

## THE STUDY OF MONOCHLORINATED PHENOLS USING HYPHENATED ELECTROCHEMICAL METHOD

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Cyclic voltammetric (CV) study of electrooxidation of monochlorophenols (2-chlorophenol, 3-chlorophenol, 4-chlorophenol) on a Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> was combined with the experiment using electrochemical quartz crystal microbalance (EQCM). For all chlorophenols the polymeric film formation on the electrode surface has been observed and the electrode surface was completely covered with polymeric film after five cycles. Partial deactivation of the electrode resulting in the formation of the more permeable film was created in the case of 2-chlorophenol and the film of 4-chlorophenol was created also with the low permeability. The influence of the scan rate on the electrooxidation of chlorophenol was evaluated. It was found that the lower electropolymerization rate and better permeability of the film was observed at higher scan rates. Valuable insights into complex electro-oxidation processes of all chlorophenols were also gained by means of the elimination voltammetry with linear scan (EVLS). The EVLS functions, eliminating two current components, reveal a strong adsorption state of 3-chlorophenol and show differences in electrochemical behavior of chlorophenols in all cycles. From the comparison of elimination results of corresponding derivatives the different mechanism of electrooxidation was suggested.

**Keywords:** Chlorophenols electrooxidation; Cyclic voltammetry; Electrochemical quartz crystal microbalance (EQCM); Elimination voltammetry with linear scan (EVLS); Pt electrode; Electrochemistry; Elimination; Chlorophenols.

Chlorinated phenols (CPs) are labelled as “priority pollutants” due to their slow degradation, bioaccumulation and extreme toxicity. They were listed among the priority environmental pollutants by the US EPA (US Environmental Protection Agency) in the Clean Water Act<sup>1</sup>. The whole group of CPs comprises tens of compounds, significantly differing from each other with their molecular structure, and consequently with their physical and chemical properties and degree of toxicity. Toxicity of CPs depends on the degree of chlorination and the position of chlorine atoms relative to the

hydroxyl groups. Toxicity of CPs increases with the number of chlorine substituents and chlorophenols with the chlorine atom in the para position are more toxic than other isomers<sup>2</sup>.

Many treatment technologies have been proposed for the destruction of chlorophenols, including biological and chemical methods, adsorption, oxidation methods (e.g., thermal combustion, wet catalytic oxidation, advanced oxidation processes) or electrochemical methods. Effective and economical anodic oxidation of pollutants requires the appropriate choice of catalytic electrode material. A lot of electrode materials have been used for electrooxidation of phenol and its derivatives, e.g., noble metals<sup>3,4</sup>, boron doped diamond<sup>5</sup>, carbon<sup>6</sup>, metal oxides electrodes<sup>7,8</sup>.

When phenol and its derivatives are electrooxidized, the phenoxy radicals are generated in the first step and can react irreversibly with other radical or with an unreacted phenate anion to form dimeric products. Such dimer can be oxidized again to produce a new radical which can couple with a phenoxy radical or with dimeric radical to produce the polymer<sup>9</sup>. Electropolymerization of phenolic compounds was observed to occur on a wide variety of anodes, such as Pt<sup>9,10</sup>, Au<sup>11</sup>, glassy carbon (GC)<sup>6</sup>, metal oxides like IrO<sub>2</sub><sup>12</sup>, PtO<sub>2</sub>, RuO<sub>2</sub><sup>13</sup> and also the boron doped diamond electrode<sup>14</sup>. A deactivation rate of the electrode due to polymerization depends on a large number of parameters, e.g., chlorophenol concentration, the nature of the electrode, the number and position of chlorine substituents, solution pH and electrode potential.

Increasing concentration of phenolic compounds allows formation of a large amount of phenoxy radicals, thus causing faster deactivation of electrode. According to Ežerskis and Jusys<sup>15,16</sup>, the polymerization rate of CPs is also dependent on the location and number of chlor atoms in the aromatic ring with the respect to the phenolic OH group. They found that full deactivation of the Pt electrode occurs in the solution of *para*-substituted chlorophenols; partial deactivation occurs in the case of phenol and *ortho*-substituted chlorophenols and weak fouling occurs in the case of *meta*-substituted chlorophenols<sup>10</sup>. Deactivation of the electrode was usually found to be more obvious in alkaline solutions, as compared to that in acidic phenolic solution<sup>12</sup>. The polymer films formed during electropolymerization on different types of anodes have different permeability characteristics which determine the rate of mass transfer of phenol. SEM results show that the polymeric films formed on Ti/IrO<sub>2</sub> and Pt anodes can not be mineralized. On the other hand, complex oxidation reactions leading to the partial combustion of polymeric materials can take place on the

Ta/β-PbO<sub>2</sub> surface due to electrogenerated OH radicals which have an oxidizing power much higher than that of intermediates formed respectively on IrO<sub>2</sub> and Pt<sup>9</sup>. Electrode potential is also an important parameter for electropolymerization of phenolic compounds. In the potential region of water stability ( $E < 2.3$  V vs SHE) direct electron transfer reactions occur on boron doped diamond (BDD) surface that result in electrode fouling due to the formation of a polymeric film on its surface. In the potential region of water decomposition ( $E > 2.3$  V vs SHE), indirect oxidation reaction can take place by electrogenerated active intermediates which can avoid electrode fouling<sup>14</sup>.

