

## Catalytic Degradation of Boscalid under Solar Radiation in Aqueous Medium: Effect of Operating Parameters

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### ABSTRACT

Boscalid is a fungicide used to combat gray mold on export fruits. However, once released into the environment, this molecule is stable in water and sediment. The objective of this study is to demonstrate the usefulness of the TiO<sub>2</sub>/clay process for the depollution of water contaminated with Boscalid. To do this, clay beads of approximately 3 mm in diameter, coated or not with TiO<sub>2</sub>, were manufactured. All experiments were conducted with aqueous solutions containing boscalid and then exposed to sunlight for 360 minutes. The results of the solar photolysis and dark adsorption tests did not reveal any decrease in the initial concentration of this molecule. On the other hand, the solar photocatalysis results showed a Boscalid disappearance rate greater than 90% for 60 g of clay balls and for an initial concentration of 500 µg/L. Application of this process to water samples also showed a compound disappearance rate of 60% and 38% for tap water and river water respectively. Furthermore, the efficiency of this water treatment process depends on the experimental conditions.

**Keywords:** Supported photocatalysis, Titanium dioxide, Clay, Boscalid

### INTRODUCTION

In most countries where agriculture occupies a prominent place, such as Côte d'Ivoire, the use of plant protection products, with a view to improving agricultural yields and reducing post-harvest production losses, is very essential for a constantly growing population (Reilly *and al.*, 2012). Studies by Diarra *and al.* (2020) have shown that many bodies of water are affected by pesticide contamination. In addition, these pesticides can remain in soils for years or even decades after their last application (Ebert *and al.*, 2000). Although they are effective in increasing food production, their use also poses environmental and health problems (Bentley *and al.*, 2010). Among these pesticides is Boscalid. This pesticide is a systemic fungicide commonly used in agriculture to control fungal diseases that can affect crops. It belongs to the carboxamide family, which is a class of chemical compounds developed specifically for its fungicidal activity (Karlsson *and al.*, 2016). Boscalid has proven efficacy in controlling various pathogenic fungi, making it a popular choice among farmers and crop protection professionals (Skanes *and al.*, 2021). However, despite its effectiveness, the extensive use of Boscalid raises environmental concerns. One of the main concerns is its persistence in the environment (Han *and al.*, 2022). Due to its chemical structure, Boscalid tends to be relatively stable and degrade slowly. This means that once applied to crops, it can persist in the environment for an extended period of time, or even indefinitely, before completely breaking down (Lagunas-Allué *and al.*, 2010). This persistence can lead to a gradual accumulation of Boscalid in soils, surface waters, and groundwater, increasing the risk of long-term contamination (Karlsson *and al.*, 2016).

Therefore, the elimination of this pesticide before their release into the environment is very important. In addition, in recent decades, many treatment methods such as photocatalysis have been used in the degradation of organic pollutants (Bouna *and al.*, 2012; Aliste *and al.*, 2021). For this purpose, titanium dioxide (TiO<sub>2</sub>) is commonly used as a photocatalyst. When TiO<sub>2</sub> is exposed to UV light, it generates electron-hole pairs that react with organic pollutants, leading to their degradation into less toxic compounds.

Photocatalysis therefore offers a promising approach for the degradation of organic pollutants in aqueous media (Akter *and al.*, 2022). It is in this context that the present study has as its general objective the degradation by the TiO<sub>2</sub>/clay process of water contaminated by boscalid. Specifically, it will be:

- Determine the hydrolysis kinetics of boscalid in aqueous medium,
- Determine the adsorption kinetics of boscalid in the presence or absence of TiO<sub>2</sub>-coated beads,
- Determine the photolysis kinetics of boscalid in aqueous medium,
- Study the influence of certain parameters such as the mass of the catalyst, the initial concentration of the pollutant and the dilution matrices on the photocatalytic degradation kinetics of boscalid.

