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Photocatalytic degradation of antibiotics: The case of sulfamethoxazole and trimethoprim

M.N. Abellán, J. Giménez *, S. Esplugas

Departament d'Enginyeria Química, Facultat de Química, Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain

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ABSTRACT

The aim of this study is the evaluation of photocatalysis to degrade two antibiotics widely used in both human and veterinary medicine: sulfamethoxazole (SMX) and trimethoprim (TMP), in aqueous medium. The degradation of SMX and TMP, and the TOC reduction, were improved when TiO_2 concentration was increased, up to 0.5 and 0.2–0.5 g TiO_2 L^{-1} in the case of SMX and TMP, respectively, where the scattering phenomena start being noticeable. The comparison between photocatalysis and photolysis shows that the SMX degradation is improved when the catalyst is present in the solution. In the case of TMP, the final degradation achieved by the two processes is similar, but the evolution during time can be clearly differentiated, indicative of different reaction pathways. Surprisingly, when monitoring the aromatic content during TMP photocatalysis, this increases to a large extent during the first 3 h. On the contrary, the photocatalytic degradation of SMX results in a gradual cleavage of the molecule, because the aromatic content decreases gradually during the photocatalytic reaction (72%). Finally, the experimental data of both antibiotics were fitted to a simple model, taking into account the effect of the radiation on the kinetic constants.

1. Introduction

A great number of works related to the presence of pharmaceuticals in water have appeared during the last decades [1,2]. These compounds can reach the water cycle by different routes: industrial via (e.g. residues from a pharmaceutical industry) and the domestic via (excretes can contain the active agents or their metabolites). Through which pharmaceuticals may end up in the sewage plants, being a large percentage discharged to the aquatic medium because they are not susceptible to abatement by biological processes. The third route would be the utilization of pharmaceuticals in agriculture, because they will be present in the manure, and therefore the pharmaceuticals or their active substances will end up in the water by leaching from the crops [3].

Although the amount of drugs introduced in the medium through these routes may be low, its continuous discharge could cause high concentrations in the long term and adverse effects in terrestrial and aquatic organisms. These effects can be slowly accumulated, so that the changes show up suddenly and irreversibly [4]. On the other hand, it could be supposed that pharmaceuticals are susceptible of degradation through micro-organisms' action, but not all drugs are biodegradable [5]. The case of antibiotics is obvious, because they are biologically active, and so they have limited biodegradability, and they would not be efficiently removed in the Sewage Treatment Plants (STPs). A clear example is the fact that, in the last decades, the increase in antibiotics consumption has resulted in the generation of more harmful bacteria, more resistant to antibiotics [6].

Sulfamethoxazole (SMX) is a synthetic antimicrobial frequently used in human medicine to treat bronchitis and urinary tract infections and also in veterinary medicine, for prevention and treatment of infections, as well as growth promoter [7]. Trimethoprim (TMP) is mainly used in the prophylaxis and treatment of urinary tract infections, as well as for prevention and treatment of respiratory or gastro-intestinal tract infections in cattle, swine and poultry [8]. Indeed, the combination of sulfonamides with trimethoprim is widely used in veterinary medicines. There are some works that report the presence of these two antibiotics in the effluents of STPs [9,10], which remarks the fact that they are not completely eliminated during the treatment.

The present study deals with the degradation of sulfamethoxazole (SMX) and trimethoprim (TMP), (Fig. 1) by means of photocatalysis with TiO_2 in suspension. As known, in photocatalysis it is used the most energetic part of the solar spectrum ($\lambda < 400$ nm), generating e^-/h^+ pairs on the semiconductor surface that can subsequently degrade organic compounds by reacting with them through redox reactions, or they can react with the water molecules

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* Corresponding author. Tel.: +34 934021293; fax: +34 934021291.
E-mail addresses: j.gimenez.fa@ub.edu (J. Giménez), santi.esplugas@ub.edu (S. Esplugas).

