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The influence of metal oxide properties on the oxidation of organics

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Dedicated to Professor E. Gileadi on the occasion of his retirement from the University of Tel Aviv and in recognition of his contribution to electrochemistry

Abstract

The ‘anodic oxidation’ of *p*-benzoquinone has been studied using a range of anode materials. The influence of the applied current density on the removal rate of *p*-benzoquinone has also been studied. An increase in the applied current density was found to increase the removal rate of *p*-benzoquinone only slightly, thus resulting in an actual decrease of the current efficiency of this process. The removal rate for *p*-benzoquinone was found to be influenced by several properties of the anode material. In fact, a relationship between properties of the anode such as its electroactive surface area and the removal rate of organics appears to exist. Crown Copyright © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Metal oxide electrodes; Anodic oxidation; *p*-Benzoquinone

1. Introduction

Many industrial wastewater streams (from e.g. petrochemical refineries, pulp and paper mills, etc.) contain toxic organic compounds such as phenols and quinones, and their treatment down to trace levels is of increasing concern. The potential use of electrochemistry for the treatment of such wastewater streams has attracted much attention [1–4]. Electrochemistry appears to be a particularly attractive method as there is no need to add chemicals to the wastewater. It has been shown that these organic pollutants can be oxidized electrochemically using metal oxides as anodes and employing ‘high’ anodic currents [1,3]. During this anodic oxidation process, the evolution of O₂ (oer) also occurs at the metal oxide (MO_x) anode surface, as shown in the reaction scheme [5]:

(It should, however, be noted that the exact pathway for the oer depends on the nature of the metal oxide anode.)

It has been suggested that the hydroxy radicals (OH[•]) generated as intermediate species at the anode surface oxidize the organic compounds to CO₂ [5]. The anodic oxidation reaction of phenol has often been studied and based on solution analysis using high performance liquid chromatography (HPLC) the following reaction scheme has been suggested [3]:

The first step of the ‘anodic oxidation’ reaction, i.e. the conversion of phenol to *p*-benzoquinone, is known to be rapid and has been reported to take place at the same rate using either antimony ‘doped’ tin-oxide (Sn(Sb)-oxide) or Pt/Pt-oxide anodes. However, the oxidation rate of the intermediate product, namely *p*-benzoquinone, to lower aliphatic acids has been re-

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ported to be more rapid using antimony doped tin oxides rather than Pt/Pt-oxide or IrO₂ as anodes. It has been further observed that metal oxide anodes such as Pt/Pt-oxide and IrO₂, which are good oer catalysts, favor the oxidation of phenol to lower aliphatic acids, while metal oxide anodes such as antimony doped tin oxide, which are poor oer catalysts, are suggested to oxidize phenol completely to CO₂ [3,5]. Based on these observations and radical trap experiments using *N,N*-dimethyl-*p*-nitrosoaniline as an OH• scavenger it has been suggested that a larger concentration of OH• is present on the antimony doped tin oxide anodes, i.e. on anodes that are poor catalysts for the oer, as compared to the noble metal oxides (e.g. IrO₂), which are good catalysts for the oer [5]. The larger OH• concentration has been suggested to be responsible for the more rapid oxidation rate of *p*-benzoquinone and the lower aliphatic acids on anodes that are poor oer catalysts [5].

There is still considerable controversy about the reaction mechanism of this anodic oxidation process. Complete product analyses as well as studies on the influence of the metal oxide properties such as the real electroactive surface area and the number of electroactive oxide sites have not been carried out. Furthermore, the development of non-toxic anode materials, as well as anodes exhibiting good efficiencies for the oxidation of organics down to low concentrations, is needed. In the present work, the oxidation rates and the current efficiencies for the oxidation of *p*-benzoquinone are obtained using a range of anode materials. An attempt is made to correlate the experimentally determined rates of oxidation and current efficiencies with specific metal oxide properties.

2. Experimental

2.1. Anode materials

A range of anode materials were used in this work and are for simplicity divided into two classes as follows:

Class 1 anodes, which are poor electrocatalysts towards the oer:

- antimony doped tin oxide (Sn(Sb)-oxide);
- fluoride doped lead oxide (PbO₂).

