



HAL
open science

Photocatalytic Degradation of Myclobutanil and Its Commercial Formulation with TiO₂ P25 in Slurry and TiO₂ / β -SiC Foams

Ignace Christian M'bra, Didier Robert, Nicolas Keller, Patrick Drogui, Albert Trokourey

► To cite this version:

Ignace Christian M'bra, Didier Robert, Nicolas Keller, Patrick Drogui, Albert Trokourey. Photocatalytic Degradation of Myclobutanil and Its Commercial Formulation with TiO₂ P25 in Slurry and TiO₂ / β -SiC Foams. *Journal of Nanoscience and Nanotechnology*, 2020, 20 (9), pp.5938-5943. <10.1166/jnn.2020.18547>. <hal-03004442>

HAL Id: hal-03004442

<https://hal.science/hal-03004442v1>

Submitted on 26 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Photocatalytic degradation of Myclobutanil and its commercial formulation with TiO₂ P25 in slurry and TiO₂/β-SiC foams.

Ignace Christian M'BRA^{1,2}, Didier Robert^{1*}, Nicolas Keller¹, Patrick Drogui³ and Albert Trokourey².

¹ Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé (ICPEES), CNRS-UMR7515 Université de Strasbourg, antenne de Saint-Avold, Université de Lorraine, 12 rue Victor Demange 57500 Saint-Avold, France

² Laboratoire de Chimie Physique, UFR Sciences des Structures de la Matière et de la Technologie (SSMT), Université Félix Houphouët Boigny d'Abidjan, 22 BP 582 Abidjan 22, Côte d'Ivoire

³ Institut National de la Recherche Scientifique (INRS-Eau, Terre et environnement), Université du Québec, 490 rue de la Couronne, Québec city, Québec, G1K 9A9, Canada

* didier.robert@univ-lorraine.fr

Date of Submission: 17 april 2019

Date of Acceptance: 12 September 2019

Abstract

Viticulture is one of the crops most subject to pest control by fungicides. Their drainage towards the fresh water affects the aquatic environment, the fauna, the flora and especially the human health. It is therefore necessary to find an adequate solution to solve this problem. Heterogeneous photocatalysis is an advanced oxidation method for the degradation and mineralization of organic pollutants in water and air using semi-conductor (e.g. TiO₂). TiO₂ P25 in suspension (0.75 g. L⁻¹) is used to treat Myclobutanil contaminated water and a commercial formulation Systhane™ 20EW, a fungicide produced by BASF. After 120 min of batch treatment under our conditions (pH = 6.7, Co = 10 mg.L⁻¹), 96% and 98% of Myclobutanil and Systhane were removed with 94% and 92% mineralization, respectively. In order to avoid the recovery of nanoparticles of TiO₂ P25 after treatment, we have taken care of β-SiC foam cells. Under the same experimental conditions, 45% and 56% of Myclobutanil and Systhane degraded after 4 h with mineralization of 29% and 27%, respectively in recirculation in a fixed-light photoreactor by UV-A lamps. These results are very encouraging: filtering is not necessary to separate the catalyst from the treated water, it is very important for large-scale use of this process.

Keywords Photocatalysis, TiO₂/β-SiC, Myclobutanil, Systhane, Fungicide.

1. Introduction

Fungicides are pesticides designated exclusively to eliminate or limit the development of plant parasitic fungi. Although there are fungicides in their natural state, their production on an industrial scale is more important to meet agricultural needs. Industrial agriculture is part of a broader consumption system that includes many other actors (gardening and green spaces) than the farmers

themselves. During the last decade, the use of fungicides in vineyard cultivation has increased by 12 % (2014-2016, in France) in pest control [1]. Powdery mildew and downy mildew are two important diseases found in vine growing according to the French institute of agronomic research (INRA) report in 2006 [2]. In this context, the growing sector is very concerned about the environmental, toxicological and health problems caused by their massive use [3].

To reduce the concentration of these toxic organic compounds in wastewater, new technologies have emerged over the last twenty years. Advanced oxidation processes (AOP) (ozonation, sonolysis, electrochemistry ...) are techniques that have generated a lot of interests in scientific research for the treatment of contaminated water [4,5]. AOPs are "green" and effective methods for the purification and disinfection of wastewater. For this purpose, the heterogeneous photocatalysis is an AOP based on the absorption of light by a semiconductor in order to photogenerate oxidizing species such as hydroxyl radicals and superoxides (OH° , O_2^\ominus) [6]. OH° free radicals are considered as the main active species for the photocatalytic oxidation of organic pollutants. One of the main advantages of heterogeneous photocatalysis is its ability to mineralize, without selectivity, most recalcitrant organic pollutants [7-9], especially fungicides and other pesticides.

