

Article

# Photocatalytic Efficiency of Suspended and Immobilized TiO<sub>2</sub> P25 for Removing Myclobutanil, Penconazole and Their Commercial Formulations

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**ABSTRACT:** Fungicide application in viticulture is a major source of surface and groundwater contamination. It is therefore essential to find solutions to stop this environmental pollution. Heterogeneous photocatalysis is an advanced oxidation method for the degradation and mineralization of organic pollutants in water. TiO<sub>2</sub> P25 photocatalyst in suspension has been used for removing the fungicides Myclobutanil and Penconazol, and their respective commercial formulations Systhane and Topas, in contaminated water. The apparent kinetic constants  $k_{app}$  of fungicides removal over 30 min batch treatment was higher for a mixture of pure molecules of Myclobutanil and Penconazol than for a mixture of their commercial formulations ( $17.5 \times 10^{-3}$  by comparison with  $10.3 \times 10^{-3} \text{ min}^{-1}$  for Myclobutanil, and  $10.0 \times 10^{-3}$  by comparison with  $2.80 \times 10^{-3} \text{ min}^{-1}$  for Penconazol). TOC removal constants  $k_{TOC}$  were similar for the two mixtures, due to the presence of mineral and organic additives in the commercial formulations. To easily recover the photocatalyst after fungicide removal, TiO<sub>2</sub> P25 has been supported on  $\beta$ -SiC foam. Fungicides degradation was lower with supported photocatalysts than with the suspension of photocatalyst nanoparticles (NPs) because of a lower concentration of active sites on the supported photocatalyst than in the catalyst suspension. However, catalyst recovery and reuse after fungicide removal is obviously easier with TiO<sub>2</sub>/ $\beta$ -SiC material than with a suspension of TiO<sub>2</sub> which requires long and expensive filtration operations.

**Keywords:** Fungicides; Photocatalysis; Myclobutanil; Penconazol; TiO<sub>2</sub>/ $\beta$ -SiC



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## 1. Introduction

While the world is facing a drastic increase in water requirements, several water sources are contaminated with organic pollutants, and therefore unsuitable for consumption. Pollution generally arises from industrial, household and agricultural activities. In viticulture, the use of fungicides has tremendously increased in the recent years [1]. A study conducted under the aegis of the French Ministry for Ecological and Inclusive Transition reveals an alarming increase in sales of insecticides, fungicides, and herbicides for 10 years in France (for example, the sales of fungicides increased by 41%) [1]. Their use by several actors in the agricultural world is responsible for health and environmental problems. This is how in-situ, soils are found with high levels of these chemicals. Pesticides drainage into water tables and water currents strongly contribute to water pollution. Aquatic species and humans are exposed to these toxic pollutants.

It is therefore urgent to effectively treat water contaminated by fungicides, for making it suitable for consumption. The ideal and economical treatment would consist (after filtration, decantation of suspended particles and solid waste) in biological removal or even mineralization of fungicides. Unfortunately, this type of treatment has its limits because there are often recalcitrant organic products which cannot be eliminated this way [2]. Simple and inexpensive solutions are then strongly required for removing these

types of pollutants. By keeping this in mind, the scientific community has effectively developed oxidation techniques called Advanced Oxidation Processes (AOP) [3] over the past twenty years. These technologies have already shown their effectiveness in the treatment of toxic and "biologically recalcitrant" organic pollutants. These processes are based on the in-situ formation of hydroxyl radicals  $\text{HO}^\bullet$  [4] which have an oxidizing power greater than that of traditional oxidants such as  $\text{H}_2\text{O}_2$  [5],  $\text{Cl}_2$  [6], or  $\text{O}_3$  [7]. These radicals are capable of partially (or totally) mineralizing most organic compounds. Among these AOPs, special attention has been paid to heterogeneous  $\text{TiO}_2/\text{UV}$  photocatalysis [8,9], due to its ability to mineralize a wide range of recalcitrant organic pollutants at room temperature and at atmospheric pressure into harmless substances [10]. Several studies have been done using titanium dioxide in suspension [11,12]. However, the post-treatment recovery of  $\text{TiO}_2$  is a difficult process to achieve due to the nanometer-size photocatalyst and the cost this can entail. Therefore, filtration and re-suspension of  $\text{TiO}_2$  should be avoided in a wastewater treatment process. Therefore, the idea of immobilizing  $\text{TiO}_2$  on a suitable and chemically inert support has started to emerge because it could avoid the expensive process of phase separation [13,14]. However, the surface of the photocatalyst is active only when illuminated by light. Thus, heterogeneous systems often suffer from mass transfer limitation due to the reduction in specific surface area of  $\text{TiO}_2$  compared to homogeneous systems. However, it should be noted that catalysts immobilization on substrates remains currently a promising alternative in heterogeneous photocatalysis.

The use of  $\beta$ -form ( $\beta$ -SiC) silicon carbide cellular foams in 3D as a macroscopic support for  $\text{TiO}_2$  P25, is the subject of our work. These foams have very interesting characteristics such as their good mechanical and thermal resistance, chemical inertness, excellent hydrodynamic properties, and above all a large specific surface area ( $20 \text{ m}^2 \cdot \text{g}^{-1}$ ). Previous studies have been carried out by removing recalcitrant organic compounds in the presence of the  $\text{TiO}_2/\beta$ -SiC material [11,15–17]. The objective of the present work is to compare the photocatalytic activity of  $\text{TiO}_2$  P25 in slurry (batch mode) with that of  $\text{TiO}_2$  P25 supported onto  $\beta$ -SiC (recirculation mode), for the removal of a mixture of either pure molecules of Myclobutanil and Penconazol, or commercial formulations of these fungicides. To do this, we have built a photoreactor to remove and mineralize these organic compounds in water under irradiation of artificial UV-A lamps.

