

*Full Length Research Paper*

# Degradation of chlorantraniliprole by photocatalysis of supported titanium dioxide: Effect of operating parameters

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The rinsing of sprayers after the phytosanitary treatment of agricultural plots generates waste water, which is discharged without prior treatment into aquatic environments. The aim of this study was to evaluate the efficiency of a supported photocatalytic process for the degradation of chlorantraniliprole in an aqueous medium. Clay balls were made in the laboratory from 40 mL of ultrapure water added to 100 g of clay powder to obtain a homogeneous paste. Beads were made and dried at 105°C for 24 h and then baked at 550°C in the oven to make them water-resistant. They were soaked in a 10 g/L ethanol solution of TiO<sub>2</sub> for 24 h, then calcined at 400°C. The photocatalysis experiments were carried out with 50 ml reactors containing 40 g of beads under sunlight in a humid tropical zone for 300 min. The results showed a decrease in the concentration of chlorantraniliprole 500 µg/L under these experimental conditions. The degradation of this insecticide is significantly improved by increasing the clay mass at pH = 6 for a concentration of 500 µg/L. In addition, the application of this photocatalytic process on environmental matrices showed that this process was effective for the depollution of drinking water and river water. The beads were reused for all experiments by recycling them by calcination at 400°C.

**Key words:** Chlorantraniliprole, supported titanium dioxide, clay beads, aqueous medium.

## INTRODUCTION

Although there are many new methods of insect control, chemical control using insecticides has long been considered a reliable method (Hafeez et al., 2019). For example, plant protection products are specifically designed to elicit a biological response in a specific organism (Li et al., 2022). However, some can also elicit the same response in nonspecific creatures following persistent exposure to even minute amounts of these

chemicals (Héma et al., 2009; Khan et al., 2022). As part of the search for alternative molecules to pyrethroids that are effective against insect pests of cotton in the Sahelian zone, chlorantraniliprole, which belongs to the anthranilic diamide family, was authorized in 2014 under the brand name CORAGEN 20 SC. It has been successfully tested at research stations and on growers' farms (Cordova et al., 2006; Lahm et al., 2007). However, despite the good

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quality of the results obtained on cotton plots, the management of sprayer rinse water near water resources located in the drinking water resources of the major cities of Côte d'Ivoire is becoming a problem in agricultural areas. Indeed, due to their high leachability and with a leaching potential index of 4.22 (Lewis and Tzilivakis, 2017; Fenoll et al., 2015), chlorantraniliprole and some of its metabolites can leach through the soil profile. In addition, chlorantraniliprole is considered persistent and mobile in surface waters and exhibits relatively high aquatic toxicity (Aliste et al., 2021). Photocatalytic degradation has been considered an effective and inexpensive tool for the removal of organic and inorganic pollutants from water (Rodrigues-Silva et al., 2013; Chong et al., 2010). Many studies have used an aqueous suspension of anatase ( $\text{TiO}_2$ ) in different physico-chemical forms, to degrade pollutants by UV illumination (Prieto-Rodríguez et al., 2013). The most commonly commercially available powder form of  $\text{TiO}_2$ , shows significant photocatalytic activity (Koltsakidou et al., 2017). However, due to its nanometric size, its use requires an additional and somewhat difficult operation to separate it from treated water. Extensive research has been reported for the immobilization of  $\text{TiO}_2$  on a photochemically stable substrate such as clay minerals (Heidari et al., 2022). The present study aims to develop a solid support (clay) easily available, recyclable, reusable and ecological to immobilize  $\text{TiO}_2$  for the application in the processes of photocatalytic degradation of chlorantraniliprole in aqueous medium. Specifically, it will involve determining the kinetics of chlorantraniliprole degradation and highlighting the influence of certain parameters such as the initial concentration of the pollutant, the initial mass of the catalyst, the pH and the dilution matrices on the kinetics of photocatalytic degradation.

## MATERIALS AND METHODS

### Chemical products

The quality of the products used is of purity greater than 95%. Carlos Erba brand analysis grade ethanol and acetone were 99.99% pure. HPLC grade acetonitrile is of 99.99% purity. The chlorantraniliprole used is a phytosanitary product called CORAGEN 20 SC with a concentration of 200 g/L. The oxidant is titanium dioxide ( $\text{TiO}_2$ ) composed of anatase of 99% purity. It was supplied by the firm Carlos Erba.

