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Spiramycin photocatalysis under artificial UV radiation and natural sunlight

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ABSTRACT

Photocatalytic processes in the presence of titanium dioxide, operating in UVA radiations, present great interest for degradation of hazardous organic contaminants. The objective of the work presented is to evaluate the performance of spiramycin (SPM) photocatalytic degradation in TiO_2 aqueous suspension using solar irradiation and artificial UVA (365 nm) light. SPM degradation and mineralization were assessed to establish the feasibility of both treatments. To achieve this study, the effect of the initial SPM concentration and the catalyst concentration on the photocatalytic degradation were optimized. Photocatalysis removal of different SPM concentrations (10, 20, 40 $mg\,L^{-1}$) was tested using $0.25\,g\,L^{-1}$ of TiO_2. SPM degradation percentage achieved after 360 min was 95.6% under both types of radiation (solar and artificial light). However, the mineralization percentage were 89.2 and 87.8% in solar and laboratory conditions, respectively. The kinetics followed the first-order and the reaction rate was well fitted with Langmuir–Hinshelwood model. Solar photocatalysis has demonstrated to be useful for the removal of SPM. The UV/TiO_2 photocatalysis process can be suggested for the SPM degradation in aqueous solution.

Keywords: Photocatalysis; Spiramycin; TiO_2; Solar; UV; Advanced oxidation processes

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1. Introduction

Although pharmaceuticals have been consumed for many decades, only during the last few years their fate and release in the aquatic environment have been recognized as one of the most urgent questions of environmental chemistry [1]. They have been recognized as an important class of organic pollutants due to their physical and chemical properties, which allow their persistence and bioaccumulation in the environment provoking negative effects in aquatic or terrestrial ecosystems in concentrations down to a few nanograms per litre [2].

Antibiotics are an important group of pharmaceuticals in today's medicine and have been detected in various compartments of the aquatic environment: waste water, surface water, ground water, and as well as in drinking water [3–6]. They are regarded as "pseudo persistent" contaminants due to their continual input into the ecosystem. Therefore, the occurrence of antibiotics in the environment has received

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considerable attention. They are generally poorly absorbed by the human body, and thus excreted either unchanged or transformed, via urine and faeces [3,7]. This is not surprising if one considers that the use of antibiotics is very large for human beings and livestock. Between 30 and 90% of the administered dose of most antibiotics is generally excreted with the urine and, often, they are not destroyed by conventional wastewater treatments [2]. Antibiotics cannot be retained through classical unit operations in water treatment plants and are, thus, released in to natural water environments [8]. These natural waters can eventually be treated for human consumption or used for different activities such as irrigation [9,10]. Accordingly, there is a need to remove these compounds from water and tertiary treatment technologies are recommended for this purpose. Among these technologies, advanced oxidation processes (AOP) have already been reported as the most appropriate ones for this task [11–13]. These techniques are based on the generation of hydroxyl radicals (OH), the second highest known oxidant species. Thus, these processes are able to oxidize and mineralize almost every organic compound [14–16].

Among the different AOPs, heterogeneous photocatalysis using UV/TiO_2 system appears as one of the most destructive technologies [17–19]. The titanium dioxide photocatalyst is widely available, inexpensive, non-toxic, and shows a relatively high chemical stability [20–23]. Additionally, the process can be carried out under ambient conditions and may lead to complete mineralization of organic carbon into CO_2, water, and inorganic ions [24,25]. Several studies have demonstrated that ultraviolet (UV) is able to decompose pharmaceuticals by direct photolysis or indirect photolysis through an AOP. Indeed, Amoxicillin [26], nitroimidazoles [27], oxytetracycline [28], and sulfamethoxazole [29] are easily degraded by UV treatment.