Different methods have been used to investigate the electropolymerization behaviours of chlorophenols and to characterize the polymeric films formed, including cyclic voltammetry (CV)<sup>15</sup>, Fourier transformed infrared (FTIR) spectroscopy<sup>16</sup>, electrochemical quartz crystal microbalance (EQCM)<sup>17</sup> and gas chromatography-mass spectrometry (GC-MS)<sup>18</sup>.

Electrochemical quartz crystal microbalance is a promising method allowing real-time measurements of electrochemically induced mass changes at electrode surface. Such dynamic monitoring of minute mass changes offers great promise for investigating the kinetics and mechanism of numerous potential-controlled surface reactions (including deposition or dissolution of surface layers or various uptake processes)<sup>11</sup>. Ureta-Zañartu et al.<sup>17</sup> used a gold electrode for the electrooxidation of CPs with emphasis in the use of the EQCM for evaluating the polymerization rate. They observed that at low potential scan rates, high CPs concentrations and high pH the formation of films with low porosity is favoured. On the contrary, at high potential scan rates and/or low CP concentrations the film was porous enough for charge transfer to continue<sup>17</sup>. Ežerskis et al.<sup>19</sup> used EQCM for electropolymerization study of CPs in alkaline solution. They found that the highest electropolymerization rate was found for *ortho*-substituted CPs indicating a weak fouling of the electrode. Low electropolymerization rates for *para*-substituted CPs suggest a low permeability of the polymer film resulting in rapid electrode fouling<sup>19</sup>.

Linear sweep voltammetry (LSV) or cyclic voltammetry (CV) are the most frequently used electrochemical methods. Elimination voltammetry with linear scan (EVLS) provides an improvement of the LSV or CV results, and makes it possible to identify the nature of the currents controlling the studied process. In a potential controlled electrochemical experiment only the total current can be measured. The methods have been termed as elimination methods because of their ability to eliminate certain selected current. In the EVLS there are two necessary conditions for elimination: (i) the total

current is formed from the sum of the particular currents and (ii) the particular currents eliminated can be expressed as the product of a scan rate function and an electrode potential function<sup>20</sup>. The application of elimination can expand the electrode working potential range beyond the ordinary limit. It can also improve the resolution of the irreversible current up to that for the reversible current, differentiate irreversible from reversible currents and make a true baseline correction<sup>21</sup>. The whole theoretical background of EVLS was described by Dračka<sup>21</sup> and Trnková<sup>22</sup>.

EVLS has been applied to the resolution of reduction signals of adenine and cytosine in short synthetic homo-oligodeoxynucleotides (dA<sub>9</sub> and dC<sub>9</sub>)<sup>23</sup> and heterooligodeoxynucleotides with different sequences of adenine and cytosine<sup>24</sup>. In comparison with the common electrochemical methods, EVLS enables one to resolve the overlapped signals by using the function which eliminates the charging and kinetic currents ( $I_c$  and  $I_k$ ) and conserves the diffusion current ( $I_d$ ). For the adsorbed electroactive substance, this elimination function gives a good readable peak-counterpeak which has successfully been utilized to the analysis of overlapped reduction signals of adenine and cytosine on hanging mercury drop electrode (HMDE).

In our paper, cyclic voltammetry with the combination of EQCM measurements were used for electrochemical oxidation of monochlorinated phenols at 5 MHz AT-cut quartz crystal Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The EVLS was used for detailed observation of oxidation parts of cyclic voltammograms for every studied monochlorophenol. The elimination function E4, E5 and E6 were used for data evaluation. As a referent current  $I$  the current measured at 50 mV/s was used, as  $I_{1/2}$  the current measured at 25 mV/s was used and as the  $I_2$  the current measured at 100 mV/s was used.

Elimination function E4 conserves  $I_d$  with simultaneous elimination of  $I_k$  and  $I_c$

$$f(I) = -11.657 I_{1/2} + 17.485 I - 5.8284 I_2. \quad (1)$$

Elimination function E5 conserves  $I_k$  with simultaneous elimination of  $I_c$  and  $I_d$

$$f(I) = 6.8284 I_{1/2} - 8.2426 I + 2.4142 I_2. \quad (2)$$

Elimination function E6 conserves  $I_c$  with simultaneous elimination of  $I_k$  and  $I_d$

$$f(I) = 4.8284 I_{1/2} - 8.2426 I + 3.4142 I_2. \quad (3)$$

When the adsorption of electroactive particles plays an important role in the electrode process and the process of electron transfer takes place in its adsorbed state, then the course of EVLS E4 function corresponds to the peak-conterpeak signal. The situation is similar in the case of EVLS functions E5 and E6. Their signals have also peak-counterpeak shapes but their courses are opposite than in the case of EVLS E4. The theoretical courses of elimination function (E4, E5 and E6) obtained using  $1/2 v_{\text{ref}}$ ,  $v_{\text{ref}}$  and  $2 v_{\text{ref}}$  are shown in Fig. 1 (the dependence of E4, E5 and E6 on  $\alpha nFE/RT$ )<sup>25,26</sup>. The potential-dependent  $x$ -axis is changed from -5 to 5 and the calculation was described in paper<sup>22</sup>.

