Application Of Advance Oxidation Processes At Laboratory Scale For Pharmaceutical Residues Degradation In Soils

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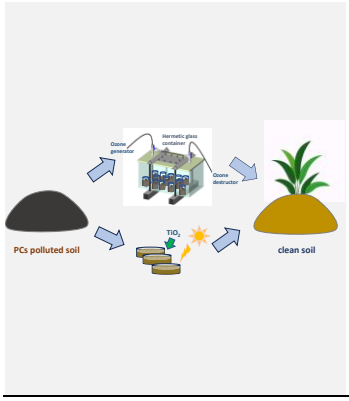

This work was aimed to study the effectiveness of two advance oxidation processes (photocatalysis and ozonation) in the degradation of carbamazepine residues in three different soil matrices. Photocatalytic treatment was carried out by means of TiO_2 P25 Degussa under solar irradiation. Ozonation treatment was conducted using a hermetic glass chamber connected to an ozone generator. A BMT 964 analyzer and an ozone destructor were also attached. Comparison of both processes showed that TiO_2 photocatalytic treatment under solar irradiation is the most efficient for carbamazepine removal after 48 hours of treatment. The results suggest that both techniques could be considered as remediation tools for the elimination of pharmaceutical residues from soils.

Introduction

A great number of pharmaceutical compounds (PCs) is often detected in the environment. Either direct discharges or indirectly through orine and feces, PCs are introduced in the sewage system and reach wastewater treatment plants (WWTP). However, WWTP conventional treatments are not designed to fully remove organic compounds occurring at trace concentrations. Besides spreading PCs pollution across water comparments, treated WWTP effluents are also a significant source of PCs accumulation in soils and crops when these waters are used for irrigation purposes, jeopardizing human health and the environment. Carbamazepine (CBZ) is a representative example of PCs pollutant. This persistent antiepilectic drug has been regularly prescribed worldwide and is frequently found in soil systems. Advanced oxidation processes (AOPs) constitute a promising technology for the remediation of polluted soils. AOPs can turn nearly all types of organic pollutants into harmless or less harmful products after direct introduction of oxidizing agents in the contaminated site and the subsequent formation of hydroxyl radicals ($OH^{\bullet}$). Their high versatility offers a wide variety of possible processes for $OH^{\bullet}$ generation, being photocatalysis and ozonation some of the most often applied. Photocatalysis use semiconductors (TiO_2, ZnO, CdS, etc.) as catalysts to generate the $OH^{\bullet}$ radicals. Among the different semiconductor materials tested, TiO_2 P25 Degussa stands out because of its photochemical stability, commercial availability, non-toxic nature and low cost, high photoactivity and ease of preparation in the laboratory. Ozonation is based on the use of ozone (O_3) for the treatment of contaminated soils. Organic contaminants can be decomposed directly by molecular ozone or through indirect reactions with $OH^{\bullet}$ (generated from O_3 decomposition) that facilitates pollutants oxidation. The aim of this work was to evaluate at laboratory scale the efficacy of two AOPs, TiO_2 photocatalysis under solar irradiation and ozonation, for the degradation of carbamazepine residues from three different soils.

Material and Methods

CBZ analytical standard (≥99.5%) and titanium dioxide P25 Degussa (99.5 %) were purchased by Merck Life Science SLU (Madrid, Spain) and Nippon Aerosil Co. Ltd. (Osaka, Japan), respectively. Physicochemical properties of the soils assayed were: soil S1 texture (18% sand, 16% silt, 34% clay), pH 7.9, OM 0.27% (w/w), EC 0.92 dS m^{-1}; soil S2 texture (34% sand, 26% silt, 40% clay), pH 7.4, OM 0.51% (w/w), EC 9.11 dS m^{-1}; soil S3 texture (10% sand, 27% silt, 62% clay), pH 8.1, OM 1.20% (w/w), EC 4.8 dS m^{-1}. Soils were spiked at 200 µg kg^{-1} of CBZ active ingredient. For photocatalytic treatment, soils were weighed in Petri plates (90 × 15 mm) and 1 g of TiO_2 Degussa P25 and 30 mL of deionized water were added. Then, samples were exposed to sunlight during 48 hours and three replicates were taken initially and at 10, 30 and 48 hours). Ozonation treatment was performed using an airtight glass container (volume 150 L) connected to an Osmaqua Ozone generator (4.49 g (O_3) h^{-1}). Samples were weighed in pyrex glass vessels (110 mm long, 80 mm diameter), introduced in the container and exposed to ozone during 6 days and three replicates were collected at scheluded times (0, 4, 24, 48, 96, 120 and 144 hours). The procedure followed for the extraction of CBZ residues in soil samples was performed as reported by Fenoll et al. [1]. Samples were analysed by HPLC-MS^2.

