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Electro-oxidation of Some Phenolic Compounds by Electrogenerated O_3 and by Direct Electrolysis at PbO_2 Anodes

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The oxidative degradation of phenolic compounds (4-chlorophenol and 4-nitrophenol) was studied using different electrochemical systems involving ozone formation at PbO_2 anodes: (i) direct electrolysis at constant current; (ii) ex-situ use of O_3 and (iii) combined use of anodically generated stream of O_3/O_2 fed into the cathode where H_2O_2 is electrogenerated by O_2 reduction. We show that the latter advanced oxidation method gives the best results: it is a Fenton-type degradation of the target pollutants taking place in the cathodic compartment by reason of the highly oxidizing environment brought about by radicals that are formed mainly in the reactions of O_3 with OH^- and HO_2^-.

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Electrochemistry along with the microbial and photochemical approaches is a well established method for the degradation of wastes. It has been frequently stressed, however, that often these methods cannot bring about complete mineralization of several compounds,[1] and to this end various methods broadly classified as AOPs (Advanced Oxidation Processes)[2] provide complementary and alternative means of environment remediation, as outlined in comprehensive recent surveys.[3,4]

These AO systems include ozone, hydrogen peroxide as well as a mixture of them called "Peroxone"[5] which can be activated by Fenton reactions leading to formation of a large amount of OH radicals and, consequently, to a highly oxidizing environment.

In our previous work,[6] H_2O_2 was electrogenerated at the cathode which was fed by a gaseous mixture of O_2 and O_3 that are, in turn, electrogenerated at the PbO_2 anode of the same electrochemical cell; the cathode also contained the target organic species to be degraded. Ozonization combined with electrolysis has been later investigated in other laboratories.[7] Herein we report on the oxidation of phenol derivatives in aqueous solutions using conventional electrolysis as well as and indirect electrochemical methods that generate the active oxidants such as O_3 and/or H_2O_2. In particular, we compare the results obtained using different oxidation methods: (i) the conventional electrolysis at PbO_2 anodes; (ii) the ex-situ method, whereby the electrochemical system is used only for the electrogeneration of O_3 at PbO_2; (iii) a combined use of electrogenerated O_3 and H_2O_2 in a Fenton-like AOP.

It is now well recognized that, in the direct electrolysis process, the oxidation of a large number of organic and inorganic compounds on different electrode materials, including PbO_2, proceeds simultaneously with the evolution of oxygen. Highly oxidizing oxygen species, such as OH radicals, formed during the anodic oxidation of water are able, in turn, to oxidize most organic compounds. There is a vast literature on this subject, concerning both conducting[8–16] and semiconductor anodes.[17–20]

At the high anodic potentials involved, the same oxygen species may react to form O_3 in addition to O_2, as illustrated by the pathway below[21–26]

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

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

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

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

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

Studies on the role of reactive oxygen intermediates in the mechanism of ozone formation at PbO_2 have been published recently.[27–30]

We show that the direct electrooxidation of an organic substrates is kinetically controlled and competes with O_2 evolution and O_3 formation. Moreover, concerning cathodically activated reactions, we show that an O_2 cathode with a graphite electrode, in weakly alkaline solutions, forms HO_2^- which reacts with O_3 when the cathode is fed by O_2/O_3, confirming the mechanism that we proposed earlier[6] where the active oxygen species are intermediates in the reaction of O_3 with co-electrogenerated H_2O_2.

Experimental

Materials and methods.—Ultrapure sulfuric acid was obtained from Merck; 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 platinized. The electrodeposition of Pt was carried out from a solution containing 32.5 g l^{-1} K_2PtCl_6 in 30 g l^{-1} 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 mm. Recent research has shown that PbO_2 electrodeposited from methanesulfonic acid features interesting, new characteristics.[31,32] In the present work, however, the oxide electrodeposition was carried out as described before[33] from a solution containing 0.1 M HNO_3 and 0.1 M $Pb(NO_3)_2$ at room temperature and at a constant current of 5 mA cm^{-2} until a PbO_2 deposit of 30.8 mg cm^{-2} was obtained.