## EXPERIMENTAL

The studied monochlorophenols were 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP), all obtained from Merck and used as received. The supporting electrolyte was 0.5 M  $\text{H}_2\text{SO}_4$ . All the solutions were freshly prepared with twice distilled

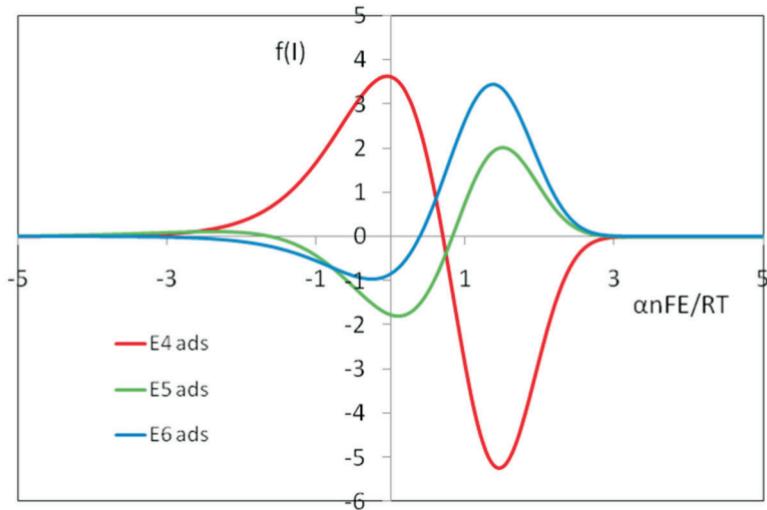


FIG. 1

The theoretical courses of EVLS functions E4, E5 and E6, eliminating two current components, on  $\alpha nFE/RT$ . The  $f(I)$  values were calculated for the parameter of  $\alpha nFE/RT$  in the range from -5 to +5. E4 (red line):  $I_d \neq 0, I_k = 0, I_c = 0; f(I) = -11.657I_{1/2} + 17.485I - 5.8284I_2$ . E5 (green line):  $I_d \neq 0, I_d = 0, I_c = 0; f(I) = 6.8284I_{1/2} - 8.2426I + 2.4142I_2$ . E6 (blue line):  $I_c \neq 0, I_d = 0, I_k = 0; f(I) = 4.8284I_{1/2} - 8.2426I + 3.4142I_2$

Millipore water. The solutions were deaerated with argon 5.0 (Messer, min. 99.999 vol.%) at 1 atm pressure for 30 min before each measurement. The experiments were carried out at room temperature. An electrochemical quartz crystal microbalance model RQCM S/N 220 (Maxtek INC., California, USA) was used. A three-electrode compartment cell, with a 5 MHz AT-cut quartz crystal Pt electrode as a working electrode, reversible hydrogen electrode (RHE) as a reference electrode and Pt sheet as an auxiliary electrode, was used. The AT-cut quartz crystals used in this study have the diameter of 25.4 mm and the thickness of 0.33 mm. Pt electrode surface was renewed electrochemically by its polarization at negative potential (-0.5 V vs SHE) for 3 min and then by its cycling (50 cycles at 50 mV/s) in the supporting electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>). For the purity control the reference CV curve of 0.5 M H<sub>2</sub>SO<sub>4</sub> (black curve in Fig. 2) was used. The scan rates of 25, 50 and 100 mV/s, all at a constant potential step of 2 mV, were employed.

EQCM was connected with Autolab potentiostat (Ecochemie, Netherlands) used for cyclic voltammograms recording. All cyclic voltammetric data obtained for each tested monochlorophenol were exported into Microsoft Excel (Microsoft, USA) for elimination procedure.