However, on an industrial scale, recovering TiO_2 nanoparticles after treatment is expensive. To overcome this difficulty, the immobilization of photocatalysts on support has been the subject of several studies in recent years. Many supports such as glass fibers, quartz fibers, cordierite monolith, alumina foams, cellulosic paper have been used to support TiO_2 [10-12]. The most used cellular foams for immobilizing photocatalysts are metallic foams (mainly made of nickel or aluminium) as well as ceramic foams (alumina or cordierite). Usually, metallic foams suffer from a low specific surface area that needs to be increased by different methods, such as chemical and/or thermal pre-treatments, or by the coating of the foam with an oxide interlayer. Alumina and cordierite cellular foams are much more resistant than polymer or carbon foams, and benefit from a reactive oxygen-containing surface, prone to bind with TiO_2 or TiO_2 precursors, even if they suffer from a relatively low specific surface area due to the high temperatures used for the ceramic shaping [13]. In our institute, the use of 3D supports based on silicon carbide foams (SiC) has been studied because they facilitate the exchange between the supported photocatalyst and the organic pollutant to be treated [6, 5]. These supports have many advantages such as their high chemical resistance, their exceptional thermal stability and their macroporosity offering a high internal surface allowing the immobilization of large quantities of photocatalysts.

Systhane 20EW, from BASF, is an effective commercial fungicide used to control powdery mildew (black rose blotch, rust) in vegetables, berries, ornamentals and vines. However, its active ingredient Myclobutanil is toxic to wildlife, harmful for aquatic life and especially for the human health [7].

Previous studies have been conducted to remove Myclobutanil or its commercial formulation in water by heterogeneous photocatalysis, but a very few in the presence of supported TiO₂ [18].

This work evaluates the influence of certain operating parameters (pH, C_{myclobutanil}) during the photocatalytic degradation of Myclobutanil and its commercial formulation (Sythane™ 20EW) in the presence of nanoparticles of TiO₂ P25 suspended and supported on alveolar foam β-SiC. The objective of this study is to determine the optimal experimental conditions for the photocatalytic degradation and mineralization of Myclobutanil in a pilot scale photoreactor with integrated photocatalyst.

2. Materials and methods

2.1. Chemicals and materials

Myclobutanil (C₁₅H₁₅N₄Cl, 99.9%, (RS) -2-p-chlorophenyl-2-(1H-1,2,4-ylmethyl) hexanenitrile from Techlab), commercial formulation Systhane™ 20EW (100 g.L⁻¹ Myclobutanil from Bayer), TiO₂ P25 (average size 20 nm, purity 97%, surface area 50m².g⁻¹ and 80% anatase, 20% rutile, Evonik industries) were used as received. Ethanol anhydride (99.8%, FLUKA) and titanium tetraisopropoxide (TTIP, C₁₂H₂₈O₄Ti, 97% SIGMA ALDRICH) were used without purification. Distilled water was used to prepare all the solutions.

2.2. Preparation of TiO₂/β-SiC foams by dipping in a suspension of TiO₂

The alveolar foams of β-SiC have been synthesized and supplied by SICAT company (Willstätt, Germany) [19]. The foam samples have a size of 9.5 cm (length) x 6 cm (width) x 1 cm (thickness), with a weight of about 20 g and a cell size of 4.5 mm. The foam was calcined at 1000 °C for 2h to remove residual organic carbon. Each β-SiC foam sample was completely immersed in the TiO₂ slurry (10 g TiO₂ P25 and 4 mL TTIP in 200 mL ethanol) during 5 minutes. The photocatalytic materials were dried at room temperature for 20 minutes, avoiding clogging of the cells. TiO₂/β-SiC foams were placed in an oven at 110 °C overnight to evaporate the residual organic compounds. TiO₂/β-SiC foams were introduced into the oven at 450 °C for 2h at a rise rate of 5 °C.min⁻¹. The average wt % of TiO₂ per foam was about 7.5 %, which corresponds to 1.5 g of TiO₂ fixed on the support [6].

