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Photocatalytic Degradation of Pyrimethanil by the Two Commercial Catalysts under Artificial Irradiation

K.Elatmani[1,3],G. Plantard[2,3], D. Sacco[2,3], V. Geotz[2], M. Belmouden[1], A. Assabbane[1], Y. Aitichou[1]
[1](Université Ibn Zohr, Cité Dakhla, 8106 Agadir, Morocco)
[2](PROcédés Matériaux et Energie Solaire, Rambla de la Thermodynamique, PROMES-CNRS, UPR 8521, 66100 Perpignan CEDEX, France)
[3](Université de Perpignan Via Domitia, 52 avenue Paul Alduy, 66860 Perpignan, France)
Corresponding Author: K.Elatmani

ABSTRACT: *Water is used by man to ensure his life and develop his economic and industrial activities. The need for better management and effective protection of the quality of surface and ground natural waters is necessary. Many conventional methods have been applied to remove pollutants from water. Alternate technologies popularly known as Advanced Oxidation Processes (AOPs) have been extensively explored for complete demineralization of these compounds for the past few decades. Among AOP's, heterogeneous photocatalysis has been used to treat several pollutants such as pesticides. Its principle is based on the production of OH◦ radical active. The aim of this work is the determination of the pyrimethanil'sphotocatalytic degradation kinetics on media as a function of the irradiation intensity. The results obtained for the degradation of the target molecule and its mineralization (TOC) as a function of the different irradiations; show the preponderant influence of this parameter on the operation of the process. The results show that the suspension form of catalyst gives better results than the supported media.*

Keywords: *Photocatalysis, Pyrimethanil, TiO_2, Pesticides*

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I. INTRODUCTION

The depollution of water has become an important issue today. Indeed, in recent decades, the massive use of crop protection products, with the aim of obtaining high yields for agriculture, has been significant. This massive use of plant protection products has a significant impact on the environment. In particular, it is responsible for the pollution of groundwater used for human consumption. It is urgent to find new methods to clean contaminated water and to have an organic pollutant content corresponding to European standards [European Directive (2000)] in water intended for human consumption, ie 0.1 μgL^{-1} for each Type of pesticide and 0.5 μgL^{-1} as the maximum value of the total pesticide concentration. For a long time, environmental concerns have been neglected at the expense of massive agriculture and at all costs. With the aim of treating contaminated water, new processes have emerged, advanced oxidation processes, the aim of which is to degrade the pollutants present in water with the ultimate goal of complete mineralization of the latter.

Advanced Oxidation Processes, such as water treatment processes operating at ambient temperature and pressure [Glaze et al. (1987)], seem to provide convincing results. In the case of photo-catalysis, the radical species are produced by photo-excitation of a photosensitive semiconductor with Ultra-violet radiation. The use of existing or industrially available photocatalytic media.

A preliminary study was carried out to verify the sensitivity of the pyrimethanil target molecule to the phenomenon of photolysis which can intervene under direct UV radiation and to quantify the importance of the adsorption phenomenon of the pollutant at the surface of the catalyst. Subsequently, the photocatalytic degradation kinetics obtained for the various media will be systematically determined, and these will be compared with each other using the two industrially available media, namely the TiO_2 nanoparticles (Degussa P-25) and The cellulosic tissue impregnated with catalyst (Ahlstrom, Grad 1048).

II. MATERIAL AND METHODS

Photocatalytic degradation of pyrimethanil was performed in a closed circuit pilot (Figure 1). It consists of a stirred glass vessel (3) (volume of 1 liter) connected to a tubular quartz or borosilicate glass reactor (2), the dimensions of which are 3.2 cm in outside diameter, a thickness of 0, 15 cm and 80 cm high. Its capacity is 0.035 l. The UV irradiation is carried out by a UV lamp (model VL-330 by the VilbertLourmat brand) whose spectrum is centered at 365 nm but extends from 300 nm to 400 nm. The latter is fixed on a sliding rail making it possible to vary its distance with the reactor and thus the intensity received by the latter. The range studied varies from 9 to 35 Wuv.m2, an intensity domain corresponding to solar radiation. The calibration of the flux induced by the lamp was carried out using a UV detector of the Lutron Electronic brand. A reflector of the parabolic collector (CPC) type is placed on the rear face of the reactor in order to homogenize the irradiation over its entire periphery. The reflector consists of a polished aluminum plate (99.85% purity), with a thickness of 0.5 mm supplied by the company SATMA whose reference is Bandoxal and exhibiting a reflectivity of 95% in the range of UV. The size of the lamp which develops a height of 90 cm, combined with the use of a CPC reflector, ensures quasi-uniform irradiation conditions over the entire surface of the reactor tube. The uniformity of the irradiation according to height was verified by measurements taken along the vertical axis indicating a dispersion of less than ± 3% relative to the mean value. The circulation of the fluid is ensured by a centrifugal pump with an inert pump head of the brand Cole Parmer Instrument with a flow rate of 1.4 L min-1. All the auxiliary tubing is made of materials that are inert with respect to the molecules studied and the choice has therefore been made of stainless steel and Teflon.