Among antibiotics, we found that Spiramycin (SPM), which belongs to the group of macrolide antibiotics, is produced by fermentation. SPM is a 16-member macrolide antibiotic used to treat infections of the oropharynx, respiratory system, genito-urinary tract, as well as cryptosporidiosis and toxoplasmosis [30]. SPM degradation has been reported [31], but no one has employed photocatalysis and especially natural solar light before. The artificial generation of photons is the most important source of costs during photocatalysis. The use of sunlight would represent, then, a more economic and ecologic alternative. With a typical UV-flux of 20–30 $W m^{-2}$, near the surface of the earth, the sun provides 0.2–0.3 mol photons $m^{-2} h^{-1}$ in the 300–400 nm range, available for the catalyst activation [14].

The aim of the present work is to study the photocatalytic degradation of SPM in a TiO_2 aqueous solution under both solar and artificial light. The effect of various parameters, such as SPM concentration and mass of catalyst on the decay of pollutant was investigated using a new reactor design.

2. Experimental

2.1. Chemical and reagents

A commercial available titanium dioxyde was used as a photocatalyst produced by the chemical factory «BIOCHEM ChemoPharma» (Quebec, Canada). This photocatalyst is in anatase form with BET specific surface area of 4.61 ($m^2 g^{-1}$) and 20.2 nm particle diameter. SPM which was purchased from Sigma-Aldrich Chemical is a mixture of three macrolide antibiotics mainly constituted of SPM I (over 92%), while SPM II and III are minor derivatives (percentages, respectively lower than 0.5 and 5%) (Fig. 1) [32,33].

2.2. Photocatalytic reactor

All the experiments were performed under natural sun and artificial light in the same tubular photoreactor shown in Fig. 2. This photoreactor is composed of 19 parallel quartz tubes, with a total mirror's area of solar irradiation caption—reflection of 0.128 m^2. The irradiated volume was 285 mL. The polluted solution with suspended TiO_2 was continuously re-circulated at the flowrate of 1.74 $L min^{-1}$, employing a peristaltic pump (Ecoline VC-280, ISMATEC) through the photoreactor and the reservoir tank (1L).

Solar photocatalytic experiments were carried out in the photoreactor developed for photocatalytic application installed at the Solar Equipment Development Unit on the north of Algeria (latitude 36°.39´; longi-

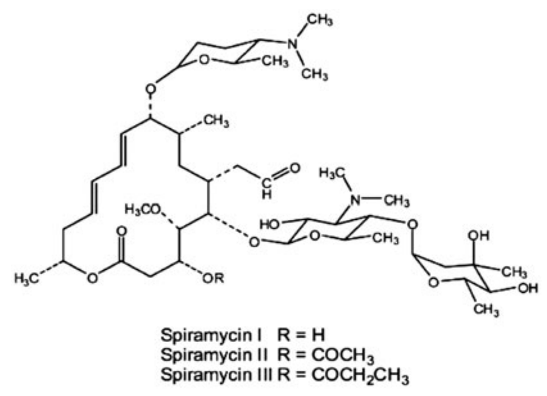

Fig. 1. Chemical structure of SPM.

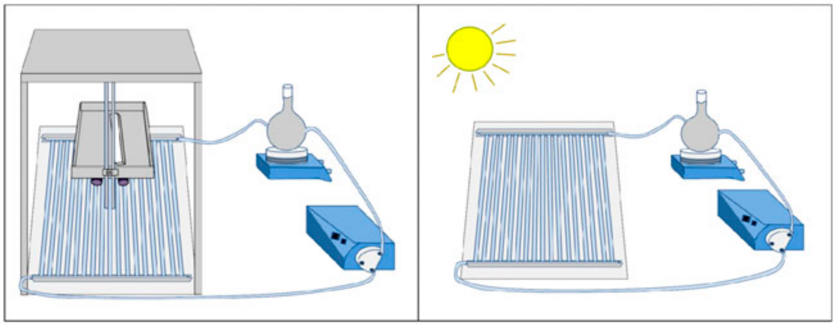

Fig. 2. Experimental setup.

tude 2˚.42´ at sea level), during the period from July to September 2012, using natural sunlight radiation. Solar radiation was measured by global radiometer (KIPP&ZONZN, CMP11) mounted on a platform horizontal tilted as the same as the reactor. In the laboratory, the same photoreactor was placed into the lamp box. The photoreactor was irradiated by a 2 Phillips PL-L 24 W/10/4P lamps ($\lambda_{max} = 365$ nm).

