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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 TiO_2 (P25) and Pd/Al_2O_3 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.

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 ($^{\bullet}OH$), 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 TiO_2) 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 Pd/Al_2O_3 catalyst, followed by heterogeneous photocatalysis, withTiO_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 $\approx 55\,m^2\,g^{-1}$; pore volume $\approx 0.65\,cm^3\,g^{-1}$) 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 Pd/Al_2O_3 catalyst with a metal load of 0.5% (w/w) supplied by BASF (BET surface area $\approx 92\,m^2\,g^{-1}$; pore volume $\approx 0.36\,cm^3\,g^{-1}$). The Pd-$\gamma$-alumina particles were provided as 2.4–4 mm diameter egg-shell spheres which were pulverized and a powdered Pd/Al_2O_3 supported catalyst was always used ($dp < 100\,\mu m$). 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 backpressure 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 $0.2\,\mu m$ 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 × 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 ±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 $^{\bullet}OH$ radical on the alkyl chain of the molecule) and other minor intermediate

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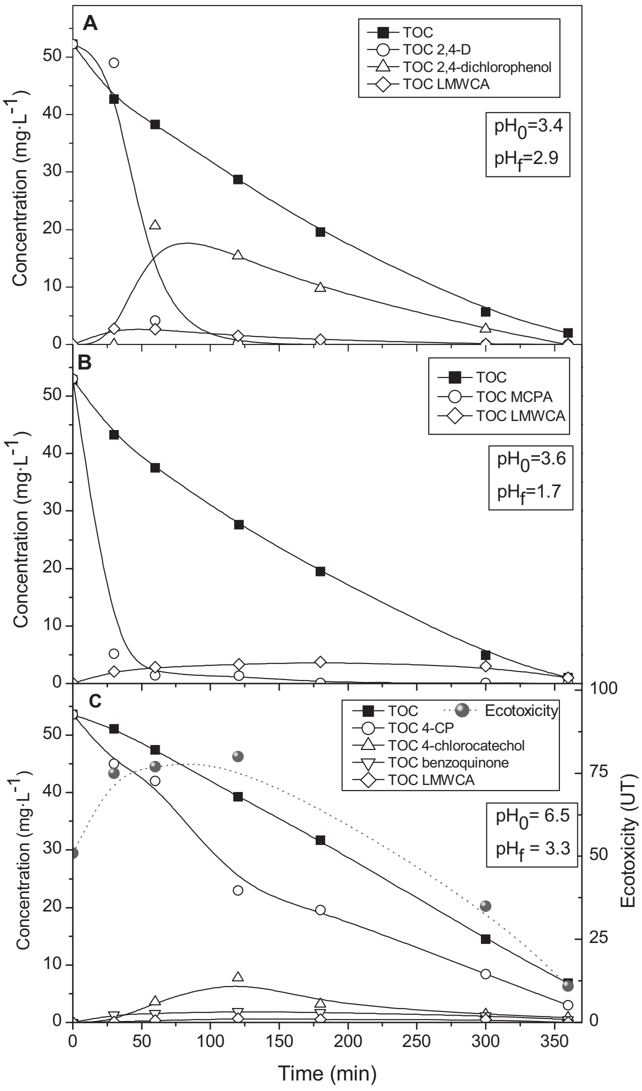

Fig. 1. Time-evolution of organochlorinated compounds, aromatic intermediates, and LMWCA expressed as TOC, during photodegradation of 2,4-D (A), MCPA (B) and 4-CP (C). (C) also includes the evolution of ecotoxicity during 4-CP photodegradation.

by-products were detected [21]. Total conversions of 2,4-D and the 2,4-dichlorophenol aromatic intermediate rose after 360 min reaction time. With respect to 4-CP photodegradation, 4-chlorocathecol and benzoquinone were the main aromatic intermediates detected, but in very low concentrations. Moreover, in all cases, the LMWCA detected were minority acetic, maleic, oxalic and formic acids. Hydrochloric acid was also observed as a consequence of the C—Cl bond rupture.

It is well known that the photocatalytic degradation of these compounds is caused by an attack of surface holes generated and/or hydroxyl radicals and depends on both the pH and irradiation wavelength [34]. Taking into account that any adsorption phenomenon was observed with these chlorinated pollutants, both during the initial dark period and during the photocatalytic process, under the operating conditions used in this work, it would seem likely that the major pathways of photocatalytic oxidation of phenoxy pesticides are through homolysis of the carbon–oxygen bond on its aromatic ring [35–37]. This step is very fast and leads to higher disappearance rates for 2,4-D and MCPA than for chlorophenols which is illustrated by the preceding figures.

