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Anodic oxidation of pentachlorophenol at Ti/SnO₂ electrodes

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Abstract The electrochemical oxidation of dilute aqueous solutions of pentachlorophenol (PCP) using Ti/SnO₂ as an electrocatalytic material has been investigated. The studies were carried out in a two-compartment electrochemical cell at three different current density values (10, 30 and 50 mA cm⁻²) at 25 °C and using 20 mg L⁻¹ of PCP in 0.1 M NaOH (pH 10) as supporting electrolyte. The PCP concentration and the by-products of the oxidized solution were monitored during the oxidation process using UV and HPLC techniques. For the three current densities investigated it was found that the rate of PCP elimination depends only on the specific electrical charge. Likewise, the oxidation mechanism was proved to occur through the participation of adsorbed hydroxyl radicals ($\cdot\text{OH}$) formed on the SnO₂ surface, whatever the current density used. However, as the applied current density was increased, a current efficiency lower than 2% was obtained, which is due to mass transfer limitations. In addition, it was observed that the PCP was mineralized to CO₂ with conversion percentages as high as 92% and at current density values as low as 10 mA cm⁻². The PCP degradation produces two other by-products of oxidation (< 10%), namely carboxylic acids, which are non-toxic compounds.

Keywords Electrocatalysis · Pentachlorophenol · Oxidation · Ti/SnO₂ electrode

Introduction

Interest in developing new and more efficient methods for the destruction of hazardous waste and the conversion of mixed waste to low-level toxicity waste continues to increase. Degradation of chlorinated phenols and their derivatives has been especially studied regarding their persistence and bioeffects in aquatic bodies. A particular case is pentachlorophenol (PCP), a broad spectrum biocide which has been historically used in a variety of herbicidal, insecticidal, fungicidal and general disinfectant applications. Owing to their high toxicity level for both human and aquatic organisms, PCP is the subject of strict regulations on its use and disposal and to new or alternative processes of degradation which must be developed [1, 2].

In the last few years, chemical [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13] and biological [14, 15, 16, 17, 18] methods have been assayed in order to remove or, better, to degrade organochlorinated compounds. Among all these methods, the chemical degradation methods seem to be the most promising for both time and efficiency of degradation, although the possibility of using combined biological-chemical processes has also been explored recently [19]. The degradation of organochlorinated compounds has been preferentially studied by the use of advanced oxidation processes in the liquid phase in which the generation of reactive intermediates – such as $\cdot\text{OH}$ radicals – is the main feature in the transformation or mineralization of the compounds, depending on the oxidation method chosen [4, 12, 20].

It is also important to emphasize that the metallic-oxide-based catalysts are still the best option for chemical oxidation by catalysis in the gas phase [21], as well as by catalysis [22] and photocatalysis [3, 4, 8, 10, 12] in the liquid phase. This fact is also true for electrooxidation methods, where the traditional electrocatalysts for degradation processes are metallic oxides such as IrO₂ [23, 24], PbO₂ [25] and Ti/SnO₂ [23, 24, 26, 27]. These electrocatalysts, used to study the electrochemical

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oxidation of non-chlorinated benzene derivatives, have shown high performance levels for conversion and/or combustion of certain hazardous organic compounds. For chlorinated compounds, the electrochemical oxidation of 2-chlorophenol and 2,6-dichlorophenol has been reported recently [28, 29]. In these works it was shown that chlorophenols can be oxidized satisfactorily on PbO_2 , SnO_2 and porous carbon felt electrodes from aqueous solutions with faradic efficiencies as high as 30%. It was shown also that the oxidation route seems to be dependent on the electrocatalytic material used: an opening of the aromatic ring on carbon felt, formation of quinone compounds on PbO_2 , and an almost instantaneous ring-opening reaction on SnO_2 electrodes were proposed as the oxidation steps involved. Nevertheless, in all cases the final products of the electrochemical oxidation were essentially aliphatic acids. On the other hand, the electrooxidation of chlorophenols produces polymeric films on the surface of Au electrodes [30]. In the case of PCP, only the electrochemical reduction on lead electrodes from water and propylene carbonate media has been studied as a degradation process until now [31]. In this work it was shown that the PCP reduction gives only chlorinated (tri- and tetrachlorophenols) compounds as reduction products, whatever the reaction media used. Even though a current efficiency of approximately 100% was reported to reduce PCP directly to 2,3,4,6-tetrachlorophenol in aqueous solution, this and others are not good results from an environmental point of view since these chlorophenols are still toxic and biorefractory compounds. Therefore, if the PCP destruction from aqueous solutions is the desired process, then other alternative electrochemical methods must be considered in order to produce biocompatible reaction products such as aliphatic acids or, better, combustion products such as CO_2 and H_2O .

