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Selective oxidation of pentachlorophenol on diamond electrodes☆

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Abstract

The influence of electrode potential on pentachlorophenol (PCP) oxidation on boron doped diamond (BDD) electrodes in a 0.1 mol L^{-1} Britton–Robinson buffer (pH 5.5) is described. Controlled potential electrolyses were carried at 0.9, 2.0 and 3.0 V vs Ag/AgCl and the solutions analysed by square wave voltammetry, high performance liquid chromatography, chloride ion selective electrode and spectroscopy in the ultraviolet–visible region. At low positive potential (0.9 V), the formation of an adherent film on the electrode surface involving the transference of 1 electron per PCP molecule was observed. The film was identified as the dimer 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone and the current efficiency was as high as 90%. At potentials close to the onset of O_2 evolution (2.0 V), the formation of the corresponding quinone (*p*-tetrachlorobenzoquinone) was detected at the beginning of the process. This was followed by further oxidation to the hydroxy-benzoquinone with a practically quantitative yield. Electrolyses carried out well into the region of oxygen evolution (3.0 V) lead to the electrochemical combustion of PCP to CO_2 and H_2O as well as to the release into solution of 5 Cl^- ions per PCP molecule destroyed.

1. Introduction

Increasing restrictions in environmental control have led to the development of electrochemical methodologies for the monitoring and elimination of toxic organic compounds in wastewater. Among such substances, pentachlorophenol (PCP) is a fungicide still widely used for wood preservation, although it is forbidden in several countries. The World Health Organisation classifies PCP as a highly dangerous substance. The human body through the respiratory or the gastrointestinal systems can absorb this pesticide producing skin and mucous irritations. Contamination with PCP can also provoke damage to the eyes, pharynx and larynx [1].

The elimination of PCP from industrial waste by incineration is highly inconvenient due to the generation of toxic combustion products such as dioxins, which are even more hazardous than PCP itself [1]. Therefore, the search for alternative methods to eliminate PCP from the environment has become an urgent task [2–4].

Electrochemical methods are a promising alternative for the complete oxidation of organic compounds prejudicial to the environment since they allow an initial transformation of the aromatic compounds into less toxic substances that can be biologically destroyed or even, in special cases, complete transformation to CO_2 and water (electrochemical combustion).

The electrochemical oxidation of chlorinated phenols has been reported by Rodgers et al. [5] and the reaction behaviour was analysed on bright Pt and on three different metal oxide surfaces, namely, PbO_2, SnO_2 and IrO_2. On Pt and at potentials more positive than 0.6 V vs HESS, the authors reported the inhibition of the active sites on the Pt surface by a monolayer of olygomers formed by a hydroxyl radical reaction. On the other hand, it was observed that on PbO_2 a direct transference of electrons to the reagent molecule occurs without inhibition of the electrode surface, while on SnO_2 and IrO_2 the hydroxyl radical reaction leading to the olygomer formation was again identified. The authors were able to determine current efficiencies as high as 50% when applying 0.1 mA cm^{-2} on the three oxide anodes tested [5].

Kazunga et al. [6] used the enzyme *Horseradish peroxydase* to promote the catalytic oxidation of PCP in aqueous medium with the pH varying between 4 and 7. The authors detected mainly the formation of the dimer 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone (PPCHD) and only traces of other soluble products. The dimer was dissolved in acetonitrile and analysed by high performance liquid chromatography (HPLC). Under typical conditions of reverse phase

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HPLC the PPCHD is capable of undergo reduction and subsequent dissociation to the original PCP molecule [6].

The electrooxidation of PCP in aqueous medium was also studied by Gattrell and Macdougall [7]. Here, the experiments were performed on pyrolytic carbon, vitreous carbon, gold and platinum electrodes in phosphate and acetate buffers with the pH varying between 6 and 7. It was concluded that the overall reaction involves the transference of one electron per PCP molecule and the main product detected was again the dimer PPCHD. This is a rather insoluble compound that precipitates on the electrode surface thus blocking the active sites. The oxidation of PCP to quinone was not detected under those experimental conditions but some polymeric species were present in solution [7].