Two different apparatus were used for analytical monitoring of the solution. Pyrimethanil is monitored using HPLC. The TOC meter can monitor the concentration of organic carbon in the medium. The by-products resulting from the degradation of the target molecule are not directly measured but theoretically determined in TOC equivalent.

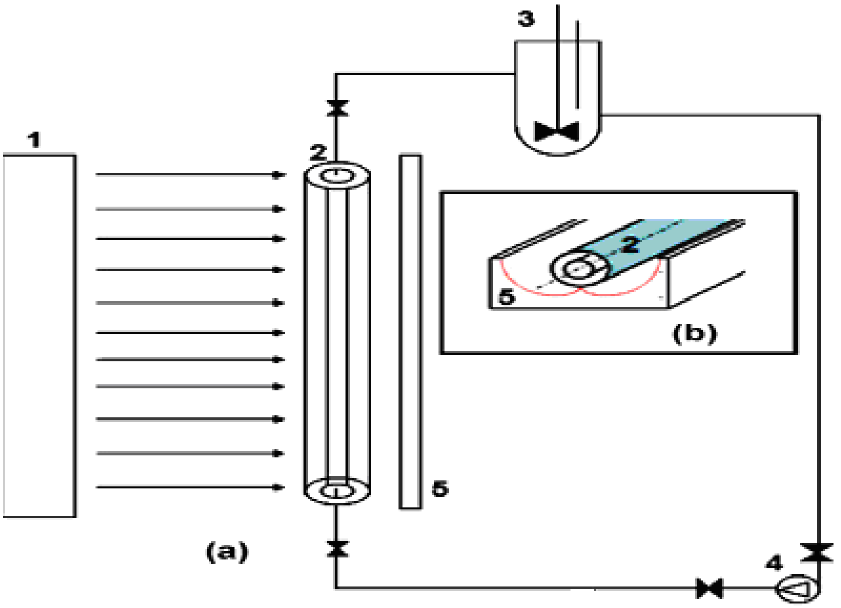


Figure 1: Diagram of the driver used. (5), Pomp (4), UV lamp (1), Reactor (2), Storage tank

III. RESULTS AND DISCUSSIONS

A. Photolysis and adsorption

The phenomenon of photolysis constitutes one of the natural degradation pathways of a molecule when it is subjected to a particular light radiation. Indeed, when this radiation can be absorbed by the molecule, it causes the photo-excitation of this molecule. The absorbed energy causes the electron excitation of the electrons constituting the peripheral layers of the atoms and of the bonds between atoms, the vibrations caused can thus cause the rupture of chemical bonding of a molecule. In our case study, it is a matter of checking whether the photolysis does not contribute to the formation of radicals by the rupture of carbon-carbon bonds. Since this natural phenomenon can have a non-negligible influence, it is important to quantify it to dissociate the processes of catalysis and photolysis.

Adsorption, on the other hand, is a spontaneous phenomenon. The molecule interacts with the surface of the solid. It is then retained for a more or less long time by the more or less solid bond formation of Wan Deer Walls type: the molecule is said to be adsorbed. The thermodynamic equilibrium between the free and the adsorbed species is reached with a more or less slow rate depending on the nature of both the adsorbent and that of the adsorbate. Determination of the equilibrium time is a preliminary step in any adsorption study. In the case of our study, it makes it possible to identify the part of the degraded molecule and that of adsorbed.