The initial TOC photodegradation rates for the three pollutants used have been calculated [38], and are summarized in Table 1.

Table 1
TOC initial photodegradation rates for 2,4-D, MCPA and 4-CP using PCO and the combination of HDC and PCO.

	PCO		HDC + PCO	
	$-r_{TOC,0}$ (mg L^{-1} min^{-1})	r^2	$-r_{TOC,0}$ (mg L^{-1} min^{-1})	r^2
2,4-D	0.23	0.956	0.24	0.967
MCPA	0.25	0.980	0.24	0.989
4-CP	0.10	0.990	0.06	0.992

The initial photodegradation rate for both phenoxy pesticides was almost the same, despite the fact that 2,4-D presents chlorine atoms that are more accessible to oxidation [39], it was photodegraded at lower irradiation times than MCPA, due to the presence of the methyl group, an electron donor that may increase the dehalogenation rate of haloaromatic pesticides [16]. On the other hand, the value obtained for the initial TOC photodegradation rate of 4-CP was half that of the chlorinated herbicides, probably as a result of the different mechanisms involved, i.e. h^+ hole-mediated in the phenoxy pesticides, and $^\bullet$OH radical-mediated in the case of the chlorophenols [16,37].

Taking into consideration that the 2,4-D and MCPA aqueous solutions consisted mainly of their anionic species due to the dissociation constant values (pK_a 2,4-D = 2.7 and pK_a MCPA = 3.1), under these conditions, where the TiO_2 photocatalyst was suspended in the acidic solution, the surface became positively charged, because of the isoelectric point of TiO_2 P25 (pH_{PIE} TiO_2 P25 = 6.3), which facilitates herbicide–photocatalyst interactions [40].

Regarding the behavior of 4-CP which has a pK_a value of 9.41, it was poorly dissociated in aqueous solution as confirmed by the initial pH value of 6.5. Under these conditions the TiO_2 photocatalyst surface is neutral and the herbicide–photocatalyst interactions are weak electrostatic forces [15], which slows down the photodegradation as demonstrated by the $r_{0,TOC}$ value.

Fig. 2 shows the evolution of chloride during the PCO process for the three pesticides studied. The efficiency of chloride release in the phenoxy pesticides was practically complete for 2,4-D and MCPA, whereas a lower formation was observed for 4-CP. Moreover, the fact that almost all the chlorine corresponding to the initial concentration of both chlorinated phenoxy herbicides was in the form of chloride ions indicates the almost complete absence of chlorinated intermediates after 360 min irradiation time, and this was confirmed by the almost complete TOC removal of phenoxy herbicides. On the contrary, in the 4-CP, chlorinated by-products were not-detected [36], and this may have resulted in the residual organic matter observed, because only 82% chloride formation and 87% TOC conversion, were obtained at the end of the photocatalytic reaction.

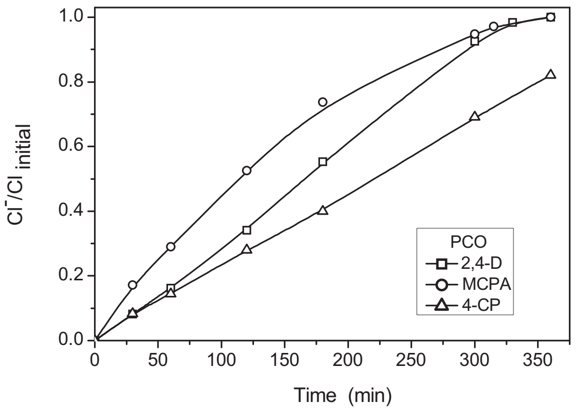

Fig. 2. Time-evolution of chloride/chlorine initial ratio during upon photocatalytic oxidation.