Oturan et al. [8] generated hydroxyl radicals on a carbon felt electrode for the destructive oxidation of pentachlorophenol. The PCP degradation was confirmed by the decrease in the total organic carbon (TOC) as well as by the increase in free chloride ions in solution. Such evidence is indicative of the complete destruction of the pesticide molecule.

This short review leads to the conclusion that the formation of chlorinated intermediates and polymeric films are the most common pathways for the reaction under mild oxidative conditions. However, hydroxyl radicals formed on the electrode surface can produce the electrochemical combustion of PCP. Meanwhile, there is a lack of a systematic study on the effect of electrode potential on the oxidation of PCP and/or related compounds carried out under similar experimental conditions using a single electrode material.

The electrode material to be used for the complete oxidation of PCP has to posses a wide electrochemical window as well as an enhanced stability in aggressive conditions to allow the generation of hydroxyl radicals. The boron doped diamond electrode (BDD) is an exceptional choice of electrode material since it presents the above characteristics in contrast with other allotropic forms of carbon such as pyrolytic and vitreous carbon electrodes [9–12]. Moreover, this material readily produces $OH^{\bullet}$ radicals on its surface at high positive potentials, thus allowing the electrochemical combustion of organic molecules present in solution [13, 14].

In this work, the oxidation mechanism of PCP was studied at different potentials by constant potential electrolysis on the BDD electrode in aqueous media. The solutions were analysed by square-wave voltammetry (SWV), HPLC and UV–vis techniques. Additionally, the concentration of chloride ions and the total organic carbon (TOC) in solution were also determined during the experiments.

2. Experimental details

Electrolyses were carried out in a three-compartment electrochemical cell with a total volume of 20 mL. The PCP solutions were prepared from a 1.0×10^{-3} mol L^{-1} stock solution. The BDD electrode (1.2 cm × 1.2 cm) was kindly furnished by Werner Haenni from Centre Suisse de Electronique et de Microtechnique SA, Neuchâtel, Switzerland [11]. The reference electrode was the Ag/AgCl/KCl 3.0 mol L^{-1} system provided with a Luggin capillary while the auxiliary one was a Pt foil. The electrochemical measurements were performed in a 0.1 mol L^{-1} Britton–Robinson (BR) buffer with pH adjusted to 5.5. For the TOC analysis, the electrolyses were conducted in a phosphate buffer having the same pH that the BR solution. Electrolyses at 0.9 V required the periodical removal of a blocking surface film by immersion in acetonitrile. For those at 2.0 and 3.0 V, a periodic reactivation of the surface was performed by applying a negative potential of about −3.0 V for 30 s every 30 min.

The electrochemical experiments were performed in a model 273A EG & G PARC potentiostat/galvanostat linked to a microcomputer and controlled by the M-270 software (EG & G PARC). The characterisation of the products obtained during the electrolyses was achieved using a high performance liquid chromatography (HPLC) instrument model LC-10AT Shimadzu linked to a UV–vis detector model SPD-10AV Shimadzu. Here, the mobile phase was a 60:40 v/v mixture of acetonitrile and water acidified by acetic acid with flow rate of 1 mL min^{-1}. The elution was performed under isocratic conditions and the wavelength monitored was 300 nm. The chromatographic column was a RP-18 LiChrosorb column (5 μm) from Merck. These analyses were performed using samples from the electrolyses in BR buffer as well as those collected in acetonitrile (below). The responses were compared with the corresponding calibration curves since in the latter case the intensity of the HPLC signal is much higher. The UV–vis spectra were obtained in a model U-2010 Hitachi spectrophotometer. The ion selective electrode used for the determination of free chloride ions in solution was the model 96-17B from Orion and the total organic carbon content was measured in a model TOC-V CPH/CPN Shimadzu instrument.

