



Degradation of Doxycycline, Enrofloxacin, and Sulfamethoxypyridazine under Simulated Sunlight at Different pH Values and Chemical Environments

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Abstract: In this work, the dissipation of the antibiotics doxycycline (DC) (from the group of tetracyclines), enrofloxacin (ENR) (a fluoroquinolone), and sulfamethoxypyridazine (SMP) (a sulfonamide) is investigated both under simulated sunlight and in the dark, at three different pH (4.0, 5.5, and 7.2), and in the presence of different salts and humic acids. The results indicate that all three antibiotics are very sensitive to photodegradation, and this sensitivity increased with rising pH values, from 4.0 to 7.2. The rise in pH also caused an increase in the degradation kinetic constants and a decrease in the half-lives of antibiotics. In general, the half-lives ranged from a few minutes to 6 h, depending on the pH conditions and the specific antibiotic, and followed the sequence DC > SMP > ENR, although at pH 5.5 the sequence changed to SMP > DC > ENR. After 24 h of simulated sunlight, mineralization was always lower than 10%, although the antibiotic was not quantifiable after the same time of exposure to light (24 h), which indicates that intermediate compounds were generated. The effect of the presence of salts on the dissipation of the three antibiotics was negligible for NaCl and NaNO₃, while NaHCO₃ did favor the dissipation of DC and ENR. The presence of humic acids showed no effect on the dissipation of SMP, and it only slightly increased the dissipation of DC and ENR. These results may be useful in the assessment of the persistence/degradation of the antibiotics studied when they reach different environmental compartments and may suffer exposure to light under different physicochemical conditions.

Keywords: Doxycycline; Enrofloxacin; Sulfamethoxypyridazine; dissipation; photolysis

1. Introduction

Water pollution is a matter of real concern worldwide, constituting a problem that makes it clearly difficult for many human communities to have access to enough amounts of safe and quality drinking water. Among the potential pollutants, in recent decades, antibiotics spread into the environment have acquired special relevance, both from discharges related with their use in veterinary medicine and in human diseases. Different groups of these emerging pollutants have been detected in aquatic environments in a variety of countries around the world [1], with especially relevant levels found in the waters and soils of China [2]. As an example, among the different antibiotics, sulfamethoxypyridazine (SMP), which belongs to the group of sulfonamides, was found in concentrations that ranged between 29–149 ng L^{-1} in rivers of Spain [3], reaching up to 630 ng L^{-1} in river waters in China [4].

Enrofloxacin (ENR), which is a second-generation antibiotic from the group of fluoroquinolones, was detected in concentrations of up to 448 ng L^{-1} in both river and sea



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). waters in China [4]. Doxycycline (DC), also a second-generation antibiotic, belonging to the tetracycline group, has been detected in concentrations of up to 47 ng L^{-1} in river waters in China [4]. This presence of antibiotics in water may favor the generation of resistances that could reduce the efficacy of these antibiotics in the future [5], especially in the presence of other environmental pollutants [6], which could lead to serious public health problems.

The degradation of antibiotics due to the effect of light (photodegradation) is a process with potential relevance in reducing their concentrations in water, due to its high photosensitivity, as has been evidenced in the case of tetracyclines [7–9], sulfonamides [10–12], and fluoroquinolones [13,14].

This photodegradation process depends on the chemical characteristics of the antibiotics, but it is also influenced by the pH of the medium, with degradation increasing as the pH rises [8,11,15]. However, other variables can also influence the photodegradation of antibiotics, such as the saline composition of the waters [16]. Likewise, the presence of soluble organic matter can exert an effect, either by favoring the photolysis [11,17], or on the contrary by slowing down photodegradation due to a screen effect [18]. Therefore, both salinity and the presence of soluble organic matter could condition the evolution of the antibiotics present in environment compartments.

In view of that background, the aim of this work is to address the susceptibility of the antibiotics DC, ENR, and SMP to be degraded by means of simulated sunlight, at three different pH values (between 4.0 and 7.2, which is a normal range in river and lake waters), while also studying the effect of different salts and the presence of soluble organic matter on the photolytic degradation of these antibiotics. Altogether, the results of this study could be useful in evaluating the possible natural evolution of these antibiotics when they are discharged as pollutants into the environment, as well as to determine the eventual influence of some physicochemical conditions that may favor their elimination by artificial photolytic procedures.