### Protocol for the production of clay balls

For the production of clay balls with or without  $\text{TiO}_2$ , two protocols were carried out in each case: calcined pure clay balls were made and the fixing of  $\text{TiO}_2$  on the calcined balls.

### Making calcined balls

To make calcined clay beads, 40 mL of ultrapure water were added

to 100 g of clay powder to obtain a homogeneous paste (Step 1). Beads of about 0.3 mm in diameter were made. These balls were then dried at 105°C (Step 2) for 24 h and then baked at 550°C in the oven to make them resistant in water (Step 3) and also to eliminate all forms of residual organic matter (Figure 1).

### Beads covered of $\text{TiO}_2$ making

The clay beads were soaked in an ethanolic solution of 20 g/L of  $\text{TiO}_2$  for three days. Then, the beads were calcined in the oven at 400°C for 2 h on a temperature ramp of 10°C/min. This ramp promotes fixation of a large quantity of  $\text{TiO}_2$ . The beads were rinsed with ultrapure water to get rid of the  $\text{TiO}_2$  residues which were not well fixed. This experiment was repeated three times to allow better fixation of the  $\text{TiO}_2$  (Figure 2).

### Clay beads characterization tests

#### Analysis by scanning electron microscopy

Scanning electron microscopy (SEM) is a surface characterization technique allowing observations down to the nanometric scale. Before being observed in the SEM, a gold/palladium (Au/Pd) deposit is made on the samples. This metallization avoids the accumulation of charge on the surface of the sample and decreases the penetration depth of the beam, thus improving the quality of the image. The SEM observations were carried out on a Philips XL 30 device at 15 kV coupled to an EDX (Energy Dispersive X-ray) microanalysis.

#### X-ray microanalysis analysis

Energy dispersive X-ray microanalysis, EDX, with a scanning electron microscope allows qualitative and quantitative analyses of small sample volumes of beads coated or not with  $\text{TiO}_2$ . Qualitative X-ray microanalysis is performed using energy dispersive element spectra.

## Experiments

### Adsorption test

Adsorption experiments were carried out in the dark both with the beads covered with  $\text{TiO}_2$  and with those not covered with  $\text{TiO}_2$ . The duration of the test is 300 min.

### Photolysis test

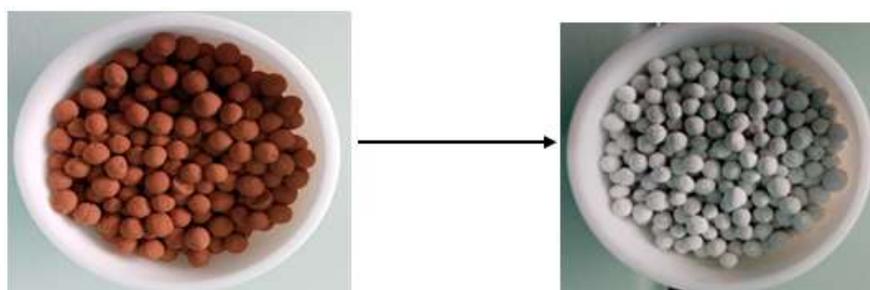
The photolysis consisted in the irradiation of the doped matrices at concentrations of 500  $\mu\text{g/L}$  under solar irradiation in the presence of beads not covered with  $\text{TiO}_2$ . The objective is to know the contribution of direct photolysis during the degradation of the chlorantraniliprole. Samples were then taken successively with Pasteur pipettes at regular time intervals during irradiation (30, 60, 120, 180, 240, and 300 min) and analyzed by high performance liquid chromatograph coupled to a UV detector.

### Experimental photocatalytic

The experimental device is composed of four 50 mL test tubes corresponding to the different times of the experiments. The water matrices were spiked with the chlorantraniliprole solutions. The



**Figure 1.** Steps in the manufacture of calcined clay beads.  
Source: Authors



**Figure 2.** Steps in the manufacture of clay balls covered with titanium dioxide.  
Source: Authors

reactors were placed under natural solar radiation. The duration of each test is 300 min. Samples are then taken successively with Pasteur pipettes at regular time intervals during the irradiation (30, 60, 120, 180, 240, and 300 min) and analyzed by high performance liquid chromatograph. After each photocatalysis test, the reactors and the clay balls were calcined in an oven at 400°C for 2 h to destroy the pesticide residues. The effect of parameters such as the mass of beads impregnated in TiO<sub>2</sub>, the concentration of the pollutant, the pH and the dilution matrices was studied under these studies conditions.

