Electrooxidation of chlorophenols at a glassy carbon electrode in a pH 11 buffer

C. Berríos^a, R. Arce^a, M.C. Rezende^a, M.S. Ureta-Zañartu^{a,*}, C. Gutiérrez^b

^a Facultad de Química y Biología, Universidad de Santiago de Chile, casilla 40, correo 33, Santiago, Chile

^b Instituto de Química Física “Rocasolano”, CSIC, C. Serrano, 119, 28006 Madrid, Spain

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Abstract

The electrochemical oxidation of three chlorophenols (CPs), namely 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) at a glassy carbon electrode in a pH 11 carbonate/hydrogen carbonate buffer electrolyte has been studied by cyclic voltammetry (CV) and impedance measurements. The three CPs show in CV an irreversible oxidation peak whose potential decreased linearly with increasing pK_a of the CPs, showing that the oxidation is the more facile the less acidic is the CP. Although the oxidation is not under diffusion control, *i.e.*, the peak potential was not directly related to the rate constant, the same slope was obtained when the potential at which the integrated charge began to increase significantly was plotted instead of the peak potential. A reversible process near -0.45 V is observed for 2,4,6-TCP from the second positive scan, which was attributed to the formation of a soluble (since this couple nearly disappeared upon solution stirring) benzoquinone. Impedance data showed that for 2-CP and 2,4-DCP the formation of the polyphenolic film begins already at 0.0 – 0.1 V, and that the film is non-porous and non-conducting. On the contrary, with 2,4,6-TCP polyphenol formation began near 0.15 V, and the film is so porous that it allows the oxidation of 2,4,6-TCP to continue.

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1. Introduction

Chlorophenols (CPs) are toxic compounds, used as herbicides and pesticides, whose chemical stability and high resistance to biological degradation lead to serious environmental contamination [1]. They are also present in industrial effluents, mainly from cellulose plants. The OH group of CPs confers them an acidic character and solubility in water. CPs have pK_a values extending from 4.7 to 9.4, the acidity, that increases with increasing number of chlorine atoms in the molecule [2,3], possibly being an indicator of their reactivity.

The major intermediates detected by HPLC in the sonochemical degradation of phenol have been hydroquinone, catechol and *p*-benzoquinone, the degradation rate being increased by salts of transition metals such as copper and iron [4]. Electrooxidation of phenol should break a carbon–carbon bond in the aromatic ring, leading to less toxic compounds. Ideally, phenol degradation

should proceed as [5,6]:

However, the transfer of the first electron yields, independently of pH, the corresponding phenoxy radical, which then reacts with another phenoxy radical or with unreacted CP to give oligomers which foul the electrode surface. Diverse mechanisms, with formation of oligomers and polymers of low molecular weight, have been proposed by Gatrell et al. [7–9]. Ezerskis and Jusys [10] reported that the degree of fouling in CP oxidation at Pt may be related to the different structure of the tars formed, which depends on the structure of the monomer. They also reported [11], using an electrochemical quartz crystal microbalance (EQCM), that 4-CP has a low electropolymerization rate on Pt, which suggests a low permeability of the polymer film. Quantum chemical studies suggest the formation of polychlorodibenzo-*p*-dioxins and dibenzofurans in the

* Corresponding author.

E-mail address: mureta@usach.cl (M.S. Ureta-Zañartu).

electropolymerization of 2-CP [12]. Recently, Ferreira et al. [13], using the EQCM, reported that the polymers formed by the electrooxidation of *m*-cresol, 2,5-dimethylphenol and 2,3,5-trimethylphenol at Au and Pt electrodes were more passivating than the polymer from the non-substituted phenol.

We have studied the electrochemical degradation of CPs on glassy carbon at pH 2 [14], on gold electrodes also at pH 2 [15], and on GC modified with polymeric films of Ni(II)tetrakisulphophthalocyanine at pH 11 [16]. The position of the Cl atom critically affects the reactivity of CPs [14,15]. The peak potential at 0.01 V s^{-1} of electrooxidation of several CPs on GC electrode in acid media increased linearly with their pK_a values [14], *i.e.*, the reactivity increased with the acidic character of the CP. On the contrary, on gold electrodes practically no differences in the peak potentials were observed, oxidation beginning always with the formation of the incipient surface gold oxide [15]. However, EQCM results showed that the extent of electrode fouling depended on the CP structure.

