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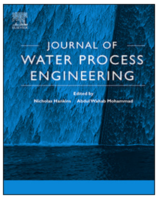

Degradation of pesticide mixture by electro-Fenton in filter-press reactor

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ABSTRACT

The efficiency of a prototype equipped with a dimensionally stable anode (DSA) and a carbon felt cathode was analysed by means of H_2O_2 production and removal of the herbicides diuron (DIU) and glyphosate (GLY) from 0.05 M Na_2SO_4 solutions, pH 3.0, by electrochemical oxidation (EO), EO with H_2O_2 electrogeneration and electro-Fenton (EF). Mineralisation current efficiencies and specific energy consumption were also determined. The best performance under galvanostatic conditions was found to be that of the EF, with 1 mM of Fe^{2+}, compressed air flux of 1 L min^{-1} and current intensity of 1.00 A, for 180 min of treatment, 34% of mineralisation, with 5% current efficiency and specific energy consumption of 0.85 kW h g^{-1} of total organic carbon was found. A maximal accumulated concentration of 78 mg L^{-1} of electrolysed H_2O_2 was achieved in 60 min, and the concentrations of DIU and GLY were reduced by 8% and 94%, respectively. There is a good correlation between the studied flux dispersion in the residence time distribution and the conversion rate verified on degradation, with 100% for GLY and 66.2% for DIU. Two organic by-products as well as short chain carboxylic acids, namely formic, citric and oxalic acid, were detected by LC–MS, and therefore, DIU and GLY degradation mechanisms were proposed.

1. Introduction

In the last decade, there has been a growing interest in finding new technologies to remove organic contaminants from water [1]. Electrochemical advanced oxidation processes (EAOPs) such as electro-Fenton (EF), are widely used in effluent treatment [2], where the continuous H_2O_2 electro-generation at the cathode fed with air or O_2, with the addition of the ferrous ion catalyst, produces the oxidant $\cdot OH$ ($E^\circ = 2.8$ V/SHE – standard hydrogen electrode) by the Fenton reaction [3–6]. One of the main applications of EAOPs is the degradation of harmful compounds provided from agricultural activity [7–12].

The high consumption of commercial pesticides in agriculture and inadequate disposal or storage of outdated products leads to herbicide accumulation in soil, air and waterbodies [13]. Among the five most commonly used herbicides in the world, diuron (DIU) ($C_9H_{10}C_{l2}N_2O$, 3-(3,4-dichlorophenyl)-1,1-dimethylurea)-1,1-dimethylurea) and glyphosate (GLY) ($C_3H_8NO_5P$, N-(phosphonomethyl) glycine) [14] are both non-selective and water soluble. These herbicides, which are classified respectively as organochlorine and organophosphorus synthetic pesticides, are persistent and accumulative pollutants [15,16].

DIU dissolves slowly into water (because of its low solubility in water – 42 mg L^{-1}) and can percolate through the soil, causing contamination of groundwater and surface water [17]. Due to its intensive use, its low volatility and its sluggish biodegradation mechanism (30–180 days half-life in soil) [18], DIU contamination is a serious environmental problem in many countries [19,20]. This herbicide has been included in the list of priority hazardous substances of the European Union [21,22] and the US Environmental Protection Agency (USEPA) [23,24]. DIU has been reported as a chemical harmful to aquatic life and flora [25,26], as well as to mankind, at risk of causing congenital malformations [27], suspected to be a carcinogen and genotoxic compound [28], and with consequences for human health and reproduction [29].

GLY is rapidly biodegraded to its main by-product, amino methylphosphonic acid (AMPA), which is more toxic and persistent than the original herbicide [30,31]. Nevertheless, the low toxicity of this herbicide to humans and animals was one of the main reasons for its great use worldwide [32] and the development of transgenic plants tolerant

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to GLY has further increased consumption [33,34]. The half-life of the commercial formulations of GLY is relatively long, between 7–70 days [35]. The USEPA has established a maximum level of GLY in drinking water of 0.7 μg mL^{-1} and the maximum residual level in most cultures is set at 0.1 μg g^{-1} by the European Union [36]. Although acute toxicity is lower than other herbicides, studies suggest that GLY is a potential endocrine disruptor [37], which may influence fetal osteogenesis [38] and be harmful to the human liver [39]. *In vitro* animal studies have revealed the mutagenic and carcinogenic effect of GLY [40], as well as its impact on the environment and aquatic life [41,42].

Therefore, studies seeking to properly address contamination issues in water bodies presenting incidence of herbicides or other endocrine disrupting compounds have become focus of growing concern [2,20,35]. Among the methods studied filter-press electrochemical reactors, with parallel plate geometry [43,44], have been studied from a theoretical and experimental point of view. These studies have demonstrated their effectiveness in a range of applications, including organic and inorganic electrosynthesis, metal ion removal, energy storage, environmental remediation and potable water treatment [45–54]. Usually, the processes' efficiency is directly related to the fluid dynamics performance in the reactors used. In literature, there are several types, modes of operation (continuous or batch), sizes and dimensions of reactors, with distinct geometry, materials and configuration of electrodes [55–58], enabling countless interaction possibilities when associated with different sources of energy [59,60] and operational conditions proposed for the system itself (volumetric flow, current density, reagent concentration, among others).

