

## Degradation of phenol using Co- and Co,F-doped PbO<sub>2</sub> anodes in electrochemical filter-press cells

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### Abstract

A comparative study on the electrooxidation of phenol in H<sub>2</sub>SO<sub>4</sub> medium using pure PbO<sub>2</sub> or F-, Co- and Co,F-doped PbO<sub>2</sub> electrodes in filter-press cells was carried out. The oxide films were obtained by galvanostatic electrodeposition using an electrolytic bath containing sodium lauryl sulfate as additive and Pb<sup>2+</sup>, F<sup>-</sup>, Co<sup>2+</sup> or Co<sup>2+</sup> + F<sup>-</sup>, under magnetic stirring (to obtain 4-cm<sup>2</sup> electrodes) or ultrasound waves (to obtain 63-cm<sup>2</sup> electrodes). The best results were attained with PbO<sub>2</sub> electrodes doped with a low-Co content (1 mM Co<sup>2+</sup> in the electrolytic bath) along with F<sup>-</sup>: the chemical oxygen demand (COD) and the total organic carbon content (TOC) of the simulated wastewaters were removed by about 75% and 50%, respectively. When pure PbO<sub>2</sub> electrodes were used, the COD and TOC removals were about 60% and 45%, respectively. For the smaller electrodes, an average current efficiency (ACE) and an energy consumption (EC) of about 16% and 70 kWh kg<sub>COD</sub><sup>-1</sup>, respectively, were obtained. For the larger electrodes, the ACE and EC values were about 18% and 105 kWh kg<sub>COD</sub><sup>-1</sup>, respectively. Stability tests of the electrodes showed that they are suitable for use in the electrochemical treatment of phenol wastewaters.

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### 1. Introduction

Phenolic compounds are commonly present in wastewater produced by several industries, among them oil refineries, coke, plastics, and chemical plants. Thus, before discharge these compounds must be removed from the wastewater due to their toxicity. Because of their refractory chemical nature, the use of biological treatments becomes inadequate [1]. As a consequence, several types of treatments have been proposed for the degradation and destruction of aromatic compounds. Among them, Fenton's oxidation processes [2,3], ozonization [4], and supercritical water oxidation [5] are being tested in different studies involving wastewater treatment. Beside these, electrochemical methods are also being tested as alter-

native and quite promising processes for this end [6–8]. In these processes, aromatic compounds can be converted into biodegradable substances or, eventually, electrochemically mineralized (electrochemical combustion) [9].

In processes involving the anodic oxidation of organic molecules or the production of ozone by electrochemical means, a high overpotential for the oxygen evolution reaction (OER) is desirable, since it leads to higher global current efficiencies. Indeed, a high overpotential is very important when electrooxidatively degrading organic compounds, despite not being the only expected characteristic for the electrode material. Some materials (e.g., Au and Pt) that present a low-OER overpotential have oxygenated species available on their surfaces (formed from the water dissociation reaction), capable of promoting the oxidation of the organic compound. But, in spite of this, their low-OER overpotential commonly leads to a low rate constant for this oxidation reaction, something undesirable beside the cost of these materials. Consequently, many authors have investigated different electrode materials (glassy carbon, tin

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dioxide, lead dioxide, boron-doped diamond (BDD), etc.) for the oxidation of phenolic compounds, at a more fundamental level as well as in electrochemical reactors, as recently reviewed in detail by Martínez-Huitile and Ferro [8]. Some of these authors followed the phenol anodic degradation determining the oxidation products and their evolution with time, showing that the nature of these products and their concentrations strongly depend on the electrode material under investigation. Furthermore, several other variables may influence the phenol electrooxidation process: solution composition and pH, phenol concentration, employed current density, and temperature. It should be noted that, in studies with the goal of electrooxidising organic compounds, phenol has been used as a model compound, i.e., the conclusions obtained from its degradation studies are assumed to be applicable to several other aromatic compounds. Taking into account that, depending on the experimental conditions, the oxidation of phenol can lead to the formation of a polymeric film on the electrode, some papers were devoted to the characterisation of these films and to understanding their formation process [21,23].

PbO<sub>2</sub> calls the attention as an electrode material due to its easy and rapid preparation, besides being of low cost and quite stable in high-applied potentials in media of different pHs. Its electrocatalytical activity as well as its stability can be significantly improved by the incorporation of doping ions into its crystalline matrix, previously added to the electrodeposition bath. Among them, Fe<sup>3+</sup> [18,24,25], Bi<sup>3+</sup> [17,18,26,27], Co<sup>2+</sup> [28], and F<sup>-</sup> [29] have been considered as good dopants towards the oxygen transfer reaction, as well as ozone production.

Several papers were published reporting on the performance of PbO<sub>2</sub> electrodes in the electrooxidation of phenol [6,10–19,30–33]. Nevertheless, not many of them deal with the effect of doping on the PbO<sub>2</sub> electrochemical performance in the treatment of wastewater containing phenolic compounds using small- [14,27] or larger scale systems [17,26].

Considering the above, the main goal of this work is the investigation of the performance of pure or Co and F (together or separately) doped β-PbO<sub>2</sub> electrodes in the electrooxidation of simulated phenol wastewaters in two different filter-press cells systems: a small-scale one (0.18 L/electrodeposited PbO<sub>2</sub>) and a larger scale one (1.0 L/sonoelectrodeposited PbO<sub>2</sub>).

