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Electrochemical oxidation of *trans*-3,4-dihydroxycinnamic acid at PbO_2 electrodes: direct electrolysis and ozone mediated reactions compared

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Abstract

A comparative study of the oxidative degradation of *trans*-3,4-dihydroxycinnamic acid was carried out using three different methods, two of which have in common the use of electrogenerated ozone as a potential oxidant: (i) direct electrolysis; (ii) external cell chemical reactions with O_3; and (iii) a 'cathodic oxidation' in which an O_2/O_3 mixture is fed into the cathodic compartment containing the organic substrate; H_2O_2 produced reacts with ozone to yield radicals that bring about the demolition of the organic compound. The nature products formed by the direct electrochemical oxidation depends on potential. The degradation of dihydroxy-acid is observed only at relatively high potentials, where radical oxygen species are formed in a high amount by the oxidation of water. At relatively lower potentials the process shows stirring dependence and leads essentially to one oxidation product which is adsorbed on the electrode. A comparative examination of the results, considering also the requested amount of ozone as a parameter, shows that the external cell and cathodic oxidation are the most efficient methods. This confirms our previous data on the oxidation of phenolic compounds, and the cathodic oxidation with ozone emerges as a promising approach in the abatement of pollutants. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Lead dioxide; 3,4-Dihydroxycinnnamic acid; Ozone; Electrocatalysis; Pollutants

1. Introduction

The electrooxidation of a large number of organic and inorganic compounds on different electrode materials, including PbO_2, proceeds simultaneously with the evolution of oxygen. Highly oxidising oxygen species, as OH radicals, are formed during the anodic oxidation of water which are able, in turn, to oxidise most organic compounds. There is a vast literature on this subject, concerning both conducting [1–9] and semiconducting anodes [10–13].

At the high anodic potentials involved, the same oxygen species may be involved in the formation of O_3 in addition to O_2 [4–20], as illustrated by the pathway below:

$$H_2O \rightarrow H^+ + (OH)_{ads} + e^- \quad (1)$$

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$$(OH)_{ads} \rightarrow (O)_{ads} + H^+ + e^- \quad (2)$$

$$2(OH)_{ads} \rightarrow O_2 + 2H^+ + 2e^- \quad (3)$$

$$2(O)_{ads} \rightarrow O_2 \quad (4)$$

$$(O)_{ads} + O_2 \rightarrow O_3 \quad (5)$$

A mechanistic study on the role reactive oxygen intermediates in the formation of ozone at PbO_2 and at platinum has been published by Wabner and Gramow [20], using *p*-nitrosodimethylaniline as a radical trap. The authors also proposed that singlet oxygen, in addition to OH radicals, can be involved in oxidation reactions.

In our recent research work [21] we have compared different methods for the abatement of pollutants involving or not ozone formation at PbO_2 anodes: (i) direct electrolysis; (ii) ex-situ use of O_3 and (iii) combined use of anodically generated O_3 and H_2O_2 produced at an O_2 cathode (cathodic oxidation). We showed that the last method gives better results in the oxidation of 4-chlorophenol.

The encouraging results stimulated our research along this direction and in the present work we examine the degradation of *trans*-3,4-dihydroxycinnamic acid (henceforth abbreviated as DHCA) as a representative phenolic acid present in wastewater from olive oil industry. The large content in phenolic compounds represent a serious problem of environmental contamination and the reduction of the pollutant content has been the target of several recent investigations using different methods [22,23].

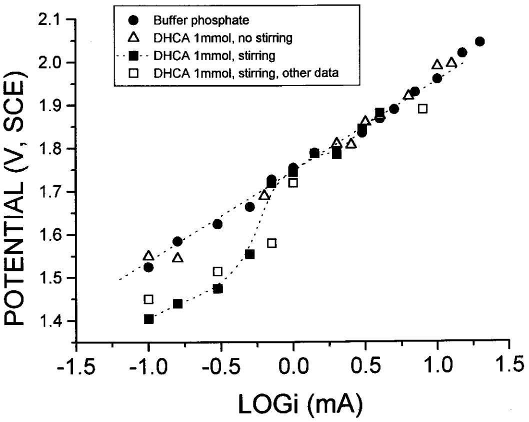

Fig. 1. Quasi- steady-state potential vs. log *i* curves for PbO_2/Pt electrodes in stirred phosphate buffer solutions (pH = 7.2) in the absence and in the presence of 0.5 mmol dm^{-3} *trans*-3,4-dihydroxycinnamic acid. Electrode geometric area: 0.42 cm^2. $T = 23°C$.