## 2. Materials and Methods

### 2.1. Chemicals and Materials

Penconazol ( $\text{C}_{13}\text{H}_{15}\text{N}_3\text{Cl}_2$ , 1-(2,4-dichloro- $\beta$ -propylphenetyl)-1*H*-1,2,4-triazole according to IUPAC, 99.9%, Techlab), Topas commercial formulation ( $100 \text{ g} \cdot \text{L}^{-1}$ , 10.2% Penconazol, Bayer-BASF), Myclobutanil ( $\text{C}_{15}\text{H}_{15}\text{N}_4\text{Cl}$ , 99.9%, (RS)-2-p-chlorophenyl-2-(1*H*-1,2,4-ylmethyl) hexanenitrile from Techlab), Systhane<sup>TM</sup> 20EW commercial formulation ( $100 \text{ g} \cdot \text{L}^{-1}$  Myclobutanil from Bayer), were used as received. Aeroxide  $\text{TiO}_2$  P25 nanoparticles were supplied by Evonik (size of primary nanoparticles ranged from 10 to 50 nm, largely distributed from 15 to 25 nm, and their BET surface area was  $60.8 \text{ m}^2/\text{g}$ ). The exact phase composition of  $\text{TiO}_2$ -P25 has been determined to be anatase (77.1%), rutile (15.9%) and amorphous  $\text{TiO}_2$  (7.0%) [18]. Ethanol anhydride (99.8%, FLUKA) and titanium tetraisopropoxide (TTIP,  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ , 97%, SIGMA ALDRICH) were used without purification. Distilled water was used to prepare all the solutions.

### 2.2. Photocatalytic Tests with $\text{TiO}_2$ P25 in Slurry

Batch mode experiments were conducted at room temperature in a glass cylinder reactor with aqueous solutions (Penconazol/Topas, Myclobutanil/ Systhane<sup>TM</sup>, mixtures) under UV-vis irradiation. The ATLAS Suntest CPS solar case simulating natural radiation and equipped with a xenon vapor lamp was used in all experiments. The photocatalyst  $\text{TiO}_2$  P25 powder [10] was introduced into 200 mL of fungicide solution (Penconazol/Topas, Myclobutanil/ Systhane<sup>TM</sup>, mixture) (between  $10 \text{ mg} \cdot \text{L}^{-1}$  and  $20 \text{ mg} \cdot \text{L}^{-1}$ ) up to a final concentration of  $0.75 \text{ g} \cdot \text{L}^{-1}$ , and the slurry was homogenised by stirring. Before irradiation, suspensions were kept in the dark for 30 min to reach the adsorption equilibrium. During the irradiation procedure, 10 mL of solution were taken at regular intervals and filtered (Whatmann, 0.45 mm). Concentrations of fungicides remaining after irradiation were determined with a LIBRA S12 UV-vis spectrophotometer ( $\lambda = 215 \text{ nm}$ ), and by TOC analysis (SHIMADZU TOC-L).

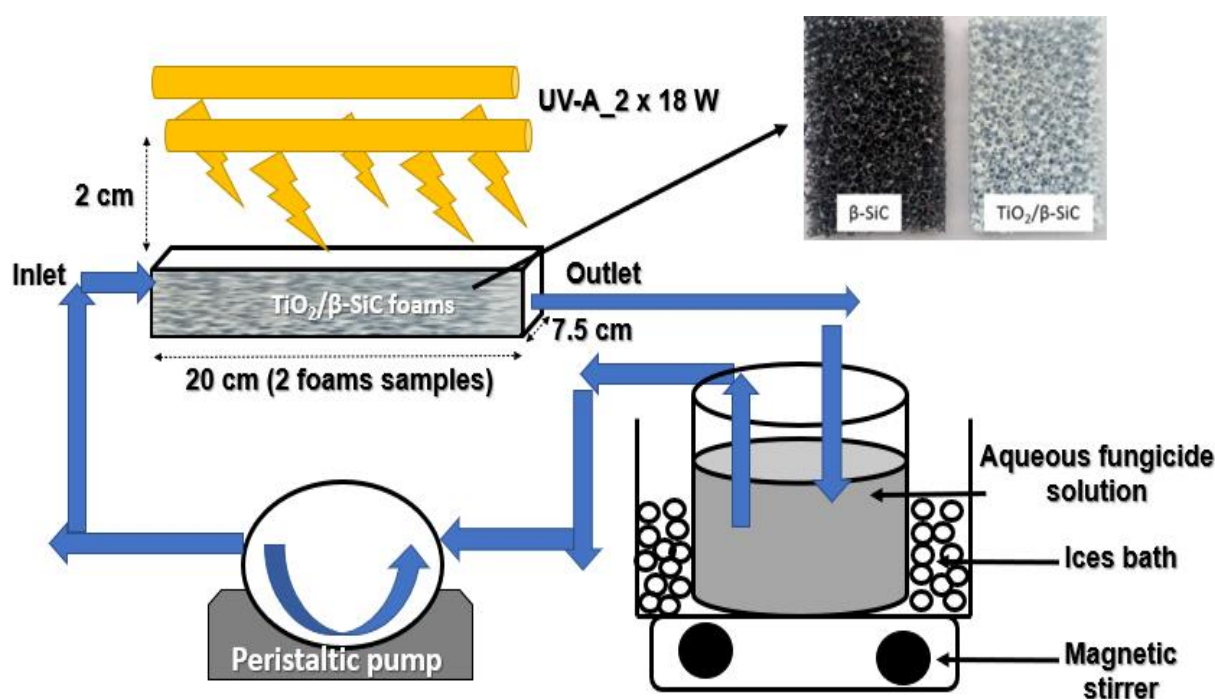
### 2.3. Preparation of $\text{TiO}_2/\beta$ -SiC by Dip Coating Method

