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Photocatalytic Removal of Pesticides Present in Agro-industrial Water Effluents

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Abstract. Pesticide residues accumulated in agricultural wastewaters constitute a potential risk for the environment and the human health. Hence, focused actions for their elimination are of high priority for both the industry and national authorities. This work evaluates the effectiveness of the photocatalytic process to decompose four representative pesticides of different physicochemical properties; chlorpyrifos an organophosphate; thiamethoxam an neonicotinoid; flonicamid a pyridine and tebuconazole a triazole, frequently detected in the water effluents generated of the fruit-industry. Their photocatalytic degradation was examined using the commercial photocatalyst Evonik P25 TiO_2 in a lab-scale batch reactor. The optimum conditions of the photocatalytic reactions were defined and the apparent reaction rate constants for the pesticide decomposition was determined. It was confirmed that the reaction rate depends on the pesticides concentrations (varying from 1 to 10 mg/L), the pH values of the solution (from strong acidic, to neutral and strong alkaline medium) and the presence of scavenger reagents (acting as reactive radicals quenchers). The photocatalytic efficiencies were evaluated taking into thorough consideration the compounds solubility and their adsorption onto the catalyst’s surface. Complete degradation of the selected pesticides was achieved after one hour illumination under UV-A light, without any formation of toxic by-products.

Keywords: degradation, pesticide, scavengers, solution pH, titanium dioxide photocatalysis

1. Introduction

Nowadays, the agricultural industry activities are related with a plethora of pesticides, like fungicides, herbicides or insecticides. Even if the pesticide usage improved and enlarged the production of cereals, fruits or vegetables sector, it has also raised potentially harmful effects for the aquatic environment and human health, negative effects, including short-term and long-term toxicity, endocrine disrupting effects or antibiotic resistance of microorganisms. Most of the pesticides are recalcitrant organic molecules, non-biodegradable and resistant in the removal from the conventional wastewater treatment plants. Characteristic examples of common pesticides are the organophosphoric pesticides of chlorpyrifos (CP), the pyridne and neonicotinoid insecticides of flonicamid (FND) and thiamethoxam (TMX), respectively, or the triazole fungicides of tebuconazole (TBZ). Among the proposed solutions for agricultural wastewater purification, the advanced oxidation technologies based on heterogeneous photocatalysis with titania (TiO_2) are a very promising treatment method [Athanasekou et al., 2018]. Titania, a non-toxic and earth abundant oxide, has the ability to degrade water contaminants pollutants by forming highly reactive and non-selective radical species under UV-A illumination [Arfanis et al., 2019].

In this work, the photocatalytic degradation of the aforementioned pesticides was studied, in order to evaluate the capability of titania under a variety of experimental conditions. The obtained results on these representative water contaminants are currently employed in the development and optimization of an innovative hybrid photocatalytic nanofiltration reactor prototype unit (PNFR), with the ability to recycle 15 m^3/day of real agro-wastewater [Athanasiou et al., 2016].

2. Materials & Methods

For the photocatalytic removal of pesticides from the water matrix, the commercial titania Evonic Aeroxide P25 was selected as model photocatalyst. The experiments were carried out in open vessel glass vials in batch-mode, using 10 mL of aqueous solutions of chlorpyrifos (CP), tebuconazole (TBZ), thiamethoxam (TMX), or flonicamid (FND). In all cases the contaminants’ concentration was 10 ppm, while 1 mg of P25 was suspended in the above solutions (0.1g/L). The vials were placed into a photoreactor with four UV-A lamps (Sylvania 15W/BLB, power density 2.6 mW cm^{-2}) in a distance of 15cm and were illuminated for 90 minutes. During the photocatalytic experiments, at precise time intervals, the catalyst was separated from the aqueous suspension through filtration with PTFE filters and the supernatant solution was measured by HPLC, in order to determine the pollutants' decomposition rate. Each experimental point in the respective graphs corresponds to consecutive photocatalytic runs, by using a new vial of 10 mL, under the same conditions.