2. Experimental

All other chemicals were Fluka reagents and were used as received. β-PbO_2 electrodes were prepared by electrodeposition at constant current from $Pb(NO_3)_2$ acid solutions onto Ti substrates previously etched in hot oxalic acid and then platinised. The electrodeposition of Pt was carried out from a solution containing 32.5 g/dm^{-3} K_2PtCl_6 in 30 g/dm^{-3} KOH at 75°C, using a constant current of 8 mA/cm^2 for 2.5 min. The approximate thickness of the resulting deposit is 0.25 μm. Lead dioxide was electrodeposited onto these substrates from a solution containing 0.1 mol dm^{-3} HNO_3 + 0.1 mol dm^{-3} $Pb(NO_3)_2$ at room temperature and a constant current of 5 mA/cm^2 until a PbO_2 deposit with an estimated thickness of 30.8 mg/cm^2 was obtained.

Electrochemical experiments were conducted using an EG&G/PARC model 273A potentiostat with EG&G software using a conventional three compartments cell. Impedance measurements were carried out using a EG&G model 5210 lock-in amplifier. A saturated calomel electrode was used as reference.

Analyses of the reaction products were conducted by HPLC using a TSP instrument equipped with a Spectro Monitor detector 5000 and a 25 cm Econosphere C 18 5U column. Ozone analysis was carried out mostly by iodometric titration. In some cases the results so obtained were checked by the spectrophotometric method.

In the oxidation experiments by the different methods, the reactions were not carried out exhaustively, and the kinetic analysis of the results is done in terms of residual DHCA as a function of time. In some cases, the chemical oxygen demand (COD) was evaluated as described in [6]. The formation of coloured compounds during electrolysis was followed by UV-visible spectroscopy using a Kontron Uvikon 940 spectrometer.

3. Results and discussion

3.1. Direct electrolysis

All experiments were conducted in a phosphate buffer electrolyte at pH 7.2. In this medium DHCA is easily soluble, whereas some solubility problems were encountered in acid solutions. On the other hand, we noticed that at pH values higher than 10 the DHCA solutions were not stable, as indicated by changes of the UV-vis spectrum with time.

In Fig. 1 are shown the steady-state polarisation curves for PbO_2 in phosphate buffer both without and with added DHCA. In the latter case one notices a pronounced stirring dependence in the lower potential region, which is actually seen only during the first run in the direction of increasing potentials. However, in

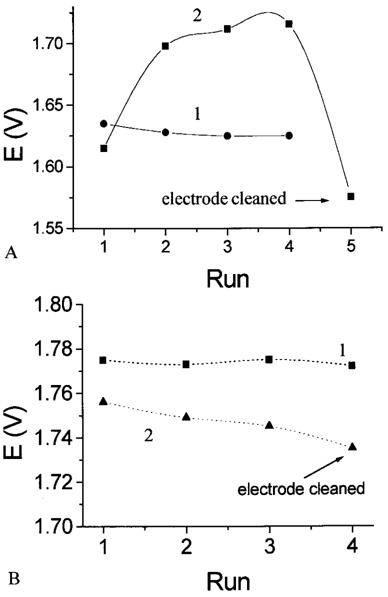

Fig. 2. Variations of the electrode potentials for repeated chronopotentiometric measurements with PbO_2/Pt electrodes in stirred phosphate buffer solutions (pH = 7.2) in the absence (curve 1) and in the presence (curve 2) of 0.5 mmol dm^{-3} *trans*-3,4-dihydroxycinnamic acid. Applied constant current: (A) 0.3 mA; (B) 1 mA. Electrode geometric area: 0.42 cm^2. $T = 23°C$.

consecutive steady-state experiments, the effect of solution stirring is no longer observed and the polarisation curves are similar to those observed with no DHCA present. As a matter of fact, for repeated runs we observed that in the low potential region the curves shifted to slightly higher potentials.

