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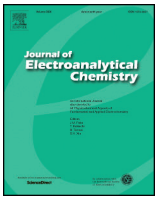

Electrochemical oxidation of phenolic wastewaters using a batch-stirred reactor with NaCl electrolyte and Ti/RuO_2 anodes

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ABSTRACT

An electrochemical oxidation (EO) process with Ti/RuO_2 anodes was applied to treat phenolic wastewaters. In order to optimise the system, different operating conditions were tested. The nature of the electrolyte and the applied current density greatly affected the process, while the concentration of the electrolyte as well as the initial pH had a sparingly impact. The optimum operating conditions attained, 10 g L^{-1} of NaCl, 119 mA cm^{-2} and initial pH 3.4, allowed the complete removal of the total phenolic content (TPh) and chemical oxygen demand (COD) when applied to a simulated phenolic mixture. SEM analysis revealed no morphological differences on the surface of the anode before and after it being used in EO. Neuronal studies were performed to verify the impact of the synthetic phenolic effluent, before and after the EO treatment, in the formation of neuronal reactive oxygen species (ROS). The treated effluent had a milder effect, compared to the raw one, but neuronal activity became enhanced after its removal. Regarding the depuration of an undiluted real olive mill wastewater (OMW) under the optimised parameters, the treatment achieved 100% of TPh removal and 17.2% of COD removal. Thus, the EO can be considered a satisfactory pre-treatment process to real wastewaters, since all phenolic content can be removed in 180 min.

1. Introduction

Water pollution and its scarcity affect millions of people, threatening the existence of humankind and constitute one of the most important environmental issues of the century. Hazardous and persistent contaminants are dangerous compounds, which appear in wastewater streams coming from industrial and agricultural activities [1–4]. The seasonally produced olive mill wastewaters (OMW) present high pollutants load and are toxic to the environment. These characteristics are mainly due to the presence of phenolic acids and polyphenols substances, which are biorecalcitrant compounds not able to be removed by biological treatment [5]. High levels of phenolic acids, that are also important antioxidants, may interfere with health. Therefore, finding a safe solution for the management of OMW, so that they do not affect human health, becomes imperative.

Advanced oxidation processes (AOPs) have been successfully applied to reduce the organic load and toxicity present in wastewaters, since they are based on the generation of powerful oxidising species (hydroxyl radicals, •OH) in solution, which are able to destroy organics up to their mineralisation. Electrochemical oxidation (EO) appears as an environmental friendly method, being easy to operate and control. This technology can achieve high efficiencies through two different mechanisms: direct and indirect anodic oxidation. In the former, pollutants are oxidised by direct charge transfer. On the other hand, in indirect oxidation, a strong oxidant can be electrochemically generated at the anode that will degrade contaminants in the bulk solution. As an example, there is the generation of hydroxyl radicals M(•OH) produced by the decomposition of water molecules on the surface of the anode (M) (Eq. (1)) [6,7].

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

In addition, NaCl is a common mediator added to the system, allowing the production of active chlorine species. The oxidation of the chloride (Cl^-) ion on the surface of the anode leads to the generation of chlorine (Cl_2) (Eq. (2)), which is further hydrolysed being disproportionated to HClO (hypochlorous acid) and Cl^- (Eq. (3)). In the bulk solution, the HClO is in equilibrium with OCl^- with pKa =

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7.55 (Eq. (4)) [8–10].

$$2\ Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{2}$$

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^- + H^+ \tag{3}$$

$$HClO \rightleftarrows H^+ + OCl^- \tag{4}$$

Moreover, it should be taken into account that during the treatment process, both oxidation mechanisms, direct and indirect, may coexist [9].

Electrochemical oxidation has already been applied to the depuration of phenolic acids and OMW, through the employment of different anode materials. In general, the anodic materials with high O_2 overpotential are preferentially selected for the EO treatment. An example is the boron-doped diamond (BDD) anode [11–14], since it generates greater amounts of reactive M(•OH) than other materials such as Pt and PbO_2. Nevertheless, the application of BDD for wastewaters depuration is limited by its high acquisition cost. Therefore, the study of other anode materials has been accomplished in order to identify more affordable electrodes as suitable alternatives to reduce initial investment and operational costs. This is the case of the dimensional stable anodes (DSA) [15–26], which have a strong interaction between their surface (M) and •OH radicals allowing the formation of superoxide MO (an oxide with higher oxidation state) according to Eq. (5). This situation occurs when higher oxidation sates are available for a metal oxide anode, above the standard potential of oxygen evolution ($E^0 = 1.23$ V vs. SHE). The redox couple MO/M acts as mediator in the selective oxidation of the organic compounds (R) (Eq. (6)), which directly competes with the side reaction of O_2 evolution that results from the chemical decomposition of the higher oxide (Eq. (7)) [2].

