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Examination of benzoquinone electrooxidation pathway as crucial step of phenol degradation process

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ABSTRACT

The electrochemical oxidation of benzoquinone on expanded graphite (EG) electrode was conducted. Electrochemical process was realized by cyclic voltammetry technique in alkaline solution. The main part of this work was devoted to examination of benzoquinone oxidation proceeding through the opening of aromatic ring accompanied by the formation of carboxylic acids. Water samples containing benzoquinone and short chain mono- and dicarboxylic acids were analyzed qualitatively and quantitatively with high performance liquid chromatography (HPLC). The validation of chromatographic method was determined for benzoquinone, oxalic acid, malonic acid, acetic acid, maleic acid, succinic acid and fumaric acid.

1. Introduction

Phenol is widely used in many industries, for example, chemical, petrochemical or pharmaceutical industry. Wastewaters from these industries often contain phenolic compounds and in this way the hazardous waste might be transported to the environment. Protection of water, air and soil against the penetration of this type of contaminants as well as the development of the appropriate degradation methods is of crucial importance. The most popular method of phenol degradation is its oxidation. Much effort is made to find out new materials and methods enabling multiple use of material in phenol oxidation.

Phenol oxidation can be carried out in different ways: catalytic oxidation, electrochemical oxidation, photodegradation or sonoelectrochemical procedures [1–10]. Low costs, high effectiveness and controlling of the regarded process make the electrochemical elimination of phenol from water especially worthy of interest. Among the materials commonly used for electrooxidation of phenol are metallic (e.g. Pt and Au), oxide (IrO_2 and PbO_2) and carbon (diamond, glassy carbon, expanded graphite) electrodes [11–15].

Expanded graphite (EG) being the products of the process of exfoliation of graphite intercalation compounds (GICs) exhibit interesting physicochemical features, such as enhanced adsorption capacity, developed surface area which allow their practical application in electrochemical processes both as an electrode material and as a catalyst [14,16].

Depending on the applied conditions, process of phenol electrooxidation proceeds through the formation of several intermediate products of different properties. It is important to determine all oxidation by-products because it allows describing the phenol oxidation pathway. The organic by-products can be divided into two main groups: sparingly water soluble and good water-soluble compounds. There are quinones in first group and carboxylic acids in the second one. Different mono- and dicarboxylic acids can be found between the oxidation products [17,18]. For analysis of these acids liquid chromatography is very useful [19–23]. Six of the dicarboxylic acids were chosen for the investigation in this work: oxalic acid, malonic acid, acetic acid, maleic acid, succinic acid and fumaric acid.

Generally, the pathway of complete phenol oxidation consists of four main steps (Fig. 1):

1. oxidation of phenol to hydroquinone and benzoquinone;
2. opening of aromatic ring to carboxylic acids;
3. degradation of carboxylic acids;
4. complete mineralization to CO_2 and H_2O.

According to some researchers, the oxidation of benzoquinone followed by the opening of aromatic ring accompanied