This phenomenon is well illustrated by the data reported in Fig. 2 referring to repeated experiments carried out at constant applied current in stirred solutions, both in the absence and in the presence of DHCA. For the case of successive runs at relatively low currents (Fig. 2A), corresponding to the stirring dependent region in the polarisation curve, the potential increases to higher values than those observed in phosphate buffer alone. If the electrode is then cleaned in a solution of CH_3COONH_4 and a new experiment is performed in the DHCA solution, the observed steady-state potential returns to a low value. This behaviour can be ascribed to the adsorption of products deriving from the oxidation of the dihydroxy-acid such as, for example, polycondensation species.

This conspicuous time dependence of the potential is not seen in analogous experiments with higher constant applied currents (Fig. 2B). In this case, the potentials measured in the absence and in the presence of DHCA differ by few tens of a mV evidently indicating that, in this region, O_2 evolution dominates the anodic process.

The results presented above indicate that the mechanism of DHCA oxidation changes with changing current or potential. To prove this convincingly, we carried out an UV-visible spectroscopy analysis of DHCA solutions following electrolysis at different constant currents corresponding to the stirring dependent and stirring independent domains of the Tafel region. In the low currents region the UV-visible spectra feature a clear isosbestic point at 340 nm, indicating that the oxidation of DHCA gives mainly one stable product, in the solution phase, which is characterised by higher absorption at the longer wavelengths (Fig. 3A). The reaction most likely corresponds to the oxidation of the OH groups of the aromatic ring to give a coloured conjugated quinone.

Conversely, a plain decrease of the absorbance above 250 nm is observed when the electrolysis is carried out in the higher current range (Fig. 3B), which indicates the degradation of the organic compound. The fact that this reaction occurs despite the steady-state electrochemical data provide no evidence of it in this region

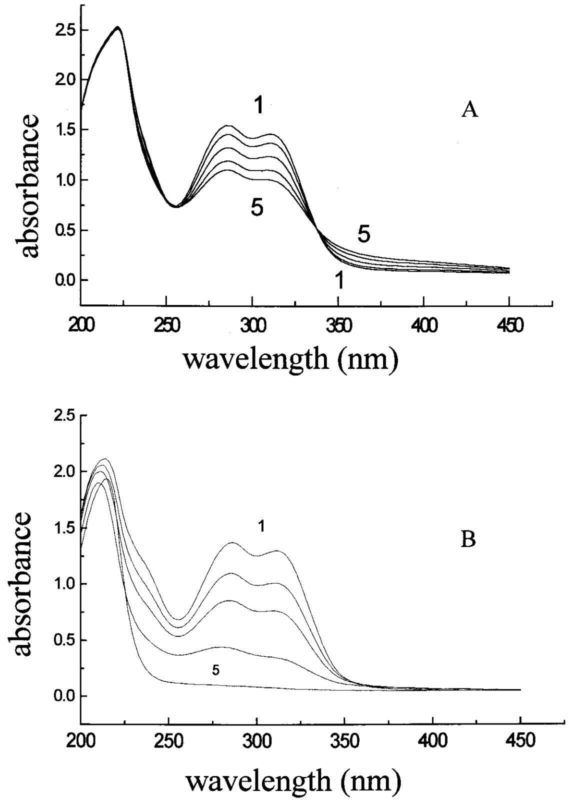

Fig. 3. UV-visible spectra as a function time of electrolysis of 0.5 mmol dm^{-3} *trans*-3,4-dihydroxycinnamic acid at PbO_2/Pt electrodes in stirred phosphate buffer solutions (pH = 7.2). Curves 1–5 correspond to: (A) 0 to 135 min at a constant current of 1.8 mA/cm^2 ($E = 1.55$ V, SCE); (B) 0 to 100 min at a constant current of 50 mA/cm^2 ($E = 2.03$ V, SCE).