Class 2 anodes, which are good electrocatalysts towards the oer and are divided into two sub-classes:

Class 2a (Ir-based oxides):

- iridium oxide (IrO₂);
- mixed iridium and titanium oxides: Ir(30%)Ti(70%)O₂;
- mixed iridium, titanium and cerium oxides: Ir(30%)Ti(20%)Ce(20%)O₂.

(The percentages in the above formulae for the Ir-based oxides are equivalent to the mole ratio of the

metal salts in the precursor solutions (see below)).

Class 2b (Pt-based anodes):

- platinum/platinum-oxide (Pt/Pt-oxide);
- Pt foil.

The Sn(Sb)-oxides were supplied by Eltech System Corp., Chardon, OH, while all other anodes were prepared as described below. Circular (1.6 cm diameter) or rectangular (1.6 × 1.6 cm) Ti plates of 99.7% purity and 0.089 cm thickness (Alfa Aesar) were used as supports for the oxides. Just prior to the deposition of the metal oxides, the Ti plates were consecutively sandblasted, ultrasonically cleaned in *iso*-propanol for 20 min, etched in boiling 10 M HCl for 1 min and then rinsed with ca. 200 ml H₂O. The PbO₂ anode was prepared using a procedure described elsewhere [4]. The PbO₂ was formed by electrodeposition at 1.7 V versus a saturated calomel electrode (SCE) from 0.1 M HNO₃ solution containing 0.5 M Pb(NO₃)₂ and 40 mM NaF. The solution was stirred rigorously during the deposition process, which took 10 min. The Ir-based oxides and the Pt/Pt-oxide electrodes were prepared by thermal decomposition of adequate mixtures of ca. 0.14 mol dm⁻³ solutions of H₂IrCl₆ (Alfa Aesar), TiCl₄ (Alfa Aesar), CeCl₃·7H₂O (Alfa Aesar) and H₂PtCl₆ (Alfa Aesar) at 450 and 550°C, respectively. The influence of the baking temperature on the properties of IrO₂ anodes was also investigated, i.e. IrO₂ anodes were also prepared at 550°C (referred to as IrO₂(550°C) in this work). The salts were dissolved in *iso*-propanol. Adequate mixtures of the precursor solution at the desired mole ratio were coated repetitively onto the titanium support by brushing. Porous oxide layers of ca. 1.2 to 1.6 mg cm⁻², and up to micrometer thickness, were formed in this manner. Other details of the preparation of these oxides are described elsewhere [6].

2.2. Cells and electrodes

A three compartment cell, in which the reference electrode was separated from the working electrode compartment by a Luggin capillary, was generally employed for the electrochemical studies. However, for the anodic oxidation of the model organic compounds, a two compartment cell was used, i.e. the reference and working electrodes were placed in the same compartment. In all electrochemical experiments the counter electrode was separated from the working electrode, i.e. the counter electrode (a Pt spiral) was enclosed in a fine glass frit or separated using a Nafion[®] membrane. Either a saturated calomel electrode (SCE), a mercury sulfate electrode (MSE) or a Pt wire were employed as reference electrodes. The latter was used only for the constant current oxidation studies of the model organic compounds. It should be noted that no use was made of the recorded potential versus the Pt wire. All potentials reported in this work are versus the SCE, and geometrical electrode areas are given.

2.3. Techniques and instrumentation

All electrochemical experiments were performed using the VoltaLab 32 electrochemical laboratory (Radiometer). Positive feedback ohmic drop compensation was performed when necessary, i.e. for high current experiments. A Shimadzu UV-1201 S UV-vis spectrophotometer was used to estimate the *p*-benzoquinone concentrations by monitoring the absorbance at 246 nm. The concentration of *p*-benzoquinone as well as intermediates and end products resulting during/ from the anodic oxidation process were also determined using a HP series 1100 high performance liquid chromatograph (HPLC). For the separation of the carboxylic acids, an ion-interaction column (Mandel), which was heated at 45°C, was employed. The UV detector was set at 210 nm. 0.01 M H₂SO₄ was used as the mobile phase and the flow rate was generally 0.3 ml min⁻¹. A C-18 column (Supelco) was also employed. The mobile phase was a mixture of 0.01 M H₂SO₄ and acetonitrile at a flow rate of generally 1 ml min⁻¹. The UV detector was set at 195 nm and the column was thermostated at 20°C. The total organic carbon (TOC) concentration was measured using a TOC-5050 Shimadzu.

