

# A comparison of electrochemical degradation of phenol on boron doped diamond and lead dioxide anodes

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Received: 2 July 2007 / Revised: 17 October 2007 / Accepted: 31 October 2007 / Published online: 16 November 2007  
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**Abstract** This work compares two electrode materials used to mineralize phenol contained in waste waters. Two disks covered with either boron doped diamond (BDD) or  $\text{PbO}_2$  were used as anodes in a one compartment flow cell under the same hydrodynamic conditions. Efficiencies of galvanostatic electrolyses are compared on the basis of measurements of Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD). Galvanostatic electrolyses were monitored by analysis of phenol and of its oxidation derivatives to evaluate the operating time needed for complete elimination of toxic aromatics. The experimental current efficiency is close to the theoretical value for the BDD electrode. Other parameters being equal, phenol species disappeared at the same rate using the two electrode materials but the BDD anode showed better efficiency to eliminate TOC and COD. Moreover, during the electrolysis less intermediates are formed with BDD compared to  $\text{PbO}_2$  whatever the current density. A comparison of energy consumption is given based on the criterion of 99% removal of aromatic compounds.

**Keywords** Electrooxidation · Boron doped diamond · Lead dioxide · Phenol · Energy consumption · Waste waters

## 1 Introduction

Phenol is taken to be a model pollutant; it is typically encountered in effluents from oil, textiles, painting,

pesticides, colouring and pharmaceutical industries. Aromatic compounds are generally toxic and those having a quinone structure have very high toxicities [1]. It is not economically viable to remove phenol from aqueous effluents by liquid–liquid extraction for concentrations below 4,000 ppm. Furthermore, at concentrations above 5 ppm biological processes are ineffective. Thus, other techniques are needed to destroy this pollutant. Electrochemical techniques which allow reduction of the quantity of organic pollutants in solution are: (a) Separation by electroflocculation [2], (b) Oxidation by electrogenerated Fenton's reagent [3, 4], (c) Direct oxidation on a suitable anode material [5–9], where organic molecules are degraded into smaller molecules by successive oxygen atom transfer until complete destruction of the carbon skeleton [10]. The complete oxidation of phenol in aqueous solution by electrochemical means has been carried out on anode materials such as  $\text{SnO}_2$  [7, 8],  $\text{PbO}_2$  [6, 11, 12],  $\text{WO}_3$  [13] and BDD [14, 15]. Stucki et al. showed that a  $\text{SnO}_2$  anode gives better results than  $\text{PbO}_2$  in COD abatement for phenol solutions [7]. Kotz et al. found that an increase in the pH of solutions improved the service life of Ti/ $\text{SnO}_2$  electrodes [16]. On the other hand, the service life of the Ti/ $\text{SnO}_2$  electrode was shown to depend on the thickness of the  $\text{SnO}_2$  active layer. Indeed, polarization under high current densities induces passivation of the titanium substrate rather quickly. Therefore, this type of electrode has not been commercially developed. At the present time, lead dioxide electrodes are commonly used for industrial use [17]. On the other hand, BDD is an innovative material having the widest electrochemical window and an excellent stability in acid or basic solutions [9, 18]. However, current technologies of BDD manufacture do not allow obtaining electrodes of industrial size [19].

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This paper examines the influence of operating parameters such as current density and flow rate to compare the two materials from the point of view of efficiency and energy consumption.

## 2 Experimental

### 2.1 Electrochemical reactor

Electrolyses were conducted in a one compartment reactor (Diacell<sup>®</sup>), under galvanostatic conditions with electrolyte recirculation. Electrodes were formed by two disks of 63 cm<sup>2</sup> active surface and separated by 10 mm. The cathode was a 1 mm thick disk of zirconium, the anode was either a Si wafer coated with a 1 μm thick layer of boron doped diamond (BDD) or a titanium disk covered with a PbO<sub>2</sub> film (supplied by de Nora, Italy). The BDD electrodes (supplied by CSEM, Neuchâtel) were made by chemical vapour deposition on a conductive substrate of polysilicium. Other details of the cell were given previously [20].

### 2.2 Operating conditions

Solutions of 0.02 M phenol (Prolabo, 99% purity) were prepared from 0.1 M sulphuric acid (Prolabo, Normapur). Electrolyses were conducted under different current densities (respectively: 47, 100 and 142 mA cm<sup>-2</sup>) at a constant electrolyte flow rate (200 L h<sup>-1</sup>). The effect of the flow rate was studied between 42 and 336 L h<sup>-1</sup>, for a current density fixed at 47 mA cm<sup>-2</sup>.

### 2.3 Analysis

Electrolyses were monitored by measuring Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD). Values of TOC were measured with a Shimadzu 5050A instrument and those of COD were determined by photometry with disposable test tubes and a pocket photometer (Dr. Lange Lasa 50 system).

Concentrations of phenol and its oxidation intermediates were followed by liquid chromatography (HPLC) of samples taken at regular intervals. A mixed column (ion exclusion and selective adsorption) PRP-X 300 (Hamilton) was used to separate aromatics and aliphatic carboxylic acids in a single injection [11]. The eluant was a mixture of 0.01 M sulphuric acid and acetonitrile. The proportions of the two components varied with time (Table 1). All compounds were detected at a wavelength of 220 nm, except the *para*-benzoquinone which was detected at 250 nm.

### 2.4 Current efficiency and energy consumption

The instantaneous current efficiency is calculated from experimental COD-values according to Eq. 1.

$$\eta = \frac{\Delta \text{COD}_{\text{exp}}}{\Delta \text{COD}_{\text{th}}} = 4FV \frac{[\text{COD}(t) - \text{COD}(t + \Delta t)]}{I \Delta t M_{\text{O}_2}} \quad (1)$$

COD ( $t$ ) and COD ( $t + \Delta t$ ) are, respectively, the concentrations of COD expressed in g L<sup>-1</sup> at times  $t$  and  $t + \Delta t$ .  $M_{\text{O}_2}$  is the dioxygen molar weight (g mol<sup>-1</sup>), and  $V$  the volume of solution ( $L$ ).