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

2.3. Photocatalytic tests with TiO₂ P25 in slurry

Batch mode experiments were conducted at room temperature in a glass cylinder reactor with aqueous solutions of Myclobutanil and Systhane 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 TiO_2 in powder (0.75 g. L^{-1}) [6] was immersed by means of stirring in a 200 mL volume of solution of Myclobutanil and Systhane (between 10 and 20 mg.L^{-1}). Before each irradiation, the suspensions were kept in the dark for 30 minutes in order to reach the adsorption equilibrium. During the irradiation procedure, 10 mL of solution were taken at regular intervals and filtered (Whatmann, 0.45 μm). The remaining concentration of Myclobutanil and Systhane was determined with a LIBRA S12 UV-vis spectrophotometer ($\lambda_{\text{max}} = 220 \text{ nm}$) and mineralization by TOC analysis (SHIMADZU TOC-L).

2.4. Photocatalytic tests with TiO_2 P25 support on $\beta\text{-SiC}$ foam

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

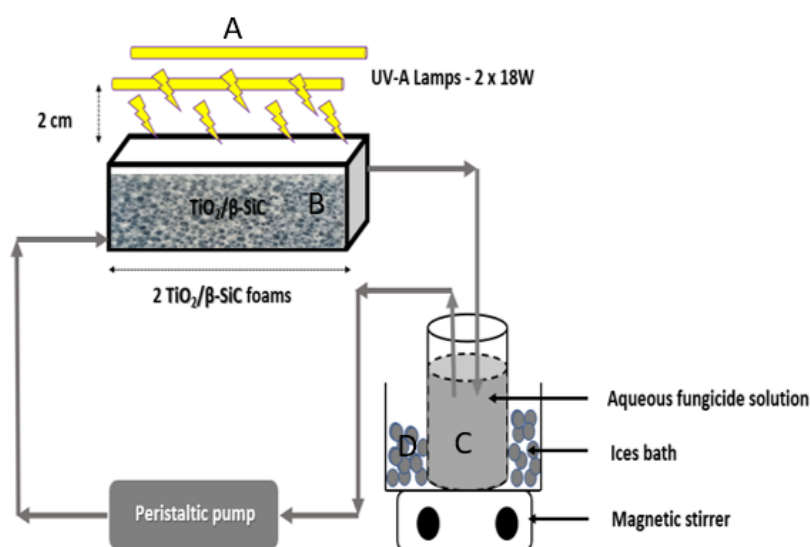


Figure 1. Experimental photocatalytic device: A (2 UV-A lamps); B (photoreactor); C (Myclobutanil or Systhane aqueous solution); D (Thermostatic bath).

3. Results and discussion

3.1. Degradation of pure Myclobutanil and Systhane by TiO₂ P25 slurry

3.1.1. Influence of initial concentration

For most of organic molecules [20, 21], the photocatalytic disappearance follows apparent first-order kinetics when the initial concentration is low enough and no catalyst saturation occurs, as in the case of Myclobutanil. For a low initial fungicide concentration, the simplest representation for the rate of photodegradation is given by $\ln C_t = -k_{app}t + \ln C_0$. This equation can be used to demonstrate the linearity of data. Its integration is given by $\ln \left(\frac{C_0}{C_t}\right) = k_{app}t$ where k_{app} is the apparent constant of the pseudo-first order rate.

Figure 2 shows the evolution of Myclobutanil concentration according to fungicide concentration. After 2 h irradiation, a total disappearance of Myclobutanil was obtained. The obtained apparent constant rate (k_{app}) have been listed in Table 1. The best result is obtained at 10 mg.L⁻¹ [22] because the photocatalyst TiO₂ P25 in suspension is less saturated and the production of free radicals is more important at the interface of this one to oxidize the molecules of the fungicide.

Regarding the kinetic variations of TOC according to the irradiation time, we noted three distinct steps in the mineralization of Myclobutanil (Figure 2). According to Malato *et al* [23], during the first step, we have the formation of hydroxy derivative of Myclobutanil without mineralization of organic carbons. Then, there is a rapid decrease of the TOC suggesting the transformation of organic carbon into mineral carbon by photooxidation into phenyl derivatives and to finish a very low abatement of TOC with formation of hardly oxidizable aliphatic molecules [6, 23].

Table 1. Pseudo-first-order rate constant k_{app} for the photocatalytic disappearance of Myclobutanil.

