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# Chemical composition and direct electrochemical oxidation of table olive processing wastewater using high oxidation power anodes

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## HIGHLIGHTS

- Table olive processing wastewater (TOW) is a notoriously polluting.
- Hydroxytyrosol is the most abundant phenolic compound identified by LC/MS in TOW.
- Remediation of TOW by electrochemical oxidation is performed.

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## ABSTRACT

Table olive processing wastewater (TOW) is a notoriously polluting due to its high organic and phenol content. To reduce them, an electrochemical process has been studied for the treatment of this effluent. Experiments were performed with a cell equipped with lead dioxide ($PbO_2$) or boron-doped diamond (BDD) as anode and platinum as cathode, where Table Olive Wastewater (TOW) were destroyed by hydroxyl radicals formed at the anode surface from water oxidation. The comparative study of both systems shows the performance of the BDD anode compared to $PbO_2$, explained by the large amounts of hydroxyl radicals generated effective at BDD anode and its synthesis characteristics.

Using LC/MS analysis, it was possible to determine hydroxytyrosol, as major phenolic compounds, in table olive processing wastewater and its concentration reach 890 mg $L^{-1}$. A possible reaction mechanism oxidation for hydroxytyrosol was proposed. The kinetics decays for hydroxytyrosol degradation on $PbO_2$ anode follows a pseudo-first order reaction with a rate constant 0.9 $h^{-1}$ for $j_{app}$ value 20 mA $cm^{-2}$.

## 1. Introduction

Olive oil and table olive production are highly important for the economies of the Mediterranean countries, constituting one of the major agro-industrial activities for countries as diverse as Italy, Spain, Greece, Turkey and Tunisia. Both agro-industrial activities result in effluents that are characterized by high organic content (Piperidou et al., 2000; Beltran-Heredia et al., 2000), seasonal generation and the presence of classes of pollutants such as polyphenols (Kyriacou et al., 2005; Aggelis et al., 2001). Actually, the manufacturing process of table olives occurs a series of steps include initial olive cleaning using pure water, debittering using sodium hydroxide, washing and fermentation using sodium chloride aqueous solutions for finishing products. For that reason, this process produced large quantities of wastewater through different stages (Lefebvre and Moletta, 2006). The Table Olive Wastewater (TOW) constitute the most heavily polluted fraction of the table olive processing, since they consist of high phenolic compounds (Marsilio et al., 2001; Bouaziz et al., 2008), sugars, acids, tannins, pectins, carotenoids, oil residues and trace amounts of various metals. In fact, wastewaters generated by olive production process, show antimicrobial, exotoxic and phytotoxic properties (Parinos et al., 2007; Chatzisymeon et al., 2008) and resisting biological degradation mainly due to their high polyphenol (Marsilio et al., 2001; Bouaziz et al., 2008) and organic content (Beltran-Heredia et al., 2000; Piperidou et al., 2000).

Currently, in Mediterranean countries, this type of wastewater is disposed of untreated to the environment, in rivers, streams and

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the sea. In the best cases, it is stored in evaporation ponds, where anaerobic conditions are quickly established leading to unpleasant odor, breading of insects and risks of surface and groundwater contamination. Consequently, TOW constitutes a serious source of environment pollution (Beltran-Heredia et al., 2000) and the treatment of this wastewater makes them into an important environmental concern. In this context, several techniques have been adopted for the treatment of TOW with special characteristics (alkaline pH and higher phenol content). These techniques are mainly based on biological degradation (Beltran et al., 2008), photo-catalytic treatment (Chatzisymeon et al., 2008), wet air oxidation (Katsoni et al., 2008, ozonation (Beltran et al., 1999), chemical oxidation with Fenton's reagent (Kotsou et al., 2004), electro-coagulation (García-García et al., 2011), ultra-filtration (El-Abbassi et al., 2014) or combined biological and chemical treatments (Benitez et al., 2001; Rivas et al., 2001), with varying degree of success. These methods are limited in terms of economic feasibility and efficiency. Over the past several years, there has been an increasing interest in the application of electrochemical oxidation processes for treatment toxic effluents due to their unique ability to oxidize or reduce contaminants in the water near the well-controlled electrode (Sirés et al., 2014; Martínez-Huitle et al., 2015). These methods are based on the formation of highly reactive chemical entities •OH, which will break down organic molecules “biologically recalcitrant” in biodegradable molecules or inorganic compounds such as $CO_2$ and $H_2O$. In addition, it has been reported that the electrochemical oxidation processes effectiveness for removing organic pollutants depends on the different operating conditions such as water hardness (presence of $Mg^{2+}$ and $Ca^{2+}$ ions) (Azerrad et al., 2016; Dos Santos et al., 2016) and high content of $PO_4^{3-}$ $SO_4^{2-}$ and $Cl^-$ ions (Antonin et al., 2015; Azerrad et al., 2016).

