



Total removal of alachlor from water by electrochemical processes



Angelo R.F. Pipi^{a,b}, Adalgisa R. De Andrade^a, Enric Brillas^b, Ignasi Sirés^{b,*}

^a Departamento de Química, Laboratório de Eletrocatalise e Eletroquímica Ambiental, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo (FFCLRP, USP), Av. Bandeirantes 3900, 14040-901 Ribeirão Preto, SP, Brazil

^b Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

ARTICLE INFO

Article history:

Received 19 March 2014

Received in revised form 11 June 2014

Accepted 13 June 2014

Available online 22 June 2014

Keywords:

Boron-doped diamond

Chloroacetanilide pesticides

Electrochemical advanced oxidation processes

Reaction pathway

Water treatment technologies

ABSTRACT

Concentrated aqueous solutions of the chloroacetanilide herbicide alachlor, a suspected human carcinogen that has been classified as a priority water pollutant by the European Commission, have been quickly degraded and even totally mineralized by different electrochemical advanced oxidation processes (EAOPs) in cells equipped with a carbonaceous air-diffusion cathode able to electrogenerate H_2O_2 on site and a Pt or boron-doped diamond (BDD) anode. The highest performance was obtained by means of the photoelectro-Fenton (PEF) process with BDD in the presence of 0.5 mM Fe^{2+} , thanks to the synergistic action of (i) electron transfer, (ii) coupled oxidation by $\cdot OH$ generated by Fenton's reaction in the solution bulk and BDD($\cdot OH$) generated at the anode surface, and (iii) photolytic and photodecarboxylation reactions allowed by UVA photons. Good results were also obtained by electro-oxidation (EO) and electro-Fenton (EF) with BDD, resulting in a much higher mineralization current efficiency than EO, EF and PEF with Pt. Based on GC-MS analyses, the initial transformation step of alachlor promoted by the EAOPs involved four different reaction pathways, namely dealkylation, cyclization, scission of the R-N bond and hydroxylation by $\cdot OH$ and BDD($\cdot OH$). Further cleavage of the resulting nine cyclic and/or aromatic by-products led to the appearance of short-chain aliphatic carboxylic acids such as acetic, chloroacetic, oxamic and oxalic. Only PEF with BDD was able to ensure the quick and total degradation of the latter two acids, therefore becoming the best available electrochemical technology at present for the degradation of alachlor. Different amounts of nitrogenated (NH_4^+ and NO_3^-) and chlorinated (Cl^- , ClO_3^- and ClO_4^-) ions were accumulated in the final solutions depending on the anode and the applied current.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Herbicides constitute the main group of chemicals for plant protection, being the chloroacetanilides vastly applied to soil to control the growth of weeds. Among the 19 chloroacetanilide herbicides listed in The Compendium of Pesticide Names, alachlor, acetochlor and metolachlor have become pre-eminent active ingredients in commercial formulations.

The main use of alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) is for pre-emergent control of annual grasses and broadleaf weeds in crop fields, primarily on corn, soybean and sorghum [1]. Its occurrence in water resources is particularly worrisome due to its possible implications on human health and toxic effects on aquatic fauna and ecosystems. The short-term exposure to alachlor causes minor eye and skin irritation but, in the long term, it may cause organ damage and even cancer [2].

* Corresponding author. Tel.: +34 934021223; fax: +34 934021231.

E-mail address: i.sires@ub.edu (I. Sirés).

In fact, it has been classified as a B2 carcinogen by the U.S. EPA [1], and it is one of the priority substances listed by the European Commission within the scope of the Water Framework Directive [3], although data indicating endocrine disruption and genotoxicity or mutagenicity *in vivo* are inconclusive [4]. According to the decision-guidance document adopted by the Secretariat of the Rotterdam Convention [5] it is not discarded that nasal tumors observed in rats are relevant in humans. Concerns are also related to the formation of a large variety of degradation products with toxicological and/or eco-toxicological impact. Consequently, at present, alachlor is considered as a severely restricted chemical. In Canada, all uses are banned since 1985 based on its unacceptable health risks, whereas some recent regulatory actions are being implemented by the European Community to ban it as a pesticide. In particular, no authorizations for plant protection products containing alachlor can be granted or renewed since December 2006.

The major source of alachlor in groundwater and surface water is through its manufacture and runoff from herbicide used on row crops, and it has even been detected in raw, tap, treated and rain

waters [6,7]. Alachlor is persistent and not readily biodegradable in water resources [5,8] and thus, conventional physicochemical processes and bioremediation are not suitable technologies to ensure its removal from water streams. In contrast, alachlor has been degraded by several advanced oxidation processes (AOPs) like gamma radiolysis [9], O₃/H₂O₂ [10], photocatalysis [11,12], ultrasonic and hydrodynamic cavitation [13–15] and UV and solar photo-Fenton [16,17]. Many of these processes still show limitations such as low removal efficiency, high operational costs or secondary pollution.

The electrochemical AOPs (EAOPs) represent an interesting alternative for the degradation of organic pollutants from aqueous media. The most powerful EAOPs are the Fenton-based ones and the electro-oxidation (EO) [18,19]. The former ones are based on the electro-Fenton (EF) process and can be considered as more environmentally-friendly than their non-electrochemical counterparts because the H₂O₂ and Fe²⁺ required to carry out the Fenton's reaction can be continuously electrogenerated in situ from compressed atmospheric air and an initial catalytic amount of iron ions. The essential component in such systems is the carbonaceous cathode, which is able to reduce the O₂ contained in the air as follows [20–22]:

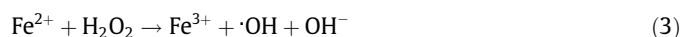


As for the EO process, also called anodic oxidation (AO) or electrochemical incineration/combustion, the key requirement is the incorporation of an anode that is able to generate ·OH from water oxidation [23–27]:

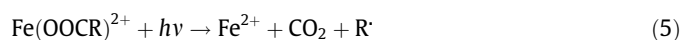


The degradation of some pesticides by EAOPs has been demonstrated using electrochemical cells equipped with low oxidation power anodes such as RuO₂ and IrO₂ dimensionally stable anodes (DSA) and Pt [28–31], although much greater performance is obtained with high oxidation power anodes like PbO₂ [32,33] and, mainly, boron-doped diamond (BDD) [34].

