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Degradation of chlorophenoxy herbicides by coupled Fenton and biological oxidation

Sonia Sanchis *, Alicia M. Polo, Montserrat Tobajas, Juan J. Rodriguez, Angel F. Mohedano

Seccion Departamental de Ingenieria Quimica, Universidad Autonoma de Madrid, Madrid 28049, Spain

HIGHLIGHTS

- Chlorophenoxy herbicides were treated by combined Fenton and biological oxidation.
- Reaction pathways for 2,4-D and MCPA Fenton oxidation were proposed.
- The optimal H_2O_2 dose was selected from biodegradability assays.
- Nearly 90% of COD removal was achieved in the combined Fenton-SBR treatment.

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ABSTRACT

A combined treatment for the degradation of the chlorophenoxy herbicides 2,4-D and MCPA in water by means of Fenton and biological oxidation has been studied. The chemical oxidation step was necessary to achieve an efficient removal of these pollutants due to their toxicity and low biodegradability. Aqueous herbicide solutions (180 mg L^{-1}) were subjected to Fenton oxidation upon different H_2O_2 doses (from the theoretical stoichiometric amount referred to initial COD to 20% of this value). The toxicity and biodegradability tests of the Fenton effluents suggested that the ones resulting upon treatment with 80% and 60% of stoichiometric H_2O_2 were the optimal for subsequent biological treatment dealing with 2,4-D and MCPA, respectively. These effluents were treated in a sequencing batch reactor achieving nearly 90% conversion of organic matter measured as COD.

1. Introduction

In the last decades, the use of agrochemicals (herbicides) has been a common practice in intense agriculture, which has considerably increased pollution problems of surface and ground water. Contamination includes point sources like water from cleaning pesticide containers and agricultural industries (10–100 mg L^{-1}) and water from pesticide manufacturing plants (1–1000 mg L^{-1}) (Malato et al., 2001). Chlorophenoxy herbicides, such as 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (4-chloro-2-methylphenoxyacetic acid), are mainly used as plant growth regulators. These herbicides are chemicals of main concern for the environment due to their toxicity (EC_{50} values of 21.1 for 2, 4-D and 11.6 for MCPA from Microtox® test and 213 and 144 mg L^{-1} from activated sludge respiration inhibition test, respectively) and low biodegradability (less than 25% of TOC reduction after 28 d) (Tobajas et al., 2010; Polo et al., 2011). These characteristics make them hardly biodegradable compounds, being detected in the effluents of wastewater treatment plants (Hu et al., 1999; Peschka et al., 2005).

To prevent the environmental hazard and human risks of herbicides it is necessary to develop methods allowing their effective breakdown. In this context, the application of Advanced Oxidation Processes (AOPs) has been considered a promising solution dealing with recalcitrant compounds (Chiron et al., 2000; Pera-Titus et al., 2004), industrial effluents (Azbar et al., 2004; Bautista et al., 2008) or landfill leachates (Wu et al., 2004; Primo et al., 2008a, 2008b). However, to achieve high percentages of mineralization, namely complete oxidation, requires in most cases costly amounts of H_2O_2. The use of coupled treatments for the efficient breakdown of organic pollutants has received increasing attention. One of the most attractive solutions appears the combination of AOPs and biological oxidation (Oller et al., 2011). Regarding herbicides removal, different AOPs like photo-Fenton (Farre et al., 2008), TiO_2 photocatalysis (Oller et al., 2007), electrochemical oxidation (Brillas et al., 2004) and ionizing radiation (Drzewicz et al., 2004) have been used coupled with biological systems.

* Corresponding author. Tel.: +34 914973598; fax: +34 914973516.
E-mail address: sonia.sanchis@uam.es (S. Sanchis).

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In particular, Fenton oxidation, based on the catalytic decomposition of H_2O_2 into hydroxyl radicals by means of Fe^{2+} at acid pH, has been used in combination with biological treatment for the removal of pentachlorophenol (Zimbron and Reardon, 2011) and 2,4-D (Sun et al., 2005). Application of Fenton oxidation as pretreatment can convert initially persistent organic pollutants into biodegradable intermediates, which could be treated in a biological system with considerable cost reduction. In this sense, the efficient use of H_2O_2 in the oxidation step is a critical issue for the economy of the treatment. Insufficient oxidation can lead to intermediates structurally similar to the starting pollutants, of even higher toxicity and recalcitrant character (Osano et al., 2002; Sinclair and Boxall, 2003; Hernando et al., 2005). Thus, establishing the optimal H_2O_2 dose to be used in the combined treatment requires evaluating the toxicity and biodegradability of the effluents going to the biological step.

Among standardized bioassays for determining the toxicity of a certain pollutant, the Microtox® test is one of the most widely used, due to its high sensitivity and precision (Dalzell et al., 2002). Although some authors have reported that EC_{50} values obtained by this method could give an overestimation of the toxic effect on the biomass of an activated sludge unit, it can be useful for a rapid toxicity detection in wastewater treatment plants since it has been found a good agreement between the response of *Vibrio fischeri* and activated sludge to different chemicals (Ricco et al., 2004; Lapertot et al., 2008; Polo et al., 2011).