The electrochemical impedance is not generally used in complex systems due to the difficult interpretation of the results. However, it has been recently used for electrodes modified with polymeric films in order to obtain qualitative information about the film properties. So, Patolsky et al. [17] determined the change of the charge-transfer resistance of enzyme monolayer-functionalized electrodes upon the precipitation on them of an insoluble product. Very recently, Pigani et al. [18] studied the electrooxidation of chlorophenols at neutral pH on a Pt electrode coated with poly(3,4-ethylenedioxy)thiophene (PEDOT), and found that fouling was much lower on Pt/PEDOT,poly(sodium-4-styrenesulphonate) than on Pt/PEDOT, LiClO_4 , which allowed to use the former for discriminating several CPs by cyclic voltammetry (CV).

In this work, we report how the voltammetric response and electrochemical impedance of three chlorophenols (2-CP, 2,4-DCP and 2,4,6-TCP) at a GC electrode in a pH 11 buffer depend on the structure of the CP.

2. Experimental

The reagents and apparatus have been already described [14]. 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and 2-chloroquinone (2-ClQ) were from Aldrich p.a., and Na_2CO_3 , NaHCO_3 , and NaOH were from Merck p.a. All the compounds were used as received. The water was deionized and twice distilled. A GC disk of 0.8 cm diameter from Pine Instruments was used as working electrode, and a Pt helix of high area as auxiliary electrode. All the potentials were measured and are referred to the mercurous sulphate electrode (MSE; 0.64 V vs. SHE). A Wenking POS72 potentiostat commanded by a personal computer (INELECSA, Spain) was used for cyclic voltammetry, and an Autolab potentiostat PGSTAT 30 (Eco Chemie, Utrecht, The Netherlands) driven by the GPES software for impedance measurements in the 100 kHz–10 mHz frequency range, with 10 steps per logarithmic decade. For the GC electrode the maximum applied potential was only 0.4 V in order to avoid its oxidation. The cell

was held at room temperature and the electrolyte deaerated with nitrogen.

After each measurement in the presence of CP the electrode was cleaned with piranha solution, rinsed with distilled water, polished to a mirror-like finish with a $0.05 \mu\text{m}$ alumina slurry in a polishing cloth (Buehler), rinsed with water, sonicated in a water bath for 10 min, and cycled repetitively at 0.1 V s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ until the double-layer current reached a given value. Before each experiment a reference CV was obtained in the pH 11 buffer electrolyte.

3. Results

3.1. Cyclic voltammetry

The first CV of the three CPs studied in this work show a chemically irreversible oxidation peak (peak 1 in Fig. 1, thin solid line) whose potential increased slightly with increasing chlorine substitution (Table 1). The peak current density (j_p) decreased with increasing chlorine substitution, the relative values for 2-CP, 2,4-DCP and 2,4,6-TCP being 1:0.7:0.4. In the negative scan, only 2,4,6-TCP shows two reduction processes in the first scan, at -0.2 and -0.5 V (peaks 2 and 2' in Fig. 1C).

For 2-CP the peak current density was of the order of that of 0.6 mA cm^{-2} calculated for an irreversible reaction involving only one electron, assuming a Tafel slope of 118 mV dec^{-1}

Fig. 1. First (thin solid line), second (dashed line) and fifth (thick solid line) CVs at 0.1 V s^{-1} of a glassy carbon electrode in a pH 11 buffer electrolyte with: (A) 1 mM 2-CP; (B) 1 mM 2,4-DCP; (C) 1 mM 2,4,6-TCP.

Table 1

Voltammetric parameters of the oxidation of several chlorophenols at a glassy carbon electrode obtained from the CVs in Fig. 1

CP	Scan number	j_p (mA cm ⁻²)	E_p (V)	Q_{an} (mC cm ⁻²)
2-CP	1	0.556	0.167	0.150
	2	0.310	0.176	0.108
	5	—	—	0.044
2,4-DCP	1	0.384	0.170	0.124
	2	0.352	0.165	0.120
	5	0.154	0.192	0.074
2,4,6-TCP	1	0.216	0.176	0.072
	2	0.238	0.182	0.070
	5	0.264	0.214	0.070

The capacitive component has been subtracted from the current densities and from the anodic charges.