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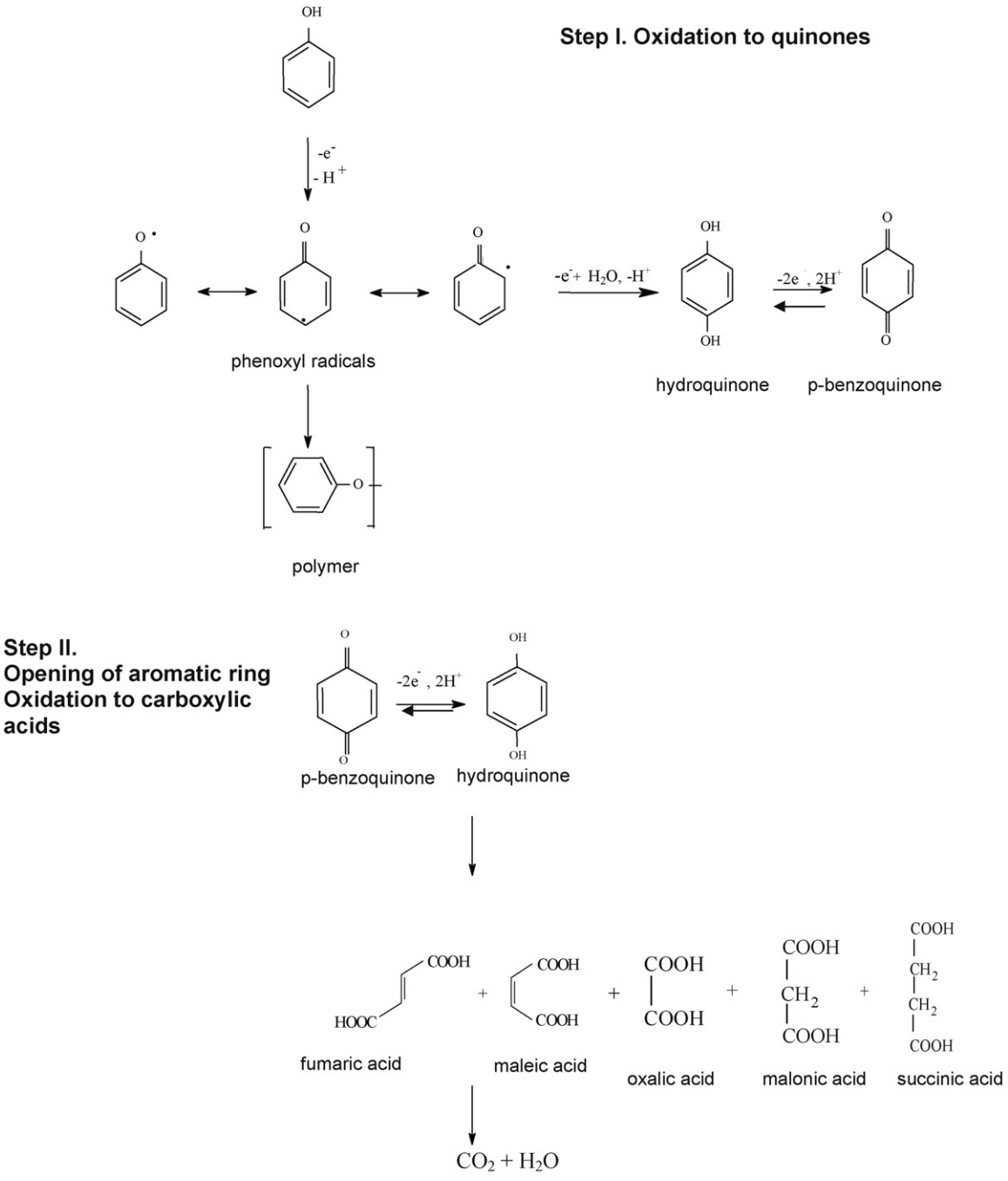

Fig. 1. Phenol oxidation pathway.

by the formation of several carboxylic acids is recognized as a rate-determining step in complete oxidation of phenol [13]. If the aromatic ring is tearing apart rapidly, the efficiency of polymeric products formation being considered as an inhibitor of complete phenol oxidation is considerably reduced [13,24]. Therefore in this work the electrochemical oxidation of benzoquinone on expanded graphite (EG) electrode was carried out. Electrochemical process was realized by cyclic voltammetry technique in alkaline solution, whereas the high performance liquid chromatography (HPLC) was used for separation and qualitative and quantitative analysis of achieved products.

2. Experimental

2.1. Electrochemical investigations

2.1.1. Preparation of electrode

Expanded graphite (EG) used as electrode material in benzoquinone electrooxidation was prepared by thermal exfoliation of graphite intercalation compound with sulfuric acid (H_2SO_4-GIC), which was beforehand synthesized by the galvanostatic oxidation of host graphite in 18 M H_2SO_4. Thermal exfoliation of H_2SO_4-GIC was performed in muffle furnace at temperature 800 °C in air for 5 min.