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Photocatalytic oxidation of six pesticides listed as endocrine disruptor chemicals from wastewater using two different TiO_2 samples at pilot plant scale under sunlight irradiation☆

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ABSTRACT

The photocatalyzed degradation of a mixture of six pesticides (malathion, fenotrothion, quinalphos, vinclozoline, dimethoate and fenarimol) with endocrine disrupting activity has been studied in sewage wastewater effluent under natural sunlight at pilot plant scale. The initial level of each pesticide was 0.30 mg L^{-1}. For this, two commercial TiO_2 nanopowders (Degussa P25 and Kronos vlp 7000) were used as photocatalysts. The operational conditions (catalyst loading, effect of electron acceptor and pH) were previously optimized under laboratory conditions using a photoreactor. The results show that the use of TiO_2 alongside an electron acceptor like $Na_2S_2O_8$ strongly enhances the degradation rate of the studied pesticides compared with photolytic tests, especially Degussa P25. The photodegradation process followed pseudo-first order kinetics in all cases. In our experimental conditions, the necessary time necessary for 90% degradation (DT_{90}) varied from 79 to 1270 min (6–108 min as normalized illumination time, t_{30W}) for malathion and fenarimol, respectively for TiO_2 vlp 7000 and 32–817 min (t_{30W} = 3–69 min) for the same pesticides, in the case of TiO_2 P25. The results confirm the efficacy of the treatment to remove recalcitrant pollutants from wastewater using natural sunlight as renewable source.

1. Introduction

The total sales of pesticides for agricultural use reached about 387 thousand tonnes in the EU-28 during 2015. Some Mediterranean countries such as Spain (20%), France (17%) and Italy (16%) lead the EU-28's pesticide market followed by other Central European States like Germany (12%) and Poland (6%) and together they reaching more than 70% of the pesticide sales in the EU-28 [1]. The European Union Directive 2009/128/EC on the Sustainable Use of Pesticides requires all Member States to assume measures to decrease the risk of pesticides for human health and the environment [2]. Many pesticides are endocrine disruptors (EDs), compounds that alter the function(s) of the endocrine system and consequently cause adverse health effects in an intact organism, or its progeny, or sub-populations [3]. In recent years, different public and private institutions have published lists of compounds suspected to be EDs. More specifically, based on the Community Strategy EDs 1999, the European Commission Institute for Environment and Health (IEH), has been developing a list of priority chemical substances based on scientific evidence showing their capacity EDs, as well as production volume, persistence and potential exposure. In 2011, the fourth and final report on the implementation of this strategy was published, emphasizing the need for an evaluation of the cumulative impact of these compounds, especially in relation to human fertility [4].

In this context, there is very clear evidence concerning the presence of many different pesticides in the aquatic environment at European Union (EU) level. Consequently, they need special consideration according the European Water Framework Directive

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(EWFD) [5]. Recent studies have pointed to the presence of different pesticides in environmental (surface-, ground- and seawater), waste- and drinking waters [6]. The EWFD proposes a strategy for the fight against water pollution. Therefore, to safeguard its citizens from harmful effects, the EU has established groundwater quality standards (0.1 $\mu g L^{-1}$ for individual pesticides and 0.5 $\mu g L^{-1}$ for the sum of all pesticides).

For its part, Directive 2013/39/EU [7] promotes the development of innovative technologies for wastewater treatment, while avoiding expensive solutions. Therefore, there is a search for effective low-cost methods to remove pollutants from water so that they do not endanger human health or the environment.

In this respect, the development of photochemical processes where sunlight is absorbed by a catalyst promoting a strong change in the structure of pollutants is of crucial relevance. Hence, the considerably increased interest in recent years in applying Advanced Oxidation Processes (AOPs) to remove pesticide residues from water as an alternative to conventional methods because they such processes allow the removal of the pesticides through mineralization instead of simply moving them from place to place [8].