3. Results and discussion

Square wave voltammetric experiments with PCP on BDD electrodes in BR buffer have been recently reported [15]. They show a single oxidation peak at around 0.80 V vs Ag/AgCl with the characteristics of an irreversible electrode reaction controlled by the adsorption of the reagent. The SWV parameters were optimised in relation to the maximum value of peak current and the maximum selectivity (half-peak width). Such procedure yielded the following values: square wave frequency (f) 100 s^{-1}, square wave amplitude (a) 50 mV and scan increment (ΔE_s) of 2 mV. Figure 1 illustrates the results and indicates the different potentials used for the electrolyses. Other details on the optimization procedure can be found elsewhere [15].

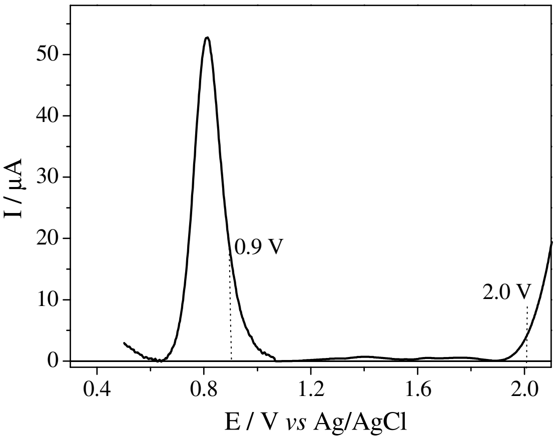


Fig. 1. Square wave voltammograms for 4.5×10^{-5} mol L^{-1} PCP in 0.1 mol L^{-1} BR buffer at pH 5.5 ($f = 100$ s^{-1}, $\Delta E_s = 2$ mV and $a = 50$ mV).

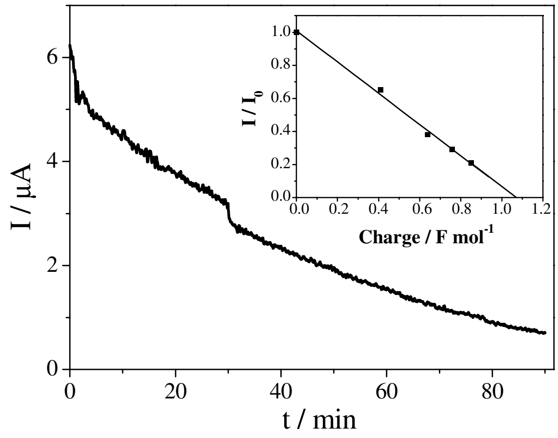


Fig. 2. Chronoamperometric response for PCP electrolysis at 0.9 V. Initial concentration of PCP 5.0×10^{-5} mol L^{-1} in 0.1 mol L^{-1} BR buffer, pH 5.5. Insert: relationship between the I/I_o and the charge passed for PCP oxidation.

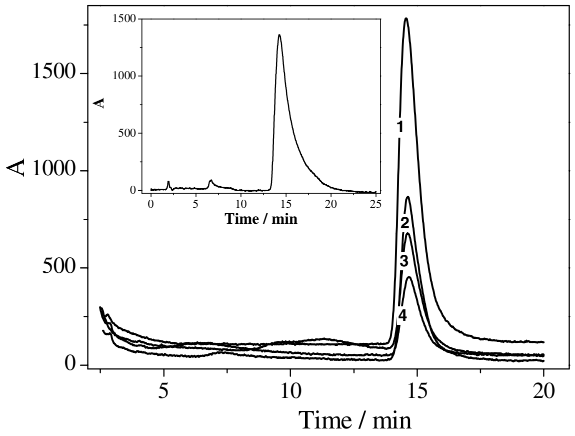


Fig. 3. Chromatograms for aqueous samples from PCP electrolysis at 0.9 V as a function of time: 0 (1), 30 (2), 60 (3) and 90 min (4). Insert: chromatographic response of the acetonitrile extract taken from the electrode surface after 30 min electrolysis (as mentioned in the Experimental section, the HPLC response for PCP is much higher when acetonitrile is used as the solvent).