Only a couple of studies have reported the electrochemical degradation of chloroacetanilide herbicides. In particular, photoelectrocatalysis with TiO₂-based anodes was proven effective for the transformation of alachlor into several intermediates [35], whereas anodic Fenton treatment was investigated for the comparative removal of alachlor, acetochlor, butachlor, metolachlor and propachlor [36]. None of these studies allowed the complete mineralization of the polluted solutions. Furthermore, the former process presents a very low efficiency due to the inherent mass transport limitations, whereas the latter requires the continuous supply of commercial H₂O₂ and the use of a membrane that leads to undesired high cell voltages. Surprisingly, the performance of electrochemical systems equipped with an air-diffusion electrode (ADE) as the cathode and a BDD anode has not been assessed yet. Under EF conditions, the decontamination could be enhanced due to the synergistic action of BDD(·OH) produced from reaction (2) and ·OH generated via Fenton's reaction (3), as recently shown by some of us for some organic pollutants [37–40].



A significant improvement could be expected under photoelectro-Fenton (PEF) conditions, since the irradiation with artificial UVA light favors the continuous regeneration of Fe²⁺ as Fenton's reagent with additional formation of ·OH from photo-Fenton reaction (4), as well as the photodecarboxylation of Fe(III)-carboxylate complexes via reaction (5) [18,38,41]:



One important niche market for the EAOPs is the integration as user-friendly, very effective processes in wastewater treatment facilities after pre-concentration of the effluent by membrane technologies [21,42]. Accordingly, this work addresses the treatment of concentrated alachlor solutions of up to 0.60 mM, i.e., 100 mg L⁻¹ total organic carbon (TOC), aiming at demonstrating the viability of the EAOPs for achieving the quick degradation and total mineralization. The progress of mineralization in systems with a Pt or BDD anode and an ADE cathode was monitored by TOC analysis, high-performance liquid chromatography (HPLC) and ion chromatography (IC). Furthermore, the main degradation by-products formed upon the electrochemical treatments have been identified by gas chromatography–mass spectrometry (GC–MS), which has allowed the identification of the primary intermediates involved in different reaction pathways.

2. Materials and methods

2.1. Chemicals

Alachlor (C₁₄H₂₀ClNO₂, 95% purity) was of technical grade from Aragonesas Agro S.A. Anhydrous sodium sulfate used as background electrolyte and ferrous sulfate heptahydrate used as Fe²⁺ catalyst source were of analytical grade supplied by Merck and Fluka, respectively. Oxalic, oxamic, acetic and chloroacetic acids were of analytical grade purchased from Merck. Solutions were prepared with high-purity water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm at 25 °C. The initial solution pH was adjusted to 3.0 with analytical grade sulfuric acid supplied by Merck, because it is the optimum value to carry out the Fenton's reaction [18]. Organic solvents, inorganic salts used for preparing the calibration curves in IC and other chemicals used were either of HPLC or analytical grade from Merck, Panreac and Sigma–Aldrich.

2.2. Electrochemical cells

Lab-scale, current-controlled electrolyses were carried out under EO, EF and PEF conditions by using an open, undivided, cylindrical glass cell containing a 100 mL solution. A double jacket for circulation of external thermostated water from a Thermo Electron Corporation HAAKE DC 10 thermostat allowed the regulation of the solution temperature at 25 °C. The solution was stirred with a magnetic bar at 800 rpm to ensure mixing and the transport of reactants toward/from the electrodes. Two different anode/cathode pairs were employed, thus constituting the Pt/ADE and BDD/ADE cells with electrodes of 3 cm² and an interelectrode distance of about 1 cm. The Pt sheet anode of 99.99% purity was supplied by SEMPSA, the BDD thin-film anode was purchased from Adamant Technologies and the carbon–PTFE ADE was purchased from E-TEK. The cathode was mounted as described elsewhere [18], being fed with compressed air pumped at 1 L min⁻¹ for continuous H₂O₂ generation by reaction (1). Before first use of both electrochemical cells, a preliminary polarization of 0.05 M Na₂SO₄ at 300 mA for 180 min allowed the removal of impurities from the BDD anode surface and the activation of the catalytic layer of the ADE.

All the trials were performed with fresh aqueous solutions of 0.05 M Na₂SO₄ at pH 3.0 (which has been found as optimal for the treatment of other aromatics with an ADE as cathode [18]) containing up to 0.6 mM alachlor, at constant current in the range 100–300 mA. The corresponding cell voltage was 7.0, 10.0 and 16.0 V using Pt, and 12.0, 16.0 and 22.0 V using BDD, at 100, 200 and 300 mA, respectively. In EF and PEF, 0.5 mM Fe²⁺ was added before current application in order to allow the Fenton's reaction (3). In the photoassisted electrolyses, the solution was irradiated with a Philips TL/6 W/08 fluorescent black light blue tube placed

Download English Version:

<https://daneshyari.com/en/article/641064>

Download Persian Version:

<https://daneshyari.com/article/641064>

[Daneshyari.com](https://daneshyari.com)