxygen in a five member ring), since most degradation products generated were products of hydroxyl radical attack to isoxazol ring [31]. The identification of degradation products of SDZ and STZ was not within the scope of the present study. However, considering the structural similarity of the three antibiotics, it can be expected that benzene ring in both SDZ and STZ would be less susceptible to hydroxyl radical attack than the pyrimidine and thiazol rings, respectively, as it is the isoxazol ring in sulfamethoxazol. So, the different reactivity of SDZ and STZ would be a consequence of the different susceptibility of these rings to hydroxyl radical attack.

The higher reactivity of SDZ in relation to STZ may be explained by the different groups attached to amide nitrogen atom [32]. The pyrimidine ring in the case of SDZ has two nitrogen atoms while the thiazol ring in the case of STZ has one nitrogen atom and one sulfur atom, less electronegative than nitrogen, resulting in lower electron density than in pyrimidine ring. The higher electron density in pyrimidine ring favors electrophilic addition of hydroxyl radical and consequently its further degradation. Furthermore, the resonance effect contributions of the substituent ring should also be considered. In SDZ, there is a larger number of possible resonance structures after hydroxyl radical addition reaction, which lowers the system energy by electron delocalization.

## 4. Conclusions

The presence of 0.20 mM Fe(III)-oxalate favored considerably the degradation of both SDZ and STZ in relation to the use of $Fe(NO_3)_3$. The positive effect of Fe(III)-oxalate on degradation may be related to the iron complexation with pyrimidine and thiazol ring, leading to a lower iron availability to react with hydrogen peroxide in a Fenton reaction. The increase of pH decreased linearly the rate constant of both SDZ and STZ. However, significant degradation was observed even at pH 6 in the presence of Fe(III)-oxalate due to complexation which contributes to stabilization of iron species. This is advantageous for a possible application since it permits the disposal of this solution without pH adjustment or its use in hybrid systems (chemical-biological) for treatment of recalcitrant contaminants. The antibiotic sulfathiazol showed to be more recalcitrant than sulfadiazine due to the lower electron density of thiazol ring when compared to pyrimidine ring, what makes it less susceptible to hydroxyl radical eletrophilic addition leading to a lower degradation rate.

## Acknowledgments

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