Samples were taken every 30 min for 6 h from the reservoir (tank) and filtered in a Millipore disk with a porosity of 0.45 µm. The pH of the reaction mixture was not adjusted (natural solution pH) and the temperature was not controlled, it was varying from 20 to 30˚C.

SPM degradation was evaluated by measuring the absorbance with a spectrophotometer UV-VISIBLE type Shimadzu UV1800. The UV absorption spectrum of SPM in aqueous solution is given in Fig. 3. The maximum absorption band is located at 232 nm. A correlation curve between SPM concentration and the absorption was pre-established.

During the experiment, total organic carbon (TOC) was measured in Shimadzu TOC-V_{CPH} in order to evaluate the mineralization degree.

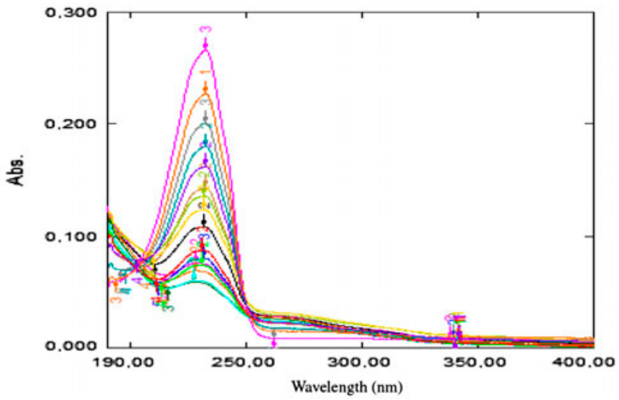

Fig. 3. UV spectra of SPM.

The photocatalytic processes were carried out in the presence of TiO_2 and were supposed to be pseudo-first-order reactions [34]:

$$r = -\frac{dC}{dt} = kC \tag{1}$$

where r is the reaction rate and k is the apparent constant.

In order to estimate the kinetics of degradation processes in the presence of TiO_2, the following relationship was improved:

$$\ln \frac{C}{C_0} = -kt \tag{2}$$

with:

$C_{0:}$ Initial pollutant concentration; mg L^{-1} and C: pollutant concentration at time t; mg L^{-1}

3. Results and discussion

3.1. Adsorption, direct photolysis, and photocatalysis

Preliminary experiments were carried out to determine the photocatalysis performance (Figs. 4 and 5). An initial three successive stages experiment was undertaken: the first stage took place at ambient temperature in the presence of TiO_2 without radiation; the second stage is in the presence of radiation without titanium dioxide; and the third under UV radiation with TiO_2 catalyst in suspension. Adsorption in Fig. 4 shows the sorption kinetics of the active substance over time. Equilibrium was reached after several hours and only 9% of the active molecule was adsorbed. In the absence of TiO_2, no significant decrease in the concentration of the active molecule was observed during the 6 h of illumination, the amount of SPM removed is less than 7%. In photocatalysis, the presence of titanium dioxide with UV radiations has increased the removal

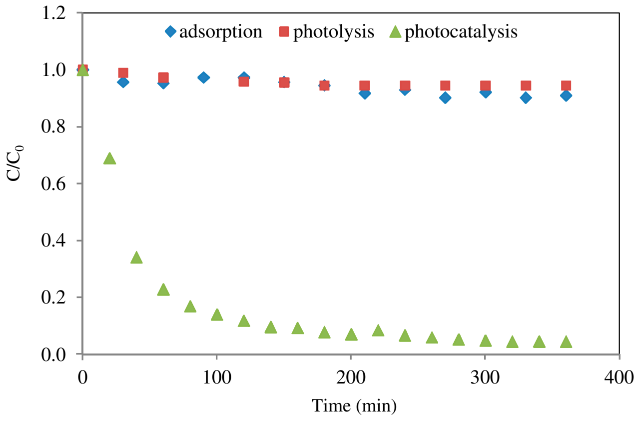

Fig. 4. Temporal evolution of SPM-reduced concentration for different processes (lamp radiation). $C_{SPM} = 10\,mg\,L^{-1}$, $C_{TiO2} = 0.25\,g\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