The electrochemical oxidation of PCP on the BDD electrode was studied by controlled potential electrolysis at room temperature. The experiments were conducted at three different applied potentials in selected regions of the voltammogram shown in Figure 1. First, the oxidation was studied just after the PCP voltammetric peak (0.9 V); in the sequence, a potential at the onset of oxygen evolution was chosen (2.0 V) and, finally, the electrochemical combustion of PCP was achieved in a region where $OH^{\bullet}$ formation is the predominant reaction (3.0 V) [13, 14]. These experiments will be separately described in the following Sections. Meanwhile, to exclude the possibility of oxidation by hypochlorite ions generated from the Cl^- freed from the PCP molecules, electrolyses were carried out at 3.0 V in the absence of PCP but containing a (five-folded) equivalent amount of NaCl. The concentration of Cl^- ions remained constant throughout the process thus proving that under those conditions Cl_2 formation does not compete with oxygen evolution.

3.1. *Electrolyses at 0.9 V*

Electrolyses at 0.9 V were carried out in BR buffer (pH 5.5) with an initial PCP concentration of 5.0×10^{-5} mol L^{-1}. Blockage of the electrode surface was clearly observed after approximately 30 min by the drop of the current to a practically zero value. The film formed on the electrode surface was removed by dissolution in acetonitrile and kept for further analysis. The process was stopped after 90 min and the exponential current-time decay during electrolysis is presented in Figure 2 together with a linear plot (insert) showing the relative variation of the current as a function of the passed charge [16]. This latter plot indicates the transference of one electron per PCP molecule.

Figure 3 shows the chromatograms recorded for samples taken from the electrochemical cell at different times during the electrolysis at 0.9 V. No other products were detected by HPLC and the PCP decay corresponds to about 80% of the original concentration. Very similar results were obtained by SWV analysis of the PCP concentration. In addition, the insert of Figure 3 shows the chromatogram recorded from the acetonitrile extract (surface film) taken after 30 min of electrolysis. In this case, the peak shape and retention time are very similar to that of pure PCP. This fact will be explained after the mechanistic discussion.

Finally, the determination of free chloride ions in solution after electrolysis at 0.9 V showed that the concentration was below the detection limit of the ion selective electrode (10^{-6} mol L^{-1}) suggesting that no Cl^- ions were released during the process.

The results presented above suggest that PCP removal from solution should occur by the formation of a surface film on the electrode. A dimerisation mechanism for PCP has been proposed by Gattrell and Macdougall [7] where the radicals initially formed by a $1e^-$ transfer

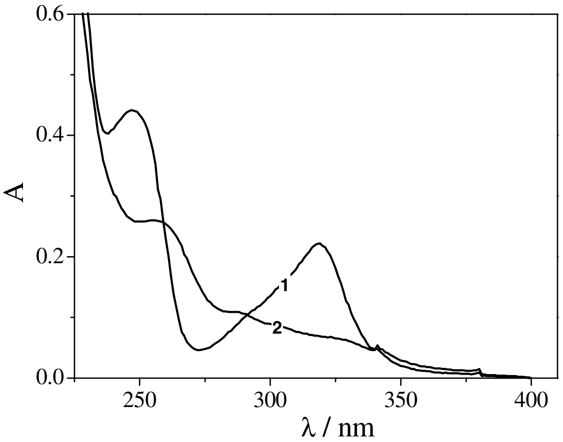


Fig. 4. UV–vis spectra obtained in acetonitrile for: 5.0×10^{-5} mol L^{-1} PCP (1) and for the film deposited on the electrode surface (2).

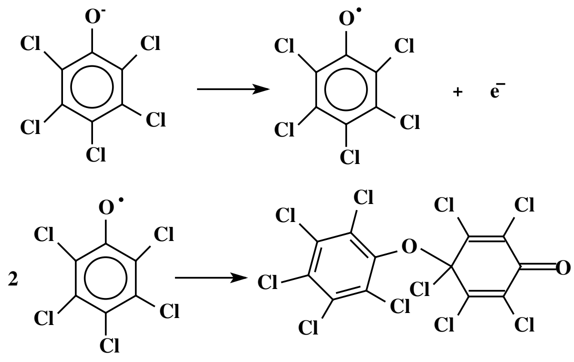
can give raise to a variety of products. Meanwhile, dimerisation through the formation of a C–C bond is less probable due to severe steric hindrance and the main products should be those involving an oxygen bridge [7].