Among these electrochemical oxidation processes, anodic oxidation (AO) method has been successfully applied to produce directly hydroxyl radicals in order to destroy organic pollutants (Wu et al., 2012). This method has proven its efficiency in the treatment of aqueous solutions loaded with toxic organic matter, since it uses electron as reagent and is environmentally clean. In this method, a current density ($j$) is usually applied to the anode surface M in order to produce hydroxyl radical M(•OH) as intermediate of water discharge by reaction (1) (Hamza et al., 2009; Samet et al., 2010; Dridi Gargouri et al., 2013):

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

The application of AO to wastewater remediation needed the use of special electrodes with high overvoltage for oxygen evolution like $SnO_2$ (Panizza and Cerisola, 2009), lead dioxide $PbO_2$ (Hamza et al., 2011; Dridi Gargouri et al., 2013) and Boron-Doped Diamond BDD (Hamza et al., 2009; Samet et al., 2010). In this frame, some previous studies have reported that $PbO_2$ and BDD are able to generate highly reactive physisorbed •OH thus leading to overall combustion of organic compounds such as pesticides (Dridi Gargouri et al., 2013; Samet et al., 2010), synthetic organic dyes (Hamza et al., 2009; Brillas and Martínez-Huitle, 2015), petroleum hydrocarbons (Gargouri et al., 2014) and phenolic compounds (Kallel Trabelsi et al., 2005).

Thus, considering that BDD and $PbO_2$ electrodes have shown good electro-catalytic activity towards the electro-oxidation of organics compound, the aim of the present work is to study the decontamination of TOW by AO process. This work was also focused on the kinetics analysis and the mineralization pathway for the major compound in TOW.

## 2. Materials and methods

### 2.1. Table olive wastewater samples

The fresh washing and debittering wastewaters were obtained from the Agro-industrial Cooperation of Chaouat (Mater, North of Tunisia). Wastewater samples were obtained from processing Meski olive cultivar in November 2015. The samples studied, taken from a same tank, debittered for 6 h and washed with water for 12 h, were stored at −20° C to prevent auto-oxidation and the subsequent polymerization of phenolic compounds.

### 2.2. Chemical products

Folin–Ciocalteau reagent and sodium bicarbonate were purchased from Sigma–Aldrich. Gallic acid and Rutin used as a standard to determine the total phenolic and total flavonoids contents respectively were also purchased from Sigma–Aldrich.

$Na_2SO_4$ was purchased from Chemi-Pharma and was used as a supporting electrolyte. $H_2SO_4$ and NaOH (Merck) were used for the pH adjustment.

### 2.3. Physico-chemical characterization of TOW

Electrical conductivity and pH, were determined according to standard protocols described by APHA, 1992.

Chemical oxygen demand (COD) was measured using a colorimetric method (Dridi Gargouri et al., 2013). Dry extract was determined by weight difference before and after drying the sample overnight at 105 °C, until a constant weight was obtained.

Total phenols were evaluated colorimetrically by Folin–Ciocalteau reagent as described by Gargouri et al. (2015). The total phenolic content was determined as GA equivalents (GAE) and the obtained values were expressed as mg of GAE per liter of TOW (mg of GAE $L^{-1}$).

Flavonoids Content (FC) of sample was determined using spectrophotometric method as described by Hajji et al. (2010) and Rutin was used as a standard.

CieLab coordinates (L*, a* and b*) for Color measurement, were directly read with a spectrophoto-colorimeter (Trintometre, Lovibond PFX 195 V 3.2, Amesbury, UK). In this coordinate system, the L* value is a measure of lightness, ranging from 0 (black) to 100 (white), the a* value ranges from −100 (greenness) to +100 and the b* value ranges from −100 (blueness) to +100 (yellowness).

### 2.4. RP-HPLC–QTOF-MS and MS/MS analysis

Analyses were made with an Agilent 1200 series rapid resolution (Santa Clara, CA, USA) equipped with a binary pump, an autosampler and a DAD. Separation was carried out with the analytical column core–shell Halo C18 (150 mm × 4.6 mm, 2.7 mm particle size) or Zorbax Eclipse Plus C18 (150 mm × 4.6 mm, 1.8 mm particle size). The system was coupled to a 6540 Agilent Ultra-High-Definition (UHD) Accurate-Mass Q-TOF-LC/MS (Palo Alto, CA, USA) equipped with an ESI interface. The gradient elution was conducted with two mobile phases, acidified water (0.5% acetic acid, v/v) (phase A) and acetonitrile (phase B), with a constant flow rate of 0.5 mL $min^{1}$. The gradient program was as follows: 0 min 99% A and 1% B, 5.50 min 93% A and 7% B, 11 min 86% A and 14% B, 17.5 min 76% A and 24% B, 22.50 min 60% A and 40% B, 27.50 min 0% A and 100% B, 28.5 min 0% A and 100% B, 29.5 min initial conditions, which were finally maintained for 5.50 min for column equilibration (total run 35 min). The injection volume was 8 mL and each extract was analyzed twice. The operating conditions briefly were: drying nitrogen gas temperature 325 °C with a flow of 10 L $min^{-1}$;