



# Electrochemical treatment of aqueous solutions of catechol by various electrochemical advanced oxidation processes: Effect of the process and of operating parameters

Aziza Hadj Ltaïef<sup>a</sup>, Adriana D'Angelo<sup>b</sup>, Salah Ammar<sup>a</sup>, Abdellatif Gadri<sup>a</sup>, Alessandro Galia<sup>b</sup>, Onofrio Scialdone<sup>b,\*</sup>

<sup>a</sup> *Electrochemistry, Materials and Environment - Faculty of Sciences of Gabes, Erriadh City, 6072 Gabes, Tunisia*

<sup>b</sup> *Dipartimento dell'Innovazione Industriale e Digitale, Ingegneria Chimica, Gestionale, Informatica, Meccanica, Università degli Studi di Palermo, Palermo 90128, Italy.*

## ARTICLE INFO

### Keywords:

Catechol  
Advanced oxidation process  
Electro-Fenton  
Anodic oxidation  
BDD

## ABSTRACT

Catechol, one of the most abundant compounds in olive mills wastewaters, which is generated in the Fenton degradation of various aromatic compounds, is a toxic, possible carcinogen, persistent pollutant and it is not readily biodegradable. Hence, its degradation requires the utilization of advanced oxidation processes (AOPs). Here, the electrochemical treatment of aqueous solutions of catechol was investigated. The utilization of various electrochemical processes, such as electro-Fenton (EF), direct anodic oxidation (AO), indirect oxidation by electro-generated active chlorine and coupled processes was investigated. Furthermore, the effect of various operating conditions (including the nature of anode for AO, the initial pH and the current density) was widely studied in order to optimize the selected electrochemical processes. For EF process, the effect of the nature of the catalyst (homogeneous FeSO<sub>4</sub> and heterogeneous pyrite and chalcopyrite) was also analysed. It was shown that both EF and AO, under proper operating conditions, allow a very high removal of the TOC, while the indirect oxidation by electro-generated active chlorine is poorly effective. The utilization of a coupled EF-AO process allowed enhancing the abatement of both catechol and TOC with respect to single processes.

## 1. Introduction

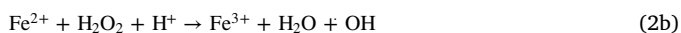
Conservation of the environment, which requires a sustainable development to avoid compromising existing natural resources, is gradually becoming a major objective. As a result, a special research area of environmental electrochemistry has been developed, which is based on the utilization of electrochemical techniques to prevent or minimize environmental pollution. Traditional physical, chemical and biological techniques are widely used for the treatment of wastewater containing biodegradable organic pollutants. They are often inadequate for treating various kinds of industrial and agricultural effluents, as they are relatively expensive, inefficient, time consuming or a secondary cause of pollution. Consequently, over the past three decades, researchers have tried to develop new and more environmentally friendly technologies for the total elimination of persistent organic pollutants from wastewater and for the quantitative and rapid mineralization of non-biodegradable organics. In this context, the use of more innovative processes such as the advanced oxidation processes (AOPs) has acquired great relevance [1]. These processes have proved to have

high efficiency with advantages such as versatility, high energy efficiency, amenability of automation, and safety because they operate at mild conditions with limited use of chemicals [2–4]. AOPs produce in situ hydroxyl radical ( $\cdot\text{OH}$ ), the strongest oxidizing agent ( $E^\circ = 2.80 \text{ V} / \text{SHE}$ ) after fluorine. These processes are especially efficient for aromatic molecules thanks to the non-selective electrophilic aromatic substitution of hydroxyl radical to aromatic moieties, leading finally to the ring opening reactions. Among them, electrochemical AOPs (EAOPs) such as anodic oxidation (AO) and electro-Fenton (EF) processes have gained much interest for the removal of organic compounds. In AO, the destruction of pollutants is mediated by hydroxyl radicals generated on the surface of the anode by the oxidation of water and its efficiency depends strongly on the anode material. In EF process, H<sub>2</sub>O<sub>2</sub>, produced at the cathode by oxygen reduction (Eq. (1)), reacts with catalytic amounts of Fe<sup>2+</sup> to generate the  $\cdot\text{OH}$  radicals in the solution (Eqs. (2a), (2b)) [5].