### Photodegradation kinetics

When photolysis or photocatalysis is used for the removal of organic pollutants in aqueous media, the degradation kinetics conforms to the Langmuir-Hinshelwood model. These kinetics describe the reactions between the OH<sup>•</sup> radicals and the adsorbed or dissolved organic molecules. This model is generally first-order kinetics. This reaction is described by Equations 1 to 3.

$$\frac{dc}{dt} = k_{app} \times t \quad (1)$$

$$\ln \left( \frac{c_0}{c} \right) = k_{app} \times t \quad (2)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

$k_{app}$  is pseudo order 1 kinetic constant;  $t_{1/2}$ : reaction half-life time

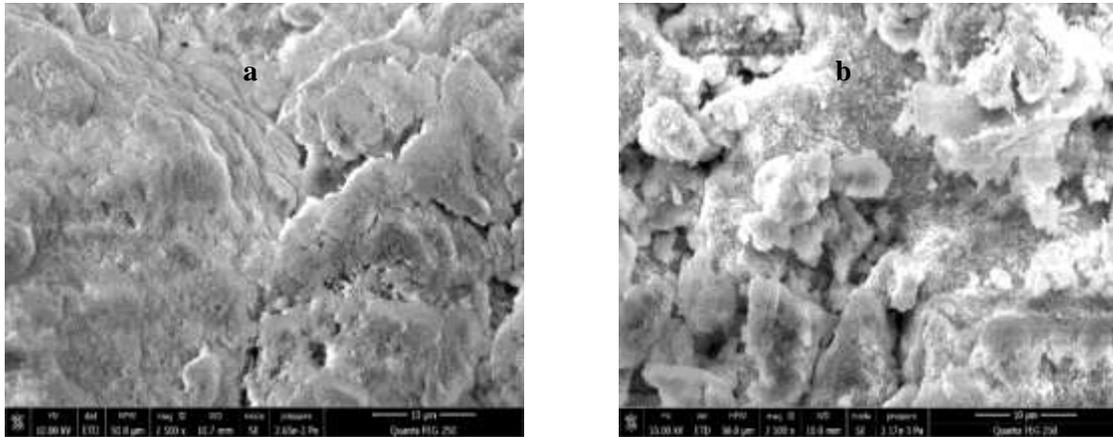
## RESULTS AND DISCUSSION

### SEM-EDX scanning electron microscopy

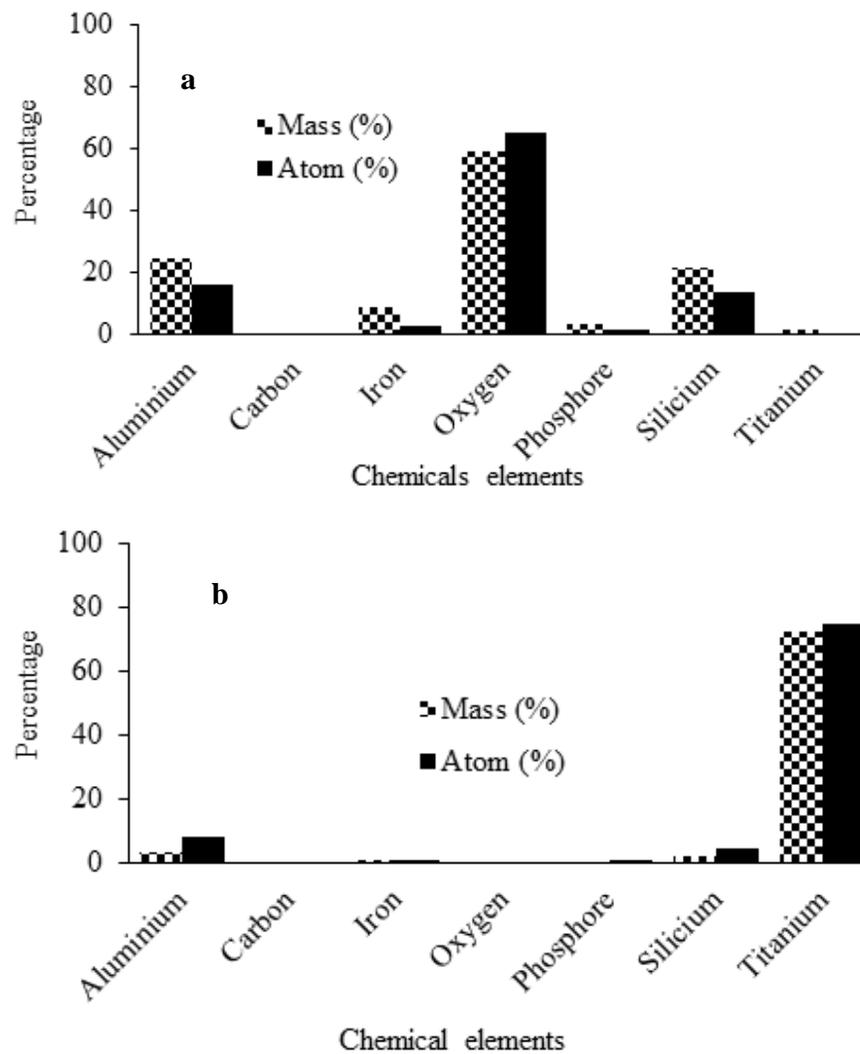
SEM analysis of the various calcined balls is as shown in Figure 3a and b. The results indicate two different topographies of the surface of the two types of clay balls. Observation of the beads coated with TiO<sub>2</sub> show a white color characteristic of the presence of titanium dioxide in Figure 3.