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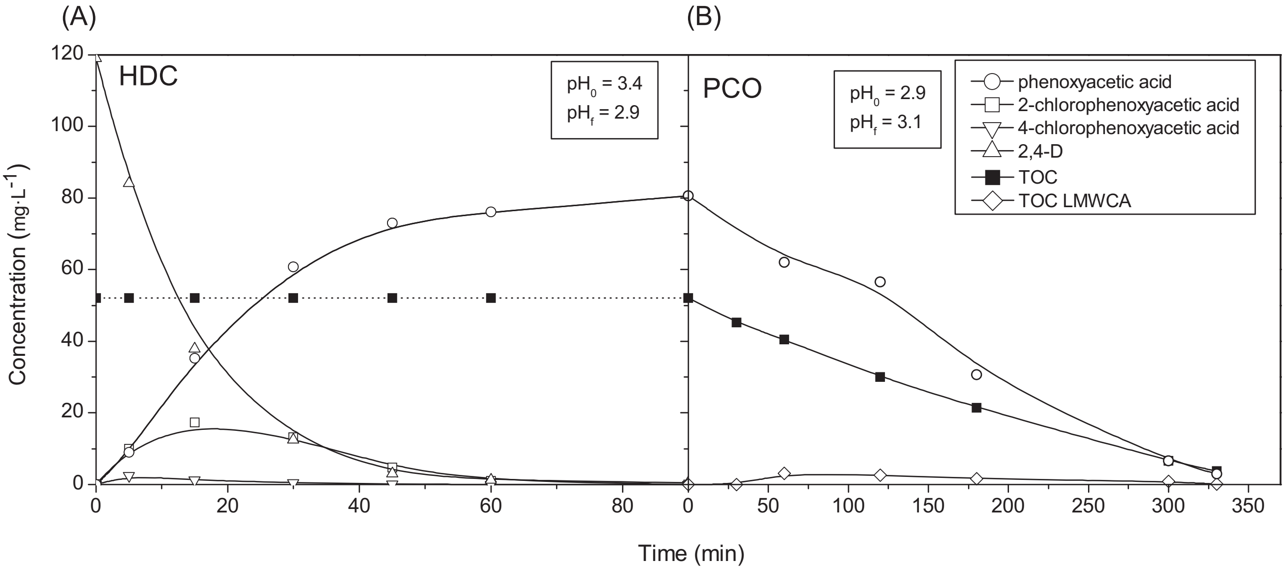

Fig. 3. Time-evolution of 2,4-D, 2-chlorophenoxyacetic, 4-chlorophenoxyacetic, phenoxyacetic acid and overall TOC concentration and TOC corresponding to LMWCA during the sequential treatment of 2,4-D. (A) 1st step: HDC and (B) 2nd step: PCO.

3.2. *Sequential treatment (hydrodechlorination + photocatalysis)*

All the chlorinated pesticides studied were treated in a sequential process, where the effluent obtained after a first step, based on HDC with Pd/Al_2O_3, was treated by PCO in a second step with TiO_2 P25. This was carried out in order to analyze whether the previous removal of chlorine from HDC in the initial organochlorinated compounds resulted in an improvement in the final efficiency of the photocatalytic process. In all cases, the HDC reaction provoked a transformation of organochlorinated compounds. C and Cl balance closed in more than 97 and 99%, respectively, indicating that the reactants and products were properly quantified in this step.

The sequential treatment of 2,4-D removal is represented in Fig. 3, where 2-chlorophenoxyacetic, 4-chlorophenoxyacetic and phenoxyacetic acids were identified as the organic reaction products during 2,4-D HDC process. According to the evolution of the concentration of the products, the HDC of 2,4-D occurred faster at the *para* than at the *ortho* position [16,39] and consequently, 4-chlorophenoxyacetic acid was detected at concentrations lower than 0.1 mM. Total dechlorination was achieved at 90 min reaction time, and phenoxyacetic acid was the only organic reaction product detected at that time. The hydrochloric acid produced during the HDC process, did not have an important influence on the variation of the effluent pH. The acidic HDC-effluent was subsequently treated by heterogeneous photocatalysis. Some residual organic matter was detected at the end of the photocatalytic process given that 92% TOC conversion was found. The absence of aromatic intermediates in the reaction media can be explained by the LMWCA (formic, acetic and maleic) plus corresponding phenoxyacetic acid detected were responsible for that residual TOC.