To confirm the dimerisation mechanism for PCP, samples of the surface film were collected in acetonitrile and analysed by HPLC and UV–vis spectroscopy. The UV–vis absorption spectra obtained for pure PCP and for the film in acetonitrile solutions are presented in Figure 4.

The spectrum of the film shows a maximum of absorption at 259 nm while for PCP its characteristic peak is around 320 nm. From data in the literature [6], the peak obtained at around 259 nm can be attributed to the dimeric compound 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone (PPCHD).

This later compound (PPCHD) is not a very stable species and may undergo decomposition when injected in the chromatographic column. As mentioned in Section 1, the dimer can be reduced back to pentachlorophenol by metallic residues present in the column [6]. According to the same authors [6], large amounts of PPCHD give rise to a HPLC peak having a retention time of about 18 min under the conditions used here. The chromatogram for the surface film dissolved in acetonitrile was already presented in the insert of Figure 3 and shows a large peak corresponding to PCP and a small shoulder at around 18 min. Therefore, the PPCHD dimer is the most probable oxidation product from PCP at 0.9 V although the formation of polymeric species should not be discarded.

The results above, together with the previous literature data [6,7], suggest a reaction mechanism for PCP oxidation on the BDD electrode at 0.9 V. Scheme 1 shows the suggested mechanism where the initial formation of the PCP radical is followed by a radical–radical coupling through the oxygen atom to form the surface film, blocking the electrode surface.



Scheme 1. Proposed reaction pathway for the oxidation of PCP on the BDD electrode at 0.9 V forming the dimer 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone.

To evaluate the consumption of organic material in the electrolytic cell, samples of the solution where analysed to quantify the total organic carbon (TOC) in solution during the electrolyses (now performed in 0.1 mol L^{-1} phosphate buffer at pH 5.5 to avoid the carbon molecules from the acetic acid in the BR buffer). The results are presented in Figure 5 and show a reduction of only 40% in the TOC by electrolysis at 0.9 V. Such reduction is much smaller than that measured by SWV and HPLC (Figure 2) and might be due to either a partial solubility of the PPCHD dimer or even to the formation of olygomers and/or polymers that remain in the cell solution.

The current efficiency (ε) for the electrode processes was calculated using the following relationship [17]:

$$\varepsilon = \frac{100 Q_{\mathrm{PCP}}}{Q_{\mathrm{PCP}} + Q_{\mathrm{Blank}}} \tag{1}$$

where the charge Q_{PCP} was obtained from the chronoamperometric curve between time 0 and 90 min and Q_{Blank} was that from an analogous experiment but without PCP added to the electrolyte. From those measurements and considering the elimination of 80% of the initial reagent concentration, the efficiency value obtained for the PCP electrolyses on the BDD electrode at 0.9 V was 96%.

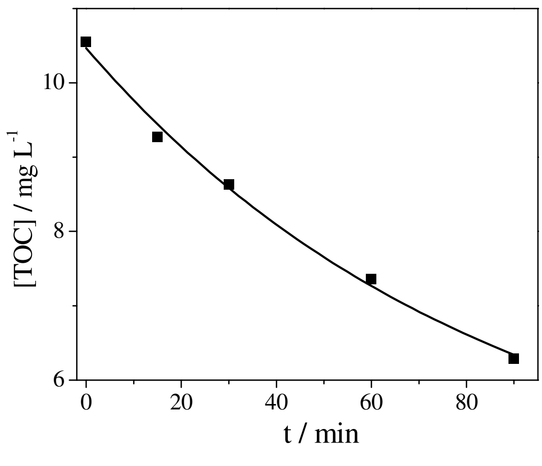


Fig. 5. Total organic carbon variation during PCP electrolysis on BDD electrode at 0.9 V in 0.1 mol L^{-1} phosphate buffer, pH 5.5.

3.2. *Electrolysis at 2.0 V*

Electrolyses at the onset of oxygen evolution (2.0 V) were conducted in 6.5×10^{-5} mol L^{-1} PCP concentration in BR buffer (pH 5.5). The currents measured at the beginning of the experiment were much higher than in the previous case and, consequently, the decay with time was much steeper, as shown in Figure 6. The linear plot in the insert of Figure 6 shows that four electrons are involved in this oxidation process.

