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Electrochemical Determination and Removal of Pentachlorophenol at Diamond Electrodes

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Abstract

This work describes the determination of pentachlorophenol (PCP) in pure and polluted waters by square wave voltammetry (SWV) and the influence of the electrode potential on PCP oxidation on boron doped diamond (BDD) electrodes. Measurements carried out in solutions of the Britton-Robinson buffer with pH = 5.5 revealed a single oxidation peak at 0.80 V *vs.* Ag/AgCl for PCP in a process that is controlled by the adsorption of the species. The detection limits obtained were 5.5 μg L^{-1} in pure water and 15.5 μg L^{-1} for water taken from a local creek, respectively. Controlled potential electrolyses were carried at 0.9, 2.0 and 3.0 V *vs.* Ag/AgCl and the solutions analysed by SWV, HPLC, chloride ion selective electrode and UV-vis spectroscopy. 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. At potentials close to the onset of O_2 evolution (2.0 V), the formation of the corresponding quinone was detected. Electrolyses carried out well into the region of oxygen evolution (3.0 V) lead to the total 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.

***Keywords*:** diamond electrode, square wave voltammetry, electroanalysis, pentachlorophenol, electrochemical combustion.

Introduction

The use of electroanalytical methods for the determination of a variety of organic and inorganic substances is steadily growing due to several improvements that have allowed the attainment of detection limits compatible with environmental regulations. Meanwhile, those methods are usually based on processes occurring at an Hg surface and the hazardous potential for human health of this and other

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heavy metals strongly indicates the necessity of seeking alternative electrode materials. Such useful alternatives have been proposed for the determination of pentachlorophenol (PCP) by oxidation on carbon paste and vitreous carbon surfaces [1, 2].

On the other hand, organo-chlorinated compounds are a serious menace to public health when present in the environment [3] and precise determinations of their concentration are much necessary. Pentachlorophenol (PCP) is a highly dangerous and persistent chemical widely used for wood preservation and can be used as model compound for the development of new analytical techniques. The allowed level of PCP established by the local environmental council [4] for waters in general is 10 μg L^{-1} although lower limits are set by other agencies.

Boron-doped diamond (BDD) electrodes have received much attention in recent times due to their very large electrochemical window resulting from the low reactivity of their surfaces [5]. As a consequence, BDD electrodes can be used at very high potential values, either negative or positive, without promoting the electrolyte decomposition [6], thus offering an excellent alternative to mercury for electroanalytical purposes. Recent works reported in the literature [7-9] have shown that several bio-molecules can be satisfactorily determined using BDD electrodes.

The elimination of PCP from industrial waste by incineration is highly inconvenient due to the generation of toxic burning products such as dioxins, which are even more hazardous than PCP itself [3]. Therefore, the search for alternative methods to eliminate PCP from the environment has become an urgent task [10-12].

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, the complete transformation to CO_2 and water (electrochemical combustion).

Gold *et al.* [13] 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 HPLC. Under typical conditions of reverse phase HPLC the PPCHD is capable of undergo reduction and subsequent dissociation to the original PCP molecule [13].

The electrooxidation of PCP in aqueous medium was also studied by Gattrell *et al.* [14]. 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. From the results 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 [14].

Oturan *et al.* [15] generated hydroxyl radicals on a carbon felt electrode aiming to the destructive oxidation of pentachlorophenol. The PCP degradation was confirmed by the decrease of the total organic carbon (TOC) as well as by the increase of free chloride ions in solution. Such evidences are indicative of the complete destruction of the pesticide molecule.

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. Straightforward, 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 the pyrolytic and the vitreous carbon electrodes [5-7, 16]. 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 [17,18].

The objective of this work is to establish an appropriate methodology for the analytical determination of pentachlorophenol in pure and natural waters by

means of square wave voltammetry, and to study the oxidation mechanism of PCP 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.

Experimental

A conventional three-electrode cell with a Ag/AgCl (3.0 mol L^{-1}) system and a Pt wire as the reference and auxiliary electrodes, respectively, was used. The BDD working electrode was a 0.62 × 1.0 cm single-faced plate, provided by Dr. W. Hänni from CSEM, Neuchâtel, Switzerland. Details of the preparation of the diamond films have been reported elsewhere [5]. Prior to the experiments the electrode was polarized at –3.0 V *vs.* Ag/AgCl for 30 s to remove the hydrophobic film that covers the surface. After each measurement with PCP the electrode was thoroughly rinsed with water to remove any possible residues and ensure the reproducibility of the experiments. Electrochemical measurements were carried out using a model 273A EG&G PARC potentiostat with the M270 software.

A 1.0×10^{-3} mol L^{-1} stock solution of the pesticide (Pentachlorophenol, Aldrich 99%) was prepared using water from the Milli-Q (Millipore) purification system. For the measurements, several supporting electrolytes were initially tested by cyclic voltammetry and the best results were obtained when a 0.1 mol L^{-1} Britton-Robinson (BR) buffer with the pH adjusted to 5.5 by the addition of proper amounts of a 1.0 mol L^{-1} NaOH stock solution was chosen. All reagents were analytical grade.