and a diffusion coefficient of 10^{-5} cm² s⁻¹ [19]. However, with electrolyte stirring the current increased only slightly, indicating that the reaction was not under diffusion control. Effectively, for 2,4,6-TCP the slope of the $\log j$ vs. $\log v$ plot was about 0.3, lower than that corresponding to diffusion, and the peak potential barely changed between 0.02 and 0.2 V s⁻¹. Therefore, the peak potential is not directly related to the rate constant, the Tafel slope and the diffusion coefficient. In the second CV the peak current decreases by nearly 50% in the case of 2-CP, but only 3% for 2,4-DCP, while it actually increases, but is shifted positively, for 2,4,6-TCP, which, furthermore, shows a very small, but significant, anodic hump at -0.45 V. The 5th CV shows that the surface is totally blocked for 2-CP, and nearly so for 2,4-DCP, while for 2,4,6-TCP it remains active, and shows a better defined hump at -0.45 V (Table 1).

A plot of peak potential at 0.01 V s⁻¹ vs. the respective pK_a for different CPs at pH 11, at which all the CPs are completely dissociated, yields a straight line with a negative slope of -0.025 ± 0.08 V (pK_a unit)⁻¹ (Fig. 2A). Actually, since the anodic peak is not diffusion-limited, its potential is not directly related to the rate constant of the reaction. Therefore, we have also plotted the potential at which the integrated anodic charge, after subtraction of the capacitive charge, increases significantly, which occurs at a net anodic charge of 0.21 mC cm⁻² (Fig. 2B). At these potentials, the anodic process has just begun, and there-

Fig. 2. Peak potentials (A) and potentials at which the anodic charge increases significantly (B) of the main anodic peak in CVs at 0.01 V s⁻¹ of several chlorophenols at a 1 mM concentration on a glassy carbon electrode in a pH 11 buffer electrolyte vs. the pK_a of the respective chlorophenol.

fore they should be related to the rate constant. As a matter of fact, the slope, 0.030 ± 0.008 , is within one standard deviation of that obtained when plotting the peak potentials. The negative sign of the slope shows that the oxidation is the more facile the less acidic is the CP. The electrooxidation of a completely dissociated CP,

becomes easier with decreasing number of electron-withdrawing chlorine substituents, since chlorine substituents decrease the electronic charge on the ring. An increasing charge on the ring favours the extraction of an electron.

It is obvious that the electrooxidation of ArOH is simply the sum of the phenol dissociation

Table 2

Voltammetric parameters of the oxidation of 2,4,6-TCP and 2-ClQ at a glassy carbon electrode obtained from the CVs in Fig. 3

[2,4,6-TCP] (mM)	Scan number	Peak 1		Peak 2		Peak 3	
		j_p (mA cm ⁻²)	E_p (V)	j_p (mA cm ⁻²)	E_p (V)	j_p (mA cm ⁻²)	E_p (V)
0.5	1	0.060	0.225	-0.049	-0.458	—	—
	2	0.030	0.321	-0.025	-0.459	0.011	-0.421
1	1	0.152	0.241	-0.042	-0.456	—	—
	2	0.072	0.253	-0.024	-0.447	0.009	-0.389
2	1	0.226	0.197	-0.128	-0.445	—	—
	2	0.105	0.205	-0.070	-0.457	0.029	-0.418
2-ClQ 0.5 mM	1	—	—	-0.023	-0.533	0.034	-0.453
	2	—	—	-0.028	-0.536	0.043	-0.452

The capacitive component has been subtracted from the current densities.

Fig. 3. CVs at 0.05 V s^{-1} at a glassy carbon electrode in a pH 11 buffer electrolyte of 2,4,6-TCP at the following concentrations: 0.5 mM (thin solid line), 1 mM (thick solid line), and 2 mM (dashed line). (A) First CV; (B) second CV. For comparison, the first (thin solid line) and tenth (thick solid line) CVs at 0.05 V s^{-1} of 0.5 mM 2-ClQ are given in (C).

and the phenoxide electrooxidation (1). Therefore, for a phenol with $\text{p}K_{\text{a}} = 1$ the *reversible, thermodynamic* standard (*i.e.*, at pH 0) potential of phenol electrooxidation would be exactly the same as that of phenoxide electrooxidation, since then the contribution of the dissociation reaction, $\Delta G^{\circ} = -RT \ln K_{\text{a}} = 2.303RT \text{p}K_{\text{a}}$, would be exactly zero. If $K_{\text{a}} < 1$, $\text{p}K_{\text{a}} > 0$, the oxidation of a phenol will be *thermodynamically* easier than that of its phenoxide. The opposite would hold true for hypothetical, very acidic phenols with $K_{\text{a}} > 1$, $\text{p}K_{\text{a}} < 0$. Obviously, all the above calculations apply to pH 0 only, at which standard potentials are calculated. While the reversible potential of phenoxide electrooxidation is unaffected by pH, that of phenol electrooxidation decreases by 59 mV per pH unit increase. In other words, the higher the pH, the more thermodynamically difficult will be the oxidation of phenoxides, as measured in the operationally relevant potential scale, which is that referred to the Reversible Hydrogen Electrode.