Alveolar foams of  $\beta$ -SiC have been synthesized and supplied by SICAT company (Willstätt, Germany). Foam samples have a size of 9.5 cm (length)  $\times$  6 cm (width)  $\times$  1 cm (thickness), with a weight of about 20 g and a cell size of 4.5 mm. The foam was calcined at  $1000 \text{ }^\circ\text{C}$  for 2 h to remove residual organic carbon. Each  $\beta$ -SiC foam sample was completely immersed in the  $\text{TiO}_2$  P25 slurry (10 g  $\text{TiO}_2$  P25 and 4 mL TTIP in 200 mL ethanol) for 5 min. Photocatalytic materials were dried at room temperature for 20 min, avoiding clogging of the cells.  $\text{TiO}_2/\beta$ -SiC foams were introduced in an oven at  $110 \text{ }^\circ\text{C}$  overnight to evaporate residual organic compounds. The temperature was then increased at  $450 \text{ }^\circ\text{C}$  for 2 h at a rise rate of  $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . The average wt% of  $\text{TiO}_2$  P25 per foam was about 7.5%, which corresponds to 1.5 g of  $\text{TiO}_2$  P25 fixed on the support [16].

Photocatalytic materials were characterized by scanning electron microscopy (SEM). SEM was performed in secondary electron mode on a JEOL-JSM-6700 microscope equipped with a field emission gun and operating with an extraction potential, between 1 and 10 kV.

#### 2.4. Photocatalytic Tests with $\text{TiO}_2$ P25 Supported onto $\beta$ -SiC Foam

Photocatalytic experiments were performed in a polypropylene recirculation mode photoreactor measuring 20 cm (length)  $\times$  7.5 cm (width)  $\times$  2.5 cm (depth). Two samples of  $\text{TiO}_2/\beta$ -SiC foam (10 cm (length)  $\times$  6 cm (width)  $\times$  1.5 cm (depth)) were introduced in the photoreactor to carry out the photocatalytic tests. The photoreactor was covered with quartz plates. Two UV-A lamps (Philips 18 W) were horizontally disposed 2 cm above the reactor to illuminate  $\text{TiO}_2/\beta$ -SiC photocatalysts (Figure 1). The irradiation wavelength was about  $368 \pm 20$  nm with an irradiance of about  $60 \text{ W}\cdot\text{m}^{-2}$  (radiometer, spectral range: 315–400 nm, HD 9021, Delta OHM, Italy). Fungicide solutions ( $10 \text{ mg}\cdot\text{L}^{-1}$ ) were circulated through the reactor system using a peristaltic pump (Master Flex, model 7520-47) at a flow rate of  $26 \text{ mL}\cdot\text{min}^{-1}$ , with a residence time of 12 min. Before each irradiation,  $\text{TiO}_2/\beta$ -SiC was maintained for 1 h in the dark. Concentrations of fungicides remaining after irradiation were determined with a UV-vis spectrophotometer and TOC analysis without filtration.