### X-ray diffraction of the different balls analysis

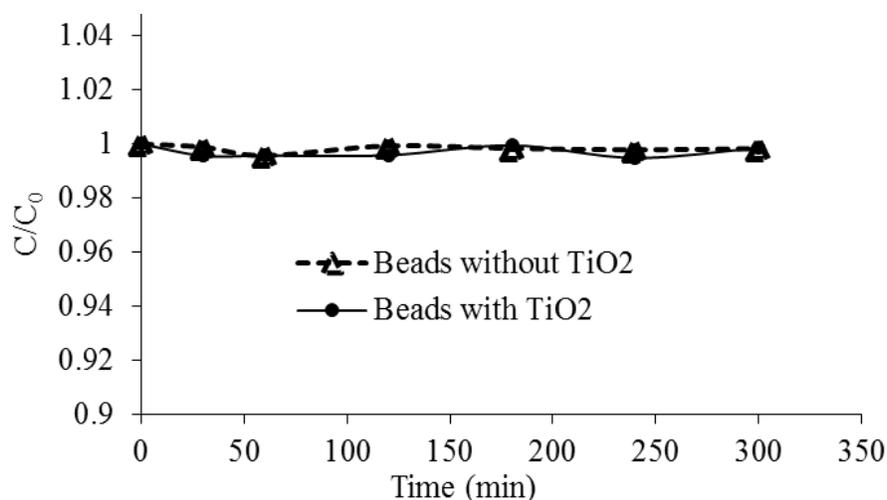
The elementary composition of the different calcined balls is as shown in Figure 4a and b. The results showed that seven (07) elements identified (O, Si, C, Ti, Al, P, Fe, S). Aluminium, silicon and oxygen are the main chemical elements in the calcined balls not covered with TiO<sub>2</sub>. As for the clay, balls are covered with TiO<sub>2</sub>, the results showed a decrease in the energies of the 7 chemical elements and a predominantly appearance of TiO<sub>2</sub>. These results confirm those obtained by scanning electron microscopy.



