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Abstract: Environmental contamination by pharmaceuticals is an emerging issue. Even if pharmaceuticals are present at very low concentrations in the aqueous environment, they make implications for human health, giving rise to phenomena of bacterial resistence. Among antibiotics, spiramycin is today used to treat a wide variety of infections. Heterogeneous photocatalytic processes in presence of UV light are successful to obtain complete mineralization of various pharmaceutical pollutants but no one has studied the photocatalytic removal of spiramycin under visible light irradiation. In this work N-doped TiO2 photocatalysts active under visible light was used to evaluate the photodegradation of this antibiotic. Photocatalytic tests were carried out in a slurry photoreactor irradiated both with UV lamps and blue LEDs with spectrum emission in the visible region. Reaction products in gas-phase were monitored by continuous analyzers, measuring CO and CO2 gaseous concentrations at the photo-reactor outlet. The only product detected during irradiation was CO2 confirming that the photocatalytic process has been proven effective in the mineralization process of spiramycin, reaching very high values of TOC removal.

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Kind Editor,
We are submitting the attached manuscript for publication in "**Chemical Engineering Journal special edition on Advances in Photocatalysis"**.
In the following I report the invitation letter from the guest Editor.
Best regards
Diana Sannino (e-mail: dsannino@unisa.it)

From: suresh.pillai@dit.ie [mailto:suresh.pillai@dit.ie]
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Cc: DIONYSDD@ucmail.uc.edu; 'Urška Lavrenčič Štangar'
Subject: Invitation to Submit an article to the Chemical Engineering Journal- Special issue on 'Photocatalysis for contaminants and microorganisms of emerging concern'

On behalf of the organising committee of JEP-2013 and the Editor of Chemical Engineering Journal, Professor D. Dionysiou, we would like to inform you that the Chemical Engineering Journal will be publishing a special issue in the area of 'Photocatalysis for contaminants and microorganisms of emerging concern'. As the guest editors of the special issue, we have noticed that you have previously published research related to environmental nanotechnology. Therefore, we would like to invite you to contribute a review article or a full research paper for peer-review and possible publication.
The subjects of the special issue include but not limited to environmental photocatalytic nanotechnology, depollution technologies using nanomaterials, AOPs/AON (Advanced oxidation technologies and nanotechnologies) on contaminants of emerging concern (pharmaceuticals, pesticides, cyanotoxins, etc), environmental sustainable nanotechnologies, and risk assessment and policy analysis of environmental technologies related to pollutants of emerging concern.

Sincerely Yours, Guest Editors

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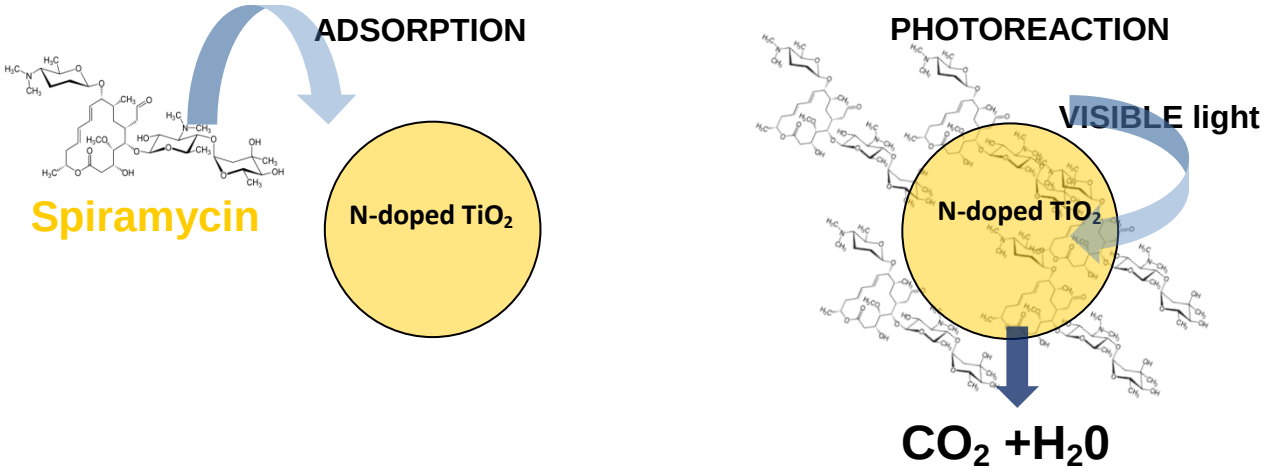
Graphical Abstract (for review)



***Highlights (for review)**

- N-doped TiO_2 photocatalyst active under visible light irradiation.
- Photocatalytic mineralization of spiramycin under visible light irradiation.
- The only reaction product detected in gas-phase was CO_2.
- Kinetic evaluations in different operating conditions.
- High photocatalytic mineralization of spiramycin of a real pharmaceutical wastewater

Photocatalytic removal of spiramycin from wastewater under visible light with N-doped TiO_2 photocatalysts

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Abstract

Environmental contamination by pharmaceuticals is an emerging issue. Even if pharmaceuticals are present at very low concentrations in the aqueous environment, they make implications for human health, giving rise to phenomena of bacterial resistence. Among antibiotics, spiramycin is today used to treat a wide variety of infections. Heterogeneous photocatalytic processes in presence of UV light are successful to obtain complete mineralization of various pharmaceutical pollutants but no one has studied the photocatalytic removal of spiramycin under visible light irradiation. In this work N-doped TiO_2 photocatalysts active under visible light was used to evaluate the photodegradation of this antibiotic. Photocatalytic tests were carried out in a slurry photoreactor irradiated both with UV lamps and blue LEDs with spectrum emission in the visible region. Reaction products in gas-phase were monitored by continuous analyzers, measuring CO and CO_2 gaseous concentrations at the photo-reactor outlet. The only product detected during irradiation was CO_2 confirming that the photocatalytic process has been proven effective in the mineralization process of spiramycin, reaching very high values of TOC removal.

Keywords: Photocatalysis; spiramycin; N-doped TiO_2; visible light; UV light; Langmuir-Hinshelwood kinetics; real pharmaceutical wastewater.