## RESULTS AND DISCUSSION

### *Cyclic Voltammetry and EQCM Measurements*

The experiment in the study of monochlorinated phenols using hyphenated electrochemical methods is presented in Fig. 2. Figure 2a shows the first five consecutive cyclic voltammograms (without stirring of the solution between scans recording) of Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1.25 mM 4-CP at scan rate of 100 mV/s. The oxidation of 4-CP during the positive-going potential sweep occurs in the potential range from 1 to 1.6 V and two oxidation peaks (p1, p2) can be observed at the first scan. The peak current decreases with increasing scan number and also the shift of second peak potential can be observed. The presence of only one oxidation peak (p3) is observed during the fourth scan. Figure 2c shows corresponding mass changes ( $\Delta m$ ) versus electrode potential. The most significant mass increase corresponds to the first scan. With the increasing scan number the  $\Delta m$  decreases indicating the polymer film formation. The electrode surface is completely covered with polymeric film after 5 cycles. Figure 2b shows the second set of five consecutive CVs (scans 6–10) measured immediately after the first set with the same solution without intermediate stirring or deaeration and without any preliminary treatment of the electrode. Differences between sixth and subsequent scans are negligible indicating thus the blocking of the electrode surface so that no further mass increase can be observed (Fig. 2d). From these CVs it is apparent that polymer film formed on the electrode surface is stable. Ežerskis and Jusys<sup>10</sup> studied the electro-polymerization of CPs in the NaOH supporting electrolyte by cyclic voltam-

metry. They observed complete deactivation of Pt electrode in the 4-CP solution resulting in the quick drop of the current after the first cycle. The partial deactivation of electrode occurs in the case of 2-CP and weak fouling of electrode occurs in the case of 3-CP solution. They stated that both the polymerization degree and the electrode deactivation ability depend on the structure and the permeability of the polymers formed, determined by the degree of chlorination and the isomerism of the monomers, their reactivity and polymerization pathways<sup>10</sup>.

The five consecutive cyclic voltammograms (without stirring of the solution between scans recording) recorded on the Pt electrode in the solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.9 mM 2-CP at a scan rate of 100 mV/s are shown in

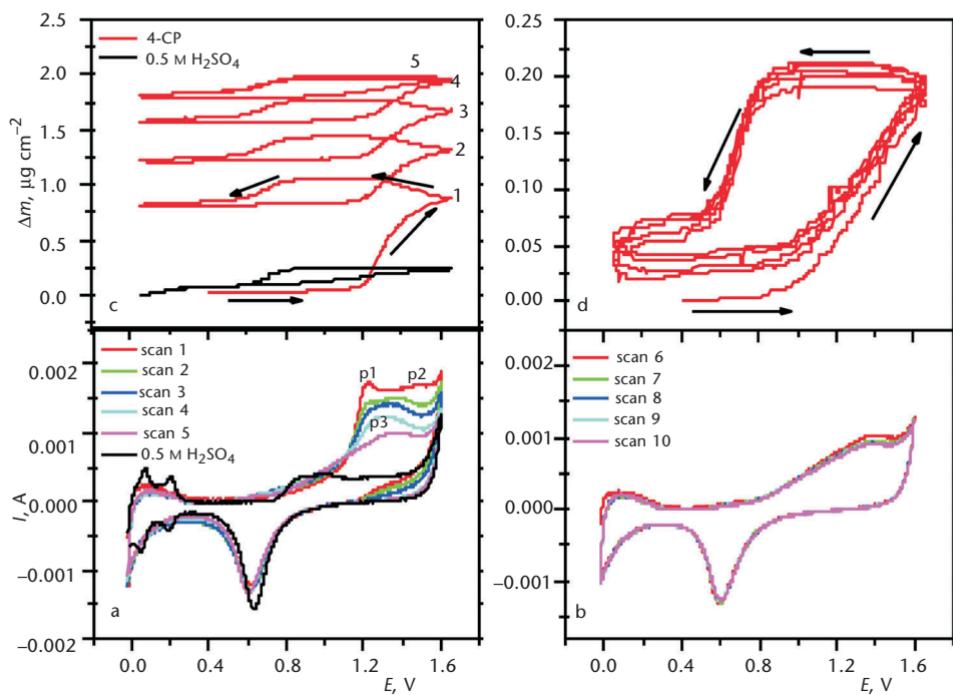


FIG. 2

a The first set of consecutive cyclic voltammograms (scans 1–5). b The second set of consecutive cyclic voltammograms (scans 6–10) at 100 mV/s in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1.25 mM 4-CP. The second set was measured subsequently after the first set of CVs without any preliminary treatment of electrode surface. The bold arrows show the scan direction. Mass response of 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1.25 mM 4-CP simultaneously recorded with c the first set of CVs. d The second set of CVs. The stabilized CV and EQCM curves of supporting electrolyte are shown in black lines

Fig. 3a. The oxidation of 2-CP occurs in the same potential range (from 1 to 1.6 V) like that for the solution of 4-CP and oxidation peak can be observed at the first scan. The peak current decreases with increasing scan number and the presence of two peaks can be observed for next scans. From the EQCM measurements it is apparent that  $\Delta m$  reaches the maximum value during the first scan and decreases with increasing scan number (Fig. 3b). After 5 cycles, the electrode surface is completely blocked with the polymeric film and no further oxidation of the 2-CP resulting in mass increase can be observed (not shown). The  $\Delta m$  measured within 5 cycles for the 2-CP (Fig. 3b) reaches higher values than  $\Delta m$  measured within 5 cycles for the 4-CP (Fig. 2c) even for the lower concentration of 2-CP (0.9 mM) than