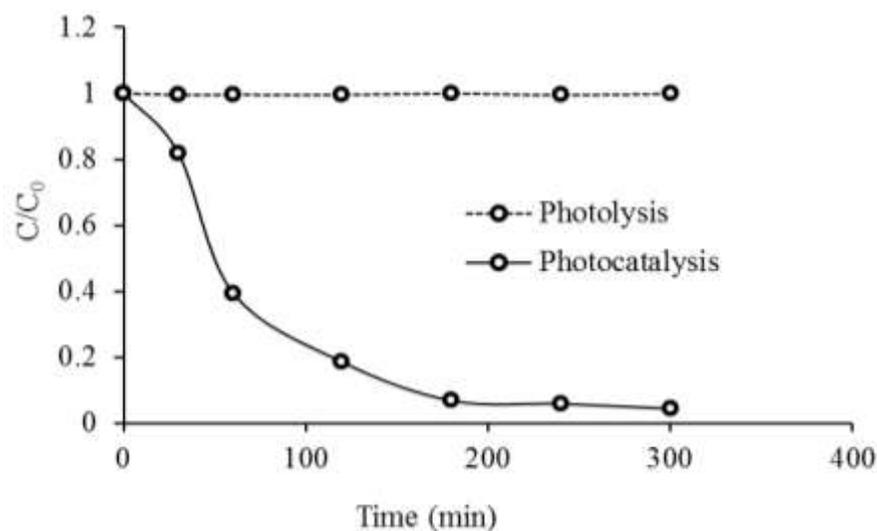
**Figure 3.** SEM images of calcined clay balls not covered with  $\text{TiO}_2$  (a) and covered with  $\text{TiO}_2$  (b).  
Source: Authors



**Figure 4.** Elemental composition of calcined clay balls (a) not covered with  $\text{TiO}_2$  and (b) covered with  $\text{TiO}_2$ .  
Source: Authors



**Figure 5.** Adsorption tests in the presence of simple clays soaked in TiO<sub>2</sub>, V = 50 mL, C<sub>0</sub> = 500 µg/l, T = 25°C, weight = 40 g; pH = 6 .  
Source: Authors



**Figure 6.** Kinetics of photolysis and solar photocatalysis of chlorantraniliprole, C<sub>0</sub> = 500 µg/L, clay weight = 40 g, V = 50 mL, pH = 6.  
Source: Authors

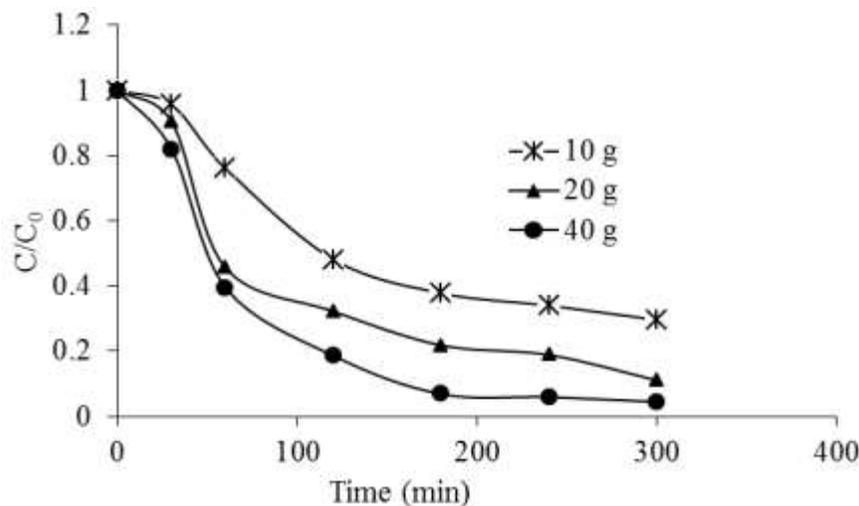
### Adsorption test

Absorption experiments were carried out on beads without TiO<sub>2</sub> and beads covered with TiO<sub>2</sub>. Figure 5 shows the adsorption kinetics of chlorantraniliprole under our experimental conditions. The two adsorption tests were carried out to evaluate the adsorption capacity of the insecticide on the beads soaked in TiO<sub>2</sub> or not. For this, control clay balls and balls soaked in TiO<sub>2</sub> as adsorbent were used during these experiments. The results indicated chlorantraniliprole is not removed by

adsorption tests. These results showed that chlorantraniliprole does not adsorb to the surface of clay materials.

### Photodegradation tests

Direct photolysis and solar photocatalysis tests were carried out by exposing reactors to room temperature illustrated in Figure 6. The direct photolysis experiment by solar exposure indicated that the initial concentration