Introduction

Pharmaceutical active compounds (PACs) have attracted much attention in recent years due to their adverse effects towards natural organisms and potential effects on human beings. The traditional plants for treatment of wastewater are able to remove microbes and organic matter, while the pharmaceuticals compounds are not oxidized. As a consequence, when this effluent is released from the treatment plants into an aquatic body, drug-tainted waters are introduced directly into the aquatic habitat. Thus PACs are progressively accumulated into the environment. In fact, several studies carried out in the past few years, have demonstrated the presence of PACs in groundwater, surface water and even in drinking water [1-5]. These drug-tainted waters must be treated for human consumption or for different human activities [6, 7].

Advanced oxidation processes (AOPs), such as ozonation, Fenton, photo-Fenton oxidation, and heterogeneous photocatalysis [8-16] have shown great efficiency in recent years as possible future complementary methods to conventional wastewater treatments [17-19]. Among these AOPs, TiO_2 photocatalysis is under developing as an affordable, effective, environmentally friendly and sustainable technology for various chemical transformations [20-28]. Several studies have demonstrated that ultraviolet (UV) and visible light is able to decompose pharmaceuticals by direct photolysis or indirect photolysis through an AOP. Indeed, Amoxicillin [29], nitroimidazoles [30], oxytetracycline [31], and sulfamethoxazole [32] are degraded by UV or visible light treatments.

Among antibiotics, spiramycin (SP) (Figure 1) is a macrolide antibiotic used to treat infections of the oropharynx, respiratory system, genito-urinary tract, as well as

cryptosporidiosis and toxoplasmosis [33]. Similarly to the other antibiotics AOPs can be applied to remove SP from water.

SP degradation has been reported under UV light irradiation in presence of TiO_2 [34], but no one has studied photocatalytic removal of SP under visible light irradiation.

However, to reach this goal, it is necessary to modify titanium dioxide in order to make it able to exploit visible light. This feature can be realized by doping TiO_2 crystal lattice with various elements. Among such modified materials, N–doped TiO_2, under visible light, exhibits stable characteristics and performance in wastewater treatment applications [35, 36]. The use of visible light would represent, then, a more economical alternative. For this reason the objective of this study is to explore the possibility of using blue LEDs as source of visible light for the photocatalytic removal of SP. The effect of various parameters, such as SP concentration and type of light sources was investigated.

1. **Materials and methods**

2.1 Materials

N-doped TiO_2 (Nt) photocatalyst was prepared by the hydrolysis reaction between the titanium tetraisopropoxide and an aqueous solution containing ammonia. More in detail, a volume of 100ml ammonia aqueous solution at 30wt %, supplied by Carlo Erba, was quickly added to 25ml of 97wt% titanium tetraisopropoxide (TTIP by Sigma Aldrich) at 0°C during a vigorous stirring of the solution in which a white precipitate was progressively formed. The precipitate was then carefully washed with bidistilled water and centrifuged to be separated. After the separation of settle solids, the obtained powders were dried and calcined at 450°C for 30 minutes, yielding N-

doped TiO_2 in anatase phase. The band–gap energy of titanium dioxide was then moved in the visible range from 3.3eV to 2.5eV [35]. The final N/Ti molar ratio was equal to 18.6 and corresponds to an optimized catalyst formulation, as found in previous works devoted to the optimization of doping process and to the evaluation of photocatalytic activity towards organic dyes [37].

A SP source, commercial antibiotic pills, was provided by Mylan generics.

2.2. Photocatalytic tests

Aqueous solutions containing SP were prepared using weighted fractions of pills dissolved in bidistilled water, to get a more realistic drug-tainted wastewater.

The experiments were realized using a pyrex cylindrical photoreactor (ID= 2.5 cm) equipped with an air distributor device (Q_{air}=250cm^3/min (STP)), magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution and temperature controller. The photoreactor was irradiated with a strip composed by 25 blue LEDs (BL strip) (provided by NEW ORALIGHT; nominal power: 5W) with wavelength emission in the range 400–550 nm [35, 37] or with four UV lamps (provided by Philips; nominal power: 32 W) with wavelength emission at 365nm. The light sources were positioned around the external surface of the photoreactor (Figure 2).

In a typical photocatalytic test, 3 g/L of photocatalyst was suspended in 100mL solution. The system was left in dark condition for 2 hours to reach SP adsorption equilibrium on catalyst surface, and then photocatalytic reaction was initiated under visible or UV light up to 7 h. Samples were taken during the tests and centrifuged for removing powders from the SP solution. The analysis of gas phase coming from the photoreactor was performed by means of a continuous CO, CO_2, non-dispersive infrared analyser (ABB Advance Optima).

The photocatalytic activity was tested in terms of the reduction of total organic carbon (TOC) that is a parameter able to analyze SP mineralization. TOC of solution has been measured from CO_2 obtained by catalytic combustion at T=680°C. CO_2 produced in gas-phase was monitored by continuous analyzers, measuring CO, CO_2 (Uras 14, ABB) and O_2 (Magnos 106, ABB) gaseous concentrations [8].

The natural pH of solution was equal to about 6 and the temperature was controlled being in the range 20-30°C. Finally, the performances of Nt photocatalyst in presence of visible light were tested in the photocatalytic treatment of a real pharmaceutical wastewater containing SP with an initial TOC content of about 20 $mg\,L^{-1}$.

3. Results and Discussion

3.1 Influence of photocatalyst and different light sources

Preliminary experiments were carried out to in order to verify that SP was degraded by heterogeneous photocatalytic process. In the absence of Nt, no significant decrease in TOC was observed during the 7h of illumination both with UV light and visible light irradiation (Figure 3). In particular, TOC removal was less than 10% in the case of visible light irradiation and 19% in the case of UV light irradiation. So, photolysis phenomena occur but in a limited extent.

The TOC profiles as function of irradiation time obtained in the presence and in the absence of Nt under the irradiation realized by UV lamps are reported in Figure 4. In dark conditions, a decrease of TOC was observed during the first hour of the test and it was unchanged in the second hour, indicating that the adsorption equilibrium of SP on catalyst surface was reached. After the dark period, the solution was irradiated

with UV light and the reaction started to occur. It can be seen that TOC value was lower when UV light was applied in the presence Nt photocatalyst. In fact, a final TOC removal reached a value of about 48%, so remarkably improved in comparison to photolysis alone.