Exp. N°	C _{Myclobutanil}	pH	k_{app} (min ⁻¹) after 30 min / R ²	TOC elimination after 1 h (%)
1	10	6.7	0.0414 / 0.98	89.45
2	15	6.7	0.0215 / 0.97	74.00
3	20	6.7	0.0131 / 0.98	50.26
4	10	4	0.0385 / 0.97	70.00
5	10	10	0.0085 / 0.98	14.74

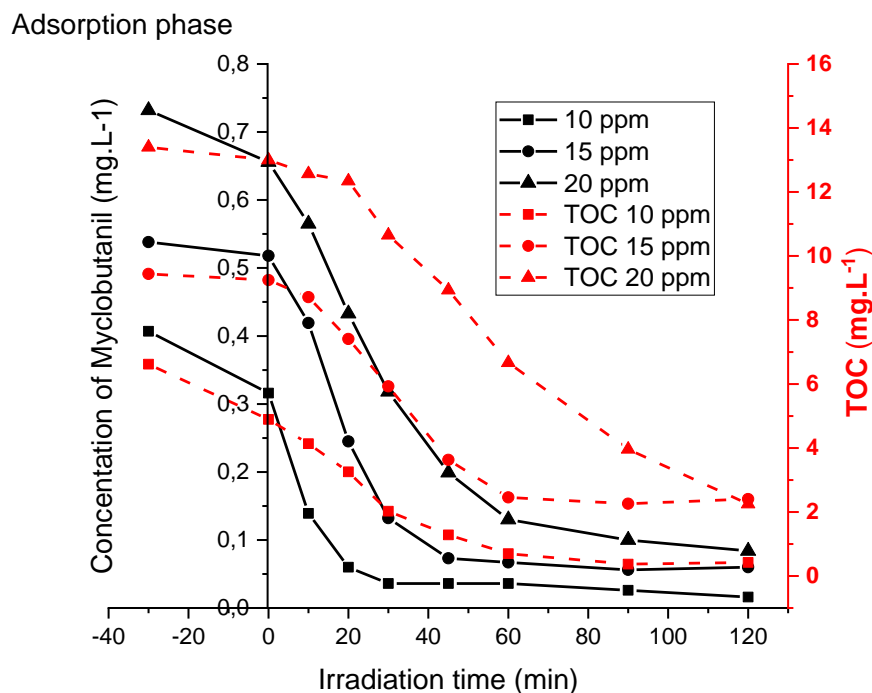


Figure 2. Kinetics of Myclobutanil disappearance and TOC evolution according to Myclobutanil concentration with TiO₂ P25 slurry.

3.1.2. Influence of solution pH

On the other hand, at natural pH no degradation has been detected in the dark after 1 h. This shows that Myclobutanil hydrolysis in water is very low. In the range of pH = 4 – 10, the Myclobutanil degradation kinetic was pH dependent (Figure 3). At pH around 4, the cyano group protonated because the pKa value of Myclobutanil is 2.30 at 25 °C [24]. At this pH the TiO₂ surface is positively charged; therefore, there are weak repulsive forces with Myclobutanil. In basic condition (pH = 10), there is a strong repulsion between the negative surface of TiO₂ and the free electron pairs of the three nitrogen atoms as well as the aromatic ring, explaining the low rate constant at pH 10 (Table 1). Finally, the best result is obtained at natural pH (6.7), because the molecule is neutral and, in this condition, the electrostatic interactions between Myclobutanil and the TiO₂ surface are weak but optimum. This is an important result for industrial applications because it will be no need to adjust pH during treatment.

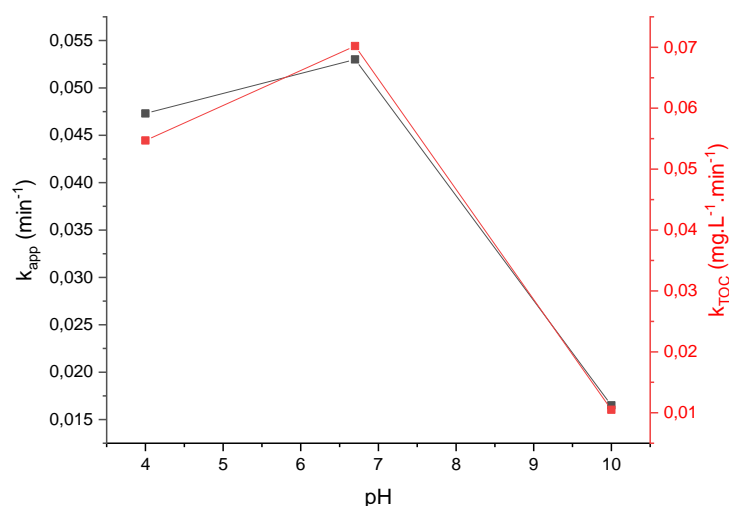


Figure 3. Evolution apparent constant rate k_{app} of Myclobutanil according to pH.