Electrochemical experiments were conducted using an EG&G model 273A potentiostat with EG&G software using a conventional, gas-tight cell with three compartments separated by glass frits that were impregnated with a Nafion solution and then dried. In all cases, SCE was used as reference electrode. A platinized Ti or a graphite sheet (7.5 cm^2 geometric area) were used as cathode.

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. The chemical oxygen demand (COD) was evaluated as described elsewhere.[13] In one experiment ozone was generated by the arc discharge method using a Fischer Ozone-Generator Instrument.

The formation of colored compounds during electrolysis was followed by UV-visible spectroscopy using a Kontron Uvikon 940 spectrometer, and the analysis of Pb^{2+} released into the solution

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was carried out by atomic absorption spectroscopy using a Perkin-Elmer 1100 spectrometer.

Results and Discussion

Direct Electrolysis Experiments.—In these experiments the organic substrate is added to the anodic compartment. Lead dioxide on Pt-Ti substrates was used as anode with Pt-Ti sheets as counter electrode. Since under some conditions ozone formation can occur, the gas evolved at the anode was collected by an argon stream and analyzed for O_3 (see experimental section).

Figure 1 illustrates the conversion of 4-chlorophenol (CPh) in 1 M H_2SO_4 as a function of time, at a constant current of 50 mA cm^{-2}. The same figure shows that the amount of O_3 detected in the O_2/O_3 gaseous mixture evolving at the anode is negligible at the beginning of the electrolysis and becomes appreciable after the concentration of CPh has decreased (not necessarily mineralized) to about 50% of its initial value. Ozone formation finally reaches a plateau as the phenol concentration approaches zero.

Since the formation of O_3 appears to provide a possible measure of efficient pollutants degradation at β-PbO_2, we carried out some experiments under conditions in which formation and detection of O_3 is improved, i.e., in buffer phosphate electrolyte at low temperatures[21] and addition of fluoride.[34,35] The oxidation of CPh was then followed at room temperature and, for comparison, at 0°C and in the presence of NaF too (Fig. 2).

From the experimental data, evaluation of the initial rate of CPh disappearance gives 0.016 mol l^{-1} min^{-1} at 0°C and 0.01 mol l^{-1} min^{-1} at 25°C; the slightly higher value at low temperature is likely due of a decreases of the OH radicals condensations reaction that leads to the parallel O_2 evolution process. Since, however, one effect of decreasing the temperature is also the enhancement of the efficiency of O_3 formation, one could possibly explain the above results on the basis of a direct reaction of the organic substrates with electrogenerated O_3 at the electrode surface. Actually, all literature data report that the reaction rates of organic species with OH radicals are at least some orders of magnitude higher than those with ozone. Nevertheless, for the sake of clarity, we checked this possibility experimentally and saw that, under the conditions given in Fig. 1, when a sufficient time has elapsed to allow O_3 formation to reach a constant value, the addition of new CPh or of the main intermediate 1,4-Benzoquinone (BQ) decreases the O_3 current efficiency instantaneously from steady-state value to approximately zero. Thus if ozone was involved in the oxidation, its reaction with the organic substrates near the surface would have to be an instantaneous process, which is not in accord with results discussed later in this work, especially in acid or neutral media (see next section). The most likely mechanism involves, instead, OH radicals as the oxidizing species and, in effect, although the reported potentials for the oxidation of CPh and NPh are 0.653 and 0.924 V vs. SCE, respectively,[36] i.e., well below the onset of O_2 evolution on PbO_2, no appreciable oxidation is observed until the discharge of water according to Reaction 1 starts.[37] These phenomena were also observed earlier for the electrooxidation of 3,4-dihydroxycinnamic acid.[6]