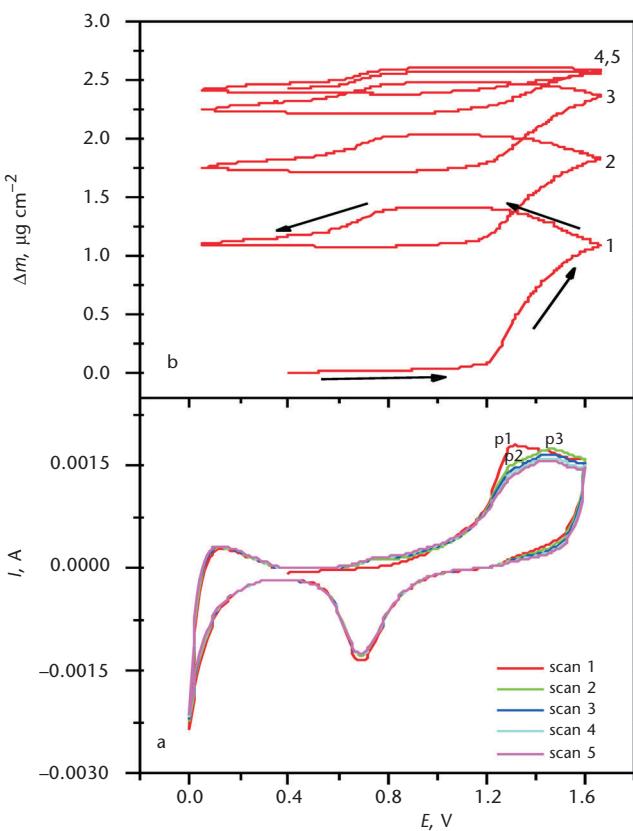


FIG. 3

a Repetitive cyclic voltammograms at 100 mV/s. b Simultaneously recorded mass response of Pt electrode in 0.5 M  $\text{H}_2\text{SO}_4$  + 0.9 mM 2-CP; the bold arrows show the scan direction

4-CP (1.25 mM). These results indicate the weak fouling of the electrode and the better permeability of polymeric film formed during the oxidation of 2-CP than that formed during the 4-CP oxidation. The same results on the Pt electrode in alkaline pH were observed by Ežerskis et al.<sup>19</sup>.

The five consecutive cyclic voltammograms (without stirring of the solution between scans recording) of Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.9 mM 3-CP at scan rate of 100 mV/s are shown in Fig. 4a. The oxidation of 3-CP occurs in the same potential region like those for 2-CP and 4-CP solutions (from 1 to 1.6 V) and only one oxidation peak can be observed at every scan. From EQCM measurements it can be observed that the polymeric film formed on the electrode surface during the 3-CP oxidation is less permeable than that in the case of 2-CP (Fig. 4b) and the measured  $\Delta m$  during the first cycle is almost twice lower for the 3-CP than that for the 2-CP. After 5 cycles, the

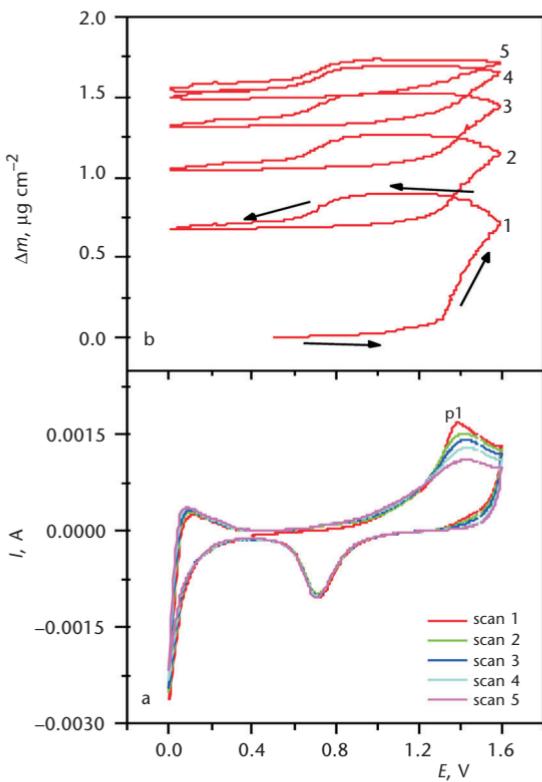


FIG. 4

a Repetitive cyclic voltammograms at 100 mV/s. b Simultaneously recorded mass response of Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.9 mM 3-CP; the bold arrows show the scan direction

electrode surface is completely blocked with the polymeric film and no further oxidation of the 3-CP resulting in mass increase can be observed (not shown).