## 2. Materials and methods

### 2.1. Chemicals

All chemicals, including Pb(NO<sub>3</sub>)<sub>2</sub> (a.r., Acros, New Jersey, USA), sodium lauryl sulfate, SLS (98.5%, Aldrich), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (a.r., New Jersey, USA), NaF (ACS reagent, Acros, New Jersey, USA), H<sub>2</sub>PtCl<sub>6</sub> (99.9%, Aldrich), phenol (Merck), *p*-benzoquinone, hydroquinone, cathecol (Acros), and methanol (HPLC grade, Mallinckrodt), were used as received. Water was purified using a Milli-Q system (Millipore). Buffer solutions used as part of the chromatographic mobile phase were prepared using sodium monohydrogenphosphate (Merck) and phosphoric acid (Merck).

### 2.2. Preparation of the pure and doped PbO<sub>2</sub> electrodes

#### 2.2.1. Small-scale electrodes (4-cm<sup>2</sup> geometric area)

The preparation of the platinised titanium plate substrate was previously described elsewhere [34,35]. The pure and doped-PbO<sub>2</sub> films were electrodeposited (20 mA cm<sup>-2</sup>) on Ti–Pt substrates using a conventional one-compartment cell. The electrolysis times were set by assuming Faradays' laws (100% efficiency) for obtaining an amount of deposited oxide equal to 50 mg cm<sup>-2</sup>. The electrodeposition bath composition consisted of 0.100 M Pb(NO<sub>3</sub>)<sub>2</sub> plus 0.5 g L<sup>-1</sup> SLS in 0.1 M HNO<sub>3</sub>. When the Co- and Co,F-doped electrodes were prepared, 0.001, 0.010 and 0.100 M Co(NO<sub>3</sub>)<sub>2</sub>, and/or 0.030 M NaF, respectively, were added to the electrodeposition bath. In all cases the electrodeposition process was carried out at 65 °C, under magnetic stirring conditions. As soon as the electrodes were produced, they were immersed in water previously heated at 65 °C and left immersed until room temperature was reached. This procedure was carried out mainly to avoid stresses in the deposits.

#### 2.2.2. Larger scale electrodes (63-cm<sup>2</sup> geometric area)

Larger Ti–Pt/β-PbO<sub>2</sub> electrodes were prepared by electrodepositing the oxide films on Ti–Pt meshes. This was done in order to further investigate the efficiency of the electrodes that presented the best performances in the electrooxidation of phenol in the small-scale system. The preparation of these larger electrodes was similar to the one described above (Section 2.2.1), except that 30 kHz/100 W ultrasound waves were applied in order to assure adequate mass transport. It is worthwhile noting that recently the use of the sonoelectrochemical technology in the deposition of electrode materials has led to quite promising and interesting results, mainly because it assures an increased mass transfer due to the reduction of the diffusion layer thickness, besides causing changes in the nucleation and crystallisation processes [36].

### 2.3. Chemical characterization of the doped PbO<sub>2</sub> films

The Co content in the doped PbO<sub>2</sub> films was determined by atomic absorption spectroscopy (Varian, AA 640 model). For such, the doped films were dissolved in a 10% HNO<sub>3</sub> plus 3% H<sub>2</sub>O<sub>2</sub> solution for 5 min at room temperature. Co-containing solutions were applied into the injection channel and the obtained results were expressed as mass percentage relative to the total mass of oxide coating.

### 2.4. Chemical characterisation of the phenol electrolysis

High-performance liquid chromatography (HPLC) was used to characterise the chemical composition of the simulated wastewater with electrolysis time (charge passed). A HP 1050 HPLC chromatograph with a 1050 M detector system was used. The mobile phase used was a mixture of 0.01 mol L<sup>-1</sup> potassium monohydrogenphosphate (pH adjusted to 3 with H<sub>3</sub>PO<sub>4</sub>) and methanol in the volumetric proportion 80:20. The flow rate used was 1.0 mL min<sup>-1</sup> and detection was monitored at λ = 254 nm. The analytical column (250 mm × 4.6 mm) used was Hipersil

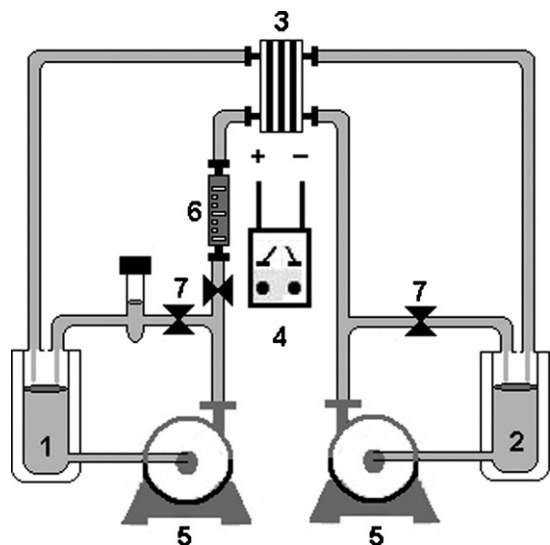


Fig. 1. Schematic representation of the system used with both small- and large-scale electrodes: (1) thermostatic anolyte reservoir; (2) thermostatic catholyte reservoir; (3) electrochemical reactor; (4) power supply; (5) pump; (6) flow meter; (7) bypass.

ODS C18. Double deionised water from a Millipore Milli-Q system was used for the preparation of all solutions.

The chemical oxygen demand (COD) of the simulated phenol wastewater was determined at different times (up to different amounts of charge passed through the cell) using a Hach DR 2000 analyser at a wavelength of 620 nm. The total organic carbon content (TOC) of the simulated wastewater was also determined at different times using a Shimadzu 5000 TOC analyser.