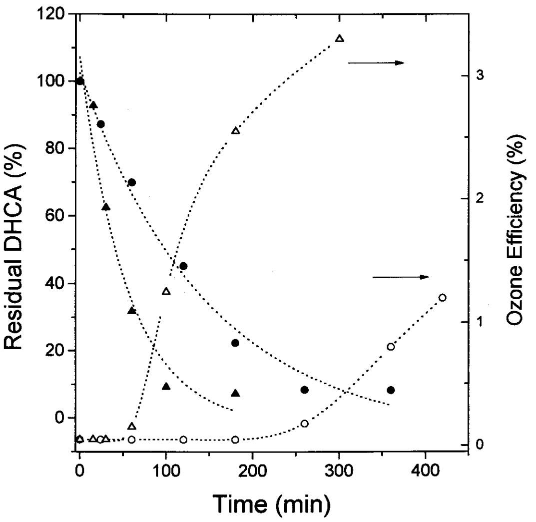

Fig. 4. Oxidation of trans-3,4-dihydroxycinnamic acid and O_3 formation at PbO_2/Pt electrodes in phosphate buffer solutions (pH = 7.2), at a constant applied current of 23 mA/cm^2 (circles) and 50 mA/cm^2 (triangles). Initial concentration: 0.5 mmol dm^{-3}.

(Fig. 1 and Fig. 2B), suggests that the process is largely controlled by the discharge of water to give highly reactive OH radicals that are able to initiate the oxidative demolition of DHCA and prevent the poisoning of the surface by adsorbed intermediates.

Fig. 4 illustrates the conversion of DHCA in phosphate buffer as a function of electrolysis time for two different values of the current density in the stirring independence range, where the evolution of both O_2 and O_3 is possible. The same figure shows that, with DHCA present, the efficiency of O_3 formation is negligible at the beginning of the electrolysis and becomes appreciable after the concentration of DHCA has decreased below ~ 20% of its initial value. Ozone formation finally reaches a plateau as the concentration of the dihydroxy-acid drops further.

In our previous work on the oxidation of 4-chlorophenol [21] we explained an analogous behaviour by a mechanism that involves the reaction of active oxygen intermediates formed upon discharge of water. These intermediates either combine to give O_2 and O_3 evolution (reactions 3–5) or react with the organic compound [for a review see [24]].

Since the steady-state approach can suffer from severe limitations, especially at high positive potentials, we conducted an impedance spectroscopy analysis in order to obtain further insights into the oxidation of DHCA occurring in parallel with O_2 evolution. Indeed the data reported in Fig. 5 show some interesting aspects from the point of view of the reaction mechanism in the higher currents range. The impedance plane exhibits a capacitive arc in the high frequency range and an inductive arc at low frequencies. The latter disappears as the positive potential (or the DHCA concentration in solution) increases.

The conditions that determine the appearance of an inductive loop have been discussed in the literature [25–28] and are associated with an electrode two-step reaction path involving an adsorbed intermediate generally written as [28]:

reactant → adsorbate + e^- step 1

reactant + adsorbate → products + e^- step 2

For this reaction sequence the predicted evolution of the impedance diagrams as a function of increasing potential involves an attenuation of the inductive loop, in agreement with the data of Fig. 5. A mechanism of this type describes, for example, the evolution of chlo-