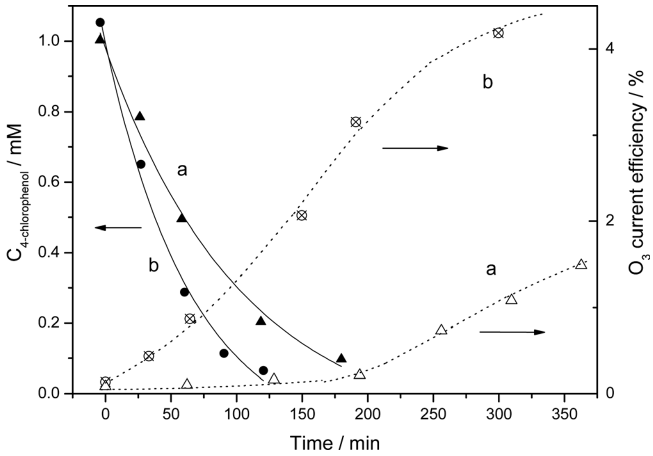

Figure 2. Oxidation of 4-chlorophenol (full symbols) and O_3 formation (open symbols) on a β-PbO_2 electrode in buffer phosphate at 25°C (a) and buffer phosphate with 0.01 M NaF at 0°C (b). Applied constant current: 50 mA cm^{-2}.

The oxidation of CPh yields mainly BQ at intermediate times of electrolysis while maleic acid is the detectable product of a prolonged experiment. BQ itself is a noxious compound and its degradation by electrochemical methods has been reported by Pulgarin et al.[38] on Ti/IrO_2 and Ti/SnO_2 electrodes and by Ge et al.[12] who used PbO_2 anodes. It is probably the result of a fast oxidation of 1,4-hydroquinone initially formed by attack of OH radicals on CPh. Figure 3 shows that under our experimental conditions, the concentration of BQ reaches a maximum after about 50 min. The interesting additional detail in this figure is that the above mentioned formation of O_3 sets in when also the intermediate BQ is consumed at the anode.

In Fig. 4 are summarized the results of CPh oxidation for different experimental conditions. We cannot discard *a priori* the possibility that the higher reactivity observed in phosphate buffer is connected with dissociation of the phenol; however, as discussed in the

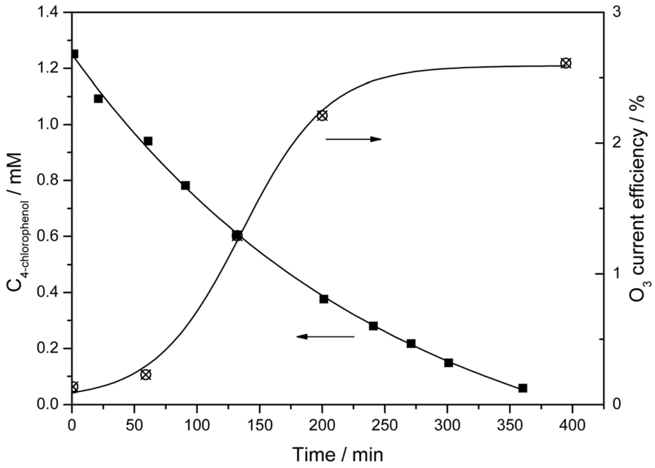

Figure 1. Oxidation of 4-Chlorophenol and O_3 formation on a β-PbO_2 electrode in 1M H_2SO_4 at a constant applied current of 50 mA cm^{-2} and T = 0°C.

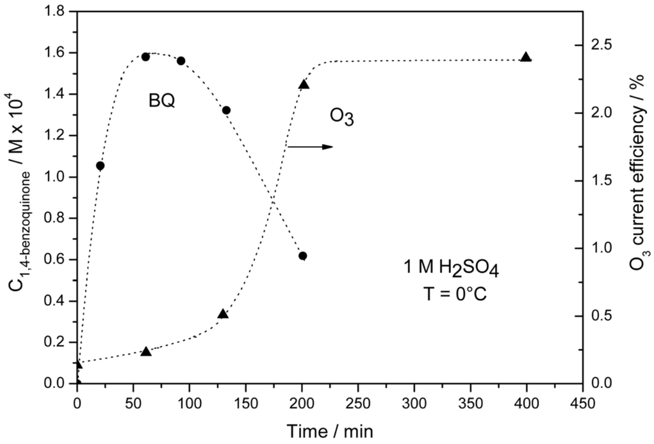

Figure 3. Formation of 1,4-benzoquinone and ozone during the electrooxidation of 1.25 mM 4-chlorophenol on a β-PbO_2 electrode in 1M H_2SO_4 at a constant applied current of 50 mA cm^{-2} and T = 0°C.