Measurements were performed using a LC-ESI(+)MS/MS system (Varian model 1200 L) operating at multiple reaction mode (MRM) with selective MRMs for each compound. Separation was achieved with a reverse-phase Zorbax SB C18 3.5 μm particle size, 150 mm× 2 mm analytical column (Agilent), using a gradient program with mobile phase A consisting of H_2O/ACN (90:10 v/v), 1 mM HCOONH4, 0.1 HCOOH and mobile phase B consisting of ACN/H_2O (90:10 v/v), 1 mM $HCOONH_4$, 0.1% HCOOH. The injection volume was 5 μL and the total run-time was 15 min.

3. Results

2.1. Photocatalytic Degradation of Pesticides

Initially, the pesticides' adsorption kinetics were determined, before the evaluation of the photocatalytic performance. In the absence of UV-A light, both flonicamid and thiamethoxam presented negligible adsorption onto the catalyst, even after 90 minutes, while tebuconazole and chlorpyrifos were adsorbed more effectively (results not shown). Considering these preliminary results, it was concluded that the 60 minutes stirring under dark conditions could ensure the required sorption-desorption equilibrium. Next, the molecules' photostability was also corroborated under UV-A illumination, since the pesticides concentration did not alter significantly in the absence of P25, especially for TMX and FND. Summarizing, the adsorption and photolysis effects should be subtracted from photocatalytic results in the case of tebuconazole and chlorpyrifos, in order to avoid problems in the results interpretation.

The photocatalytic degradation experiments with the non-polar and water insoluble chlorpyrifos and tebuconazole revealed that TiO_2 is highly effective in removing these contaminants. Interestingly, the total process lasted less than 15 minutes, complicating the identification of accurate degradation kinetics. Since in most of the relevant studies of CP much more concentrated pesticide solutions (up to 100 ppm) are used, it was assumed that the competitive phenomena of contaminants' photolysis, photocatalysis and adsorption are accelerating their removal in the tested conditions. In any case, the complete mineralization of CP and TBZ was proven under TOC measurements, establishing the photocatalytic degradation with P25 as an efficient method for the chlorpyrifos and tebuconazole pesticides removal from water.

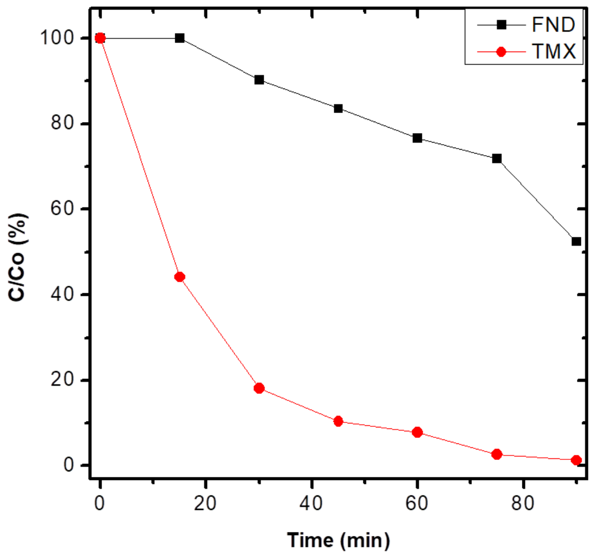

Figure 1. Kinetics of photocatalytic degradation of thiamethoxam (TMX) and flonicamid (FND) using titania P25

The photocatalytic degradation kinetics of the polar and water soluble thiamethoxam and flonicamid were tested (Figure 1). The neonicotinoid thiamethoxam presented high photodegradation rates, reaching complete removal after 60 minutes and no toxic by-product residuals in the solution. As expected, the pryridne flonicamid was more resistant is photocatalysis, presenting ~48% removal after the experiment [Garrido et al. 2019]. In order to calculate the first-order rate constant (K_{app}, $ln\frac{C_t}{C_0} = K_{app}\, t$) and the initial reaction rates ($r_{r,0}$, $r_{r,0} = K_{app} C_0$), the photocatalytic experiments had been repeated at 6 different concentrations of the solutes. The estimated values for thiamthoxam and flonicamid are ensuring that the reactions satisfy the first-order kinetics of the Langmuir–Hinshelwood law [Papageorgiou et al., 2012].

