



Treatment of actual effluents produced in the manufacturing of atrazine by a photo-electrolytic process



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HIGHLIGHTS

- Photo-assisted electrochemical treatment for a real industrial effluent.
- Direct electrochemical process occurs on turbulent flow and low current density.
- Mediated anodic oxidation occurs on laminar flow and high current densities.
- None of the organics in the industrial waste is refractory to the treatment.

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ABSTRACT

The photo-assisted electrochemical degradation of a real effluent of the atrazine manufacturing process containing atrazine, simazine, hydroxy-triazine and propazine was carried out galvanostatically using a pilot-scale tubular flow reactor prototype containing DSA[®] and Ti as cathode. The effluent was mainly characterized by a high amount of NaCl, required in the synthesis route used, and it was used as taken in the factory. The variables for process optimization were the current density (3.0, 6.0, and 9.0 mA cm⁻²) and flow rate (300 and 3,000 L h⁻¹). These later values produces laminar and turbulent flow regimes, with Reynolds numbers of 1,100 and 11,000, respectively. None of the four organics contained in the waste is refractory to the photo-electrochemical treatment and they are depleted with the photo-electrolytic technology using large current densities and appropriate electric charge passed. Both direct electrochemical process and mediated anodic oxidation occur during the treatment. First process occurs at turbulent flow condition and low current densities, while the chemical oxidation process happens at laminar flow condition and high current densities. Atrazine and propazine are efficiently removed at laminar flow conditions, with an almost total depletion for the largest current densities. On the contrary, simazine is efficiently removed in turbulent flow conditions and intermediate current density, with removals higher than 90% for 20 kWh m⁻³. These results have great significance because they demonstrate the applicability of the electrochemical technology in the treatment of real industrial wastes with a cell specially designed to attain high efficiency in the removal of pollutants.

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1. Introduction

Herbicides are chemicals used to eliminate vegetation that acts like parasites in specific plantations. They can be organic or inorganic and the choice between them is dependent of some properties such as selectivity, water solubility, chemical stability,

adsorption strength on colloids, etc. The classification of the herbicides is usually based on the chemical formulae; however, it must be stressed that any relationship between the chemical structure and the biochemical behavior is extremely difficult to understand (Audus, 1967). Among the enormous variety of herbicides, atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), a s-triazine group of herbicide, is one of the most used worldwide for the control of broadleaf weeds, being suitable for the cultivation of sugar cane, corn and sorghum. Atrazine is industrially synthesized by the nucleophilic substitution reaction of alkyl amines with

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cyanuric chloride (Mtyopo, 2004; Pathak and Dikshit, 2011). In the first step, cyanuric chloride reacts with isopropylamine to produce the 2,4-dichloro-6-isopropylamino-*s*-triazine intermediate. The second step involves the reaction between that intermediate with monoethylamine in which the second chloro atom of the triazine ring is displaced. Fig. SM-1 (in supplemental material) summarizes the steps involved in the atrazine production² for the sake of clarity.

The reaction is carried out in an organic medium in the presence of water. In order to avoid an acidification of the reaction medium, sodium hydroxide is added during the synthesis with the consequent production of a high amount of NaCl. Thus, the final industrial effluent resulting of atrazine production is a concentrated solution containing NaCl contaminated with atrazine and different reaction by-products, such as propazine, simazine, and hydroxy-triazines. The inadequate disposal of this effluent can cause serious problems to the human and aquatic lives (Hayes et al., 2011; Oturan et al., 2012). Moreover, there is the necessity to treat those pollutants due to the increasingly rigid environmental regulations (Hessel et al., 2007; Rao and Chu, 2013).

Considering all the available methods to treat effluents containing organic compounds (Martínez-Huitle and Brillas, 2009; Poyatos et al., 2010; Frangos et al., 2016), the electrochemical one, particularly the anodic oxidation, might be the option due to its high organic removal rates and easy implementation (Rodrigo et al., 2014; dos Santos et al., 2015a; dos Santos et al., 2015b). Another important requirement of this method is a high ionic conductivity, which is not a problem in effluents like those generated in the atrazine manufacturing process (Sires et al., 2014).