A number of factors should be considered during the design of an electrochemical reactor: size and geometry, fluid flow and electrodes reaction kinetics, current intensity, potential difference and concentration distribution, heat transfer, costs and operational simplicity. The fluid flow pattern affects reactor performance, and this pattern is defined primarily by the shape of the inlet and outlet manifolds. Thus, a detailed study on the hydrodynamics of these systems needs to be performed to obtain the fluid velocity profile and detect the zones of stagnation and other non-idealities [61].

The flow hydrodynamics inside a reactor can be studied using the stimulus-response method to determine the residence time distribution (RTD) – an empirical approximation that can be used to describe the flow in the equipment [62,63]. This method involves injecting an inert tracer (dissolved dye or salt) into the reactor inlet and measuring it as a function of time and concentration at the outlet [64–67]. The most commonly used signal as stimulus function is the instantaneous concentration pulse at the input of the reactor [68–70]. The output response allows determining the irregularities in the flow conditions, which can be corrected by making changes in the geometry [71]. The response function can be processed to obtain the characteristic parameters of the proposed model to describe the hydrodynamic behaviour [72]. This experimental method allows easy handling and low operational cost and is commonly used to validate mathematical models of RTD [69].

This study aims to characterise the hydrodynamic behaviour inside a prototype consisting of a continuous flow filter-press reactor by studying the RTD and evaluating its efficiency in the degradation of herbicides DIU and GLY through the EAOPs, electrochemical oxidation (EO), electrochemical oxidation with hydrogen peroxide electrogeneration (EO + H_2O_2) and electro-Fenton (EF), utilising carbon felt cathodes and DSA (dimensionally stable anodes). The reactor performance will be evaluated by the decay of the DIU and GLY mixture concentration by high-performance liquid chromatography (HPLC) and total organic carbon (TOC) concentration, which provide information on the degradation efficiency and mineralisation (conversion to CO_2), respectively. In addition, the degradation by-products (aromatic compounds and carboxylic acids) was investigated using liquid chromatography coupled to mass spectrometry (LC–MS). The toxicity of the solution was evaluated before and after treatment using lettuce seeds as the biosensor. The production of H_2O_2 was also analysed under different current intensities.

2. Experimental

2.1. Materials

Commercial DIU from Nortox® 500 SC (500 g L^{-1}) and commercial GLY from Nufarm (480 g L^{-1}) were used in this study. Sodium sulphate (Na_2SO_4, 99.0%) from Synth (Brazil) was used in the support electrolyte, and ferrous sulphate heptahydrate ($Fe_2(SO4)_3{\cdot}7H_2O$, 99.0%) from Vetec (Brazil) was used as a catalyst in EF. Sulfuric acid (H_2SO_4, 95.0–98.0%) from Sigma-Aldrich (Germany) and sodium hydroxide (NaOH, 95.0–100.5%) from CAQ (Brazil) were used to adjust the pH. All solutions were prepared with ultrapure water, obtained by a water ultra-purification system (Gehaka, model MS2000), with a nominal resistivity of 18.18 mΩ.cm at 25 °C.

2.2. Prototype for filter-press electrochemical reactor and experimental plant

A suitable filter-press reactor [73] consisting of 4 acrylic plates, where 2 presented slots that house an electrode, with a total volume of 2.4×10^{-5} m^3, was used with novel flux configuration. The cathode compartment was completely filled with a carbon felt electrode, type RVG 4000 [74], from Mersen (France), with an electroactive area of 22.08×10^{-2} m^2. In the anode occupying the entire compartment, expanded $Ti/Ru_{0.36}Ti_{0.64}O_2$ DSA plates with a total area of 1.44×10^{-2} m^2, manufactured by De Nora® (Brazil), were installed. The acrylic plates were sealed by Viton® gaskets, and the compartments were divided by a Nafion® N117 membrane (DuPont, USA). A reservoir of 1×10^{-3} m^3 equipped with a mechanical stirrer (40 rpm), was connected to the reactor through two peristaltic pumps model 646, from Fisher Scientific and Milan, for the individual feeding of the reactor compartments. The reactor contains flow diffusers at the inlet and outlet of the slots, consisting of 23 holes of 1.5×10^{-3} m in diameter, to evenly distribute the flow inside. The volumetric working flow was adopted as 2.08×10^{-6} m^3 s^{-1} to feed the reactor compartments. For both compartments, an upward feed was imposed. The reactor assembly scheme and the experimental plant are shown in Fig. 1 and the reactor dimensions and compartment characteristics in Table 1.

2.3. Method for residence time distribution (RTD)

The stimulus-response technique was employed using a black 5 dye (991.82 g mol^{-1}), from Aupicor Química (Brazil), with a concentration of 1.5 g L^{-1} as the tracer. The volume of pulse injection used in each run was 0.4 mL per compartment, and it was injected using a syringe. Upon injection, the samples were collected in batches, sequentially, every 3 s, in triplicate. Dye concentration was determined by measuring the light absorption at $\lambda = 597$ nm with a Varian Cary 50 Bio UV–vis spectrophotometer.

To determine the flow pattern inside the reactor, the following calculation procedure was implemented [75]: where C(t) is the continuous concentration recorded at the output; E(t) is the distribution of these times and is given by Eq. (1).

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \tag{1}$$

Eq. (2) represents the mean residence time, which indicates the average time the molecules remained in the system.

$$\tau = \int_0^\infty tE(t)dt \tag{2}$$

The dimensionless time, θ, which corresponds to the time in relation to the mean residence time of the fluid in the reactor, and the