Analytical curves were obtained by the standard addition method. The recovery experiments were carried out by adding a known amount of PCP to the supporting electrolyte followed by standard additions. All measurements were performed in triplicate. The effect of interferences was evaluated using water samples collected from a local creek (Monjolinho River) at three different points

of São Carlos city, namely, before (point 1), in the middle (point 2), and after crossing town (point 3). The measurements were performed without pre-treatment of the solutions but the pH was properly adjusted to the desired value.

Electrolyses were carried out in a three-compartment electrochemical cell with a total volume of 20 mL (the BDD working electrode was a 1.2 × 1.2 cm). 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 re-activation of the surface was performed by applying a negative potential of ca. -3.0 V during 30 seconds every 30 minutes.

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 mixture of acetonitrile and water acidified by acetic acid in the proportion of 60:40:5.5 v/v/v, respectively, with flow rate of 1 mL min^{-1} while the elution was performed under isocratic conditions. The wavelength monitored was 300 nm. The chromatographic column was a RP-18 LiChrosorb column (5 μm) from Merck Inc. 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.

Results and discussion

The square wave voltammograms recorded on the BDD electrode had similar features to those initially obtained by cyclic voltammetry showing an irreversible response for a single process with a peak potential of *ca.* 0.80 V *vs.* Ag/AgCl. Fig. 1 presents the result obtained for a 5.0×10^{-5} mol L^{-1} PCP solution on the BDD electrode clearly showing the irreversible nature of the electron transfer process.

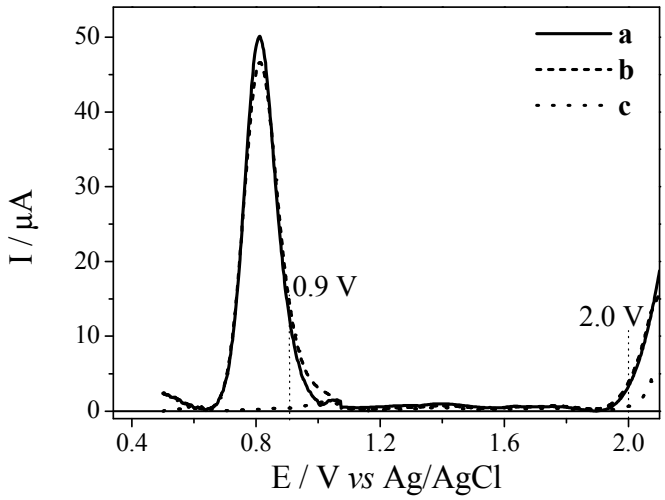


Figure 1. SWV response of the BDD electrode in 4.5×10^{-5} mol L^{-1} PCP (0.1 mol L^{-1} BR buffer, pH = 5.5, a = 50 mV, ΔE_s = 2 mV, f = 100 s^{-1}). Curves corresponding to: total (a); direct (b) and reverse (c) currents. Two of the potentials used for the electrolyses are also shown in the figure.

After the optimization of the experimental parameters of the square wave voltammetry, better results were obtained at frequency (f) of 100 s^{-1}, pulse amplitude (a) of 50 mV and scan increment (ΔE_s) of 2 mV.

Analytical curve for PCP

Fig. 2 shows the square wave voltammograms obtained for the oxidation of pentachlorophenol (PCP) at different concentrations in 0.1 mol L^{-1} BR buffer, pH = 5.5, prepared with pure water and taken after optimization of the experimental parameters. The different curves were obtained using the standard addition method and the BDD electrode. The insert in Fig. 2 corresponds to the analytical curve, that is, the linear dependence of I_p with PCP concentration for the studied interval (0.1 to 6.0×10^{-5} mol L^{-1}).

For the determination of the detection limit (DL), the standard deviation of the mean value for ten voltammograms of the blank (S_B), the slope of the straight line in the analytical curve and equation (1) were used [19]. The calculated value of DL for the BDD electrode was 2.0×10^{-8} mol L^{-1} (or 5.5 μg L^{-1}).