Methods for measuring biodegradability include OECD tests (OECD, 1992, 1993), which are commonly used to predict the potential hazard of a pollutant in a natural environment and thus low biomass concentrations and fairly large experimental times are employed. Recently, Polo et al. (2011) have proposed a new biodegradability test to predict in an easy and rapid way the behavior of a target compound or a wastewater in a biological reactor by means of respirometry. This test is based on the direct relationship between the specific oxygen uptake rate (SOUR) and the biomass activity. The bioassay simulates the typical operation conditions of an activated sludge unit, using a high biomass to COD ratio, which allows a significant reduction of the testing time to no more than 24 h, comparable to the common hydraulic retention times in a conventional biological aerobic reactor.

The removal of the biodegradable oxidation byproducts generated upon Fenton oxidation can be carried out by means of different biological treatments, using sequencing batch reactors (SBR) (Farre et al., 2008; Ballesteros Martin et al., 2009), immobilized biomass reactors (Oller et al., 2007) or aerated biofilters (Wang et al., 2012). SBR have been widely used in the last decades for industrial wastewater treatment (Wilderer et al., 2001; Singh and Srivastava, 2011) due to their low area and energy requirements, easy control and the possibility of nutrients removal by combining anaerobic, anoxic and aerobic stages in the same reactor (Zanetti et al., 2012). In addition, SBR allow changes in the operational and control strategies, so they are suitable for the treatment of variable organic loads (Monsalvo et al., 2009, 2012).

In this work, the combination of Fenton and biological oxidation in SBR is proposed for the removal of the chlorophenoxy herbicides 2,4-D and MCPA. Optimization of the hydrogen peroxide dose is analyzed through toxicity and biodegradability assays of the resulting Fenton effluents.

2. Materials and methods

2.1. Fenton oxidation

The experiments were carried out in batch mode in a 3 L glass reactor at controlled temperature (30 °C) and stirred at 200 rpm. The initial pH was adjusted around 3, which is within the optimal range for Fenton oxidation (Zazo et al., 2007; Bautista et al., 2008). The starting concentration of 2,4-D and MCPA was fixed at 180 mg L^{-1}, since these herbicides can appear at concentrations up to their solubility limits in point-pollution sources, such as effluents from agricultural industries and pesticide containers cleaning. The dose of hydrogen peroxide was varied between the theoretical stoichiometric amount for complete oxidation up to CO_2, H_2O and HCl to a 20% of that value, maintaining a H_2O_2/Fe^{2+} ratio of 10/1 (M/M). The experiments were made by duplicate.

The evolution of the concentration of herbicide, TOC and H_2O_2 upon reaction time was followed at every H_2O_2 dose tested. Final samples were also analyzed for COD, BOD_5 and reaction byproducts, as well as ecotoxicity (Microtox®). Respirometric tests for biodegradability assessment were also performed. The samples were previously neutralized with NaOH 6 N and filtered (Albet FV-C).

2.2. SBR experiments

The biological treatment of the effluents from Fenton oxidation was performed in a 3 L SBR. It was equipped with pH and dissolved oxygen probes to evaluate the biomass activity by respirometry. Air was introduced through a ceramic diffuser at a flow rate of 9 L min^{-1} to avoid oxygen limitations. Peristaltic pumps were used to feed and discharge the bioreactor, as well as for the addition of sodium hydroxide solution (12 N) for pH control.

The experiments were conducted at 30 °C, 200 rpm and pH 7 in sequences of 8 h as follows: anoxic filling (1 h), aerated reaction (5.5 h), settling (1 h) and draw (0.5 h), using a hydraulic retention time of 12 h. Samples were withdrawn along the biological process for measuring TOC, COD, organic byproducts and inorganic nitrogen species. SOUR profiles were also recorded during the aerobic stages.

Biomass concentration was maintained around 1 g VSS L^{-1} and a cell retention time of 30 d was used. The organic load was different for each herbicide, since the only carbon source was that provided by the corresponding effluents from Fenton oxidation. Ammonium sulfate and phosphoric acid were used as nitrogen and phosphorous sources, respectively, and mineral salts ($CaCl_2$, KCl y $MgSO_4$) were also added as micronutrients supply at COD:N:P:micronutrients ratio of 100:5:1:0.05 (w/w).

2.3. Inoculum source

The inoculum used in the bioreactor was collected from an activated sludge sewage treatment plant. The biological sludge was maintained with sodium acetate (150 mg COD L^{-1}) and glucose (150 mg COD L^{-1}) as carbon sources in a SBR operated at 25 °C for its use as inoculum in the BOD_5 and biodegradability tests.

2.4. Biodegradability and ecotoxicity tests

The biodegradability of the effluents from Fenton oxidation was assessed by respirometry, in a LSS respirometer (Chica et al., 2007), following the fast biodegradability procedure established by Polo et al. (2011). The sample (1 L) was mixed with biomass (350 mg VSS L^{-1}) and aeration was maintained for 24 h, continuously measuring SOUR and TOC. For the sake of reproducibility, the respirometric tests were carried out by duplicate. The reaction vessels, placed in a thermostatic bath and continuously stirred by magnetic bars, were stoppered so that oxygen transfer from the gas to the liquid can be neglected.

BOD_5 measurements were carried out in a Velps Scientifica equipment, following the standard procedure 5210 (APHA, 1992). A sample volume of 400 mL was used, with a biomass concentration of 75 mg VSS L^{-1}. N-allylthiourea was added as nitrification