

Reaction scheme for the electrochemical treatment of alachlor in water by the photoassisted process photoelectro-Fenton with BDD and Pt anodes

Angelo R. F. Pipi¹, Adalgisa R. De Andrade¹, Enric Brillas², Ignasi Sirés²

¹Departamento de Química da Faculdade de Filosofia, Ciências e Letras da Faculdade de Ribeirão Preto Universidade de São Paulo.

Av. Bandeirantes, 3900. 14040-901. Ribeirão Preto-SP. Brazil.

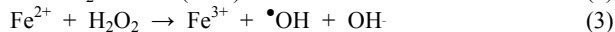
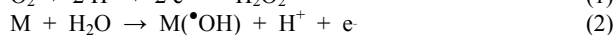
angelfav@gmail.com, ardandra@ffclrp.usp.br

²Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Química Física, Facultat de Química, Universitat de Barcelona.

c/Martí i Franquès 1-11, 08028 Barcelona, Spain. brillas@ub.edu, i.sires@ub.edu

Alachlor is a chloroacetanilide herbicide that displays toxic and genotoxic effects [1]. The treatment of persistent organic molecules found in waters can be made by various processes, including three promising electrochemical advanced oxidation processes (EAOPs) studied in this work: electro-oxidation (EO), electro-Fenton (EF) and photoelectro-Fenton (PEF).

The degradation was carried out at controlled temperature (25°C) in an undivided and open electrolytic cell containing 100 mL of 0.6 mM alachlor in 0.05 M Na₂SO₄ at pH 3.0, in the presence of 0.5 mM FeSO₄ in EF and PEF. The applied current was 100, 200 and 300 mA. Pt or boron-doped diamond (BDD), each with an area of 3 cm², was used as the anode, whereas a carbon-PTFE air-diffusion electrode was employed as the cathode since it is able to electrogenerate H₂O₂ from O₂ reduction (1). The mineralization of the organic toxic compound is due to the oxidative action of both, hydroxyl radicals M(•OH) formed from water oxidation at the anode surface according to reaction (2), and hydroxyl radicals produced in the solution bulk by Fenton's reaction(3) in EF and PEF [2].



The total organic carbon (TOC) was analyzed for determining the rate and efficiency of the mineralization process of the pollutant with the electrolysis time up to 6 h. From the results of the evolution of TOC, it can be inferred that BDD leads to a higher degradation efficiency than Pt. Moreover, the PEF process presents a quicker TOC removal compared to the other EAOPs, reaching 90% of degradation in 4 h, as shown in Figure 1. Regarding the effect of the applied current, this was not very significant in any of the cases under study.

On the other hand, the disappearance of the initial herbicide was monitored by reverse-phase HPLC.

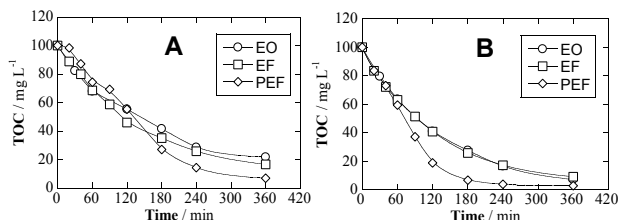


Fig. 1. TOC removal with electrolysis time at two different current density values for the three EAOPs: (A) 100, (B) 300 mA. Conditions: 0.6 mM alachlor, 0.05 M Na₂SO₄, pH 3.0; 0.5 mM FeSO₄ in EF and PEF.

The trends agree with a pseudo-first order kinetics in all cases. For PEF, we observed the complete destruction of alachlor after only 30 min, using either Pt or BDD anodes. Again, the applied current did not have much effect on the destruction kinetics, as depicted in Figure 2.

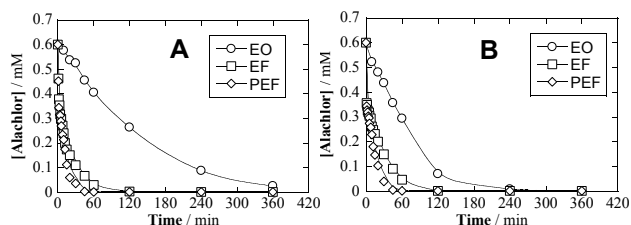


Fig. 2. Time course of alachlor at two different current density values for the three EAOPs: (A) 100, (B) 300 mA. Conditions: see Figure 1.

The electrolyzed solutions were also analyzed using ion-exclusion HPLC, detecting the presence of oxalic, oxamic, maleic, malic, tartaric, acetic and formic acids as short-chain intermediates. In the case of PEF, it was possible to observe a larger number of acids. Measurements were also performed by ion chromatography to determine and quantify the released inorganic ions like Cl⁻, ClO₃⁻ and ClO₄⁻. All three appeared at different concentrations using the BDD anode, whereas only chloride was detected by using Pt, reaching 0.6 mM at 6 h. Finally, GC-MS measurements were conducted to identify key intermediates formed during the removal of alachlor. Such analyses revealed the formation of 10 by-products, most of them exhibiting a benzenic structure (Figure 3), thus allowing the proposal of a plausible reaction pathway.

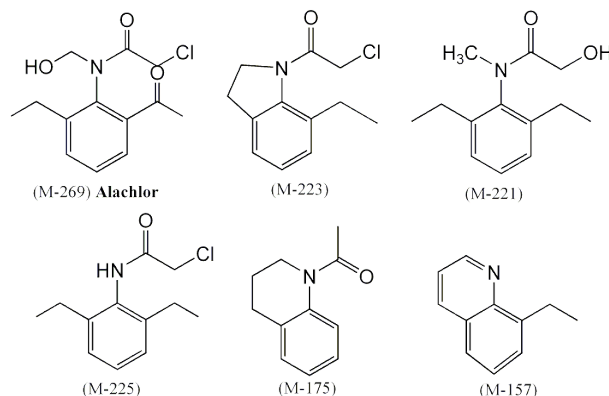


Fig. 3. Structures of alachlor and some by-products found by GC-MS during the electrolyses.

Acknowledgements

The authors acknowledge funding from MICINN through CTQ2010-16164/BQU project, co-financed with FEDER funds and support from the Fundo de Amparo a Pesquisa do Estado de São Paulo (FAPESP).

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