## 2. Materials and Methods

### 2.1. Reagents and solvents

TiO<sub>2</sub> is composed of 95% anatase. The boscalid used comes from a phytosanitary product called CUMURA 50 SC with a concentration of 500 g/L. It was used for solutions for photodegradation testing. The acetonitrile was 99% pure and supplied by Carlo Erba. The ultrapure water was produced at the MiliQ quality laboratory (Resistivity: 0.5 Ω.cm<sup>-1</sup>).

### 2.2. Protocol for the development of clay supports.

Clay supports have been developed in the form of spherical balls, thus allowing optimal exposure of their surface to light. For the manufacture of these clay balls, with or without TiO<sub>2</sub>, two protocols were put in place in each case: the making of pure clay balls and the impregnation of the clay balls in a TiO<sub>2</sub> solution.

#### 2.2.1. Manufacturing of high-temperature calcined clay balls

To make the balls, 40 mL of ultrapure water was added to 100 g of clay powder to obtain a homogeneous paste. Balls of approximately 0.3 mm in diameter were shaped. The balls were then dried at 105 °C for 24 hours and then fired at 550 °C in an oven to make them water-resistant and to eliminate any form of residual organic matter.

#### 2.2.2. Fabrication of TiO<sub>2</sub>-coated beads

The clay beads were immersed for three days in an ethanolic TiO<sub>2</sub> solution at 20 g/L. Then, they were calcined in an oven at a temperature of 400 °C for 2 hours, according to a temperature ramp of 10 °C/min, thus promoting an increased fixation of TiO<sub>2</sub>. Subsequently, the beads were rinsed with ultrapure water to remove the TiO<sub>2</sub> residues that were not firmly fixed. This experiment was repeated three times.

#### 2.2.3. Experiments performed

Three experiments were performed: a hydrolysis experiment, an adsorption experiment, and an experiment combining hydrolysis and solar photocatalysis. Boscalid hydrolysis tests were performed in a 500 µg/L doped solution, at free pH (pH = 6) for 25 days in the dark, at a concentration of 500 µg/L. For the adsorption experiments, TiO<sub>2</sub>-coated and uncoated clay beads were used in dark conditions, with a test duration of 360 minutes. Finally, for the hydrolysis and solar photocatalysis experiments, the TiO<sub>2</sub>-coated beads were exposed to sunlight for a period of 25 days at a concentration of 500 µg/L and pH 6.

#### 2.2.4. Hydrolysis tests

Boscalid hydrolysis tests were carried out in the dark in a solution spiked at 500 µg/L and an initial pH of 6 for a period of 25 days. Photolysis consisted of irradiating matrices doped with a concentration of 500 µg/L under solar irradiation in the presence of clay beads not covered with TiO<sub>2</sub>. The objective was to determine the contribution of direct photolysis to the degradation of the boscalid molecule. Samples were taken successively with Pasteur pipettes at regular time intervals during irradiation (30, 60, 120, 180, 240 and 300 minutes) and analyzed by high-performance liquid chromatography coupled with a UV detector.

### 2.2.5. Experimental protocol of photocatalytic tests

The experimental setup consists of quartz reactors with a capacity of 100 mL, adapted for the different stages of the experiments. The water matrices were enriched with boscalid solutions. The reactors were exposed to natural solar radiation, each test lasting 300 minutes. At regular intervals during irradiation (30, 60, 120, 180, 240 and 300 minutes), samples were taken successively using Pasteur pipettes and then analyzed by high-performance liquid chromatography. After each photocatalysis test, the reactors and clay balls were calcined at 500 °C for 2 hours in order to destroy pesticide residues and to be able to reuse them for the following experiments. The effect of operating parameters such as TiO<sub>2</sub>-impregnated bead mass, pollutant concentration, pH and dilution matrices were studied.