$$M(^{\bullet}OH) \rightarrow MO + H^+ + e^- \tag{5}$$

$$MO + R \rightarrow M + RO \tag{6}$$

$$MO \rightarrow M + \frac{1}{2} O_2 \tag{7}$$

DSA are titanium anodes coated with mixed metal oxide compositions comprising different elements such as iridium, ruthenium, platinum, rhodium or tantalum [27]. Different oxides such as IrO_2, RuO_2, SnO_2 have already been applied to the treatment of model aqueous solutions containing phenolic compounds typically found in OMW [15, 28–32]. Only few studies have described the use of titanium based-alloys (Ti/RuO_2, Ti/IrO_2, Ti/TiRuO_2, Ti/Pt, and Ti/Ta/Pt/Ir) to treat real OMW [19–26,33–35]. According to Chatzisymeon et al. [25] and Papastefanakis et al. [26], the Ti/IrO_2 and Ti/RuO_2 anodes exhibit good activity to the depuration of this kind of wastewaters. Although, these effluents have a complex composition, which may compromise the activity and stability of the electrodes, a significant reduction of total organic pollution (chemical oxygen demand, COD = 5–71% and total organic carbon, TOC = 20–67%) and an interesting removal of colour (50–100%), phenolic content (75–96%) and ecotoxicity may be attained.

This work addresses the use of an EO process to remove a mixture of six phenolic compounds typically found in OMW by using Ti/RuO_2 anodes. These anodes have already demonstrated high electrocatalytic activity for Cl_2 evolution, being generally used in the chlor-alkali process [36]. Therefore, in this study, their performance was tested by evaluating the effect of different operating conditions such as the nature and concentration of the electrolyte, the applied current density and the initial pH, with the aim to attain an efficient and cost-effective treatment. In addition, changes in anode surface morphology were assessed through SEM analysis. To the best of our knowledge, it is the first time that a set of studies, performed in mammalian brain slices, addressed the influence of the raw and treated synthetic effluents in neuronal activity. Moreover, the best operating conditions were applied to a real undiluted OMW in order to verify the possibility of application of the mentioned technology.

2. Experimental

2.1. Synthetic and real effluents

Six phenolic acids, commonly found in OMW, were selected to prepare a simulated phenolic mixture [37] with a concentration of 100 mg L^{-1} of each acid: 3,4,5-trimethoxybenzoic (Alfa Aescar, 99%), 4-hydroxybenzoic (99%, Alfa Aescar), gallic (98%, Fluka), protocatechuic (97%, Sigma), trans-cinnamic (99%, Sigma) and veratric (99%, Acros Organics). No further purification was applied to them before use. A real wastewater was collected from a mill located in the Extremadura region of Spain and the experiments were performed with the filtered effluent. The filtration step was necessary in order to avoid electrode plugging during electrolysis [31]. The main features of the synthetic and real wastewater are displayed in Table 1. Both effluents have an acidic character, high phenolic content and organic matter load (chemical oxygen demand – COD). According to the Portuguese Decree-Law 236/98 of 1st August, an effluent can be directly discharged into an aquatic medium if COD value is lower than 150 mgO_2 L^{-1}.

2.2. Electrochemical oxidation procedure

The oxidation process was performed in a Perspex batch-stirred reactor at atmospheric pressure [38,39]. Ti/RuO_2 material, commercially obtained, was used as anode and stainless steel (SS) as cathode, each with an effective area of 21.1 cm^2. The electrodes were parallel to each other, with a distance of 10 mm, linked to a DC power supply HY3010 Kaise ($I = 1.2$–2.5 A). In each experiment, the reactor was filled with 1 L of synthetic effluent or with real effluent, and samples were periodically withdrawn and centrifuged at 3500 rpm (Nahita 2655) for further analysis. The conductivity of the electrolyte was measured using a Consort C863 unit and different concentrations of NaCl (1.8–20 g L^{-1}) or Na_2SO_4 (4–20 g L^{-1}) salts were added to the synthetic effluent to promote higher conductivity to the solution (above 2.5 mS cm^{-1}). In the experiment with the real effluent, 5 g L^{-1} of NaCl were introduced in the system, to work with the same conductivity as the one leading to the best degradation conditions for the synthetic effluent. The initial pH of the medium was varied between 3 and 9, using NaOH at 3 M or H_2SO_4 at 2 M whenever necessary. This parameter was followed using an HANNA pH meter but not adjusted during the treatment time.

Some experiments were randomly run in duplicate to ensure the reproducibility of the results.

2.3. Analytical techniques

Samples were analysed for total phenolic content (TPh) using the colourimetric Folin Ciocalteau method. This technique consists in the introduction of 20 μL of sample, 1.58 mL of distilled water and 100 μL of the Folin-Ciocalteu reagent in a 2 mL cuvette. After 3–6 min, 300 μL of a saturated sodium carbonate solution were added and the cuvettes were left in the dark for 120 min. The absorbance was determined with a T60 PG Instruments spectrophotometer, at 765 nm, against a blank containing 20 μL of distilled water instead of the sample. TPh

Table 1
Main characteristics of the synthetic and real effluents.

Characteristics	Synthetic effluent	Real effluent [37]
pH	3.4 ± 0.3	3.3 ± 0.4
Conductivity (mS cm^{-1})	0.14 ± 0.01	5.94 ± 0.03
TPh (mgGA L^{-1})	323 ± 7	740 ± 9
COD (mgO_2 L^{-1})	1118 ± 41	22,650 ± 1302