The analysis of gases coming from the photoreactor showed the presence of only CO_2 during the UV light irradiation, confirming the occurring of the mineralization of SP (Figure 5). It is important to underline that no formation of CO_2 was detected in absence of light irradiation. This last experimental result shows that the TOC reduction obtained in dark conditions was due to only adsorption of SP on Nt surface.

Through a comparison between the amount of carbon consumed during the photocatalytic reaction (as assessed by TOC analysis) and the amount of carbon released as CO_2, the total carbon mass balance was closed to about 95±5%, evidencing that SP is selectively converted to CO_2. It is possible to affirm that total mineralization of SP was obtained in presence of photocatalyst.

It was also performed visible light driven photocatalytic removal of SP over the Nt using the light emitted by BL and results are presented in Figure 6. It is observed that SP photolysis shows a progressive removal of TOC up to a value lower than 10% after 7 h of irradiation. In contrast, the presence of Nt showed higher removal rate with a final TOC removal of 45 % after 6 h of irradiation. This enhanced photocatalytic ability in presence of visible light is ascribed to nitrogen insertion in the crystalline structure of titania.

3.1 Effect of Spiramycin concentration

The effect of the SP concentration has been studied with an initial TOC ranging between 40 and 170 mgL^{-1}. The mineralization in terms of TOC removal achieved after 4 hours under the visible light for 40, 60, and 170 mgL^{-1} of initial TOC, were 74, 68, and 40%, respectively (Figure 7).

3.2 Kinetic modelling

3.2.1 Adsorption in dark conditions

For the evaluation of SP adsorption on the active surface [38], the following equation was used:

$$TOC^{*} = \frac{b \cdot TOC_d}{1 + b \cdot TOC_d} \qquad \text{Eq. 1}$$

Where:

TOC^{*}: amount of SP adsorbed on catalyst in dark conditions [g /g]

TOC_m: maximum absorbable value of TOC*

TOC_d: concentration of SP in solution after dark adsorption [mg L^{-1}]

b: adsorption equilibrium constant [L mg^{-1}]

Eq.1 can be rearranged to give:

$$\frac{TOC_d}{TOC^{*}} = \frac{1}{b \cdot TOC_m} + \frac{1}{TOC_m} \cdot TOC_d \qquad \text{Eq. 2}$$

Accordingly, a plot of TOC_d/TOC^{*} as a function of TOC_d produces a straight line with: slope=$1/TOC_m$ and intercept=$1/b*TOC_m$ (Figure 8).

The value of b was calculated from Eq. 2 utilizing the data reported in Figure 8 and it was equal to 0.0089 [L mg^{-1}].

3.2.2 Evaluation of rate constant

The mathematical model has been realized considering that in the batch reactor under blue LEDs irradiation, occur mainly the total oxidation of SP to CO_2.

Mass balance on SP concentration (expressed as TOC) can be written as:

$$V \cdot \frac{dTOC(t)}{dt} = r(TOC, I) \cdot W_{Nt} \qquad \text{Eq. 3}$$

Where:

TOC(t) :TOC at given reaction time, [g L^{-1}]

-r: reaction rate, [g L^{-1} h^{-1}]

W_{Nt}: amount of catalyst effectively irradiated [35, 37], [g]

The initial conditions are:

t=0 $\qquad\qquad$ $TOC=TOC_0$

The kinetic expressions is well described with the classic Langmuir- Hinshelwood (L-H) mechanism [39] in terms of mineralization of SP as in the following:

$$-r = K \cdot \frac{b \cdot TOC}{1 + b \cdot TOC} \cdot \frac{I \cdot \alpha}{1 + I \cdot \alpha} \qquad \text{Eq. 4}$$

Where:

K=kinetic constant [mg g^{-1} h^{-1}]

α= light absorption coefficient [cm^2 mW^{-1}]

I= light intensity reaching the photocatalyst surface [mW cm^{-2}].

Eq. 4 is similar to the Langmuir-Hinshelwood rate law used in other studies regarding the mathematical modelling of methylene blue degradation [37].

This equation takes into account also the influence of light intensity. In fact, only a fraction of nominal radiation reaching the photocatalyst particles is absorbed by itself. This effect was considered utilizing the parameter α. This parameter depends only on the reactor configuration and light sources and not on the liquid medium; its value is equal to 0.000925 [cm^2 mW^{-1}] and it is the same used in a previous work [37]. Moreover, it is important to consider that the light penetration inside the reactor core depends on type of pollutant (in this case SP) and on the catalyst concentration [37]. This suggests that only a part of the light intensity entering in the reactor, will be reach the photocatalyst particles. To consider this screening effect, a first order correlation (similar to Lambert-Beer law) for the effective light energy received by the Nt particles [37] was used:

$$I = I_0 \cdot e^{-[Nt] \cdot k_I} \qquad \text{Eq.5}$$

Where:

k_I= specific extinction coefficient per unit catalyst mass [L mg^{-1}]

I= light intensity reaching the photocatalyst surface [mW cm^{-2}].

I_0= nominal light intensity= 32 mW cm^{-2}

[Nt]= catalysts dosage [mg L^{-1}].

Eq. 4, coupled with Eq. 5, together with the initial condition, was solved with Euler iterative method to identify the constants K and k_I by fitting experimental data reported in Figure 9 as a function of irradiation time. The fitting procedure was realized by using the least squares approach obtaining the value of K: 6.04 [mg g^{-1} h^{-1}], and k_I: 0.349 [L mg^{-1}]. After obtaining the model parameters, the experimental data obtained with different initial TOC were fitted to analyse the ability of the

model to predict the experimental data. The obtained results are shown in Figure 10. In this series of experiments, the incident light intensity (I_0) and Nt dosage are kept constant. The calculated values in both cases are in good agreement with the experimental data. It is important to note that also for the higher TOC_0 (170 ppm), this system is able to predict the mineralization trend with a single value of kinetic constant. This last result is in contrast with literature works about kinetic degradation of antibiotics in liquid phase that report different values for mineralization constant [32].

3.3 Photocatalytic performance of Nt under visible light on a real wastewater coming from a pharmaceutical plant for production of spiramycin

The treatment of real wastewater sample was effected because it could be more difficult its depollution due to the wide variety of the products in variable composition. The performances of Nt photocatalyst on real wastewater coming from a pharmaceutical plant for production of spiramycin was shown in Figure 11. In the case analyzed, the initial value of TOC_0 was about 20 mg L^{-1}. In dark conditions the decrease of TOC was equal to 24%. After the dark period, visible light source was turn on and the mineralization process started determining a decrease of TOC. The value of TOC reached after 40 minutes of irradiation was about 3 ppm corresponding to almost 83 % of conversion.