The aim of this work is to study the electrochemical oxidation of dilute aqueous solutions of PCP as a function of the anodic conditions by using SnO_2 -coated titanium (Ti/SnO_2) anodes as electrocatalysts.

Experimental

The PCP oxidation experiments were made in a two-compartment electrochemical cell with the reaction compartment of 250 mL capacity, as shown schematically in Fig. 1. The anode was made of SnO_2 -coated titanium [23, 24, 26, 27] and the cathode was a UHP graphite rod (EG&G PARC) enclosed in a 10 mL porous porcelain pot. The anolyte composition was 20 mg L^{-1} PCP in 0.1 M NaOH (pH 10) and the catholyte was 0.1 M NaOH. The pH of the anolyte was kept constant during the electrolysis by continuous introduction of a 1 M NaOH solution and its temperature was fixed at 25 °C. The current density for the electrolysis (j_{appl}) was kept constant at the desired level (10, 30 and 50 mA cm^{-2}) from a Tacussel model PJT24-1 (24V-1A) potentiostat-galvanostat. The PCP concentration as well as the oxidation by-products formed during the electrolysis experiments were followed using a Varian model 9050/9012 HPLC, with a $\mu\text{Bondapak NH}_2$ -5 reversed-phase column and a variable wavelength UV-vis detector. The most suitable mobile phase was acetonitrile/0.05 M

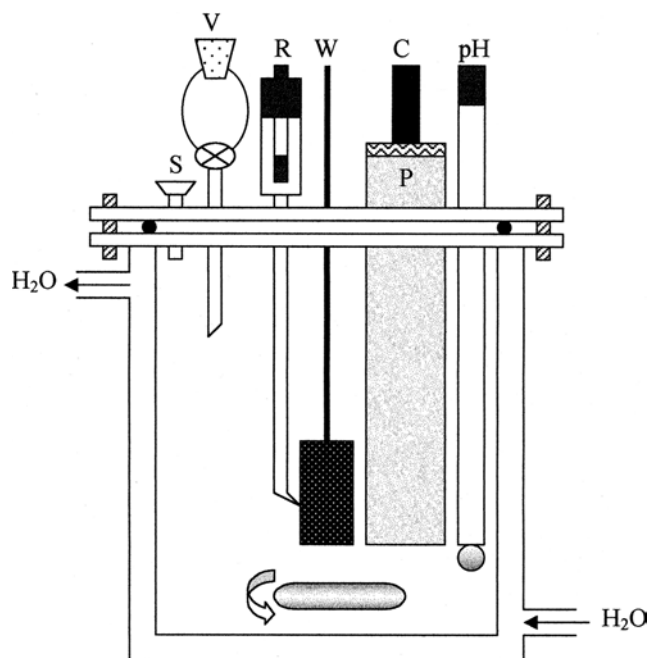


Fig. 1 Diagram of the two-compartment electrochemical cell used for studying electrocatalytic oxidation of PCP. C, counter, R, reference, and W, working electrodes, respectively; pH, pH meter; P, porcelain pot; V, addition flask (1 M NaOH); S, sample holder; H_2O , from the water thermostat (25 °C)