## 2.5. Phenol electrooxidation

### 2.5.1. Small-scale electrodes

The small-scale electrodes were used in the electrooxidation ( $100 \text{ mA cm}^{-2}$ ) of 0.18 L of the simulated phenol wastewater ( $500 \text{ mg L}^{-1}$  phenol in  $0.5 \text{ M H}_2\text{SO}_4$ ) in an acrylic filter-press reactor (at the maximum possible flow rate:  $\sim 50 \text{ L h}^{-1}$ ) with separate anodic and cathodic compartments (see system setup in Fig. 1);  $0.5 \text{ M H}_2\text{SO}_4$  was used as catholyte. The gap between the membrane and the electrodes was about 0.2 cm. This separation was accomplished by using a Nafion 117 (Du Pont) cationic membrane, since it is stable in the chosen electrolysis conditions. The wastewater was kept at  $40^\circ\text{C}$  in all the experiments, since this temperature is normally considered as the highest limit for discharge by treatment plants into municipal sewer systems. These experiments were carried out until the total charge passed was equal to four times the theoretical value necessary for the complete mineralization of the phenol molecules contained in the sample of simulated wastewater.

### 2.5.2. Larger scale electrodes

The larger scale electrodes were used in the electrooxidation ( $100 \text{ mA cm}^{-2}$ ) of 1.0 L of the simulated phenol wastewater ( $1000 \text{ mg L}^{-1}$  phenol in  $0.5 \text{ M H}_2\text{SO}_4$ ) in a polypropylene filter-press reactor (at the maximum possible flow rate:  $\sim 75 \text{ L h}^{-1}$ ),

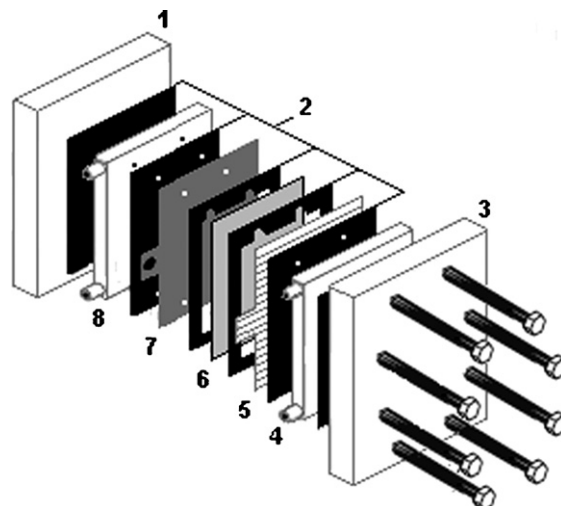


Fig. 2. Schematic representation of the large-scale electrode filter-press reactor used in the simulated wastewater electrolyses. (1) and (3) End plates; (2) silicone gaskets; (4) anodic compartment; (5) working electrode (anode); (6) membrane; (7) counter electrode (cathode–nickel plate); (8) cathodic compartment.

also with separate anodic and cathodic compartments;  $0.5 \text{ M H}_2\text{SO}_4$  was used as catholyte. In this system, the gap between the membrane and the electrodes was about 0.4 cm (Fig. 2). In these experiments, the chemical composition of the simulated wastewater after different electrolysis times was analysed using HPLC, besides determining its COD and TOC. The total amount of charge passed was also equal to four times the theoretical value necessary for the complete mineralization of the phenol molecules contained in the sample of simulated wastewater.

## 2.6. Electrode stability

For the doped electrode that presented the best performance in the phenol electrooxidation in the small-scale system, a stability test (up to 50 h) was performed by anodic polarization at  $100 \text{ mA cm}^{-2}$  [37] in a  $0.5 \text{ M H}_2\text{SO}_4$  solution at  $40^\circ\text{C}$ ; for comparison purposes, the same test was done for the pure  $\text{PbO}_2$  electrode. In these tests a conventional one-compartment cell was used and two DSA–Ru (Denora) plates were used as counter electrodes. The anode potential was monitored with time, and the electrode would be considered as deactivated if its potential became equal to that of the Ti–Pt substrate under the same experimental conditions [37].

After each stability test, mass loss of the electrode  $\text{PbO}_2$  film was checked, after drying it at  $90^\circ\text{C}$  for 1 h.

## 3. Results and discussion

### 3.1. Electrode preparation

The influence of the  $\text{Co}^{2+}$  concentration in the electrodeposition bath on the Co amounts deposited in the produced  $\text{PbO}_2$  films, in the absence or presence of F, was investigated and the obtained results are shown in Table 1. Regardless of the presence of  $\text{F}^-$ , the Co content in the  $\text{PbO}_2$  films increases with the  $\text{Co}^{2+}$  concentration in the electrodeposition bath. A 10-fold

increase in the  $\text{Co}^{2+}$  concentration in the electrodeposition bath resulted in an increase of between 2.0 and 2.5 times in the Co content in the films, reaching a value of approximately 0.1% (m/m). These results could be expected taking into account the greater availability of  $\text{Co}^{2+}$  ions in the bath to be incorporated into the films. As already pointed out, the presence of  $\text{F}^-$  ions did not promote a greater incorporation of Co into the films, contrary to what should be expected due to the formation of the  $[\text{Co}(\text{OH}_x)\text{F}_y]^{(2-x-y)}$  complex in solution [28]. A similar behaviour was observed when the  $\text{PbO}_2$  films were doped with Fe and F [35] and was explained as due to the presence of SLS in the electrodeposition bath, which by being weakly adsorbed on the electrode surface hinders the approach of the complex to the electrode surface and thus acts as a steric barrier for the incorporation of the dopant (through the complex) into the oxide.