$$DL = \frac{3S_B}{b} \quad (1)$$

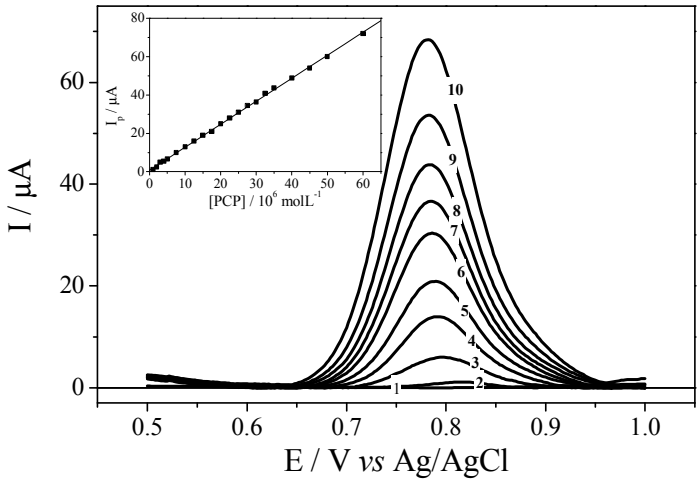


Figure 2. Analytical curve - SWV response of the BDD electrode for different PCP concentrations: 0 (1), 1.0 (2), 3.0 (3), 10.0 (4), 15.0 (5), 25.0 (6), 30.0 (7), 35.0 (8), 45.0 (9) and 60.0×10^{-6} mol L^{-1} (10) in 0.1 mol L^{-1} BR buffer, pH = 5.5, with a = 50 mV, ΔE_s = 2 mV, f = 100 s^{-1}. Insert: linear dependence of the peak current with PCP concentration.

The reproducibility of the method was determined by successive measurements of 5 different PCP solutions of 5.0×10^{-5} mol L^{-1} with a coefficient of variation of 1.8%, while the repeatability calculated at the same concentration level furnished a coefficient of variation of 1.3% (n = 5).

The same routines described before were followed to compare the results obtained through the diamond with those of a conventional technique as high performance liquid chromatograph (HPLC). The analytical curve in pure water solutions for HPLC was also obtained by the standard addition in the same interval for the SWV (0.1 to 6.0×10^{-5} mol L^{-1}). The principal results obtained with both techniques are collected in table 1.

The results showed that the SWV and HPLC methodologies for PCP determination in pure water are in agreement.

Table 1. Analytical characteristics of the analytical curves and detection limits for PCP in pure water obtained by SWV (BDD electrodes) and HPLC.

Parameter	SWV (BDD - electrode)	HPLC
b	1.93	1.63×10^{9}
r	0.9995	0.9993
S_B	1.34×10^{-8}	298.87*
DL / ($\mu g\ L^{-1}$)	5.5	3.0
% Recovery	100.0	96.0

***** The standard deviations of the smaller value that intercept y in analytical curve (n = 6).

Effect of interferences and recovery experiments

To evaluate the effect of interferences on the analytical response of the BDD electrode, SWV studies similar to those described in the previous section were performed using contaminated water samples from a local creek (Monjolinho river). To highlight the interferences effect those samples were used to propose both the stock solution and the supporting electrolyte. Fig. 3 presents the analytical curves obtained on the BDD electrode by the standard addition method for PCP concentrations varying from 0.1 to 6.0×10^{-5} mol L^{-1} in 0.1 mol L^{-1} BR buffer, pH = 5.5, for the different water samples.

The corresponding detection limits (*DL*) were again calculated by means of equation (1) plus a linear regression analysis of the straight lines in Fig. 3 and are collected in Table 2 together with the other relevant parameters. They show how the presence of organic matter in the water sample increases the *DL* value considerably and the reason for that could be one or more of several effects. Firstly, the oxidation of PCP on BDD is preceded by an adsorption step that might be hindered by other organic molecules previously present on the surface. Secondly, humic substances dissolved in the contaminated water could interact with PCP thus reducing its effective concentration at the interface. Finally, unknown electroactive species may suffer oxidation in the same potential region of PCP with the consequent increase in the residual current of the blank solution. All these phenomena will increase the measured *DL* value.

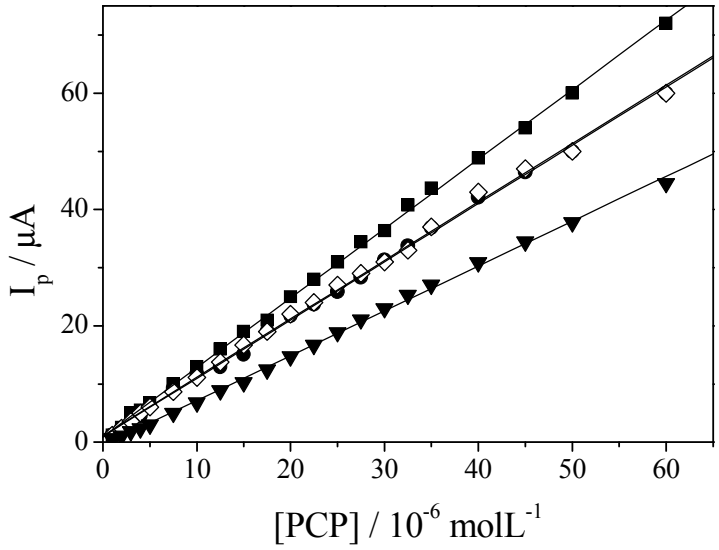


Figura 3. Analytical curves for PCP in solutions prepared with pure water (■) and with samples collected at: point 1 (●), point 2 (◇) and point 3 (▼) of the Monjolinho creek. Same experimental conditions as in Fig. 6.