At pH 2, at which all the CPs, even the more acidic one (pentachlorophenol), are undissociated, the contribution of the dissociation reaction to the *reversible, thermodynamic* potential would be, for a $\text{p}K$ increase of 4.68 (from pentachlorophenol, $\text{p}K = 4.75$, to 2-CP, $\text{p}K = 9.43$), an increase of 0.28 V. At pH 2 this increase of 0.27 V has to be added to the unknown decrease of the *reversible* potential of phenoxide electrooxidation at pH 11, at which all the CPs, even the less acidic one, 2-CP, are completely dissociated. Assuming that the observed decrease of 0.15 V of the peak potential with increasing $\text{p}K$ at pH 11 is the same as the unknown decrease of the (pH-independent) reversible potential of phenoxide electrooxidation, the addition to it of the calculated, thermodynamic increase of 0.28 V due to the phenol dissociation yields for pH 2 a net *increase* of the reversible potential of undissociated phenol electrooxidation of 0.13 V. This is in fair agreement with the observed increase of the peak potential at pH 2 of 0.18 V [14], which is only 0.05 V higher. Actually this agreement is rather surprising, since for several CPs the rate constant does not necessarily

bear a monotonic relationship with the corresponding reversible potential.

3.1.1. 2,4,6-TCP

The effect of the CP concentration and potential scan rate were studied with 2,4,6-TCP, since it produced less fouling. The voltammetric parameter $d \log(j_{\text{p}})/d \log(v)$ was about 0.4, and the peak potential was independent of the scan rate, which pointed to a kinetically controlled reaction. Effectively, stirring barely increased the currents.

Fig. 3 shows the first (Fig. 3A) and second (Fig. 3B) CVs at 0.05 V s^{-1} for 0.5; 1 and 2 mM and 2,4,6-TCP in the pH 11 buffer electrolyte. The treatment with piranha solution attacked the GC electrode, as clearly shown by differences in the double-layer current (Fig. 3). Although the scan rate is just half that in Fig. 1, the reversibility of the process at about -0.5 V increases dramatically. In the first scan the peak potential of the main anodic peak is *lower* for 2 mM 2,4,6-TCP ($E_{\text{p}}^{(1)} = 0.197 \text{ V}$) than for 1 mM 2,4,6-TCP ($E_{\text{p}}^{(1)} = 0.241 \text{ V}$), pointing to a higher fouling (the peak potential of a diffusion-controlled voltammetric peak should be independent of concentration, irrespective of its Nernstian or non-Nernstian character). The peak current density increased with the concentration without reaching saturation (Table 2).

The chemically reversible process near -0.5 V should correspond to a species in solution, because its current density decreases with electrolyte stirring. Therefore, the phenoxy radical is rapidly oxidized before significant polymerization can occur. Fig. 3C shows the first and tenth CVs at 0.05 V s^{-1} of 0.5 mM 2-ClQ on GC at pH 11. The quinone/hydroquinone process appears at about the same potential as the reversible process in 2,4,6-TCP, although the formation of an O= group in carbon 4 requires the expulsion of the chlorine atom in that position. 1,2-Benzoquinone is very unstable, and 1,3-benzoquinone does not exist. The solution did not become turbid upon addition of an AgNO_3 solution, but this test is not conclusive, since the chloride

concentration would be very low. It has been reported that the formation of a quinone-like compound involves dechlorination of the CP [20]. Ezerskis et al. [11] claim, with basis on EQCM data, that for monomers with chlorine atoms in *ortho* and *para* positions the electropolymerization occurs with dechlorination, which may be more important when the chlorine atom is in the *para* position only. The same authors [21] concluded, with basis on gas chromatography–mass spectrometry (GC–MS), that CP polymerization occurs by two routes: (i) the quinol–ether route (without chlorine elimination) and (ii) the nucleophilic-radical substitution (SRN1) route (with some elimination of chlorine from *ortho* and/or *para* positions). Thus, very probably the low polymerization rate of 2,4,6-TCP is related with its high dechlorination rate.