4. Conclusions

The removal of spiramycin in N-doped TiO_2 suspension was investigated for the first time under visible light. The results showed that the photocatalytic process seems to be very efficient in the mineralization of spiramycin. During irradiation time, the only product detected in gas phase was CO_2 confirming that the photocatalytic

process has been proven effective in the mineralization of spiramycin, reaching very high values of TOC removal. Kinetic evaluations evidenced that the mineralization process can be described with a single value of reaction constant, also at very high initial concentration of antibiotic.

The system is also able to mineralize the spiramycin and all the organic compounds present in a real pharmaceutical wastewater reaching high values of depollution in short times. Photocatalytic visible treatment of spiramycin containing streams with N-doped titania appeared a very promising method for wastewater treatment.

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Figure1

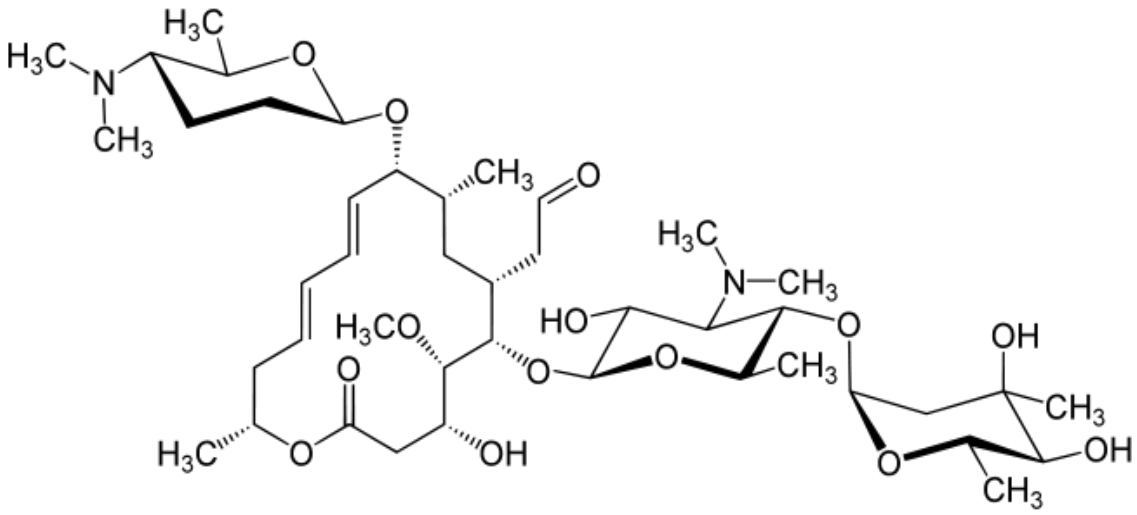

Figure 1 Chemical structure of SP

Figure2

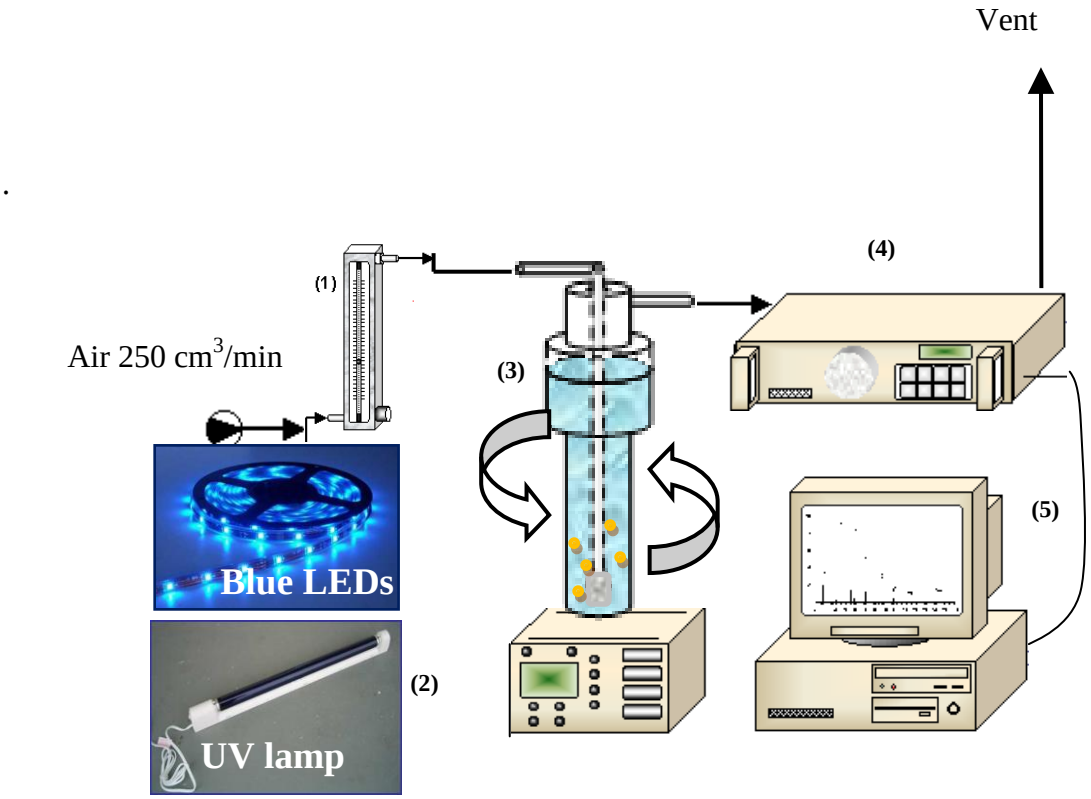

Figure 2 Experimental set up apparatus (1) rotameter; (2) magnetic stirrer; (3) photoreactor; (4) CO,CO_2 analyzer, (5) personal computer for data acquisition.