3.1.3. Photocatalytic degradation of pure Myclobutanil compared to Systhane

If we compare the degradation kinetics of Systhane (commercial formulation) with its active molecule (Myclobutanil), we show that Myclobutanil degrades faster (0.0414 min^{-1}) than Systhane (0.0275 min^{-1}) (figure 4). This result shows that the formulation contains the active molecule (19.42 wt %) with a significant amount of organic additive compounds (aromatic hydrocarbons, cyclohexane, naphthalene, 80.58 wt %). However, during the adsorption phase, Systhane is adsorbed more on the surface of the photocatalyst than Myclobutanil because some additives absorb at the same wavelength as Myclobutanil. This phenomenon is confirmed by the kinetics of mineralization of the two solutions to be treated. After 120 min of irradiation, for 10 mg.L^{-1} of solution, the elimination of TOC was 6.2 mg.L^{-1} and 13.6 mg.L^{-1} respectively for Myclobutanil and Systhane.

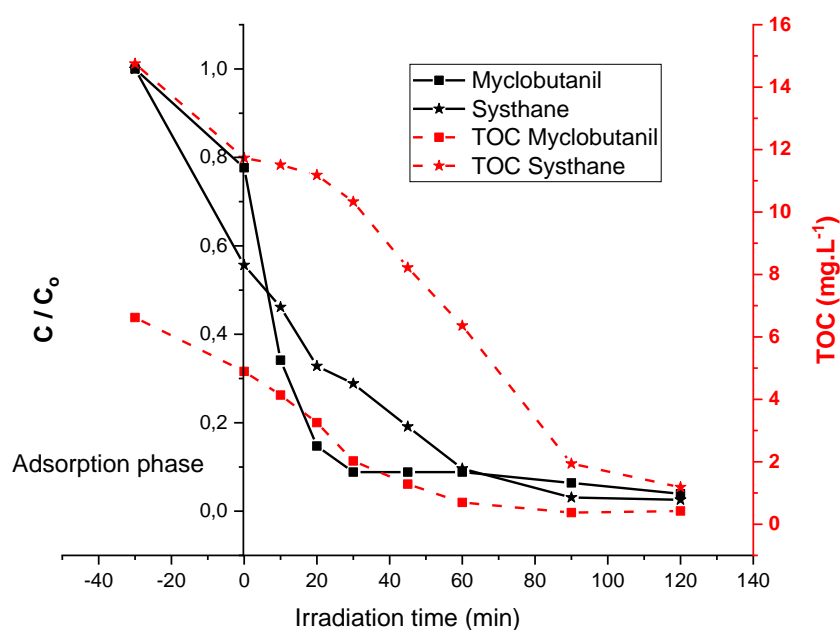


Figure 4. Photocatalytic degradation kinetics and TOC evolution of pure Myclobutanil compared to Systhane.

3.2. Photocatalytic elimination of Myclobutanil and Systhane by TiO_2 P25 supported on $\beta\text{-SiC}$ foams

In the previous section, we have shown the photocatalytic efficiency of TiO_2 on the degradation of Myclobutanil and its commercial formulation (Systhane). In order to solve the problem of photocatalyst recovery after treatment, we immobilized TiO_2 nanoparticles on cellular foams $\beta\text{-SiC}$. This photocatalytic support has already been used as a support for TiO_2 for the treatment of air [25-26] and water [14-15]. All photocatalytic experiments with our materials were performed in a fixed-bed photoreactor illuminated by UV-A lamps in order to increase the photocatalytic activity of TiO_2 .

After the preparation of $\text{TiO}_2/\beta\text{-SiC}$ materials, their morphologies were characterized at SEM (Figure 5). Figure 5A shows cracks on the surface of the TiO_2 film on the support without TTIP. This is due to drying the material at room temperature (dip-coating phase) or during the calcination phase at 450°C . in the oven. However, in the presence of TTIP, the surface is homogeneous (Figure 5B). This shows that adding TTIP in the TiO_2 suspension improved the stability of the film on the photocatalytic support as it acts as a binder.