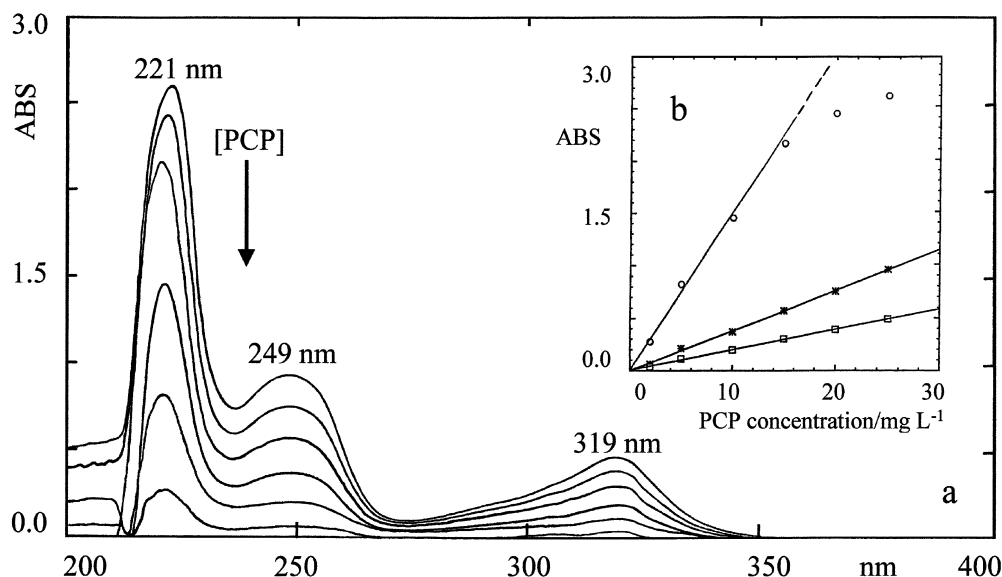
KH_2PO_4 buffer (50% v/v, pH 4.6) at a flow rate of 1.0 mL min^{-1} and the wavelengths for analytical detection were 319 nm for PCP and 252 nm for the oxidation by-products. In addition, the disappearance of PCP during electrolysis was also monitored by spectrophotometric measurements at an analytical wavelength of 319 nm using a Philips model 8710 UV-vis spectrophotometer. In a similar way, the $\cdot\text{OH}$ radical formation was monitored by using the disappearance of the *N,N*-dimethyl-*p*-nitrosoaniline (RNO) used as an $\cdot\text{OH}$ radical scavenger and which absorbs at 440 nm. The CO_2 produced by electrochemical oxidation of PCP and dissolved as sodium carbonate in the alkaline solution was determined by stoichiometric back-titration with standard 0.1 M HCl solution.

Results and discussion

UV spectroscopic characteristics of PCP in aqueous media

Like benzene, the UV spectrum of PCP exhibits three absorption bands whose wavelength values are shifted towards more positive values due to the strong substitution of the benzene ring as well as to the influence of the aqueous media used as solvent. In 0.1 M NaOH (pH 10) + $x \text{ mg L}^{-1}$ PCP solutions the observed wavelength values were 221, 249 and 319 nm, these values being associated with the ${}^1\text{B}_u$, ${}^1\text{L}_a$ and benzenoid absorption bands, respectively [32, 33]. Figure 2a shows the UV spectrum of PCP as a function of PCP concentration, and Fig. 2b the corresponding Beer's law applied to each of the absorption bands observed, for which the following molar absorptivities (ϵ) were

Fig. 2 **a** UV absorption spectra of 0.1 M NaOH (pH 10) + x mg L⁻¹ PCP solutions as a function of PCP concentration, $0 < x \leq 25$ mg L⁻¹. **b** Beer's law applied to each of the absorption bands observed: squares, 319 nm; asterisks, 249 nm; circles, 221 nm



calculated: $\epsilon_{319} = 5.1 \times 10^3$, $\epsilon_{249} = 1.0 \times 10^4$ and $\epsilon_{221} = 3.8 \times 10^4$ L mol⁻¹ cm⁻¹.

From these results, we chose the wavelength at 319 nm as that at which quantitative analysis of PCP concentration was to be performed, since Beer's law is not completely obeyed at 221 nm and the absorption band at 249 nm is the most sensitive to the substituent effects.