Figure3

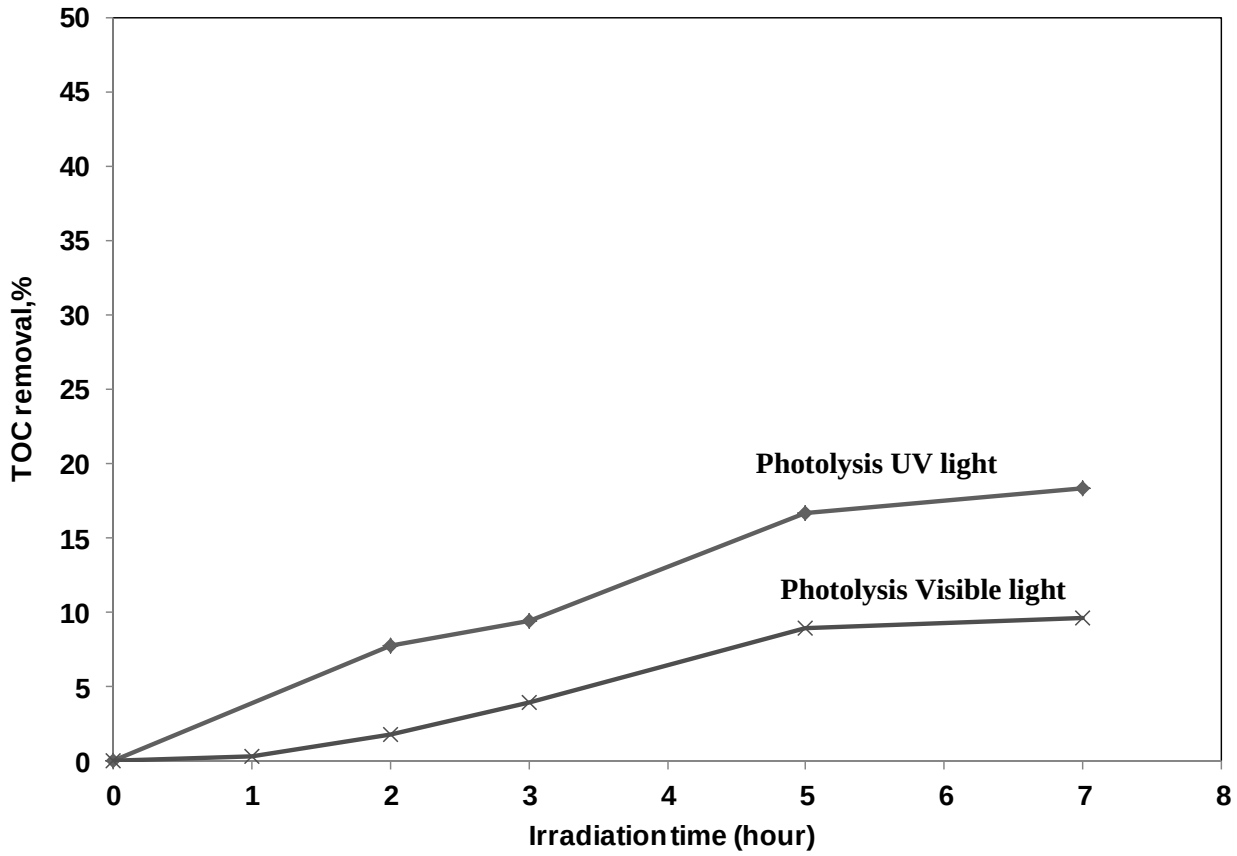

Figure 3 Comparison between photolysis under visible light and UV light

Figure4

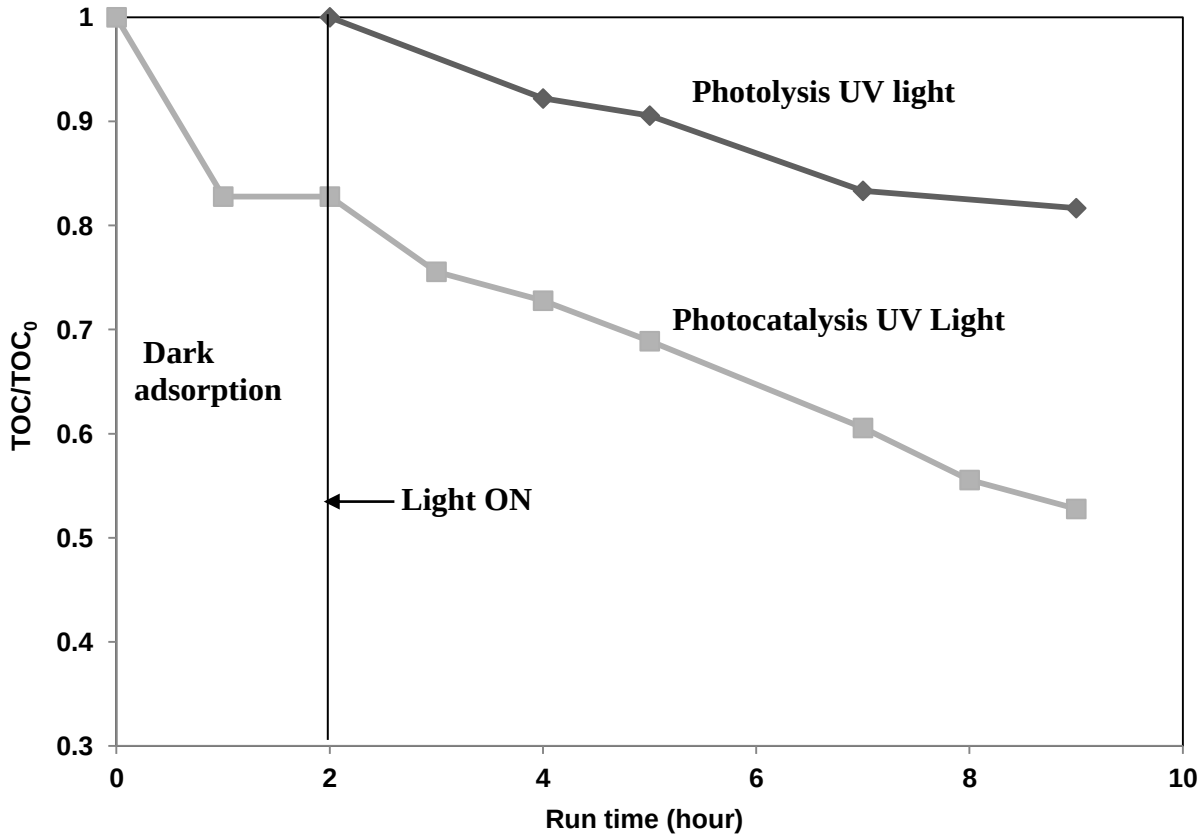

Figure 4 Comparison between photolysis and photocatalysis (Nt dosage: 3g/L) using UV light sources