**Figure 7.** Effect of catalyst concentration, pH = 6,  $C_0 = 500 \mu\text{g/L}$ ,  $T = 25^\circ\text{C}$ .  
Source: Authors

of PAC did not change. These results are in agreement with those obtained by Lin et al. (2017). These authors have also shown that a pesticide cannot be degraded by direct photolysis under similar conditions since this anticancer molecule does not have chromophores which absorb UVA (N'guettia et al., 2017). Unlike photolysis, the solar photocatalysis experiment indicated a break in slope. This rupture is followed by a decrease in the initial concentration of chlorantraniliprole during the solar irradiation. This decrease in initial concentrations would reflect a photocatalytic oxidation of phytosanitary pollutants by  $\text{OH}^\bullet$  radicals. Indeed, most of these processes combine two or three reagents (oxidants) to produce  $\text{OH}^\bullet$  radicals (Fenoll et al., 2015; Gad-Allah et al., 2011). Free radicals are highly active species capable of reacting rapidly and non-selectively on most organic compounds, deemed to be difficult to oxidize biologically or by conventional chemical treatments (Simon et al., 2008; Magnone et al., 2019).

#### Effect of $\text{TiO}_2$ concentration

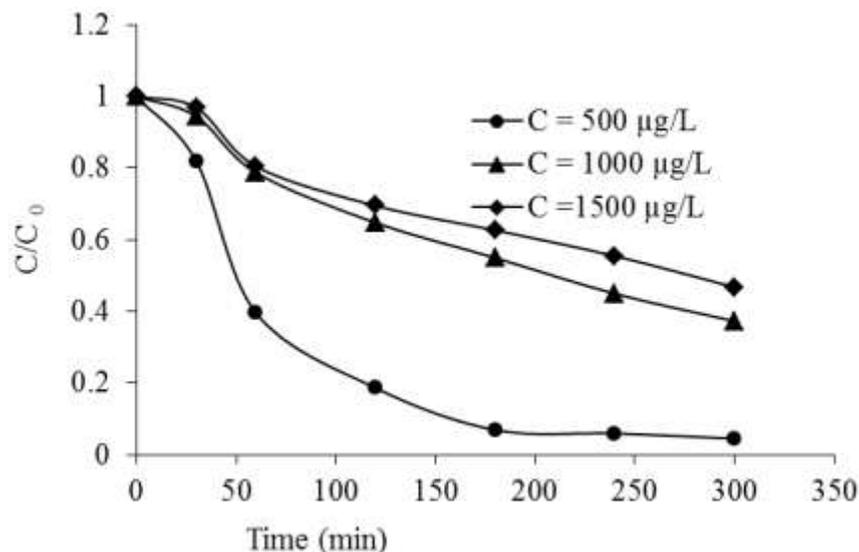
To study the effect of catalyst mass, we increased the mass of beads covered with  $\text{TiO}_2$  from 10 to 40 g. Figure 7 shows the evolution of the disappearance of chlorantraniliprole for these different masses of the catalyst. The results showed that whatever the mass of balls coated with  $\text{TiO}_2$ , 50% of the concentration of the pollutant is degraded after 1 h of reaction. After 300 min of experiment, the rates of disappearance obtained from this insecticide were 70.40, 88.91, and 95.54%. The increase in the mass of the beads covered with the catalyst induces a strong disappearance of chlorantraniliprole in the doped solutions. However, the

mass of beads coated with  $\text{TiO}_2$  is not proportional to the rate of degradation obtained. This could result in a disparity of the  $\text{TiO}_2$  fixed on the surface of the beads. The maximum speed is reached for a mass of 40 g of the  $\text{TiO}_2$  catalyst. These results are similar to those of Xekoukoulotakis et al. (2011) and Michael et al. (2013). These authors have shown that this efficiency reflects an abundant production of hydroxyl radicals. This efficiency would be due to an increase in the exposed surface of the  $\text{TiO}_2$  fixed on the clay beads.

