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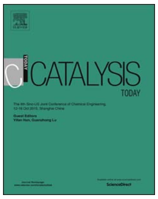

Degradation of herbicide S-metolachlor by electrochemical AOPs using a boron-doped diamond anode

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ABSTRACT

The degradation and mineralization ability of electrochemical processes like electro-oxidation with electrogenerated H_2O_2 (EO-H_2O_2), electro-Fenton (EF) and UVA-assisted photoelectro-Fenton (PEF) has been comparatively studied for solutions of the herbicide S-metolachlor. Solutions of 100 mL have been treated using an undivided cell equipped with an air-diffusion cathode and a boron-doped diamond (BDD) anode. The effect of pH, current density, and Fe^{2+} and S-metolachlor concentrations has been thoroughly studied. The total organic carbon removal profiles have demonstrated the feasibility of almost overall mineralization by EF and PEF after 9 h at 300 mA. The herbicide decays in both treatments informed about the complexation of Fe(III) ions formed from Fenton's reaction, which decelerated S-metolachlor removal. However, the high oxidation power of BDD anode allowed the gradual mineralization of such complexes. The identification of chlorinated and non-chlorinated degradation byproducts by GC–MS has allowed the proposal of main degradation routes.

1. Introduction

The large consumption of herbicides worldwide contributes in a very significant manner to environment contamination and, as a result, public health is currently at stake [1]. The herbicide S-metolachlor (ST, $C_{15}H_{22}ClNO_2$, 2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-[(1S)-2-methoxy-1-methylethyl]acetamide) is a selective chloroacetanilide herbicide that has been applied since the 1970s to more than 70 different crops to control small leaf weeds in the pre and post-emergence period [2]. Its high water solubility (480 mg L^{-1} at 20 °C), low vapor pressure (1.73×10^{-3} Pa at 20 °C) and large half-life owing to its slow degradation by photolysis (70 days exposure to sunlight) or hydrolysis (30 days at pH 5–9) led to classify S-metolachlor residues as persistent [3,4]. Its large usage and relatively low adsorption in soil cause a considerable discharge into groundwater, thus compromising water quality [5]. Although ST is classified as moderately toxic (Class III) [4,6], its negative impact on aquatic microorganisms like phytoplankton [7], fish [8] and crustaceans [9], as well as on certain types of human cells [10] has been reported. Several authors have investigated the performance of various methods to treat water containing this and other herbicides. TiO_2 photocatalysis [11], photo-Fenton with artificial and natural light [12,13], electro-Fenton (EF) [14–20], and UVA- or solar-assisted photoelectro-Fenton (PEF) with in situ H_2O_2 electrogeneration [16,20–22] have yielded very positive results.

The electrochemical advanced oxidation processes (EAOPs) like electro-oxidation with electrogenerated H_2O_2 (EO-H_2O_2), EF and PEF have been progressively receiving increasing interest for the removal of toxic organic contaminants from water due to their great performance, in combination with simple setups, safe procedures and affordable costs [23–28]. They promote the oxidation of organic compounds upon in situ generation of hydroxyl radical ($\cdot$OH), which exhibits a high redox potential (E° = 2.8 V/SHE), yielding a high degree of mineralization [29–32].

In EO, which is the most widely employed EAOP, the formation of physisorbed $\cdot$OH (M($\cdot$OH)) occurs at the surface (M) of a non-active anode such as boron-doped diamond (BDD) from water oxidation at high applied current or potential, as shown in reaction (1) [30]. BDD is the most effective anode among those tested so far, having demonstrated its effectiveness also for the total degradation of herbicide residues [18,30]. Apart from its large overpotential for O_2 evolution and low adsorption of any species including $\cdot$OH, BDD presents very appealing technological properties such as a high mechanical, thermal and chemical resistance [32].

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$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (1)$$

The EO process can be combined with the cathodic electrogeneration of H_2O_2, yielding the so-called EO-H_2O_2. Several kinds of carbonaceous materials have been used for this purpose, being carbon-PTFE-based air-diffusion cathodes especially useful because of their large ability to favor the two-electron reduction of gaseous O_2 from reaction (2):

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

Additional amounts of $\cdot OH$ in bulk solution can be generated in EF from the catalytic decomposition of H_2O_2 by Fe^{2+} at pH 3.0, following Fenton‘s reaction (3). The catalytic cycle can be maintained since Fe^{3+} can be reduced at the cathode to regenerate Fe^{2+} via reaction (4) [29]. The oxidation ability of EF process can be enhanced upon irradiation with UVA light (λ_{max} = 360 nm), yielding the so-called PEF process, which promotes the photoreduction of Fe(III) species from reaction (5), giving rise to additional amounts of $\cdot OH$, and the photodecomposition of Fe(III)-carboxylate complexes from reaction (6) [29–32]. Note that H_2O_2 is not photolyzed to $\cdot OH$ radical because this would require higher energy such as that provided by UVC light (λ_{max} = 254 nm) [29].

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

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (5)$$

$$Fe(OOCR)^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\bullet} \quad (6)$$

Aiming to evaluate the comparative performance of EO-H_2O_2, EF and PEF to degrade the herbicide S-metolachlor, this paper presents a thorough investigation on the behavior of ST solutions treated in an undivided BDD/air-diffusion cell. The effect of pH on the oxidation ability of EO-H_2O_2 was studied. The influence of the applied current, and the Fe^{2+} and ST concentrations in EF was assessed from total organic carbon (TOC) and high-performance liquid chromatography (HPLC) measurements. The main reaction byproducts were identified by gas chromatography-mass spectrometry (GC–MS).