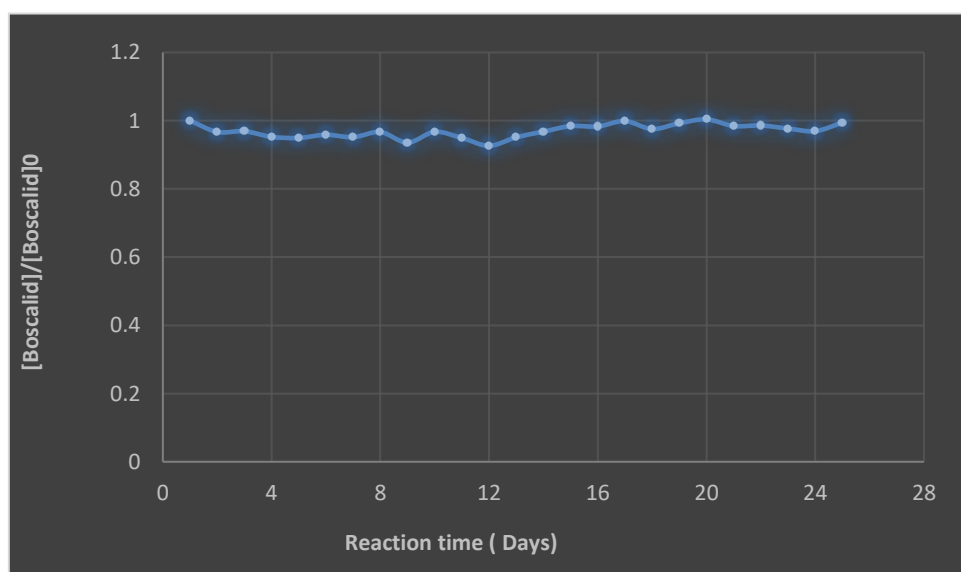
### 2.2.6. Chromatographic analyses

The analyses were carried out by high-performance liquid chromatography of the Agilent 1260 Infinity II brand. The chromatograph was calibrated with standard solutions of concentrations 0, 50, 500, 5000, 10000 and 150000 µg/L. The mobile phase is composed of 85% acetonitrile and 15% water, while the stationary phase is made up of a Kromasil C18 column. The boscalid molecule was detected at a wavelength of 254 nm with a retention time of 3.692 minutes.

## 3. Results

### 3.1. Boscalid hydrolysis kinetics

Figure 1 presents the results of boscalid hydrolysis experiments in the absence of non-TiO<sub>2</sub>-coated beads, carried out in ultrapure water.

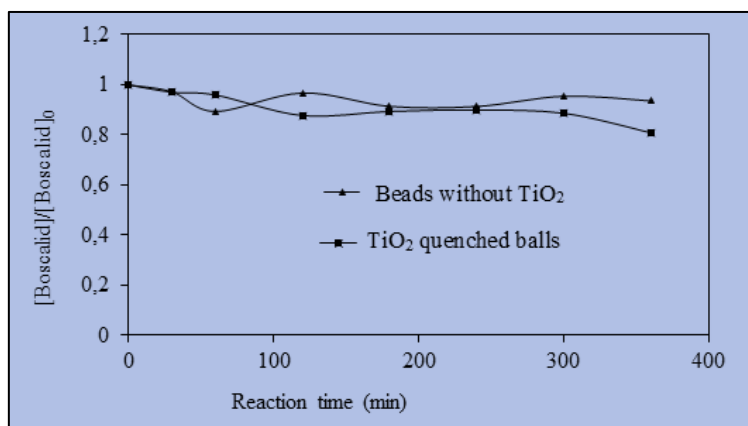


**Figure 1: Hydrolysis kinetics of boscalid, pH = 6, T° = 25 °C**

The results of this specific experiment indicate that the initial concentration of boscalid did not vary over the course of the experiment. This means that, despite the experimental conditions and the elapsed time, the initial concentration of boscalid remained constant. There was no significant degradation or change in the concentration of boscalid over time in this specific experiment. These results suggest that hydrolysis was not an effective mechanism for the degradation of boscalid in ultrapure water in this experimental setup. Indeed, studies conducted by the US Environmental Protection Agency have shown that boscalid is stable to hydrolysis at pH 5, pH 7, and pH 9 at 25°C (US-EPA, 2010). Based on the results obtained at 25 °C, the parent compound is not expected to hydrolyze in the environment, making hydrolysis an insignificant fate process for boscalid (US-EPA, 2010).

### 3.2. Boscalid adsorption kinetics

Figure 2 presents the results of boscalid adsorption experiments in the presence or absence of TiO<sub>2</sub>-coated beads in doped ultrapure water.