After a given number of potential cycles, that increases with the scan rate and the 2,4,6-TCP concentration, the main anodic peak nearly disappears, indicating a complete fouling, the reduction peak at -0.5 V disappears, and a new reduction peak appears at -0.7 V (Fig. 4). Thus, in 1 mM 2,4,6-TCP solution 11 CVs at 0.05 mV s $^{-1}$ are needed to observe this fouling (Fig. 4C). Therefore, it is clear that there is some reaction other than that leading to the quinone-like species that eventually produces a fouling of the electrode. On the contrary, repetitive cycling of 0.5 M 2-chloroquinone at the same pH did not produce any change.

The Tafel plot for 2,4,6-TCP oxidation at a GC electrode evaluated from the foot of the anodic peak in Fig. 4B was 0.114 V, showing that the first charge transfer was rate-determining. Although similar values were obtained for the three CPs in Fig. 1, the subsequent reaction steps are different: while the reaction

products of 2- and 2,4-DCP foul the electrode surface, those of 2,4,6-TCP remain mainly in solution, although repetitive cycling does produce fouling.

3.2. Electrochemical impedance

The time required for determining a Nyquist plot was nearly 2 h. From a previous work [22] it is known that in the pH 11 buffer electrolyte the bare GC electrode behaves as a CPE without charge transfer, because at low frequencies (0.1–10 Hz) the phase angle is somewhat lower than 90° , and the slope of the $\log Z$ vs. $\log f$ plot is about -0.9 . Furthermore, the total impedance does not depend on the potential.

For each CP data were obtained three times for the same electrode: (i) freshly piranha-cleaned and stabilized by 5 RCVs at pH 11 GC electrode in 1 mM CP, without any previous CV in the presence of CP (sample 1); (ii) GC electrode after 5 RCVs in the presence of CP (sample 2) and (iii) the resulting GC electrode in the pH 11 buffer electrolyte (sample 3). The Nyquist plots of bare GC in the pH 11 buffer electrolyte, and of samples 1 for the three CPs, are plotted in Fig. 5. At 0.05 V, at the foot of the anodic peak, the three CPs show similar curves, with a much lower imaginary component than that in base electrolyte. At 0.15 and 0.25 V, at potentials straddling the main anodic peak, quite surprisingly, the curves for 2-CP and 2,4-DCP tend towards that in base electrolyte. It can be seen in the insets that a faradaic process is evident for 2,4,6-TCP, but that at low frequencies the imaginary component remains constant while the real component increases with decreasing frequency. This is not the classical diffusional (Warburg) behaviour for a solution species, and could be due

Fig. 4. Influence of the scan rate and the concentration of 2,4,6-TCP on the first CVs at a glassy carbon electrode in a pH 11 buffer electrolyte. (A) First four CVs at 0.02 V s $^{-1}$ of 2 mM 2,4,6-TCP 4 CVs; (B) first six CVs at 0.05 V s $^{-1}$ of 2 mM 2,4,6-TCP; (C) six CVs at 0.05 V s $^{-1}$ selected from the first 12 ones of 1 mM 2,4,6-TCP.

Fig. 5. Nyquist plots of a glassy carbon electrode in a pH 11 buffer electrolyte (∇) and in the presence of 1 mM 2-CP ($\square$); 2,4-DCP ($\circ$) and 2,4,6-TCP ($\triangle$), at the following potentials: (A) 0.05 V; (B) 0.15 V; (C) 0.25 V; (D) 0.35 V; (E) 0.45 V; and (F) 0.55 V. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Fig. 6. Plots of log impedance vs. applied potential at the following constant frequencies: (1) 10^{-2} Hz; (2) 10^{-1} Hz; (3) 1 Hz; (4) 10 Hz; (5) 10^2 Hz; (6) 10^3 Hz and (7) 10^4 Hz, of a glassy carbon electrode in a pH 11 buffer electrolyte in the presence of: (A) 1 mM 2-CP; (B) 1 mM 2,4-DCP.

Fig. 7. Plots of log impedance vs. applied potential at the following constant frequencies: (1) 10^{-2} Hz; (2) 10^{-1} Hz; (3) 1 Hz; (4) 10 Hz; (5) 10^2 Hz; (6) 10^3 Hz and (7) 10^4 Hz, of a glassy carbon electrode in a pH 11 buffer electrolyte in 1 mM 2-CP. (A) sample 1; (B) sample 2.

to diffusion through the polyphenolic film. At 0.35–0.45 V, well past the peak potential, the curves for the three samples 1 are very similar. At 0.55 V a faradaic process is observed only for 2,4,6-TCP (Fig. 5F), probably reflecting a degradation of the polymeric film.