**Figure 1.** Experimental photocatalytic device with  $\text{TiO}_2/\beta$ -SiC.

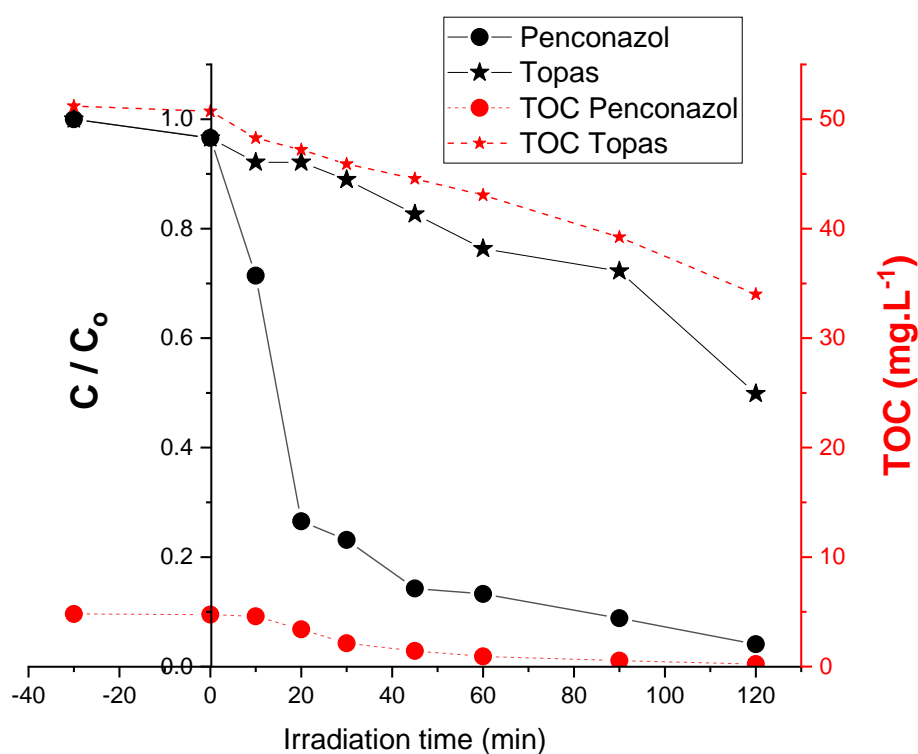
### 3. Results and Discussion

#### 3.1. Photocatalytic Degradation of Pure Penconazol and of Topas Formulation

##### 3.1.1. With the $\text{TiO}_2$ P25 Photocatalyst Suspension

Photocatalytic elimination kinetics of Penconazol and its commercial formulation Topas, were determined with  $\text{TiO}_2$  P25 in suspension. Figure 2 shows the fungicide disappearance, as well as TOC variation as a function of irradiation time. According to Table 1, the apparent rate constant of Penconazol disappearance  $k_{pen}$  is approximately five times greater than that ( $k_{top}$ ) of Topas solution. After one-hour treatment, 86.74% of Penconazol are eliminated in the pure molecule solution whereas only 23.66% of the fungicide is removed from the commercial Topas formulation. Remember that Penconazol represents approximately 10.20% by mass of Topas solution, the remaining 89.80% comprising cyclohexanone and 2-methylpropanol. During the treatment, OH free radicals responsible for the molecular degradation, attack both Penconazol molecules and the additives. These additives compete on the active sites of the  $\text{TiO}_2$  P25 photocatalyst. Therefore, degradation kinetics of Penconazol are slower in Topas formulation than in the pure molecule solution.

On the other hand, the comparison of TOC variations shows that during 60 min, the mineralization rate constant is approximately two times greater for Topas than for Penconazol (Table 1). As indicated above, the additives present in the Topas solution participate to the kinetics of molecules removal. Hence, TOC elimination is higher in the commercial formulation than in the pure molecule solution.



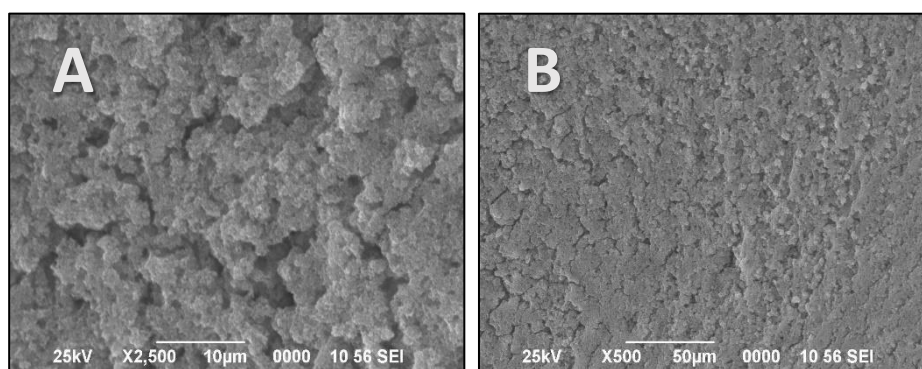
**Figure 2.** Photocatalytic degradation kinetics and TOC variation of a pure Penconazol solution and of Topas formulation using TiO<sub>2</sub> P25 photocatalysts in slurry.

**Table 1.** Removal Rate of Penconazol and TOC in pure solution and in Topas formulation by TiO<sub>2</sub> P25 in slurry over 60 min of UV-A irradiation.

Photocatalytics Parameters	Pur Penconazol	Topas Formulation
$k_{app} (\text{min}^{-1}) \times 10^{-3}/R^2$	51.2/0.98	2.80/0.98
Percentage of Penconazol removed	86.73%	23.66%
$k_{TOC} \times 10^{-3} (\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1})/R^2$	68.9/0.98	139.2/0.98
Percentage of TOC removed	80.78%	15.88%

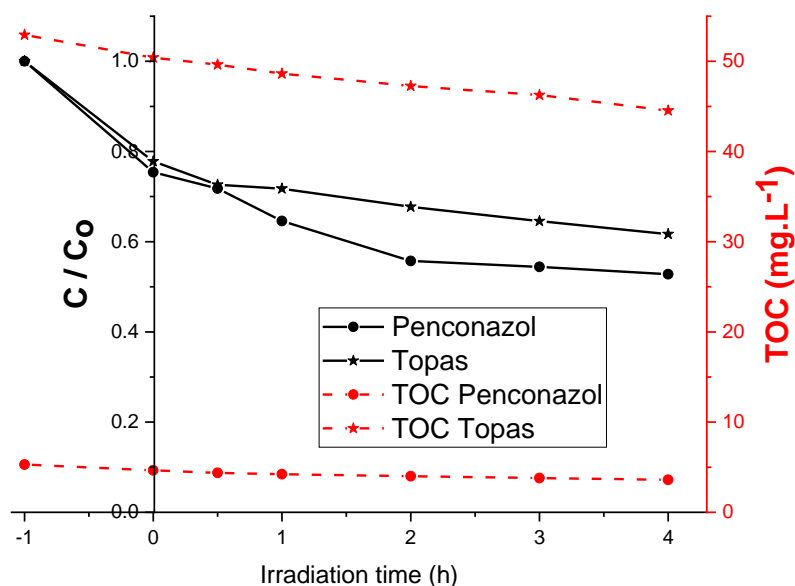
### 3.1.2. Photocatalytic Degradation with Supported TiO<sub>2</sub>/β-SiC Photocatalyst