2.4. Solutions

Phosphate buffer (pH 6.8) was used as the electrolyte solution and *p*-benzoquinone (Aldrich) was used as the model organic compound. For some studies, the organics were also dissolved in 0.01 M H₂SO₄ and 0.1 M Na₂SO₄ (pH ca. 2) solutions. All chemicals were ACS grade and high resistivity (18 MΩ) H₂O was used. The experiments were performed at 25°C. High purity argon was used to deoxygenate the solutions prior to the cyclic voltammetric studies.

3. Results and discussion

3.1. Operational life-time of metal oxide anodes

The anodic oxidation process of organics is carried out at 'high' anodic currents, thus resulting in a very positive anode potential. Under these conditions, only a few materials are stable, thus limiting the materials that can be used as anodes for this process [7]. Anodes made of non-toxic noble metal oxides such as Pt-oxides and Ir-oxides, are well known to have long lifetimes (several thousand h), however, they are very costly, while the stability of the very toxic antimony doped tin oxides is insufficient for practical applications [8]. The operational life-time of the anode used in an industrial process is of high relevance due to economical as well as environmental concerns. The latter is of particular

importance when metal oxides made of toxic metals, such as lead, tin and antimony are considered to be used for the treatment of wastewater streams.

3.2. Oxidation of *p*-benzoquinone

Phenol has been used frequently as a model organic compound to study the anodic oxidation process [1–3]. However, during the anodic oxidation, phenol polymerizes at the anode surface [9]. This results in surface fouling of the anode and decreases the active electrode area, thus making the evaluation of the effectiveness of different anodes for the oxidation of organic compounds difficult. Therefore, the anodic oxidation studies reported in this work were carried out using *p*-benzoquinone as a model organic compound. *p*-Benzoquinone, a very toxic compound, is produced as an intermediate during the anodic oxidation of phenol and its further reaction to the less toxic aliphatic acids appears to be a critical step in the anodic oxidation of phenol (i.e. reaction (1)). It should be noted that the anodic oxidation of *p*-benzoquinone has been studied in prior work [10,11]. Pulgarin et al. [10] studied the anodic oxidation of large concentrations of *p*-benzoquinone solutions at pH 2.5 using Sn(Sb)-oxides and IrO₂ as anodes, while Feng et al. [11] used Fe doped PbO₂ anodes for the anodic oxidation of *p*-benzoquinone solutions in acetate buffer solutions (pH 5).

In this work, generally 20 ml of 5×10^{-4} M *p*-benzoquinone solutions in phosphate buffer pH 6.8 were used for the anodic oxidation studies. This concentration was selected as preliminary studies showed that the *p*-benzoquinone concentration decreases when the solutions are exposed to air on open-circuit. The decrease in the *p*-benzoquinone concentration was, however, found to be small with time for concentrations at or below 5×10^{-4} M *p*-benzoquinone. It should be noted that decreases in the *p*-benzoquinone concentration were found to take place over a broad pH range (tested for pH ca. 0–12). This decrease is likely to be related to condensation/polymerization reactions of *p*-benzoquinone known to occur in acidic and alkaline solutions [12,13]. For the anodic oxidation, a geometrical anode area of 1.7 cm² (1.4 × 1.2 cm) was exposed to the electrolysis solution. Preliminary studies showed the rate of *p*-benzoquinone removal to be slow, hence, 'anodic oxidation' studies were generally carried out until the concentration of *p*-benzoquinone was reduced to half of its original value. In this work, the rate of 'oxidation' of *p*-benzoquinone ($v_{\text{ox,org}}$) was calculated as the time in minutes needed to decrease the *p*-benzoquinone concentration from 5 to 2.5×10^{-4} M. The current efficiency (I_{eff}) is equivalent to the number of electrons used for the 'anodic oxidation' of *p*-benzoquinone (from 5 to 2.5×10^{-4} M) versus the total number of electrons passed. For this calculation, it was

assumed that only one electron is involved in the ‘anodic oxidation’ of *p*-benzoquinone, as the mechanism of the *p*-benzoquinone oxidation is not understood in detail (discussed below).