Fig. 4 shows the sequential treatment for MCPA. During the HDC reaction (Fig. 4A) 2-methylphenoxyacetic acid and hydrochloric acid were the only reaction products detected under the operating conditions used. The total conversion of MCPA was achieved at 30 min reaction time, no important changes in effluent pH were detected during the experiment. The resultant acidic effluent from

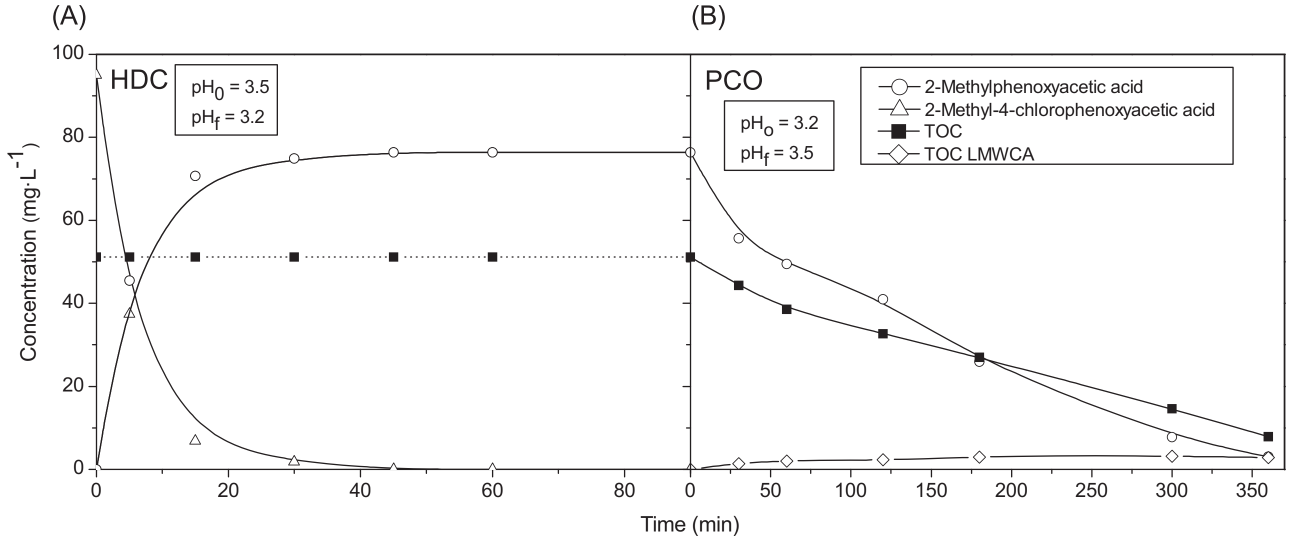

Fig. 4. Time-evolution of MCPA, 2-methylphenoxyacetic acid and overall TOC concentration and TOC corresponding to LMWCA during the sequential treatment of MCPA. (A) 1st step: HDC and (B) 2nd step: PCO.

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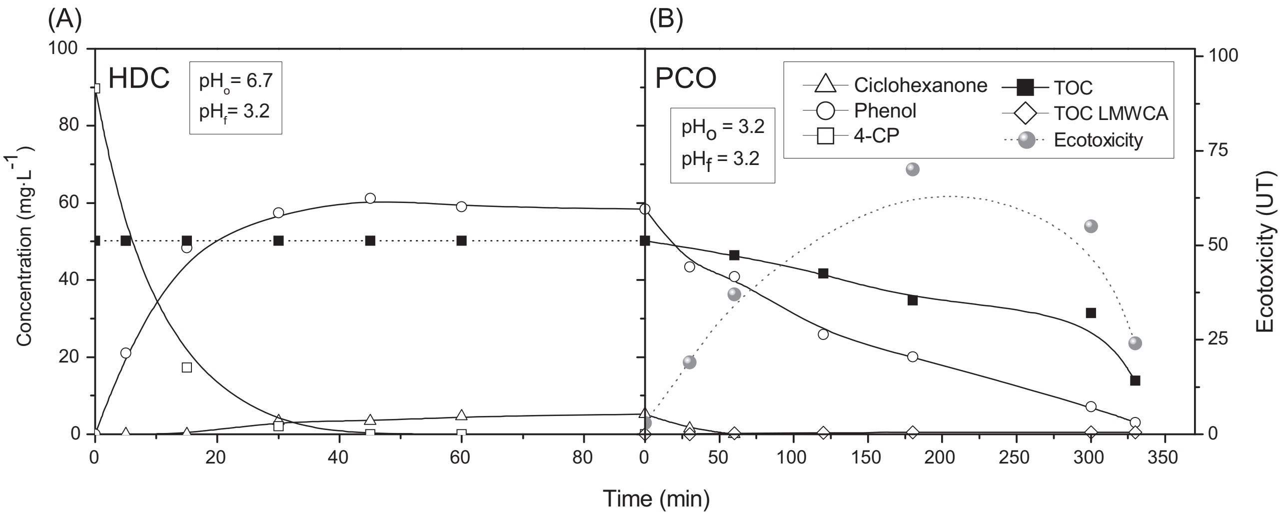