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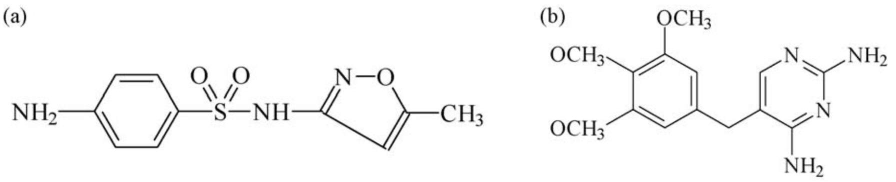

Fig. 1. Structures of the antibiotics: sulfamethoxazole (a) and trimethoprim (b).

to generate hydroxyl radicals, which can be responsible as well of the degradation of the organic pollutants present in the medium. The most employed catalyst is the titanium dioxide, and the medium where the reaction takes place is normally water [11]. The main advantages of this technology are [12]: (1) good stability of TiO_2 in a wide range of pHs and work conditions; (2) the low cost of TiO_2; (3) relatively low selectivity, this means that it can be successful to degrade a large variety of toxic compounds; (4) complete mineralization can be achieved. Moreover, the present study is dealing with the differences found between photocatalysis and the photolytic reaction on both antibiotics, and it intends to establish kinetic equations where the influence of the radiation has been taken into account in a simple way, in order to obtain suitable kinetic constants for a subsequent scaling-up.

2. Materials and methods

2.1. Chemicals and analytical methods

The water used to prepare the different solutions, as well as the solvent for the HPLC, was Milli-Q water (18 μS cm^{-1}). The water used to clean the system was deionized water. Sulfamethoxazole and trimethoprim were supplied by Sigma–Aldrich. The catalyst employed was titanium dioxide Degussa P25. Before analysis by HPLC or TOC, samples were filtered by using 0.22 μm Durapore PVDF filters (Millipore). Sulfamethoxazole and trimethoprim were analyzed in a Waters' HPLC (photodiode array detector 996, auto sampler 717, controller 600) equipped with Millennium software. The reverse-phase column was a Tracer Extrasil ODS2. The mobile phase (flow rate of 1 mL min^{-1}) was, for sulfamethoxazole, a solution of 40% acetonitrile (Panreac) and 60% water (pH adjusted at 3 with phosphoric acid) and, for trimethoprim, was acetonitrile and water (20/80) buffered at pH 3 with phosphoric acid and 0.01 M Na_2HPO_4 (Panreac). The absorption spectra of sulfamethoxazole and trimethoprim were determined in a spectrophotometer (PERKIN ELMER, Lambda20), being the maximum absorption at 270.5 and 204 nm, respectively. Therefore, these are the wavelengths chosen for the detection of these compounds in the HPLC. The total organic carbon was measured using a TOC analyzer (Shimadzdu TOC-VCSN) provided with an auto-sampler. The reagents used to perform the BOD and COD tests were supplied by Panreac and all of them were of analytical grade.

2.2. Reactors and procedure

The device used consists of a solar simulator CO.FO.ME.GRA (Milan, Italy) and a tubular quartz reactor located at the bottom of the solar simulator in the axis of a parabolic mirror. The lamp is a Xenon lamp (PHILIPS XOP-15 OF, 1500 W) and it is placed at the top of the solar simulator, in the axis of a parabolic mirror. The simulator is also supplied with a radiation-limiting filter (280 nm), located below the lamp, in the upper part of the simulator. The reactor is charged with the suspension formed by the antibiotic solution plus the catalyst, and the resulting suspension is recirculated to a reservoir tank (1 L) which is continuously stirred, in order to have a solution well mixed throughout the experiment. Samples are withdrawn periodically during 6 h of reaction. These samples are filtered to get rid of the catalyst and be able to analyze them through HPLC and TOC devices. Further details about the operation of the system, as well as the procedure, have been already explained elsewhere [13,19].

2.3. Actinometric experiments

Actinometric experiments were performed to determine the radiation entering the reactor. The method is based on the well-known photochemical decomposition of oxalic acid in the presence of uranyl [14]. In basis of the available data (reactor geometry, lamp spectrum and quantum yield), the incident photon flow for the different conditions was found. An annular two-layered reactor (jacketed tubular annular reactor) was used to estimate the photon flow absorbed by the suspension in each experimental condition. The installation and procedure were the same explained above, and only reactor was changed. This jacketed reactor was also made in quartz and it is formed by two concentric chambers with tubular geometry. The inner reactor (26 cm length and 1.95 cm inner diameter) was filled with the TiO_2 suspension (plus the pollutant solution) in study for different concentrations of catalyst. In the outer jacket (26 cm length and 2.95 cm outer diameter), the actinometric solution was circulated as described in the case of degradation experiments. Due to the narrow dimensions of the jacket (0.5 cm), part of the light crossed through the actinometric solution and arrived to the TiO_2 suspension. A part was absorbed and the rest was reflected or transmitted to the jacket again. Therefore, this scattered light could be measured. With this system it was possible to determine the radiation absorbed by the studied suspension, by deducting with a blank (no catalyst in suspension), and as function of the amount of TiO_2 loaded and the pollutant used.