The $v_{\text{ox,org}}$ and, therefore, I_{eff} values determined for the ‘anodic oxidation’ of *p*-benzoquinone using a particular current density (j) and anode material were found to be very reproducible ($\pm 5\%$) with time. This suggests that these anodes do not exhibit a loss of activity for the ‘anodic oxidation’ of *p*-benzoquinone (which could, e.g. result from the formation of an organic polymeric film or loss of the oxide coating used as anode) with time of electrolysis. This was tested for up to 30 h on Sn(Sb)-oxides and up to 100 h on IrO₂

and Pt/Pt-oxide, respectively. It should also be noted that a different anode was used for each oxidation experiment at a particular j . Furthermore, the $v_{\text{ox,org}}$ and I_{eff} values were essentially the same for the anodic electrolysis of 5×10^{-4} M solutions in pH 6.8 phosphate and pH 2 sulfate solutions, indicating that the rate of *p*-benzoquinone oxidation is independent of pH (within the range tested). It is also noteworthy that the rate of the *p*-benzoquinone oxidation was found to be the same using different rotation rates to stir the solution, suggesting that the *p*-benzoquinone oxidation reactions studied in this work are not mass transport controlled.

3.2.1. The influence of j on $v_{\text{ox,org}}$ and I_{eff}

In the first oxidation studies the dependences of $v_{\text{ox,org}}$ and I_{eff} of *p*-benzoquinone on the applied current density was studied using three different anodes, namely IrO₂, Pt/Pt-oxide and Sn(Sb-doped) oxide as shown in Fig. 1(a) and (b), respectively.

It is seen in Fig. 1(a) that the rate of *p*-benzoquinone removal at a particular current density depends on the nature of the anode material used. This could be due to various factors such as differences in the nature of the radicals produced in the H₂O discharge reaction and/or different concentrations of radicals at the anode surface; this is further discussed in the following section. Fig. 1(a) also shows that $v_{\text{ox,org}}$ increases somewhat with increasing current density, however, the increase is not proportional to j so that I_{eff} actually decreases as higher current densities are applied, as shown in Fig. 1(b). In fact, an increase in j from 5 to 50 mA cm⁻² diminishes I_{eff} by ca. 5 times, and vice versa. The small dependence of the *p*-benzoquinone reaction rate on j is not yet understood. It could suggest that the concentration of the radical species formed at the three anode surfaces (i.e. Pt/Pt-oxide, IrO₂ and Sn(Sb-doped) oxide) does not depend strongly on current density and, hence, on potential for the experimental conditions used here. However, it is also known that *p*-benzoquinone undergoes condensation/polymerization reactions in acidic and alkaline solutions [12,13]. This results in a variety of products, their nature being also influenced by the presence of O₂ [12]. An increase in j results in pH changes near the electrode surfaces as well as in an increase production of O₂ (see reaction 1 (1.1, 1.2, 1.3)). Therefore, the slight increase in $v_{\text{ox,org}}$ observed in Fig. 2(a) may be due to the formation of condensation/polymerization products.

3.2.2. I_{eff} values obtained using a range of anodes at 10 mA cm⁻²

In this section I_{eff} values for the anodic oxidation of 5×10^{-4} M *p*-benzoquinone were obtained using a range of different anode materials and applying 10 mA cm⁻², as shown in Table 1. It is seen that I_{eff} decreases

Fig. 1. The dependence of the oxidation rate ($v_{\text{ox,org}}$) of *p*-benzoquinone on the current density using (□) IrO₂, (△) Pt/Pt-oxide, (◇) Sn(Sb-doped) oxide as anodes. For the anodic oxidation, a 5×10^{-4} M *p*-benzoquinone solution in phosphate buffer (pH 6.8) was used (a, top). The dependence of the current efficiency (I_{eff}) of *p*-benzoquinone on the current density using (□) IrO₂, (△) Pt/Pt-oxide, (◇) Sn(Sb-doped) oxide anodes. For the anodic oxidation, a 5×10^{-4} M *p*-benzoquinone solution in phosphate buffer (pH 6.8) was used. I_{eff} was estimated assuming a one-electron reaction (b, bottom).