Fig. 5. Time-evolution of 4-CP, phenol, cyclohexanone and overall TOC concentration and TOC corresponding to LMWCA during the sequential treatment of 4-CP. (A) 1st step: HDC and (B) 2nd step: PCO. (B) also includes the evolution of ecotoxicity versus time during the 2nd step of the sequential treatment.

catalytic HDC was treated by PCO (Fig. 4B); at the end of the process (360 min) 83% TOC conversion and 95% conversion for 2-methylphenoxyacetic acid was achieved, which indicates the existence of some non-identified intermediate organic compounds in addition to the LMWCA (formic, acetic and maleic acids) detected.

According to previous results, the phenoxyacetic herbicides (2,4-D and MCPA) were efficiently removed by both the single PCO treatment and the combined process, with an identical initial TOC rate (Table 1) and practically complete mineralization. The effluents from 2,4-D and MCPA after HDC were composed of hydrochloric aqueous solutions of phenoxyacetic and 2-methylphenoxyacetic acids, respectively. These were almost completely dissociated due to their dissociation constant values (pK_a phenoxyacetic acid = 3.12 and pK_a 2-methylphenoxyacetic acid = 3.23). Under these conditions, as was observed during the single process, the TiO_2 photocatalyst surface suspended in the acidic solution became positively charged and phenoxyacetate–photocatalyst interactions were enhanced [41]. The lower TOC conversion achieved by the combined process could be related to the absence of chlorine in the organic molecule that could have had a synergic effect during the photocatalytic degradation [42,43].

The sequential treatment of 4-CP (Fig. 5) shows that the HDC of 4-CP (Fig. 5A) leads to the formation of phenol and cyclohexanone in addition to hydrochloric acid, which caused an important decrease in the pH of the reaction medium. After 45 min operation some of the phenol concentration was transformed to cyclohexanone. Consequently, at the total conversion of 4-CP, the organic content of the acidic effluent transferred to the photocatalytic stage was composed of 94% phenol and 6% cyclohexanone (Fig. 5B). At the beginning of the PCO stage, cyclohexanone was totally removed, but a low concentration of phenol remained at the end with 72% TOC removal. Longer irradiation times are well known to lead to total phenol mineralization by photocatalysis with TiO_2 P25 [44].

Analogously to 4-CP PCO, the initial compounds fed to the second PCO stage are found in the non-dissociated phenol and cyclohexanone forms that do not have any affinity to the TiO_2 positively charged surface (because of the hydrochloric acid present in the after-HDC effluent) and the combined degradation was $r_{0,\mathrm{TOC}}$ which is even worse than for the single PCO.

Fig. 6 shows a general view of the dechlorination capacity, during the HDC reaction in the combined process for the three herbicides studied. Fig. 6 can be compared with Fig. 2 which shows the chlorine release during a single photocatalytic degradation. These figures also show that the complete chlorine removal for 2,4-D, MCPA and 4-CP compounds was achieved at 90 min. A comparison of the initial chloride formation rates (Table 2) between both the single and the combined processes reveal significant differences, with values showing rates differing by at least one order of magnitude.

3.3. *Ecotoxicity*

The ecotoxicity values of the final effluents were measured and compared with those of the initial solutions. Table 3 shows that the photodegradation of 2,4-D and MCPA did not result in an increase in the effluent ecotoxicity. Although a small quantity of oxidation products remained after 6 h, these by-products only corresponded to the LMWCA detected in the aqueous solution, without significance in terms of toxicity. In the case of 4-CP photodegration, the fact that no total organic matter was removed by the end of the photocatalytic process means that the treated effluent was significant in terms of its ecotoxicity. The evolution of ecotoxicity values versus irradiation time for the photodegradation of 4-CP was also studied (Fig. 1C). This figures shows that at the initial time the resulting effluent was more toxic than the starting solution. This could be related to the presence of low concentrations of benzoquinone in the reaction effluent, a compound characterized by high