#### Effect of pollutant concentration

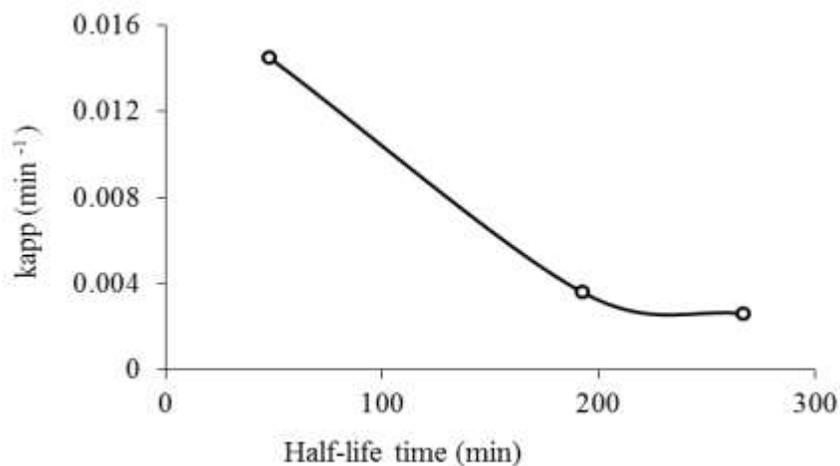
Figure 8 shows the degradation kinetics of chlorantraniliprole in the different reactors. The degradation of the substrate is therefore inversely proportional to the initial concentration of the latter. This fact would be explained by a weaker participation of photons as the concentration of the solute increases; consequently a saturation of the sites of sites of the production of  $\text{OH}^\bullet$  radicals. The reduction rates of the initial concentration of the pollutant are 95.54, 62.74, and 53.26%, respectively for the 500 concentrations; 1000 and 1500  $\mu\text{g/L}$  of pollutant. This phenomenon can be explained by the reduction in the photodegradation of  $\text{h}^+$  holes and/or  $\text{OH}^\bullet$  radicals on the surface of the catalyst due to the covering of the active sites by the pollutant, or by the reduction in intensity of the radiation absorbed at the level of the catalyst caused by the molecules of the pollutant (Simon et al., 2008).

Figure 9 shows the rate equations for the degradation of chlorantraniliprole at different concentrations. The expression of the equation  $\ln\left(\frac{C_0}{C}\right) = kt$  is straight with



**Figure 8.** Effect of chlorantraniliprole concentration, weight of beads-TiO<sub>2</sub> = 40 g; T = 25°C, pH = 6.

Source: Authors



**Figure 9.** Right-hand equation as a function of irradiation time in ultrapure water.

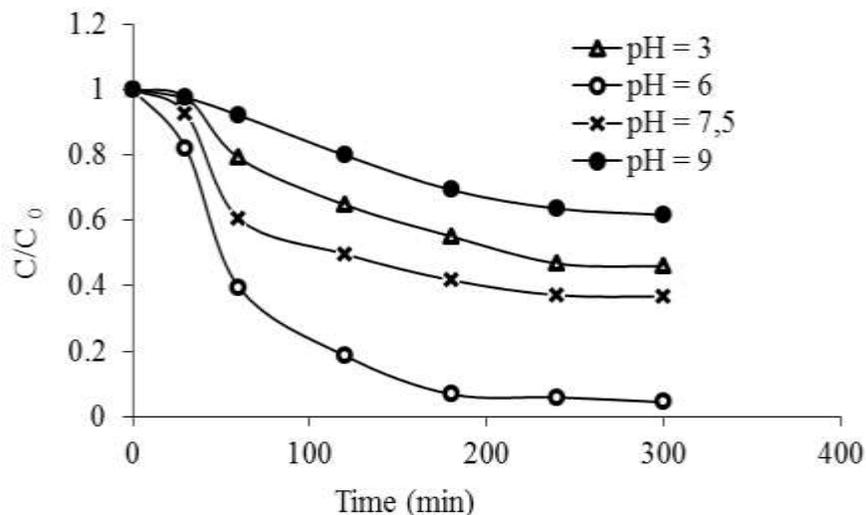
Source: Authors

correlation coefficients  $R^2$  equal to 0.99 for the different concentrations of pollutants. The disappearance kinetics of chlorantraniliprole follows a first-order law. The values of the kinetic constants are  $2.6 \cdot 10^{-3}$ ,  $3.4 \cdot 10^{-3}$  and  $1.45 \cdot 10^{-2} \text{ min}^{-1}$ . The results indicated that the rate constant ( $k_{app}$ ) decreases with increasing substrate concentration. And as a result, half-life times were reduced from 267 to 48 min for chlorantraniliprole concentrations of 500 to 1500 µg/L. In fact, in water, chlorantraniliprole is persistent under aerobic conditions with a half-life varying from 125 to 231 days (median of 178 days). It is moderately persistent under anaerobic conditions (half-life = 42 days)