### 3.2. Phenol electrooxidation

#### 3.2.1. Small-scale electrodes

First the phenol electrooxidation at the different obtained  $\text{PbO}_2$  electrodes was investigated by COD and TOC measurements. These experiments were carried out in order to identify the electrode compositions that led to better oxidation performances so as to prepare similar larger scale electrodes to be used in experiments where the identification and quantification of the main oxidation products would be carried out by HPLC.

From the results presented in Table 1, it can be seen that for the pure oxide electrode after a total charge passed ( $Q_F$ ) of  $16.7 \text{ Ah L}^{-1}$  the COD and TOC decreased by almost 60% and 45%, respectively. At the beginning of the electrolysis, the simulated wastewater quickly became yellowish, a coloration that disappeared after the charge passed reached a value of about  $12 \text{ Ah L}^{-1}$ . In these experiments the oxidation products were not identified; however, it is well known that the formation of *p*-benzoquinone (yellow when in solution) is quite probable in this process, particularly when the medium is acidic [6,10–15,17–19,31,38].

Furthermore the COD results presented in Table 1 indicate that the performance of the pure  $\text{PbO}_2$  electrode may be further improved by the incorporation of dopants such as F and Co. The doping of the electrode with F or Co only has a significant effect on the COD removal, but the organic-charge mineralization pro-

cess (TOC) is barely altered. On the other hand, the doping of the electrode with a high Co content (10 mM Co-doped  $\text{PbO}_2$ ) had a negative effect, since the COD removal is smaller (despite the TOC removal being practically the same) than that attained when the 1 mM Co-doped  $\text{PbO}_2$  electrode was used, differing by about 22%. It should be noted that electrodes with a higher Co content had a lower OER overpotential [39], thus favouring the selective oxidation of phenol. COD and TOC removals for the 1 mM Co,F-doped  $\text{PbO}_2$  electrode are quite similar to the ones attained with the electrode doped with F only, although the former presented a slightly higher TOC removal.

A possible explanation for the better performance of the Co-doped electrodes is that low Co contents in the Co- or Co,F-doped  $\text{PbO}_2$  electrodes modify the superficial properties of the films, improving the phenol adsorption on their surfaces (pre-adsorption), which would lead to an increased residence time of the species at the electrode surfaces [18]. This would justify the best results for these electrodes in the COD removal, since the probability of successful oxidation is increased.

The average current efficiencies (ACE) for the electrooxidations after a  $Q_F$  of  $16.7 \text{ Ah L}^{-1}$  were calculated using the following equation [22]:

$$\text{ACE} = \frac{[(\text{COD})_0 - (\text{COD})_t]FV}{8It} \times 100 \quad (1)$$

where  $(\text{COD})_0$  and  $(\text{COD})_t$  are the initial COD ( $\text{g L}^{-1}$ ) and the COD after a time  $t$  (s), respectively,  $I$  is the applied current (A),  $F$  the Faraday constant, and  $V$  the simulated-wastewater volume (L). The obtained ACE values from 10.9% to 17.5% were quite low, as expected since the value of  $Q_F$  is four times the theoretical value necessary for the complete mineralization of the amount of phenol contained in the sample of simulated wastewater. In any case, ACE decreases with the Co-doping content. This trend occurs because an increase in the Co-doping in the oxide films leads to a decrease in the OER overpotential [39] (vide supra). It should be noted that electrode passivation due to polymeric film formation can be practically neglected, since the experimental conditions tested here are considered to be unfavourable to this formation: low pH of the simulated wastewater and constant removal of reaction products from the electrode surface promoted by the wastewater flow in the filter-press reactor.

Table 1

Co content of the different small-scale ( $4 \text{ cm}^2$ ) doped  $\text{PbO}_2$  electrodes and their performances (pure and F-doped  $\text{PbO}_2$  electrodes also included) toward COD and TOC removal in the electrolysis ( $100 \text{ mA cm}^{-2}$ ,  $Q_F = 16.7 \text{ Ah L}^{-1}$ ) of a simulated phenol wastewater ( $500 \text{ mg L}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$ ). Average current efficiencies (ACE) and energy consumptions (EC) also shown

Electrode	Co content (mass%)	COD removal (%)	TOC removal (%)	ACE (%)	EC ( $\text{kWh kg}_{\text{COD}}^{-1}$ )
Ti-Pt/ $\text{PbO}_2$	–	58.4	43.6	12.8	89.0
Ti-Pt/ $\text{PbO}_2$ -F	–	74.2	46.7	17.5	65.2
Ti-Pt/ $\text{PbO}_2$ -Co (1 mM) <sup>a</sup>	0.04	71.6	45.1	14.3	79.8
Ti-Pt/ $\text{PbO}_2$ -Co (10 mM) <sup>a</sup>	0.12	49.5	43.2	10.9	100.4
Ti-Pt/ $\text{PbO}_2$ -Co,F (1 mM) <sup>a,b</sup>	0.04	74.2	49.3	15.7	72.7
Ti-Pt/ $\text{PbO}_2$ -Co,F (5 mM) <sup>a,b</sup>	0.08	58.4	48.4	14.2	80.3
Ti-Pt/ $\text{PbO}_2$ -Co,F (10 mM) <sup>a,b</sup>	0.10	43.8	37.0	11.2	101.6

<sup>a</sup>  $\text{Co}^{2+}$  concentration in the electrodeposition bath.

<sup>b</sup> 30 mM  $\text{F}^-$  in the electrodeposition bath.