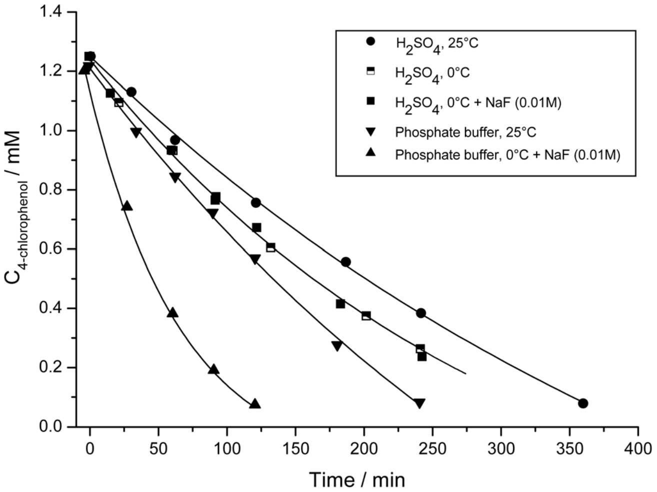

Figure 4. Effect of the electrolyte and temperature on the electrooxidation of 4-chlorophenol on a β-PbO_2 electrode. Applied constant current: 50 mA cm^{-2}.

next section, dissociation in the *p*H range from 0 to neutrality is weak (1% at *p*H 7.2). In H_2SO_4 the reactivity of the non-dissociated species is slightly higher for NPh than CPh, indicating an attack by OH radicals rather than direct electron transfer. The oxidation of 1.2 mM NPh at 50 mA cm^{-2} is essentially completed after 6h, and we observed maleic acid and a stoichiometric amount NO_3^- as the final products. 1,4-benzoquinone is observed as a reaction intermediate in this case too; its concentration, however, was one order of magnitude lower than that observed in the case of CPh oxidation (Fig. 3), seemingly suggesting a more efficient ring opening process for NPh.

Reactions with Ex-situ Generated Ozone.—This AOP approach using ozone for the abatement of pollutants is probably the most extensively investigated and the object of a large number of publications and reviews.[39]

In the present work, the gas evolved at the PbO_2 anode ($O_3 + O_2$) is collected and passed through an external vessel containing the phenolic compounds in H_2O. As O_3 is present at low concentrations in the mixture, the rate of ozone consumption will be also limited by mass transfer of O_3 from the gas phase to the liquid (aqueous) phase. Under these conditions the rate of O_3 formation will depend also on the apparent volumetric mass transfer coefficient (k_La) of the investigated system. For this reason the results reported in this section are compared at a constant gas flux.

Degradation can be initiated by a direct reaction with O_3 (Pathway I)[40] or by a highly oxidizing environment created by reactions of O_3 decomposition (Pathway II). In the latter case, a possible route includes the following reactions[39,41]

$$O_3 + OH^- \rightarrow O_2^- + HO_2^\bullet \qquad [6]$$

$$O_3 + OH^- \rightarrow {}^\bullet O_3^- + {}^\bullet OH \qquad [7]$$

$$^\bullet O_3^- + H_2O \rightarrow {}^\bullet OH + OH^- + O_2 \qquad [8]$$

In accordance with the above reactions, ozone stability in aqueous solutions is reported to decrease as the *p*H increases.[42] In the case of direct ozonation (Pathway I) one should also consider that the reaction of O_3 with dissociating organic compounds is reported to increase by several orders of magnitude as the *p*H approaches the dissociation constant. If pK is the phenol dissociation constant then the degree of dissociation is:[39]

$$\alpha = 1/(1 + 10^{pK-pH}) \qquad [9]$$

and the ozonation reaction rate constant of a phenol XROH is[39]