2. Material and methods

2.1. Chemicals

S-metolachlor (Pestanal®) with purity > 98% was obtained from Sigma-Aldrich. Vetec Quimica Fina supplied the $Fe_2SO_4{\cdot}7H_2O$, Na_2SO_4 and concentrated H_2SO_4. A Gehaka DG500 UF system was employed to produce pure water (resistivity > 18 MΩ cm) needed to prepare all solutions to be degraded. Other chemicals used in various analytical techniques were obtained from J.T. Baker and Vetec Quimica Fina.

2.2. Electrolytic system

Comparative treatments of 100 mL of ST solutions with 0.050 M Na_2SO_4 were carried out by EO-H_2O_2, EF and PEF using an open, undivided glass cell (capacity of 150 mL) with a jacket for recirculation of water at 25 °C. During the trials, solutions were stirred using a magnetic follower. All details on the power source employed to operate galvanostatically and the UVA lamp to irradiate the solutions in PEF can be found elsewhere [20,33]. The BDD anode and carbon-PTFE air-diffusion cathode (3 cm^2 each) used in all the experiments, conveniently cleaned and activate prior to first use [20], were purchased from NeoCoat and E-TEK, respectively. In order to ensure the H_2O_2 production along the electrolyses, the cathode was connected to an air pump (flow rate of 1 L min^{-1}). It must be noted that the use of such a small electrolytic system limits the current efficiency of electrode reactions, particularly the ST removal with BDD($^{\bullet}$OH) that is controlled by the mass transport of organic pollutants.

2.3. Instruments and analytical procedures

The degradation of ST was monitored by HPLC using a Thermo Scientific Finnigan chromatograph equipped with: (i) an autosampler, (ii) a photodiode array detector (set a constant wavelength of 215 nm), and (iii) a 5 μm Agilent Technologies Zorbax Eclipse XDB-C-18 column (250 mm × 4.6 mm). The mobile phase consisted in a 40:60 (v/v) H_2O/CH_3CN mixture eluted at a flow rate of 0.6 mL min^{-1}. At selected treatment times, samples were collected, immediately diluted with CH_3CN and then filtered (0.45 μm PTFE filters). Chloride, chlorate, ammonium and nitrate ions were quantified following standard procedures [34,35]. The pH monitoring, TOC analysis and calculation of mineralization current efficiency (MCE) for each assay were performed as described in previous studies [20,36]. The number of electrons *n* involved in the theoretical global mineralization process of ST was 74 according to reaction (7), which considers the quantitative formation of ammonium (95% of initial N was accumulated as NH_4^+ and 5% as NO_3^-) and chloride ions (subsequently transformed into chlorate ions).

$$C_{15}H_{22}ClNO_2 + 28H_2O \rightarrow 15CO_2 + NH_4^+ + Cl^- + 74H^+ + 74e^- \quad (7)$$

Worth mentioning, the MCE is an average value that considers globally the organic matter to be mineralized, thus ignoring the particular role of reaction intermediates which have variable oxidation state of carbon.

The main byproducts formed upon treatment of 100 mL of ST solutions by EAOPs were identified by GC–MS using a NIST05-MS library. For this, the samples were treated by liquid-liquid extraction method using $C_2H_2Cl_2$ [20]. GC–MS analysis was made with an Agilent Technologies system composed of a 6890N GC, fitted with a nonpolar Teknokroma Sapiens-X5MS or polar Agilent 19091N-133 HP Innowax column, and a 5975C MS operating in electron impact mode at 70 eV. The temperature ramp was: 36 °C for 1 min, 5 °C min^{-1} up to 250 °C (polar) or 320 °C (non-polar) and hold time 10 min. The temperature of the inlet, source and transfer line was 250, 230 and 250–300 °C, respectively.

3. Results and discussion

3.1. Effect of initial pH on the EO-H_2O_2 treatment

For some pollutants, the initial pH is an important parameter in the EO-H_2O_2 treatment because it may affect the protonation/deprotonation equilibria and various reactions where protons have a role, including for example the adsorption of the molecule on the electrodes. Solutions with 0.28 mM ST and 0.050 M Na_2SO_4 were treated at initial pH of 3.0, 5.0 or 9.0 at 300 mA for 540 min. The ST concentration decay shown in Fig. 1a highlights its total disappearance thanks to the oxidation by BDD($\cdot$OH), requiring 240 min at pH 3.0 and 5.0 and 360 min at pH 9.0. Nevertheless, the degradation was slighly faster at pH 3.0, which can be explained, at least in part, by the higher concentration of protons that favored the cathodic formation of H_2O_2 from reaction (2) [37]. This suggests a certain contribution of H_2O_2 to the oxidative degradation of ST. The slighly slower ST decay at pH 9.0 could also be related to the competitive oxidation of OH^- to O_2 at BDD without production of hydroxyl radicals [38], which causes a lower generation of BDD($^{\bullet}$OH) from reaction (1). The inset panel of Fig. 1a presents the good fitting obtained from a pseudo-first-order kinetic analysis of the previous decays for the first 30 min, yielding apparent rate constant (k_{app}) values of 0.014, 0.010 and 0.011 min^{-1} at pH 3.0, 5.0 and 9.0, respectively (see Table 1).

Fig. 1b shows no substantial difference between the TOC removals achieved in EO-H_2O_2 at those three pH values until 6 h of electrolysis, which agrees with the behavior of another herbicide like mecoprop [21]. At 9 h, however, the mineralization attained was 96% at pH 3.0,