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Applicability of electrochemical oxidation using diamond anodes to the treatment of a sulfonylurea herbicide

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ABSTRACT

In this work, the electrolysis of chlorsulfuron (CSF, a sulfonylurea herbicide) with conductive-diamond anodes is studied. The influences of the nature of the supporting electrolyte (0.05 mol dm⁻³ NaCl and Na₂SO₄), the applied current density (30 and 100 mA cm⁻²) and the initial herbicide concentration (20,50 ad 100 mg dm⁻³) have been evaluated. Total mineralization of the herbicide was attained regardless of the supporting electrolyte medium used, although electrolyte clearly influenced on the efficiency and rate of the oxidation process. Likewise, the process was found to be more efficient at low current densities. Results point out the importance of mediated electrochemical processes in the removal of CSF. This influence was confirmed by additional tests in which the electrolysis was combined with UV light or ultrasound irradiation: the use of UV irradiation results in a less efficient process, while US improves importantly the rate of the mineralization as compared to the single electrolytic process. The strong oxidation conditions of electrolysis leads to the formation of reaction intermediates (2-amino-4-methoxy-6-methyl-1,3,5-Triazine, 2-chlorobenzenesulfonamida and oxalic acid) in agreement with the mechanisms proposed in the literature for other AOPs.

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1. Introduction

In recent years, one group of phytochemicals, pesticides, has been the subject of growing concern among environmental agencies and the scientific community. This concern is for their high risks to both human health and the environment, which are often associated with their limited biodegradability, high vapor pressure and lipid affinity [1–4]. Thus, many treatment technologies are being developed for both soil and water treatment to minimize the effects of their occurrence on the environment and public health. The novel soil treatments aim to constrain pollution and remove it by means of *in situ* technologies (without excavation to preserve the characteristics of the soil). In particular, one of the most desired characteristics of such a treatment is its ability to effectively transfer the pollutant from the soil to an aqueous phase, known as flushing fluid. Electrochemically based processes, such as electrokinetic soil fences and electrokinetic soil flushing, are very promising for helping solve this serious environmental problem [2,5,6]. They have been studied recently for the remediation of soil spiked with pesticides, and the results are, thus far, fairly positive:

it was demonstrated that pesticide can be efficiently transferred from the soil to the flushing fluid, thereby transforming the soil remediation problem into an easier wastewater treatment issue.

Regarding the removal of pesticides from water, many Advanced Oxidation Processes (AOPs), such as ozonation, photochemical oxidation, photolysis with H₂O₂ and O₃, Fenton processes, and photocatalysis, have been proposed and tested [7–12] over the last decade. These AOPs are characterized by the generation of very reactive and oxidizing free radicals in aqueous solutions, particularly hydroxyl radicals. Most of them show great efficiency, but the results are strongly influenced by the characteristics of the pesticide, and the occurrence of refractory species is occasionally a major problem.

Currently, one of the most interesting AOPs is electrolysis, which has been demonstrated to be a very efficient technology for the removal of organic pollutants [9,13–15], including pesticides. The results obtained with this technology depend strongly on not only the operating conditions but also the anode material used. Diamond coatings have demonstrated brilliant performance due to their intrinsic properties, which lead to the efficient production of hydroxyl radicals. This radical is a very powerful oxidant (E⁰: 2.80 V vs. SHE), and it is ultimately responsible for the formation of other oxidants, such as peroxosulfates, peroxophosphates, peroxocarbonates, ozone and hydrogen peroxide [16–18]. The hydroxyl

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radicals and many other mediated oxidants that are produced at high concentrations on the surface of a diamond are responsible for the severe oxidation conditions attained [15,19,20]. The interaction of these oxidants with pesticides is a factor of major significance, as demonstrated in previous works in which electrolysis, sono and photoelectrolysis were used to destroy pesticides [21–23]. The literature [24,25] indicates that US irradiation can help improve the mass transfer to anodic surfaces during electrolysis and promote the decomposition of water, thereby producing hydroxyl radicals. Alternately, the use of light irradiation mainly permits the homogeneous activation of oxidants occurring in the bulk phase [26]. Likewise, recent studies have demonstrated that a combination of technologies was a very efficient process, even more so than expected, according to the addition of effects of the single processes [22,27,28].

There are many types of pesticides, and they exhibit very different physico-chemical properties. Sulfonylureas, which form a group of highly selective herbicides, are used worldwide for weed and grass control and in some crops. In particular, chlorsulfuron (CSF) has great phytotoxicity, even at low concentrations. Its bio-refractory nature thus necessitates the development of new treatment technologies to eliminate this type of pesticide from contaminated water and soil [29,30].

The purpose of the present study is to evaluate the applicability of the electrochemical oxidation of chlorsulfuron with diamond anodes. The effects of the supporting electrolyte, current density and initial herbicide concentration are studied, with the intention of elucidating how the mediated electrolytic process affects chlorsulfuron oxidation. Additionally, to clarify the role of mediated oxidation, electroirradiated tests (with irradiation of UV light or ultrasounds) are carried out.