3. Results and discussion

3.1. Degradation experiments

The degradation studies were firstly focused on the effect of the amount of catalyst on the process. The working range was 0.1–2.0 g TiO_2 L^{-1} in suspension. As it can be observed in Fig. 2a, SMX degradation undergoes initially a fast increase, but this rate decreases as long as the reaction goes longer. A plausible explanation would be the generation of its oxidation products, which would compete with the parent compound for the oxidizing species and for the available radiation, and thus, the reaction rate would diminish. The degradation would improve as long as more catalyst is added to the solution, because there is more light absorption by the catalyst, giving rise to the generation of more oxidizing species. However, for catalyst concentrations higher than 0.5 g L^{-1}, the degradation can be hardly improved. After 6 h of photocatalytic reaction, the degradation reaches values of 88% for 1.0 g L^{-1} and it only increases to 91% when [TiO_2] = 2.0 g L^{-1}. This is probably due to the increase of the scattering phenomena.

Regarding the TOC conversion (Fig. 2a), no mineralization is observed at short times for catalyst concentrations lower than 0.5 g TiO_2 L^{-1}. It can be seen that the mineralization percentage is lower than that corresponding to the sulfamethoxazole degradation. This is due to the presence of oxidation products in the

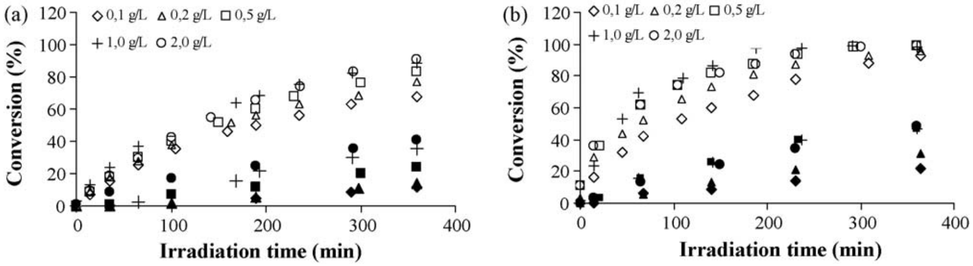

Fig. 2. Antibiotic degradation (empty symbols) and TOC removal (full symbols) for sulfamethoxazole (a) and trimethoprim (b) during the experimental time ($[SMX]_0 = 100$ mg L^{-1}, $[TMP]_0 = 100$ mg L^{-1}, not-buffered pH, $T = 25$ °C, $V_T = 1$ L, flow rate = 28 mL s^{-1}, and irradiation time = 6 h).

medium, because the TOC embraces the entire organic load of the samples, and therefore, not only the degradation of the parent compound is measured, but also the global degradation of all compounds in the solution. When there is not catalyst in the solution, very low values of TOC removal are obtained (Fig. 3a), pointing out that the oxidation products are not susceptible to photolysis, or photolysis advances much more slowly than photocatalysis. Concerning SMX mineralization, these rates increased more than degradation at higher TiO_2 concentration.

Regarding the results obtained with TMP, Fig. 2b shows that the optimum amount of catalyst to be used with this antibiotic is located between 0.2 and 0.5 g L^{-1}. A final degradation higher than 95% can be achieved for 0.2 g TiO_2 L^{-1} and, for concentrations higher than this value, the degradation is 100% in all cases, which means that this compound is more easily degraded by photocatalysis than SMX. In general, the tendencies in the photocatalytic series are very similar: fast increase at the beginning and then the slope starts to be lower. The photolytic rate's decrease could be explained by the generation of intermediates that compete for the oxidizing species in solution.

Concerning the influence of the catalyst (TiO_2) concentration, it can be observed again, in this Fig. 2b, the scattering phenomena occurring when the amount of catalyst starts being higher than the optimum, which hinder the increase of the reaction rate.