Results and Discussion

Influential parameters of both techniques (catalyst loading, moisture content and ozone dosage) were previously optimized. Figure 1 depicts the evolution of CBZ residues during photocatalytic and ozonation treatments. In both treatments, the highest degradations corresponded to soil S1, with the lesser OM content. For the rest of soils,

degradations were lower as the OM content increased (soil S1 > soil S2 > soil S3). OM can enhance the sorption of pollutants and as a result inhibite degradation [2]. In addition, OM can acts as $OH^{\bullet}$ scavenger and react with these radicals faster than soil pollutants [3]. Residual levels found in photocatalytic treatment after 48 hours of accumulated solar irradiation ranged from 0.25 to 36.7 μg kg^{-1}, for soils S1 and S3, respectively. In the case of ozonation treatment, residuals levels after 48 hours of exposure varied from 8.54 to 107.8 μg kg^{-1}, for soils S1 and S3, respectively. TiO_2 photocatalytic treatment under solar irradiation seems to be more effective for CBZ removal. However, the increase of ozone exposure time to 144 hours enhanced CBZ degradation. Residual levels found at the end of ozonation treatment were 0.07, 0.5 and 42.6 μg kg^{-1} for soils S1, S2 and S3, respectively. The reactive species, O_3, and $OH^{\bullet}$ radicals, appears to be responsible for the increased pesticide removal [4].
The occurrence of transformation products of CBZ was also studied by HPLC-MS^2.

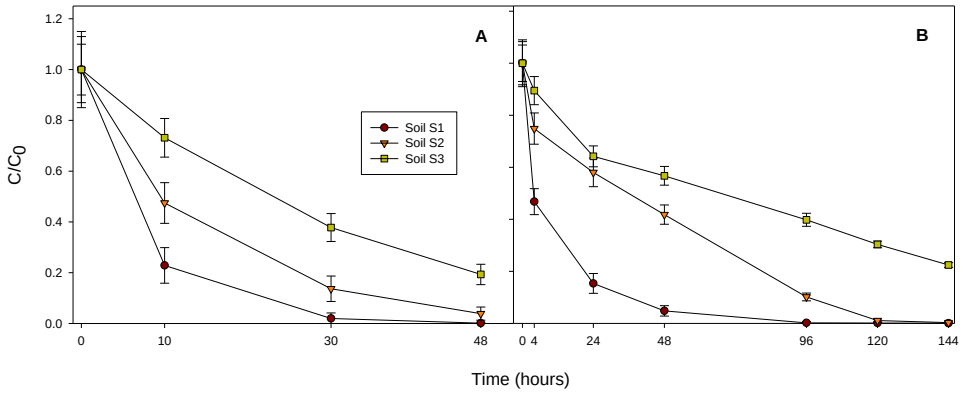

Figure 1. Concentration-time course of CBZ residues in the different soils during degradation experiments (A: TiO_2 photocatalytic treatment under solar irradiation; B: ozonation treatment).

Conclusions

Results indicate that both treatments can be proposed as suitable technologies for removing organic compounds in soils. TiO_2 photocatalytic treatment under solar irradiation was proven to be more effective than ozone exposure after 48 hours of treatment. The low-cost of reactives and the use of renewable energy source like sunlight make this treatment more attractive, particularly in Mediterranean countries where many places reach 3000 h of sunlight per year.

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