To facilitate the simultaneous voltammetric determination of PCP decay and the compound formed by oxidation (below), SWV analysis of the solution at different times during the electrolysis at 2.0 V was carried out after an initial polarisation at 0.0 V. The results are presented in Figure 7 (curves 1–3) together with the response obtained for a 5.0×10^{-5} mol L^{-1} *p*-chloranil solution under the same experimental conditions (curve 4). In all cases, the *p*-chloranil molecules at the interface are reversibly reduced at the initial potential to its hydroquinone form thus showing an oxidation peak at about 0.18 V in the anodic sweep. That peak at 0.18 V goes through a maximum after approximately 80 min electrolysis and then diminishes with time. No other electroactive species could be detected in these experiments but certainly *p*-chloranil is being further oxidised under these conditions.

A similar behaviour was observed with the UV–vis measurements (Figure 8) where the PCP band at 320 nm diminishes with time and the new band at around 290 nm grows initially and then decays. This latter band corresponds to *p*-chloranil (curve 4) and confirms the previous SWV results.

The chromatograms obtained for the PCP solution at different electrolysis times (Figure 9) showed a peak characteristic of *p*-chloranil with a retention time of 6.6 min as determined from a standard sample (curve 4). They also show the appearance of another oxidation product with a retention time of 3.9 min. After 100 min electrolysis at 2.0 V, the *p*-chloranil peak has almost

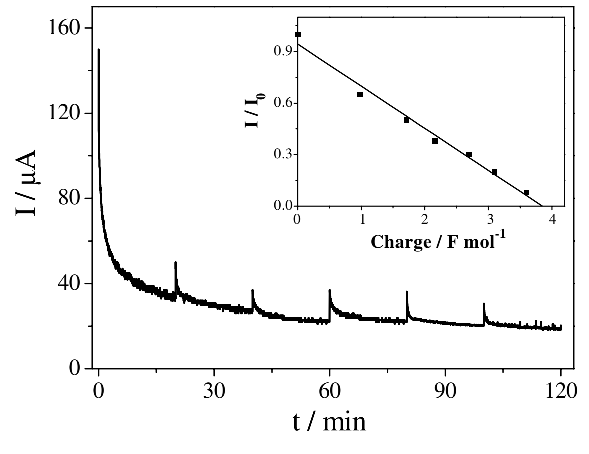


Fig. 6. Chronoamperometric response for PCP electrolysis at 2.0 V. Initial PCP concentration of 6.5×10^{-5} mol L^{-1} in 0.1 mol L^{-1} BR buffer, pH 5.5. Insert: relationship between the I/I_o and the charge passed for PCP oxidation.

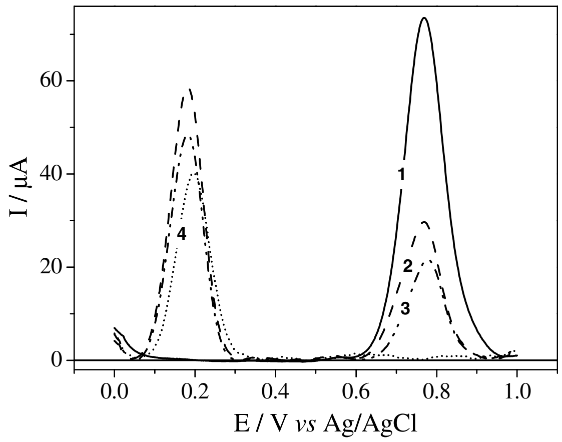


Fig. 7. Square wave voltammograms in 0.1 mol L^{-1} BR buffer pH 5.5 ($f = 100$ s^{-1}, $a = 50$ mV and $\Delta E_s = 2$ mV) recorded after initial polarisation at 0.0 V for the solution under electrolysis at 2.0 V at different times: 0 (1), 80 (2) and 120 min (3) and for 5.0×10^{-5} mol L^{-1} *p*-chloranil standard solution under the same experimental conditions (4).