With regards to the TOC removal (Fig. 2b), all series show an increasing linear tendency during the reaction time. The TOC removal increases when the catalyst concentration does it, up to an amount of catalyst of 0.2–0.5 g L^{-1}. For concentrations higher than 0.5 g TiO_2 L^{-1}, the TOC removal remains constant with final values of 50% after 6 h of irradiation, due to the increasing presence of oxidation products (TMP degradation is also higher with higher $[TiO_2]$), and the scattering effects between the particles of the catalyst.

The most interesting point here is the different behaviors of the two antibiotics, regarding the lower optimum catalyst obtained in the case of TMP. A series of experiments were made to assess the adsorption of both compounds on the surface of the catalysts, but similar results were found (a maximum of 5% after 24 h). The difference might be the higher sensitivity of TMP for light absorption, as it will be seen in the next section when explaining the photolytic process on both antibiotics.

3.2. Photolysis vs. photocatalysis

When the effectiveness of photocatalysis and photolysis are compared in the degradation of compounds in water, the former usually yields to a higher degradation rate than the latter, due to the enhancing effect of the catalyst on the use of the light. A first clue about the importance of the photolysis can be obtained comparing the absorbance spectrum of the target compounds with the emission spectrum of the lamp. Obviously, if the compounds can absorb light in the region of the lamp emission, both the catalyst and the molecules will compete for the photons.

SMX absorbs light within the range between 240 and 310 nm, which means that it cannot be assured if its degradation is due to the photocatalysis or due to a parallel photolysis process. Thus, the catalyst and the SMX molecules are competing for the photons of the system. Similarly, TMP can also absorb radiation up to a wavelength of 310 nm, which is almost the limit of emission of the lamp with filter (around 290 nm). The interesting issue is to determine the effect of photolysis on the photocatalytic treatment of these antibiotics. Two preliminary experiments were made to measure the effect of the photolysis: one experiment without any catalyst and one experiment with catalyst (Fig. 3).

When the catalyst is present in the system the final SMX degradation is almost 83%, and this value drops to 38% when only the light degrades the target compound (Fig. 3a). The TOC removal achieved with photocatalysis and photolysis is 24% and 2.5%, respectively. It seems that, although the radiation can degrade the parent compound to some extent, it is more difficult and thus more slowly to degrade the oxidation compounds generated from the photolytic reaction. Therefore, it can be concluded that SMX is prone to be degraded by photolysis, but this effect is less important on the reaction intermediates, because the TOC removal is much lower that the degradation values. Anyway, the effect of photolysis might be reduced when the catalyst is added to the system, because the molecules of the catalyst will compete with the molecules of SMX for the radiation absorption.

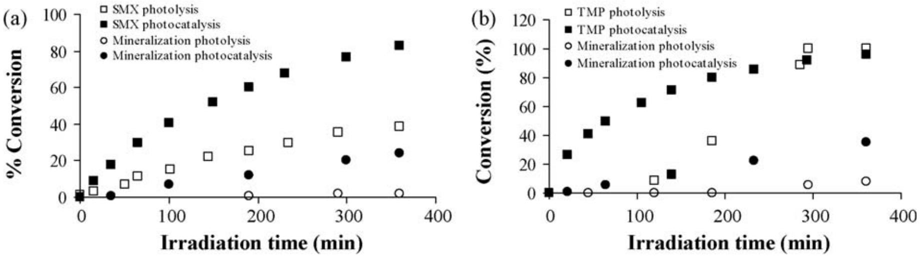

Fig. 3. Sulfamethoxazole (a) and trimethoprim (b) degradation and TOC removal during the experimental time with catalyst (full symbols) and without catalyst (empty symbols) ($[SMX]_0 = 100$ mg L^{-1}, $[TMP]_0 = 100$ mg L^{-1}, $[TiO_2] = 0.5$ g L^{-1}, not-buffered pH, flow rate = 28 mL s^{-1}, $T = 25$ °C, and $V_T = 1$ L).