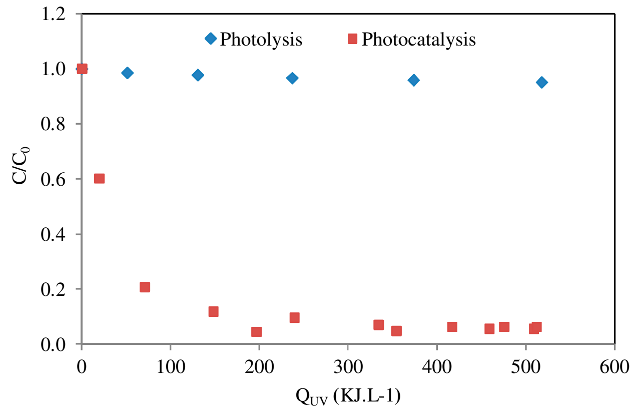

Fig. 5. Temporal evolution of SPM-reduced concentration for different processes (solar radiation). $C_{SPM} = 10\,mg\,L^{-1}$, $C_{TiO2} = 0.25\,g\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

efficiency up to 90%. Thus, in comparison to the mechanism of photocatalytic degradation, the kinetics of adsorption and photolysis were negligible [35].

The same experiments were carried using sunlight which has various intensities of radiation during a day. The results are expressed as a function of accumulated UV energy received by the reactor per volume unit of treated solution. Eq. (3) is commonly used when working with the solar resource. This dimension makes possible the comparison of degradation kinetics for different operating conditions (irradiation surface and reactor volume) regardless of the weather conditions and the resulting solar irradiation [35–38].

$$Q_{UV} = \frac{S}{V_T} \cdot \int_0^t I(t)d(t) \qquad (3)$$

where Q_{UV} is the quantity of UV energy ($J\,m^{-3}$) harnessed by the process, I is the UV radiation intensity ($W\,m^{-2}$) measured by the radiometer, S is the irradiated surface area (m^2), V_T is the reactor volume (m^3), and t is the duration of irradiation (s).

The photocatalytic degradation rate of SPM is very significant for solar treatment. However, the direct solar photolysis of this pollutant is negligible (5%).

3.2. Spiramycin photocatalytic degradation

3.2.1. Effect of the catalyst amount

The main objectives chased in this case were the comparison of these two light sources for SPM photocatalytic treatment performance. Several catalyst loads were used; 0.05, 0.1, 0.25, 0.5, 0.75, 1 and $1.25\,g\,L^{-1}$ for the different radiation sources tested, solar and lamp light (Figs. 6 and 7). In both cases, as the catalyst load increased in this range, the degradation observed was also important. The degradation of SPM increases with the concentration of titanium dioxide until a maximum of around 96% using $0.25\,g\,L^{-1}$ of catalyst. Beyond this value, the degradation remains approximately constant and the rate constant evolution is low. This behavior is explained by the fact that above the optimal concentration of TiO_2, particles cause a screening effect between them and the sunlight, and thus reduce the formation of hydroxyl radicals responsible on the oxidation reaction of the pollutant [39,40].

In order to avoid the deposition of the catalyst in the reactor and also for the economic reasons, we have considered in this study the value of $0.25\,g\,L^{-1}$ as an optimal concentration of TiO_2.