Table 2. Parameters from the analytical curves and detection limits for PCP in pure and contaminated waters (BDD – electrode).

Sample	*r*	S_B / (μA)	*b* / (A / mol L^{-1})	*DL* / (μg L^{-1})
Milli-Q	0.9996	0.0083	1.200	5.5
Point 1	0.9992	0.009	1.002	7.2
Point 2	0.9990	0.015	1.004	12.0
Point 3	0.9993	0.015	0.771	15.5

The same routines described before were followed to compare the behavior of the diamond with that of a conventional mercury electrode. Thus, after optimization of the experimental conditions, a single and irreversible reduction peak was observed at ca. – 0.78 V *vs.* Ag/AgCl for PCP in a phosphate buffer with pH = 9.0.

A similar set of experiments was carried with the Hg electrode and Fig. 4 presents the analytical curves for PCP concentrations varying from 0.5 to 8.0 × 10^{-6} mol L^{-1}. The detection limits (DL) calculated for the Hg electrode are collected in Table 3.

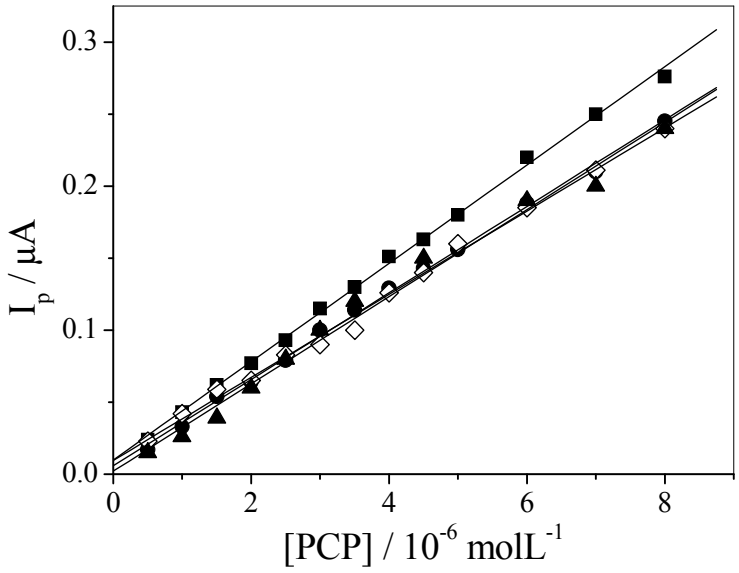


Figure 4. Same as in Fig. 3 but using the Hg electrode in phosphate buffer, pH = 9.0.

Table 3. Parameters from the analytical curves and detection limits for PCP in pure and contaminated waters (Hg-electrode).

Water sample	*r*	S_B (n A)	*b* / (A / mol L^{-1})	*DL* (μg L^{-1})
Milli-Q	0.9992	0.165	0.0341	4.0
Point 1	0.9989	0.250	0.0300	6.6
Point 2	0.9976	0.500	0.0288	14.0
Point 3	0.9961	0.650	0.0285	18.0

Although the Hg electrode furnishes lower values for the DL in pure or slightly contaminated water (point 1), it is clear from the results in Tables 2 and 3 that the BDD electrode is less sensitive to impurities. Thus, for the two more impure samples (points 2 and 3) the DL on BDD is smaller than that on Hg. The reason for that must be associated to quantitative differences in the adsorption processes on both electrode materials and needs further investigation.

Recovery experiments were carried out for each of the samples under investigation and the results are collected in Table 4. They clearly demonstrate that the diamond electrode allows an excellent percentage of recovery even in

highly polluted water samples thus offering the possibility of analytical determinations in environmental matrices.

Table 4. PCP recovery measurements for BDD and Hg electrodes in pure and contaminated waters.

Boron-doped diamond electrode		**Mercury electrode**	
Water sample	**%** Recovered	Water sample	**%** Recovered
Milli-Q	100	Milli-Q	96
Point 1	98	Point 1	95
Point 2	98	Point 2	93
Point 3	97	Point 3	92

Electrooxidaton of PCP

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 values of the applied potential in selected regions of the voltammogram shown in Fig. 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 total combustion of PCP was achieved in a region where $OH^{\bullet}$ formation is the predominant reaction (3.0 V). These experiments will be separately described in the following sections.

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}. A 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 Fig. 5 together with a linear plot (insert) showing the relative

variation of the current as a function of the passed charge [20]. This latter plot indicates the transference of one electron per PCP molecule.

Fig. 6 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 ca. 80% of the original concentration. Very similar results were obtained by SWV analysis of the PCP concentration. In addition, the insert of Fig. 6 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 those of pure PCP. This fact will be explained after the mechanistic discussion.