$$k_{obs} = k_{ndis}(1-\alpha) + k_{dis}\alpha \qquad [10]$$

where k_{dis} and k_{ndis} refer to dissociated and non-dissociated XROH, respectively. Taking the relevant k and pK values from literature,[43] the calculation of k_{obs}, for a *p*H 7.5, gives $1.2 \times 10^7\ M^{-1}\ s^{-1}$ and $1.07 \times 10^7\ M^{-1}\ s^{-1}$ for CPh and NPh, respectively. The calculated rates remain comparable at *p*H 6.5, and this does not reflect the trend shown by experimental data (see curves NPh-a and NPh-b in Fig. 5). Reaction with radicals is the alternative route that is often invoked, which becomes evidently more pronounced as *p*H increases. By comparison with the above k values, reaction rates with OH radicals are of the order[39] of $10^{10}\ M^{-1}\ s^{-1}$. We do not wish to enter into details of the mechanism since this issue is the object of a vast literature.[39] Our intention is that the results should provide a comparison with the analogous experiments described in the next section (vide infra) in which H_2O_2 is additionally co-electrogenerated.

It is finally important to note that disappearance of the main intermediate initially observed (BQ) is fast and little dependent on *p*H (Fig. 5). It is, however, converted into secondary intermediates which cause the solution to become intensely brown colored. We have not investigated on the chemical nature of these intermediates but they are likely products of condensation of 1,4-benzoquinone as reported previously.[13] Particularly in the case of CPh, in contrast to a relatively fast conversion, the color disappears slowly. Thus, while the conversion of CPh is essentially complete after 120 min, it takes about 300 min for a COD value of 10 to be measured.

Pathways I and II are the ones likely to occur in the absence of added impurities but it is noteworthy that the decomposition of ozone can be catalyzed by a number of species such as Fe^{2+} and manganese[44] giving highly oxidizing intermediates; however, this method involves a separation of the inorganic species following the treatment. A "cleaner" O_3/H_2O_2 approach[39] has gained considerable popularity and a particular case of this method is discussed in the following section.

Indirect oxidation with simultaneously electrogenerated O_3 and H_2O_2.—In the approach described here, the organic substrate is present in the cathodic compartment and hydrogen peroxide is conveniently generated in-situ, at a graphite cathode, when a O_2/O_3 mixture produced at the PbO_2 anode is collected by a stream of an inert gas and swept at a constant flux through the catholyte.[6] The attention attracting term "*cathodic oxidation*" has also been used in this connection.[45]

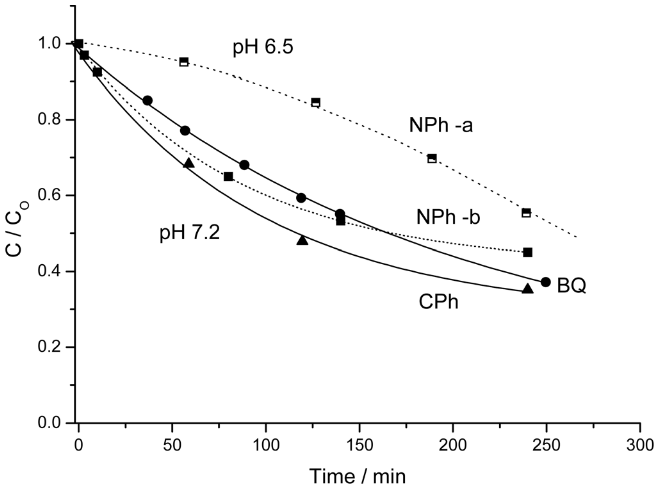

Figure 5. Use of electro-generated ozone for the ex-situ chemical oxidation of test organic compounds in water. Ozone was generated at a β-PbO_2 electrode in phosphate buffer + NaF at 0°C (*p*H 7.2) and 50 mA cm^{-2} (current efficiency: 6–7%). Degradation of 4-nitrophenol was tested both in pure water (*p*H 6.5, NPh-a) as well as at *p*H 7.2 (NPh-b).