The energy consumption (EC) for the removal of 1 kg of COD (measured in kWh kg<sub>COD</sub><sup>-1</sup>) was obtained by the use of the following equation [40]:

$$EC = \frac{tUI/V}{\Delta COD} \times 10^3 \quad (2)$$

where  $t$  is the electrolysis time (h),  $U$  the average electrolysis cell voltage (V),  $I$  the applied electrolysis current (A),  $V$  the simulated-wastewater volume (L), and  $\Delta$ COD the difference in COD (mg L<sup>-1</sup>).

As it can be seen in Table 1, the electrodes that presented the lowest EC values are the ones whose ACE values are highest. Rajkumar et al. [40] reported an EC value of 154 kWh kg<sub>COD</sub><sup>-1</sup> for the electrooxidation of phenol (500 mg L<sup>-1</sup>, 0.5 L, 27.7-cm<sup>2</sup> electrode, and 72 mA cm<sup>-2</sup>) using a Ti/TiO<sub>2</sub>-RuO<sub>2</sub>-IrO<sub>2</sub> electrode. However, this was attained only after Cl<sup>-</sup> (2500 mg L<sup>-1</sup>) was added into the solution. Yavuz and Koparal [41] using a Ti/TiO<sub>2</sub>-RuO<sub>2</sub> electrode and also investigating the electrooxidation of phenol (200 mg L<sup>-1</sup>, 0.5 L, four 6-cm<sup>2</sup> plates, and 15 mA cm<sup>-2</sup>) reported an EC value of 150.3 kWh m<sup>-3</sup> (corresponding to 366.6 kWh kg<sub>COD</sub><sup>-1</sup>). The fact that EC is much better for the PbO<sub>2</sub> electrode, even without Cl<sup>-</sup> addition, should be expected because the OER overpotential is much lower in dimensionally stable anodes (DSA), as it is the case of the Ti/TiO<sub>2</sub>-RuO<sub>2</sub>-IrO<sub>2</sub> and Ti/TiO<sub>2</sub>-RuO<sub>2</sub> electrodes; in another words, DSAs should not be expected to be good electrodes for wastewater electrooxidation. On the other hand, Iniesta et al. [26], using a pure PbO<sub>2</sub> electrode (63-cm<sup>2</sup> electrode and 100 mA cm<sup>-2</sup>) to degrade a real wastewater (containing 23 mg L<sup>-1</sup> phenol in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, along with other organic matter – COD<sub>0</sub> = 5700 mg L<sup>-1</sup>), reported a quite low EC value: 0.15 kWh L<sup>-1</sup> = 30 kWh kg<sub>COD</sub><sup>-1</sup>. However, it should be noted that the treated wastewater also contained a high Cl<sup>-</sup> concentration (7500 mg L<sup>-1</sup>).

Boron-doped diamond has been reported as an excellent electrode material for the electrooxidation of wastewater [8]. Thus, an electrolysis using a Nb/BDD electrode [20] was carried out using the same experimental conditions as with the PbO<sub>2</sub> electrodes, in order to compare their performances. The COD and TOC removals (85.2% and 83.4%, respectively) attained using the BDD electrode, for the same value of  $Q_F$ , were higher (with an ACE of 20.9%), confirming the excellent performance of this electrode material [8,16,42]. On the other hand, recently we compared the performance of BDD and PbO<sub>2</sub> electrodes in the electrooxidation of the Blue Reactive 19 dye, and the PbO<sub>2</sub> electrodes presented a similar performance [35]. From the above presented results, it can be concluded that the electrooxidation performances of the F-, 1 mM Co- and the 1 mM Co,F-doped electrodes were quite similar. However, for further investigation in the larger scale system, a Co-doped electrode should be chosen considering that Co doping might increase the oxide stability. Specifically, the 1 mM Co,F-doped electrode was chosen because of its higher ACE and lower EC values; a pure PbO<sub>2</sub> electrode and the 5 mM Co,F-doped electrode were also used for comparison purposes.

### 3.2.2. Larger scale electrodes

During the experiments using the larger electrodes, HPLC was used to determine the chemical composition of the simulated wastewater, besides monitoring its degradation through COD and TOC measurements. The main compounds found in the electrooxidised wastewater were phenol, hydroquinone, *p*-benzoquinone and fumaric acid. As it can be seen in Fig. 3 and Table 2, when either the pure or the Co,F-doped PbO<sub>2</sub> electrodes were used, phenol was always completely oxidised. On the other hand, the concentration of *p*-benzoquinone was always greater than that of hydroquinone, but both of them pass through a maximum at  $Q \leq 10$  Ah L<sup>-1</sup> and then decrease as the electrolyses proceed. These results show that the *p*-benzoquinone formation rate is greater than its degradation rate; thus and not surprisingly, the benzoquinone electrooxidation reaction can be considered as the limiting step in the phenol degradation. Tahar and Savall [13], using Ta/PbO<sub>2</sub> electrodes (in different conditions: 2000 mg L<sup>-1</sup> phenol, at 70 °C), also reported that the limiting step for this reaction was the *p*-benzoquinone degradation. In their work, hydroquinone was almost undetectable and all the *p*-benzoquinone was consumed after a  $Q$  of ~50 Ah L<sup>-1</sup>.