2. Materials and Methods

2.1. Chemical Reagents and Quantification of the Three Antibiotics

The three antibiotics used in the experiments were provided by Sigma-Aldrich (Buchs, Switzerland), with purity \geq 98.0% for SMP and ENR, and \geq 95.0% for DC. The chemical reagents used for HPLC analyses (acetonitrile, phosphoric acid, oxalic acid, and triethanolamine) were of high purity analytical grade, supplied by Sigma-Aldrich (Madrid, Spain). All solutions were prepared with Milli-Q water.

The quantification of the antibiotics was carried out by means of an HPLC equipment (Dionex Corporation, Sunnyvale, CA, USA) connected to an ultraviolet-visible detector (UVD170U) and using a Luna C18 column obtained from Phenomenex (Alcobendas, Spain). The mobile phase consisted of 0.01 M acetonitrile and phosphoric acid for SMX and ENR, while this was 0.02 M acetonitrile and oxalic acid/0.01 M triethanolamine in the case of DC. For the detection of SMP, a wavelength of 270 nm was used, while it was 360 nm in the case of ENR and DC. The values of the detection limits were 0.22, 0.05, and 0.04 mg L⁻¹ for DC, ENR, and SMP, respectively [19]. In the selected samples, which were subjected to 0 and 24 h of simulated sunlight exposition, total organic carbon (TOC) was measured using a Multi N/C 2100 (Analytikjena, Jena, Germany) device, this being performed to quantify the degree of mineralization affecting to each antibiotic. In addition, spectrometry was used to determine changes in absorbance for all three antibiotics at the same times of exposition (0 and 24 h).

2.2. Photodegradation Experiments

The degradation of the three antibiotics (SMP, ENR, and DC) was studied under simulated sunlight and in the dark, in aqueous media with solutions in which the antibiotic concentration was 50 μ mol L⁻¹, working at three different pHs (4.0, 5.5 and 7.2). The simulated sunlight was provided by a xenon lamp (Atlas Suntest CPS + Atlas, Linsengericht, Germany) having 550 W m⁻² power and 285 nm quartz filters. Exposure times ranged from 0.5 to 72 h. Some of the photodegradation experiments were carried out in the presence of different salts (NaCl, NaNO₃, and NaHCO₃, which were at concentrations ranging between 0 and 500 mg L⁻¹),

and were provided by Sigma Aldrich (Madrid, Spain). These experiments were carried out both under simulated sunlight (1 h of exposure) and in the dark. The effect of the presence of humic acids (as an example of soluble organic matter) was studied in the same way as with salts, but using humic acids concentration ranging between 0 and 10 mg L⁻¹. The elemental composition of the humic acids was 518 g kg⁻¹, 40 g kg⁻¹, and 40 g kg⁻¹ of C, N, and H, respectively. Functional groups distribution was as follows: total acidity 599 cmol kg⁻¹, COOH groups 330 cmol kg⁻¹, and total OH groups 291 cmol kg⁻¹ [20].

2.3. Modeling

The experimental data were fitted using an exponential decay model (Equation (1)):

$$\frac{C}{C_0} = e^{-kt} \tag{1}$$

where C/C_0 is the fraction of the initial concentration (C_0) that remains in the suspension after a given time *t* (expressed in min) and *k* (min⁻¹) is the dissipation kinetic constant. The half-life (t^{1/2}, expressed in h) of each compound was calculated as per Equation (2):

$$t^{\frac{1}{2}} = \frac{\ln 2}{k} \tag{2}$$

3. Results and Discussion

Figure 1 shows the dissipation results of the three antibiotics studied (DC, ENR, and SMP), both under simulated sunlight and in the dark. No dissipation took place in the dark (Figure 1b,d,f), keeping the C/C_0 ratio very close to 1, meaning that hydrolysis and biodegradation can be ruled out under these conditions and for the period of time here studied (between 0 and 72 h).



Figure 1. Degradation kinetics of the three antibiotics: (**a**) Doxycycline (DC) under simulated sunlight; (**b**) DC in the dark; (**c**) Enrofloxacin (ENR) under simulated sunlight; (**d**) ENR in the dark; (**e**) Sulfamethoxypyridazine (SMP) under simulated sunlight; (**f**) SMP in the dark. The values of the coefficients of variation were $\leq 10\%$ in all cases.