These two phenomena, which can also take place in parallel, in this case they potentially compete with the phenomenon of photocatalysis. The quantification of these phenomena has therefore been carried out prior to the studies carried out with the catalyst.

The tests were carried out in the "pilot" assembly described in the previous chapter (FIG. 1), under artificial irradiation with a lamp whose spectrum is centered at 365 nm. The experimental conditions were as follows:
-Pyrimethanil volume in the 1L glass vessel at initial pH not very different from 8.5.
- Irradiated volume of tubular reactor of 55.4 cm3
- Irradiation provided by the lamp is 35W.m-2
- Mass of TiO2 (Degussa P-25) in the solution of 0.71 g for the follow-up of the kinetics of adsorption.

The samples taken during the monitoring of this adsorption kinetics are filtered using a 4 mm PTFE filter and a porosity of 0.45 µm and then analyzed by HPLC.

The adsorption experiments are carried out in the dark in the presence of a suspension of Titanium dioxide. A stirring of 90 minutes in the dark is sufficient to reach the equilibrium of adsorption of pyrimethanil. Our results in FIG. 2 indicate a maximum adsorption of 10% of the solute, as soon as the UV lamp is switched on, the phenomenon of Photocatalysis begins causing a decrease in pyrimethanil concentration.

In the absence of the photocatalyst TiO2, the irradiation of the reaction mixture leads to apesticide disappearance of the order of 5% after 19 hours. Pyrimethanil absorbs practically no radiation emitted by the lamp. It thus appears that the contribution of direct photolysis is therefore negligible in a wavelength range close to 365 nm. These two phenomena will beconsidered negligible in our study.

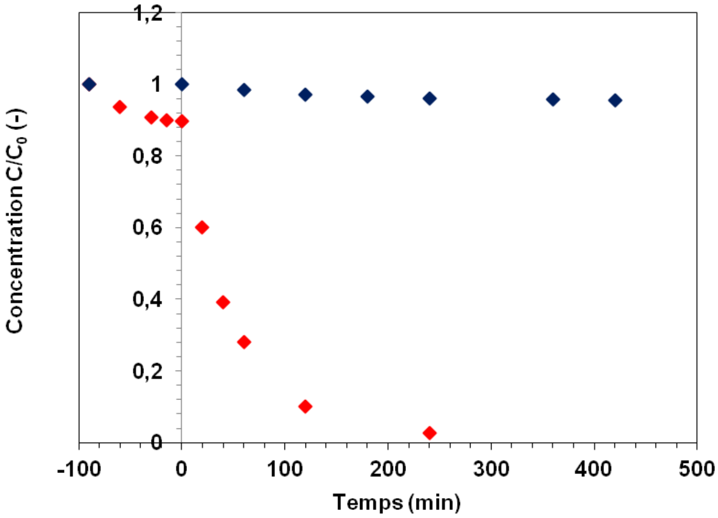
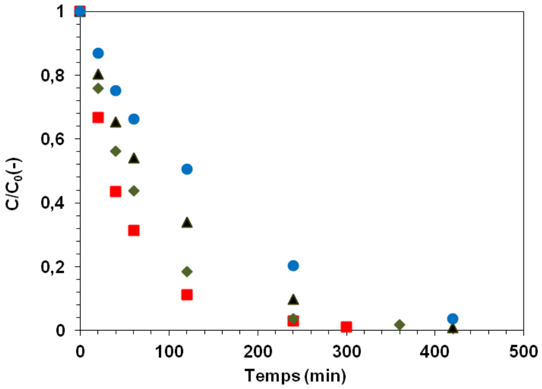
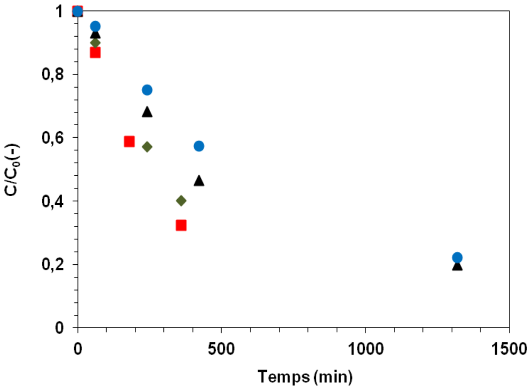


