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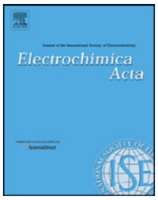

Electrochemical removal of phenol in alkaline solution. Contribution of the anodic polymerization on different electrode materials

Noureddine Belhadj Tahar[a], André Savall[b,*]

[a] *Département de Chimie, Faculté des Sciences de Monastir, Université de Monastir, Route de Kairouan, 5000 Monastir, Tunisia*
[b] *Laboratoire de Génie Chimique, CNRS, Université Paul Sabatier, 118, Route de Narbonne, 31062 Toulouse cedex 9, France*

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ABSTRACT

The removal of organic pollutants based on electropolymerization on an anode was performed in the case of phenol in alkaline solution. The polymer formed by a process involving less than two electrons per molecule of phenol, is then precipitated by decreasing the pH and finally filtered and disposed. The electrochemical polymerization of phenol ($C_0 = 0.105$ M) in alkaline solution (pH = 13) at 86 °C has been studied by galvanostatic electrolysis, using a range of anode materials characterized by different O_2-overpotentials (IrO_2, Pt and β-PbO_2). Measurements of total organic carbon and HPLC have been used to follow phenol oxidation; the morphology of the polymer deposited on the electrode surface has been examined by SEM. Experimental data indicate that phenol concentration decreases by oxidation according to a first order reaction suggesting a mass transport limitation process. Polymeric films formed in alkaline solution did not cause the complete deactivation of the anodes. SEM results show that the polymeric films formed on Ti/IrO_2 and Pt anodes cannot be mineralized. On the other hand, complex oxidation reactions leading to the partial incineration of polymeric materials can take place on the Ta/β-PbO_2 surface due to electrogenerated $HO^\bullet$ radicals which have an oxidizing power much higher than that of intermediaries formed respectively on IrO_2 and Pt. It is assumed that the polymer films formed on these anodes have different permeability characteristics which determine the rate of mass transfer of the phenol. The fractions of phenol converted in polymers were 25, 32 and 39% respectively with Ti/IrO_2, Pt and Ta/β-PbO_2, a series of materials in which the O_2-overvoltage increases.

1. Introduction

Electrochemical oxidation has been proposed as an efficient method for the treatment of wastewater polluted by organics since mineralization of organic pollutants can be completely achieved at different anode materials: SnO_2 [1–6], PbO_2 [1,7–12] and boron doped diamond (BDD) [13–17]. BDD is considered as a promising material; however, BDD electrodes are still under development in view to increase their robustness and to reduce fabrication costs of equipments [17]. In wastewater treatment the removal of phenols is of great importance due to their toxicity [10]. Destruction of phenols by electrochemical oxidation has been investigated intensively; however, this technique of mineralization suffers from low reaction rates and low current efficiencies [18,19]. The main reason for the low oxidation rate is electrode fouling. Phenols are well known for their ability to foul anodes; the tarry deposit is attributed to anodic polymerization [20]. Electropolymerization of phenols has been studied on different electrodes such as Au [21], glassy carbon [20], Pt [4,5,22–25], PbO_2 [26] and BDD [13,14]. From these investigations a global mechanism is commonly accepted for electropolymerization of phenol [21,22,27–30]; at pH value higher than phenol pK_a (9.89), phenate anion gives rise, during the first step of oxidation, to phenoxy radical:

$$C_6H_5O^- \rightarrow C_6H_5O^\bullet + 1e^- \tag{1}$$

A phenoxy radical can react irreversibly with an other radical or with an unreacted phenate anion via C–C or C–O coupling to form dimeric products [5,19,22,24,29–34]. For example:

$$2C_6H_5O^\bullet \xrightarrow{\text{C–C Coupling}} \underset{\text{Dimer}}{HOC_6H_4C_6H_4OH} \tag{2}$$

$$2C_6H_5O^\bullet \xrightarrow{\text{C–O Coupling}} \underset{\text{Dimer}}{C_6H_5OC_6H_4OH} \tag{3}$$

Such dimer can be oxidized again to produce a new radical which can couple with a phenoxy radical or with other dimeric radical to produce the polymer. For example:

$$C_6H_5OC_6H_4OH \xrightarrow{-e^-,\,-H^+} C_6H_5OC_6H_4O^\bullet \tag{4}$$

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* Corresponding author. Tel.: +33 5 61556110; fax: +33 5 61556139.
E-mail address: savall@chimie.ups-tlse.fr (A. Savall).

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$$C_6H_5OC_6H_4O^{\bullet} \xrightarrow[-(n-1)e^-,\,-(n-1)H^+]{nC_6H_5O^{\bullet}} \underset{\text{Polymer}}{C_6H_5O[C_6H_4O]_nC_6H_4OH} \quad (5)$$

Gattrell and Kirk [20,35] reported that tars formed by electropolymerization of phenol show low permeability and strong adhesion to the electrode. The formation rate of tars depends on phenoxy radical concentration which can be limited by decreasing the concentration of phenol. This film was considered to be composed of (i) a tightly adsorbed layer of products of oxidation and polymerization covered with (ii) polymeric and oligomeric layers [36,37]. The tightly adsorbed layer is unaffected by oxygen evolution while the upper layers can be disrupted by gas evolution. Therefore, oxygen evolution is beneficial to prevent complete deactivation of the electrode by a thick polymeric film; however, electron transfer remains hindered by a barrier at the electrode surface.