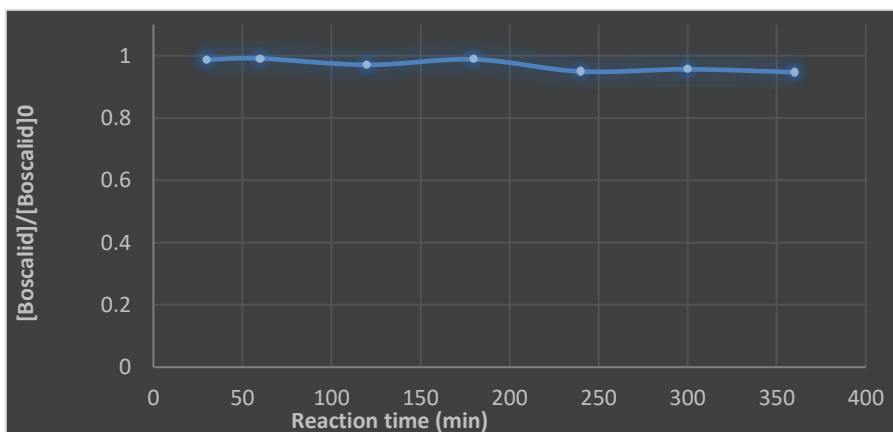


**Figure 2: Adsorption kinetics of boscalid pH = 6, T° = 25 °C**

In both cases, the results showed that the initial concentration of boscalid did not change during these experiments.

### 3.3. Photolysis of boscalid

Figure 3 presents the degradation kinetics of boscalid in the spiked solutions prepared from ultrapure water.



**Figure 3: Kinetics of degradation of boscalid by photolysis, pH = 6, T° = 25 °C**

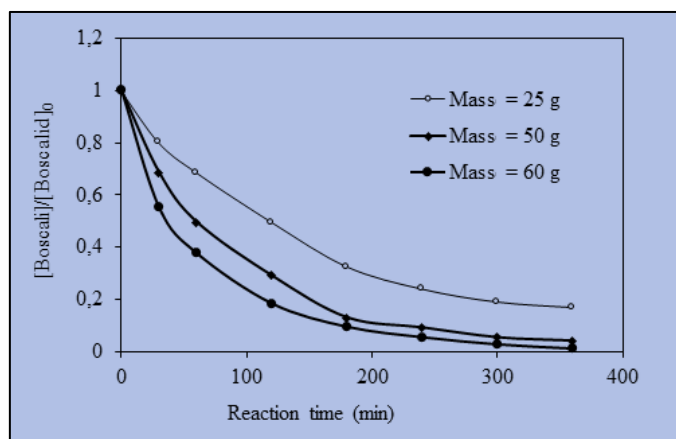
The results showed that the degradation rate is 5%. This indicates that Boscalid is stable to photolysis in water. This stability of boscalid could be explained by its chemical structure. Indeed, boscalid is a fungicide that belongs to the chemical family of carboxamides. It has a diphenyl ether-carboxamide nucleus and is endowed with a cyano group that gives it high chemical stability. The chemical structure of boscalid contains functional groups that are not easily degraded by light. In particular, the nitrile group (-C≡N) present in the boscalid molecule is not very reactive and does not absorb light photons efficiently, which makes the molecule quite stable to photolysis in water. In addition, the presence of other functional groups such as phenyl and methoxy groups in the structure of boscalid also contribute to its stability to photolysis. This chemical structure of boscalid allows it to resist photolysis in water; that is, under the effect of light, boscalid is stable to photolysis in water.

### 3.4. Photocatalysis of boscalid

This study investigated the efficiency of photocatalytic degradation of boscalid by TiO<sub>2</sub>. The photocatalysis experiments elucidated the degradation rate of boscalid according to three parameters as a function of time: the effect of the mass of TiO<sub>2</sub>-coated beads, the initial concentration of boscalid, and the effect of dilution matrices.