To calculate the half-lives, the exponential decay model previously shown (Equation (2)) was used, which fitted well, judging by the high R^2 values obtained (between 0.956 and 0.984) (Table 1).

Table 1. Results of the exponential decay model (Equations (1) and (2)) in samples prepared with filtered milliQ water (FMW) at different pH values; *k*: rate constant (h⁻¹); $t_{1/2}$: half-life (h). Average values \pm standard error.

Doxycycline	k (h $^{-1}$)	<i>t</i> _{1/2} (h)	R ²
pH 4.0	0.106 ± 0.007	6.5 ± 0.4	0.969
pH 5.5	0.208 ± 0.013	3.3 ± 0.2	0.984
pH 7.2	0.988 ± 0.097	0.7 ± 0.1	0.956
Enrofloxacin			
pH 4.0	0.472 ± 0.051	1.5 ± 0.2	0.988
pH 5.5	0.844 ± 0.107	0.8 ± 0.1	0.984
pH 7.2	3.833 ± 0.254	0.2 ± 0.1	0.986
Sulfamethoxypyridazir	ie		
pH 4.0	0.122 ± 0.025	5.7 ± 1.4	0.917
pH 5.5	0.111 ± 0.012	6.2 ± 0.7	0.976
pH 7.2	0.205 ± 0.020	3.4 ± 0.3	0.980

3.1. Effect of pH on the Photodegradation of the Three Antibiotics

At pH 4, with 0.25 h of simulated sunlight, DC dissipated only 9%, increasing to 13% at pH 5.5 and to 36% at pH 7.2. With 1 h of exposure to simulated sunlight, the dissipation percentages were 10%, 21%, and 52% for pH 4.0, 5.5, and 7.2, respectively. This increase in DC dissipation with pH is shown graphically in Figure 1a. For DC, the kinetic constants increased with increasing pH, while the half-life values decreased, going from 6.5 h at pH 4.0 to 0.7 h at pH 7.2 (Table 1). Other authors [8,21,22] presented data of the same order regarding photodegradation of other tetracycline antibiotics, also with a decrease in half-lives with increasing pH.

For 0.25 h of simulated sunlight exposure, the antibiotic ENR dissipated 16% at pH 4.0, 31% at pH 5.5, and 49% at pH 7.2, while for 1 h of exposure, the percentages were 44%, 53%, and 91% for pH 4.0, 5.5, and 7.2, respectively. In this case, the dissipation was faster than for DC and also increased with growing pH values (Figure 1c). For ENR, the half-lives also decreased with increasing pH, going from 1.5 h at pH 4.0 to 0.2 h at pH 7.2 (Table 1). Data of the same order, but with values lower than those obtained in this work, were reported by Prabhakaran et al. [23], corresponding to other fluoroquinolones, such as difloxacin.

Regarding the antibiotic SMP, it behaved similarly to DC at pH 4, with 8% dissipation after 1 h of exposure to simulated sunlight; however, SMP dissipation showed no increase when pH raised to 5.5 (the dissipation percentage remained at 8%), but rose to 30% for pH 7.2. This behavior can also be observed when analyzing Table 1, where the kinetic constants and half-lives of SMP are similar at pHs 4.0 and 5.5, but they increase at pH 7.2. SMP shows half-lives of the same order as other sulfonamides, such as sulfachloropyridazine, but much lower than those of sulfadiazine and sulfamethazine [11].

For pH 4.0 and 7.2, the half-lives follow the sequence DC > SMP > ENR, but the sequence changes to SMP > DC > ENR for pH 5.5, mainly because SMP has similar half-lives values at pH 4.0 and pH 5.5 (Table 1).