The scan rate is other factor which has the great influence on the electro-oxidation of chlorophenols. For 2-CP, the oxidation peak current decreases with the decreasing scan rate (Fig. 5a). We have also observed the shift of oxidation and the reduction peak potential to less positive values with the decreasing scan rate (Fig. 5a) during the first scans. The presence of the second oxidation peak was observed at the second scan for the scan rate of

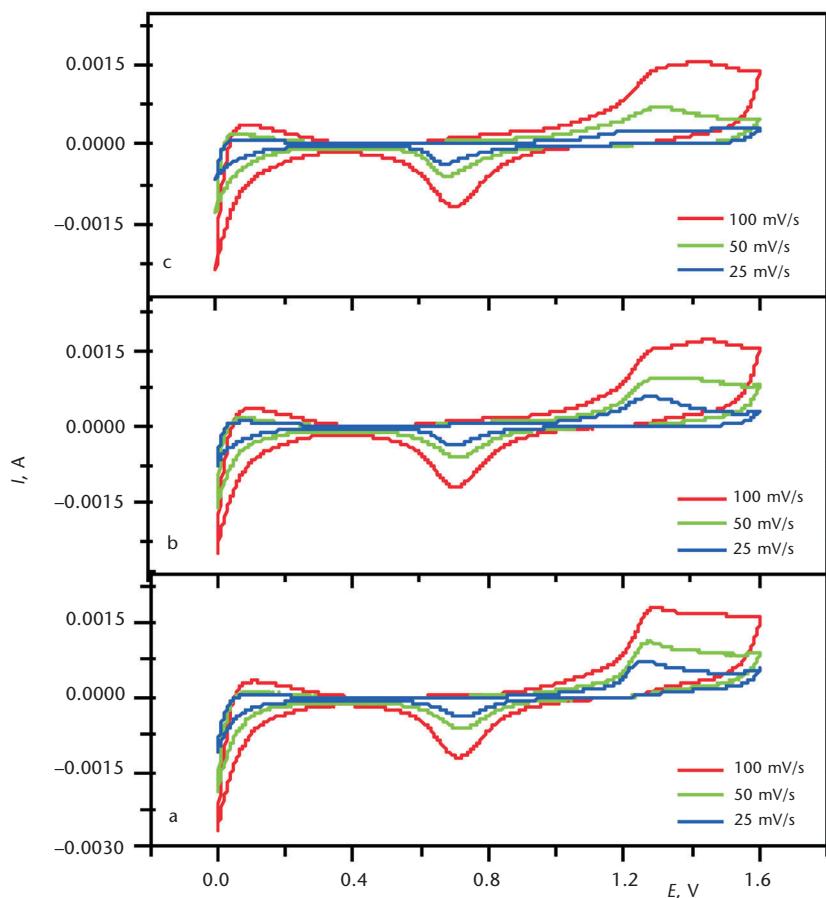


FIG. 5

The cyclic voltammograms recorded at 100, 50 and 25 mV/s: a during first cycles, b during second cycles and c during third cycles on Pt electrode in 0.5 M  $\text{H}_2\text{SO}_4$  + 0.9 mM 2-CP

100 mV/s but on the CV for the scan rate of 25 mV/s, the only one peak can be observed (Fig. 5b). The reduction peak potential is shifted to more positive values during the second (Fig. 5b) and the third scans (Fig. 5c). The decrease of the oxidation peak current with the increasing scan number is apparent for every tested scan rate (Fig. 5) indicating thus the polymer film

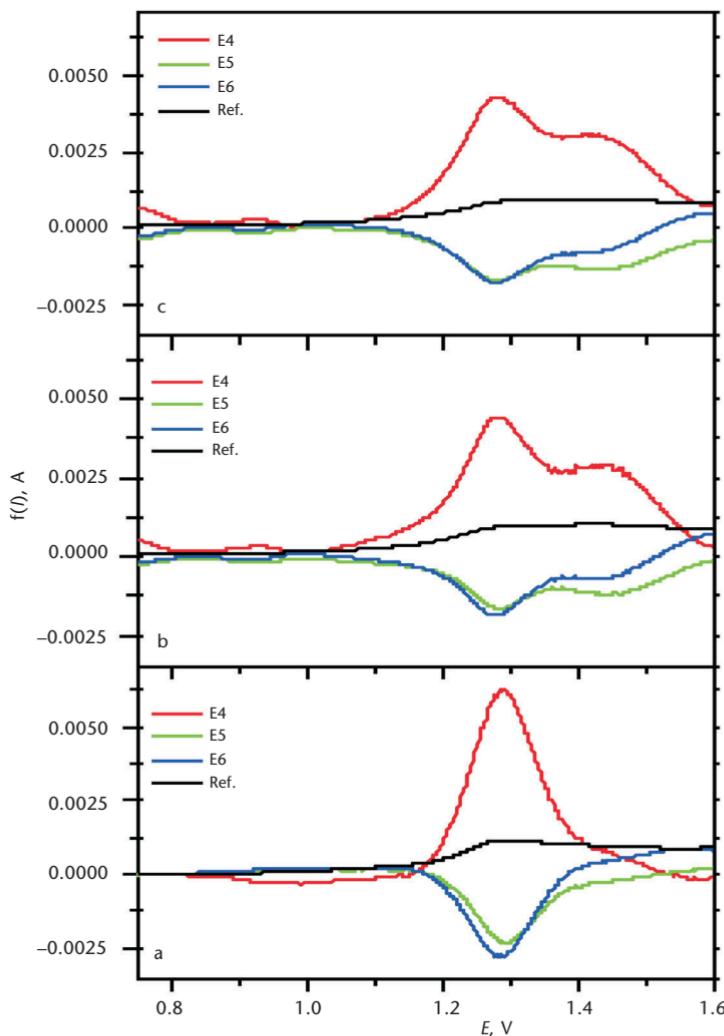


FIG. 6  
Elimination voltammograms of 2-chlorophenol: a first cycle, b second cycle, c third cycle