The variation of the phenol (Ph) concentration with time (see Fig. 3) clearly shows a first-order exponential decay, typical of reactions controlled by mass transport. Considering that the rate equation for this reaction can be written as

$$d[\text{Ph}] = -k_{\text{ap}}[\text{Ph}] dt \quad (3)$$

where  $k_{\text{ap}}$  is the reaction apparent rate constant, the rearrangement of this equation as  $d[\text{Ph}]/[\text{Ph}] = -k_{\text{ap}} dt$  followed by its integration from  $[\text{Ph}]_0 \rightarrow [\text{Ph}]$  and from  $0 \rightarrow t$ , yields the equation:

$$\ln \left( \frac{[\text{Ph}]}{[\text{Ph}]_0} \right) = -k_{\text{ap}} t \quad (4)$$

Considering that the number of electrons directly or indirectly transferred after the adsorption of phenol on the electrode surface is unknown, it is possible to estimate the apparent mass transport

Table 2

Reaction apparent rate constant ( $k_{\text{ap}}$ ), apparent mass transport coefficient ( $k_{\text{m}}$ ), compounds' concentrations, COD and TOC removals, average current efficiencies (ACE) and energy consumptions (EC) in the electrolysis (100 mA cm<sup>-2</sup>) of a simulated phenol wastewater (1000 mg L<sup>-1</sup> phenol in 0.5 M H<sub>2</sub>SO<sub>4</sub>) using larger scale (63 cm<sup>2</sup>) pure and Co,F-doped PbO<sub>2</sub> electrodes

	Pure PbO <sub>2</sub>	1 mM Co,F-doped PbO <sub>2</sub>	5 mM Co,F-doped PbO <sub>2</sub>
$k_{\text{m}}$ ( $\times 10^{-5}$ m s <sup>-1</sup> )	14.6	8.73	14.1
$k_{\text{ap}}$ (h <sup>-1</sup> )	3.32	1.98	3.21
[Phenol] (mg L <sup>-1</sup> )	–	–	–
[Benzoquinone] (mg L <sup>-1</sup> )	43.1	82.2	182.0
[Hydroquinone] (mg L <sup>-1</sup> )	2.2	3.9	19.0
[Fumaric acid] (mg L <sup>-1</sup> )	8.65	2.86	26.8
COD removal (%)	63.4	75.4	48.8
TOC removal (%)	43.4	50.7	36.6
ACE (%)	14.6	18.2	11.6
EC (kWh kg <sub>COD</sub> <sup>-1</sup> )	132	105	165

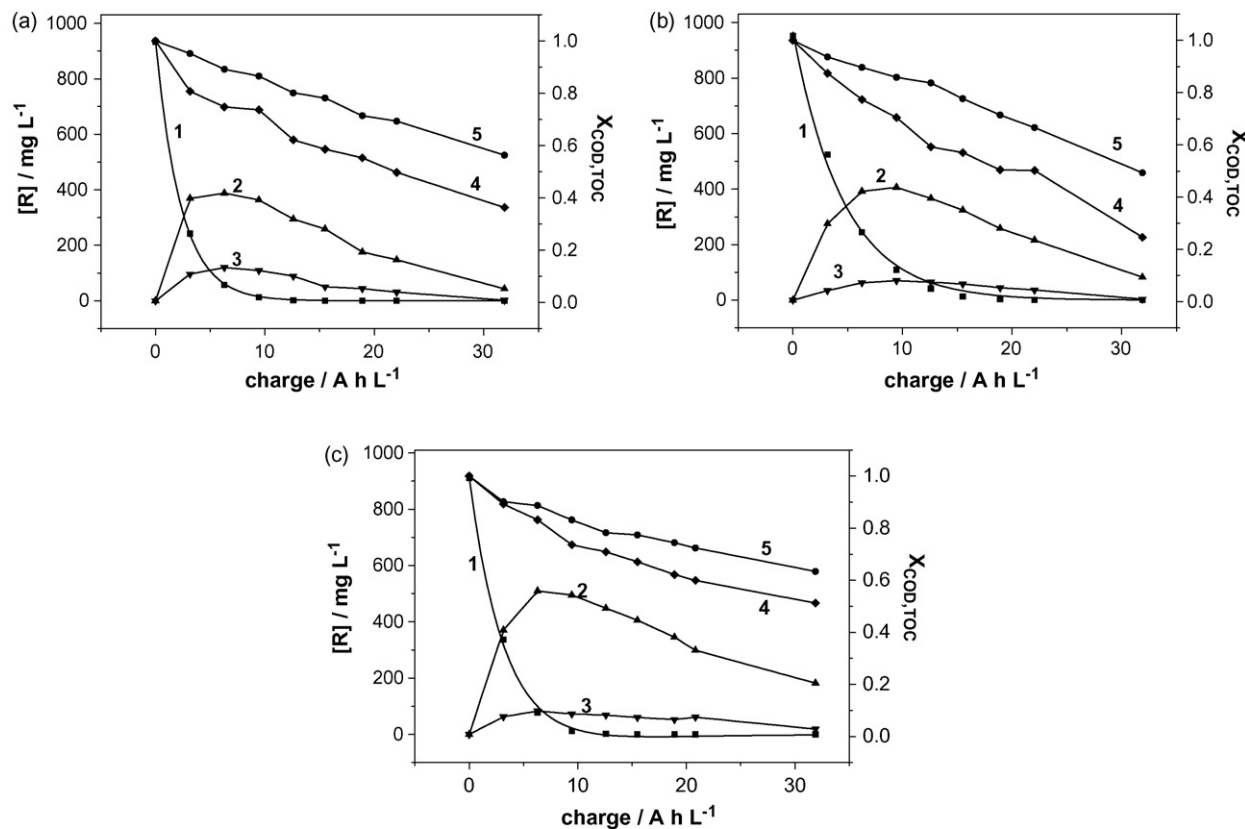


Fig. 3. Phenol, *p*-benzoquinone, and hydroquinone concentrations and normalized COD and TOC vs. charge passed for the electrooxidation ( $100 \text{ mA cm}^{-2}$ ) of the simulated phenol wastewater ( $1000 \text{ mg L}^{-1}$ ,  $1 \text{ L}$ ,  $40^\circ\text{C}$ , and  $\sim 120 \text{ L h}^{-1}$ ) using the following electrodes: (a) pure  $\text{PbO}_2$ , (b)  $1 \text{ mM Co,F-doped PbO}_2$  and (c)  $5 \text{ mM Co,F-doped PbO}_2$ . (1) Phenol, (2) *p*-benzoquinone, (3) hydroquinone, (4) normalised COD ( $X_{\text{COD}}$ ), (5) normalised TOC ( $X_{\text{TOC}}$ ).