Electrochemical oxidation of PCP

The oxidative degradation of PCP was carried out on Ti/SnO₂ anodes as electrocatalysts at three j_{appl} values: 10, 30 and 50 mA cm⁻², through 240 min of electrolysis time. The progress of the reaction was followed by taking small samples of the reaction solution at periodic intervals, followed by UV and HPLC analysis for PCP content. Thus, the variation in the PCP concentration as a function of the electrolysis time at different j_{appl} values are shown in Fig. 3a. The oxidation curves reveal a rapid removal of PCP at high j_{appl} values and a more gradual removal at low j_{appl} values. This trend is expected, owing to the greater ability of the anodic electrocatalytic surface sites to mineralize, or at least partially oxidize, aromatic compounds to CO₂. When the PCP concentration data are represented as a function of the specific electrical charge passed (A h L⁻¹) (Fig. 3b), the oxidation curves show the same dependence on the amount of charge passed whatever the value of j_{appl} used.

The results described above show that: (1) the Ti/SnO₂ electrocatalysts are not only efficient to oxidize phenol from aqueous solutions [34] but also to oxidize the corresponding chlorinated derivatives, such as PCP, and (2) the oxidation of PCP on Ti/SnO₂ electrocatalysts occurs by the same reaction mechanism whatever the value of j_{appl} used. This high electrochemical activity is due to the high concentration of ·OH radicals on the

electrocatalyst surface, directly involved in the oxidation reaction of PCP. In alkaline solutions the ·OH radicals are produced by a charge transfer step which involves hydrated hydroxyl ions [35, 36]:

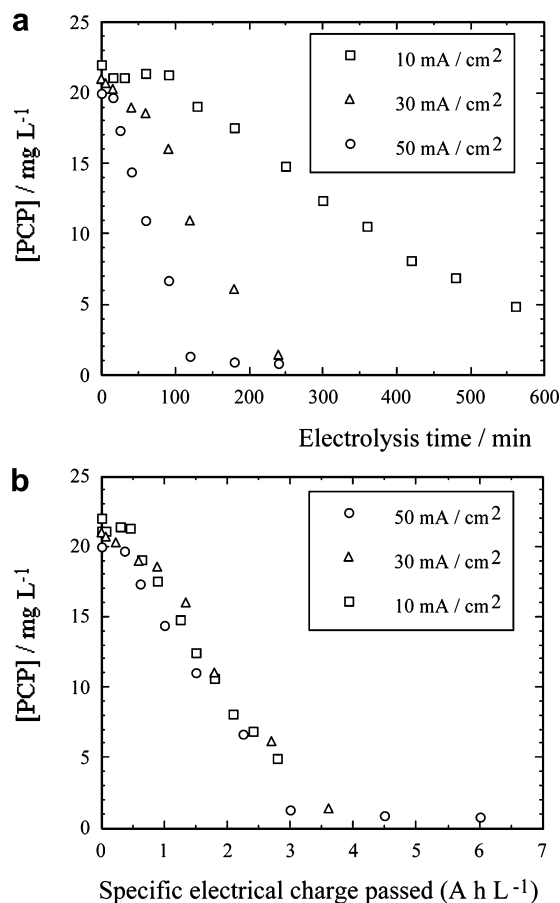


Fig. 3 **a** Plot of [PCP] vs. time of electrolysis for the 0.1 M NaOH (pH 10) + 20 mg L⁻¹ PCP solution. **b** Plot of [PCP] vs. specific electrical charge passed (A h L⁻¹) for the 0.1 M NaOH (pH 10) + 20 mg L⁻¹ PCP solution



In this work, the formation of $\cdot\text{OH}$ radicals was always confirmed by using RNO as an $\cdot\text{OH}$ radical scavenger [37, 38]. For this a 0.1 M NaOH + 2×10^{-5} M RNO solution was electrolyzed at 30 mA cm^{-2} during an electrolysis time of 90 min and the corresponding UV spectrum obtained at 10 min intervals (Fig. 4a). The disappearance of RNO was analyzed at 440 nm as a function of j_{appl} and is expressed as a first-order plot in Fig. 4b. As can be observed, the electrochemical formation rate of $\cdot\text{OH}$ radicals increases as j_{appl} increases ($k_{10} = 0.0056 \text{ min}^{-1}$, $k_{30} = 0.0125 \text{ min}^{-1}$ and $k_{50} = 0.0404 \text{ min}^{-1}$) and, hence, their accumulation on the SnO_2 surface also increases. Consequently, the higher elimination of PCP at a given electrolysis time should be observed at the higher j_{appl} used.