We limited experiments to the case of CPh as a test substrate since NPh could undergo reduction reactions at the cathode, making a comparison with other methods difficult. Experiments were conducted in buffer phosphate (*p*H 7.2) and buffer borate + 1 M NH_4PF_6 (*p*H 9). The choice was dictated by the necessity to maximize the amount of O_3 formation and for this purpose the solution in the anode compartment was also added with NaF and kept at a temperature of 0°C. Current efficiencies for ozone formation at a current of 50 mA cm^{-2} were 8–10% in buffer phosphate and 10–12% in buffer borate.

The results for the advanced oxidation of CPh by cathodically activated O_2/O_3 are shown in Fig. 6 (curves 4, 5) and compared, in the same figure, with the data discussed in the previous sections obtained with the external cell O_3 approach (curves 2, 3) and direct electrolysis (curve 1). The comparison is done in the *p*H range from 6.5 to 9 where the stability of H_2O_2 in the presence of O_3 decreases with increasing *p*H (Ref. 42) and even a relatively low concentration of hydrogen peroxide can cause formation of a high concentration of OH radicals through reaction with ozone.[39]

It is clear that the O_2/O_3 cathodic activation AO method always offers the best results. We observed that the methods based on the use of O_3 generally feature an improved degradation of the organic substrate as *p*H increases from neutral to weakly alkaline media. As discussed above, this is due to reaction of the phenolate XRO^- directly with O_3 and/or indirectly with OH radicals (Reactions 6–8). Additionally, we have proposed earlier[6] that in the neutral or weakly alkaline *p*H range (7–9) reaction of O_3 with hydrogen peroxide

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^- + O_2 \qquad [11]$$

contributes significantly to creating a highly oxidizing environment leading to degradation of the organic pollutants. Reaction 11 can occur in addition to or instead of the above mentioned Reactions 6–8; the rate constant for Reaction 12 ($2.8 \times 10^6\ M^{-1}\ s^{-1}$) is several orders of magnitude higher than those of Reactions 6–8.[46]

In a recent paper, Kishimoto et al.[7] have questioned the possible involvement of hydrogen peroxide on the ground that, "a cathodic reaction with higher standard potential generally occurs prior to reactions with lower potential". Accordingly, the four-electrons reduction of oxygen, e.g., in alkaline solutions

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- (0.401\ V\ vs\ NHE) \qquad [12]$$

is expected, contrary to experience, to be favored over the two-electrons route

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- (-0.0649\ V\ vs\ NHE) \qquad [13]$$

Likewise the electrochemical reduction of O_3 should be favored over that of O_2, and the direct reduction of O_3 to ${}^{\bullet}O_3^-$ should play a key role in the mechanism.[7] The cited authors favor a debatable mechanism in which O_2 reduction and the consequent hydrogen peroxide formation has no role. Formation of H_2O_2 from O_2, predominantly present in the O_2/O_3 mixture, is seemingly not considered in other published work.[47] It seems therefore appropriate to discuss these issues in some detail.

In our experiments, the potential of the graphite cathode reached values between − 0.9 and − 1.0 V when the PbO_2 anode worked under conditions of O_3 generation, i.e., typically at 2.0 to 2.1 V, and thus reduction of O_2 needs to be considered and discussed. Indeed, an ample literature has much to recommend consideration of the role played by O_2 reduction in the system described herein (Reaction 12 and 13). In particular, it has long been established that on some electrode materials, including graphite, O_2 reduction follows a two-electron route yielding hydrogen peroxide.[48–51] However, in order to collect additional data that can buttress conclusions on the reduction processes involved, we performed the experiments described in the following.

Ozone is a rather small fraction of the total gas evolved at the anode, i.e., typically 18 mg l^{-1} or ~ 1% v/v (STP) in the present case. Then with pure O_2 bubbling, under otherwise identical operative conditions as with O_2/O_3, analysis of the catholite during 20 min showed that hydrogen peroxide is produced at an average rate of 4 mg l^{-1} min^{-1}. For a comparison, in the experiment with O_2/O_3 and 18 mg l^{-1} O_3 in the gas phase, the amount of dissolved ozone was about 4 mg l^{-1} at 20°C in agreement with the value calculated according to literature.[52] As a consequence, at steady state conditions, ozone can react with an excess HO_2^- according to fast Reaction 12 giving rise to a highly oxidizing environment.