Among AOPs, heterogeneous photocatalysis (based on the generation of •OH and other highly reactive radicals) using different semiconductors has been extensively reviewed in the recent literature due to its efficiency in the abatement of pesticides and other pollutants [9–12]. Due to the low cost and mild conditions, the use of natural sunlight irradiation in tandem with a solid semiconductor has become a technique of environmental interest for the treatment of pesticide-polluted wastewater [5]. Among the different semiconductors investigated as likely photocatalysts, titanium dioxide (TiO_2) is the best known due to its properties that include high photoactivity, non-toxic nature, low cost, commercial availability, photochemical stability, possibility of doping and/or coating on solid support [13,14]. Currently, it is difficult to find a photocatalyst showing activity higher than that of TiO_2 Degussa P25 [15] which has a wide band-gap energy of 3.2 eV ($\lambda < 380$ nm). Different strategies for achieving TiO_2 visible light active have been proposed [16]. The band gap of the TiO_2 can be narrowed by doping titania with carbon. As a result, carbon doped TiO_2 (Kronos vlp 7000) can be used not only under UV radiation, but also under the visible light spectrum with a wavelength of >400 nm due to a lower band-gap energy of 2.4 eV ($\lambda < 535$ nm).

The main purpose of this paper was to assess the efficiency of heterogeneous photocatalysis to degrade residual concentrations of several pesticides catalogued by the IEH as EDs in sewage wastewater effluents. For this, two different commercial TiO_2 samples (Degussa P25 and Kronos vlp 7000) were used as semiconductors in tandem with $Na_2S_2O_8$ as electron acceptor under natural sunlight and at pilot-plant scale. Previously, influential parameters in the process such as catalyst loading, effect of electron acceptor and pH were optimized in a photochemical reactor at laboratory scale.

2. Materials and methods

2.1. Pesticides and reagents

The analytical standards of malathion, fenotrothion, quinalphos, vinclozoline, dimethoate and fenarimol of >98% purity were purchased from Dr. Ehrenstorfer Co (Ausgburg, Germany). The main physical-chemical characteristics [17] of the pesticides studied are shown in Table 1. Dichloromethane and acetone for residue analysis, sodium chloride and anhydrous sodium sulphate were purchased from Scharlab (Barcelona, Spain). Sodium persulfate (98%) was supplied by Panreac Química (Barcelona, Spain). Pure water was obtained from a Milli-RX purification system from Millipore. TiO_2 P25 Degussa (99.5%, powder 32 nm) was supplied from Nippon Aerosil Co Ltd (Osaka, Japan) and TiO_2 Kronos vlp 7000 (carbon doped Anatase, 87.5%, 15 nm) was obtain from Kronos Titan Gmbh (Leverkusen, Germany).

The sewage wastewater effluent was obtained from a wastewater treatment plant located in Las Torres de Cotillas (Murcia, Spain) with an average daily of capacity of 5000 m^3/day. In this plant, mechanical pre-treatment is followed by an aerobic biological process as secondary treatment, to end with disinfection by ultraviolet light. The composition of the sewage wastewater effluent used in this study is shown in Table S1 (ESM).

2.2. Photocatalyst characterization

The photocatalysts were characterized for Diffuse Reflectance Spectroscopy (DRS), X-Ray Diffractometry (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), and Energy Dispersive X-Ray (EDX) attached to SEM according to the methodology published in a previous paper by Fenoll et al. [18]. The surface area of titania samples was measured following the BET method.

2.3. Photocatalysis experiment using artificial light

Previous experiments were carried out at laboratory scale under artificial irradiation with the six pesticides and different levels of catalyst, oxidant and pH to obtain the optimal operational

Table 1
Physical and chemical characteristics of the pesticides used in this study.

Pesticide CAS	Group (Formula)	Molecular weight	Log K_{ow}	S_W [a]	Aqueous hydrolysis [b]	GUS index [c]
Fenarimol 60168−88-9	Pyrimidine ($C_{17}H_{12}Cl_2N_2O$)	331.2	4.07	13.7	Stable	3.23 (H)
Vinclozoline 50471−44-8	Oxazole ($C_{12}H_9Cl_2NO_3$)	286.1	3.42	3.4	1.3	2.45 (M)
Fenitrothion 122−14-5	Organophosphate ($C_9H_{12}NO_5PS$)	277.2	2.80	38.0	183	0.48 (L)
Quinalphos 13593−03-8	Organophosphate ($C_{12}H_{15}N_2O_3PS$)	298.3	3.31	17.8	39	1.10 (L)
Malathion 121−75-5	Organophosphate ($C_{10}H_{19}O_6PS_2$)	330.4	2.12	148	6.2	-1.28 (L)
Dimethoate 60−51-5	Organophosphate ($C_5H_{12}NO_3PS_2$)	229.3	0.98	39,800	68	1.06 (L)

[a] Water solubility (mg L^{-1}).
[b] DT_{50} (days) at 20 °C and pH 7.
[c] Groundwater Ubiquity Score (GUS) Index. Leachability in parentheses: (L, Low; M, Medium; H, High).