According to Table 1, SPM degradation follows the pseudo-first-order kinetic model. The apparent rate

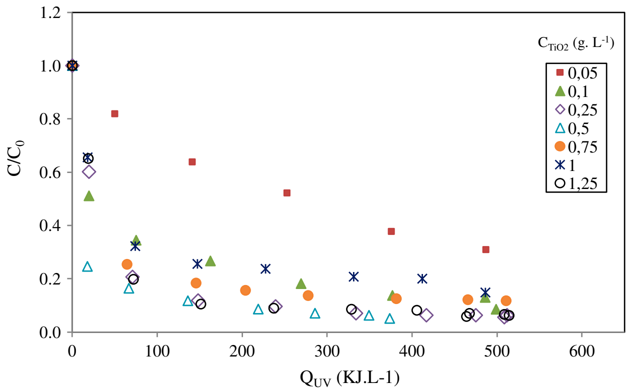

Fig. 6. Solar photocatalytic treatment of SPM as a function of the quantity of accumulated energy for different catalyst concentration. $C_{SPM} = 10\,mg\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

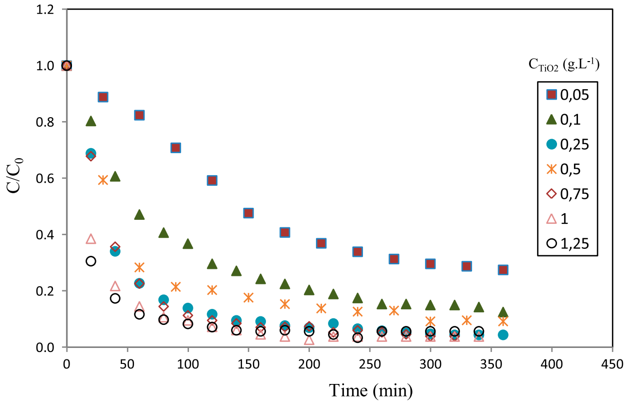

Fig. 7. Temporal evolution of SPM elimination rate for different catalyst concentration (lamp radiation). $C_{SPM} = 10\,mg\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

constants for each TiO_2 concentration were determined by linear regression form (ln (C/C_0) versus time). The slope of the straight lines corresponding to the kinetic rate constants of degradation increases with the amount of TiO_2 until it reaches an optimum value under sunlight.

3.2.2. Effect of Spiramycin concentration

The effect of the SPM concentration has been studied in a range between 10 and 40 mg L^{-1} for the optimum TiO_2 concentration already found ([TiO_2] = 0.25 g L^{-1}) in both cases (solar and artificial radiation).

The obtained results (Figs. 8 and 9) show that the SPM removal is very fast that its concentration decreases. The degradation percentages achieved after 360 min under the solar light for 10, 20, and 40 mg L^{-1} of SPM were 95.6, 92.2, and 94.4%, respectively (Fig. 8). SPM removal under simulated sunlight after 360 min was 95.6, 89.9, and 78.4% for the three different SPM concentrations, respectively (Fig. 9).

The rate constant is reversely dependent on the initial concentration of SPM in the solution; it is the highest for the lowest pollutant concentration and decreases with increasing concentrations.

Kinetics were fitted as a function of time ($C = f(t)$) for the two experimental (UV/Solar light). Kapp values could be respectively obtained from the slopes of the regression curves representing –ln(C/C_0) versus time. Obtained results are summarized in Table 2. As SPM concentration increased, low kinetic constant were obtained in both cases. As seen, the initial reaction rate for SPM photocatalytic degradation increases increasing SPM initial concentration from 10 to 40 mg/L [40].

3.2.3. Mineralization

Mineralization was followed for some experiments at different SPM concentration (Figs. 10 and 11). Mineralization achieved after 360 min at the laboratory reactor with UV lamp for 10, 20, 40 mg L^{-1} was 87.8, 83.1, and 64.8%, respectively. Percentages of mineralization under solar radiation were 89.2, 84.5, and 68.8% for the same different SPM concentrations. Generally, mineralization was slower than degradation due to the formation of intermediate products.