For an electrochemical reactor working in galvanostatic conditions the electrolysis energy is given by Eq. 2:

$$E = \int_t U(t) I dt \quad (2)$$

The voltage of the cell  $U(t)$  is given by the following sum of terms:

$$U = U^0 + \eta_A + \eta_C + \sum RI \quad (3)$$

where,  $U^0$  is the potential at nil current,  $\eta_A$  and  $\eta_C$  are the anodic and cathodic overvoltages, respectively, and ( $RI$ ) is the ohmic drop through the solution of resistance  $R$ . The cell voltage was directly measured during electrolyses. For all electrolyses, for all three current densities and for both of the two electrode materials, a decrease in voltage is observed over the course of the process. The variation in cell voltage results mainly from the change in ohmic drop of the solution due to change in composition. This decrease never exceeded 10%; thus, an average value of the cell voltage was used to calculate the energy consumption. At a current density of 47 mA cm<sup>-2</sup>,  $U(t) = 4.5$  V for a PbO<sub>2</sub> anode and 5.6 V for a BDD anode.

## 3 Results and discussion

Previous studies carried out on various anode materials showed that the main intermediates in phenol oxidation are: hydroquinone (HQ), catechol, benzoquinone (BQ) followed by maleic, oxalic and formic acids [6, 8, 11, 15]. However, the amount of each intermediate depends on the catalytic activity of the anode and on the reactor type (with or without separator). In the present work, galvanostatic electrolyses of 0.02 M phenol solutions were carried out using a one compartment reactor under the same hydrodynamic conditions. Current density was either lower or higher than the limiting current density  $i_{\text{lim}}^{\circ}$  (108 mA cm<sup>-2</sup>) calculated with the initial COD-value by the following equation [21]:

**Table 1** Eluent composition as function of time in HPLC analysis

Time/min	Acetonitrile/% vol
0–5	5–25
5–15	25–40
15–17	40
17–20	40–5

Components: 0.01 M H<sub>2</sub>SO<sub>4</sub> and acetonitrile. Column: PRP-X300 (length = 250 mm, diameter = 4.1 mm). Flow rate = 1.3 mL min<sup>-1</sup>

$$i_{\text{lim}}^0 = 4Fk_m[\text{COD}]^0 \quad (4)$$

where  $F$  is the Faraday constant (C mol<sup>-1</sup>),  $k_m$  is the mass transfer coefficient (m s<sup>-1</sup>) and  $[\text{COD}]^0$  is the initial COD (mol m<sup>-3</sup>).

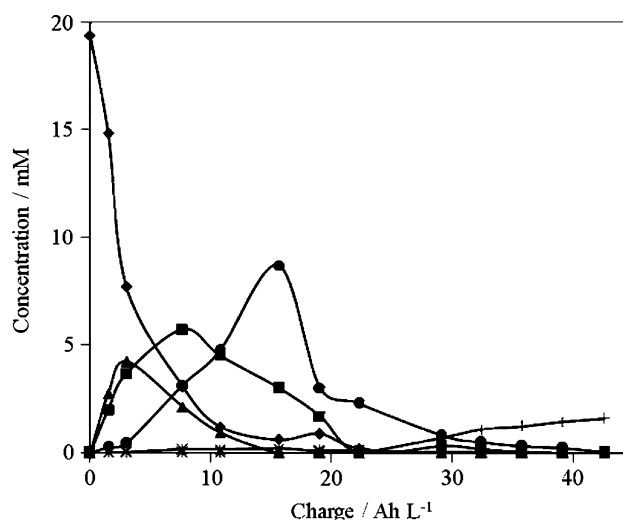
The aim was to compare the performance of the anode materials (BDD and PbO<sub>2</sub>).

### 3.1 Intermediates in phenol degradation

#### 3.1.1 Electrolysis at $i < i_{\text{lim}}^0$

Figure 1 shows the concentration variations of phenol and its oxidation products on the PbO<sub>2</sub> electrode during galvanostatic electrolysis. Phenol disappeared completely towards 20 Ah L<sup>-1</sup> while the main intermediates were HQ, *p*-BQ and oxalic acid. Maleic acid (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) was formed in very small quantities compared to the results of Belhadj Tahar and Savall [11] obtained with a two-compartment reactor. This can be explained by its hydrogenation into succinic acid (C<sub>4</sub>H<sub>6</sub>O<sub>4</sub>) on the cathode [22]. This assumption was experimentally confirmed during electrolyses of a 0.05 M maleic acid solution carried out under galvanostatic conditions (40 mA cm<sup>-2</sup>) in the reactor with or without separator. Without separator, succinic acid was formed with a maximum concentration of 0.007 M and the same electrolysis conducted with a Nafion membrane did not produce any succinic acid [23].

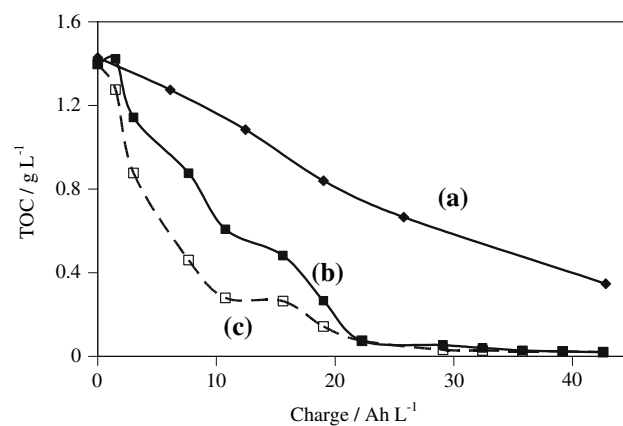
In the case of PbO<sub>2</sub> anode (Fig. 1), and in a reactor without separator, the BQ/HQ redox couple reacts reversibly between anode and cathode [6]; this could explain the large amount of HQ obtained in our experiments compared with results of Belhadj Tahar and Savall [11]. It was also observed that the solution became orange very quickly (30 min or 1.5 Ah L<sup>-1</sup>). The colour intensified between 6 and 15 Ah L<sup>-1</sup> and became persistent when *p*-BQ disappeared (for charges higher than 15 Ah L<sup>-1</sup>) until 40 Ah L<sup>-1</sup>. Indeed, a sample of the electrolysed solution tested by HPLC showed a peak at 450 nm (characteristic of a coloured compound) at a retention time similar to that for HQ. The coloured intermediate is probably a phenol oligomer [6, 11, 24] having the same retention time of HQ;



