



Application of electrochemical advanced oxidation processes to the mineralization of the herbicide diuron



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HIGHLIGHTS

- Greater diuron degradation using BDD/air-diffusion cell compared to Pt/air-diffusion.
- Mineralization up to 93% by UVA photoelectro-Fenton in a 100 mL stirred tank reactor.
- Mineralization up to 70% by solar photoelectro-Fenton in a 2.5 L pre-pilot flow plant.
- Oxalic and oxamic acids detected as final carboxylic acids.
- Release of NH_4^+ and Cl^- , partially oxidized to ClO_3^- and ClO_4^- ions.

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ABSTRACT

Here, solutions with 0.185 mM of the herbicide diuron of pH 3.0 have been treated by electrochemical advanced oxidation processes (EAOPs) like electrochemical oxidation with electrogenerated H_2O_2 (EO- H_2O_2), electro-Fenton (EF) and UVA photoelectro-Fenton (PEF) or solar PEF (SPEF). Trials were performed in stirred tank reactors of 100 mL and in a recirculation flow plant of 2.5 L using a filter-press reactor with a Pt or boron-doped diamond (BDD) anode and an air-diffusion cathode for H_2O_2 electrogeneration. Oxidant hydroxyl radicals were formed from water oxidation at the anode and/or in the bulk from Fenton's reaction between added Fe^{2+} and generated H_2O_2 . In both systems, the relative oxidation ability of the EAOPs increased in the sequence EO- H_2O_2 < EF < PEF or SPEF. The two latter processes were more powerful due to the photolysis of intermediates by UV radiation. In the stirred tank reactor, the PEF treatment with BDD was the most potent method, yielding 93% mineralization after 360 min at 100 mA cm^{-2} . In the flow plant, the SPEF process attained a maximum mineralization of 70% at 100 mA cm^{-2} . Lower current densities slightly reduced the mineralization degree in SPEF, enhancing the current efficiency and dropping the energy consumption. The diuron decay always obeyed a pseudo-first-order kinetics, with a much greater apparent rate constant in EF and SPEF compared to EO- H_2O_2 . Oxalic and oxamic acids were detected as final carboxylic acids. Ammonium and chloride ions were also released, the latter ion being partially converted into chlorate and perchlorate ions at the BDD surface.

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1. Introduction

Recently, several electrochemical advanced oxidation processes (EAOPs) are being developed for water remediation (Martínez-Huitle and Ferro, 2006; Panizza and Cerisola, 2009; Klavarioti et al., 2009). These methods are based on the *in situ* generation

of $\cdot\text{OH}$, which reacts with most organics up to their mineralization to CO_2 , water and inorganic ions due to its high standard redox potential ($E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/SHE}$). The most powerful EAOPs generate H_2O_2 from the two-electron reduction of injected O_2 (Brillas et al., 2009; Sirés and Brillas, 2012):



Good efficiencies for H_2O_2 generation from reaction (1) have been reported for carbonaceous cathodes like carbon sponge (Özcan et al., 2008), carbon-felt (Dirany et al., 2012), graphite-felt

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(Panizza and Oturan, 2011), boron-doped diamond (BDD) (Ramírez et al., 2013) and carbon-PTFE O₂⁻ or air-diffusion electrodes (El-Ghenymy et al., 2013).

The most popular EAOP is anodic oxidation or electrochemical oxidation (EO), where organics are oxidized at high current by physisorbed M(·OH) formed during the anodic water discharge to O₂ (Martínez-Huitle and Ferro, 2006; Aquino Neto and De Andrade, 2009a,b):

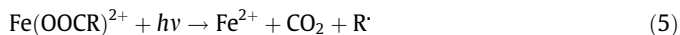


The best anode known for EO is the BDD thin film (Panizza and Cerisola, 2009). When an undivided cell with an O₂⁻ or air-diffusion cathode is used, the method is so-called EO with electrogenerated H₂O₂ (EO-H₂O₂) (Sirés et al., 2007; Cavalcanti et al., 2013).

The oxidation ability of EO-H₂O₂ is enhanced in electro-Fenton (EF) by adding a small amount of Fe²⁺ to the solution at pH ca. 3, thus reacting with generated H₂O₂ to give ·OH and Fe³⁺ in the bulk from Fenton's reaction (3) (Brillas et al., 2009):



In photoelectro-Fenton (PEF), the solution is irradiated with artificial UVA light (Sirés et al., 2007; Anotai et al., 2011; De Luna et al., 2012; Garcia-Segura et al., 2012). When sunlight is used, the method is so-called solar PEF (SPEF) (Flox et al., 2007; Almeida et al., 2011; Salazar et al., 2012). In both EAOPs, the radiation causes: (i) the photolysis of Fe(OH)²⁺, the pre-eminent Fe³⁺ species at pH ~ 3, from photo-Fenton reaction (4), and (ii) the photodecarboxylation of some generated Fe(III)-carboxylate complexes from reaction (5).