Figure5

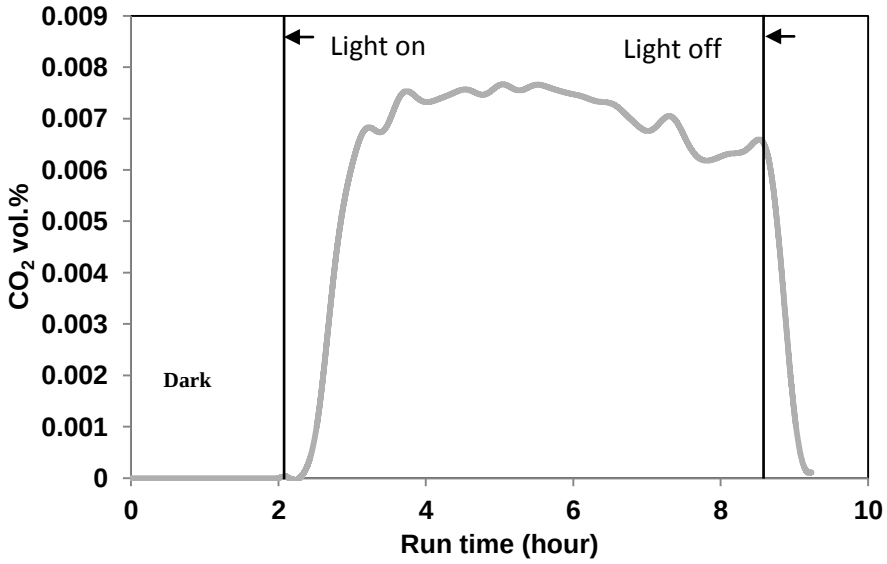

Figure 5 Gas phase analysis during photocatalysis in presence of UV irradiation.

Figure6

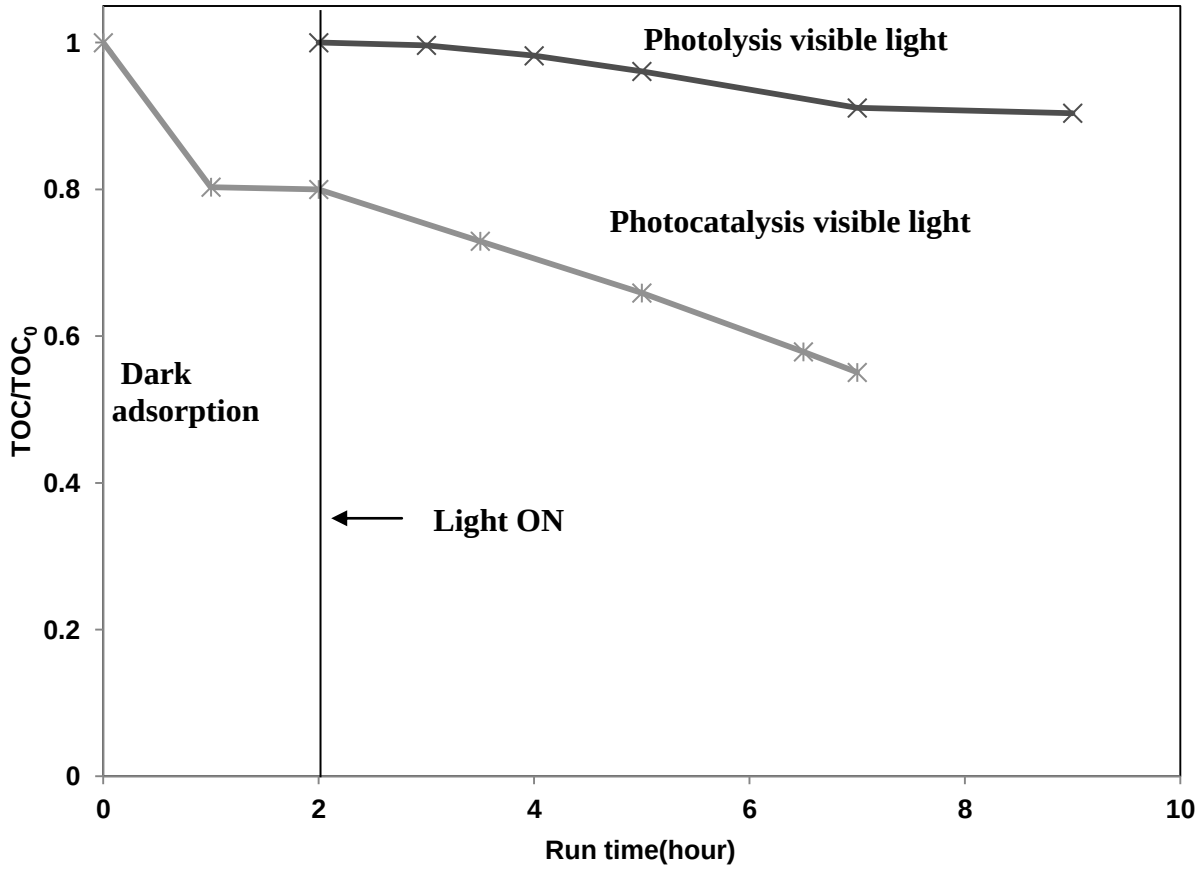

Figure 6 Comparison between photolysis and photocatalysis (Nt dosage : 3g/L) using visible light (blue LEDs)sources