Fig. 2. Typical cyclic voltammograms for Ir based oxides in phosphate buffer (pH 6.8) obtained at 100 mV s⁻¹ between 0 and 1.7 V vs. a saturated calomel electrode (SCE). (—) shows the CV for IrO₂ and (---) shows the same for Ir(30%)Ti(70%)O₂.

Table 1

I_{eff} values for the anodic oxidation of 5×10^{-4} M *p*-benzoquinone at 10 mA cm⁻² for a range of anodes

Anode material	$I_{\text{eff}}/\%$
Pt	2.5
PbO ₂	0.6
Sn(Sb)-oxide	0.55
Pt/Pt-oxide	0.55
IrO ₂ (550°C)	0.55
IrO ₂ (450°C)	0.45
Ir(30%)Ti(70%)O ₂	0.3
Ir(30%)Ti(20%)Ce(50%)O ₂	0.3

Table 2

$Q_{\text{Ir-oxide}}$ and E_{anode} values for Ir-oxide based anodes

Anode material	$Q_{\text{Ir-oxide}}/\text{mC cm}^{-2}$ ^a	$E_{\text{anode}}/\text{V vs. SCE}$ ^b
IrO ₂ (550°C)	2.7	1.61
IrO ₂	11	1.49
Ir(30%)Ti(70%)O ₂	25	1.33
Ir(30%)Ti(20%)Ce(50%)O ₂	25	1.34

^a The $Q_{\text{Ir-oxide}}$ values were extracted from raw CV data between 0.1 and 1 V vs. SCE for the Ir based oxides (see text).

^b The E_{anode} values were obtained after 10 min at 10 mA cm⁻² in 0.5 M H₂SO₄ vs. SCE and were corrected for IR-drop.

with the anode in the following order: Pt foil $\gg$ PbO₂ > Sn(Sb) oxide $\approx$ Pt/Pt-oxide $\approx$ IrO₂(550°C) > IrO₂ > Ir(30%)Ti(70%)O₂ $\approx$ Ir(30%)Ti(20%)Ce(50%)O₂. These results indicate that the Pt foil anode clearly shows the highest current efficiency for the removal of *p*-benzoquinone. PbO₂ shows only a slightly better efficiency for the removal of *p*-benzoquinone than Sn(Sb)oxide, and the non-toxic noble metal oxides, i.e. Pt/Pt-oxide and the IrO₂ anodes baked at 550°C. In fact, I_{eff} found for the latter three oxides is the same. Furthermore, I_{eff} is seen to be different for the two IrO₂ anodes baked at 450 and 550°C. This clearly indicates that factors other than the chemical nature of the metal oxide anodes influence the performance towards the oxidative removal of organics. Also, the I_{eff} value found for the Ir(30%)Ti(70%)O₂ and Ir(30%)Ti(20%)Ce(50%)O₂ anodes is only 1.3 times smaller than that obtained for the IrO₂ anode, even though a much larger amount (3.3 times more) of precious Ir salt was used for the IrO₂ preparation than for the two mixed oxides. Again, it should be noted that mass transport limitations within the solution are not thought to influence the I_{eff} value (Table 1), as the stirring rate was not found to influence $v_{\text{ox,org}}$ and I_{eff} .

3.2.3. Properties of Ir-based oxides and their possible influence on I_{eff}

IrO₂ is known to be an excellent electronic conductor and to have a high internal porosity. In fact, the

