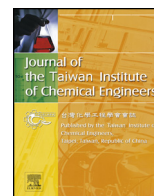




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Photocatalytic ozonation of 4-chloro-2-methylphenoxyacetic acid and its reaction intermediate 4-chloro-2-methyl phenol

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ABSTRACT

Aqueous 4-chloro-2-methylphenoxyacetic acid (MCPA) has been treated by the systems UVA/TiO₂/N₂, O₃, TiO₂/O₃, UVA/O₃, UVA/TiO₂/O₂, and UVA/TiO₂/O₃. Under the conditions investigated ($T = 20\text{ }^{\circ}\text{C}$, $\text{pH} = 4.5$, $Q_{\text{gas}} = 30\text{ L/h}$, $V = 1\text{ L}$, $C_{\text{O}_3} = 5\text{ ppm}$, $C_{\text{MCPA}} = 5\text{ ppm}$, $C_{\text{TiO}_2} = 0.5\text{ g/L}$), MCPA is removed in less than 30 min. Photocatalytic ozonation is the most efficient process both in terms of MCPA removal rate (100% conversion in less than 15 min) and mineralization extent (60% after 3 h and 25 °C). 4-Chloro-2-methyl phenol (CMP) is detected in those systems combining TiO₂ and UVA radiation. The presence of ozone involves the complete depletion of CMP following its generation. The direct rate constant between CMP and ozone corroborates the high reactivity observed ($7.2 \pm 0.3 \times 10^4\text{ (M s)}^{-1}$, $4.4 \pm 0.2 \times 10^5\text{ (M s)}^{-1}$, and $2.9 \pm 0.7 \times 10^6\text{ (M s)}^{-1}$ at pHs 4, 7 and 10, respectively). Identified intermediates detected in the UVA/TiO₂/O₃ applied to MCPA correspond to oxygenated species derived from the parent compound after loss of some substitution groups. No significant toxicity of intermediates is observed in BOD₅, *Daphnia parvula*, and *Culex pipiens* larvae tests.

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1. Introduction

4-Chloro-2-methylphenoxyacetic acid (MCPA) is a widely used herbicide of the chlorophenoxy type family. Phenoxy herbicides act by simulating the action of natural hormones to produce uncoordinated plant growth. Their action is selective as they are toxic to dicotyledonous plants. The acid is the parent compound, but a number of formulations in use contain the more water soluble amine salts or the ester derivatives, which are readily dissolved in an organic solvent. Regulatory agencies in their evaluations of these two constituents have found MCPA unlikely to be human carcinogen; however, a number of epidemiologic studies have found positive associations between exposure to chlorophenoxy compounds and an increased risk of some lymphohematopoietic cancers, primarily non-Hodgkins lymphoma, but also Hodgkin's disease, soft-tissue sarcoma, and to a lesser extent, leukemia [1].

MCPA can be easily degraded in aqueous solution by means of TiO₂ mediated photocatalysis in the presence of UVA or visible light [2,3]. MCPA photocatalysis leads to the complete removal of

the parent compound in a relatively short period of time; however, the herbicide is not completely mineralized and some intermediates accumulate in the reaction media [4]. 4-Chloro-2-methyl phenol (CMP) is the main intermediate that accumulates in the MCPA photocatalytic process. CMP is generated from MCPA by direct photolysis and $\bullet\text{OH}/\text{h}^+$ reaction (higher CMP yield). CMP is more toxic than the parent compound [5]. Accordingly, water treatment technologies dealing with MCPA removal should take into consideration the evolution of this byproduct. The accumulation of CMP in the Degussa P-25 mediated photocatalysis has been previously experienced [6].

In the present study, the photocatalytic ozonation of MCPA is investigated and compared to other systems such as single ozonation, photolytic ozonation, catalytic ozonation and photocatalysis. Use of ozone in photocatalytic processes shows some advantages if compared to the system in the absence of ozone, namely the presence of an additional oxidant (O₃) reacting with organic molecules by direct or indirect ($\bullet\text{OH}$) pathways, additional generation of free radicals by ozone photolytic scission, potential catalytic ozone decomposition by the TiO₂ surface, etc. [7].

Photocatalytic ozonation has normally been applied by using UV-C radiation, few works have applied cheap black light lamps (UVA radiation), [8,9]. Additionally, the number of studies focused on the photocatalytic ozonation of pesticides is also limited. Some

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works can be listed. Rajeswari and Kanmani [10] combined UVA radiation and ozone in the presence of titanium dioxide and carbaryl as model pollutant. Under their experimental conditions, 76.5% of total organic carbon (TOC) removal and increase of the five day biological oxygen demand–chemical oxygen demand ratio (BOD₅/COD) were reported. Farré and co-workers [11,12] conducted a preliminary chemical treatment of pentachlorophenol, isoproturon, diuron, alachlor and atrazine pesticides in aqueous solutions analyzing the toxicity of the effluent after the treatment. Beduk and collaborators [13] carried out the photocatalytic ozonation in the presence of UV-C radiation of the organophosphorus pesticides malathion and parathion. Cernigoj and co-workers [14,15] also studied the photocatalytic ozonation of thiacloprid and neonicotinoid insecticides.

In this work the influence of pH, photocatalyst and MCPA initial concentration has been assessed in the UVA/TiO₂/O₃ system. Additionally, the response of CMP toward the studied technologies has also been investigated. Toxicity tests have completed the work.

2. Experimental

2.1. Photoreactor and procedure

A 1 L capacity perfectly mixed borosilicate glass photoreactor was used in all the experiments. The reactor was placed in the middle of a 31 cm external diameter pipe (54 cm height). The internal wall of the pipe was covered by aluminum foil to increase the photons reflection toward the reaction media. Four black light lamps (41 cm length) were evenly distributed and attached to the pipe. The lamps (LAMP15TBL HQPOWER™ manufactured by Velleman®) had a nominal power of 15 W mainly emitting within the range 350–400 nm, the maximum being located at 365 nm. Actinometry experiments in the presence of ferryxalate led to a value of 6.86×10^{-5} Einstein/min/L when 4 lamps were used.