Figure7

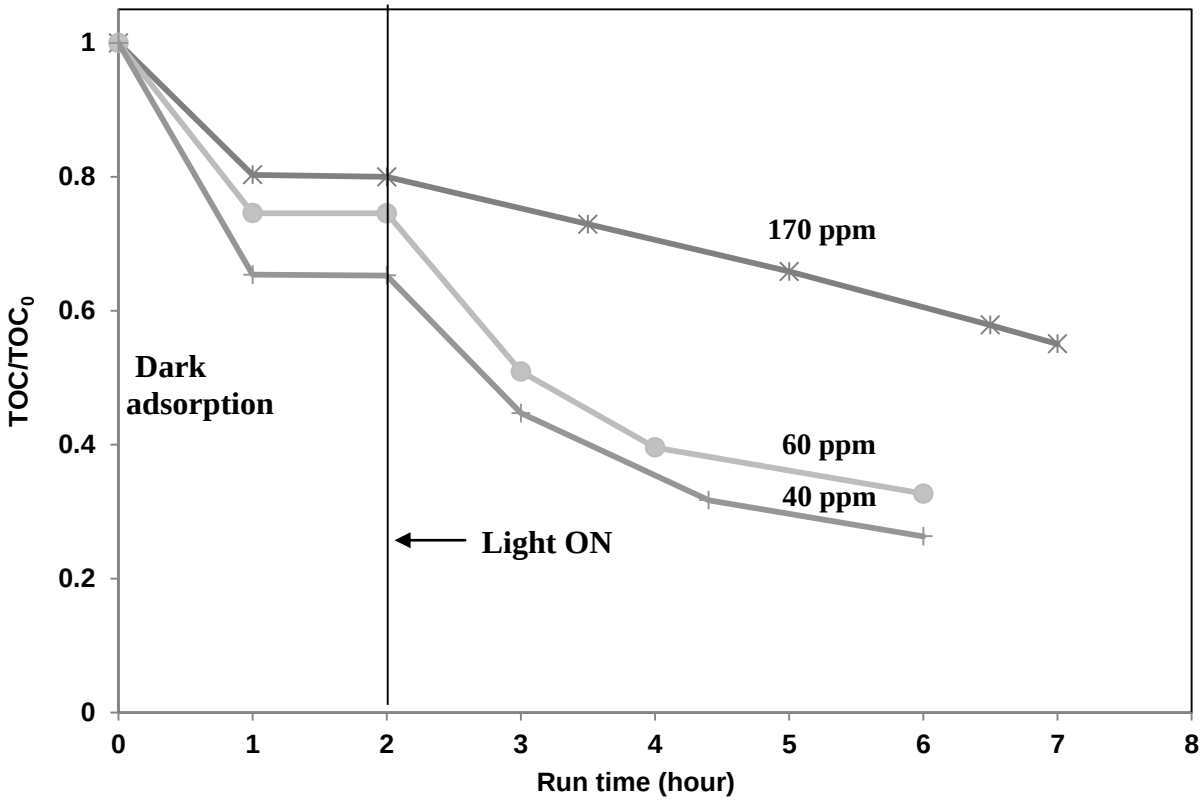

Figure 7 Evaluation of SP mineralization under visible light with different initial TOC_0.

