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Technical Note

Study of the toxicity of diuron and its metabolites formed in aqueous medium during application of the electrochemical advanced oxidation process "electro-Fenton" ☆

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ABSTRACT

Diuron (*N'*-[3,4-dichlorophenyl]-*N*,*N*-dimethylurea) is a herbicide belonging to the phenylurea family, widely used to destroy weeds on uncultivated surfaces. Because of its toxicity for aquatic organisms and suspicion of being carcinogenic for humans, diuron is the object of growing environmental concern. Therefore, we have developed the electro-Fenton method, an electrochemical advanced oxidation process (EAOP), to degrade diuron in aqueous medium, and we have studied the evolution of the toxicity of treated solution during the process. Indeed, the EAOPs catalytically generate hydroxyl radicals that oxidize the persistent organic pollutants, and can ultimately destroy and mineralize them. But, sometimes, relatively toxic organic metabolites are formed during the oxidation reaction. In this work, the evolution of toxicity of diuron aqueous solutions was studied at different initial concentrations, during treatment by the electro-Fenton method. Samples were collected at various electrolysis times and mineralization degrees during the treatment. The toxicity of the samples was measured using the bacteria *Vibrio fischeri* (Microtox) and the green alga *Scenedesmus obliquus*. Our results demonstrated that the toxicity of diuron aqueous solutions (concentrations = 3.0–27.6 mg L^{-1}) varied considerably with time. The formation and disappearance of several metabolites, having toxicity often stronger than that of the initial herbicide, were observed. To improve the efficiency of water decontamination, the electro-Fenton method should be applied during a time long enough (several hours) and at relatively high electrolysis current (I = 250 mA) to reach a nearly complete mineralization of the herbicide in the aqueous medium.

1. Introduction

Phenylurea derivatives have been put on the market during the 60s, and they have been widely applied as herbicides since then, although their use was recently banned or at least restricted in several European countries, due to growing environmental concerns. These compounds can enter in plants through the roots, and then they are carried by means of the sap towards leaves where they inhibit photosynthesis. Among these phenylureas, diuron (*N'*-[3,4-dichlorophenyl]-*N*,*N*-dimethyl-urea) is a systemic herbicide more particularly used to eradicate weeds in the non-agricultural areas, including roadsides, railways, parks, etc. (often located at the proximity of drainage systems and feeders) as well as in the wine growing regions. Most commercial preparations containing diuron are classified in the category of harmful chemicals, and they are generally considered as dangerous for aquatic life and flora (for instance, LC_{50} = 5.6 mg L^{-1} in the case of trout) as well as for mankind, for which the risk of provoking congenital malformations has been reported (Morgan and Kicentjuk, 1992; Tomlin, 1997). In addition, diuron is suspected to be a carcinogenic and genotoxic compound (Canna-Michaelidou and Nicolaou, 1996).

Taking into consideration these various problems generated by diuron, and also its degradation in the environment, it seemed very important to develop efficient processes aimed to rapidly destroy diuron and its oxidation products in natural waters, and to monitor the evolution of the toxicity during the degradation reaction. Indeed, several groups have developed an intensive effort of research on the chemical (Gallard and De Laat, 2001), physicochemical (Bouras et al., 2007), photochemical (Mazellier et al., 1997; Tixier et al., 1999), heterogeneous photocatalytical (Malato et al., 2003),

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electrochemical (Edelahi et al., 2003; Polcaro et al., 2004) and microbiological (Tillmanns et al., 1976; Tixier et al., 2000) degradation methods of diuron, and the diuron transformation products. In contrast, there has been relatively few works on its degradation kinetics (Salvestrini et al., 2002). Most detected degradation metabolites are constituted by diuron de-methyl derivatives, such as DCPMU [3-(3,4-dichlorophenyl)-1-methylurea], DCPU [3-(3,4-dichlorophenylurea] and 3,4-DCA (3,4-dichloroaniline) (Salvestrini et al., 2002). It is well documented that diuron itself and its transformation products generally present toxic effects on mammals, and might have serious consequences on the human health and reproduction (Malpuech-Brugere et al., 2001; Giacomazzi and Cochet, 2004). For instance, it was reported that a concentration of 5 mM of 3,4-DCA was able to destroy the human spermatozoids within 30 min (Malpuech-Brugere et al., 2001).

Therefore, this work included two main parts: application of the electro-Fenton method to the degradation of diuron, and study of the evolution of toxicity of diuron solutions during electro-Fenton treatment. In the first part, we investigated the diuron degradation kinetics and formation of metabolites during the application of the electrochemical advanced oxidation process (EAOP), namely "electro-Fenton" process, to diuron aqueous solutions by using high performance liquid chromatography (HPLC) analysis. The process is based on the *in situ* electro-generation of ·OH radicals, according to the electrochemically-assisted Fenton's reaction (Oturan et al., 1999; Boye et al., 2003; Brillas et al., 2004a; Diagne et al., 2007):

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \quad (1)$$

Hydrogen peroxide and ferrous ions are simultaneously produced in an aqueous medium by the bi-electronic reduction of the dissolved molecular oxygen (reaction (2)) (Oturan et al., 1992a; Brillas et al., 2004b) and ferric ions (initially introduced at a catalytic concentration) (reaction (3)) (Oturan et al., 1992b, Boye et al., 2002; Kesraoui-Abdessalem et al., 2008)

