



Effective monitoring of the electro-Fenton degradation of phenolic derivatives by differential pulse voltammetry on multi-walled-carbon nanotubes modified screen-printed carbon electrodes



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ABSTRACT

This work illustrates a fast, sensitive and selective electroanalytical methodology for simultaneous determination of phenolic derivatives. Optimization of differential pulse voltammetry (DPV) conditions and electrochemical study by cyclic voltammetry (CV) of phenolics are included. Differential pulse voltammetry at screen-printed carbon electrodes (SPCE) was selected for the sensitive detection of *m*-Cresol and Tert-butylhydroquinone. The introduction of Multi-walled Carbon-Nanotubes with acid groups, MWCNT-COOH, as modifier on working SPCE enhances the performance of electrode surface with a highly catalytic activity on it, allowing a 5-fold higher sensitive analysis than unmodified SPCE, with a limit of detection as low as about 1 μ M. This simple and low-cost methodology has been applied, for first time, to monitoring the electro-Fenton degradation of *m*-Cresol, giving selective information of the reactant loss and products formation. Aromatic intermediates (monohydroxy, polyhydroxy and quinone phenolic derivatives) have been identified and followed during the electrolysis process. The electro-Fenton with iron on activate carbon is 4-fold faster than with other catalyst. The results are validated by chromatographic (HPLC) technique. The electroanalytical methodology described, in conjunction with the use of small SPCE as sensor transducer, can be implemented for continuous monitoring of end-point of the electro-Fenton reaction at industrial level in wastewater remediation plants, indicating the two main stages of electro-Fenton during the electrolysis.

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1. Introduction

The rapid in situ determination of phenolic pollutants and their derivatives is an important environmental challenge because of the easy penetration of such species through membranes or skins of plants, animals and humans, with toxic effects [1,2], but not all phenolics are toxic and some of them are used as additives. Fig. 1 illustrates the structure of three phenolics with different uses and properties. On one hand, thymol is one of the most important phenolic oils of thymus, an aromatic and medicinal plant with applications in pharmaceutical and food industries, which has been reported to have antibacterial, antiox-

idative, and mammalian age delaying properties [3]. On the other hand, tert-butylhydroquinone (TBHQ), is a highly effective synthetic antioxidant and, in food industry, it is used as preservative (E319) and the maximum TBHQ allowed is 0.02% of the weight of the food product, regulated by U.S. Food and Drug Administration [4] and by European Food Safety Authority [5]. In opposite way, cresols are classified by the US Environmental Protection Agency (US-EPA) as pesticide, showing chronic effects at 12 mg L⁻¹ of the quantitative structure-activity relationship [6], being the most toxic the *p*-Cresol isomer while the *m*-Cresol is the less of the three isomers.

The US-EPA [7] and the European Environmental Agency (EEA) [8] include eleven substituted phenols classified as hazardous for human health and assigns them a maximum admissible concentration range of 60–400 μ g/L in relation with their toxicity degree. Thus, such situation requires the development of economic and ecological techniques to eliminate phenolics in contaminated environment.

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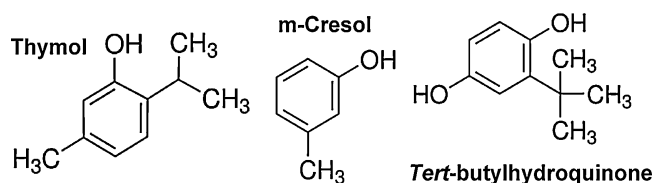


Fig. 1. Structures of phenolics used in this work (source: Sigma–Aldrich Chemicals).

In this context, removal of phenolic derivatives from industrial wastewater has generated considerable attention of society and achieving a safety level ($0.1\text{--}1.0\text{ mg L}^{-1}$) is difficult [9]. Recently, advanced oxidation processes (AOPs), which can produce oxidizing hydroxyl radicals, have proved to be an efficient procedure for the treatment of different organic pollutants such as phenolic derivatives [10,11]. Among them, electro-Fenton has received great attention for the removal of harmful organics in waters due to the advantages of this treatment such as continuous electro-generation of H_2O_2 , a short reaction time and Fe^{2+} generation by direct reduction of Fe^{3+} on the cathode [12,13]. One of the advantages of the foam materials is their high reaction surface. Based on previous paper [14], using nickel foam as cathode, the production of hydroxyl radicals is improved. Furthermore, there is not leaching of nickel ions because the regeneration of Ni^{2+} on Ni over the influence of an electric field is possible. For this reason, the electrode keeps its structure and composition along the treatment. In order to improve the efficiency of this treatment the use of heterogeneous electro-Fenton process has been postulated. Nowadays, different catalysts have been used in heterogeneous electro-Fenton reactions such as iron–alginate gel, iron–carbon, iron–zeolite, magnetite, iron–hydrogels. [15–19]. By use of heterogeneous catalysis the reuse of iron and the operation in continuous mode are possible [15,20].