Previously to the photodegradation experiments, the mixture water + photocatalyst was stirred for 60 min in the dark to achieve the MCPA adsorption equilibrium on the photocatalyst surface. Oxygen or a mixture oxygen–ozone was continuously bubbled into the water bulk by means of a diffuser placed at the reactor bottom. The gas flow rate was kept constant at 30 L/h in all the experiments. Photocatalysts were maintained in suspension by magnetic stirring. Prior to the analysis, the solid was removed from samples by filtration through Millex-HA filters (Millipore, 0.45 μm).

Ozone was produced from pure oxygen by using a Sander Laboratory Ozone Generator. Dissolved ozone in solution was determined by the indigo method, the analysis is based on the decoloration of the 5,5,7-indigotrisulfonate [16]. Ozone in the gas phase was monitored by means of an Anseros Ozomat ozone analyser. The analysis was based on the absorbance at 254 nm. All experiments were conducted at the natural pH of the solutions, with no addition of buffering substances.

2.2. Materials

Pure MCPA from Aldrich (>99%) was used in different experiments, the rest of chemicals were purchased from Sigma-Aldrich and used as received (acetaminophen >99%, CMP 97%, phosphoric acid 85%). Organic solvents were HPLC grade obtained from Panreac. Commercial TiO₂ Degussa P25 photocatalyst (70% anatase and 30% rutile) was used with an average particle size of 30 nm and BET surface area of 50 m²/g. Water purified by a Milli-Q water system (Millipore) was used in the preparation of solutions and suspensions.

2.3. Analysis

MCPA and CMP were analyzed by high-performance liquid chromatography (Agilent 1100). The column used was a Kromasil

100 5C18. The mobile phase acetonitrile/water/phosphoric acid 85% (40:54:6) was pumped at a flow rate of 1 mL/min. Detection was conducted at 230 nm. In the case of acetaminophen, the reference compound in rate constant determination experiments, the mobile phase was changed to acetonitrile/water/phosphoric acid (18:76.5:8.5), and detection was conducted at 244 nm. Byproducts were tentatively identified by HPLC coupled to mass spectrometry. The detector was a quadrupole-time-of-flight mass spectrometer (Agilent Technologies 6520, Accurate-Mass Q-TOF LC/MS) equipped with a dual ESI electrospray interface. The analytical operating conditions were as follows: capillary 3500 V; nebulizer, 30 psi; gas flow, 5 L/min; gas temperature 300 °C; skimmer voltage, 65 V; octapole rf, 750 V; fragmentor, 100 V. The mass spectra were processed by means of the Agilent Mass Hunter Qualitative Analysis B.04.00 software.

In order to assess the degree of mineralization, total organic carbon was determined by a Shimadzu TOC 5000A analyzer by directly injecting the aqueous solution. The pH of the reaction media was measured by means of a Radiometer Copenhagen pH-meter. pH adjustment was carried out by addition of NaOH or perchloric acid. Biological oxygen demand after five days determination was conducted by the respirometric method, based on the absorption of the CO₂ generated in the microbial metabolism by solid NaOH.

2.4. Ecotoxicity bioassays with *Daphnia parvula* and *Culex pipiens* larvae

The acute toxicity tests using *Daphnia parvula* were conducted using US EPA standard operating procedures [17]. This procedure was extrapolated to carry out similar trials with mosquito *Culex pipiens* larvae. A culture for *D. parvula* or *C. pipiens* larvae was received from installations of Extremadura's University, where organisms were naturally cultured in artificial ponds.

20 young *D. parvula* or 15 s-instar *C. pipiens* larvae were placed in 100 mL of test solution using a disposable plastic transfer pipette, and were subjected to 16:8 light:dark photoperiods at room temperature. Survival numbers were recorded and monitored at 6, 24 and 48 h for *D. parvula*; 24, 46, 72 and 96 h for *C. pipiens*. Organisms were not fed during the experiments. In ecotoxicity tests, commercial MCPA (MCPA 60% from KENO-GARD®) or CMP solutions were prepared in mineral water (10.7 mg/L HCO₃⁻, 5.3 mg/L SO₄²⁻, 19.0 mg/L, Cl⁻, 2.7 mg/L, Ca²⁺ 2.7 mg/L Mg²⁺, 14.7 mg/L, Na⁺, and 14.3 mg/L SiO₂). pH was adjusted to 7 ± 0.1. Three blank tests, without MCPA or CMP addition, were considered per each run.

Initially trials were carried out at various parent compound initial concentrations in order to determine the concentration which causes the 50% mortality (LC₅₀). Organisms were exposed to nine concentrations (1000, 500, 250, 125, 62.5, 31.2, 15.6, 7.8, and 3.9 mg/L of MCPA; or 10, 5, 2.5, 1.25, 0.62, 0.31, 0.15, 0.08 and 0.04 mg/L for CMP). After this preliminary study, samples from photocatalytic ozonation experiments at different stages of oxidation extent (0, 25, 50, 75, 100% of initial MCPA removal) were taken. An additional sample was also considered when TOC removal reached the steady state level.

3. Results and discussion

3.1. Preliminary experiments: Technologies comparison

3.1.1. 4-Chloro-2-methylphenoxyacetic acid oxidation

Some preliminary experiments were initially carried out to compare the performance of individual systems derived from the UVA/TiO₂/O₃ technology. Fig. 1 shows the results obtained in terms of MCPA normalized degradation and TOC conversion when an

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