Enhanced Degradation Of Cyanantraniliprole And Chlorantraniliprole In Soil By Solar Photocatalysis

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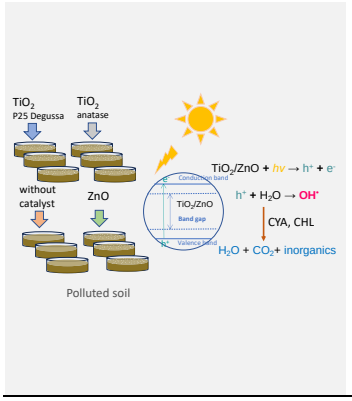

In this work, we have studied the photo-degradation of two anthranilic diamide (cyantraniliprole and chlorantraniliprole) insecticides in soil using ZnO, TiO_2 P25 Degussa and TiO_2 anatase as catalysts under solar irradiation. An analytical methodology based on a green sample treatment procedure and liquid chromatography with mass spectrometry (LC-MS) using triple quadrupole (QqQ) analyzer has been used for determination and identification of these insecticides and their main transformation products. Comparison of these catalysts showed that ZnO is the most efficient for the removal of studied pollutants. The results confirm the efficacy of the treatment to remove recalcitrant pollutants from soil using natural sunlight as renewable source.

Introduction

Anthranilic diamides, such as cyantraniliprole (CYA, 5-bromo-2-(3-chloropyridin-2-yl)-*N*-[4-cyano-2-methyl-6-(trideuteriome-thylcarbamoyl)phenyl] pyrazole-3-carboxamide) and chlorantraniliprole (CHL, 3-bromo-*N*-(4-chloro-2-methyl-6-((methylamino)carbonyl)phenyl)-1-(3-chloro-2-pyridinyl)-1*H*-pyrazole-5-carboxamide), are a group of insecticides widely used against *Lepidoptera* insects via activation of ryanodine receptors (RyRs). These compounds could be found in soils because of their use in different crops. Therefore, innovative and sustainable technologies for the remediation of pesticide contaminated soils are necessary in order to protect consumers and environment. In recent years, photocatalysis using semiconductor oxides as catalysts has been used to destroy organic pollutants in water and soil. Among these materials, titanium dioxide (TiO_2) and zinc oxide (ZnO) are the most widely photocatalysts studied. TiO_2 is a polymorphous compound, which exists in three crystallographic phases (rutile, anatase, and brookite) of which only anatase is functional as photocatalyst. TiO_2 P25 Degussa is a mixed-phase titania photocatalyst, containing both anatase (70%) and rutile (30%) crystallites. The aim of this work was to evaluate at laboratory scale the efficacy of the use of different semiconductor oxides for the photocatalytic solar degradation of cyantraniliprole, chlorantraniliprole and their main transformation products from soil.

Material and Methods

Analytical standards of CYA (≥ 98 %) and CHL (≥ 99 %) were purchased from Chem Service, Inc (PA, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Zinc oxide (ZnO 99.99 %, 5 m^2 g^{-1}, <210 nm) was purchased from Alfa Aesar (Karlsruhe, Germany). Titanium dioxide P25 Degussa (99.5 %, 50 m^2 g^{-1}, <21 nm) was supplied from Nippon Aerosil Co., Ltd. (Osaka, Japan). Titanium dioxide anatase (99.7 %, 45-55 m^2 g^{-1}, <25 nm) was purchased from Sigma-Aldrigh (Madrid, Spain). Physicochemical properties of the selected soil were: silty clay loam texture (19.9 % sand, 51.6 % silt, 28.5 % clay); pH 7.9; OM 0.03 % (w/w); EC 2.14 dS m−1. Soil was spiked with active ingredients of cyantraniliprole and chlorantraniliprole to reach a level of 1000 µg kg^{-1} for each one. Then, 30 g of polluted soil were weighed in the corresponding Petri plates (90 × 15 mm) and 1 g of catalyst (ZnO, TiO_2 anatase and TiO_2 Degussa P25) was added. In addition, 30 mL of deionized water was also added. Soil samples were exposed to sunlight during the photoperiod. The extraction of insecticide residues from soil samples was conducted according to the procedure developed by Fenoll et al. [1]. Identification and quantification of TPs were carried out using a 1260 Infinity UHPLC combined with an Agilent 6465BA QqQ Mass Spectrometer (LC-MS/MS). The analytical column was a Zorbax Eclipse XDB-C8.