We verified that the reaction of O_3 with peroxide is indeed fast in an experiment in which a stream of O_2/O_3 generated, this time, by arc discharge (80 mg l^{-1} O_3 at 70 ml min^{-1}) was fluxed for 2 min through a 3 ml of 8 mM H_2O_2 at *p*H 9. We observed a decrease of the peroxide concentration by over an order of magnitude, and no dissolved ozone was measured. For prolonged experiments ($t > 4$ min), the concentration of ozone dissolved in water increased again and reached 17 mg l^{-1}, i.e., the value measured in an analogous experiment with no added H_2O_2.

In a further searching experiment, a gaseous mixture of O_2/O_3 was again generated by the discharge method and bubbled into the cathode compartment of an electrochemical cell until the measured concentration of ozone in solution was constant. The measured amount of O_3 in the gas phase was 20 mg l^{-1}.

Curve a in Fig. 7 is the reduction of O_2/O_3 at the graphite cathode in pre-saturated solutions and curve b in the same figure refers to an analogous experiment but in a pure O_2 saturated electrolyte. Comparison of the data reveals that at potentials more negative of − 0.25 V the current is essentially due to O_2 reduction; some difference in the current can be attributed to a difference in gas flux, and it is clear that reduction currents clearly attributable to O_3 are observed at potentials more positive than − 0.2 V only.

To sum up the discussion on the nature of active oxygen species, a predominant role of O_2 reduction appears reasonable in view of the fact that ozone represent typically 1–2% v/v of the gas evolved at the anode, and even considering that its reported solubility in water is 10 times higher than that of O_2, the overall contribution as electroactive species should be small, taking into account also that its two-electron reduction

$$O_3 + H_2O + 2e^- \rightarrow 2OH^- + O_2 \qquad [14]$$

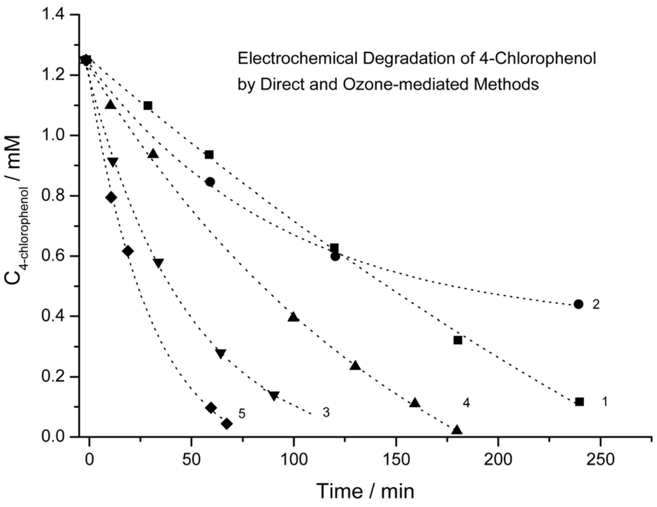

Figure 6. Comparison of different methods for the oxidation of 1.25 mM 4-chlorophenol using β-PbO_2 electrodes in neutral or weakly alkaline media at 25°C: (1) direct electrolysis at *p*H 7.2 (phosphate buffer); (2) ozone-mediated ex-situ method, in water at *p*H 6.5; (3) ozone-mediated ex-situ method, in water at *p*H 9 (borate buffer); (4) cathodic O_2/O_3 approach at *p*H 7.2 (phosphate buffer); (5) cathodic O_2/O_3 approach at *p*H 9 (borate buffer). See text for full explanation.