Morphologies of TiO<sub>2</sub>/β-SiC materials were characterized by SEM. SEM picture (Figure 3A) of the TiO<sub>2</sub> film on the support prepared without TTIP [19] shows cracks at the surface of the material. This is due to drying the material at room temperature (dip-coating phase) or to the calcination phase at 450 °C, because thermal expansion coefficients of the support and the catalyst are different. However, in the presence of TTIP, the surface is more homogeneous (Figure 3B), showing that the addition of TTIP to the TiO<sub>2</sub> suspension improved the stability of the catalyst film on the support, since TTIP acts as a binder. Photocatalytic materials prepared with TTIP were used to perform all photocatalytic experiments for the removal of Penconazol and its commercial formulation Topas.



**Figure 3.** SEM pictures of the surface of TiO<sub>2</sub> P25 films coated on β-SiC alveolar foams with (A) without addition of TTIP and (B) addition of TTIP in TiO<sub>2</sub> slurry.

Kinetics of photocatalytic degradation of Penconazol (pure and in Topas) by the  $\text{TiO}_2/\beta\text{-SiC}$  material are shown in Figure 4. UV measurements at 215 nm performed for determining disappearance kinetics of the active molecule show similar adsorption percentages for Penconazol (24.59%) and Topas (22.19%), after one-hour adsorption in the dark. However, TOC determinations show a decrease of  $2.52 \text{ mg}\cdot\text{L}^{-1}$  and  $0.64 \text{ mg}\cdot\text{L}^{-1}$  TOC for Topas and Penconazol respectively, after one hour adsorption. This difference reflects the adsorption of the additives present in the commercial formulation. Over 4 h irradiation, Penconazol degrades faster than Topas (Figure 4). However, after 2 h irradiation, the degradation rate of pure Penconazol decreases because of the competition existing between by-products and the molecule on the active sites of the photocatalyst. In the literature, Penconazol molecule is stable and hardly biodegradable in an aqueous medium. Therefore, the amount of TOC removed is four times lower than for Topas (Table 2).



**Figure 4.** Photocatalytic degradation's kinetics and TOC variation of a pure Penconazol solution and of Topas formulation by the use of  $\text{TiO}_2/\beta\text{-SiC}$ .

**Table 2.** Removal rate of Penconazol and TOC in pure solution and in Topas formulation by the use of  $\text{TiO}_2/\beta\text{-SiC}$  over 60 min of UV-A irradiation.

Photocatalytic Parameters	Pur Penconazol	Topas Formulation
$k_{\text{app}} \times 10^{-3} (\text{min}^{-1}) R^2$	3.59/0.97	2.89/0.92
Percentage of Penconazol removed	35.41%	28.24%
$k_{\text{TOC}} \times 10^{-3} (\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1})/R^2$	9.18/0.98	35.67/0.99
Percentage of TOC removed	20.23%	8.13%

### 3.2. Photocatalytic Degradation of Myclobutanil in Pure Solution and in Systhane<sup>TM</sup> Formulation

#### 3.2.1. With $\text{TiO}_2$ P25 Suspension

Results of photocatalytic degradation of Myclobutanil in pure solution and in commercial formulation with  $\text{TiO}_2$  P25 in suspension were obtained by M'Bra et al. [11]. They are summarized in Table 3 and were obtained under the following optimal experimental conditions:  $C_0 = 10 \text{ ppm}$ ;  $\text{pH} = 6.7$ ;  $C_{\text{TiO}_2} = 0.75 \text{ g}\cdot\text{L}^{-1}$ ;  $V_{\text{solution}} = 200 \text{ mL}$ ; Irradiation time = 120 min; UV-vis irradiation in batch mode.

The authors have shown that Myclobutanil degraded faster in a pure aqueous solution ( $41.4 \times 10^{-3} \text{ min}^{-1}$ ) than in the commercial Systhane formulation ( $21.2 \times 10^{-3} \text{ min}^{-1}$ ). Like for Penconazol, the percentage of TOC removed is lower with Systhane than with the solution of pure Myclobutanil, which is explained by the presence of organic additives in the commercial formulation.

**Table 3.** Removal rate of Myclobutanil and TOC in pure solution and in Systhane formulation by the use of  $\text{TiO}_2$  P25 in slurry over 60 min of UV-A irradiation.