porosity, i.e. internal surface area of Ir based oxides, is influenced by the temperature used to decompose the precursor salt as well as by the addition of foreign metal salts such as Ti and/or Ce [6]. It is further known that the oer takes place only at the Ir sites within these oxides, i.e. the Ti and Ce sites are not involved [6]. Changes in the oxide surface area influence the number of electroactive Ir sites, which, in turn, influence the oxide's activity towards the oer and the E_{anode} value at a particular *j*. The number of electroactive Ir sites (which is related to the electroactive surface area) can be estimated from the cyclic voltammetric (CV) characteristics of these oxides [6]. This is shown in Fig. 2 for the typical example of IrO₂ (—) and Ir(30%)Ti(70%)O₂ (---) electrodes cycled at 100 mV s⁻¹ in phosphate buffer. The charge passed between ca. 0.1 and 1 V reflects the electrochemical conversion of Ir sites at the solution|oxide interface and within the oxide. It is proportional to the number of electroactive Ir sites present within the oxide film ($Q_{\text{Ir-oxide}}$), while the large increase in the anodic current at more positive potentials results from the oer. The value of $Q_{\text{Ir-oxide}}$ equals the integrated area (i.e. the current multiplied by the potential in the CV between 0.1 and 1 V) divided by the sweep rate, in this case 100 mV s⁻¹. It is clearly seen in Fig. 2 that the $Q_{\text{Ir-oxide}}$ values as well as the activity for the oer are different for the IrO₂ and the Ir(30%)Ti(70%)O₂. It is also noteworthy that the $Q_{\text{Ir-oxide}}$ value for a particular Ir based oxide was found to be the same using phosphate buffer and 0.5 M H₂SO₄ solutions. Furthermore, the $Q_{\text{Ir-oxide}}$ values were independent of the sweep rate for values ≤ 100 mV s⁻¹.

Table 2 summarizes the $Q_{\text{Ir-oxide}}$ values for the four Ir based oxides used in this work indicating almost ten-fold differences in the number of electroactive Ir sites within the four Ir-based oxides. The values of E_{anode} measured at 10 mA cm⁻² in 0.5 M H₂SO₄ are also listed in Table 2. It is seen that the E_{anode} value decreases with the metal oxide anode as follows: IrO₂(550°C) > IrO₂ > Ir(30%)Ti(70%)O₂ $\approx$ Ir(30%)Ti(20%)Ce(50%)O₂, i.e. in the inverse order as $Q_{\text{Ir-oxide}}$. This dependence of E_{anode} on the metal oxide anode material is the same as found for I_{eff} . This could suggest that the experimentally observed differences in I_{eff} (Table 1) are related to differences in the E_{anode} values (maybe due to adsorption of the organic involved in the 'oxidation' reaction, as investigated in more detail in parallel work [14]). However, it is also possible that the differences in I_{eff} (Table 1) are due solely to different surface areas of the oxide, suggesting that the oer occurs at the internal and external sites of the oxide, while the oxidation of organics occurs predominantly at the external sites of the oxide. Furthermore, these results suggest that metal oxides which exhibit a lower activity towards the oer (i.e. with decreased number of electroactive sites for the oer and

lower porosity) are better anodes for the oxidative removal of organics.

It should be noted that the E_{anode} values of the Ir(30%)Ti(70%)O₂ and the Ir(30%)Ti(20%)Ce(50%)O₂ anodes increased over an extended period of electrolysis time at high anodic currents. This increase in E_{anode} indicates changes in oxide properties as well as a short lifetime of these anodes. Furthermore, the differences in E_{anode} for the four Ir based oxides (Table 2) appear to

Fig. 3. SEM showing the top view for a Pt/Pt-oxide made at 550°C using the thermal decomposition method. The SEM shows a 1 k × magnification.

Fig. 4. Concentration time profile for the anodic oxidation of 5×10^{-4} M p -benzoquinone in phosphate buffer (pH 6.8). (Δ) shows the concentration profile for p -benzoquinone and ($\times$) shows the same for maleic acid (a, top). The dependence of the total organic carbon concentration (TOC) ($\diamond$) observed during the anodic oxidation of 5×10^{-4} M p -benzoquinone in phosphate buffer (pH 6.8). The anodic oxidation was carried out at 10 mA cm^{-2} and a 10 cm^2 Pt foil was used as anode (b, bottom).

be large as compared to the $Q_{\text{Ir-oxide}}$ values. This may be related to the fact that E_{anode} was measured for extensively used oxide anodes and needs to be investigated further.