### 3.5. Effect of TiO<sub>2</sub>-coated bead mass

In the present case, clay beads were used to provide a solid support for TiO<sub>2</sub> particles to improve their photocatalytic efficiency. The masses of clay beads were varied to study their effect on the degradation of boscalid as shown in Figure 4.

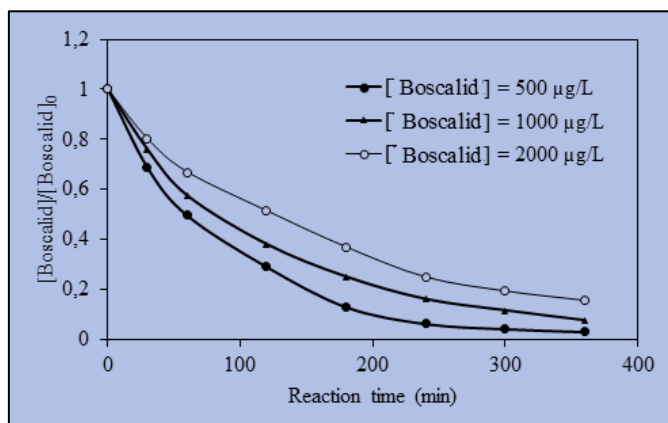


**Figure 4: Effect of mass of TiO<sub>2</sub>-coated beads, pH = 6, T° = 25 °C**

The results show that the degradation rate of boscalid evolves in the order of increasing masses of 25, 50 and 60 g. The degradation rates are 83.20%, 96% and 99% after 6 hours, respectively. The photocatalytic degradation process involves the use of TiO<sub>2</sub> catalyst, which absorbs photons of light and produces electron and hole pairs. These electrons and holes react with reactive species present in the solution, such as boscalid, to produce oxidizing species that can degrade the organic compound (Xekoukoulotakis *and al.*, 2011). The results showed that the efficiency of boscalid degradation increased with the mass of clay beads. This can be explained by the fact that larger masses of clay beads allow a greater dispersion of TiO<sub>2</sub> particles, which increases their contact with boscalid and therefore their photocatalytic efficiency. Photocatalytic degradation of boscalid in the presence of clay ball masses and TiO<sub>2</sub> is an efficient process that depends on the clay ball mass used. This method can be used to remove pesticide residues from water and other solutions, thus providing an environmentally friendly solution for pollution remediation.

### 3.6. Effect of Boscalid concentration

Figure 5 presents the results of the effect of the initial concentration of Boscalid on the degradation kinetics.



**Figure 5: Effect of initial Boscalid concentration, pH = 6, T° = 25 °C**

It is evident from this figure 5 that for boscalid concentrations of 500; 1000, 2000 µg/L, the results showed a decrease in the degradation kinetics of boscalid beyond 500 µg/L. Under these working conditions, the mass would be more suitable for concentrations less than or equal to 500 µg/L. The studies carried out by Roumayssaa (2012) examined the effect of pesticide concentration on photocatalytic degradation by TiO<sub>2</sub> fixed on different supports. For example, they examined the effect of the initial concentration of imazalil, a fungicide on photocatalytic degradation by TiO<sub>2</sub> fixed on clay beads. The results showed that the degradation rate decreased at higher concentrations of imazalil. The results also showed a decrease in degradation kinetics at higher concentrations. These results are consistent with the results mentioned in the question, which show a decrease in the photocatalytic degradation kinetics of boscalid TiO<sub>2</sub> beyond 500 µg/L in doped ultrapure water matrices. Thus, concentrations lower than or equal to 500 µg/L would be more suitable to optimize the efficiency of the photocatalytic degradation of this substance.

### 3.7. Effect of dilution matrices

Figure 6 presents the degradation kinetics of boscalid in different water matrices including ultrapure water, tap water and river water.