Photocatalytic Parameters	Pur Myclobutanil	Systhane <sup>TM</sup> Formulation
$k_{\text{app}} (\text{min}^{-1}) \times 10^{-3}/R^2$ after 30 min	41.4/0.98	21.2/0.99
Percentage of Myclobutanil removed	91.15%	90.38%
$k_{\text{TOC}} \times 10^{-3} (\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1})/R^2$	70.2/0.98	88.5/0.98
Percentage of TOC removed	89.45%	56.89%

### 3.2.2. Photocatalytic Degradation with Supported TiO<sub>2</sub>/β-SiC Photocatalyst

Results of photocatalytic degradation of Myclobutanil and its commercial formulation with TiO<sub>2</sub>/β-SiC are shown in Table 4. They were obtained under the following optimal experimental conditions: two TiO<sub>2</sub>/β-SiC samples; C<sub>0</sub> = 10 ppm; pH = 6.7; Flow rate = 26 mL·min<sup>-1</sup>; V<sub>solution</sub> = 500 mL; Irradiation time = 4 h; UV-A irradiation in the recirculation mode (Figure 1).

The authors have shown that Myclobutanil in pure solution degraded faster ( $5.24 \times 10^{-3} \text{ min}^{-1}$ ) than in Systhane formulation ( $3.20 \times 10^{-3} \text{ min}^{-1}$ ), due to the presence of organic additives which compete with the degradation of Myclobutanil in Systhane formulation. Degradation rate constants are lower in the case of the TiO<sub>2</sub>-P25 photocatalyst supported on β-SiC than in suspension. This is explained on the one hand by the decrease in the available surface of supported TiO<sub>2</sub> particles compared to the suspension and on the other hand by a recirculation reactor system which causes a dead volume of non-irradiated fungicide solution.

**Table 4.** Removal rate of Myclobutanil and TOC in pure solution and in Systhane™ formulation by the use of TiO<sub>2</sub>/β-SiC over 60 min of UV-A irradiation.

Photocatalytic Parameters	Pur Myclobutanil	Systhane™ Formulation
$k_{\text{app}} (\text{min}^{-1}) \times 10^{-3}/R^2$	5.24/0.99	3.20/0.99
Percentage of Systhane removed	32.51%	44.72%
$k_{\text{TOC}} \times 10^{-3} (\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1})/R^2$	10.71/0.98	21.71/0.98
Percentage of TOC removed	18.63%	19.29%

### 3.3. Photocatalytic Degradation of Fungicide Mixtures

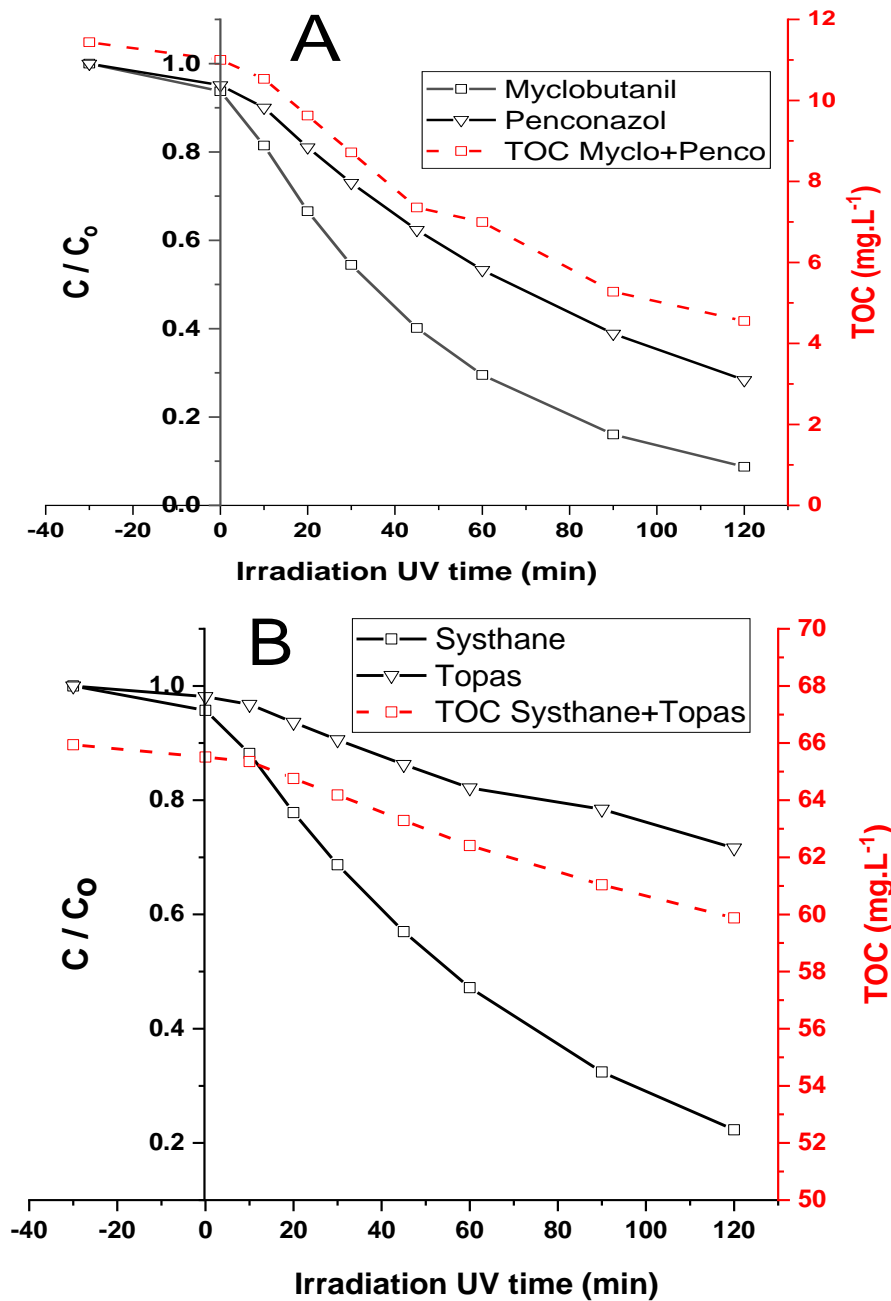
Among the numerous fungicide treatments carried out on vineyards, there is often an association of two fungicides. It is therefore important to evaluate the performance of photocatalytic degradation process on mixtures of pure active molecules (Penconazol and Myclobutanil) but also on mixtures of their Topas and Systhane commercial formulations. We believe that our study will complement the work undertaken by Pichat et al. in 2004 [20].