**Fig. 1** Concentration variation of organic compounds during phenol oxidation:  $\blacklozenge$  phenol,  $\blacksquare$  hydroquinone,  $\times$  cathecol,  $\blacktriangle$  *p*-benzoquinone,  $*$  maleic acid,  $\bullet$  oxalic acid,  $+$  formic acid. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Flow rate = 200 L h<sup>-1</sup>. Reactor without separator; Anode: PbO<sub>2</sub> (63.6 cm<sup>2</sup>); cathode: Zr.  $i = 47 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^0 = 108 \text{ mA cm}^{-2}$

however, it was not possible to either identify it, or quantify it. Consequently, the concentrations of HQ presented in Fig. 1 are not exactly representative of the real values and give only a trend as to its variation.

Figure 2 presents a comparison between the experimentally measured values of TOC (a) and the values calculated (b and c) from concentrations of the identified compounds (Fig. 1). In Fig. 2 the TOC is calculated with (b), and without (c), the contribution of the HQ concentration is shown in Fig. 1. In both cases, the calculated TOC-values are lower than the experimental ones from the beginning of electrolysis. Thus, the identified intermediates



**Fig. 2** Comparison between experimental TOC (a) and calculated TOC taking into account HQ (b) or not (c) during phenol oxidation. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Flow rate = 200 L h<sup>-1</sup>. Reactor without separator; Anode: PbO<sub>2</sub> (63.6 cm<sup>2</sup>); cathode: Zr.  $i = 47 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^0 = 108 \text{ mA cm}^{-2}$

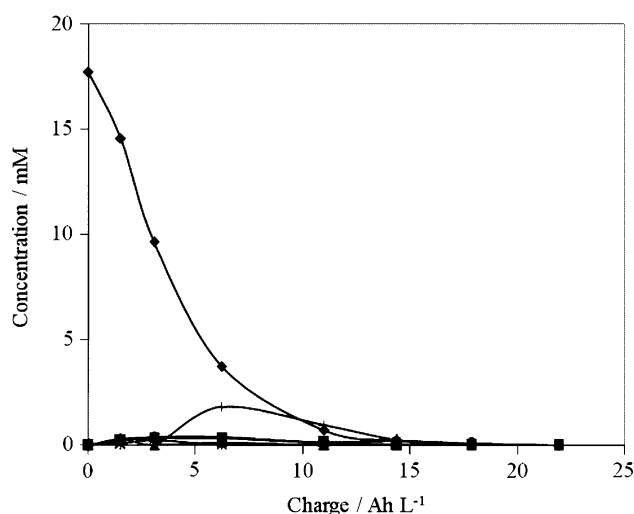
represent only a small part of the actual TOC in the solution. For example, for a charge of  $42 \text{ Ah L}^{-1}$ , the TOC is still high ( $\sim 0.35 \text{ g L}^{-1}$ ) while the calculated TOC by HPLC evaluation is almost zero ( $0.02 \text{ g L}^{-1}$ ). This significant organic carbon, not identified by HPLC, can be justified by the insoluble oligomers generated by anodic oxidation.

Figure 3 shows that, in the case of an electrolysis conducted on a BDD electrode, phenol totally disappeared after a charge of  $13 \text{ Ah L}^{-1}$ . All the detected and identified intermediates were in small quantities and, among these, formic acid was the most abundant. Hydroquinone and oxalic acid had low but perceptible concentrations, while only traces of *p*-BQ ( $C < 1 \text{ mM}$ ) were observed with a light yellow colour which appeared at the beginning of electrolysis for a short period. Catechol was not detected. Without a separator, the reduction of *p*-BQ is possible, but the HQ and *p*-BQ oxidation rates are so fast on BDD that these two intermediates do not reach significant concentrations. Cañizares et al. [15] also found very low amounts of *p*-BQ, HQ and carboxylic acids, whereas oxalic acid was the main intermediary in terms of carbon, and represented  $< 5\%$  of the initial carbon.

### 3.1.2 Electrolysis at $i > i_{\text{lim}}^{\circ}$

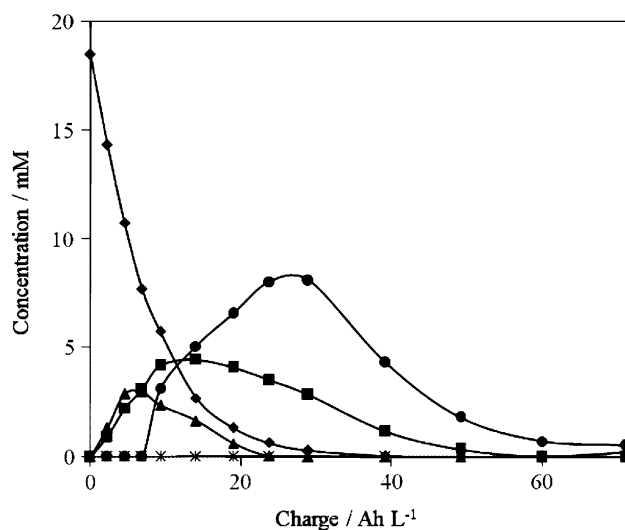
Figure 4 shows that phenol concentration on the  $\text{PbO}_2$  anode practically reached zero towards  $40 \text{ Ah L}^{-1}$ . Aromatic compounds were totally removed at  $60 \text{ Ah L}^{-1}$ . The intermediates were the same and had similar profiles to those in the previous experiment ( $i = 47 \text{ mA cm}^{-2}$ ). However, the maximum concentrations of HQ and BQ were slightly lower. The strong orange colour appeared at the beginning of electrolysis and disappeared towards  $60 \text{ Ah L}^{-1}$ . At the same time, the difference between measured and calculated TOC, with or without the contribution of the peak of HQ, remains important for this current density (not shown), throughout the electrolysis ( $500 \text{ mg L}^{-1}$  for a charge of  $70 \text{ Ah L}^{-1}$ ).