With regards to TMP (Fig. 3b), there is a remarkable difference when the catalyst is present in the system. When the degradation is carried out only with light, the shape of the curve is exponential, i.e., the reaction rate seems to be very slow at short times, and it increases a lot at longer reaction times (from 300 min). On the contrary, the shape of the curve when the catalyst is present is logarithmic, which might mean that the photolytic degradation of this antibiotic has a completely different pathway from that belonging to the photocatalytic process. In fact, it seems that this compound is hard to be degraded by photolysis at the beginning of the reaction and, as soon as the first oxidation products arise in the medium, the reaction rate increases exponentially, which could be due to the different kinetics followed by the photolytic process. The percentages of degradation in the photolytic and photocatalytic treatment are 99% and 96%, respectively, which means that photolysis is equally efficient than photocatalysis. Regarding the TOC reduction, the tendency in both cases is linear and ascendant, but the final value is different: 7% with photolysis and 35% with photocatalysis.

3.3. Determination of the specific ultraviolet absorbance

Specific UV Absorbance (SUVA) is the absorbance of a sample at 254 nm, normalized for dissolved organic carbon (DOC, mg C L^{-1}). Weisshaar et al. [15] reported that this parameter is strongly related to the aromatic percentage (obtained by ^{13}C NMR), and other authors have equally used the SUVA as an indicator of the aromatic content of a sample [16,17].

The absorbance of the samples has been measured during a standard reaction ([antibiotic] = 100 ppm, $[TiO_2] = 0.5\ g\ L^{-1}$ and free pH), in order to obtain the SUVA for SMX and TMP. The aromatic content of the samples corresponding to the degradation of SMX decreases along the reaction time, up to 72% of reduction at the end of the experiment (15 h). This decrease demonstrates the gradual cleavage of the aromatic rings along the reaction of photocatalysis, resulting in smaller molecules. However, some aromatic level (~28%) remains after 15 h of irradiation, when the degradation of the target compound has already been 99%, and the corresponding TOC removal of 51%.

Surprisingly, the aromatic content of TMP increases during the first 3 h, and then it starts decreasing until the end of the experiment, but it does not reach the initial value even after 15 h of reaction. The increase in this parameter suggests the formation of intermediates more aromatic than the parent compound, after an incomplete oxidation, probably during the early stages of the oxidation reaction. In this way, TMP could undergo reactions of dimerization, or the bonding of the trimethoxybenzyl and the pyrimidine ring by the loss of a functional group $-C_xH_y$. Unfortunately, there is very limited bibliography about how TMP degrades during advanced oxidation processes or during photochemical reactions. An example of the latter is the work made by Dedola et al. [18], in which some photoreactions of TMP in solution (acetonitrile and benzophenone) are reported. The most interesting aspect of this work is that this antibiotic can oxidize into a diastereoisomeric tetraarylethanes, more aromatic than the parent compound.

3.4. Kinetic study

In general, the reaction rate (r) can be expressed using the following equation:

$$r = k\,f(C) \tag{1}$$

where k is the kinetic constant and $f(C)$ is a function of the target compound's concentration.

In order to obtain a kinetic equation which correlates the reaction rate (r) with the concentration of the target compound (C), mass balances have to be applied. The hypothesis taken into account for the system employed in the present work have been explained already elsewhere [19]. According to all these assumptions, the application of the mass balance to the system leads to

$$V_p r = -V_T \frac{dC}{dt} \tag{2}$$

where V_p is the photoreactor volume, V_T is the total volume of the system, C is the concentration of the substance to be degraded, collected from the reservoir tank, and t is the reaction time.

Due to the influence that the radiation absorbed by the catalyst ($F_{abs,cat}$) has on the system, the global kinetic constant will depend on this parameter (among others, like reactor's geometry, flow rate, etc.). The radiation absorbed by the catalyst depends on the concentration of TiO_2 and on the concentration of the other species present in the medium, because the latter can absorb part of the radiation emitted by the light source. The way of tackling the behavior of light in heterogeneous systems is not an easy task. Some authors [20,21] have tried to conceive a rigorous radiation model, which must be solved by complex mathematical equations. Other possible way to study the radiation is considering the system been divided into layers [22]. In a simpler way, the dependence of the radiation on the reaction rate has also been explained by Ollis [23], who stated that kinetic and equilibrium constants are influenced by the volumetric rate of radiation absorption, and this influence can vary among the different reactions, being the general dependence of the reaction rate (r) is proportional to I^a, where: $0.5 < a < 1.0$, depending on the volumetric rate of radiation absorption. In this work, a first simple approach was used by introducing an experimental estimation of the radiation absorbed by the catalyst ($F_{abs,cat}$) into the kinetic equation. Thus, the determination of the radiation absorbed by the catalyst ($F_{abs,cat}$) was made with actinometries (oxalic acid – uranile). Eq. (3) enables the calculation of this variable.