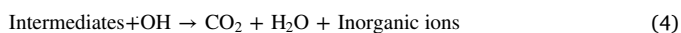
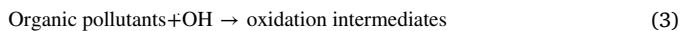


\* Corresponding author.

E-mail address: [onofrio.scialdone@unipa.it](mailto:onofrio.scialdone@unipa.it) (O. Scialdone).



These formed  $\cdot\text{OH}$  react rapidly on organics, leading to their oxidation/mineralization according to the following equations:



The advantages of this process with respect to conventional Fenton process is the continuous electro-generation of  $\text{H}_2\text{O}_2$  inside the reactor and the cathodic regeneration of  $\text{Fe}^{2+}$  from cathodic reduction of  $\text{Fe}^{3+}$ .

Catechol is one of the most plentiful compounds in olive mills wastewaters (OMW) [6]. Furthermore, it is generated in the Fenton degradation of aromatic compounds [7] and it is the first intermediate produced by the degradation of tyrosol by electro-Fenton [8] (one of the most relevant compounds in OMW). It is a toxic, persistent pollutant and it is not readily biodegradable under environmental conditions because of its aromatic structure [9]. The International Agency for Research on Cancer (IARC) has classified catechol as possibly carcinogenic to humans (Group 2B) [10]. For these reasons, several technologies have been investigated for the removal of catechol from wastewater and aqueous solutions, including biological methods [11,12], adsorption [13,14], ozonation process [15,16], advanced photo-oxidation process [17] and Fenton and photo-Fenton [9,18].

In this experimental work, an in-depth study on the electrochemical treatment of catechol is reported. The main aim of the work is to evaluate the potential utilization of various electrochemical processes (namely, AO, EF, oxidation by electro-generated active chlorine and coupled processes) for the degradation of such phenolic compound in aqueous solutions. Furthermore, the effect of various operating conditions (including the nature of anode for AO, the initial pH and the current density) was widely investigated in order to optimize the selected electrochemical processes. For EF process, the effect of the nature of the catalyst ( $\text{FeSO}_4$ , pyrite and chalcopyrite) was also analysed. At the end of this work, the two more promising processes (AO and EF) were coupled to achieve a more effective degradation of catechol.

## 2. Experimental

### 2.1. Electrolysis system

Electrolyses were performed in a cylindrical, undivided tank glass cell under vigorous stirring performed by a magnetic stirrer with 50 mL of solution. Saturated calomel electrode (SCE) was used as reference electrode and all potentials reported in this study are referred to it. Different kinds of anode and cathode were used depending on the selected process:

- (i) Direct anodic oxidation (AO): Boron-doped diamond (BDD, wet surface area  $1.53 \text{ cm}^2$ , from Condias, supported on Nb, 5000–6000 ppm boron) or  $\text{Ti}/\text{IrO}_2\text{--Ta}_2\text{O}_5$  (Dimensionally Stable Anodes, DSA, surface area  $1.21 \text{ cm}^2$ , from De Nora SpA) were used as anodes and Ni plate as counter electrode;
- (ii) Indirect anodic oxidation by electro-generated active chlorine: the above mentioned  $\text{Ti}/\text{IrO}_2\text{--Ta}_2\text{O}_5$  (from De Nora SpA) was used as working electrode and Ni plate as cathode;
- (iii) Electro-Fenton (EF) process: the working electrodes used was Carbon Felt (surface area  $1.97 \text{ cm}^2$ , from Carbone Lorraine), while the counter electrode was the above-mentioned DSA electrode.
- (iv) For EF-AO coupled process, the BDD anode and the carbon felt cathode were used.

In all experiment the distance between the two electrodes were lower than 5 mm.