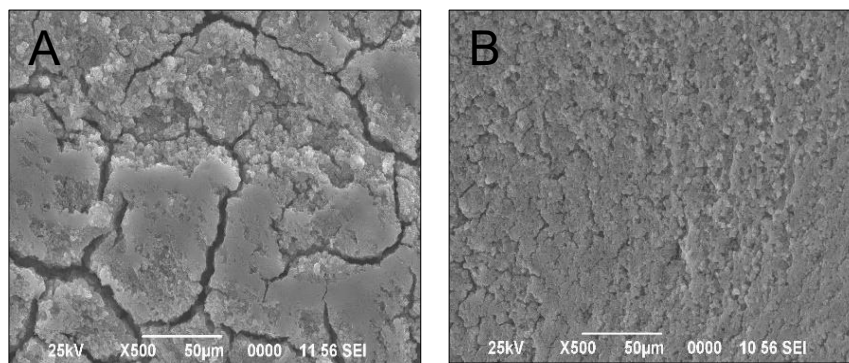


Figure 5. SEM pictures of the surface of TiO₂ P25 films coated on β -SiC alveolar foams with A) without addition of TTIP and B) addition of TTIP in TiO₂ slurry.

Photocatalytic materials prepared with TTIP were used to perform all photocatalytic experiments for the removal of Myclobutanil and its commercial formulation (Systhane). This formulation contains only 19.42 wt %, the remaining 80.58 wt % being composed of aromatic hydrocarbons, cyclohexane and naphthalene. Figure 6 shows the kinetics of degradation of Systhane and Myclobutanil. After one hour of adsorption, we had a strong adsorption of Systhane (32.98 %) compared to Myclobutanil (7.92%). The other compounds contained in Systhane are adsorbed on TiO₂/ β -SiC and especially the aromatic compounds absorbing practically at the same wavelength ($\lambda = 220$ nm) as Myclobutanil. Therefore, we have a significant elimination of Systhane (55.69 %) compared to Myclobutanil (44.54%). Their apparent disappearance rate constants are 0.00206 min⁻¹ and 0.00241 min⁻¹ for Myclobutanil and Systhane respectively (Table 2). The constant rate of Systhane mineralization (0.01359 mg.L⁻¹.min⁻¹) is greater than that of Myclobutanil (0.00670 mg.L⁻¹.min⁻¹). The other organic compounds present in the Systhane solution are certainly oxidized. The influence of pH has also been studied with the catalyst-coated foams. The results are similar to those obtained in suspension.

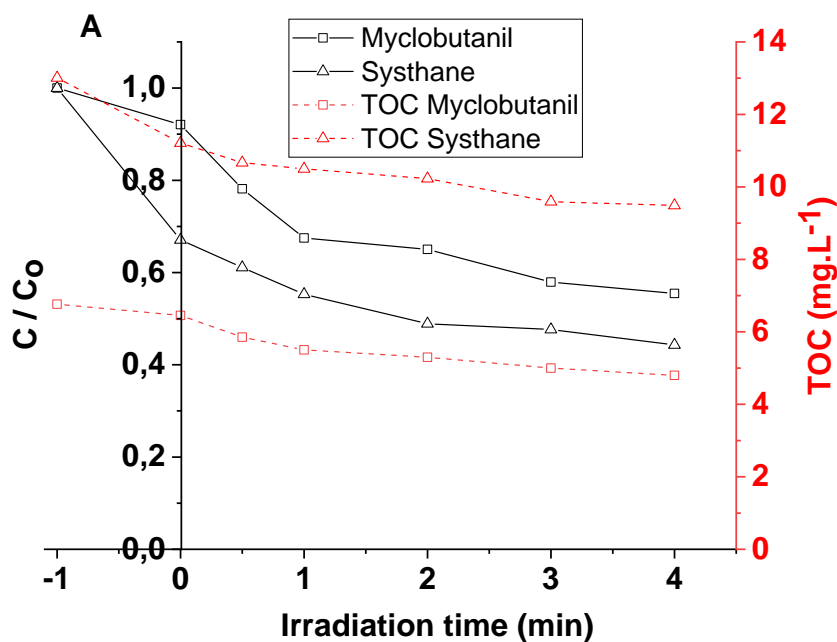


Figure 6. Photocatalytic degradation kinetics and TOC evolution of pure Myclobutanil and Systhane in the presence of TiO₂/β-SiC