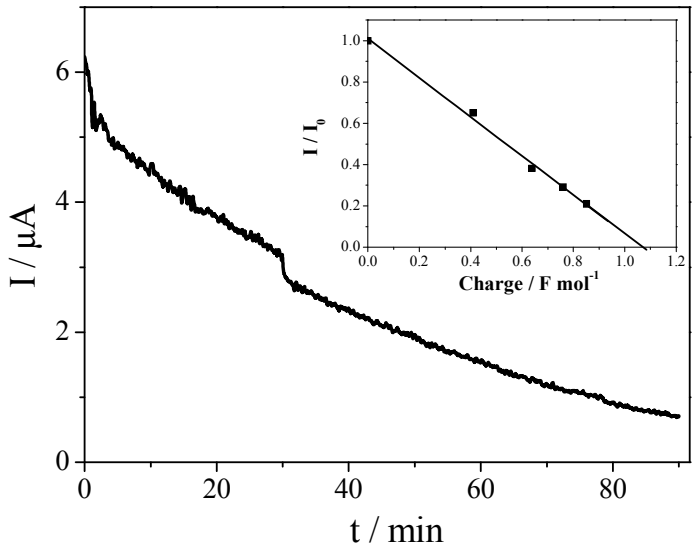


Figure 5. Chronoamperometric response for PCP electrolysis at 0.9 V. Initial concentration of PCP 5.0×10^{-5} mol L^{-1} in 0.1 mol L^{-1} BR buffer, pH 5.5. Insert: relationship between the I/I_o and the charge passed for PCP oxidation.

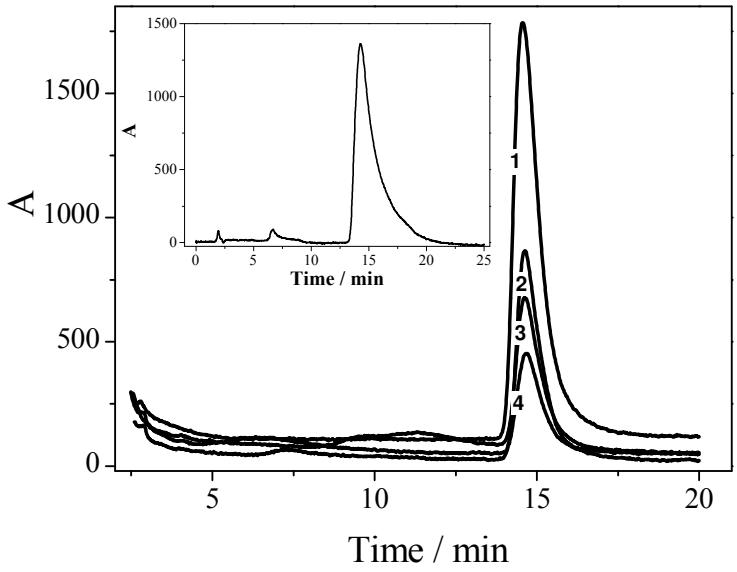


Figure 6. Chromatograms for PCP electrolysis at 0.9 V as a function of time: 0 (1), 30 (2), 60 (3) and 90 minutes (4). Insert: chromatographic response of the acetonitrile extract taken from the electrode surface after 30 min electrolysis.

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 *et al.* [14] where the radicals initially formed by a 1 e^- transfer 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 [14].

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 Fig. 7.

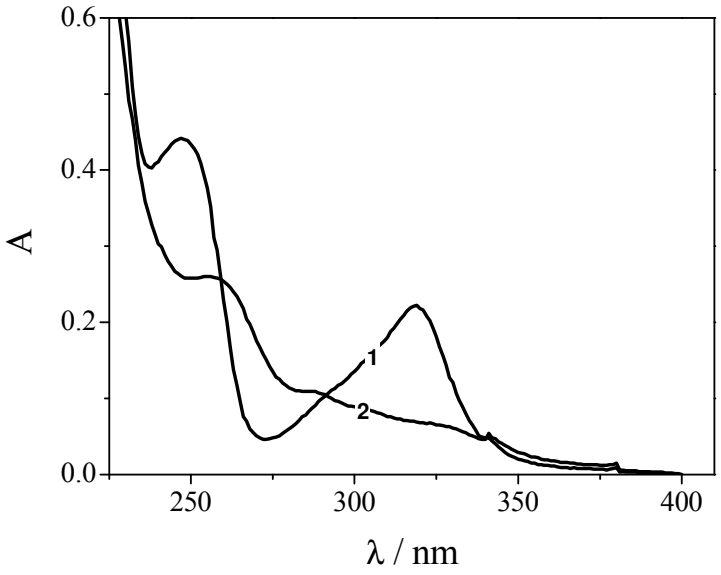


Figure 7. UV-vis spectra obtained in acetonitrile for 5.0×10^{-5} mol L^{-1} PCP (1) and for the film deposited on the electrode surface (2).

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 [13], 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 latter compound (PPCHD) is not a very stable species and may undergo decomposition when injected in the chromatographic column. As it was mentioned in the introduction section, the dimer can be reduced back to pentachlorophenol by metallic residues present in the column [13]. According to the same authors [13], large amounts of PPCHD give rise to a HPLC peak having a retention time of ca. 18 minutes under the conditions used here. The chromatogram for the surface film dissolved in acetonitrile was already presented in the insert of Fig. 6 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.

