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Comparison of different photocatalytic treatments to detoxify pesticide-polluted water

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PURPOSE OF THE ABSTRACT

Currently, the pollution of soil and water bodies (via point sources of diffuse) by pesticides used in agriculture can pose an important threat to aquatic ecosystems and drinking water resources. Therefore, low-cost, innovative and sustainable wastewater treatment technologies are necessary to avoid the discharge of pesticides into natural aquatic ecosystems, as mentioned in the European Directive on water policy (2013/39/EU).

This study aims to demonstrate a technically feasible alternative to remove pesticide residues from water by photocatalysis. For this, the photocatalyzed degradation of eight pesticides was investigated by heterogeneous (ZnO and TiO2) and homogeneous (Fe2+/Fe3+) photocatalysis at lab-scale using a photoreactor. Figure 1 shows the structure of the studied pesticides. Ferrous (FeSO4x7H2O) and ferric salts (Fe2(SO4)3xH2O), titanium dioxide (TiO2) P25 Aeroxide (99.5% purity, 55 m2 g-1 BET surface area, <21 nm particle size) and Zinc oxide (ZnO) (99.9% purity, 7 m2 g-1 BET surface area, 194 nm particle size) were used as photocatalysts and H2O2 and Na2S2O8 as oxidants.

The concentration of photocatalysts and oxidants were optimized in deionized water (18 M? cm resistivity) using a 2 L photoreactor at lab-scale as previously described by Vela et al. (2015). The emission of the lamp was in the range 300-460 nm (major emission output at 366 nm). The temperature was controlled and fixed at 23 ºC ± 1ºC by means of a thermostat pumping water through the glass jacket.

Pesticide residues from water were isolated with acetonitrile and analysed following the method proposed by Fenoll et al. (2011). Chromatographic analysis were carried out using an HPLC system Agilent Series 1100 (Agilent Technologies Santa Clara, CA, USA) equipped with a reversed phase C8 analytical column of 150 mm × 4.6 mm and 5 µm particle size (Zorbax Eclipse XDB-C8) coupled to an Agilent G6410A triple quadrupole mass spectrometer fitted to an ESI interface operating in positive ion mode.

The photodegradation of the pesticides was modelled assuming a pseudo-first-order kinetics (-dC/dt = kappC ? ? Ct = C0?e-Kapp??t or lnC0/Ct = kapp?t) where kapp (time-1) is the apparent reaction rate constant.

For heterogeneous treatments, the appropriate amount of photocatalyst (200 mg L-1 of TiO2 or 200 mg L-1 of ZnO) in tandem with Na2S2O8 (250 mg L-1) used as electron acceptor was added in each case. To achieve the maximum pesticide adsorption onto surface of the semiconductor the solutions were maintained for 30 min in the dark, prior to irradiation. In the case of homogeneous treatment (photo-Fenton), the used [Fe2+]/[Fe3+] and [H2O2] were 10 mg L-1 and 80 mg L-1, respectively. Several samples were taken during the photoperiod (120

min). Parallel, a photolytic test was performed in absence of any photocatalyst. All trials were replicated three times. Table 1 shows the rate constants obtained in each case.

As can be observed, the mean rate constants (n=8) were in the order: ZnO + $S_2O_8^{2-}$ pH 7 > TiO_2+ $S_2O_8^{2-}$ pH 7 > ZnO pH 7 > TiO_2 pH 7 > Fe(III) pH 3 > Fe(III) pH 5 > Fe(II) pH 3 > Fe(II) pH 5. The obtained results show that the use of semiconductor materials like ZnO and TiO_2 in tandem with $Na_2S_2O_8$ quickly reduce the initial amount of pesticides in water in our experimental conditions. Therefore, the use of heterogeneous solar photocatalysis can be considered as a suitable technology for removing pesticides from water especially in some areas of the Mediterranean Basin such as south-eastern Spain where shortages of irrigation water is a major problem but receives more than 3000 h of sunlight per year.

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FIGURES

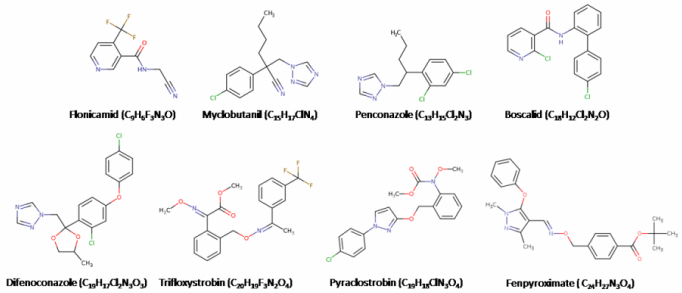

FIGURE 1

Figure 1

Structures of the studied pesticides.

Pesticide	Catalyst/pH							
	Fe(II) pH 5	Fe(III) pH 5	Fe(II) pH 3	Fe(III) pH 3	TiO_2 pH 7	ZnO pH 7	TiO_2+ $S_2O_8^{2-}$ pH 7	ZnO + $S_2O_8^{2-}$ pH 7
Boscalid	0.0070	0.0150	0.0106	0.0324	0.0643	0.0766	0.0749	0.0876
Difenoconazole	0.0333	0.0544	0.0469	0.0856	0.0637	0.0841	0.1750	0.5648
Fenpyroximate	0.0150	0.0202	0.0312	0.0361	0.1965	0.2280	0.2923	0.2664
Flonicamide	<0.0001	0.0011	<0.0001	0.0021	0.0061	0.0079	0.0198	0.0703
Myclobutanil	0.0194	0.0287	0.0302	0.0706	0.0323	0.0416	0.0894	0.6835
Penconazole	0.0184	0.0524	0.0275	0.0857	0.0382	0.0620	0.1827	0.6411
Pyraclostrobin	0.0310	0.0462	0.0452	0.0500	0.0646	0.0948	0.1380	0.5307
Trifloxystrobin	0.0195	0.0246	0.0310	0.0322	0.0941	0.1069	0.2198	0.2875

FIGURE 2

Table 1

Constant rates (min-1) calculated following a pseudo-first order model at lab-scale.

KEYWORDS

pesticides | heterogeneous photocatalysis | photo-Fenton | water

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