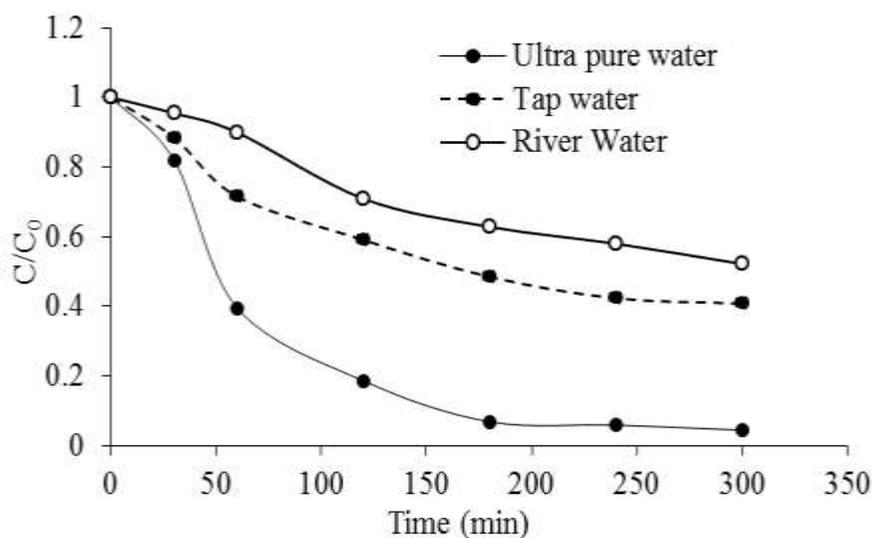
at 25°C. In addition, metabolites such as (2-[3-bromo-1-(3-chloro-2-pyridinyl)-1H-pyrazol-5-yl]-6-chloro-3,8-dimethyl-4(3H)-quinazolinone), is also persistent in aerobic soils where its half-life ranges from 646 to 785 days. In water, this metabolite is persistent with half-lives of 121 to 680 days (aerobic) and 701 days (anaerobic).

#### **Effect of pH**

Figure 10 shows the degradation kinetics of chlorantraniliprole at different values of pH. The variation



**Figure 10.** Degradation kinetics of chlorantraniliprole as a function of pH,  $C_0 = 500 \mu\text{g/L}$ , weight = 40 g. Source: Authors



**Figure 11.** Degradation kinetics of chlorantraniliprole according to the dilution matrices,  $C_0 = 500 \mu\text{g/L}$ , weight = 40 g. Source: Authors

of the pH makes it possible to highlight the ionic forms of the organic molecules in this study. Depending on the value of this pKa, we varied the pH values of the solutions to be irradiated from 3 to 9. In the case of chlorantraniliprole, the pKa value is 10. This shows that chlorantraniliprole would practically exist in its cationic form in aqueous environmental media. These results revealed that the cationic form of chlorantraniliprole is eliminated at different pH values of the spiked waters.

**Effect of water matrices**

The influence of environmental water matrices was studied. The aim is to optimize the removal process of chlorantraniliprole from ordinary waters. For this, drinking water or tap water was used in addition to ultra-pure water as shown in Figure 11. The results indicated a gradual disappearance of this molecule in tap water than in river water spiked at  $500 \mu\text{g/L}$ . These results showed a

difference in the degradation rates of chlorantraniliprole in these matrices which would be linked to the chemical composition of the irradiated matrices. These results are in agreement with those of Pereira et al. (2013) and Sheng et al. (2013). These authors indicated that  $\text{HCO}_3^-/\text{CO}_3^{2-}$  ions which are abundant in tap water or organic matter present in river water can trap OH radicals or attach themselves to  $\text{h}^+$  holes. Also, these effects are complex due to the ability of some of them to compete with organic compounds for oxidizing species (Calza et al., 2006) or to adsorb on the active surface sites of the catalyst depending on the ionic strength. These mechanisms can reduce the overall catalytic activity and therefore the rate of degradation of organic molecules (Dionysiou et al., 2000).

## Conclusion

Photocatalytic oxidation  $\text{TiO}_2$  fixed on clay balls under artificial light offers an interesting alternative for the detoxification of water polluted by chlorantraniliprole. Increasing the mass of beads covered with  $\text{TiO}_2$  improved the degradation rate of this insecticide in this study. On the other hand, the concentration of the pollutant should be optimized with the mass of balls covered with  $\text{TiO}_2$ . For this study, the optimal pH value is between 6 and 10. Under these conditions, this solar photocatalytic process could also be effective for the depollution of environmental matrices.

## CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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