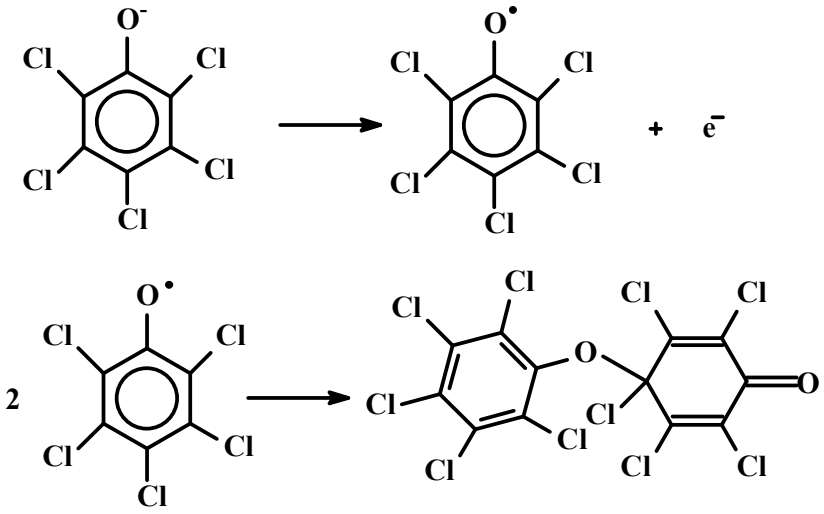
The above results, together with the previous literature data [13,14], allowed to propose a reaction mechanism for PCP oxidation on the BDD electrode at 0.9 V. Scheme I shows the suggested mechanism where the initial formation of the PCP

radical is followed by a radical-radical coupling through the oxygen atom to form the surface film, blocking the electrode surface.

The current efficiency (E) for the electrode processes was calculated using the following relationship [21]:

$$E = \frac{100 Q_{PCP}}{Q_{PCP} + Q_{Blank}} \qquad (2)$$

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%.



Scheme I. 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.

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 stepper, as shown in Fig. 8. The linear plot in the insert of Fig. 8 shows that four electrons are involved in this oxidation process.

SWV analysis of the solution at different times during the electrolysis at 2.0 V are presented in Fig. 9 (curves 1-3) and revealed the transformation of PCP into a new electroactive species having a peak potential of ca. 0.18 V. This is practically the same peak potential obtained in experiments using a 5.0×10^{-5} mol L^{-1} p-tetrachlorobenzoquinone (p-chloranil) solution in the same base electrolyte (curve 4 in Fig. 9). Meanwhile, 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.

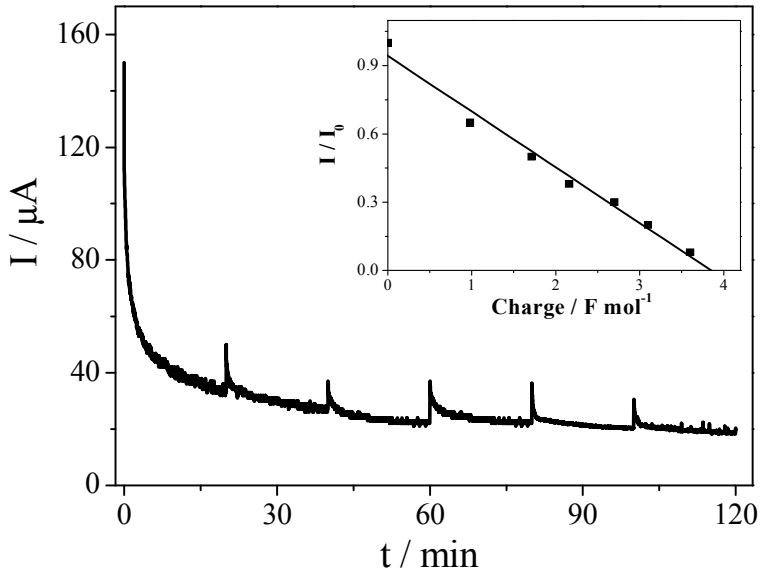


Figure 8. Chronoamperometric response for PCP electrolysis at 2.0 V. Initial PCP concentration of 6.5×10^{-5} mol L^{-1} in 0.1 mol L^{-1} BR buffer, pH 5.5. Insert: relationship between the I/I_o and the charge passed for PCP oxidation.

The chromatograms obtained for the PCP solution at different electrolysis times (Fig. 10) 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 completely

disappeared while the other one has increased significantly. This is further evidence that p-chloranil undergoes a subsequent oxidation under these conditions. On the other hand, the insert in Fig. 10 indicates that approximately 86% of the initial PCP concentration was consumed after 2 h electrolysis. This information together with equation (2) and the data extracted from Fig. 8 reveal a current efficiency of 90% for the electrolysis at 2.0 V.