Table 2: Rate of reduction of Myclobutanil and of Systhane and TOC during their elimination by TiO₂/β-SiC

Photocatalytic parameters	Pur Myclobutanil	Systhane
k_{app} (min ⁻¹) after 1 h / R ²	0,00206 / 0.98	0,00241 / 0.97
Elimination fungicide (%)	44,54	55,69
Elimination TOC (mg. L ⁻¹)	1,963	3,523
k_{TOC} (mg. L ⁻¹ .min ⁻¹) / R ²	0,00670 / 0.98	0,01032 / 0.98
Elimination TOC (%)	29,03	27,08

4. Conclusion

The photocatalytic degradation of Myclobutanil and its commercial formulation (Systhane) in aqueous solution has been investigated in the presence of TiO₂ P25 slurry and supported on β-SiC foams under UV-vis irradiation. In our conditions, Myclobutanil and Systhane can be degraded efficiently with TiO₂ suspension 91.15 % and 90.38 % respectively after 60 min illumination. Various experimental parameters influencing the kinetics were investigated such as pH, and Myclobutanil concentration in our conditions. The results showed that the optimum concentration of fungicide was 10 mg.L⁻¹ and it was necessary to work at natural pH. In the case of the use of supported photocatalysts (TiO₂/β-SiC foam), degradation kinetics are lower than for suspensions. However, after 4 h of treatment, we degraded 44.54 % and 55.70 % of Myclobutanil and Systhane respectively and

mineralized 29 % of Myclobutanil and 27 % of Systhane. These are very encouraging results because there is no need to filter to separate the catalyst from the treated water which is very important for a large-scale use of this process. Finally, the use of the supported catalyst showed a change in the mineralization kinetics since the reaction is closer to a pseudo-zero than to an order-one.

Acknowledgments

The European Fund for regional development (EFRE/FEDER) is acknowledged for partially supporting the work, in the frame of the project PHOTOPUR, within the Program Interreg V Rhin Superior and the Sciences Offensive.

References

1. <https://www.notre-planete.info/actualites/1398-statistiques-utilisation-pesticides-France>.
2. Institut National de la Recherche Agronomique (INRA), <http://www.inra.fr/Chercheurs-etudiants/Systemes-agricoles/Tous-les-dossiers/Vignes-resistantes-aumildiou-et-a-l-oidium-un-deploiement-responsable/Les-differentes-varietes-resistantes-au-mildiou-et-a-l-oidium>.
3. Gerage, J.M.; Meira A.P.G.; da Silva, M.V. **2017**. Food and nutrition security: pesticide residues in food. *Nutrire.*, 42, 3.
4. Deng, Y.; Zhao R. **2015**. Advanced oxidation processes (AOPs) in wastewater treatment. *Current Pollution Reports.*, 1, 167-176.
5. Vaiano V.; Iervolino G.; Rizzo L.; Sannino D. **2017**. Advanced Oxidation Processes for the Removal of Food Dyes in Wastewater. *Current Organic Chemistry.*, 21, 1068-1073.
6. M'Bra I.C.; García-Muñoz P.; Drogui P.; Keller N.; Trokourey A.; Robert D. **2019**. Heterogeneous photodegradation of Pyrimethanil and its commercial formulation with TiO₂ immobilized on SiC foams. *Journal of Photochemistry and Photobiology A: Chemistry.*, 368, 1-6.
7. Lofrano G.; Libralato G.; Casaburi A.; Siciliano A.; Iannece P.; Guida M.; Pucci L.; Dentice EF. Carotenuto M. **2018**. Municipal wastewater spiramycin removal by conventional treatments and heterogeneous photocatalysis. *Science of The Total Environment.*, 624, 461-469.
8. Oller I.; Gernjak W.; Maldonado M.I.; Pérez-Estrada L.A.; Sánchez-Pérez J.A.; Malato S. **2006**. Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale. *Journal of Hazardous Materials*, 138, 507-517.
9. Robert D.; Piscopo A.; Weber J.V. **2004**. First approach of the selective treatment of water by heterogeneous photocatalysis. *Environmental Chemistry Letters.*, 2, 5-8.
10. Yuningrat N.W.; Parwata I.P.; Jastrissia P.F.D.; Oviantari M.V.; Mudianta I.W. **2018**. Landfill Leachate Degradation by TiO₂-Immobilized White Cement. *Molekul.*, 13, 18-22.
11. Chen L.; Zheng K.; Liu Y. **2017**. Geopolymer-supported photocatalytic TiO₂ film: Preparation and characterization. *Construction and Building Materials.*, 151, 63-70.