Our group has demonstrated that in EF, PEF and SPEF, aromatics are more quickly destroyed by ·OH in the bulk than by BDD(·OH) (Flox et al., 2007; Ruiz et al., 2011; Salazar et al., 2012), allowing the use of less powerful anodes like Pt (Almeida et al., 2011; El-Ghenymy et al., 2013). However, more research efforts are necessary to clarify the effect of the anodes in such EAOPs, as well as to gain a better understanding of their potential scale-up from small stirred tank reactors to flow plants for their application at industrial level.

Phenylurea herbicides are applied to the pre- and post-emergence control of weeds in many crops and also on roads and railways. Among phenylureas, diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea, see chemical structure in Fig. 1) is widely used in many formulations and has been found in natural waters (Oturan et al., 2008). It presents toxic effects on mammals and might have serious consequences on human health and reproduction (Giacomazzi and Cochet, 2004). The destruction of diuron has been

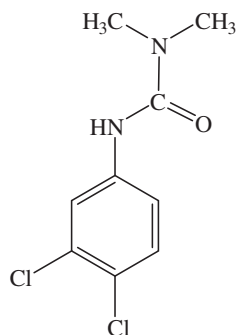


Fig. 1. Chemical structure of the herbicide diuron.

tested by physicochemical methods (Bouras et al., 2007), AOPs like Fenton (Gallard and De Laat, 2001), photo-Fenton (Djebbar et al., 2008), photolysis (Djebbar et al., 2008) and TiO₂ photocatalysis (Katsumata et al., 2009), and microbiological degradation (Tixier et al., 2000). Higher degradation rates for diuron have been found by EAOPs. Polcaro et al. (2004) reported an almost total mineralization of 41.8 mg L⁻¹ diuron at pH 7 by EO with BDD in an undivided flow cell at 15–51 mA cm⁻². No aromatic byproducts were detected and stoichiometric amounts of Cl⁻ and NH₄⁺ ions were released. Almost total mineralization was also found by treating 27.6 mg L⁻¹ diuron in 0.05 M Na₂SO₄ with 0.2 mM Fe³⁺ at pH 3.0 by EF in an undivided Pt/carbon-felt reactor at 250 mA (Oturan et al., 2008, 2010). In previous work, we studied the EO degradation of 50 mg L⁻¹ diuron in 1.5 M Na₂SO₄ or in 1.5 M Na₂SO₄ + NaCl using a divided cell with a dimensionally stable anode at 25–100 mA cm⁻² (Pipi et al., 2013), but almost total mineralization was only feasible in the presence of Cl⁻ due to the more potent destruction by chlorinated active species formed from anodic oxidation of Cl⁻.

This paper aims to study the comparative mineralization of a 0.185 mM (42.9 mg L⁻¹) diuron solution at pH 3.0 by EO-H₂O₂, EF, PEF and SPEF in undivided cells with an air-diffusion cathode. The oxidation ability of these EAOPs in 100 mL stirred tank reactors with a Pt or BDD anode was clarified. The treatments were further scaled-up to a 2.5 L flow plant with a BDD/air-diffusion filter-press cell, which was coupled to a solar photoreactor for SPEF.

2. Experimental

2.1. Chemicals

Reagent grade diuron (>98% purity) from Sigma–Aldrich was used as received. Anhydrous sodium sulfate, ferrous sulfate heptahydrate and oxalic and oxamic acids were of analytical grade from Merck and Fluka. Solutions degraded in stirred tank reactors were prepared with high-purity water obtained from a Millipore Milli-Q system (resistivity > 18 MΩ cm), whereas those treated in the flow plant were prepared with deionized water. The initial solution pH was adjusted to 3.0 with analytical grade sulfuric acid from Merck.

2.2. Electrolytic systems

The electrolytic trials at laboratory scale were conducted in open, undivided and cylindrical tank reactors containing a 100 mL solution and with a double jacket for circulation of external thermostated water 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. The cells contained either a 3 cm² Pt sheet from SEMPSA or a 3 cm² BDD thin-film electrode from Adamant Technologies as the anode and a 3 cm² carbon-PTFE air-diffusion cathode from E-TEK. The cathode was mounted as described elsewhere (Isarain-Chávez et al., 2010), being fed with an air flow of 1 L min⁻¹ for H₂O₂ generation. The trials were performed at constant current density (*j*) provided by an Amel 2053 potentiostat–galvanostat. In PEF, the solution was irradiated with a Philips TL/6W/08 lamp, which emitted UVA light with λ_{max} = 360 nm, supplying a photoionization energy of 5 W m⁻² determined with a Kipp & Zonen CUV 5 radiometer.

Treatments with a 2.5 L recirculation flow plant were performed as reported elsewhere (Flox et al., 2006, 2007; Ruiz et al., 2011). The diuron solution was degraded at 25 °C and liquid flow rate of 200 L h⁻¹. The electrolytic reactor was an undivided filter-press cell with a 20 cm² BDD thin-film anode from Adamant Technologies and a 20 cm² carbon-PTFE air-diffusion cathode from E-TEK. The cathode was fed with air pumped at an overpressure of

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