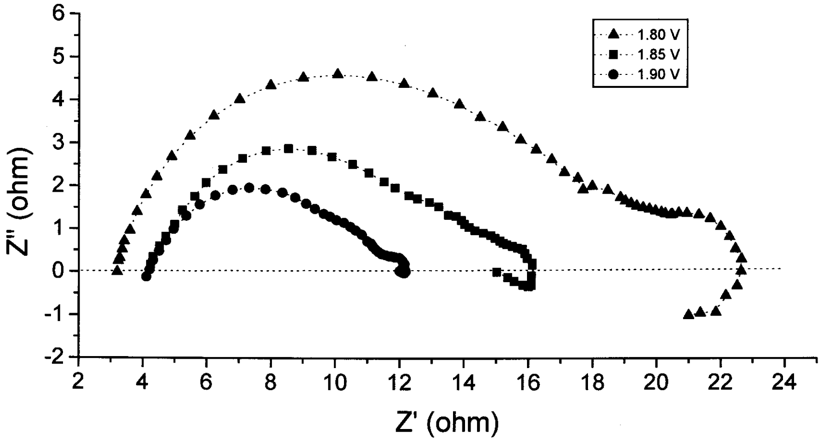

Fig. 5. Nyquist impedance plots at different potentials for PbO_2/Pt electrodes in phosphate buffer solutions (pH = 7.2) containing 0.5 mmol dm^{-3} *trans*-3,4-dihydroxycinnamic acid. Electrode geometric area: 0.42 cm^2.

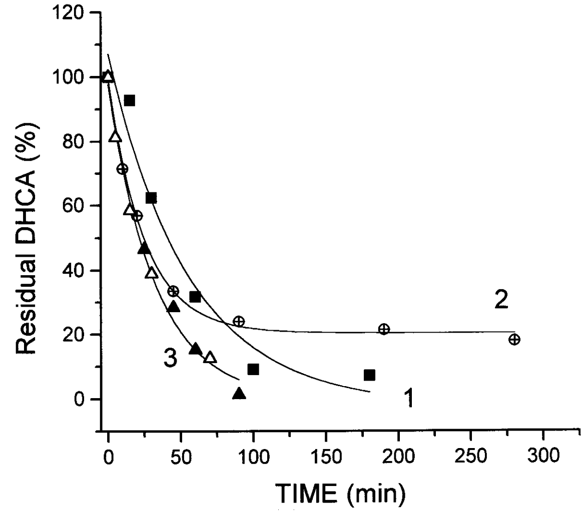

Fig. 6. Comparison of different methods for the oxidation of *trans*-3,4-dihydroxycinnamic acid (0.5 mmol dm^{-3}): (1) direct electrolysis method at 50 mA/cm^2; (2) external-cell chemical oxidation with O_3 electrogenerated on PbO_2 with a current efficiency of 6–7% at 50 mA/cm^2 and 22°C; (3) cathodic oxidation experiment (see text), O_3 electrogenerated on PbO_2 with a current efficiency of 6–7% at 50 mA/cm^2 and 22°C.

rine, the dissolution of metals ([28] and refs. therein) and the oxidation of carboxylic acids [29]. The last case, i.e. the decarboxylation reaction:

$$R-COO^- \rightarrow (R-COO)_{ads} + e^- \tag{6}$$

$$(R-COO)_{ads} + R-COO^- \rightarrow \text{products} + e^- \tag{7}$$

provides a possible explanation of the impedance results. We then propose that, to some degree, this process occurs in parallel with the above discussed reaction of DHCA with OH^- radicals formed by the discharge of water.

3.2. External cell reactions with electrogenerated ozone

This approach exploits the chemical reaction of DHCA with O_3 that is formed at a PbO_2 anode. The electrogenerated gas ($O_3 + O_2$) was flowed through an external vessel containing DHCA in phosphate buffer, following the reaction course by HPLC or UV-visible spectroscopy.

Typical results are illustrated by curve 2 in Fig. 6, for an ozone current efficiency of 6–7% at 50 mA/cm^2 and room temperature. From this summary figure we can now compare the results of the chemical reaction with O_3 with those of the direct electrolysis (curve 1), under the same conditions of applied constant current. It is interesting to note that while the rate of disappearance of DHCA is initially higher for ex-situ method than for the electrolytic reaction, for prolonged experiments the concentration of the substrate remains essentially constant. This occurs because ozone is consumed by secondary reactions with intermediates [30].

Since the ozonization reaction is generally first order in ozone and in the organic substrate [23], one obvious way of keeping the reaction going is, therefore, that of increasing the yield of O_3 formation. We could achieve this by using metal doped PbO_2 anodes [8]. Thus, for example, we obtained current efficiencies of 6.8 and 8.85% for Fe(III) and Co(II) modified PbO_2 [31] at 20°C and 100 mA/cm^2. Lowering the temperature to $+5 \pm 2$°C increased the yields to 18 and 12%, respectively, for an applied current of 50 mA/cm^2.