The same data shown in Fig. 5 are presented as $\log Z$ vs. potential plots for several frequencies in Fig. 6 for each CP, in order to better show the differences between the three CPs.

3.2.1. 2-CP oxidation

For sample 1 (freshly cleaned GC electrode in 1 mM 2-CP), at frequencies ≤ 0.1 Hz the impedance increased from 0.00 to 0.10 V (lines 1 and 2 in Fig. 6A), reflecting the beginning of the formation of a polyphenolic film. At frequencies of 1–100 Hz the impedance remained almost constant with potential (lines 3, 4 and 5). And at frequencies ≥ 1 kHz the impedance increased, especially between 0.10 and 0.20 V, at the main anodic peak (lines 6 and 7 in Fig. 6A), this increase being clearly due to the formation of a non-conducting polyphenolic film. Therefore, formation of this film begins already at the foot of the main anodic peak, and is completed at the peak potential.

At frequencies lower than 1 Hz no differences were observed between the impedance curves in the presence (sample 2) or the absence (sample 3) of 2-CP in the electrolyte, evidencing the presence of a non-conducting polyphenol film, whose impedance did not change with potential. In the range 10 Hz–1 kHz the impedance decreases with increasing potential, this being far more noticeable with sample 3, probably due to a degradation of the polyphenolic film (plots of samples 2 and 3 are not shown).

3.2.2. 2,4-DCP

With sample 1 the initial impedance increase at all frequencies is due to the electrode fouling (Fig. 6B). This behaviour is different from that of 2-CP, with which the initial impedance increase was noticeable only up to 0.1 Hz. Another difference is that with 2,4-DCP the impedance curves at 1 and 10 kHz do not coincide.

3.2.3. 2,4,6-TCP

The impedance plots of 2,4,6-TCP (Fig. 7) are very different from those of 2-CP and 2,4-DCP, as was to be expected from the very different Nyquist plots. Oxidation without fouling produces a decrease of the impedance at frequencies < 1 Hz from 0.00 to 0.15 V, the peak potential, signalling that a faradaic process unobscured by electrode fouling is occurring. The impedance increases at increasing potentials, since the time required by this staircase program is much longer than that in a CV.

Plot 7B of sample 2 clearly shows that the polyphenolic film is porous, since it is similar to plot 7A of sample 1. The impedance decrease at higher potentials could be attributed to a degradation of the polymeric film.

In summary, while with 2-CP and 2,4-DCP fouling starts already at 0.05 V, with 2,4,6-TCP it begins at a slightly higher potential, 0.15 V, and, furthermore, the polyphenolic film is so porous that it allows the oxidation of 2,4,6-TCP to proceed even in sample 2.

4. Conclusions

The joint use of cyclic voltammetry and impedance techniques is a promising approach for the study of the elec-

trooxidation of different CPs at a GC electrode, highlighting their similarities and differences.

- The Tafel slope, near 0.118 V dec^{-1} , shows that the first electron transfer is rate-determining for all three CPs.
- The peak potentials of CP oxidation at GC in a pH 11 buffer electrolyte, at which all the CPs are fully ionized as phenoxides, decreased linearly with increasing $\text{p}K_{\text{a}}$, since the electronic density at the ring increased with decreasing chlorine substitution, which favored the extraction of an electron from the ring.
- The peak potentials of CP oxidation at GC decreased linearly with the $\text{p}K_{\text{a}}$ at pH 2. The change of sign of the slope with respect to that at pH 11 is due to the fact that the contribution of the phenol dissociation to the reversible electrooxidation potential predominates over the behaviour of the phenoxides.
- The formation of the oligomers is favored for 2-CP and 2,4-DCP because in them carbon 6, which, being in *ortho* position with respect to the phenolic carbon, is therefore the likely reaction center, is free, while it is occupied in 2,4,6-TCP.
- The impedance measurements clearly show that the polyphenolic film fouling the electrode surface is non-porous and non-conducting for 2-CP and 2,4-CP, while in the case of 2,4,6-TCP it is porous and allows the oxidation of 2,4,6-TCP in solution to continue.

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