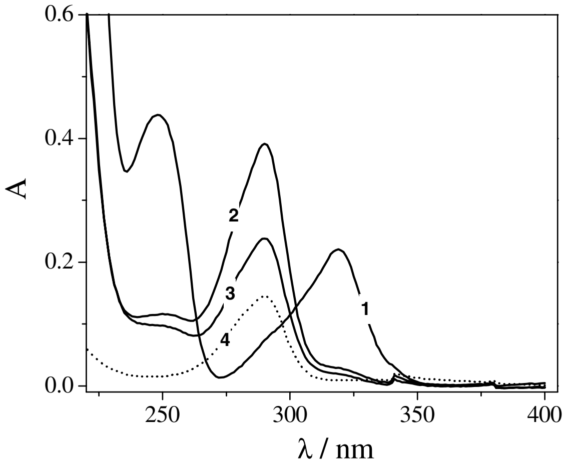


Fig. 8. UV–vis spectra for the electrolysis of PCP at 2.0 V as a function of time: 0 (1), 80 (2) and 120 min (3) and for 3.0×10^{-5} mol L^{-1} *p*-chloranil standard solution (4).

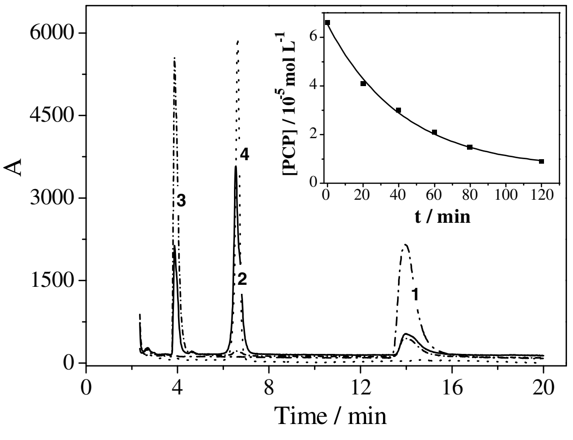


Fig. 9. Chromatograms for samples from PCP electrolysis at 2.0 V as a function of time: 0 (1), 100 (2), 120 min (3) and for 5.0×10^{-5} mol L^{-1} *p*-chloranil standard solution (4). Insert: variation of PCP concentration during electrolysis at 2.0 V.

disappeared completely while the other one has increased significantly. This is further evidence that *p*-chloranil undergoes a subsequent oxidation under these conditions. The insert in Figure 9 indicates that approximately 86% of the initial PCP concentration was consumed after 2 h electrolysis. This information together with equation [1] and the data extracted from Figure 6 reveals a current efficiency of 90% for the electrolysis at 2.0 V.

The concentration of free chloride ions in solution was measured as 1.1×10^{-4} mol L^{-1} at the end of the electrolysis at 2.0 V. This value corresponds to the removal of two chloride atoms per PCP molecule. In addition, analysis of the TOC showed very small changes during electrolysis with the carbon concentration varying from 12.55 mg L^{-1} to 11.95 mg L^{-1}. This is an indication that neither the organic molecules nor the carbon atoms were removed from solution.

The experimental results obtained for the electrolysis at 2.0 V are in total agreement with the literature [7, 8, 18] showing that the PCP anion is initially oxidized by two electrons to the corresponding radical cation that immediately reacts with water to form *p*-chloranil. In the sequence, *p*-chloranil undergoes nucleophilic addition of water, resulting in the formation of a trihydroxybenzene derivative that is further oxidised to the corresponding quinone, following the Scheme 2 depicted below.

3.3. *Electrolysis at 3.0 V*

After 90 min electrolysis at 3.0 V, 95% of the initial 6.5×10^{-5} mol L^{-1} PCP concentration in BR buffer (pH 5.5) was consumed, as shown by the HPLC results presented in Figure 10. No other products could be detected by SWV, HPLC or UV–vis. analyses of the solution. Moreover, the PCP depletion in solution was accompanied by an equivalent increase of free chloride ions as also shown in Figure 10 where 5 Cl^- per PCP consumed were measured. This indicates that the original molecule and/or its oxidation fragments have been completely dechlorinated during the process.