An increase in the degradation rate as a function of increasing pH was previously described for other sulfonamides [11,24] and for other kinds of antibiotics, such as tetracyclines [8,25], or other antibiotics, such as ciprofloxacin and trimethoprim [26]. This increased pH-dependent degradation can be due to changes in absorbance and in the molecules of the antibiotics. In general, changing the pH between 4 and 7.2 does not produce significant modifications in the absorption spectra, except for a slight shift towards the ultraviolet in the case of SMP (Figure 2). On the other hand, there are important changes in speciation. At acidic pH (4.0), the three antibiotics are fundamentally protonated, especially ENR, while increasing the pH results in the appearance of zwitterionic and negatively charged species for the three antibiotics here studied (Figure 2), with which this aspect seems to be more relevant in the dissipation of these antibiotics, favoring electronic excitation by the light source, as highlighted in previous publications for tetracycline [27] and for oxytetracycline [22]. The various species may have different degrees of sensibility to light, as pointed out by Boreen et al. [28], who indicated that the quantum yield (moles of a compound that are transformed per mole of photons that are absorbed by the compound) for sulfadiazine, sulfamethazine, and sulfachloropyridazine is higher for the anionic species than for the neutral ones. Similar results were found for sulfadiazine y sulfamethoxazole [29] and for other organic molecules, such as benzothiazols [30]. In addition, it has been previously described that, during the photodegradation process, H_2O_2 is produced together with an increase in OH⁻ ions, and it is more markedly as the pH was increased, thus favoring the presence of reactive oxygen. This has been shown during photodegradation of tetracycline, although this is dependent on the wavelengths used [27,31], and it has also been shown for sulfonamide molecules [32]. Similar results (in the sense of the formation of reactive oxygen species) have been described for doxycycline [33].



Figure 2. Antibiotic absorption spectra and speciation at different pHs (4.0, 5.5, and 7.2). (**a**) Doxycycline (DC) spectrum and DC speciation; (**b**) Enrofloxacin (ENR) spectrum and ENR speciation; (**c**) Sulfamethoxypyridazine (SMP) spectrum and SMP speciation.

Figure 3 shows the results of the changes in absorbance of the antibiotics after 24 h of simulated sunlight, indicating that the absorbance peaks at which the three antibiotics (DC, ENR, and SMP) were measured to disappear. However, when total organic carbon (TOC) is measured (Figure 4), the results indicate that mineralization is very scarce, being 7% for DC, 0% for ENR, and 4% for SMP, evidencing the formation of metabolites for the three antibiotics.



Figure 3. Antibiotic absorption spectra after 0 and 24 h of exposition to simulated sunlight at pH 5.5. (a) Doxycycline (DC); (b) Enrofloxacin (ENR); (c) Sulfamethoxypyridazine (SMP).



Figure 4. Total organic carbon (TOC) values after 0 and 24 h of exposition to simulated sunlight at pH 5.5. Doxycycline (DC); Enrofloxacin (ENR); Sulfamethoxypyridazine (SMP). Coefficients of variation were always lower than 7%.

3.2. Effect of Different Salts and Humic Acids on the Photodegradation of the Three Antibiotics

The results corresponding to the study of the effects of the presence of different salts (NaCl, NaNO₃, and NaHCO₃) and soluble organic matter (humic acids) on the degradation of the three antibiotics are shown in Figures 5–7.



Figure 5. Doxycycline (DC) degradation under simulated sunlight and in the dark, in the presence of different salts or humic acids. (a) Presence of NaCl under simulated sunlight; (b) Presence of NaCl in the dark; (c) Presence of NaNO₃ under simulated sunlight; (d) Presence of NaNO₃ in the dark; (e) Presence of NaHCO₃ under simulated sunlight; (f) Presence of NaHCO₃ in the dark; (g) Presence of humic acids under simulated sunlight; (h) Presence of humic acids in the dark. Coefficients of variation were always lower than 10%.



Figure 6. Cont.



Figure 6. Enrofloxacin (ENR) degradation under simulated sunlight and in the dark, in the presence of different salts or humic acids. (a) Presence of NaCl under simulated sunlight; (b) Presence of NaCl in the dark; (c) Presence of NaNO₃ under simulated sunlight; (d) Presence of NaNO₃ in the dark; (e) Presence of NaHCO3 under simulated sunlight; (f) Presence of NaHCO₃ in the dark; (g) Presence of humic acids under simulated sunlight; (h) Presence of humic acid in the dark. Coefficients of variation were always lower than 10%.



Figure 7. Cont.