$$F_{abs} = V_T \frac{c_{ox,0} - c_{ox}}{t} \frac{1}{\sum_\lambda f_\lambda \phi_\lambda [1 - \exp(-\alpha_\lambda d)]} \tag{3}$$

F_{abs} is the radiation absorbed by the actinometer, V_T is the total volume of the system, c_{ox} is the oxalic concentration at any time, $c_{ox,0}$ is the oxalic acid concentration at the initial time, f_λ is the fraction of radiation at the wavelength λ, ϕ_λ is the quantum yield of actinometer at the wavelength λ, α_λ is the absorptivity of the reaction medium at the wavelength λ, d is the way followed by the light inside the reactor (in this case is the diameter of the reactor). The wavelength range considered for this calculation has been the range within 300 and 388 nm, where the TiO_2 can absorb the light. The results for F_{abs} and $F_{abs,cat}$ are presented in Table 1.

$F_{abs,cat}$ has been calculated by deducting F_{abs} at different amounts of TiO_2 to F_{abs} ($0.0\ g\ L^{-1}$). Obviously, this calculation would only be an approximation, since the losses of radiation by scattering phenomena have not been taken into consideration. As soon as the radiation absorbed by the catalyst ($F_{abs,cat}$) is known, a simple correction can be introduced in the kinetic model

Table 1
Radiation absorbed by the actinometer and by the catalyst, within the range 300–388 nm (where the TiO_2 can absorb the light).

$[TiO_2]$ ($g\ L^{-1}$)	F_{abs} (μEinstein s^{-1})	$F_{abs,cat}$ (μEinstein s^{-1})
0.0	7.38	0.00
0.1	6.61	0.78
0.2	5.58	1.79
0.5	4.67	2.71
1.0	3.81	3.57
2.0	2.47	4.91

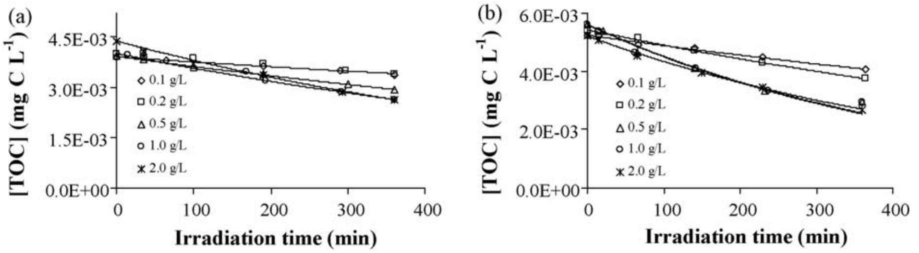

Fig. 4. Fittings of the experimental data to Eq. (7) for (a) sulfamethoxazole ($[SMX]_0 = 100\ \mathrm{mg\ L^{-1}}$) and (b) trimethoprim ($[TMP]_0 = 100\ \mathrm{mg\ L^{-1}}$) ($T = 25\ ^\circ\mathrm{C}$, $V_T = 1$ L, flow rate = 28 mL $\mathrm{s^{-1}}$, and irradiation time = 6 h).

Table 2
Values of the kinetic constants (k, k' and k'') corresponding to sulfamethoxazole and trimethoprim, (Eq. (7)) for the different values of TiO_2 concentration.

Sulfamethoxazole			
$[TiO_2]$ (g L^{-1})	$K(\times 10^5\ s^{-1})$	K' (Einstein^{-1})	K'' ($s^{-0.5}$ Einstein$^{-0.5}$)
0.1	8.12 ± 0.17	105 ± 12.70	0.092 ± 0.011
0.2	9.56 ± 0.42	53 ± 7.70	0.071 ± 0.010
0.5	14.81 ± 0.01	55 ± 5.50	0.090 ± 0.009
1.0	24.92 ± 0.16	70 ± 7.40	0.132 ± 0.014
2.0	30.35 ± 0.19	62 ± 6.60	0.137 ± 0.015
Trimethoprim			
$[TiO_2]$ (g L^{-1})	$K(\times 10^4\ s^{-1})$	K' (Einstein^{-1})	K'' ($s^{-0.5}$ Einstein$^{-0.5}$)
0.1	1.49 ± 0.04	192 ± 24.30	0.169 ± 0.021
0.2	2.19 ± 0.01	122 ± 12.80	0.164 ± 0.017
0.5	4.72 ± 0.02	174 ± 18.20	0.287 ± 0.030
1.0	4.66 ± 0.01	130 ± 13.30	0.246 ± 0.025
2.0	3.92 ± 0.01	80 ± 8.20	0.177 ± 0.018

employed, as indicated in Eqs. (4) and (5).