Results and Discussion

Catalyst loading and moisture content were previously optimized. Figure 1 shows the evolution of insecticide residues during the experiment. ZnO and TiO_2 P25 Degussa have higher disappearance rates than TiO_2 anatase. Thus, the residual levels of CYA and CHL at the end of the experiment using ZnO were 1.10 and 1.06 µg kg^{-1}, respectively. In the case of TiO_2 P25 Degussa, the residual levels after 23 hours of light exposure were 25.6 and 39.2 µg kg^{-1}, respectively. Residual concentrations of 77.5 and 114.9 µg kg^{-1}, respectively, were found when TiO_2 anatase was used. In the absence of a catalyst, the photolytic decomposition of these compounds occurs at a slower rate and only a 70 % and 23 %, respectively, reduction of its concentration is achieved after 23 hours of accumulated irradiation.

ZnO appears to be more effective on CYA and CHL oxidation than TiO_2 under solar of irradiation. The observed differences between ZnO and TiO_2 are certainly

related to the different properties of the photocatalyst [2]. Thus, ZnO has a lower specific surface area and higher particle size than TiO_2. In addition, the apparent extra reaction rate of ZnO under solar irradiation is very likely due to the fact that it absorbs large fraction of the solar spectrum and absorption of more light quanta than TiO_2 [3] However, ZnO can be photocorroded when ZnO is used as photocatalyst [4].

The presence of transformation products of CYA and CHL was also studied by HPLC-MS^2.

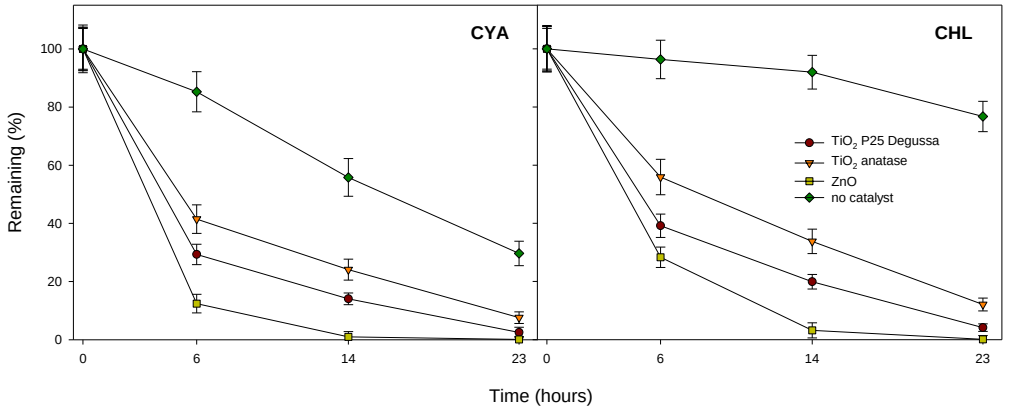

Figure 1. Degradation of Cyanantraniliprole (CYA) and Chlorantraniliprole (CHL) during the different treatments under solar irradiation.

Conclusions

In summary, the use of heterogeneous solar photocatalysis can be considered as a suitable technology to remove CYA, CHL and their transformation products from soil especially in some areas of the Mediterranean Basin, where solar irradiation is highly available (more than 3,000 h of sunshine per year on average in some areas) making this process quite attractive.

Acknowledgments

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