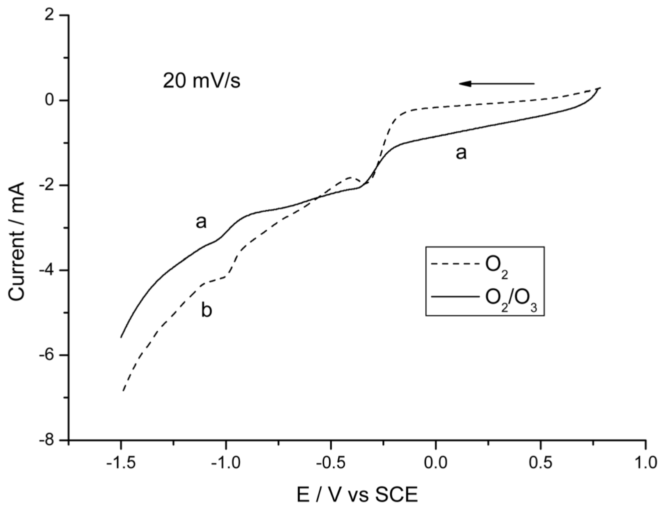

Figure 7. Linear sweep voltammetry curves for a graphite cathode in a 1 M NH_4PF_6 electrolyte (*p*H 9 buffer) saturated with O_2/O_3 (curve a) or with pure O_2 (curve b). Scan rate: 20 mV/s.

appears more plausible than a one-electron reduction in the cathodic potential range of interest in this work.

On the basis of our data we cannot support the key role of O_3^- from electroreduction of O_3 proposed by some authors.[7,47] Assuming[7] parallel one-electron and two-electron reductions of O_3, the subsequent reaction of O_3^- should be that with water to give OH radicals (Reaction 8, *vide supra*, $k = 20–30\ M^{-1}\ s^{-1}$)[39]. On the other hand, according to the cited authors, the main source of hydroperoxy species is the reaction of O_3 with OH^- (Reaction 6, *vide supra*, $k = 70\ M^{-1}\ s^{-1}$).[46] Our results actually show efficient formation of hydrogen peroxide, then both the above cited processes cannot compete with Reaction 12 which is several orders of magnitude faster.

We think that a final comment is due on this complex system: it concerns the role of H_2O_2 itself, in the absence of ozone, in the degradation of the target phenol. It has, in fact, been recently shown that H_2O_2 electrogenerated at carbon cathodes can bring about an efficient degradation of chlorophenols present in the catholyte.[53] We then examined the abatement of 4-chlorophenol at a O_2-reducing cathode under the same conditions described above but in the absence of O_3 and found that, in experiments carried out on the same time scale as those with O_3, no significant decrease of the COD was observed despite a fast disappearance of the initial phenol. We only observed accumulation of intermediate products, among which we detected 2-hydroxy-1,4-benzoquinone and 2,5-dihydroxy-1,4-benzoquinone. The results are at variance with those of the above cited authors[53] and one possible reason is the difference in current density: 39 mA cm^{-2} in their work and 4–5 mA cm^{-2} in the present one. We can therefore claim that the use of an O_3/O_2 cathode is a better choice in that it allows efficient removal of the pollutant under milder experimental conditions.

Conclusions

The present work is a comparative investigation of the oxidation of phenolic compounds using electrochemical methods. Three different methods were employed having in common the formation of ozone as a potential oxidant: (i) direct electrolysis (ii) ex-situ use of electrogenerated 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 degradation of the organic compounds. According to the results described in this work, what we called *direct electrolysis* actually turns out to be a process mediated by oxygenated radical intermediates. Subsequently, the active oxygen intermediates can react with the phenolic compounds.

The homogeneous decomposition of the organic species, which is the basis of the ex-situ method, can compete with direct electrolysis on weakly alkaline solutions since degradation of the phenols is initiated by radicals formed in the reaction of O_3 with OH^-, with HO_2^- or with phenates.

On the basis of the data collected for CPh, the so called "cathodic oxidation" approach offers the best advantages, and results can be further improved since there are promising developments in the study of efficient systems for the electrochemical ozone production. In a perspective development of the research it would be interesting to examine the oxidation of organic species with O_2/O_3 as a function of the applied cathodic potential and of the amount of O_3 in the gas phase so as to create conditions for O_3 reduction to be the preferred process or, in other words, establish the role of active oxygen intermediates.

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