Thus, at an anodic condition of 50 mA cm^{-2} , for which a current of about 3 A h L^{-1} were passed after 120 min of electrolysis time (Fig. 3b), 94.7% of the PCP contained in the electrolyzed solution was eliminated. For this same electrolysis time, but with a j_{appl} value of 10 mA cm^{-2} , the PCP elimination was 39.3% of the initial concentration because only 1.2 A h L^{-1} (Fig. 3b) were passed through the electrocatalytic system.

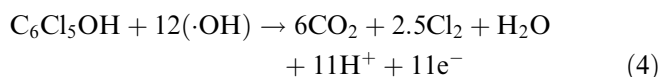
The theoretical specific electrical charge ($[\text{A h L}^{-1}]_{\text{theor}}$) needed for the complete oxidation of PCP (20 mg L^{-1}) considering the anodic reaction:



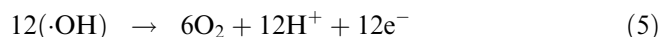
(with $\text{H}_2\text{O} + \text{e}^- \rightarrow 0.5\text{H}_2 + \text{OH}^-$ as the complementary cathodic reaction), is:

$$0.02 \frac{\text{g PCP}}{\text{L}} \left(\frac{\text{mol PCP}}{266.5 \text{ g PCP}} \right) \left(\frac{23 \text{ mol e}^-}{\text{mol PCP}} \right) \times \left(\frac{96,485 \text{ C}}{\text{mol e}^-} \right) \left(\frac{\text{h}}{3600 \text{ s}} \right) = 0.05 \text{ A h L}^{-1} \quad (3)$$

At 50 mA cm^{-2} and 120 min of electrolysis time the specific electrical charge observed ($[\text{A h L}^{-1}]_{\text{obs}}$) is about 3 A h L^{-1} (Fig. 3b). Therefore, the current efficiency for the PCP oxidation, defined as ($[\text{A h L}^{-1}]_{\text{theor}} / [\text{A h L}^{-1}]_{\text{obs}}$), should be 1.7%, i.e. 98.3% of the applied current has been used for the side reaction of O_2 evolution. This low current efficiency for the oxidation reaction is due to the fact that the electrogenerated $\cdot\text{OH}$ radicals are in competition between the oxidation of PCP (desired reaction):



and O_2 evolution (side reaction):



according to the general scheme of the oxidation reaction by Comninellis and co-workers [26]. Moreover, the low PCP concentrations used in this work (20 mg L^{-1}) favor the side reaction (5). This set of anodic reactions (1, 3 and 4) allows us to explain why it is necessary to keep constant the pH of the electrolyzed solution, otherwise the high consumption of OH^- ions and the high production of H^+ ions will shift the pH toward more acid values, such as was observed for a test reaction and whose results are summarized in Table 1.

It is also important to point out that the cell potential values remain almost constant during all the electrolysis time used to eliminate PCP from the studied solutions, as can be verified from data of Table 1 for the test reaction. This fact makes evident the high stability of the Ti/ SnO_2 anodes used as electrocatalysts to eliminate PCP from aqueous solutions, which are promising results to consider this type of material in the use of electrochemical methods for the treatment of wastewater.