Figure 5a shows results for an electrolysis at a current density of  $142 \text{ mA cm}^{-2}$  on a BDD anode. The phenol disappeared totally at about  $40 \text{ Ah L}^{-1}$ , and for this same charge, all aromatic compounds were removed. The concentrations of all intermediates were very low or even zero and, in contrast to the experiment under  $47 \text{ mA cm}^{-2}$  (Fig. 3), formic acid was not detected in significant quantities. A slight yellow tint was observed, in agreement with the very small quantity of *p*-BQ measured by HPLC ( $< 1 \text{ mM}$ ). Furthermore, the calculated and measured TOC were closer than for the  $\text{PbO}_2$  electrode (Fig. 5b), so the compounds identified by HPLC represented the major part of the intermediates of phenol oxidation.

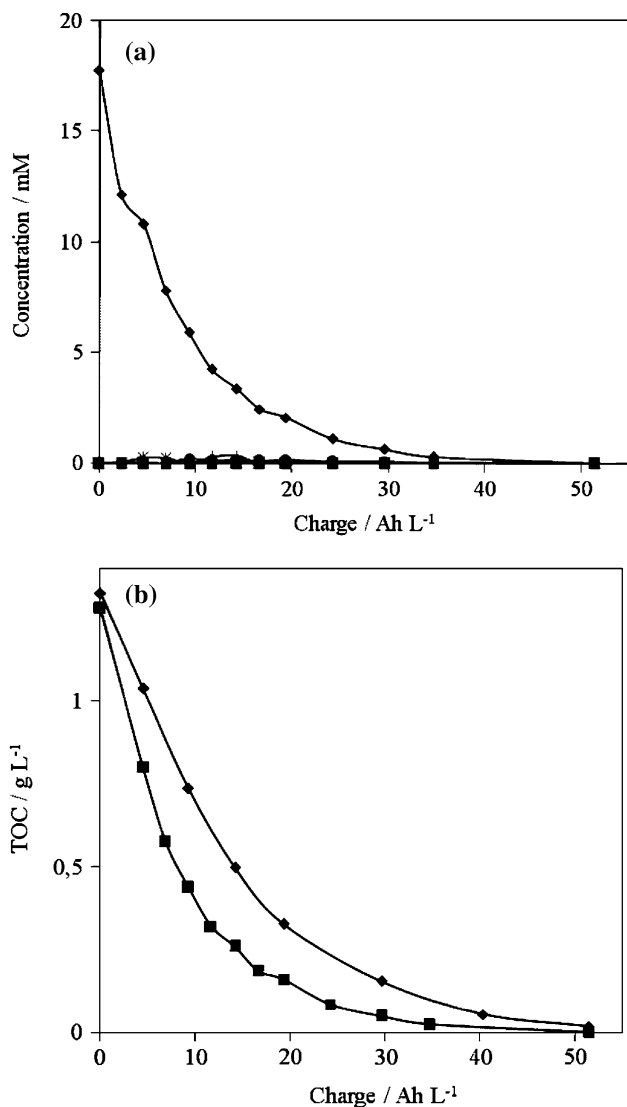


**Fig. 3** Concentration variation of organic compounds during phenol oxidation:  $\blacklozenge$  phenol,  $\blacksquare$  hydroquinone,  $\times$  cathecol,  $\blacktriangle$  *p*-benzoquinone,  $*$  maleic acid,  $\bullet$  oxalic acid,  $+$  formic acid. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M  $\text{H}_2\text{SO}_4$ . Flow rate =  $200 \text{ L h}^{-1}$ . Reactor without separator; Anode: BDD ( $63.6 \text{ cm}^2$ ); cathode: Zr.  $i = 47 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^{\circ} = 108 \text{ mA cm}^{-2}$

Electrolyses carried out under a current density of  $47 \text{ mA cm}^{-2}$  (lower than  $i_{\text{lim}}^{\circ}$ ) on a BDD anode gave complete phenol removal for a lower charge than for a current of  $142 \text{ mA cm}^{-2}$  (compare Figs. 3, 5). On the other hand, under  $142 \text{ mA cm}^{-2}$  (higher than  $i_{\text{lim}}^{\circ}$ ), the two electrode materials require the same time to totally remove the phenol (Figs. 4, 5). However, for complete disappearance of the intermediates, the  $\text{PbO}_2$  anode requires a longer electrolysis time.

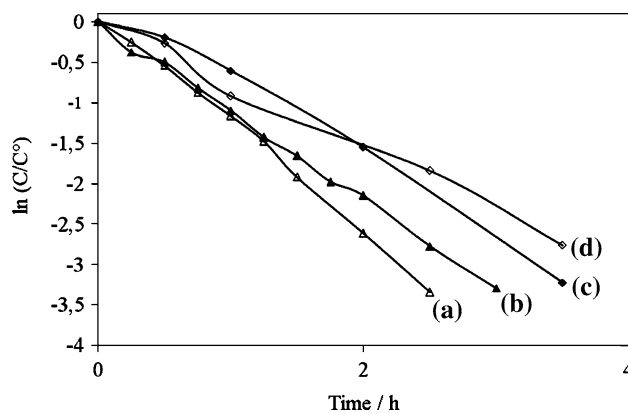


**Fig. 4** Concentration variation of organic compounds during phenol oxidation:  $\blacklozenge$  phenol,  $\blacksquare$  hydroquinone,  $\times$  cathecol,  $\blacktriangle$  *p*-benzoquinone,  $*$  maleic acid,  $\bullet$  oxalic acid,  $+$  formic acid. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M  $\text{H}_2\text{SO}_4$ . Flow rate =  $200 \text{ L h}^{-1}$ . Reactor without separator; Anode:  $\text{PbO}_2$  ( $63.6 \text{ cm}^2$ ); cathode: Zr.  $i = 142 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^{\circ} = 108 \text{ mA cm}^{-2}$



