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# Degradation of tyrosol by a novel electro-Fenton process using pyrite as heterogeneous source of iron catalyst

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## ABSTRACT

Tyrosol (TY) is one of the most abundant phenolic components of olive oil mill wastewaters. Here, the degradation of synthetic aqueous solutions of 0.30 mM TY was studied by a novel heterogeneous electro-Fenton (EF) process, so-called EF-pyrite, in which pyrite powder was the source of  $\text{Fe}^{2+}$  catalyst instead of a soluble iron salt used in classical EF. Experiments were performed with a cell equipped with a boron-doped diamond anode and a carbon-felt cathode, where TY and its products were destroyed by hydroxyl radicals formed at the anode surface from water oxidation and in the bulk from Fenton's reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  generated at the cathode. Addition of  $1.0 \text{ g L}^{-1}$  pyrite provided an easily adjustable pH to 3.0 and an appropriate  $0.20 \text{ mM Fe}^{2+}$  to optimize the EF-pyrite treatment. The effect of current on mineralization rate, mineralization current efficiency and specific energy consumption was examined under comparable EF and EF-pyrite conditions. The performance of EF-pyrite was 8.6% superior at 50 mA due to self-regulation of soluble  $\text{Fe}^{2+}$  by pyrite. The TY decay in this process followed a pseudo-first-order kinetics. The absolute rate constant for TY hydroxylation was  $3.57 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , as determined by the competition kinetics method. Aromatic products like 3,4-dihydroxyphenylethanol, 4-hydroxyphenylacetic acid, 4-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid and catechol, as well as *o*-benzoquinone, were identified by GC-MS and reversed-phase HPLC. Short-chain aliphatic carboxylic acids like maleic, glycolic, acetic, oxalic and formic were quantified by ion-exclusion HPLC. Oxalic acid was the major and most persistent product found. Based on detected intermediates, a plausible mineralization pathway for TY by EF-pyrite was proposed.

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## 1. Introduction

Olive oil mill wastewaters (OMWWs) is thought to be one of the most polluting effluents produced by the food processing industry, being characterized by a high chemical oxygen demand (COD) (Mulinacci et al., 2001; Rodis et al., 2002). The untreated release of OMWWs to water bodies constitutes a danger for the environment because their phenolic compounds of low molecular weight are responsible for toxicity on seed germination (Aliotta et al., 2002), aquatic organisms (Fiorentino et al., 2003) and bacteria (Yesilada and Sam, 1998). Tyrosol (4-hydroxyphenylethanol, TY) is a major component of the polyphenolic fraction of OMWWs, which ranges between 0.5 and 25 g L<sup>-1</sup> (McNamara et al., 2008). Since these compounds possess interesting antioxidant properties, it has been proposed their recovering as an alternative source of biologically active polyphenols (Khoufi et al., 2008). Selective phytotoxicity on tomato and vegetable marrow (Capasso et al., 1992) and toxicity to several plants and microbes (Colarieti et al., 2006) from tyrosol wastewaters have been reported.

The treatment of OMWWs is still a major industrial challenge because of their negative impact on the environment. In view of the growing stringent regulations concerning public waste disposal, there is great interest in the development of new powerful oxidation technologies for the treatment of these wastewaters. Common physical and physicochemical processes such as precipitation, coagulation-flocculation and filtration remain inefficient to solve the problem (Capasso et al., 1995; Ginos et al., 2006).

Over the last two decades, advanced oxidation processes (AOPs) based on the in situ generation of the strong oxidants such as hydroxyl radical ( $\cdot\text{OH}$ ), have become important technologies for water remediation because they are able to effectively destroy refractory pollutants, including phenolic compounds (Namkung et al., 2008; Brillas et al., 2009; Klavarioti et al., 2009; Oturan and Aaron, 2014; Sirés et al., 2014).  $\cdot\text{OH}$  has so high standard redox potential ( $E^\circ = 2.80 \text{ V/SHE}$ ) that can mineralize most organics to  $\text{CO}_2$  and inorganic ions when starting pollutant includes heteroatoms. Among the AOPs, the Fenton reagent (mixture of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  ion) has attracted great attention due to its strong oxidative capacity on organic contaminants (Kallel et al., 2009; Emami et al., 2010). Recently, an alternative electrochemical AOP (EAOP) such as electro-Fenton (EF) is being developed. This electro-oxidation process involves the continuous supply of  $\text{H}_2\text{O}_2$  to the contaminated solution from the two-electron reduction of injected  $\text{O}_2$  gas at a carbonaceous cathode, mainly carbon-felt (Drogui et al., 2001; Bellakhal et al., 2006; Balci et al., 2009; Oturan et al., 2011b) and carbon-polytetrafluoroethylene (PTFE)  $\text{O}_2$ -diffusion (Ammar et al., 2006; Ruiz et al., 2011; Garcia-Segura et al., 2012) electrodes from reaction (1):

