



Degradation of organochlorinated pollutants in water by catalytic hydrodechlorination and photocatalysis



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ABSTRACT

The degradation of chlorinated herbicides (MCPA and 2,4-D) and 4-chlorophenol (4-CP) by photocatalytic oxidation (PCO) and the combination of catalytic hydrodechlorination (HDC) and photocatalysis, at ambient conditions, has been studied. Commercial TiO₂ (P25) and Pd/Al₂O₃ catalysts were used for PCO and HDC, respectively. MCPA and 2,4-D were transformed upon photo-oxidation to intermediate products and almost total mineralization was achieved. However, in the case of 4-CP, a conversion of only 82% of chloride formation and 87% TOC were obtained. In spite of the fact that the HDC reaction resulted in a total dechlorination of organochlorinated pollutants combined with an important decrease of the effluent ecotoxicity, the percentage of mineralization obtained in the combined process (HDC-PCO) was slightly lower than in the PCO treatment. Thus, the HDC-PCO process is not justified versus a single PCO treatment.

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1. Introduction

Nowadays the extensive and sometimes excessive use of pesticides has led to surface water and groundwater pollution. Chlorophenoxy herbicides, like 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-dichlorophenoxyacetic acid (2,4-D), are commonly used for the control of broadleaved weeds in a variety of places including home lawns, cereal and grain crops, commercial areas, commercial turf, and forests [1]. Consequently, it may be washed down into surface waters, mainly in the anionic form. In addition, chlorophenols which occur as end products or intermediates in the manufacture of herbicides, disinfectants, wood preservatives, personal care formulations, dyes and wood preservatives can be also formed by the chlorination (during disinfection of water and wastewater) of humic matter [2]. These compounds are usually found in aqueous wastes from cleaning herbicide containers in the agricultural industries and in wastewaters from herbicide manufacturing plants in a wide range of concentrations (1–1000 mg L⁻¹) and at low concentrations in municipal wastewater treatment plants [3,4].

Many research efforts have been devoted to developing processes for the removal of these compounds from soil and water by means of biological, chemical and photochemical methods [5]. In this context, catalytic hydrodechlorination (HDC) represents a detoxifying technology for the conversion of organochlorinated pollutants to less toxic compounds (non-chlorinated compounds) [6,7]. This work has demonstrated its ability to deal with aliphatic and aromatic organochlorinated compounds, such as chloroethylenes, chlorobenzenes or chlorophenols or even more complex molecules such as the chlorinated herbicides alachlor, diuron or clopyralid in water using supported catalysts based on precious metals, especially Pd, as the active phase [8–11].

Meanwhile, Advanced Oxidation Processes (AOPs) are effective remediation methods which use high oxidation-potential sources to produce the primary oxidant species, the hydroxyl radical ([•]OH), which reacts rapidly, and unselectively, with most organic compounds. As a result of the non-specific and high electron affinity of the hydroxyl radical, the degradation products can be hydroxylated or partially oxidized intermediates, dimerized compounds, carbon dioxide, and mineral acids [12].

In the case of photocatalytic oxidation (PCO), the photoexcitation of a semiconductor (mostly TiO₂) under irradiation with light of suitable wavelength, generates an e⁻/h⁺ pair, creating the potential for both reduction and oxidation processes to occur at the surface of the semiconductor, for nearly all substrates investigated [13].

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Although a number of possible degradation pathways can be envisioned, the formation and subsequent reactions of the hydroxyl radicals, very strong oxidizing agents, generated from the oxidation of water molecules and hydroxyl ions by photo-excited TiO_2 , are generally accepted as the predominant degradation pathway of organic substrates in oxygenated aqueous solutions [14–16]. In particular, halogenated organic compounds (alkanes, alkenes and aromatic compounds) were reported to undergo complete mineralization in water suspensions of TiO_2 , with the formation of CO_2 , H_2O and mineral acids [17].

In spite of the fact that it has been shown that some organochlorinated pollutants, such as 4-chlorophenol (4-CP) or 2,4-D, can be successfully degraded by various AOPs, including the Fenton reaction [18], photo-Fenton [5], UV/ H_2O_2 process [19,20], heterogeneous photocatalysis (UV/ TiO_2) [21,22], anodic Fenton [23], ozonation [24], and catalytic ozonation [25], the oxidation of these pollutants requires special attention because in some cases, the toxicity of the original effluents can increase by the formation of toxic intermediates [26,27].

During the last decade, there has been a growing interest in the development of more efficient strategies to treat wastewater with organochlorinated compounds. The use of sequential or simultaneous hybrid configurations can improve both their detoxification and final mineralization [28,29]. The combination of an AOP process with a biological treatment to achieve complete mineralization at moderate costs is really interesting but it is necessary that the AOP treatment involved provides a highly biodegradable effluent without components which are toxic to microorganisms [26]. On the other hand, a hybrid AOP process based on the combination of catalytic wet peroxide oxidation (CWPO) and photocatalysis produced a rapid breakdown of the aromatic compounds, associated with the CWPO process, and effective mineralization of the resulting low molecular weight carboxylic acids (LMWCA) by photocatalytic oxidation [30]. Another strategy is to couple an advanced reductive catalytic process, such as hydrodechlorination, with an AOP. In this case, the combination of HDC followed by CWPO has been found to be an effective solution for the abatement of chlorophenols in water [27]. HDC undertakes an essential detoxification by means of the transformation organochlorinated compounds into their dechlorinated species and avoids the formation of condensation by-products, and CWPO leads to high mineralization in a shorter time than by CWPO alone.