coefficient,  $k_m$  from  $k_{\text{ap}}$ , since [13]:

$$k_{\text{ap}} = k_m \left( \frac{A}{V} \right) \quad (5)$$

where  $A$  is the electrode area and  $V$  is the volume of electrolysed wastewater.

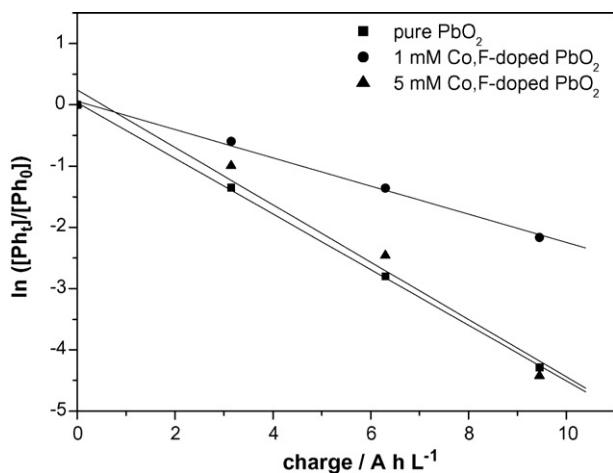


Fig. 4. Natural logarithm of the normalized phenol concentration vs. charge passed for the electrooxidation of the simulated phenol wastewater using different electrodes (data from Fig. 3).

Fig. 4 shows that  $\ln([Ph]/[Ph]_0)$  varies linearly with  $Q$ , confirming that the reaction is controlled by mass transfer when carried out using either the pure or the Co,F-doped  $\text{PbO}_2$  electrodes. The smallest values of  $k_{\text{ap}}$  and  $k_m$  were obtained for the  $1 \text{ mM Co,F-doped PbO}_2$  electrode, coherent with the data in Figs. 3(b) and 4 that show a somewhat slower decrease of the phenol concentration with time when this electrode was used. However, when the values of the COD and TOC removals are compared (see Table 2), the best performance is the one presented by the  $1 \text{ mM Co,F-doped PbO}_2$  electrode, which also presents the highest value of ACE and the lowest of EC. It should be noted that the values of ACE and COD and TOC removal using the larger electrodes are in the same range as those obtained using the smaller ones (vide supra); however, the EC values are greater for the larger electrodes, due to greater cell voltages associated to larger gaps between electrodes.

As pointed out before, at the end of the electrolyses phenol was always completely consumed, while *p*-benzoquinone, hydroquinone and fumaric acid remained in the simulated wastewater in different concentrations (see Table 2). As far as the consumption of the aromatic compounds is concerned, the pure  $\text{PbO}_2$  electrode presented the best performance, since the corresponding remaining *p*-benzoquinone and hydroquinone concentrations are the lowest,  $43.1$  and  $2.2 \text{ mg L}^{-1}$ , respectively (along with  $8.65 \text{ mg L}^{-1}$  for fumaric acid). It should be noted though that the sum of these remaining concentrations corresponds to only  $9.8\%$  and  $7.8\%$  of the remaining COD and

TOC, respectively, indicating that at the end of the electrolysis other non-identified organic compounds were present in the wastewater, possibly aliphatic acids; this is also confirmed by the electrolyses carried out with the other electrodes. The results here reported are coherent with mechanisms reported in the literature, as recently briefly reviewed by Yavuz and Koparal [41], that is: phenol oxidation to aromatic (benzoquinone and hydroquinone) and aliphatic (fumaric acid) intermediates, followed by final mineralization to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The results presented in Table 2 show that the 1 mM Co,F-doped  $\text{PbO}_2$  electrode clearly presents a better performance in the oxidation of aliphatic acids (the fumaric acid concentration is much lower), leading to a higher removal of the organic load. Again, a possible explanation might be that the low Co content in the electrode modifies the superficial properties of the film, improving the fumaric acid adsorption on its surface.

The data hereinbefore presented showed that the 1 mM Co,F-doped  $\text{PbO}_2$  electrode despite being slower in degrading phenol presented the best performance from the point of view of COD and TOC removal, along with the highest ACE and the lowest EC ( $105 \text{ kWh kg}_{\text{COD}}^{-1}$ ) values. Thus it is interesting to estimate the cost of removing 1 kg of COD from the simulated wastewater containing phenol ( $1000 \text{ mg L}^{-1}$ , corresponding to a COD of  $2286 \text{ mg L}^{-1}$ ) using this electrode. Considering that in Brazil the average cost of the kWh is  $\sim\text{US\$ } 0.14$  ( $\sim\text{R\$ } 0.30$ ), the cost of removing 1 kg of COD from the simulated wastewater would be  $\sim\text{US\$ } 14.70$  ( $\sim\text{R\$ } 31.50$ ); in another words, at this cost, about  $0.44 \text{ m}^3$  of the simulated wastewater could be partially treated. This cost is higher than the one associated to a biological treatment; however, for the phenol concentration here investigated, biological treatments are mostly inapplicable due to high toxicity.