Fig. 4 Typical absorption spectra of a 0.1 M NaOH (pH 10) + 2×10^{-5} M RNO solution obtained at 10 min intervals during 90 min of galvanostatic electrolysis at 30 mA cm^{-2} . Inset: first-order plot of the disappearance of RNO at different j_{appl} values

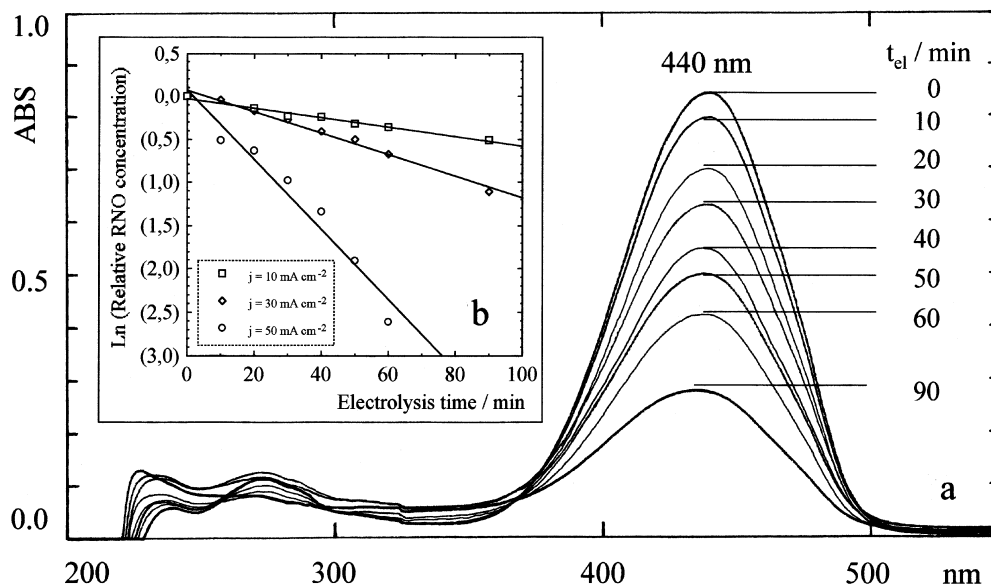


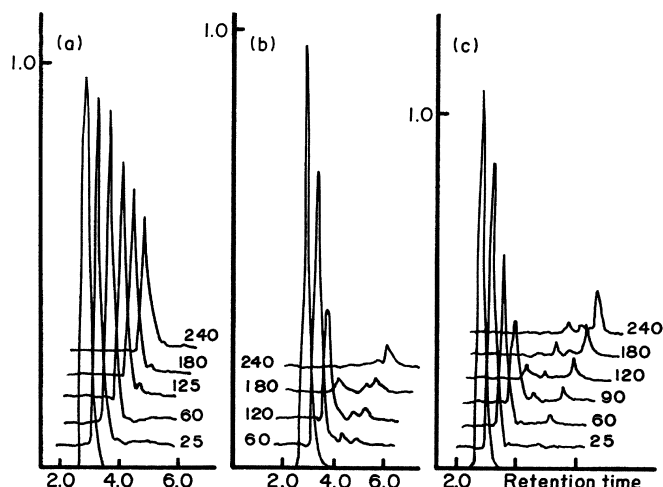
Table 1 Cell potential and solution pH (no control) of the test reaction as a function of the electrolysis time

Electrolysis time (min)	Cell potential (V, RHE)	pH of the electrolyzed solution
0	3.50	10.0
10	3.51	3.0
20	3.49	2.5
30	3.48	2.0
40	3.41	2.0
50	3.37	2.0
60	3.35	2.0
90	3.21	1.7
120	3.17	1.5
180	3.15	1.3
240	3.06	0.5

By-product distribution of PCP oxidation

In order to know if the electrochemical oxidation of PCP on Ti/SnO₂ anodes as electrocatalysts produces chlorine species or CO₂ as final reaction products, an HPLC analysis of the electrolyzed solution was undertaken as a function of the electrolysis time at all current densities used. Some typical HPLC chromatograms are shown in Fig. 5. After a first inspection of the HPLC chromatograms the occurrence of a strong mineralization of PCP at high j_{appl} values could be suggested, but the amount of CO₂ produced must be determined in order to estimate the percentage of PCP mineralized to CO₂ under each anodic condition of electrolysis.