**Fig. 5** Concentration variation of organic compounds (a) ◆ phenol, ■ hydroquinone, × cathecol, ▲ *p*-benzoquinone, \* maleic acid, ● oxalic acid, + formic acid and variation of ◆ experimental and ■ calculated TOC (b) during phenol oxidation. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Flow rate = 200 L h<sup>-1</sup>. Reactor without separator; Anode: BDD (63.6 cm<sup>2</sup>); cathode: Zr.  $i = 142 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^{\circ} = 108 \text{ mA cm}^{-2}$

For the electrolyses of Figs 1, 3–5, Fig. 6 presents the variation of the logarithm of the dimensionless phenol concentration as function of time. There is a greater difference between current densities than between anode materials. The phenol oxidation rate becomes faster by increasing the current density. In the case of electrolyses carried out at 142 mA cm<sup>-2</sup> (curves a and b) and up to about 75 min (around 12 Ah L<sup>-1</sup>), meaning about 76% of phenol removal, the concentration profiles are very close. The quasi-linear profile of the logarithm of the phenol concentration is coherent with assuming that the first step in its oxidation is mass transfer limited. Assuming that the



**Fig. 6** Dimensionless concentration variation of phenol during galvanostatic electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub> at two current density and on two anode materials. Flow rate = 200 L h<sup>-1</sup>. Reactor without separator; anode and cathode surface = 63.6 cm<sup>2</sup>. Cathode: Zr.  $i = 142 \text{ mA cm}^{-2}$  (a): PbO<sub>2</sub> and (b): BDD;  $i = 47 \text{ mA cm}^{-2}$  (c): BDD and (d): PbO<sub>2</sub>

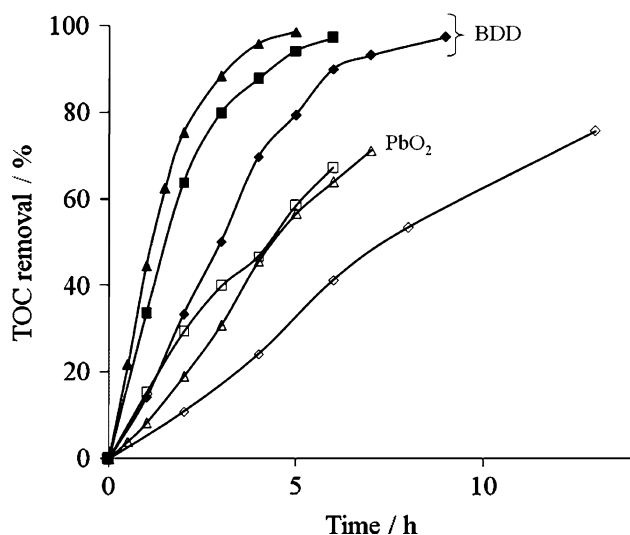
kinetics of 76% phenol degradation follows pseudo first order kinetics, the pseudo rate constant is 0.9 and 0.83 h<sup>-1</sup> on BDD and PbO<sub>2</sub>, respectively. Polcaro et al. [25] obtained the same kinetic behaviour in galvanostatic electrolysis ( $i > i_{\text{lim}}^{\circ}$ ) of solutions of phenol and its intermediates with a kinetic rate constant close to 0.7 h<sup>-1</sup>.

Phenol disappears with practically the same rate on the two materials but, in contrast to lead dioxide, the diamond totally transforms phenol at once into CO<sub>2</sub> and water (Fig. 5b). For electrolyses carried out at 47 mA cm<sup>-2</sup>, curves c and d on Fig. 6 show that the phenol oxidation rate is similar on the two materials. These curves are almost linear, suggesting a phenol disappearance rate by a mass transfer controlled process.

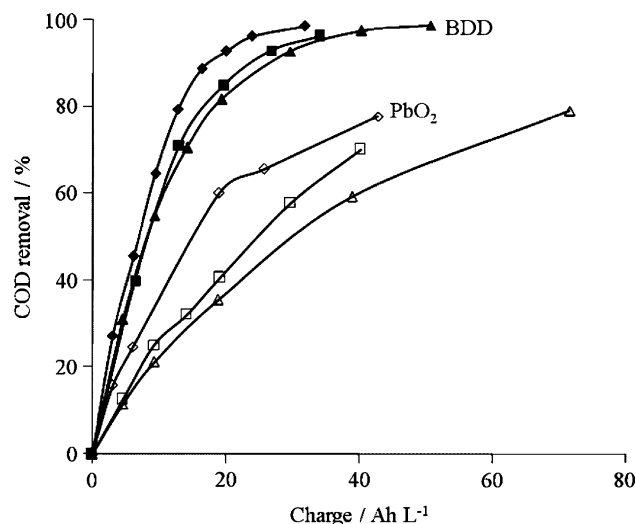
Differences observed between curves a and d (for PbO<sub>2</sub>) on the one hand, and b and c (for BDD) on the other hand, result probably from oxygen evolution, which increases with current density and improves mass transfer [24].

### 3.2 Influence of the current density

Figure 7 presents the variation of the TOC removal as a function of time for three current densities on BDD and PbO<sub>2</sub> anodes. In every case presented, the BDD efficiency was higher than that on PbO<sub>2</sub>. The PbO<sub>2</sub> electrode did not give an abatement higher than 80% in the time considered (about 10 h), Fig. 7 shows that the time of treatment decreases when the current density increases, and that the TOC removal can reach 95% with a BDD anode in <5 h (for a ratio A/V = 63/1,000 cm<sup>-1</sup>). Whatever, the electrode material, the TOC abatement is obtained at the same electrolysis time for the two higher current densities (100 and 142 mA cm<sup>-2</sup>) and did not vary significantly. To