formation. The most permeable polymeric film corresponds to the higher scan rate (100 mV/s), the oxidation process takes place even after the third cycle. The oxidation of 2-CP has occurred mainly in the first and second scans for the scan rate of 25 mV/s, the electrode was completely inactivated with the polymeric film after third scan (not shown).

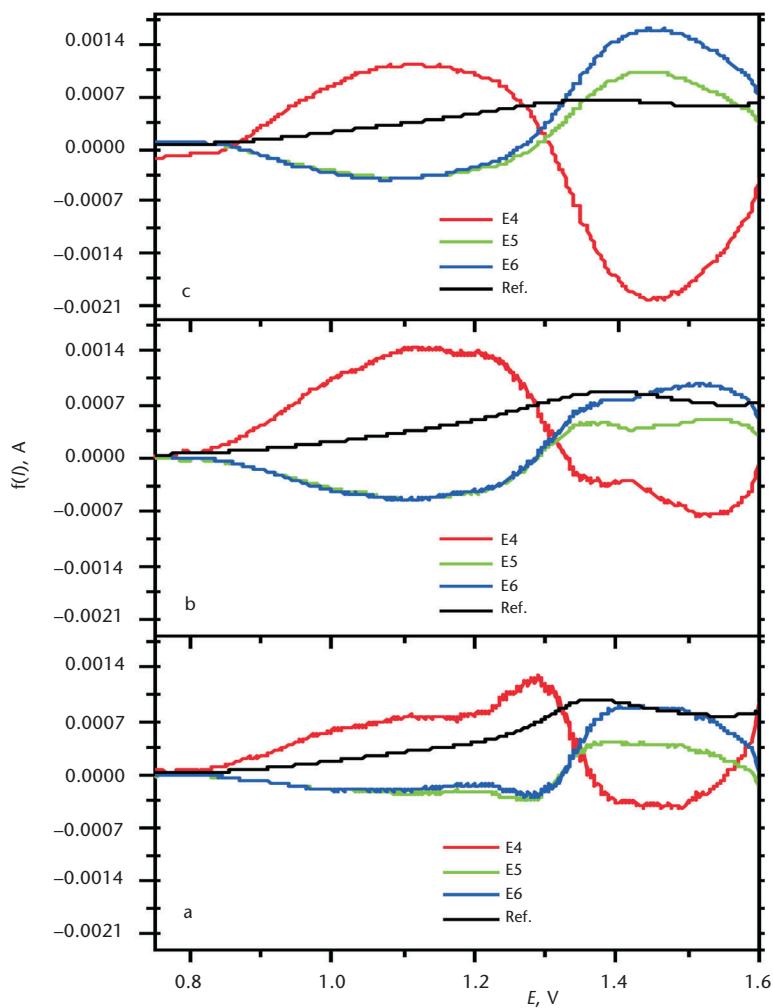


FIG. 7  
Elimination voltammograms of 3-chlorophenol: a first cycle, b second cycle, c third cycle

*EVLS Results*

Elimination functions E4, E5 and E6 for the first, second and third cycles of 2-CP oxidation are shown in Fig. 6. Scan rates of 25, 50 and 100 mV/s, and Eqs (1)–(3) have been used for their calculations. The elimination of data