Finally, the total organic carbon present in solution after 90 min electrolysis at 3.0 V diminished from 12.5 to 3.1 mg L^{-1}. This corresponds to 75% of that initially measured thus suggesting that a great proportion of the pesticide molecules has undergone a complete oxidation to CO_2 and H_2O in accordance with the reaction [8]:

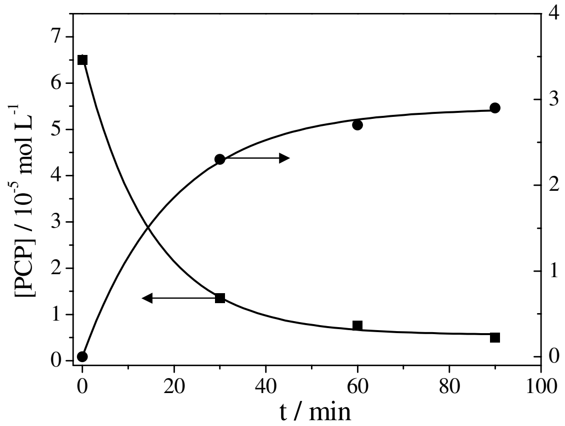


Fig. 10. Variation of PCP (■) and chloride ions concentration (●) with time for electrolysis at 3.0 V.

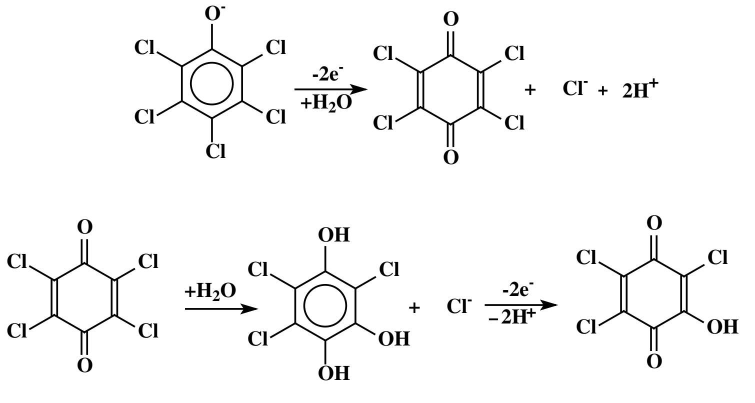
$$C_6Cl_5OH + 11\,H_2O \rightarrow 6\,CO_2 + 5\,HCl + 18\,H^+ + 18\,e^-$$

The remaining 25% should correspond to non-oxidized PCP (5%) and to other non-chlorinated and not mineralized intermediates (20%). Nevertheless, the majority of the PCP molecules was oxidised via $OH^{\bullet}$ radicals formed on the electrode surface resulting in the electrochemical combustion of the organic species.

The current efficiency for the process was not calculated in this case due to the intense oxygen evolution that occurs during electrolysis under these experimental conditions.

4. Conclusions

The electrochemical oxidation of pentachlorophenol on boron-doped diamond (BDD) electrodes is strongly dependent on the applied potential. Thus, under fairly mild conditions (0.9 V vs Ag/AgCl) a dimerization process leads to the formation of an insoluble species than can be removed from the solution. This could offer



Scheme 2. Reaction pathway for the oxidation of PCP on the BDD electrode at 2.0 V.

the possibility of a low-cost treatment for polluted wastewater if properly optimized.

At more positive potentials (2.0 V), an initial step converts PCP into *p*-tetrachlorobenzoquinone (*p*-chloranil) and this is followed by further oxidation to the corresponding hydroxy-quinone with almost quantitative yield.

Finally, the enhanced ability of BDD electrodes to generate $OH^\bullet$ radicals and to promote the electrochemical combustion of organic molecules is again demonstrated using a heavily chlorinated molecule. In this case, all chlorine atoms in the molecule appear in solution as Cl^- ions thus proving that no volatile chlorine-containing species were generated during the oxidation process that, in turn, converted most of the pesticide molecules in CO_2 and water.

Acknowledgements

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