$$r = k' F_{\mathrm{abs,cat}} f(C) \tag{4}$$

$$k' = \frac{k}{F_{\mathrm{abs,cat}}} \tag{5}$$

In addition, other kinetic constant has been considered (k''), assuming that the reaction rate depends on the volumetric rate of radiation absorption to the half ($r \propto I^{0.5}$). Accordingly, Eq. (6) has been used on this purpose.

$$k'' = \frac{k}{(F_{\mathrm{abs,cat}})^{0.5}} \tag{6}$$

The proposed kinetic model for this study is a very simple equation that is expressed as Eq. (7):

$$r = \frac{\mathrm{d}C_{\mathrm{TOC}}}{\mathrm{d}t} = kC_{\mathrm{TOC}} \tag{7}$$

The reaction rate corresponds to a first-order kinetics equation, and it is expressed as the rate of the degradation of all molecules present in the solution, as TOC concentration rate. These equations have been chosen because the TOC parameter includes all species present in the solution, at any time of the reaction. The fittings of the experimental data to this kinetic model are presented in Fig. 4. As it can be observed, the chosen model can fit quite well the experimental data obtained with SMX and TMP experiments. In order to confirm if these models can be used for a subsequent scaling-up, the kinetic constants obtained (k, k' and k'') at different TiO_2 concentrations must be first compared. Their values are shown in Table 2.

There is a gradual increase of the global constants k, as long as the amount of loaded catalyst grows. In some cases, this increase becomes smoother when $[TiO_2]$ is ≥ 0.5 g L^{-1}, which could be expected due to scattering phenomena, besides the higher generation of the intermediates when increasing TiO_2 concentration, which will lead to a competition between these and the target compound. The values of k' result well enough for the SMX (60 Einstein^{-1}) in the range $[TiO_2]$ = 0.2–2.0 g L^{-1}, because the others undergo higher variations (>30%), when calculating them from the average of the evaluated constants. On the other hand, the best results for TMP can be considered to be k'', being the average value 0.185 $s^{-0.5}$ Einstein$^{-0.5}$, because in the rest of cases the kinetic constants undergo higher deviations with their average value (>20%), besides the case of k within the range 0.5–2.0 g TiO_2 L^{-1} ($4.43 \times 10^{-4}\ s^{-1}$).

4. Conclusions

As a whole, the photocatalytic treatment applied to the degradation of SMX and TMP can be considered as an interesting and alternative process to the existing conventional ones. Both SMX and TMP are prone to undergo photolysis degradation below 310 nm. The amount of TiO_2 has an important influence on the reaction rate, being improved when the amount of catalyst in solution increases. The optimum catalyst concentration can be located between 0.5 and 1.0 g TiO_2 L^{-1} for SMX, and between 0.2 and 0.5 g TiO_2 L^{-1} for TMP. The aromatic content of the TMP solution increases during the first 3 h of reaction, which may be indicative of the generation of dimers/polymers, and after that it starts decreasing, not reaching the initial value of this parameter even after 15 h, contrary to SMX solutions, that reduce the aromatic content during the experiment.

Relatively low deviations between the global kinetic constants have been obtained with the proposed kinetic equations, even when the influence of the radiation is not considered. When introducing this parameter in the equations, slightly better results can be obtained when the latter is in the form $F_{\mathrm{abs,cat}}^{0.5}$. With SMX, the best values are k' with 60 Einstein^{-1}. On the other hand, with TMP the best results are k'', with an average value of 0.185 s$^{-0.5}$ Einstein$^{-0.5}$. These constants have been chosen because they undergo small variations with the amount of catalyst loaded in the system, and thus they could be in principle suitable to be used in a scaling-up study.

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