Figure 2: Kinetics of the disappearance of pyrimethanil in the absence of the catalyst (♦) (photolysis); Adsorption of pyrimethanil (t <0); Photocatalytic treatment in the presence of TiO_2 / UV (♦) for t> 0. Influence of irradiation on the Degussa P-25

The first experiments are carried out with the industrial photocatalyst in the form of a powder which exhibits the best reactivities because of their granulometry. We carried out our experiment in a tubular reactor with a concentration of our solute pyrimethanilof 15 mg.L-1. The different irradiation intensities selected range from 9 $WUV.m^{-2}$ to 35 WUV.m-2. The catalyst concentration $C(TiO_2)$ and the thickness (L) were matched to the configuration (geometry and diameter) of the photoreactor to absorb 90% of the incident UV radiation. In our case, the experiments were carried out in a reactor with a radius of r = 1.4 cm, which corresponds to an optimal concentration of: Copt = 0.71 g L^{-1}. The samples were analyzed simultaneously by HPLC and the total organic carbon analyzer (TOC). The results obtained are shown in the figures (FIG. 3 and FIG. 4).





B.

Figure 3: Evolution of the relative concentration of pyrimethanil as a function of time (min) for different irradiations (WUV.m-2): 9(●), 17(▲), 27(♦),35(■)

Figure 4: Evolution of the relative TOC concentration as a function of time (min) for different irradiations (WUV.m-2): 9(●), 17(▲), 27(♦),35(■)

These figures show respectively the evolution of the non-dimensional C/ C_0 concentration (ratio between the final concentration (C) at time t in mg L-1 of solute and the initial concentration (C0) of the solute expressed in mg.L^{-1} at the time T = 0) to pyrimethanil, and TOC (total organic carbon) as a function of time for different irradiations. The relative C/C_0 concentration varies according to the 80% (9 WUV.m^{-2}) irradiations in 100% (35WUV.m^{-2}) in a time period of 4h (240) min. The TOC profiles allow simultaneous monitoring of the mineralization of pyrimethanil as a function of time. This mineralization is between 30% and 50% in the same time interval and represents only 70% for 6 hours of irradiation. It can, therefore, be concluded that the kinetics of degradation is dependent of irradiation, as it is a factor of importance that can be limiting.

Kinetic aspects of industrial catalysts

The degradation of the target molecule was monitored under the same conditions with two industrial media, namely, the TiO_2 nanoparticles, which is the reference catalyst (Degussa P-25) and the TiO_2 impregnated cellulosic tissue with lower performances but Easy to implement (Ahlstrom, grad 1048). In order to define media processing capacities, it is necessary to determine the kinetics representative of the process of photodegradation. Since there is no universal kinetic law to describe the process of photodegradation, many laws are proposed in the literature expressing the dependence of velocity on concentration and intensity [Goetz et al (2009), Emeline and Al (2000)]. To facilitate the processing of the photocatalytic responses and to obtain a quantitative comparison criterion, we will work mainly on the initial kinetics which will be treated according to a pseudo-first order law with a kinetic "constant" depending on the irradiation. A pseudo-first order kinetics leads to equation 1 [Correia (2011), Emeline et al. (2000)].

$$\frac{C}{C_0} = \exp\left(-k(I)t\right) \qquad \textbf{(1)}$$

C Concentration in the reactor (mg.L^{-1})
C_0 Initial Concentration (mg.L^{-1})
K Kinetic Constant (mn^{-1})
I Intensity (W.m^{-2})
T Duration of Irradiation (min)

For each intensity studied, the expression of the natural logarithm of the C/Co ratio as a function of time is represented by a line whose steering coefficient k (I) varies as a function of intensity. The figures (FIGS. 5 and 6) indicate the results obtained for the degradation of the target molecule for the two industrial catalysts considered.