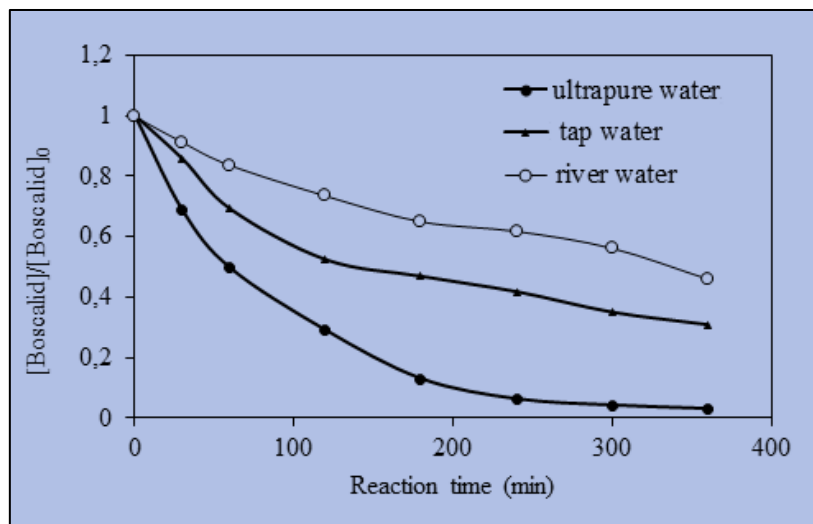


Figure 6: Effect of dilution matrices,  $T^{\circ} = 25^{\circ} \text{C}$

The results of the analysis show that the measured yield rates are 96%, 70% and 54% respectively for ultra-pure water, tap water and river water spiked with boscalid standard solutions. In addition, these results show that water quality has an impact on the efficiency of the decontamination process. Indeed, the degradation rate of boscalid is faster in tap water than in river water, which means that the photocatalytic catalyst is more effective in removing boscalid in tap water than in river water. The residual concentrations of boscalid are also different between the two water matrices, which can be attributed to the presence of contaminants and ions in the water that can interfere with the photocatalytic reaction. These results highlight the importance of considering water quality when choosing the method used to remove specific contaminants. Indeed, these results show that the photocatalytic degradation of boscalid depends on the composition and quality of the water in which it is found. The study compared the efficiency of photocatalytic degradation of boscalid in the presence of ultrapure water, tap water and river water. In general, ultrapure water showed better efficiency in the photocatalytic degradation of boscalid. This is due to its purity, which reduces the presence of contaminants and ions that could inhibit the photocatalytic reaction. In addition, ultrapure water may contain a higher concentration of photons, which promotes the photocatalytic reaction. In other words, the quality of the water in which the substance to be degraded is located is important for the efficiency of the photocatalytic reaction, and ultrapure water may be the best option to promote this reaction. However, it is important to note that the results may vary depending on the chemical composition of the substance to be degraded and the characteristics of each water matrix, and further studies may be necessary to better understand the effects of water quality on the photocatalytic degradation of different substances. As for tap water, the quality of the water may vary depending on its location. The photocatalytic degradation of boscalid may therefore be more or less effective depending on the content of contaminants, ions, and organic substances present in tap water. However, it is generally possible to achieve significant degradation of boscalid using a photocatalytic catalyst. Finally, river water can contain significant amounts of organic matter, nutrients, sediment, and other contaminants that can interfere with the photocatalytic reaction. This can make boscalid degradation more difficult and less efficient than in the presence of ultrapure water or tap water. However, it is still possible to use a photocatalytic catalyst to degrade boscalid in river water, although this may require longer treatment times or higher catalyst usage.

### 4. Conclusion

The use of clay balls as a material allowed to fix on its surface by calcination. The experiments carried out by adsorption and hydrolysis showed that the initial concentration of boscalid did not decrease. On the other hand, this study demonstrated that boscalid could be degraded by solar photocatalysis. Indeed, the photocatalysis experiments indicated a significant reduction in the initial concentration of boscalid under the experimental conditions. The fixation of  $\text{TiO}_2$  on materials appears as an alternative to resolve the issue of  $\text{TiO}_2$  suspension in the effluents treated by these photocatalytic processes. However, the performance of this process could be improved depending on the working conditions, in particular the increase in the mass of the balls which improves the efficiency of the process, at relatively low concentrations in dilution matrices containing few organic and inorganic compounds.