#### 3.3.1. Photocatalytic Degradation of Fungicide Mixtures with TiO<sub>2</sub> P25 Suspension

Figure 5 shows degradation kinetics of Myclobutanil and Penconazole mixtures in pure solutions (Figure 5A) and in mixtures of commercial Systhane and Topas formulations (Figure 5B). After 30 min adsorption, removal rates of the active compounds are 6.26% and 4.89% respectively for Myclobutanil and Systhane; 4.28% and 1.86% respectively for Penconazol and Topas. During irradiation in presence of TiO<sub>2</sub>-P25 suspensions, mixtures of pure fungicides degrade faster than when present in their commercial formulations. Table 5 shows the various fungicide removal rates, as well as their apparent disappearance and mineralization rate constants. More TOC was removed from the commercial mixture than from the pure fungicide mixture. This result is due to the presence of additives in the commercial mixture, because the radicals attack not only the fungicides, but also the additives.

**Table 5.** Removal rates of Myclobutanil/Penconazol mixtures and TOC in pure solutions and in mixtures of Systhane and Topas commercial formulations, by the use of TiO<sub>2</sub> P25 suspension over 60 min irradiation.

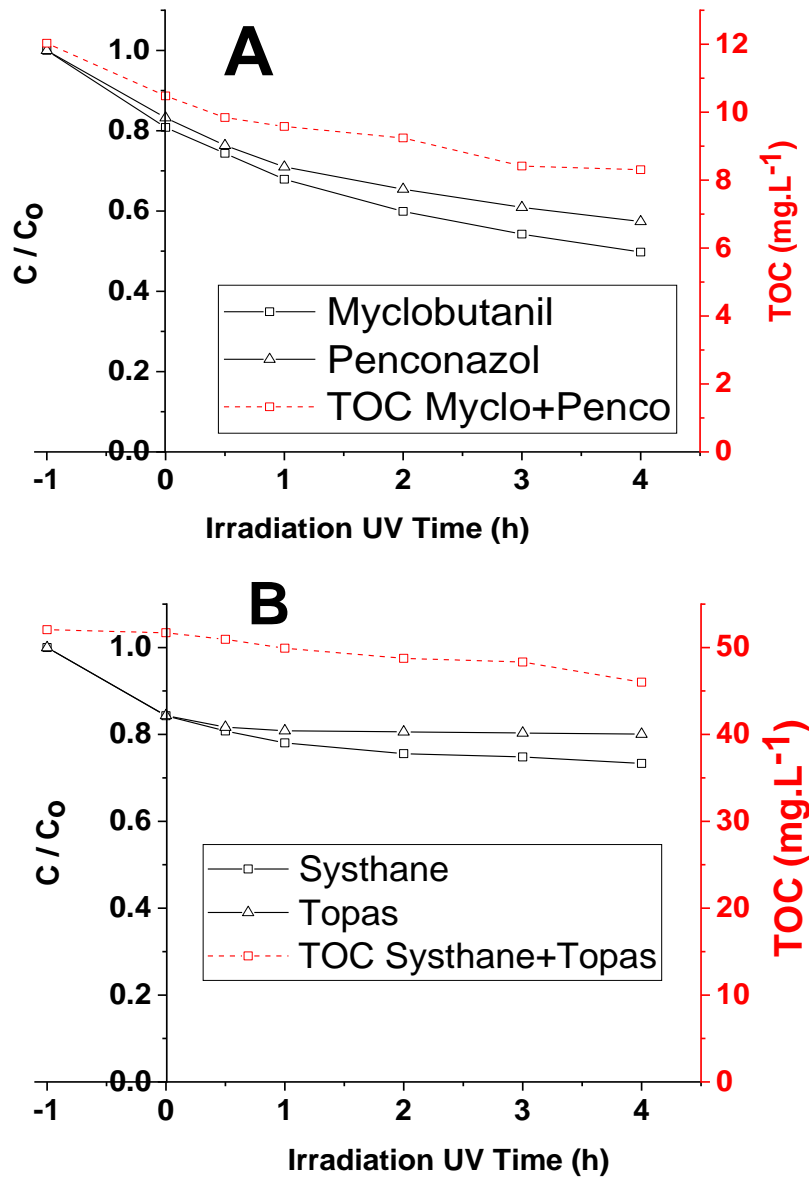
Photocatalytic Parameters	Pure Fungicides Mixture		Commercial Fungicides Mixture	
	Myclobutanil	Penconazol	Systhane™	Topas
$k_{\text{app}} \times 10^{-3} (\text{min}^{-1})/R^2$ after 30 min	17.50/0.99	10.00/0.99	10.3/0.98	3.28/0.98
Percentage of fungicide removed	70.48%	46.74%	52.82%	17.86%
$k_{\text{TOC}} \times 10^{-3} (\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1})/R^2$	63.90/0.98		62.10/0.98	
Percentage of TOC removed	47.58%		5.35%	