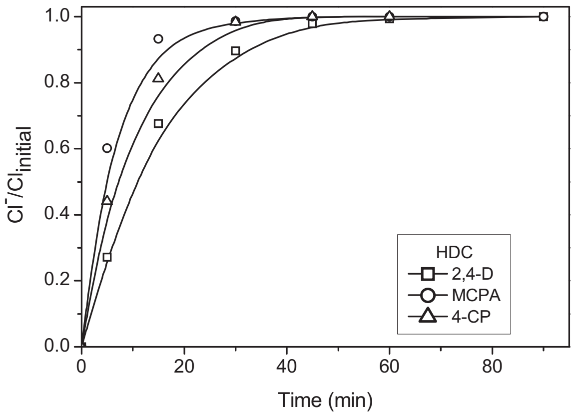

Fig. 6. Time-evolution of chloride/chlorine initial ratio during the first step (HDC reaction) of the sequential treatment.

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Table 2
Initial rate of chloride formation for 2,4-D, MCPA and 4-CP in the single photodegradation and HDC stage of sequential process.

	PCO		HDC + PCO	
	$r_{Cl^-,0}$ (mmol L^{-1} min^{-1})	r^2	$r_{Cl^-,0}$ (mmol L^{-1} min^{-1})	r^2
2,4-D	3.4×10^{-3}	0.998	4.6×10^{-2}	0.988
MCPA	2.0×10^{-4}	0.998	5.5×10^{-2}	0.999
4-CP	1.7×10^{-3}	0.999	6.1×10^{-2}	0.998

Table 3
Ecotoxicity measurements in the single photocatalysis (PCO) and sequential process: HDC + photocatalysis (PCO).

	PCO		HDC + PCO	
	Initial UT	Final UT_{PCO}	After HDC UT_{HDC}	Final $UT_{HDC+PCO}$
2,4-D	0.7	0.4	0.2	2.5
MCPA	1.1	<0.02	0.4	4.1
4-CP	51	11	2.5	24

ecotoxicity ($EC_{50} < 0.01$ mg L^{-1}). The evolution of this intermediate during the reaction is consistent with the shape of the ecotoxicity curve that revealed a maximum at intermediate times [45].

The efficiency of HDC for the abatement of ecotoxicity was evaluated after the first step of sequential treatment. The values obtained are indicative of the reduction in ecotoxicity achieved by HDC [7] while, in general, the PCO treatment resulted in an increase in ecotoxicity values, which was significant in the case of 4-CP sequential treatment. In spite of the fact that non-aromatic intermediates were detected, the ecotoxicity values revealed that the non-identified reaction compounds are more toxic than the starting compounds, phenol and cyclohexanone (Fig. 5B). Once again, the ecotoxicity curve showed a maximum followed by a progressive decrease associated with the removal of TOC. Therefore, a longer irradiation time must be provided to reach negligible ecotoxicity values [16,46].

4. Conclusions

Heterogeneous photocatalysis, with commercial P25 TiO_2, has proved to be a fairly good process for the degradation of the MCPA, 2,4-D and 4-CP at ambient operating conditions.

Photocatalytic oxidation was faster for the MCPA and 2,4-D than 4-CP because the oxidation starts with the homolysis of the carbon–oxygen bond on the aromatic ring, and both phenoxy herbicides were almost completely mineralized.

In the sequential treatment, with a first step of HDC, it was possible to totally dechlorinate all the starting compounds with higher dechlorination rates than in the single photocatalytic oxidation. However, the first step did not result in any improvement in TOC removal taking into account the overall treatment. Although no significant ecotoxicity values were found in the resulting effluent from MCPA and 2,4-D treatment, it must be emphasized that long irradiation times were necessary to reduce effluent ecotoxicity in the case of 4-CP, because of the formation of oxidation intermediates more ecotoxic than the starting compound.

Therefore, after analyzing the advantages and drawbacks of the single (PCO) and the combined processes (HDC + PCO) it can be concluded that PCO was better in terms of effluent mineralization and TOC initial degradation rate. The use of a combined HDC–PCO process could only be justified in cases where rapid dechlorination was associated with a significant reduction in ecotoxicity.

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