The aim of this work is to evaluate and compare the performance of the photocatalytic oxidation of three chlorinated pollutants, 2,4-D, MCPA and 4-CP, with a sequential process based on a first step of catalytic hydrodechlorination, with a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, followed by heterogeneous photocatalysis, with TiO_2 P25. The major drawbacks and benefits presented by both a single and a coupled advanced catalytic processes (HDC and PCO) have been analyzed.

2. Material and methods

Two different processes were carried out: (a) the single process, based on a photocatalytic only run, and (b) the sequential process, consisting of a first HDC stage followed by a second stage of PCO run which is fed with the effluent leaving the HDC treatment.

PCO experiments were carried out with a commercial titania catalyst Evonik TiO_2 P25 (BET surface area $\approx 55 \text{ m}^2 \text{ g}^{-1}$; pore volume $\approx 0.65 \text{ cm}^3 \text{ g}^{-1}$) which presents a mix of crystalline structure, 85% of anatase phase and 15% of rutile. The processes were performed in a semicontinuous slurry-photoreactor set in a Multirays apparatus (Helios Italquartz) enclosed by ten 15 W fluorescent lamps (6 UV blacklight lamps and 4 Day-light lamps) with 38.4 W m^{-2} irradiance measured by a Kipp & Zonen model CUV-4 broadband UV radiometer with UV range (306–383 nm).

To minimize light scattering by the photocatalyst particles and to avoid appreciable saturation by the substrate, 200 mg L^{-1} of TiO_2 P25 was employed. In all cases the inlet chlorinated herbicide concentrations had 50 mg L^{-1} Total Organic Carbon (TOC), corresponding to 115, 93 and 89 mg L^{-1} 2,4-D, MCPA and 4-CP, respectively.

The HDC runs were performed in a semicontinuous stirred tank reactor from Autoclave Engineers using a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst with a metal load of 0.5% (w/w) supplied by BASF (BET surface area $\approx 92 \text{ m}^2 \text{ g}^{-1}$; pore volume $\approx 0.36 \text{ cm}^3 \text{ g}^{-1}$). The Pd - γ -alumina particles were provided as 2.4–4 mm diameter egg-shell spheres which were pulverized and a powdered $\text{Pd}/\text{Al}_2\text{O}_3$ supported catalyst was always used ($d_p < 100 \mu\text{m}$). An aqueous solution of the original organochlorinated compounds 50 mg L^{-1} TOC, was placed in the reactor and hydrogen was continuously fed at a flow rate of 25 N mL min^{-1} . A temperature of 30°C , a pressure of 1.2 bar, 200 mg L^{-1} of catalyst loading and a stirring velocity of 700 rpm were always used. A constant gas flow rate and reactor pressure were maintained by means of a mass flow controller and a back-pressure control valve, respectively. The reactor was heated to the reaction temperature, which was measured and controlled by a thermocouple in the liquid phase.

Liquid samples were periodically taken from each reactor, the catalyst was separated by filtration using a $0.2 \mu\text{m}$ pore size PTFE filter and analyzed. The reaction compounds were analyzed by GC with a flame ionization detector (GC 3900 Varian) using a 30 m length \times 0.25 mm i.d. capillary column (CP-Wax 52 CB) and by HPLC (Varian Prostar 325) with a UV detector using a C18 as stationary phase (Valco Microsorb-MW 100-5 C18) at 280 nm and a mixture of acetonitrile:acidic water (acetic acid 0.1 wt.%) as the mobile phase at 0.5 mL min^{-1} . LMWCA and chlorides were analyzed by an Ion Chromatograph with chemical suppression (Metrohm 883 IC) and a conductivity detector using a Metrosep A supp 7-250 column (250 mm length, 4 mm diameter) as the stationary phase. The TOC content of the aqueous samples was also quantified using an infrared-detector TOC-VCSH/CSN Shimadzu analyzer. The pH was measured with a pH meter (CRISON). Ecotoxicity measurements were carried out using a bioassay following the standard Microtox test procedure (ISO 11348-3, 1998) [31], based on the decrease in light emission by the marine bacteria *Vibrio fischeri* (*Photobacterium phosphoreum*), using a Microtox M500 Analyzer (Azur Environmental).

All the experiments were performed in duplicate and the data reproducibility was always better than $\pm 5\%$.

3. Results and discussion

3.1. Single photocatalysis process

Fig. 1 shows the results of the photocatalytic degradation for 2,4-D, MCPA and 4-CP, expressed as TOC concentration. The reduction in TOC during irradiation time confirmed that 2,4-D (Fig. 1A), and MCPA (Fig. 1B), were being transformed by photo-oxidation to intermediate products which evolve to CO_2 and H_2O as the reaction proceeds, while the results of 4-CP photodegradation (Fig. 1C) presented a parallel evolution for TOC and 4-CP concentration throughout the reaction, which indicates the presence of minor photo-oxidized by-products.

With regard to the presence of photo-oxidized intermediates that could contribute to the modification of toxicity during the photodegradation reaction [32], 2,4-D concentration dramatically decreased at 60 min when 2,4-dichlorophenol was found to be the major aromatic intermediate, which is more persistent and toxic than 2,4-D [33]. Furthermore, 2,4-dichlorophenol (whose formation can be explained by considering the attack of an $\bullet\text{OH}$ radical on the alkyl chain of the molecule) and other minor intermediate

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