**Fig. 7** TOC removal during phenol oxidation. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M  $\text{H}_2\text{SO}_4$ . Flow rate =  $200 \text{ L h}^{-1}$ . Reactor without separator; Anode: BDD (full symbols) or  $\text{PbO}_2$  (open symbols); cathode: Zr for different current densities:  $\diamond$  47;  $\square$  100 and  $\triangle$   $142 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^\circ = 108 \text{ mA cm}^{-2}$



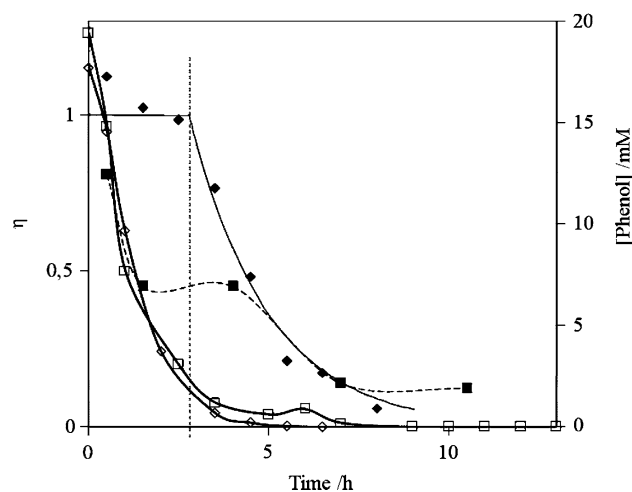
**Fig. 8** COD removal during phenol oxidation. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M  $\text{H}_2\text{SO}_4$ . Flow rate =  $200 \text{ L h}^{-1}$ . Reactor without separator; Anode: BDD (full symbols) or  $\text{PbO}_2$  (open symbols); cathode: Zr for different current densities:  $\diamond$  47;  $\square$  100 and  $\triangle$   $142 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^\circ = 108 \text{ mA cm}^{-2}$

estimate the electrolysis performance in terms of current efficiency (Eq. 6), it is convenient to represent the COD variation as a function of the charge (or time). Figure 8 confirms that COD removal is more effective with a BDD anode than with  $\text{PbO}_2$ , whatever the current density value. On a BDD anode COD removal was very close to 100%, while under the same conditions a  $\text{PbO}_2$  anode hardly achieved 80%. COD removal, represented as function of charge, increases with decrease in applied current density for the two materials. Furthermore, Fig. 8 shows that results with BDD corresponding to the three current densities are very close to some of the others, in contrast to the representative curves for  $\text{PbO}_2$ .

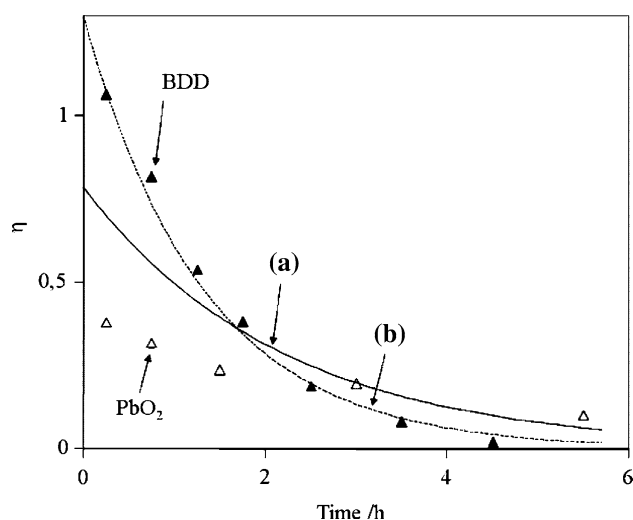
The experimental COD-values give an estimate of the instantaneous current efficiency. As such, for electrolyses conducted on BDD and  $\text{PbO}_2$ , and for a current density of  $47 \text{ mA cm}^{-2}$ , Fig. 9 presents the variations of (a) the instantaneous current efficiencies  $\eta$  (calculated from experimental results using Eq. 1), (b) the theoretical efficiency represented as a continuous line and (c) the phenol concentration. In the case of the BDD electrode, the instantaneous current efficiency  $\eta$  is in good agreement with Eq. 1 applied for theoretical COD. On the other hand,  $\eta$  calculated from COD measurements for electrolysis conducted on  $\text{PbO}_2$  (dotted line, Fig. 9) are lower than for the BDD electrode in the zone limited by charge transfer. Under this current density ( $i = 47 \text{ mA cm}^{-2}$ ), the change in the kinetic regime of COD occurs after about 3 h and coincides with more than 80% removal of the initial concentration of phenol. Figure 9 gives a good illustration of

the large difference between kinetic regimes when one speaks about COD removal and the oxidation rate of the initial phenol molecule which, according to Fig. 6, is essentially controlled by mass transfer.

In Fig. 6, we saw that the rate of the initial oxidation of phenol during electrolysis at  $142 \text{ mA cm}^{-2}$  was the same whatever the electrode material. As the profiles of COD



**Fig. 9** Comparison between BDD and  $\text{PbO}_2$  anode on variation of experimental (symbols), theoretical (line) instantaneous current efficiency:  $\diamond$  BDD,  $\square$   $\text{PbO}_2$  and on variation of phenol concentration:  $\diamond$  BDD,  $\square$   $\text{PbO}_2$  during electrolysis of 1 L of 0.02 M phenol solution in 0.1 M  $\text{H}_2\text{SO}_4$ . Flow rate =  $200 \text{ L h}^{-1}$ . Reactor without separator; Anode: BDD or  $\text{PbO}_2$  ( $63.6 \text{ cm}^2$ ); cathode: Zr.  $i = 47 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^\circ = 108 \text{ mA cm}^{-2}$ . Critical time = 2.8 h