Many phenols have been oxidized on anode materials having high oxygen overpotentials such as PbO_2 [38] and BDD [13,14,38]. It is now generally assumed that, in the potential region of water decomposition, mineralization of organics occurs by transfer of oxygen atoms from the active electrogenerated hydroxyl radicals (Reaction (6)):

$$H_2O \xrightarrow{-e^-,\,-H^+} HO^{\bullet} \quad (6)$$

Thus, the polymeric film can be oxidized by hydroxyl radicals as soon as its formation at the electrode surface that prevents fouling. The aim of these works was the efficient mineralization of organic pollutants thanks to high oxidizing power of hydroxyl radicals. However, low current yields are caused by the concurrent reaction of oxygen evolution:

$$2HO^{\bullet} \xrightarrow{-2e^-,\,-2H^+} O_2 \quad (7)$$

On the other hand, formation of polymer, occurring by direct electron transfer in the potential region of water stability, could be convenient in wastewater treatment with respect to energy consumption since less than two electrons is required per phenol molecule to trigger polymerization [29,33]. The removal of some phenolic compounds from aqueous solutions based on electropolymerization was recently attempted [33,39–41]. By this method phenol is immobilized as a solid polymer on the anode surface by electrolysis at a low anodic current density in neutral solution. Gattrel et al. and Kuramitz et al. have used as anodes respectively a granular activated carbon [33] and a bundle of carbon fiber [39–41] having large surface area to remove successfully phenols from very diluted solutions. This method represents a simple and clean technique for the complete removal of phenolic compounds in aqueous solution. However, after use, the carbon fiber and the granular activated carbon passiveted by the film of polymer must be regenerated. Zareie et al. [42] have shown that the removal of phenol from wastewater in the form of a solid polymer suspended in the reactor can be achieved using a carbon electrode and high anodic current density in the presence of NaCl ($120\,g\,l^{-1}$); these authors suggested that most of the phenol oxidation occurs in the solution bulk without electrode fouling. One can object that this process uses a large amount of salt and would form toxic organohalogeno compounds.

In a previous work [26], we underlined that electropolymerization of phenol could help to improve the efficiency in wastewater treatment. The effects of initial phenol concentration, anodic current density, pH and process temperature on phenol oxidation were studied using a Ta/β-PbO_2 anode in batch runs. It has been shown that 15% of the starting phenol can be removed as polymers under the best operating conditions. In our knowledge, the direct quantification of phenol conversion into polymer as a suspension in the electrolytic solution was not the object of any study. It was also shown that the fraction of starting phenol converted into polymer increases substantially with temperature from 25 to 65 °C [26]. Gattrell and Kirk [20] have also observed during electrolysis of phenol in sulphuric acid aqueous solution on Pt that electrode passivation was reduced or prevented by increasing temperature.

Table 1

Experimental conditions for β-PbO_2 electrodeposition. 1 M $Pb(NO_3)_2$; temperature: 65 °C; electrodeposition time for each current density value: 30 min.

Substrate	J ($mA\,cm^{-2}$)	Nature of deposit
Tantalum	100	Adherent, rough, with many big pinholes, mat and grey in color.
Niobium	100	Adherent, smooth, uniform, without pinholes, mat and grey in color.

The efficiency of phenol removal by electropolymerization is strictly related to the operating conditions and the nature of the anode material. The aim of the present work is to investigate and to compare the efficiency of three electrode materials (IrO_2, Pt and β-PbO_2), which have different oxygen overpotentials, for removal of phenol in aqueous solution by electropolymerization. Furthermore, the effect of the nature of the substrate (Ta or Nb) used for the electrodeposition of β-PbO_2 on the electropolymerization of phenol was tested. Batch runs were carried out, using these anodes, in alkaline media ($pH > pK_a$) in view to increase the solubility of polymers and therefore to reduce fouling. As the effect of varying temperature from 25 to 65 °C was previously found to be a positive fact [26], all the experiments were conducted at a temperature equal to 86 °C.

2. Experimental

2.1. Preparation of β-PbO_2 anode

β-PbO_2 deposits were electrochemically prepared on rectangular plates of massive niobium or tantalum (70 mm × 10 mm × 1 mm) from lead nitrate solution. Tantalum and niobium have very good chemical and electrochemical stability. β-PbO_2 was deposited on these substrates by anodic oxidation of lead nitrate solution at low anodic current density [43–45].

2.1.1. Surface treatment

Tantalum and niobium plates were sandblasted and then etched. The losses in mass per unit of surface area due to this surface treatment were 0.73 ± 0.12 and $0.44 \pm 0.08\,mg\,cm^{-2}$ respectively for tantalum and niobium plates. More details on the surface treatment procedure are given in our previous work [9,26].

2.1.2. Anodic deposition of β-PbO_2

Pure β-PbO_2 was obtained by electrolysis of $Pb(NO_3)_2$ solutions using anodic constant current densities higher than $100\,mA\,cm^{-2}$. The deposition procedure was previously described [9,26]; the operating conditions are summarized in Table 1.

2.2. Preparation of Ti/IrO_2

Conductive metal oxide IrO_2 was deposited on a titanium substrate (70 mm × 10 mm × 1 mm) by the thermal decomposition technique [46,47].

2.2.1. Surface treatment

Titanium substrate underwent the same mechanical surface treatment as tantalum and niobium ones. The average loss in mass was $0.16 \pm 0.05\,mg\,cm^{-2}$. Chemical etching was then carried out using boiling concentrated hydrochloric acid (32% by mass)