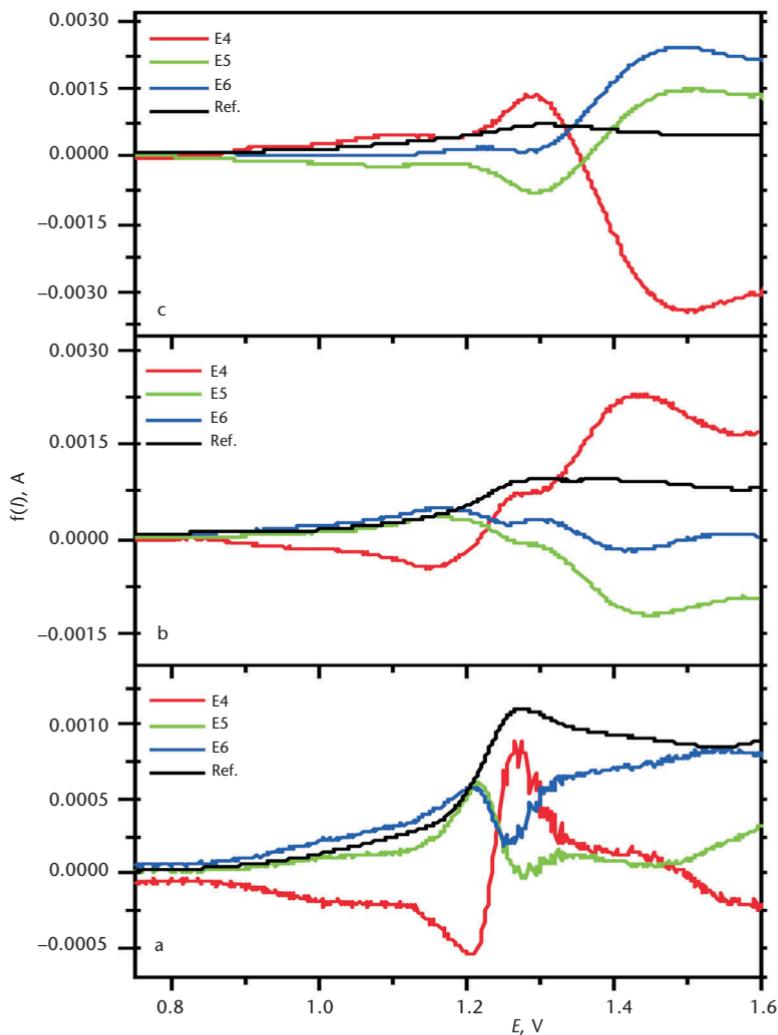


FIG. 8  
Elimination voltammograms of 4-chlorophenol: a first cycle, b second cycle, c third cycle

amplified the original LSV signal approximately six times. In accordance with CV/QCM experiments, which indicate the formation of less compact polymer film for 2-CP than to other derivatives, the presence of one oxidation peak can be observed in the first cycle (Fig. 6a). The appearance of the second peak revealed the oxidation of another intermediate for the second and third cycles (Figs 6b and 6c). According all EVLS functions, the 2-CP electrooxidation does not take place in an adsorbed state because elimination functions used do not provide typical peak-counterpeak signals<sup>25</sup>. It should be noted that these signals in E4 and in E5 together with E6 have opposite courses (Fig. 1). In contrast to 2-CP, derivate 3-CP underlie to electrode process in adsorbed state and the typical shape of peak-counterpeak is clearly visible for all cycles (Fig. 7). It clearly follows from Fig. 7a that the species oxidation undergoes in the adsorbed state but the sensitivity of elimination curves is lower compared to reference LSV curve. The increase of oxidation signal of the third cycle by EVLS was not as like as enhancement of 2-CP oxidation signals at potential area of oxidation (Fig. 7c).

The most apparent changes in elimination signals are shown in Fig. 8, where the 1st, 2nd and 3rd cycle elimination voltammograms of 4-CP oxidation are shown. Despite of difference in the scale of  $f(I)$  axis, we can say that oxidation signal is much smaller than for another CPs. Elimination functions for all 3 cycles indicate different mechanism of oxidation process for each cycle (Figs 8a, 8b and 8c). It is assumed that kinetics (minimum of E4 at 1.2 V) is taking place in the first cycle (Fig. 8a) and disappears in the third cycle. The second cycle (Fig. 8b) signifies the transit state between the first and the third cycles. In the third cycle (Fig. 8c), the adsorbed state has been indicated because of the presence of peak-counterpeak.

According to EVLS results, we can conclude that 3-CP and 2-CP were the most and the least adsorbed chlorophenols, respectively. The most complex mechanism in the oxidation process can be expected in the case of 4-CP.

## CONCLUSIONS

The electrochemical oxidation of all chlorinated phenols is the irreversible process with the loss of the first electron. After this the radical of corresponding phenol is formed and this radical may easily polymerize. It can lead to the production of polymerization compounds in a complex reaction pathway. This type of polymerization causes the electrode fouling which is a general problem in the direct electrochemical oxidation (electrochemical incineration – ECI) of phenolic compounds. The mechanism and reaction of intermediates of electrochemically induced chlorophenol oxidation de-

pend on the type of electrode used, on pH and solution components, and also on the particular oxidized chlorophenol.

In this study, we investigated three monochlorophenols (Cl in 2, 3 and 4 positions) at Pt electrode (polycrystal) in acidic solutions (0.5 M H<sub>2</sub>SO<sub>4</sub>). Moreover, EQCM was employed for study of polyphenyl layers on Pt electrode surface. Both voltammetric (CV and EVLS) and EQCM behavior is indicative of the formation of a compact and insulating polymer film blocking access of the monomer to the surface of the electrode. In accordance with CV/EQCM experiments, the polymer film is formed during 5 cycles and the mass changes ( $\Delta m$ ) were similar for 2-CP and 4-CP. In the case of 3-PC the mass change ( $\Delta m$ ) was highest and EVLS proved the main role of the adsorption.

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