Figure 7. Sulfamethoxypyridazine (SMP) degradation under simulated sunlight and in the dark, in the presence of different salts or humic acids. (**a**) Presence of NaCl under simulated sunlight; (**b**) Presence of NaCl in the dark; (**c**) Presence of NaNO₃ under simulated sunlight; (**d**) Presence of NaNO₃ in the dark; (**e**) Presence of NaHCO₃ under simulated sunlight; (**f**) Presence of NaHCO₃ in the dark; (**g**) Presence of humic acids under simulated sunlight; (**h**) Presence of humic acids in the dark. Coefficients of variation were always lower than 10%.

Regarding DC, Figure 5b,d,f show that no degradation occurs in the dark when salt concentration is increased (range between 0 and 500 mg L^{-1}). Under simulated sunlight (Figure 5a,c,e), the behavior was similar, except in the case of NaHCO₃, finding a total dissipation of DC for high concentrations of this salt (Figure 5e).

An absence of influence of salts such as NaCl and NaNO₃ on the photolysis of other antibiotics has been previously reported for sulfonamides [11] and tetracycline [27]. The increase in DC dissipation when adding NaHCO₃ is probably related to a rise in pH for high concentrations of NaHCO₃, going from pH around 6.0 for low concentrations to pH of 8.5 for high concentrations of NaHCO₃, so it seems to be an indirect effect, as previously indicated by Chen et al. [27] for tetracycline, who reported that the degradation kinetic constant increases up to a pH value around 8, with subsequent increases in NaHCO₃ not affecting that kinetic constant, since the pH value also remains constant.

The effect of the presence of dissolved organic matter (humic acids) on the dissipation of DC was not significant, both under simulated sunlight (Figure 5g) and in the dark (Figure 5h).

Regarding the antibiotic ENR, the effect of the presence of salts on its dissipation was similar to that exerted on DC, not observing repercussions attributable to NaCl and NaNO₃, both under simulated sunlight in the dark, but with an effect of NaHCO₃ being detected under simulated sunlight (Figure 6). The presence of humic acids produced a slight increase in dissipation under simulated sunlight (Figure 6g).

Regarding the antibiotic SMP, the effect of salts and humic acids on its dissipation was non-existent, both under simulated sunlight in the dark (Figure 7).

Note that the effect of humic acids on the dissipation of antibiotics probably depends on the concentration of these organic components, since at low concentrations they can function as promoters of the photosensitivity of antibiotics molecules, while at high concentrations, humic acids can hinder the photodegradation by increasing turbidity [34,35]. This would be one of the reasons why some contradictory results have been found, since Conde-Cid et al. [11] observed that humic acids exerted an effect increasing the dissipation of sulfonamides, while Chen et al. [27] did not detect the effect of the presence of such substances on the dissipation of tetracycline. These differences in results may be due to the variated effects that dissolved organic matter can have on the various antibiotics. In fact, Biošic et al. [18] observed that the presence of humic acids increased the photodegradation of sulfamethazine, while it inhibited the photodegradation of sulfadiazine. However, the opposite results may also be due to the type of dissolved organic matter, as mentioned by Bahnmüller et al. [29], who reported different effects of two types of fulvic acids on the photodegradation of sulfadiazine and sulfamethoxazole.

4. Conclusions

In general, the three antibiotics studied (DC, ENR, and SMP) were sensitive to light, showing quite fast photodegradation kinetics, which indicates that photolysis may be an important process favoring the removal of these antibiotics from waters, both in natural water bodies and wastewater. The dissipation of the antibiotics increased for growing values of the solution pH, showing higher scores for the kinetic constants of dissipation, while decreasing their half-live values. The calculation of the half-lives was carried out by means of an exponential decay model, which fitted well judging by the high R^2 values obtained. Regarding the presence of different salts, NaCl and NaNO₃ did not show an effect on the dissipation of the three antibiotics, while NaHCO₃ increased the dissipation of DC and ENR (with no effect on SMP). The presence of humic acids showed a slight effect increasing the dissipation of DC and ENR, with no effect on SMP. The overall results of this study could be useful in the assessment of the time-course evolution of the antibiotics analyzed when they reach the environment as pollutants, taking into account their possible exposure to natural sunlight. In the same way, the results obtained could be useful when designing artificial systems intended for the removal of these antibiotics based on the use of media that promote their photodecomposition.

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