The effect of increasing the amount of O_3 is illustrated in Fig. 7A, where curves 1, 2 refer to the con-

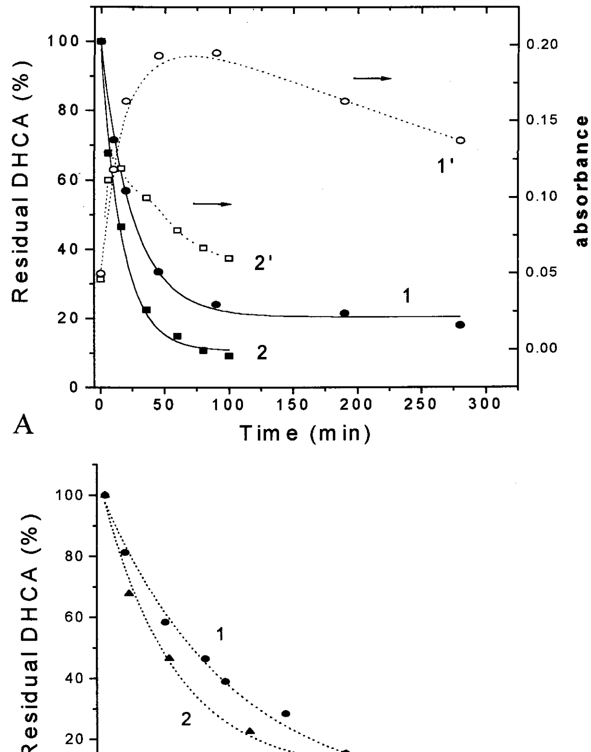

Fig. 7. Effect of an increase in the amount O_3 on the chemical oxidation of *trans*-3,4-dihydroxycinnamic acid in phosphate buffer solutions (pH = 7.2). Graph A: the current efficiency of O_3 electrogeneration was 6–7% for curve 1 and 14–16% for curve 2; curves 1′ and 2′ show the formation and disappearance of coloured intermediates. Graph B: comparison of the external-cell data (1) and cathodic oxidation (2) using O_3 electrogenerated with current efficiencies of 6–7% and 14–16%, respectively.

sumption of DHCA and curves 1′, 2′ to the bleaching of coloured intermediates as measured by the absorbance in the visible spectrum. It is clear that the latter process strongly conditions the rate of ozonization of DHCA. We have not tried to establish the exact nature of the coloured intermediates; HPLC data indicate a mixture of compounds probably originating from the reaction of some unstable intermediates [32].

The homogeneous phase reaction of O_3 with organic compounds, has been previously investigated [23,30,32–36]. In principle, the oxidation can be initiated either by the direct attack of O_3 on the organic substrate or by secondary oxidants, such as OH^- radicals, originating from the O_3 decomposition [32,35]:

$$OH^- + O_3 \rightarrow O_2^- + H_2O^\bullet \qquad (8)$$

$$O_3 + OH^- \rightarrow O_3^- + OH^\bullet \qquad (9)$$

$$O_3^- + H_2O \rightarrow OH^\bullet + OH^- + O_2 \qquad (10)$$

In accord with the above reactions, ozone stability in aqueous solutions is reported to decrease as the pH increases [37], and the contribution of the radical chain route correspondingly augments.

3.3. Cathodic oxidation with O_3/H_2O_2

The term cathodic oxidation has been used in connection with the use of oxygen cathodes that produce hydrogen peroxide as a mediator in oxidation processes [38]. In this case, the organic substrate is present in the cathodic compartment and its degradation is initiated by hydroxylation with OH radicals produced by the decomposition of hydrogen peroxide. In principle, the oxidation efficiency can be increased by the use of a Fenton system based on the addition of iron salts. In this work, however, we chose the O_3/H_2O_2 approach [21] in which an O_2 stream is used to sweep the O_2/O_3 gas mixture produced at the PbO_2 anode into the cathodic compartment.