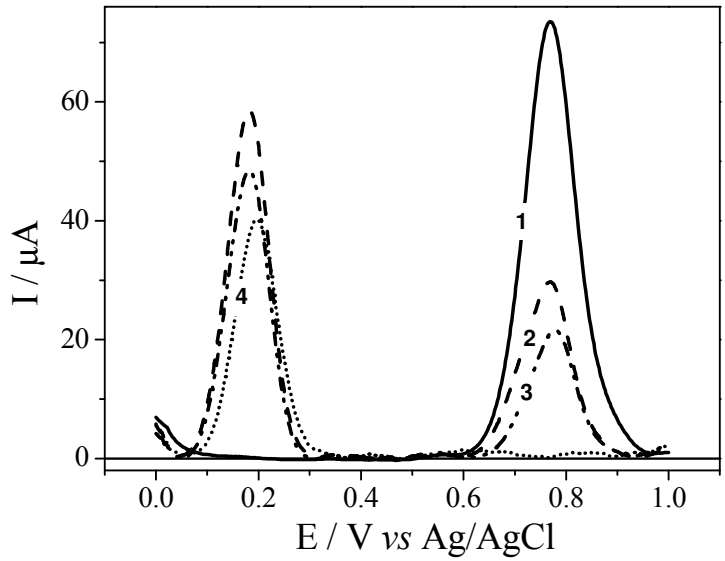


Figure 9. Square wave voltammograms in 0.1 mol L^{-1} BR buffer pH 5.5 (f = 100 s^{-1}, a = 50 mV and ΔE_s = 2 mV) for PCP during electrolysis at 2.0 V at different times: 0 (1), 80 (2) and 120 min (3) and for 5.0×10^{-5} mol L^{-1} *p*-chloranil standard solution in the same electrolyte (4).

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.

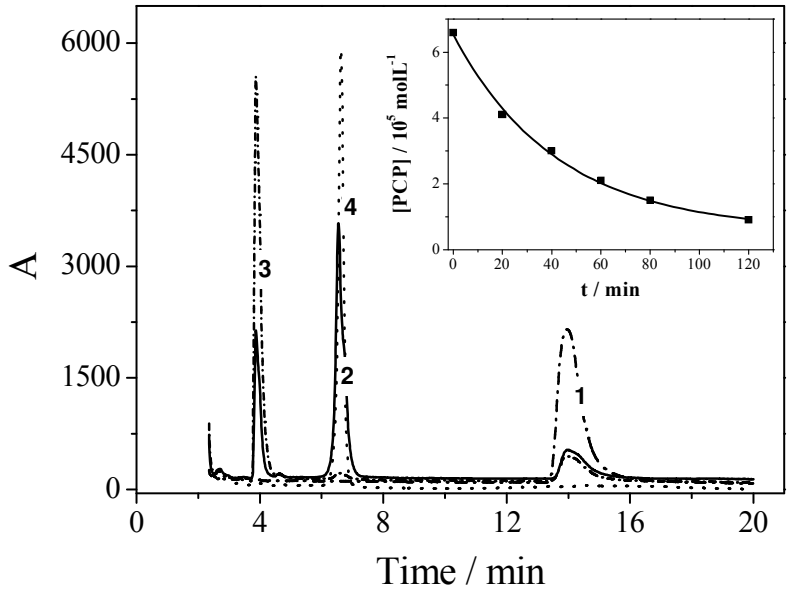
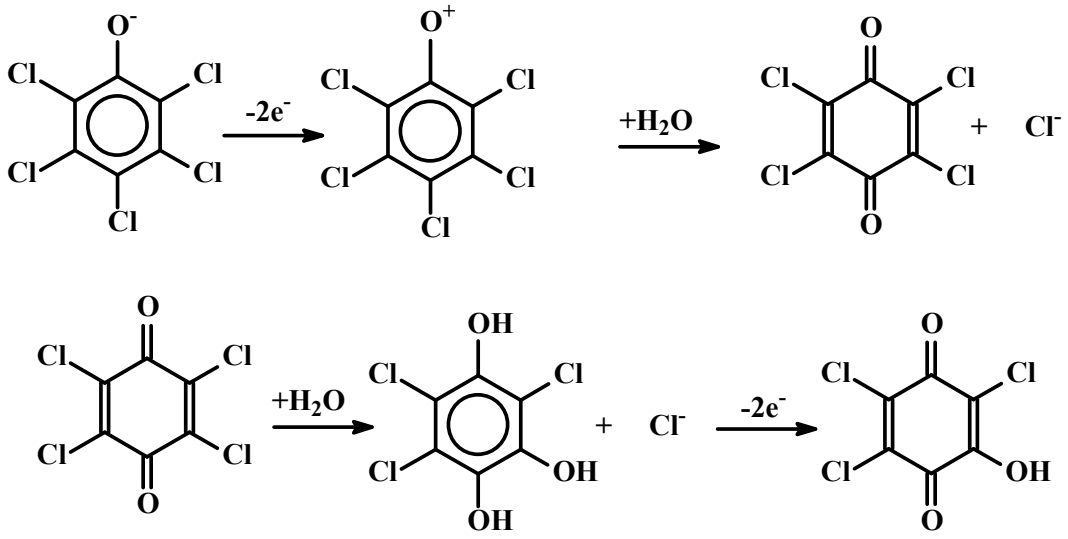


Figure 10. Chromatograms for PCP electrolysis at 2.0 V as a function of time: 0 (1), 100 (2), 120 minutes (3) and for 1.0×10^{-4} mol L^{-1} p-chloranil standard solution (4). Insert: variation of PCP concentration during electrolysis at 2.0 V.

