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Photocatalytic degradation of fungicides in real agro-wastewater using TiO2/Na2S2O8 at pilot plant scale under natural sunlight

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PURPOSE OF THE ABSTRACT

Pesticides are used in modern agriculture to prevent or control weeds, insect infestation and diseases on commodity crops in an effort to improve production efficiency and to maintain food quality. However, numerous negative environmental and health effects have been associated with these chemicals. The pesticide residues contained in the wastewater produced in the farms from remnants in containers and treatment tanks, rinse from tanks after treatments and cleaning of machines and equipment is a current European problem, in special in Mediterranean farms. The European Union Directive 2009/128/EC on the Sustainable Use of Pesticides [1] forces Member States to adopt the necessary measures to ensure that the operations by professional users and where applicable by distributors do not endanger human health or the environment. However, no real solution is currently available enabling farmers to manage agro wastewater polluted with pesticide residues, though there are some recommendations. Consequently, there is an urgent need to apply efficient, economical and sustainable remediation technologies available for farmers to these waste waters. Photocatalysis in presence of TiO2, under natural sunlight as the source of irradiation, has been efficiently used for treatment of water containing pesticide residues. TiO2 Degussa P-25 is the most commonly used semiconductor metal oxide in the field of photocatalytic water treatments [2].

The aim of this work was to remove residues of four fungicides (triadimenol, triadimefon, metalaxyl and myclobutanil), commonly used in vegetable crops, in agro-wastewater produced in farms. For this, we have used a pilot facility, natural sunlight and titanium dioxide (TiO2) in tandem with Na2S2O8.

The experiment was carried out in a pilot plant placed in Murcia (SE of Spain) using natural sunlight during the spring of 2017. The pilot plant consists of one photoreactor module with four borosilicate tubes connected to water storage tank and recovery membrane system as depicted in Figure 1. Additionally, a recovery system is integrated in the pilot plant consisting of a ultrafiltration membrane type filter enclosed in a Mann+Hummel U860 cartridge. The accumulated UVA radiation (KJ m-2) was measured during the process by use of an integrated photoradiometer. The trial was initiated with the addition of 300 mg L-1 of Na2S2O8 and 300 mg L-1 of TiO2 to the corresponding reaction tank. Several samples were taken at regular intervals during the photoperiod.

The amount of photocatalyst and oxidant are two important parameters that can affect the degradation rates of the fungicides. The photodegradation rate increases by increasing TiO2 from 100 to 200 mg L-1. However,

minimal differences were observed when the catalyst loading was increased from 200 to 400 mg L-1. Thus, 300 mg L-1 of TiO2 was selected.

On the other hand, the electron-hole recombination is one of the main drawbacks in the application of heterogeneous photocatalysis using different semiconductor oxides as it causes waste of energy. The addition of an electron acceptor, such as Na2S2O8 captures the photogenerated electron and reduces the probability of recombination with the positive hole. In order to examine the role of Na2S2O8, experiments of the photocatalytic degradation of fungicides using different initial concentrations of the oxidant were conducted. Thus, 300 mg L-1 of Na2S2O8 was selected.

Different fungicide concentration were found in the wastewater, varying the initial concentration. The results are illustrated in Figure. 2. In general, in the presence of TiO2 P25 Degussa/Na2S2O8 (300 mg L-1 /300 mg L-1), the rate of degradation decreases when the fungicide concentration increases due to insufficient quantity of ?OH, as the generation of these species is constant for a given concentration of the photocatalyst [3]. Finally, complete disappearance (>95%) was achieved after approximately 7000 KJ m-2 of accumulated sunlight irradiation.

FIGURES



FIGURE 1 Figure 1 Scheme for the treatment plant.

FIGURE 2

Figure 2 Decay curves of fungicides in wastewater for different treatments using TiO2 P25 Degussa/Na2S2O8.

KEYWORDS

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