4. Conclusion

The degradation of SPM in TiO_2 suspension was investigated under the solar irradiation and artificial UV irradiation. The results show that the photocata-

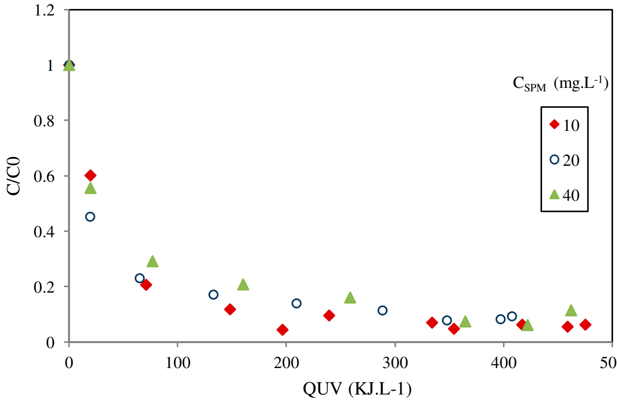

Fig. 8. Solar photocatalytic treatment of SPM as a function of the quantity of accumulated energy for different SPM concentrations. $C_{TiO2} = 0.25\,g\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

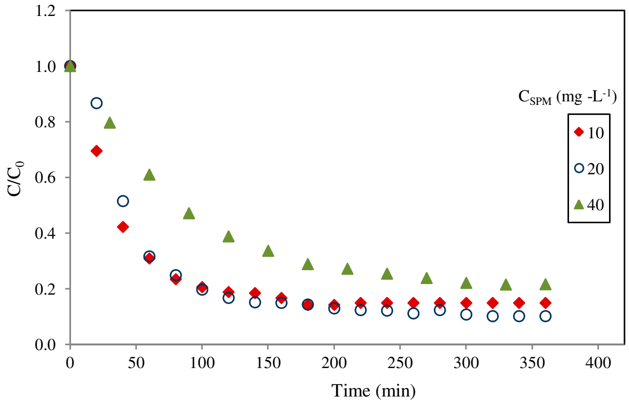

Fig. 9. Temporal evolution of SPM elimination rate for different SPM concentration (lamp radiation). $C_{TiO2} = 0.25\,g\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

Table 1
Value of kinetic constants, times of half reaction for different TiO_2 concentration under UV and solar radiation

UV lamp radiation					Solar radiation			
TiO_2 ($g\,L^{-1}$)	k_{app} (min^{-1})	R^2	r_0 ($mg\,L^{-1}\,min^{-1}$)	$t_{1/2}$ (min)	k_{app} (min^{-1})	R^2	r_0 ($mg\,L^{-1}\,min^{-1}$)	$t_{1/2}$ (min)
0.05	0.0037 ± 0.0008	0.9950	0.0332	187.3	0.0073 ± 0.0005	0.9995	0.0699	95.0
0.10	0.0118 ± 0.0013	0.9981	0.1271	58.7	0.0186 ± 0.0045	0.9946	0.1932	37.3
0.25	0.0195 ± 0.0040	0.9959	0.2468	29.5	0.0242 ± 0.0053	0.9946	0.2522	28.6
0.50	0.0222 ± 0.0040	0.9942	0.1827	38.1	0.0226 ± 0.0069	0.9868	0.2225	30.7
0.75	0.0268 ± 0.0023	0.9987	0.2666	28.3	0.0198 ± 0.0047	0.9934	0.1950	35.0
1.00	0.0307 ± 0.0092	0.9950	0.4022	17.4	0.0161 ± 0.0040	0.9926	0.1671	43.1
1.25	0.0310 ± 0.0155	0.9895	0.4738	14.9	0.0251 ± 0.0072	0.9911	0.2491	27.6

Table 2
Value of kinetic constants, times of half reaction, and SPM abatements for different SPM concentration under UV lamp and solar radiation