A number of methods have been developed to monitor electro-Fenton degradation, where GC–MS [21,22], UV–vis spectroscopy [19], HPLC and IC [23,24] are the most common techniques to follow the evolution of electrolysis; however, little attention has been paid to the use of electroanalytical techniques [25,26] and to our knowledge no references were found to monitor degradation of cresols.

The electroanalytical techniques, in particular Cyclic (CV) and Differential Pulse Voltammetry (DPV), are good tools for the study of electrochemical mechanisms and for the sensitive detection and quantification of pollutants [27], respectively, being possible to reach detection limits as low as ppt level [28] and to apply directly to opaque media giving information of reactant and products. The selectivity shown by the DPV technique is the other advantage. Furthermore, voltammograms can reflect all oxidation/reduction steps of electroactive compounds and valuable information not only on the parent substrate but also on the electrochemically-generated species that can concurrently be obtained [29–31].

In this work, the electrocatalytic behavior of MWCNT–SPCE towards the oxidation of phenolic derivatives (TBHQ, thymol and *m*-Cresol) is described. In addition, the electrochemical mechanism in the electrooxidation of phenolics for their detection is investigated using CV and DPV. The applications of the modified SPCE with MWCNT as the catalytic sensor in the voltammetric detection of *m*-Cresol, and for the selective detection of *m*-Cresol in presence of TBHQ additive were also investigated. Finally, this optimized methodology was applied to monitor the electro-Fenton degradation of *m*-Cresol. Thus, the rate constant determination can be obtained electrochemically by monitoring directly *m*-Cresol loss and, simultaneously, by monitoring the product generation. Then, the electrochemical measurements have been proved to be a powerful tool to study the mechanism of this type of reaction since

they allow the determination of rate constants and, depending on the nature of the phenolic derivative, the estimation of product yields, as has been carried out in this study. Furthermore, reliable information about the incorporation of this methodology to monitor the electro-Fenton has been collected. The use of screening technique for fast identification of the two main stages during electrolysis: aromatic intermediate and carboxylic acids production, which could be useful for researchers working in this field, is extensively discussed.

2. Material and methods

2.1. Reactants

Reagents were of maximum purity available and were used without further purification. *m*-Cresol, thymol and tert-butylhydroquinone (TBHQ) were purchased from Aldrich. The chemicals used in the preparation of the universal phosphate buffer solution, PBS, were purchased from Fluka. All solutions were prepared by using Milli-Q grade water. The phenolic stock solutions (stored in amber Eppendorf tubes at -20°C) were diluted to the required concentration by the electrolyte (0.1 M of PBS at pH 2 or electro-Fenton electrolyte, typically 0.01 M $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$ at pH 2). All reagents used in the electro-Fenton assays were provided by Sigma–Aldrich.

2.2. Voltammetric analysis

Cyclic and Differential Pulse Voltammetric measurements were obtained with a potentiostat/galvanostat AUTOLAB PGSTAT10 connected to the SPCE, through a connector DropSens DSC, where the electrochemical cell is placed, in conjunction with the three electrode systems described below. The system was controlled by General Purpose Electrochemical experiments software 4.9 (GPES 4.9). The cell configuration consists of working electrode: carbon (DRP-C110) and MWCNT-COOH as modifier on carbon (DRP-C110CNT) from DropSens Company (Spain), with a 4 mm diameter; a pseudo-reference electrode of silver, and a carbon counter electrode. The volume dispense on is $50\ \mu\text{L}$, enough amount to cover the three electrodes system. All potentials given hereafter will be relative to above mentioned Ag pseudo-reference electrode. The voltammetric measurements were carried out under room temperature.

The CVs were usually recorded in the potential range from -0.5 to $+1.3$ V, that is, $\Delta U = 1.8$ V, with a scan rate of $50\ \text{mV s}^{-1}$ and a step potential of 5 mV, unless otherwise indicated. When using DPV, the conditions were as follows: step potential of 5 mV; pulse amplitude, ΔE , of 50 mV, modulation time of 0.05 s, interval time of 0.5 s; and scan rate of $9.9\ \text{mV s}^{-1}$. The potential was scanned, usually from -0.3 to $+1.5$ V. The residual current measurements were carried out in a quiescent solution of electrolyte in presence of oxygen. A “cleaning” step was required between successive runs and previously to any measurement. For that, 5 cycles by CV in the potential range from -1.0 to $+1.5$ V at $50\ \text{mV s}^{-1}$ in 0.1 M H_2SO_4 solution was applied.

2.3. Electro Fenton remediation

The heterogeneous electro-Fenton degradation of *m*-Cresol was carried out in a cylindrical glass reactor with a working volume of 0.15 L at room temperature. The electric field was applied by a 1.6 mm thick nickel foam cathode (Goodfellow Cambridge Ltd, United Kingdom) and a BDD anode (DIACHEM®, Germany). The electrodes (surface $11\ \text{cm}^2$) were placed opposite to each other at 1 cm above the bottom of the cell and with an electrode gap of

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