3.2.4. Properties of Pt based anodes and their possible influence on I_{eff}

Fig. 3 shows the typical SEM top view for a Pt/Pt-oxide made at 550°C using the thermal decomposition method. It is seen that this Pt/Pt-oxide is very porous, i.e. the surface area and the number of electroactive sites are clearly much larger than for a Pt foil. This likely suggests that the larger I_{eff} values found using the Pt foil rather than the Pt/Pt-oxide as anode (i.e. Table 1) is again related to differences in the electroactive surface area as well as E_{anode} consistent with the case of the Ir based oxides discussed above.

3.2.5. Product analysis

The solution products resulting from the anodic oxidation of p -benzoquinone were analyzed using HPLC. The TOC was also analyzed and was found to be constant (within the experimental error of ca. $\pm 3\%$) during the ‘anodic oxidation’ of $5\text{--}2.5 \times 10^{-4}$ M p -benzoquinone for all anodes used in this work. The HPLC analysis showed that the anodic oxidation of $5\text{--}2.5 \times 10^{-4}$ M p -benzoquinone did not result in production of lower aliphatic acids as would be expected according to reaction 2. Instead, p -benzoquinone reacted to form an as yet unidentified species. It is noteworthy that its nature is likely to be different from the species formed in acidic or alkaline solutions left in air and at open-circuit. This was indicated in the different retention times of the HPLC data obtained using the C-18 column for these solutions. In previous anodic oxidation studies of p -benzoquinone carried out using PbO₂ anodes, Feng et al. [11] also found an unidentified species, which they believed to be oligomeric in nature. Anodic oxidation studies carried out over longer time periods showed that this species is oxidized to lower aliphatic acids (see below).

3.2.6. Long term anodic oxidation of p -benzoquinone using Pt anodes

In this section, the possibility of completely converting p -benzoquinone to less toxic compounds using noble metal anodes for the anodic oxidation was investigated. A 10 cm^2 Pt foil was used for the ‘anodic oxidation’ of 40 ml of 5×10^{-4} M p -benzoquinone in phosphate buffer (pH 6.8) carried out over long time periods. For the anodic oxidation a current density of 10 mA cm^{-2} was applied. Fig. 4(a) shows the dependence of the p -benzoquinone concentration versus the electrolysis time. It is seen that the p -benzoquinone concentration decreases with electrolysis time. The concentration time profile of maleic acid, which was identified using HPLC and UV–vis spectroscopy as a main

intermediate product, is also shown in Fig. 4(a). It is seen that the oxidation of the maleic acid takes place at a slow rate. However, its concentration steadily decreases. Furthermore, it is seen in Fig. 4(b) that the total organic carbon concentration (TOC) also decreases with the electrolysis time consistent with the observed decrease in the concentration of *p*-benzoquinone and maleic acid. Acetic or fumaric acid as well as low concentrations of oxalic and formic acids were also found to be produced during the anodic oxidation. Furthermore, after 30 h of anodic oxidation, the not yet identified intermediate product (see above) was not detectable by either HPLC or UV–vis spectroscopy.

It should be noted that similar results have been reported for the oxidation of phenol using Pt as the anode [3].

4. Summary and conclusions

The ‘anodic oxidation’ of *p*-benzoquinone has been studied using a range of anode materials. It has been shown that the removal rate for *p*-benzoquinone depends on the nature of the anode material consistent with prior work [3,5,10,11]. However, it was found that the rate of *p*-benzoquinone removal depends not only on the ‘chemical nature’ of the anode material, but appears to be also influenced by the anode morphology. In fact, different *p*-benzoquinone removal rates were found using iridium oxide anodes, which were prepared using the thermal decomposition method, but employing different temperatures. Overall, the results presented in this work suggest that the efficiency for the removal of *p*-benzoquinone is improved using anode materials that have a low porosity, and hence, only a few electroactive sites for the oer. However, for a complete understanding of the mechanism of the ‘anodic oxidation’ reaction of *p*-benzoquinone, i.e. the intermediate product found during this process has to be identified. Furthermore, the suggested relationship between the number of electroactive sites available for

the oer and the current efficiency needs to be tested using organic pollutants other than *p*-benzoquinone in order to establish its general applicability. It is noteworthy that Tahar and Savall [15] also observed a similar relationship between the number of electroactive sites of the anode for the oer and the ‘anodic oxidation’ rate of phenol.

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