2.2. Effect of solution pH

As the pH of real water varies with climate conditions and effluents, the effect of pH environment on the photodegradation kinetics of TMX and FND was examined [Arfanis et al., 2017]. No alterations on the adsorption capacity of pesticides onto TiO_2 was expected through charge interactions, because titania has a zero charge point close to 5, while thiamethoxam has no dissociation constant (pK_a) and FND does not dissociate in the tested pH values (pK_a = 11.6, max adjusted pH =10). For this reason, any change of the degradation rates with pH should be only attributed to the variation of the active species concentration in the solution. As shown in Figure 2, the photodegradation rates of thiamethoxam were similar at pH 7 and 9, whereas at pH=3 the photodegradation rate attenuates significantly. In contrast, the photocatalytic degradation of flonicamid in acidic medium was enhanced, while the alkaline medium did not improve the removal efficiency.

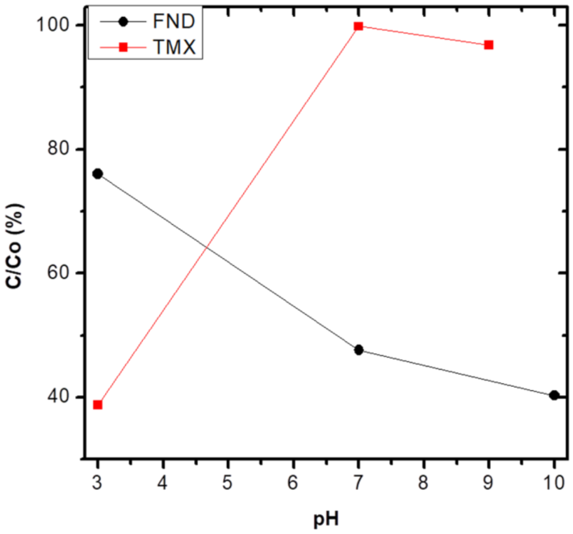

Figure 2. Effect of pH environment in the photocatalytic removal of of thiamethoxam (TMX) and flonicamid (FND)

2.3. Trap Experiments

In order to understand better the role of pH medium during the photocatalysis, radical tap experiments were performed using appropriate additives as quenchers: benzoquinone (BQ) as scavenger for super oxide anion radicals ($O_2^{\cdot -}$), potassium bromate ($KBrO_3$) for electrons, potassium iodide (KI) for holes and isopropanol (IPA) for hydroxyl radicals. Regarding the overall experimental results with quenchers, it was observed for both pesticides that the photocatalytic removal efficiency was totally hinder in the absence of hydroxyl radical and holes, whereas the absence of superoxide radicals and electrons had a less negative impact in photocatalysis. Thus, it is concluded that photocatalytic oxidation pathways are the primal removal mechanism of thiamethoxam and flonicamid, though reduction reactions also occurs.

4. Conclusions

In this study, the photodegradation of chorpyrifos, tebuconazole, thiametoxam and flonicamid pesticides, accumulated and frequently detected in wastewaters of fruit industry, was achieved. After 90 minutes of UV-A illumination, the pesticides were totally removed from the solution in the presence of the commercial titania photocatalyst Aeroxide P25, while no toxic by-products were detected during the process. Extensive examination was evaluated the effect of solution acidity on the photocatalytic efficiencies, and all the variations were sufficiently explained. Last, the photocatalytic oxidation pathways were recognized as the main degradation mechanism for both thiametoxam and flonicamid, where the photogenerated hydroxyl radical were the most reactive species. These results are verifying the advantageous performance of TiO_2 materials against a variety of pesticides with different physicochemical properties, under a variety of experimental conditions. Moreover, these findings are demonstrating that the integration of titania catalysts in the up-scaled hybrid photocatalytic nanofiltration membrane reactor is a very promising technology for the agricultural wastewaters purification.

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