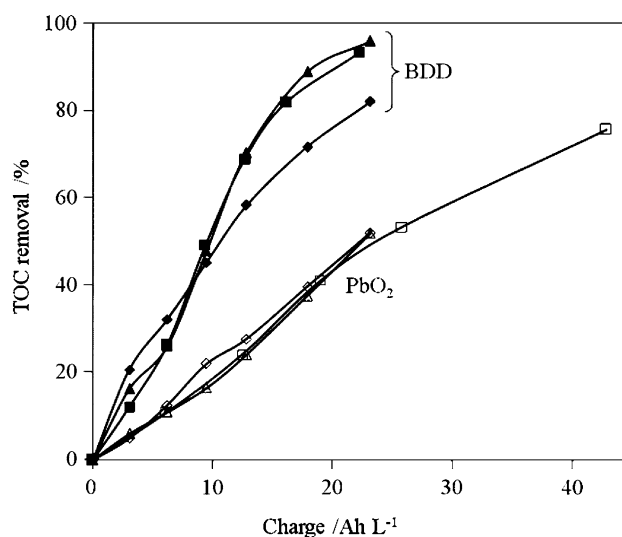
**Fig. 10** Experimental variation of instantaneous current efficiency (symbols) on BDD or PbO<sub>2</sub> anode during electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub> and theoretical variation (line) for two mass transfer coefficient values: (a):  $k_m = 2 \times 10^{-5} \text{ m s}^{-1}$ ; (b):  $k_m = 3.3 \times 10^{-5} \text{ m s}^{-1}$ . Flow rate = 200 L h<sup>-1</sup>. Reactor without separator; Anode: BDD or PbO<sub>2</sub> (63.6 cm<sup>2</sup>); cathode: Zr.  $i = 142 \text{ mA cm}^{-2}$ ;  $i_{\text{lim}}^{\circ} = 108 \text{ mA cm}^{-2}$

removal between the two materials are very different (Fig. 9), experimental current efficiency is presented in Fig. 10, together with the theoretical current efficiency. The efficiency obtained with the PbO<sub>2</sub> electrode is much lower than that obtained with BDD. For example at 0.75 h, the current efficiency is 81% with BDD while it hardly reaches 30% with PbO<sub>2</sub>. Even under a mass transfer regime, the PbO<sub>2</sub> electrode is globally less effective than BDD. However, for BDD, the experimental points are not in agreement with the theoretical curve (a) calculated with  $k_m$  equal to  $2 \times 10^{-5} \text{ m s}^{-1}$  (Fig. 10). The value of the mass transfer coefficient, can be adjusted to take into account modifications to the hydrodynamics due to oxygen evolution on the anode [26]. Taking the value of  $3.3 \times 10^{-5} \text{ m s}^{-1}$  for the mass transfer coefficient instead of  $2 \times 10^{-5} \text{ m s}^{-1}$ , a new curve of theoretical efficiency (b) can be superimposed on the experimental points.

### 3.3 Influence of flow rate

For an electrolysis conducted under the following conditions:  $i = 47 \text{ mA cm}^{-2}$ ,  $\Phi = 200 \text{ L h}^{-1}$  and  $C^0 = 20 \text{ mM}$ , the rate of COD abatement is controlled by charge transfer up to  $7.7 \text{ Ah L}^{-1}$  ( $4.3 \text{ Ah L}^{-1}$  for  $\Phi = 42$ ; and  $9.8 \text{ L h}^{-1}$  for  $\Phi = 336 \text{ L h}^{-1}$ , see Fig. 11).

Figure 11 presents the variation of TOC removal as function of charge during electrolysis of phenol solutions under a current density of  $47 \text{ mA cm}^{-2}$ , on both anode materials, and for flow rates of: 42, 200 and 336 L h<sup>-1</sup>.

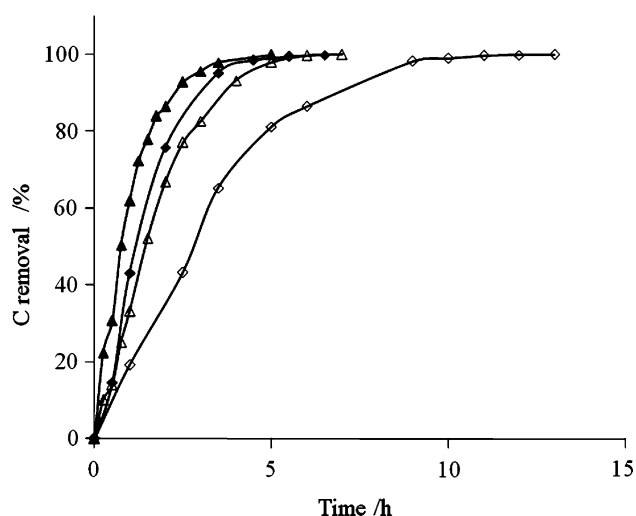


**Fig. 11** TOC removal during phenol oxidation. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Different flow rates:  $\blacklozenge$  42;  $\blacksquare$  200 or  $\blacktriangle$  336 L h<sup>-1</sup>. Reactor without separator; Anode: BDD or PbO<sub>2</sub> (63.6 cm<sup>2</sup>); cathode: Zr.  $i = 47 \text{ mA cm}^{-2}$

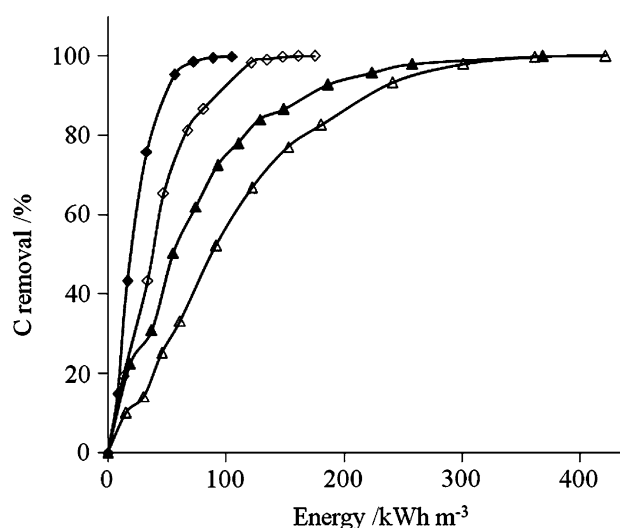
Curves on Fig. 11 clearly show a very marked difference between the efficiency of the two materials whatever the flow rate. The profile of TOC removal represented as a function of charge is identical for all flow rates in the case of lead dioxide. This means that diffusion is not the restricting factor on the overall process of phenol degradation on PbO<sub>2</sub>. In other words, analysed in terms of TOC (Fig. 11) or COD (not shown), the limitation of mineralization results from the relatively low capacity of PbO<sub>2</sub> to transfer oxygen atoms via hydroxyl radicals. Experiments performed with the BDD electrode show that, in a first zone up to about  $8 \text{ Ah L}^{-1}$ , TOC removal curves have a close resemblance for the three flow rates. On the other hand, above this charge, the TOC removal increased with increase in flow rate, this observation is in good agreement with the change in kinetic regime. Beyond this charge, results of electrolyses conducted with the two higher flow rates were similar. The same result were found by Cañizares et al. [15] who showed that the behaviour of several phenolic aqueous wastes on BDD is limited by the production of hydroxyl radicals and not by the mass transfer of the species at the electrode.