12. He Y.; Sutton N.B.; Rijnaarts H.H.; Langenhoff A.A. **2016**. Degradation of pharmaceuticals in wastewater using immobilized TiO₂ photocatalysis under simulated solar irradiation. *Applied Catalysis B: Environmental.*, 182, 132-141.
13. Raupp G.B., Alexiadis A., Hossain Md.M., Changrani R., (2001) First-principles modeling, scaling laws and design of structured photocatalytic oxidation reactors for air purification, *Catal. Today* 69, 41-49
14. Rico-Santacruz M.; García-Muñoz P.; Keller V.; Batail N.; Pham C.; Robert D.; Keller N. **2018**. Alveolar TiO₂-β-SiC photocatalytic composite foams with tunable properties for water treatment. *Catalysis Today.* 328, 235-242.
15. Marien C.B.; Le Pivert M.; Azaïs A.; M'Bra I.C.; Drogui P.; Dirany A.; Robert D. **2018**. Kinetics and mechanism of Paraquat's degradation: UV-C photolysis vs UV-C photocatalysis with TiO₂/SiC foams. *Journal of hazardous materials.* 370, 164-171.
16. Nagel D.A.; Hill E.J.; O'Neil J.; Mireur A.; Coleman M.D. **2014**. The effects of the fungicides fenhexamid and myclobutanil on SH-SY5Y and U-251 MG human cell lines. *Environmental toxicology and pharmacology.*, 38, 968-976.
17. Blair A.; Ritz B.; Wesseling C.; Freeman L.B. **2015**, Pesticides and human health. In.: BMJ Publishing Group Ltd
18. Fenoll J.; Garrido I.; Pastor-Belda M.; Campillo N.; Viñas P.; Yañez M.J.; Vela N.; Navarro S. **2017**. Solar detoxification of water polluted with fungicide residues using ZnO-coated magnetic particles. *Chemical Engineering Journal.*, 330, 71-81.
19. Nguyen P.; Pham C. **2011**. Innovative porous SiC-based materials: From nanoscopic understandings to tunable carriers serving catalytic needs. *Applied Catalysis A: General.*, 391, 443-454.
20. Rahman M.A.; Muneer M. **2005**. Photocatalysed degradation of two selected pesticide derivatives, dichlorvos and phosphamidon, in aqueous suspensions of titanium dioxide. *Desalination.*, 181, 161-172.
21. Qamar M.; Muneer M.; Bahnemann D. **2006**. Heterogeneous photocatalysed degradation of two selected pesticide derivatives, triclopyr and daminozid in aqueous suspensions of titanium dioxide. *Journal of Environmental Management.*, 80, 99-106.
22. Saien J.; Khezrianjoo S. **2008**. Degradation of the fungicide carbendazim in aqueous solutions with UV/TiO₂ process. Optimization, kinetics and toxicity studies. *Journal of Hazardous Materials.*, 157, 269-276.
23. Agüera A.; Almansa E.; Tejedor A.; Fernández-Alba A.R.; Malato S.; Maldonado M.I. **2000**. Photocatalytic Pilot Scale Degradation Study of Pyrimethanil and of Its Main Degradation Products in Waters by Means of Solid-Phase Extraction Followed by Gas and Liquid Chromatography with Mass Spectrometry Detection. *Environmental Science & Technology.*, 34, 1563-1571.
24. Liu G.; Li L.; Huang X.; Zheng S.; Xu D.; Xu X.; Zhang Y.; Lin H. **2018**. Determination of triazole pesticides in aqueous solution based on magnetic graphene oxide functionalized MOF-199 as solid phase extraction sorbents. *Microporous and Mesoporous Materials.*, 270, 258-264.
25. Kouamé A.N.; Masson R.; Robert D.; Keller N.; Keller V. **2013**. β-SiC foams as a promising structured photocatalytic support for water and air detoxification. *Catalysis today*, 209, 13-20.

26. Doss N.; Bernhardt P.; Romero T.; Masson R.; Keller V.; Keller N. **2014**. Photocatalytic degradation of butanone (methylethylketone) in a small-size TiO₂/β-SiC alveolar foam LED reactor. *Applied Catalysis B: Environmental.*, 154-155, 301-308.