### 3.3. Electrode stability

As noted recently [35], electrodes are considered viable for practical applications when they present characteristics such as high efficiency for the reaction of interest, low cost, easiness of production, and physical and chemical stabilities in aggressive media. Thus, to check on these stabilities, a stability test was carried out for the electrode with best performance in the electrooxidation of the simulated phenol wastewater, i.e., the 1 mM Co,F-doped  $\text{PbO}_2$  electrode (the same test was done for the pure  $\text{PbO}_2$  electrode). The service lifetime for these electrodes could be defined as the time at which the anode potential becomes equal to the value for the platinised titanium substrate ( $\sim 1.8 \text{ V vs. SCE}$ ) in the same experimental conditions. In accordance with Fig. 5, both electrodes show good electrochemical stability, indicated by the stability of their potential values; these results indicate that these electrodes' service lifetimes are greater than 50 h in the experimental conditions tested. Moreover, the 1 mM Co,F-doped  $\text{PbO}_2$  electrode also presented good chemical stability, since at the end of 50 h of electrolysis it lost only 0.13% of its mass (a rate of mass loss about 0.06% per day). In the case of the pure  $\text{PbO}_2$  electrode this mass loss was  $\sim 4.5$  times greater, indicating that the doping with Co and F results in higher corrosion resistance. This may result from the fact that the

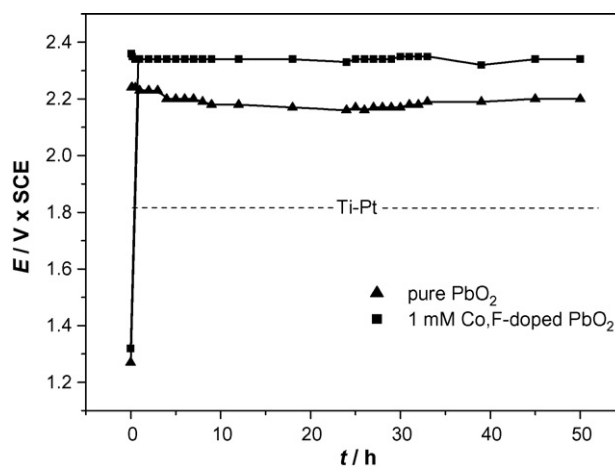


Fig. 5. Electrode stability tests: electrode potential vs. time for the electrolysis ( $100 \text{ mA cm}^{-2}$ ,  $40^\circ\text{C}$ ) of  $0.5 \text{ M H}_2\text{SO}_4$  using pure and 1 mM Co,F-doped  $\text{PbO}_2$  electrodes.

Co-doped films are more compact, as verified by MEV analyses [39]. Previously, when this same stability test was carried out for a 1 mM Fe,F-doped  $\text{PbO}_2$  electrode used in the electrooxidation of a simulated BR-19 dye wastewater [35], an opposite result was obtained, since the Fe,F-doped electrode presented a lower corrosion resistance than the pure electrode. Recently, Zhou et al. [43] compared the service lifetime of a pure  $\beta\text{-PbO}_2$  electrode and a  $\beta\text{-PbO}_2$  electrode modified with a fluorine resin (at  $120 \text{ mA cm}^{-2}$ ,  $9 \text{ M H}_2\text{SO}_4$ ,  $90^\circ\text{C}$ ). Under these drastic conditions, they found that the pure  $\beta\text{-PbO}_2$  electrode was not stable; it lost 6.74% of the oxide mass after 2 days. On the other hand, the  $\beta\text{-PbO}_2$  electrode modified with a fluorine resin was found to be very stable and its service lifetime was estimated as being roughly 10.4 years.

## 4. Conclusions

Small-scale pure, Co-, F- and Co,F-doped  $\text{PbO}_2$  electrodes as well as larger scale pure and Co,F-doped  $\text{PbO}_2$  electrodes were prepared onto platinised titanium substrates by anodic oxidation of solutions containing different  $\text{Co}^{2+}$  to  $\text{Pb}^{2+}$  ratios in the electrodeposition bath. The addition of SLS to the electrodeposition bath led to oxide films of much better quality; however, for the Co,F-doped films, this additive inhibited a greater incorporation of Co into the films in the presence of  $\text{F}^-$  ions in the bath. In the case of the larger scale electrodes, the use of ultrasound waves was necessary in order to obtain films with an adequate quality.

The results obtained by using pure, Co- and Co,F-doped  $\text{PbO}_2$  electrodes in the electrooxidation of phenol showed that the doping of the oxide by adding 1 mM  $\text{Co}^{2+}$  (alone or along with  $\text{F}^-$ ) to the electrodeposition bath leads to better performances in the effective degradation of that compound (monitored by COD and TOC). At the same time, the degradation of reaction intermediates such as *p*-benzoquinone and hydroquinone becomes less effective. The use of oxide electrodes with higher Co contents favours selective electrooxidation, yielding higher concentrations of the reaction intermediates at the end of the

electrolyses; this behaviour is due to the increased OER electrocatalytic activity brought on by the higher Co contents in the PbO<sub>2</sub>.

The results of stability tests for the pure and the 1 mM Co,F-doped PbO<sub>2</sub> electrodes showed their chemical and electrochemical stability to be suitable for their use in the electrochemical treatment of phenol wastewaters, but the Co,F-doped electrode is more stable. Finally, considering that the energy consumption might be high for the total degradation of these wastewaters, their electrooxidation could be carried out as a pre-treatment, such that the more toxic compounds would be partially oxidised and then completely digested by bacteria used in a biological treatment. This is something currently under investigation.

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