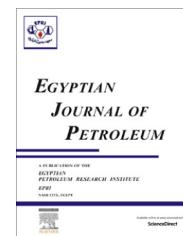




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FULL LENGTH ARTICLE

Electrochemical oxidation behavior of some hazardous phenolic compounds in acidic solution

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Abstract The electrochemical oxidation of phenol, resorcinol and pyrogallol was investigated in sulfuric acid solution. Cyclic voltammetry and electrochemical impedance spectroscopy, EIS, were used. The mechanism of the electrochemical oxidation process was proposed and discussed. The process includes a selective oxidation and PtO_x formation. EIS measurements were carried out to further examine the reaction kinetics involved in the phenolic compounds electro-oxidation. The EIS responses were found to be strongly dependent on electrode potentials. The result showed the presence of an oxidation peak in the region around 1 V vs SCE to all conditions evaluated. In cyclic voltammetric experiments a gradual decrease of the oxidation peak with the number of cycles was observed. This suggests the deactivation or blockage of the electrode surface by the adsorption of substances and/or phenoxy radical polymerization.

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1. Introduction

The electrochemical oxidation of hazardous organic species is a promising method for wastewater remediation. Phenols are a large group of pollutants in industrial effluents and, due to their low degradability by conventional effluent treatment, even at low concentrations they present toxicity and bioaccumulation problems [1]. Phenolic compounds are present in effluents from coke production, food industries, chemical industries, such as those associated to the production of resins

and pesticides, and petroleum refineries [2]. Many different technologies are in use or have been proposed for the recovery or destruction of phenols [3,4]. Among these technologies, there are processes dealing with collapse of micro bubbles [5], anodic polymerization [6–8], oxidation by photocatalysis or by hydrogen peroxide [9–12], as well as electrooxidation with various electrode materials [13–16].

The electrochemical oxidation of organic substances is a promising technique for the treatment of industrial effluents and the electrooxidation of phenol has been evaluated by different authors [17–21]. Comminellis and Pulgarin [17] studied the anodic oxidation of phenol on platinum and concluded that the most important parameters for this study are the phenol concentration and pH. They have not reported any blocking effect on the electrode surface. Arslan et al. [18] studied, besides the effect of temperature and pH, the influence of the phenol concentration in the process of phenol electrooxidation

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on platinum. They found a dependence of the peak potential on concentration and on temperature, and this dependence was more pronounced for the highest values of concentration and temperature studied. The authors reported the blocking of the electrode surface for high concentrations of phenol in alkaline medium and a phenol polymerization on the electrode surface explained this process. Kennedy et al. [20] investigated the oxidation and polymerization of aminophenolic compounds in neutral solutions and they proposed a mechanism of substitution reaction, followed by oxidation and polymerization. Pacheco et al. [21] evaluated the degradation of phenol, catechol and cresol on boron doped diamond electrodes and concluded that the degradation process increases with increasing current densities. The effect of the solute concentration was also investigated; the results have shown that under conditions of diffusive control the degradation is independent of the concentration. Li et al. [19] investigated the electrochemical degradation of phenol on platinum electrodes in comparison with oxide electrodes, obtaining similar results for platinum and Ti/RuO₂ electrodes.

Although different works are associated to the electrooxidation of phenols, the study of this process is still a matter of research, since this technique is able to achieve good destruction rates. The electrooxidation of phenol occurs through the formation of the phenoxy radical, which either reacts with other species present in the solution generating products, or reacts with other phenol molecules producing a dimeric radical. This radical can be oxidized following two different paths: the formation of polymers or quinones, depending on the conditions used. For high phenol concentrations and basic medium, polymerization is favored, while for low phenol concentrations and acid medium the formation of quinones is privileged [22]. From the oxidation reaction of quinone, carboxylic acids are obtained. These products are difficult to oxidize, but are biodegradable compounds, and therefore the electrooxidation process can be associated to a biological process [23,24]. Electropolymerization of phenol beings with the formation of the phenoxy radical, or it can react with a molecule of phenol to give predominantly a para-linked dimeric radical. This radical may be further oxidized to form a neutral dimer or it may attach another molecule. The dimer may be further oxidized create oligomers to polymers. Formation of the insoluble polyphenol results in deactivation of electrode surface. The relative rates of the two pathways (polymerization and forming quinonic structure) depend on the phenols concentration, the nature of electrode, pH, solvent, additives, electrode potential and current density [25]. Electropolymerization of phenols occur on different electrodes, such as Fe, Cu, Ni, Ti, Au, Pt and other type of electrodes [26]. Deactivation of electrode due to the phenol polymerization is more characteristic in alkaline medium. Insoluble high molecular weight species blocks the electrode surface and prevents effective electrooxidation of phenol.