The experimental results obtained for the electrolysis at 2.0 V suggest that the PCP molecule is initially oxidised to the radical cation that reacts with water to form p-chloranil. In the sequence, p-chloranil is further oxidised to the corresponding hydroxy-quinone, following the scheme II depicted below [15,22]:



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

Electrolysis at 3.0 V

As expected, electrolyses performed at 3.0 V resulted in the total combustion of PCP since now the process occurs via $OH^{\bullet}$ radicals formed on the electrode surface. After 90 min electrolysis, 95% of the initial 6.5×10^{-5} mol L^{-1} PCP concentration in BR buffer (pH 5.5) were consumed as shown by the HPLC results presented in Fig. 11. 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 Fig. 11 where 5 Cl^- per PCP molecule were measured. This indicates that the original molecule and/or its oxidation fragments have been completely dechlorinated during the process.

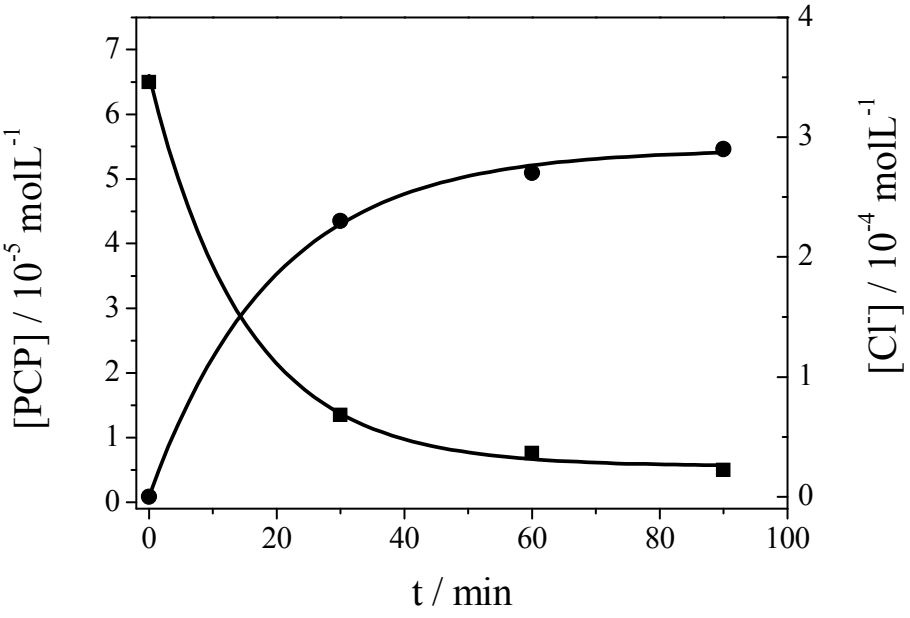


Figure 11. Variation of PCP (■) and chloride ions concentration (●) with time for electrolysis at 3.0 V.

Finally, the total organic carbon present in solution after the electrolysis at 3.0 V was 75% of that initially measured, thus suggesting once more that the pesticide molecule has undergone a complete oxidation to CO_2 and H_2O in accordance with the reaction [15]:

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

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.

Conclusions

The oxidation of PCP on a BDD electrode occurs in an irreversible manner with the species adsorbed on the surface. Optimization of the experimental parameters yielded a detection limit for PCP of 5.5 μg L^{-1} in pure water that increases up to 15.5 μg L^{-1} as a function of the degree of contamination of the water sample while the recovery efficiencies were close to 100%. The *DL* in pure water is low enough to comply with the limits imposed by environmental and/or health authorities for human consumption while in polluted matrices it is just above that limit. The results reported here demonstrate that the combination of square wave voltammetry and the boron-doped diamond electrode is a feasible alternative for the analytical determination of PCP and related molecules in either pure water or polluted natural matrices.

In addition, the electrochemical oxidation of pentachlorophenol on boron-doped diamond electrodes was shown to be strongly dependent on the applied potential. Thus, under fairly mild conditions (0.9 V *vs.* Ag/AgCl) a dimerisation process leads to the formation of an insoluble species that can be removed from the solution. This could offer the possibility of a low-cost treatment for polluted wastewater if properly optimised.

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 total 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 was generated during the oxidation process.

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