### 2.2. Chemicals

Electrolyses were usually performed at room temperature with an initial catechol concentration of 0.45 mM. The Catechol ( $\text{C}_6\text{H}_6\text{O}_2$ ) used was of reagent grade, with purity > 98%, supplied by Fluka. The supporting electrolyte was in most cases composed by 0.1 M  $\text{Na}_2\text{SO}_4$  (Sigma-Aldrich), while in some experiments 0.1 M NaCl (Sigma-Aldrich) was added to the system. Sulfuric acid from Sigma-Aldrich and Sodium hydroxide from Applichem were added in solution to adjust pH to the desired value. During Electro-Fenton experiment the catalysts used were of two types: synthetic and natural. As synthetic catalyst 0.5 mM of ferrous sulphate heptahydrate, ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , in analytical grade from Fluka) was used. Pyrite ( $\text{FeS}_2$ ) and chalcopyrite ( $\text{CuFeS}_2$ ) used in this work were extracted from Jendouba (Tunisia). They were milled with a ceramic mortar and sieved (< 80  $\mu\text{m}$ ). To remove surface impurities, the resulting powder was ultrasonicated in 95% of ethanol for 5 min, washed with 1 M  $\text{HNO}_3$ , rinsed with deionized water and further with 95% of ethanol and finally dried at 30 °C. The working concentration was 1 g/L. All solutions were prepared with distilled water. The use of the two catalysts pyrite and chalcopyrite required the addition of air or  $\text{O}_2$  to facilitate the dissolution. Electro-Fenton experiments were performed with oxygen.

### 2.3. Instruments and analytical procedures

Galvanostatic mode electrolyses were performed with an AMEL 2055 potentiostat/galvanostat. The solution pH was measured with a Crison GLP 22 pH-meter. The removal of catechol was monitored from the decay of the absorbance (A) using Agilent Cary 60 UV Spectrophotometer. The concentration of catechol was determined at  $\lambda = 270 \text{ nm}$ .

The mineralization of the starting pollutant during the electrochemical processes was assessed from the decay of the total organic carbon (TOC). This parameter was analysed by a TOC analyser Shimadzu VCSN ASI TOC-5000 A. The TOC value is given in milligrams of carbon per litre (mg/L), performing the average of three consecutive measurements with a precision of about 2%. The percentage of TOC removal was then calculated from:

$$\%X(\text{TOC}) = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} * 100 \quad (5)$$

where  $\text{TOC}_t$  and  $\text{TOC}_0$  are the experimental TOC values at time  $t$  and initial time, respectively.

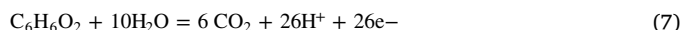
The calibration of the equipment was made using potassium hydrogen phthalate standards in the range between 0 and 50 mg/L.

The presence of carboxylic acids (oxalic, maleic, malonic and lactic acids in analytical grade from Sigma-Aldrich) was identified by Prevail Organic 5  $\mu$  column under the following conditions: the mobile phase was a buffer solution containing  $\text{KH}_2\text{PO}_4$  (Sigma Aldrich 99%) and  $\text{H}_3\text{PO}_4$  at a pH of 2.5, prepared with water Sigma Aldrich G-chromasolv for gradient elution.

The current efficiency (CE) for the removal of TOC was defined as follows:

$$CE = nFVC^0X(\text{TOC})/(It) \quad (6)$$

where  $C^0$  is the initial concentration of catechol in  $\text{mol L}^{-1}$ ,  $n$  is the number of electrons exchanged during the mineralization of catechol according to Eq. (7),  $V$  is the volume of the cathodic solution and  $F$  the Faraday constant ( $96,487 \text{ C mol}^{-1}$ ).



## 3. Results and discussion

As previous mentioned, various electrochemical processes can be potentially used for the treatment of wastewater contaminated by

Download English Version:

<https://daneshyari.com/en/article/6477034>

Download Persian Version:

<https://daneshyari.com/article/6477034>

[Daneshyari.com](https://daneshyari.com)