Figure8

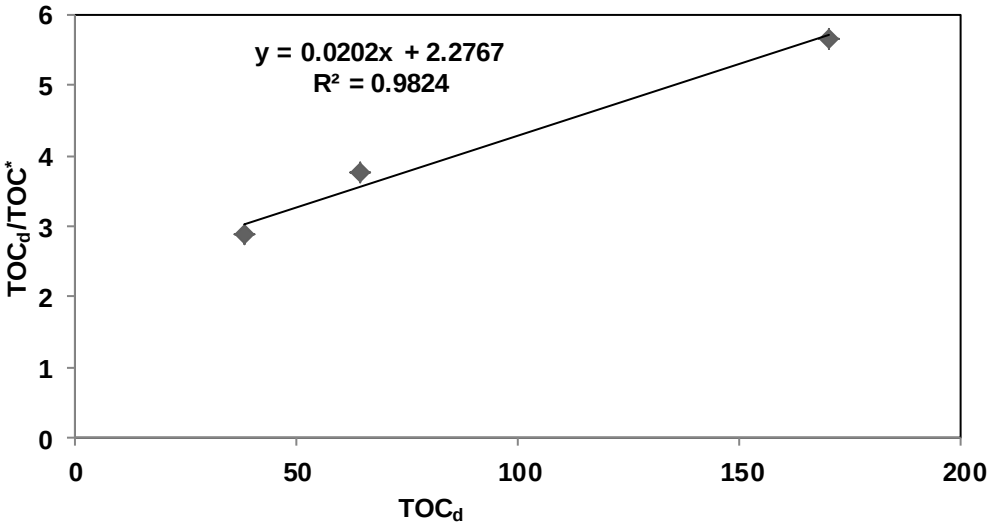

Figure 8 Evaluation of SP adsorption constant

Figure9

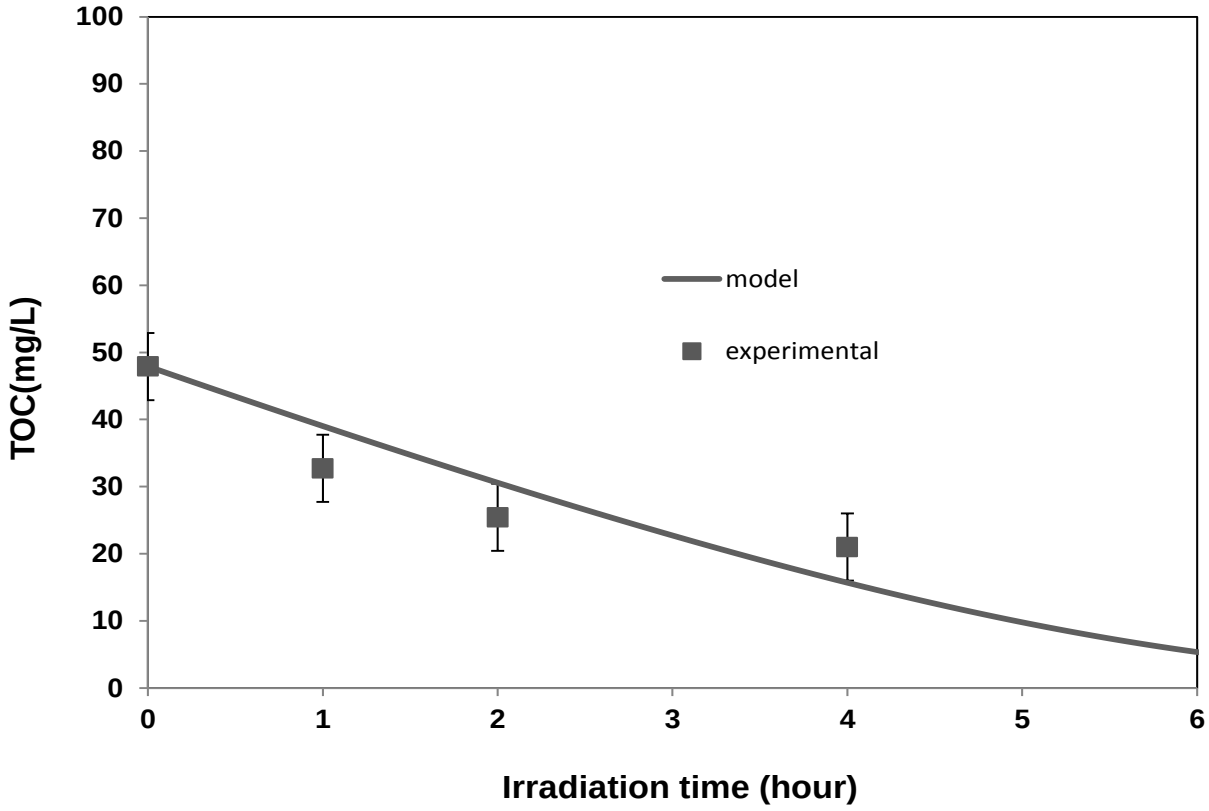

Figure 9 Comparison between model calculation and experimental data to find the reaction constant

Figure10

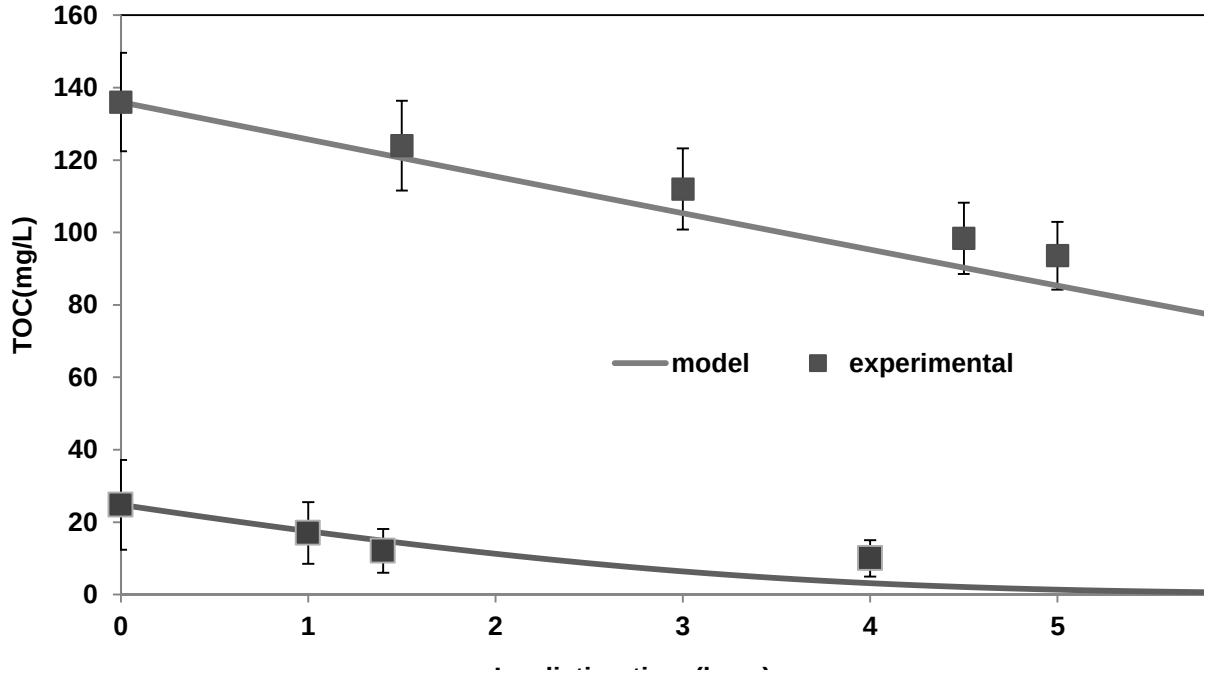

Figure 10 Experimental and predicted data as a function of initial TOC_0

Figure11

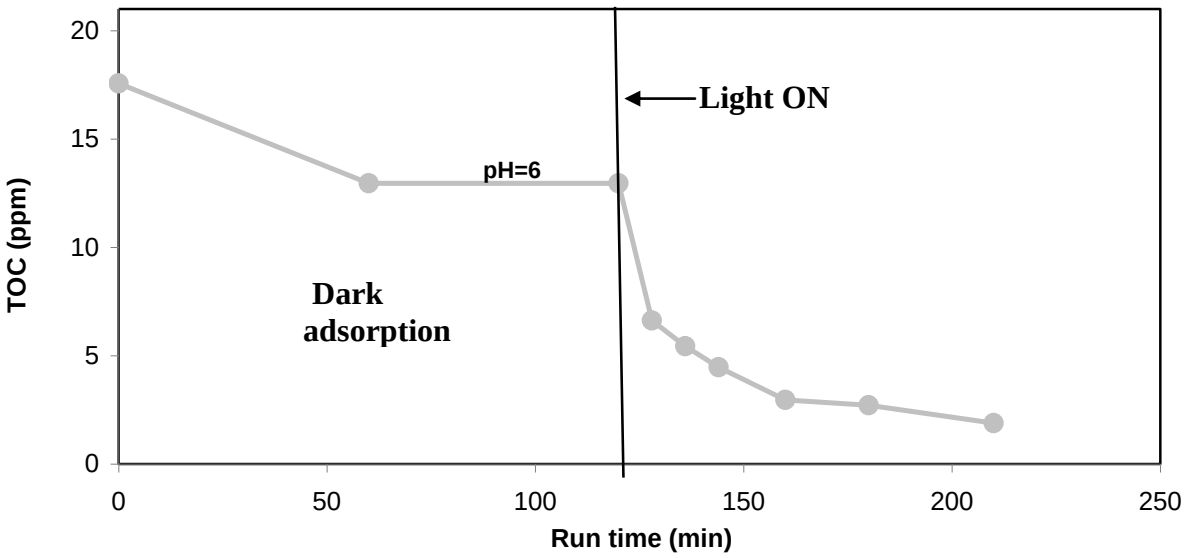

Figure 11 Photocatalytic results on the real pharmaceutical wastewater using blue LEDs light