The most important parameter in the anodic oxidation technology is the electrode material. Among the most common studied materials, the dimensionally stable anodes (DSA[®]) have been successfully used over the years in the chlor-alkali industry³ and their applications to the degradation of organic substances have been the subject of many studies (Martínez-Huitle and Brillas, 2009; Poyatos et al., 2010; Malpass et al., 2013; Santos et al., 2016). According to the model proposed by Comninellis (1994), oxide electrodes used for combustion/electrochemical conversion of organic pollutants in aqueous solution can be classified as “active” and “non-active”. For both types of materials the mechanism occurs with the initial formation of adsorbed hydroxyl radical ($\cdot\text{OH}$), which can lead to formation of higher oxides (“active”) that will promote subsequent oxidation processes or in the case of “not active” oxide materials, the hydroxyl radical interacts directly with organic species leading to complete combustion. Malpass and Motheo (2008) considering the mechanism proposed by Comninellis observed that in the oxidation process the characteristics and concentration of the organic species are as important as the nature of the electrode material.

Besides this classification considering the electrode material, the anodic oxidation processes can be classified as direct or indirect (Panizza and Cerisola, 2009). In the direct processes, the organic species undergo an adsorption process for charge transfer to occur and in the indirect processes, oxidizing species are generated on the electrode surface which diffuses away from it to interact with organic species in the solution bulk (Hermes and Knupp, 2015). In the last case the oxidizing species formed depend on the nature of the ions present in solution which may, for example, generate active chlorine (Cl_2 , HClO and ClO^-) when the solution contains chloride ions. Furthermore, the efficiency of oxide electrodes, particularly DSA[®], for an oxidation process can be increased by irradiating their surface with ultraviolet radiation (Catanho et al., 2006; Tauchert et al., 2006; Malpass et al., 2007a, 2009, 2010a; Li et al., 2011; Sathishkumar et al., 2014; Hermes and Knupp, 2015).

The effect of different supporting electrolytes in the

electrochemical oxidation of atrazine was studied using a commercial DSA[®](Ti/Ru_{0.3}Ti_{0.7}O₂) (Malpass et al., 2006). The authors reported that the removal of atrazine and total organic carbon (TOC) was only achieved at appreciable rates in NaCl medium and that the TOC removal was dependent on the NaCl concentration in solution. In addition, the photo-assisted electrochemical degradation of atrazine was also studied with substantial reduction of the energy required when photochemical and electrochemical techniques were applied simultaneously (Malpass et al., 2007a). The electrochemical and photo-assisted electrochemical degradation of atrazine were also studied by using SnO₂-containing DSA[®] with different nominal composition (Malpass et al., 2010b). The authors reported that the photo-assisted degradation led to almost complete removal of atrazine in 1 h of electrolysis while the degradation efficiency did not appear to be affected by the content of SnO₂. On the other hand, complete COD removal was dependent on the electrode composition.

A possible drawback during the anodic oxidation of organics in chloride containing media is the formation of organochlorine species. These species are organic compounds containing chloro atoms covalently bonded to their structures in which some of them present significant toxicity to living organisms. Concerning to this subject, Malpass et al. (2012) reported a toxicity decrease during photo-electrochemical degradation of atrazine in chloride containing medium using an aquatic crustacean known as *Artemia-nauplii*. As expected, it was observed that the solution toxicity increased during the anodic oxidation treatment in the presence of NaCl; however, when the photo-assisted electrochemical method was used, the toxicity decreased.

Thus, the aim of the present study is to evaluate the application of a photo-assisted electrochemical method at a pilot scale prototype to treat a real industrial effluent originated from atrazine production. The complexity of the effluent and the large size of the electrochemical cell are two of the main points of this work, which tries to determine if the electrochemical technology can be applied in real environmental remediation cases.

2. Materials and methods

2.1. Chemicals

All chemicals, including atrazine (Chem Service 98.9%), Na₂S₂O₃ (a.r., Vetec), NaCl (a.r., Synth), K₂Cr₂O₇ (a.r., Synth), AgNO₃ (a.r., Merck), NaOH (a.r., Qhemis), acetonitrile (HPLC grade, JT Baker, Mexico), and methanol (HPLC grade, JT Baker, Mexico) were used as received. Double deionised water (Millipore Milli-Q system, resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$ at 25 °C) was used in dilutions, preparation of standard solutions and cleaning of chromatographic columns.

2.2. Atrazine effluent

The real effluent containing atrazine was supplied by NORTOX S/A, Brazil. The approximate concentration of that compound in the effluent was 30 mg L⁻¹. Other substances may also be present, such as simazine and propazine, both at a concentration of 5 mg L⁻¹ and hydroxy-triazine. The physicochemical characteristics of the as received effluent can be seen in Table SM-1 of the supplementary material section. One important characteristic was the large amount of chloride ions contained, which is a consequence of the synthetic route used to produce atrazine. This concentration was determined by titration after appropriate dilution, according to the argentometric method described in the literature (Eaton et al., 1995). Thus, all the experiments were carried out with the effluent in the condition of as received.

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