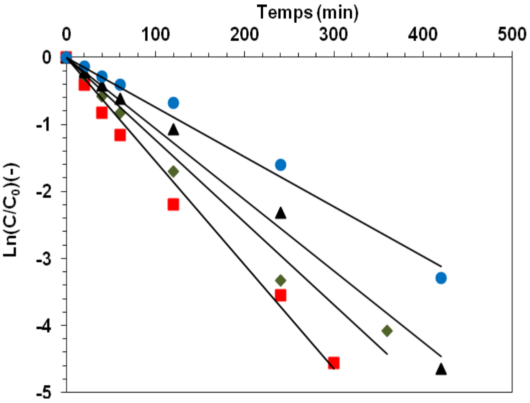


Figure 5: Expression of the logarithm of the relative pyrimethanil concentration as a function of time (min) for different irradiations (WUV.m^{-2}): 9(●), 17(▲), 27(♦),35(■) by the catalyst P-25

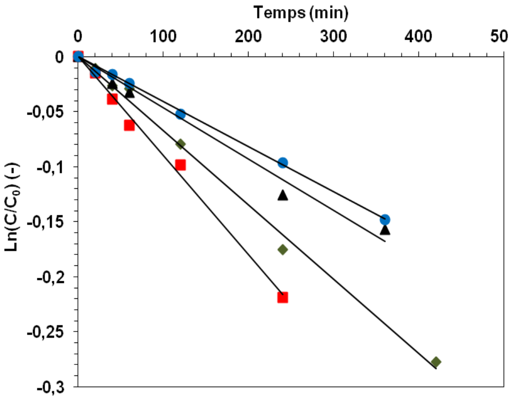


Figure 6: Expression of the logarithm of the relative pyrimethanil concentration as a function of time (min) for different irradiations (WUV.m^{-2}): 9(●), 17(▲), 27(♦),35(■) by the catalyst Ahlstrom

To express the dependence of the degradation rate on the light intensity, the kinetic constant k is extracted from the kinetics from equation 1. The kinetic pseudo-constants of k (I) are shown in the figures (Figures 7 and FIGS. 8) as a function of the irradiation. The results obtained show proportionality between the kinetic constant and the intensity. The linear dependence of the kinetic "constants" of pyrimethanil degradation and mineralization (TOC) as a function of irradiation for the P-25 catalyst is supported by correlation coefficients of 0.99 for pyrimethanil and 0.95 For the TOC. In the case of the Ahlstrom catalyst, our results indicate that the kinetic "constant" as a function of irradiation evolves in the same way. The correlation coefficients are respectively 0.94 and 0.99 for pyrimethanil and TOC.

As expected, the rate of degradation increases with the intensity of irradiation for the two catalysts studied and the only differences are the higher rate constants for P-25 than for the Ahlstrom catalyst. These results are in agreement with those obtained for the kinetics of degradation of polluting molecules [Malato et al (2009), Huang et al (2000)]. It is noted that the velocity changes linearly as a function of the intensity applied to the irradiation domain considered corresponding to the range of solar irradiation.

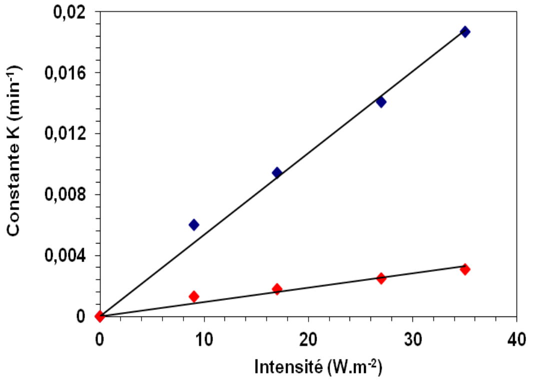


Figure 7: Evolution of the degradation kinetics of pyrimethanil (♦) and TOC (♦) as a function of the irradiation (WUV.m-2) by the catalyst P-25

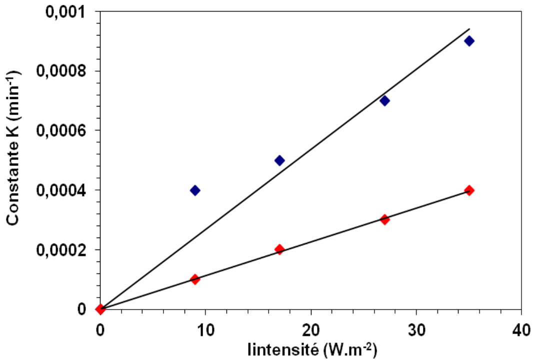


Figure 8: Evolution of the degradation kinetics of pyrimethanil (♦) and TOC (♦) as a function of the irradiation (WUV.m-2) by the catalyst Ahlstrom