2. Experimental methodology

2.1. Chemicals

All chemicals, including anhydrous sodium sulfate, sodium chloride (Fluka, Spain), and chlorsulfuron (Sigma-Aldrich), were analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity = 18.2 M Ω cm at 25 °C) was used to prepare all solutions.

2.2. Electrochemical cell

The galvanostatic electrolyses were carried out in a single-compartment electrochemical flow cell using 1 dm³ of solution. The flow rate was kept constant at 26.4 dm³ h⁻¹, and the temperature was maintained at 25 °C. Boron-doped Diamond Electrodes (Adamant Technologies) were used as both anode and cathode. Both electrodes were circular (100 mm in diameter), with a geometric area of 78 cm². The interelectrode gap was approximately 9 mm. The investigated variables in the electrochemical degradation of the herbicide were i) the nature of the supporting electrolyte (NaCl and Na₂SO₄) by keeping the ionic strength at 0.05 mol dm⁻³, ii) the applied current density (30 and 100 mA cm⁻²) and iii) the initial herbicide concentration (20, 50 and 100 mg dm⁻³).

Irradiated experiments were carried out in the electrolysis setup using the same fluid-dynamic conditions. To achieve this, the setup was equipped with an ultrasound source (UP200S ultrasound horn, Hielscher Ultrasonics GmbH, equipped with a titanium glass horn measuring 40 mm in diameter and 100 mm in length) and a UV lamp (Vilber Lourmat filtered lamp, VL-215.MC, with a power of 4 W). The ultrasound generator irradiates energy into an auxiliary tank, whereas the UV lamp is located immediately in front of the

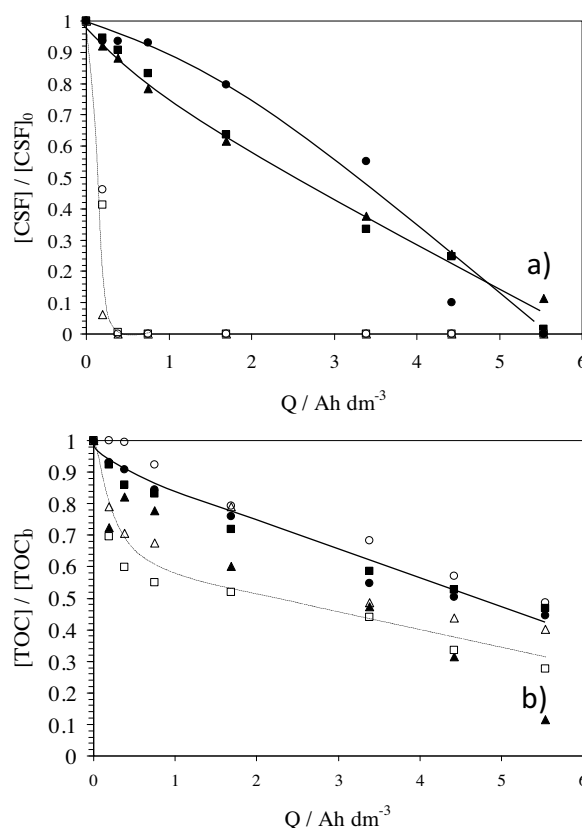


Fig. 1. Influence of the initial concentration on (a) the removal of pollutants and (b) the mineralization of the solution as a function of the applied charge (Q) during the electrochemical oxidation containing NaCl (empty points-dashed lines) and Na₂SO₄ (full points-continuous line) as the supporting electrolyte. (▲, △) 20 mg dm⁻³, (■, □) 50 mg dm⁻³ and (●, ○) 100 mg dm⁻³. Conditions: 0.05 mol dm⁻³ of the supporting electrolyte and $j = 30$ mA dm⁻².

electrochemical cell and irradiates directly to the anodic surface to promote the activation of the electrochemically formed oxidants (a quartz plate and a lattice cathode of stainless steel are used). A detailed description of the electrochemical cell can be found elsewhere [23].

2.3. Analysis procedures

The pesticide removal was monitored by chromatographic analysis and considering the total organic carbon (TOC). HPLC (Agilent 1100 series) using analytical column Phenomenex Gemini 5- μ m C18 was used for quantification. The mobile phase consisted of 40% acetonitrile and 60% water (0.1% H₃PO₄), with a flow rate of 0.4 cm³ min⁻¹. The detection wavelength used was 225 nm, and the oven temperature was maintained at 25 °C. The volume injection was set to 50 μ L. The TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Measurements of the pH were carried out with an InoLab WTW pH-meter. All samples extracted from the electrolyzed solution were filtered with 0.45- μ m nylon filters before analysis.

Chloride anions (Cl⁻, ClO₃⁻, ClO₄⁻) were determined by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1 \times 10⁻³ dm³ min⁻¹. Hypochlorite (HClO⁻) was determined by titration with 0.001 M As₂O₃ in 2.0 M NaOH. Peroxosulfate was quantified iodometrically according to Kolthoff and Carr [31].

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