### 3.4 Energy consumption

The aim of this section is to calculate the energy consumption for electrochemical treatment of phenol solutions using the two electrode materials. The energy consumption was calculated for the treatment of 1 m<sup>3</sup> of solution and for a plant having the same surface/volume ratio as the laboratory cell ( $0.0636 \text{ cm}^{-1}$ ). The electrode surface would be



**Fig. 12** Aromatic concentration removal as function of time during phenol oxidation. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Flow rate = 200 L h<sup>-1</sup>. Reactor without separator; Anode: BDD (full symbols) or PbO<sub>2</sub> (open symbols); cathode: Zr: i: ◆ 47 or ▲ 142 mA cm<sup>-2</sup>;  $i_{lim}^{\circ} = 108$  mA cm<sup>-2</sup>



**Fig. 13** Aromatic concentration removal as function of energy consumption during phenol oxidation. Electrolysis of 1 L of 0.02 M phenol solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Flow rate = 200 L h<sup>-1</sup>. Reactor without separator; Anode: BDD (full symbols) or PbO<sub>2</sub> (open symbols); cathode: Zr: i: ◇ 47 or △ 142 mA cm<sup>-2</sup>;  $i_{lim}^{\circ} = 108$  mA cm<sup>-2</sup>

6.36 m<sup>2</sup> and would be obtained by using several electrodes. Whilst it is possible today to have PbO<sub>2</sub> electrode units (deposited on titanium) of the order of one square metre, BDD elements with an identical surface are not yet commercially available. Keeping the same A/V ratio, using the same current densities, composition of the solution and the same gap between electrodes, the voltage experimentally obtained in the laboratory cell can be used in this upper scale.

The criteria chosen to compare various experiments was the toxicity removal; where toxicity is essentially relevant to the presence of aromatic compounds. Indeed, phenol is a toxic compound, but quinones produced by its oxidation are even more toxic [1]. A solution was considered to be detoxified when the total concentration of aromatic intermediates was less than 1% of the initial phenol concentration. It was shown in part 4.1 that the amount of HQ, was not accurately measured in the case of the PbO<sub>2</sub> electrode due to the presence of coloured compounds having the same retention time. But we noted also that the HQ peak disappeared with the disappearance of colour. Using the concentration removal of aromatic compounds defined by Eq. 5, one can estimate the energy consumption with a PbO<sub>2</sub> anode.

$$C_{\text{removal}} = \frac{C_{\text{phenol}}^0 - C_{\text{arom}}}{C_{\text{phenol}}^0} \times 100. \quad (5)$$

The abatement of aromatic compounds (Eq. 5) is represented on Fig. 12 as function of time. Like in Figs. 7 and 8, the BDD electrode gives a better abatement than the PbO<sub>2</sub> electrode as function of time. An experiment using a

PbO<sub>2</sub> electrode under 47 mA cm<sup>-2</sup> was considerably less effective than that using BDD electrode. However, experiments conducted at 47 mA cm<sup>-2</sup> with BDD and 142 mA cm<sup>-2</sup> with PbO<sub>2</sub> reach 99% of aromatic removal in about 5 h (Fig. 12). For these experiments, the energy consumption is shown in Fig. 13. To remove 99% of aromatic compounds, the energy required is 80 kWh m<sup>-3</sup> (BDD, 47 mA cm<sup>-2</sup>) and 330 kWh m<sup>-3</sup> (PbO<sub>2</sub>, 142 mA cm<sup>-2</sup>). The diamond electrode is more energetically effective than PbO<sub>2</sub>. This difference is directly linked to electrolysis time which follows from electrocatalytic activity. Indeed, it should be remembered that, with a current density lower than the limiting value, the electrocatalytic activity of lead dioxide is less than that of diamond. To complete this economic evaluation, the capital cost of electrodes and their life time need to be taken into account.

## 4 Conclusions

The comparison of the performance of two electrode materials (PbO<sub>2</sub>, BDD) used in the same electrolysis device for the degradation of phenol as a model molecule have allowed us to show the difference of activity of these materials towards phenol and its intermediates. Under charge transfer control, phenol removal and strong TOC and COD abatement are reached much more quickly with BDD than with PbO<sub>2</sub>. When the kinetics are initially controlled by mass transfer, the rate of disappearance of phenol is the same on the two materials but in terms of



TOC or COD removal, BDD is more effective. Furthermore, the number and amount of intermediates are higher with PbO<sub>2</sub>. Therefore, it can be concluded that electrocatalytic activity of BDD is better, because the number of exchanged electrons for each molecule is close to its maximum value. Cell voltages measured for a given current density are similar with the two materials; thus the main criteria to determine energy consumption is the time required to reach complete removal of phenol and its aromatic intermediaries.

Using a device with a surface/volume ratio of 0.0636 cm<sup>-1</sup>, under a current density of 47 mA cm<sup>-2</sup>, a removal of 99% in aromatic compounds was obtained in about 5 h on a BDD anode. In this case the energy required was 80 kWh m<sup>-3</sup>, while the same abatement was reached with a PbO<sub>2</sub> anode under a current density of 142 mA cm<sup>-2</sup> but for an energy consumption of 330 kWh m<sup>-3</sup>.

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