C. The kinetic "constants" of degradation of pyrimethanil and TOC obtained for irradiation of 35WUV.m^{-2} using catalyst P-25 show a ratio between them, this ratio approaches 4 for an irradiation of 10 WUV.m-2. The same remark is also required for the Ahlstrom catalyst with higher degradation constants than the mineralization constants. This difference is related to the measured phenomenon. Mineralization involves degradation of the target molecule and by-products. As a result, the process is slower and involves greater consumption of radicals**.**

D. Accumulated energy

When one wishes to envisage an operation of depollution directly from solar energy, it is interesting, as for any process based on the use of this resource, to compare the performances as a function of the amount of energy received. Indeed, as has been shown, the catalysts integrated into a photoreactor, develop performances highly dependent on the irradiation conditions (FIG. 7 and FIG. 8). The solar resource available at the surface of the earth is inherently intermittent (weather hazards, monthly and seasonal cycles of sunshine) [Galvez et al. (2003)], the time-based processing capacities established in the case of Our experiments under constant UV radiation are therefore not directly representative of the external irradiation conditions. A direct comparison of the experiments is nevertheless possible whatever the irradiation conditions (artificial irradiation at different intensities or solar irradiation) subject to expressing the concentration profiles of pyrimethanil and TOC depending on the UV energy received or accumulated By a unit of reactor volume. This magnitude is expressed in equation 2 originally proposed by Blanco et al (2003).

$$Q_{uv} = \frac{S}{V_T} . \int_0^{t_i} I(t).dt \quad \textbf{(2)}$$

Is the energy accumulated at each instant ti (min) where a sample is taken during the experiment, I (t) is the irradiation provided by the UV lamps (Wm-²), S (55.4 cm^3 for the reactor in the "loop" circuit), VT is the total volume of solution to be treated (1 L in our case). The results will be expressed as a function of the accumulated energy per liter of solution to be treated.

The pollutant concentration profiles as a function of the amount of energy are shown in FIGS. 9 and 10. In the irradiation domain considered corresponding to the intensity range received at the surface of the earth, it can be seen that the velocity of degradation depends on the quantity of photons received independently of the intensity applied.

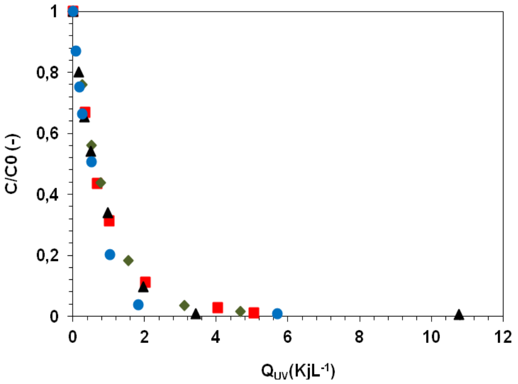


Figure 9: Evolution of the pyrimethanil concentration as a function of the accumulated energy per liter of solution to be treated with the catalyst P-25

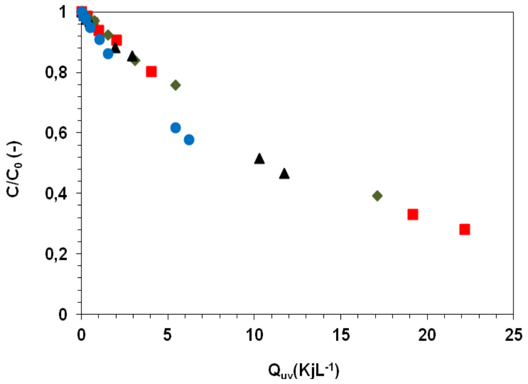


Figure 10: Evolution of the pyrimethanil concentration as a function of the accumulated energy per liter of solution to be treated with the catalyst Ahlstrom

IV. CONCLUSION

The results obtained for the degradation of the target molecule and its mineralization (TOC) as a function of the different irradiations that cover the intensity range of solar UV radiation show the preponderant influence of this parameter on the operation of the process. In accordance with the results obtained in the literature [Herrmann (1999), Malato et al. (1996)], it appears that the degradation kinetics obtained with the suspension is very much superior to those obtained with the supported media. The representation of the concentration profiles as a function of the accumulated energy which results for each of the media in a single curve irrespective of the intensity of irradiation demonstrates experimentally all the importance related to the management of the photon transfer which constitutes the real engine of the photocatalytic phenomenon.

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