**Figure 5.** Photocatalytic degradation kinetics of mixtures of (A) pure solutions of Myclobutanil-Penconazol and (B) Systhane-Topas commercial formulations, by the use of TiO<sub>2</sub> P25 suspension.

### 3.3.2. Photocatalytic Degradation of Fungicide Mixtures with Supported TiO<sub>2</sub>/β-SiC Photocatalyst

Figure 6 shows degradation kinetics of Myclobutanil-Penconazole in mixtures of pure solutions (Figure 6A) and of Systhane and Topas commercial formulations (Figure 6B). After one-hour adsorption, removal rates of the active compounds are almost similar for the two mixtures. Proportions of fungicide removed are 19.20% and 15.71% for Myclobutanil and Systhane, respectively, and 16.78% and 15.63% for Penconazol and Topas, respectively. When TiO<sub>2</sub>/β-SiC materials are irradiated, pure fungicide mixtures degrade faster than when present in their commercial formulations. Table 6 shows the various rates of fungicide removal, as well as their apparent disappearance and mineralization rate constants. Results show a higher TOC removal in the commercial mixture than in the pure fungicide mixture. This phenomenon was observed with TiO<sub>2</sub> P25 nanoparticles in suspension. Thus, additives of the commercial mixture disrupt the action of OH<sup>•</sup> radicals on active compounds. Radicals attack not only fungicides but also additive compounds. Therefore, degradation and removal kinetics of TOC molecules decrease (Tables 5 and 6).



**Figure 6.** Photocatalytic degradation kinetics by the use of TiO<sub>2</sub>/β-SiC (A) of a Myclobutanil-Penconazol mixture and (B) of a Systhane-Topas mixture.

**Table 6.** Removal rates of Myclobutanil/Penconazol and TOC, in a mixture of pure fungicide solution and of Systhane and Topas commercial formulations, in recirculation mode by TiO<sub>2</sub>/β-SiC over 60 min of UV-A irradiation.

Photocatalytic Parameters	Pure Fungicides Mixture		Commercial Fungicides Mixture	
	Myclobutanil	Penconazol	Systhane™	Topas
$k_{app} \times 10^{-3} \text{ (min}^{-1})/R^2$	3.23/0.99	2.88/0.99	2.10/0.98	1.83/0.98
Percentage of fungicide removed	32.10%	29.02%	21.95%	19.14%
$k_{TOC} \times 10^{-3} \text{ (mg} \cdot \text{L}^{-1} \cdot \text{min}^{-1})/R^2$	21.13/0.98		17.13/0.98	
Percentage of TOC removed	20.38%		4.11%	

#### 4. Conclusions

The present work assessed the efficiency of photocatalytic degradation of active molecules of pure fungicides (Myclobutanil and Penconazol) in aqueous solution but also by their commercial formulations (Topas and Systhane). Two photocatalytic systems were used, the first with TiO<sub>2</sub>-P25 suspended in water and the second with TiO<sub>2</sub>-P25 supported on β-SiC foams, under UV-vis irradiation. Results showed slower degradation kinetics of the active molecules with the supported photocatalysts than with TiO<sub>2</sub> in suspension. This is a logical result because active sites of the supported photocatalyst are reduced compared to the suspended catalyst. However, TiO<sub>2</sub>/β-SiC material can be easily recovered and reused after fungicide degradation, whereas TiO<sub>2</sub> P25 recovery in slurry requires long and expensive filtration operations.



Fungicide removal with the supported photocatalyst led to a significant reduction in the concentration of pure active molecules with reasonable treatment times and irradiance (about 50% fungicide degradation in 2 h under our conditions). Concerning the processing of commercial formulations, degradation kinetics of the active molecules were slower due to the presence of mineral and organic additives. Nevertheless, our results have shown that it is possible to degrade and mineralize commercial formulations of fungicides. We think these results are encouraging for photocatalytic removal of fungicides removal at industrial scale, especially when using the TiO<sub>2</sub>/β-SiC material which can easily be recycled. Our future work will consist on the one hand in assessing interactions of the components of fungicide formulations on the photocatalytic performances of our system, and on the other hand in optimizing the process in order to reduce the processing time of commercial formulations of fungicides.

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### Author Contributions

Conceptualization, N.K. and D.R.; Methodology, I.C.M. and D.R.; Formal Analysis, I.C.M. and D.R.; Writing—Original Draft Preparation, I.C.M.; Writing—Review & Editing, D.R.; Supervision, A.T. and D.R.; Project Administration, N.K.; Funding Acquisition, N.K. and D.R.

### Ethics Statement

Not applicable.

### Informed Consent Statement

Not applicable.

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### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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