The results for the cathodic oxidation of DHCA are plotted as curve 3 in the summary Fig. 6 and as curve 1 in Fig. 7B. It is noteworthy that UV-vis spectroscopic measurements show that DHCA undergoes no change at an O_2 cathode in the absence of O_3. In Fig. 6 the data of curve 3 can be compared with the results of the direct electrolysis and with the chemical oxidation. It is apparent that, under the same conditions of applied constant current and O_3 yield, the cathodic oxidation provides the more efficient method.

This conclusion is still valid if a comparison is made between the results of Fig. 6 (curve 3) and those of Fig. 7A (curve 2) obtained upon increasing the efficiency of O_3 electrogeneration. To facilitate the comparison, the data are plotted again in the graph of Fig. 7B. The salient point is that the chemical oxidation (curve 2) is but slightly more efficient than a cathodic oxidation process (curve 1) in which about 50% less ozone is used. Actually, this improvement is not even observed on the whole time scale of the experiments (Fig. 7B): in the long run, the situation is inverted, and COD measurements after a reaction time of 120 min gave values that were lower for the cathodic oxidation than for the external-cell method by a factor of 1.5–1.7.

The behaviour described above can explained an effective contribution of the radical route under the operating conditions of the cathodic oxidation process. In fact, hydrogen peroxide formed at a graphite cathode reacts with O_3 giving rise to a highly oxidising environment due to the occurrence of reaction:

$$O_3^- + HO_2^- \rightarrow OH^\bullet + O_2^- + O_2 \qquad (11)$$

in addition to the above mentioned reactions [8–10] and to the direct oxidation of DHCA by O_3. The latter pathway probably prevails under initial conditions, as it seems to be indicated by the fact that at relative short times curves 2, 3 in Fig. 6 tend to converge. The mechanism of this reaction is very likely similar to proposed for the analogous case of *p*-coumaric acid, involving the attack of the acrylic double bond by ozone as the first step [35]. As the concentration of the organic substrate decreases, the radical route would constitute the prevailing oxidation mode. This can provide an explanation of why the cathodic oxidation approach gives overall better results.

4. Concluding remarks

The oxidative degradation of *trans*-3,4-dihydroxycinnamic acid was investigated using three different methods, two of which have in common the use of electrogenerated ozone as a potential oxidant: (i) direct electrolysis; (ii) external cell chemical reactions with O_3 and (iii) a cathodic oxidation in which an O_2/O_3 mixture is fed into the cathodic compartment, where the H_2O_2 produced reacts with ozone to yield radicals that bring about the demolition of the organic compounds.

The direct electrolysis is a complex process in which the nature of the oxidation processes depends on potential. At relatively low potentials the process shows stirring dependence and leads essentially to one oxidation product in solution and to adsorbed species on the electrode. At some higher potential the reaction becomes stirring independent and poorly distinguishable from the O_2 evolution. Nevertheless, the demolition of the organic substrate is observed in this potential range, and this suggest a mechanism in which the active oxygen radical intermediates, formed from the discharge of water, act as oxidation mediators. The reaction of these intermediates with the organic substrate competes with the process of O_3 formation: no O_3 was detected until the concentration of the di-hydroxyacid dropped below ~20% of its initial value. Interestingly, in our cited work on the oxidation of 4-chlorophenol we observed the same behaviour.

From an analysis of impedance data in the region of high potentials, it seems possible to conclude that, in addition to the processes involving the reaction of DHCA with oxygen radical species, an electron transfer reaction takes place that can be ascribed to the decarboxylation of the acid.

The homogeneous chemical decomposition of DHCA by ozone is the basis of the ex-situ and methods. It involves the direct reaction of O_3 with the organic substrate and/or a radical chain reaction initiated by radicals formed in the reaction of O_3 with OH^- (reactions 8–10) or with HO_2^- (reaction 11). The latter pathway is favoured by an increase of the pH. The examination of the results shows that the ex-situ and cathodic oxidation with ozone are the most efficient methods. This confirms the conclusions of our previous investigation on the oxidative degradation of 4-chlorophenol and indicates this method as a promising one in the abatement of noxious chemicals.

Acknowledgements

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