Thus, as CO₂ reacts with the alkaline solution it was measured as CO₃²⁻/HCO₃⁻ by back-titration with standardized HCl. This analytical method allows us to measure the percentage of PCP mineralized to CO₂ at any time of the electrolysis reaction (Table 2). In addition, the oxidation by-products identified by their retention time obtained from corresponding standard compounds were essentially aliphatic acids (AAc, fumaric and maleic) and aromatic intermediates (ArI, such as 2,3,5,6-tetrachloro-1,4-benzoquinone and chloroani-

**Fig. 5** Typical HPLC analysis ($\lambda = 252$ nm) for the PCP solutions electrolyzed at **a** 10, **b** 30 and **c** 50 mA cm⁻² as a function of the time of electrolysis (indicated on the corresponding HPLC chromatogram)

lic acid). Table 2 summarizes the analytical results for the PCP oxidation.

As can be observed, at 30 and 50 mA cm⁻² there is an almost complete elimination of PCP and the generation of small quantities of oxidation by-products, <9% AAc and <3% ArI. The high production of CO₂ on Ti/SnO₂, including that observed at j_{appl} values as low as 10 mA cm⁻², confirms the active nature of this electrocatalyst toward the mineralization of PCP, though an almost instantaneous ring-opening reaction has already been published for the electrochemical oxidation of phenol on SnO₂ anodes [39].

Conclusions

The results obtained for the anodic oxidation of PCP in alkaline solution, using Ti/SnO₂ as an electrocatalytic material, allows us to conclude that:

Table 2 Product distribution of the PCP oxidation on Ti/SnO₂ anodes in 0.1 M NaOH (pH 10) as a function of the electrolysis time at different anodic conditions of electrolysis^a

t (min)	10 mA cm ⁻²				30 mA cm ⁻²			50 mA cm ⁻²			
	PCP	CO ₂	AAc	ArI	PCP	CO ₂	AAc	PCP	CO ₂	AAc	ArI
0	100	0	0	0	100	0	0	100	0	0	0
5	91.4	8.1	–	0.6	–	–	–	94.7	4.9	0.4	0
15	87.5	11.4	0.2	0.1	–	–	–	89.8	8.9	1.0	0.5
25	82.8	15.6	0.4	0.1	86.2	13.0	0.8	75.9	21.3	2.1	1.0
40	81.6	16.4	–	0.9	71.5	27.5	1.0	62.9	33.5	2.6	1.2
60	75.4	22.2	0.8	1.6	65.1	33.7	1.2	47.3	47.7	3.7	1.6
90	67.5	29.9	1.0	1.5	41.8	55.8	2.4	23.3	68.8	5.6	2.7
120	60.3	36.4	0.6	2.2	27.6	67.6	4.8	5.3	84.8	7.4	3.0
180	47.7	48.7	1.6	2.1	4.4	89.2	6.4	3.2	86.3	8.5	2.3
240	34.5	61.4	2.1	2.0	1.2	91.9	7.0	1.8	86.8	9.0	2.7

^aPCP = pentachlorophenol ([PCP]₀ = 20 mg L⁻¹); AAc = aliphatic acid (e.g. maleic and fumaric); ArI = aromatic intermediates (such as 2,3,5,6-tetrachloro-1,4-benzoquinone and chloroanilic acid). The values are reported as a percentage relative to the total amount of compounds in the analyzed sample

1. The Ti/SnO₂ anodes exhibit good electrocatalytic properties to oxidize PCP from aqueous solutions as well as extreme stability under high anodic conditions.
2. The best percentage of PCP elimination is achieved at high anodic conditions ($\geq 30 \text{ mA cm}^{-2}$), even though the current efficiency cannot be better than 2%.
3. On Ti/SnO₂ anodes, PCP was almost completely oxidized to CO₂ and the few oxidation by-products formed at all anodic conditions studied ($\geq 10 \text{ mA cm}^{-2}$) – mainly maleic acid – were organic species which are, in general, biocompatible compounds.
4. These results demonstrate that electrocatalytic methods of oxidation can be envisaged as adequate alternatives for the treatment of wastewater containing hazardous organochlorinated (non-biocompatible) compounds.

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