## REFERENCES

1. Akter S., Islam Md. S., Kabir Md. H., Shaikh Md. A. A. and Gafur Md. A. (2022) UV/TiO<sub>2</sub> photodegradation of metronidazole, ciprofloxacin and sulfamethoxazole in aqueous solution: An optimization and kinetic study. *Arab. J. Chem.* 15, 103900.
2. Aliste M., Garrido I., Pérez-Lucas G., Navarro S. and Fenoll J. (2021) Photocatalytic Oxidation of Chlorantraniliprole, Imidacloprid, Pirimicarb, Thiamethoxam and Their Main Photoreaction InterMediates as Impacted by Water Matrix Composition under UVA-LED Exposure. *Catalysts* 11, 609.
3. Bentley K. S., Fletcher J. L. and Woodward M. D. (2010) Chlorantraniliprole: an insecticide of the anthranilic diamide class. In *Hayes' Handbook of Pesticide Toxicology* Elsevier. pp. 2231–2242.
4. Bouna L. (2012) Functionalization of clay minerals of Moroccan origin by TiO<sub>2</sub> for the elimination by photocatalysis of organic micropollutants from aqueous environments. INPT.
5. Diarra, M., Léonce D. K., Soro D.B., Roland N. K., Bini K. D., Dibi B., Mamadou K., Ardjouma D., Karim S. T., 2020. Level of contamination of surface water by phytosanitary products: case of the water reservoir of the Lobo watershed (Central-West of Côte d'Ivoire)
6. Ebert D. and Harder U. (2000) Boscalid: The degradation behaviour of 14C-BAS 510 F in different soils (DT50/DT90). *BASF AG Agrar. Limburgerhof.*
7. Han, L., Xu, M., Kong, X., Liu, X., Wang, Q., Chen, G., Xu, K., Nie, J., 2022. Deciphering the diversity, composition, function, and network complexity of the soil microbial community after repeated exposure to a fungicide boscalid. *Environmental Pollution* 312, 120060. <https://doi.org/10.1016/j.envpol.2022.120060>
8. Karlsson A. S., Weihermüller L., Tappe W., Mukherjee S. and Spielvogel S. (2016) Field scale boscalid residues and dissipation half-life estimation in a sandy soil. *Chemosphere* 145, 163–173.
9. Lagunas-Allué, L., Martínez-Soria, M.-T., Sanz-Asensio, J., Salvador, A., Ferronato, C., Chovelon, J.M., 2010. Photocatalytic degradation of boscalid in aqueous titanium dioxide suspension: Identification of intermediates and degradation pathways. *Applied Catalysis B: Environmental* 98, 122–131.
10. Reilly, T.J., Smalling, K.L., Orlando, J.L., Kuivila, K.M., 2012. Occurrence of boscalid and other selected fungicides in surface water and groundwater in three targeted use areas in the United States. *Chemosphere* 89, 228–234.
11. Skanes, B., Ho, J., Warriner, K., Prosser, R.S., 2021. Degradation of boscalid, pyraclostrobin, fenbuconazole, and glyphosate residues by an advanced oxidative process utilizing ultraviolet light and hydrogen peroxide. *Journal of Photochemistry and Photobiology A: Chemistry* 418, 113382. <https://doi.org/10.1016/j.jphotochem.2021.113382>.
12. US-EPA (2010). Environmental Fate and Ecological Risk Assessment for Boscalid. New Use on Rapeseed, including Canola (Seed Treatment).
13. Xekoukoulotakis, N.P., Drosou, C., Brebou, C., Chatzisyneon, E., Hapeshi, E., Fatta-Kassinou, D., Mantzavinos, D., 2011. Kinetics of UV-A/TiO<sub>2</sub> photocatalytic degradation and mineralization of the antibiotic sulfamethoxazole in aqueous matrices. *Catalysis Today*, Selected contributions of the 6th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA 6), 13th to 16th June 2010. 161, 163–168. <https://doi.org/10.1016/j.cattod.2010.09.027>.
14. Roumayssaa H., 2012. Les espèces actives durant la dégradation photocatalytique : application aux pesticides. Thèse de Doctorat, l'Université de LYON, 168p

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