UV lamp radiation						Solar radiation				
C_{0SPM} (mgL^{-1})	k_{app} (min^{-1})	X (%)	R^2	r_0 ($mg\,L^{-1}\,min^{-1}$)	$t_{1/2}$ (min)	k_{app} (min^{-1})	X (%)	R^2	r_0 ($mg\,L^{-1}\,min^{-1}$)	$t_{1/2}$ (min)
10	0.0201 ± 0.0023	95.6	0.9984	0.2468	29.5	0.0242 ± 0.0053	95.6	0.9946	0.2522	28.6
20	0.0182 ± 0.0038	89.9	0.9952	0.3520	38.1	0.0213 ± 0.0055	92.2	0.9913	0.3875	32.5
40	0.0083 ± 0.0005	78.4	0.9996	0.3270	83.5	0.0184 ± 0.0031	94.4	0.9964	0.7035	37.7

lytic process UV/TiO_2 seems to be very efficient in the removal of antibiotics resistant to conventional techniques. Solar photocatalytic degradation rate can reach 96% during 360 min of treatment; important mineralization (>68%) could also be observed during the treatment. This process was also developed using a Philips UV lamp around 90% of degradation and more than 64% of mineralization were obtained. For the similar degradation rate in both cases, the solar photocatalysis can be recommended for its low energy cost and very good efficiency.

Acknowledgements

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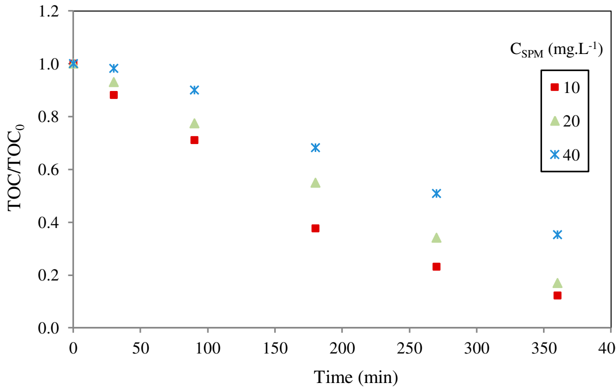

Fig. 10. Mineralization of SPM for different concentration (lamp radiation). $C_{TiO2} = 0.25\,g\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

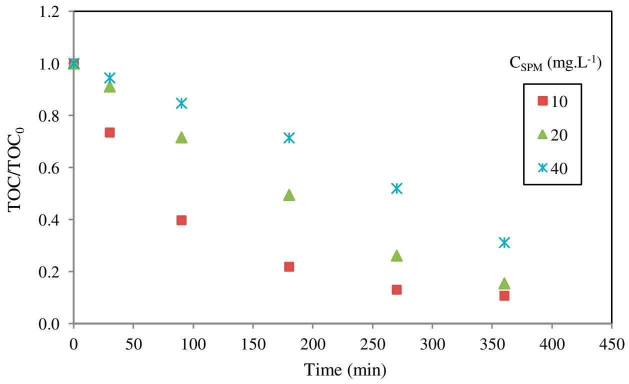

Fig. 11. Mineralization of SPM for different concentration (solar radiation). $C_{TiO2} = 0.25\,g\,L^{-1}$, $Q = 1.74\,L\,min^{-1}$.

Symbols

AOP — advanced oxidation processes

C_0 — initial pollutant concentration, $\mathrm{mg\,L^{-1}}$

C — pollutant concentration at time t, $\mathrm{mg\,L^{-1}}$

I — UV radiation intensity, $\mathrm{W\,m^{-2}}$

K_{app} — apparent constant kinetic, $\mathrm{min^{-1}}$

Q — flow rate, $\mathrm{L\,min^{-1}}$

Q_{UV} — quantity of UV energy, $\mathrm{J\,m^{-3}}$

r_0 — initial rate of SPM degradation, $\mathrm{mg\,min^{-1}}$

r — reaction rate, $\mathrm{mg\,min^{-1}}$

R^2 — linear regression coefficient

S — irradiated surface area, m^2

SPM — spiramycin

t — duration of irradiation, s

$t_{1/2}$ — half-time reaction, min

TiO_2 — titanium dioxide

TOC — total organic carbon, $\mathrm{mg\,L^{-1}}$

UV — ultra violet

V_{T} — reactor volume, $\mathrm{m^3}$

$X\%$ — SPM reduced percentage (%)

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