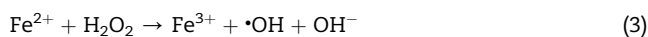


In an undivided cell and in the absence of a reducing agent,  $\text{H}_2\text{O}_2$  thus obtained is oxidized at the anode to  $\text{O}_2$  via formation of the weak oxidant hydroperoxyl radical ( $\text{HO}_2\cdot$ ) by

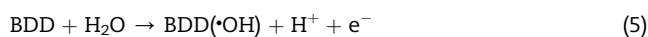
reaction (2) and then, it is accumulated in the medium until a steady concentration depending on the applied current, just when the rates of reactions (1) and (2) become equal (Brillas et al., 2009).



In acidic medium, the oxidizing power of  $\text{H}_2\text{O}_2$  is strongly enhanced by adding a small amount of  $\text{Fe}^{2+}$  ion to form  $\text{Fe}^{3+}$  ion and homogeneous  $\cdot\text{OH}$  via Fenton's reaction (3), with an optimum pH of 2.8 (Sirés et al., 2006; Panizza and Oturan, 2011; Oturan et al., 2012). An advantage of EF over the classical chemical Fenton's reagent is that Fenton's reaction (3) is electrocatalyzed because  $\text{Fe}^{2+}$  ion is rapidly regenerated from reduction of  $\text{Fe}^{3+}$  ion at the cathode by reaction (4) (Brillas et al., 2009).



When an undivided cell is utilized in EF, aromatic pollutants are removed primordially by oxidation with homogeneous  $\cdot\text{OH}$  formed from Fenton's reaction (3) and in much lesser extent with heterogeneous  $\text{M}(\cdot\text{OH})$  formed from water oxidation at the surface of a high  $\text{O}_2$ -overpotential anode M (Ammar et al., 2006; El-Ghenymy et al., 2014). In the case of a boron-doped diamond (BDD) thin-film electrode, which is the most potent anode known, this in situ electrolysis reaction can be written as follows (Marselli et al., 2003):



The generated  $\text{BDD}(\cdot\text{OH})$  is able to destroy aliphatic carboxylic acids, which are very slowly attacked by homogeneous  $\cdot\text{OH}$  (Brillas et al., 2009).

Despite its strong oxidation ability, the classical EF process has some critical limitations such as the need of operating at pH 3 for an optimal run and the loss of soluble iron catalyst as hydroxide precipitate (Sirés et al., 2014). These drawbacks can be overcome by using a Fe containing solid catalyst as source of  $\text{Fe}^{2+}$  ion instead of a soluble iron salt. Several authors have shown that classical Fenton reaction can be catalyzed by using either  $\text{Fe}_2\text{O}_3$  as heterogeneous catalyst permitting to operate at neutral pH (Costa et al., 2008; Huang et al., 2012) or zero-iron valent at pH 2–4 (Kallel et al., 2009). Expósito et al. (2007) reported the effective catalysis in the EF process to degrade aniline at pH 3.0 using mineral iron oxides like magnetite ( $\text{Fe}_3\text{O}_4$ ) and wustite ( $\text{FeO}$ ). More recently, pyrite ( $\text{FeS}_2$ ) as heterogeneous catalyst has been used to enhance the degradation of trichloroethylene, diclofenac, pyrene and toluene by Fenton's reagent (Che et al., 2011; Bae et al., 2013; Choi et al., 2014a, 2014b). The improvement of Fenton-pyrite process compared to classical Fenton was ascribed to the self-regulation of iron ions in solution by the following reactions in the presence of  $\text{O}_2$  (Arienzo, 1999; Che et al., 2011; Bae et al., 2013):

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