It is well known that cyclic voltammetry is one of the primary research means for the oxidation of organisms in electrochemical oxidation. Iotov and Kalcheva adopted cyclic voltammetry technology exclusively to study the oxidation of phenol at a platinum/gold electrode in an acid medium [27]. The electrode behavior of aniline at several conditions was investigated on a platinum, glassy carbon, and carbon fiber electrode using voltammetry techniques [28]. Kuramitz et al.

investigated the electrochemical behavior of p-nonylphenol by voltammetric techniques [29].

This work is aimed to study the electrochemical oxidation behavior of phenol, resorcinol and pyrogallol at platinum electrode in of 0.5 M H₂SO₄ solution.

2. Experimental details

Phenol, resorcinol and pyrogallol were obtained from Sigma and were used without further purification. The chemical structure of the different compounds is shown in Fig. 1. Deionized water was used for the preparation of the different solutions. Stock solutions of the different investigated materials were prepared by dissolving an appropriate amount in deionized water. Temperatures were kept constant by water circulation trough the double wall of the cell. The electrochemical cell was a three-electrode all-glass cell, the counter and working electrodes were platinum and the reference electrode was saturated calomel electrode (SCE), whose all potentials were referred. The electrolyte solutions were 0.5 M H₂SO₄ containing different concentration of phenols (0, 1, 5, 10, 15 and 20 mM). The cyclic voltammograms experiments and electrochemical impedance spectroscopic investigations were performed using a Voltalab PGZ 100 "All-in-one" Potentiostat/Galvanostat. The cyclic voltammetry measurements were carried out using a different potential scan rate (10, 25, 50, 75, 100, 150 and 200 mV/s). The total impedance, Z, and phase shift, θ , were measured in the frequency range from 0.1 to 10⁵ Hz. The superimposed ac-signal amplitude was 10 mV peak to peak.

3. Results and discussion

3.1. Cyclic polarization measurements

Typical examples of cyclic voltammograms recorded for clean bright platinum sheet in 0.5 M H₂SO₄ solution in absence and presence 10 mM of phenol, resorcinol and pyrogallol are shown in Fig. 2. In 0.5 M H₂SO₄ solution, monolayer oxide formation occurred in the region above 0.60 V on the anodic swept and the reduction of oxide gives cathodic peak at about 0.47 V on the reverse scan. When phenolic compounds are added to 0.5 M H₂SO₄ solution, phenol and resorcinol oxidation displays one oxidation peak at potential range of 0.7–1.2 V, while pyrogallol displays two oxidation peaks at potential range of 0.4–0.55 V (Peak A1) and of 0.7–1.1 V (Peak A2).

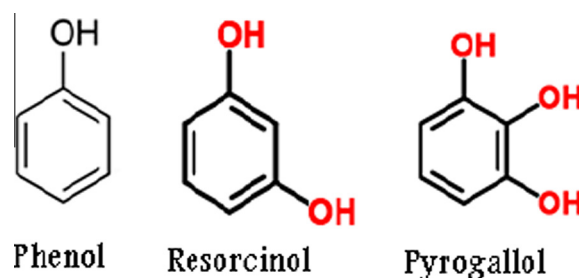


Figure 1 Structure of phenolic compounds.

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