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

On the one hand, the electro-generated ferric ions are reduced in the reaction (3) at the cathode (Oturan and Pinson, 1995; Sirés et al., 2007a; Özcan et al., 2008) in order to catalyze the reaction (1), and, on the other hand, molecular oxygen, utilized in reaction (2), is yielded at the anode by oxidation of water, according to the reaction (4):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (4)$$

As discussed in detail previously (Oturan and Oturan, 2005; Hammami et al., 2007; Sirés et al., 2007b), the hydroxyl radicals formed by Eq. (1) are very strong oxidants in solution, capable of oxidizing a very large variety of organic pollutants, including the phenylurea pesticides, until their total mineralization.

In the second part, we simultaneously determined the evolution of the toxicity of these diuron aqueous solutions with the electrolysis time. Indeed, it is worthwhile stressing that the treatment of aqueous solutions of toxic organic pollutants by advanced oxidation processes is not necessarily accompanied by a decrease of the toxicity, since the oxidation reaction might lead to the formation of intermediates and/or metabolites more toxic than the initial pollutant. The toxicity measurements of diuron aqueous solutions were carried out during the electro-Fenton treatment by means of two methods, including the bioluminescence Microtox method, based on the measurement of the bioluminescence of the marine bacteria *Vibrio fischeri* (Arufe et al., 2004; Girotti et al., 2008), and the growth of a green alga culture (*Scenedesmus obliquus*) (Couderchet and Vernet, 2003).

2. Experimental

2.1. Chemicals and instrumentation

Diuron and 3,4-DCA were purchased from Riedel-de-Haën. DCPMU, DCPU and formamide (FA) were provided from the CIL Cluzeau and Sigma Aldrich companies. Deionized water used for the preparation of the working solutions and HPLC eluting solutions was obtained from a Millipore Milli-Q (simplicity 185) system with resistivity > 18 MΩ cm at room temperature. Methanol (quality Chromanorm) was purchased from VWR international.

For the electrolyses, a stabilized power supply and a one-compartment electrochemical cell were used. The cathode was a 3D carbon felt electrode of 60 cm^2 of area (Carbone–Lorraine) and the anode was a cylindrical platinum grid of 4.5 cm of height and 3 cm of internal diameter. The degradation of the aqueous solutions (pH = 2.8–3.0) of diuron at various initial concentrations (C_0 = 3.0, 4.9, 8.9, 9.8, 14.7 and 27.6 mg L^{-1}), was performed in volumes of solution of 300 mL, at various constant current intensity values (I = 30, 50, 100, 200 mA). A moderate oxygen flow was sent through the treated solutions for 5 min prior to the electrolysis. A catalytic amount (0.2 mM) of ferric ions ($Fe_2(SO_4)_3 \cdot 5H_2O$) was added to the solution before starting the electrolysis. The pH of aqueous solutions, initially adjusted at a value of 3.0, was found to vary very little during the electrolysis, reaching finally a value of 2.8 at the end of treatment.

The evolution of the treated diuron aqueous solutions with electrolysis time was followed by HPCL analysis, using a Merck Lachrom chromatograph, equipped with a reversed-phase column (Purospher RP-18, 5 μm, 4.6 × 250 mm, Merck) and a diode array detector (model DAD L-7455). The sample volumes were 20 μL. A water–methanol 40:60 v/v mixture was used as elution solution at a flow rate of 0.8 mL min^{-1}. The diuron metabolites were identified by comparing their retention times to those of the standard compounds. The mineralization percentage of the treated diuron solutions was measured in terms of total organic carbon (TOC) by means of a Shimadzu instrument (Shimadzu TOC-VSCH analyzer).

2.2. Toxicity measurements

2.2.1. Microtox method

For this test, the measurements were carried out with the bioluminescent marine bacteria *V. fischeri*, provided by Hach Lange France SAS, by means of the Microtox M 2055 system, according to the international standard process (OIN 11348-3). The bioluminescence measurements were realized on solutions containing various diuron initial concentrations (C_0 = 4.9, 8.9, 14.7 mg L^{-1}), electrolyzed at several constant current intensities (I = 30, 50, 100, 200 mA), and on a blank (C_0 = 0 mg L^{-1}). The bioluminescence intensity of bacteria was measured after 5 and 15 min of exposition to these treated diuron solutions.

2.2.2. Green alga test

In the case of this test, three diuron initial concentrations (C_0 = 3.0, 10.0 and 27.6 mg L^{-1}) plus the blank (C_0 = 0 mg L^{-1}) were used after electrolysis at several constant current intensities. *S. obliquus* algae were grown in 250 mL flasks containing 120 mL of a nutrient mineral medium (Couderchet and Böger, 1993) on an orbital agitator (110 rpm) at 22 ± 1 °C and under continuous light (photosynthetically active radiation 100 ± 10 μmol s^{-1} m^{-2}). Samples (1.5 mL) of an exponentially-growing alga suspension were put in multi-well plates with 24 wells containing 0.1 mL of the solution under study, in the above-mentioned conditions. At the beginning of incubation, the concentrations in wells (calculated on the basis of the diuron initial