



## Electropolymerization of chlorinated phenols on a Pt electrode in alkaline solution Part I: A cyclic voltammetry study

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### Abstract

Cyclic voltammetry studies were carried out on a platinum electrode in alkaline 1 M NaOH solutions containing 0.1 M of phenol, monochlorophenols, dichlorophenols, trichlorophenols and pentachlorophenol in order to compare their electropolymerization ability and the degree of deactivation of the electrode. These show that fouling of the Pt electrode occurs during the electrooxidation of all the phenols studied. Almost full deactivation of the electrode occurs in the case of phenol and 3-chlorophenol after five cycles, while 4-chlorophenol, 3,4-dichlorophenol, 2,4-dichlorophenol and 2,4,5-trichlorophenol deactivate the electrode completely after the first cycle. Partial deactivation of the electrode occurs in the case of 2-chlorophenol, 2,3-dichlorophenol, 2,6-dichlorophenol, 2,5-dichlorophenol and 2,4,6-trichlorophenol. A weak fouling of the electrode occurs in the case of 3,5-dichlorophenol, 2,3,6-trichlorophenol and pentachlorophenol. Such differences in the degree of electrode deactivation may be explained by the different structure (permeability) of the polymeric tars formed. The structure of the tars depends on the monomer structure. Presumably, more regular and dense polymer structures deactivate the electrode more rapidly. More branched, irregular high molecular weight substances deactivate the electrode more slowly.

### 1. Introduction

The electrochemical oxidation of hazardous organic species is a promising method for waste-water remediation [1–15]. Halogenated phenols constitute a large group of organic pollutants due to their slow degradation, bio-accumulation and extreme toxicity. Such chlorinated phenols, as 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol, are among the most important pollutants (Environment Protection Agency, USA) [16].

In the first step of electrooxidation of phenol and its derivatives, phenoxy radicals are generated, which can be either oxidized further or be coupled, forming ether- and quinone-type oligomeric or polymeric compounds [17–30]. The possible electrooxidation pathways for phenol are shown in Figure 1 [19].

Insoluble high molecular weight species block the electrode surface and prevent effective electrooxidation of phenols. Electropolymerization of phenols occur on different electrodes, namely, Fe, Cu, Ni, Cr, Ti, Zn, Au, Pt [23, 31] and Ag [32]. A deactivation rate of the electrodes due to polymerization depends on a large variety of parameters, such as phenolic compound concentration, its adsorption ability, the nature of the electrode, solution pH, solvent, additives, electrode potential and current density [17]. An increase in

phenolic compound concentration enables formation of a larger amount of phenoxy radicals, which are involved in electropolymerization processes, causing faster deactivation of the electrode. Oxidation of dimethylphenol on different electrodes was shown to be faster on noble metals, such as platinum and gold [23]. Deactivation of the electrode is more characteristic in alkaline medium [23]. It has also been shown that the formation of oligomers in the case of electro-oxidation of 2,6-dimethylphenol in acetonitrile solution is more pronounced than polymerization and this leads to the formation of dimer, trimer and tetramer structures [33]. A weaker electrode fouling occurs on the metal oxide (e.g., [2]) or boron-doped diamond [34] electrodes.

Mechanistic studies of the electrooxidation of various phenol derivatives show that polymerization of phenolic compounds mainly occurs via *ortho* and *para* positions and as a result 1,2,4-, 1,2,6- and 1,2,4,6-polyphenol derivatives are formed. This is explained by formation of the radical which is preferably stabilized at *ortho* and *para* positions as confirmed by theoretical electron orbital calculations [18, 35]. In the case of phenol polymerization the most energetically favoured route for coupling is a sandwich-type structure leading to carbon–carbon coupling through *ortho–para* and *ortho–ortho* links. A less favourable route involves planar structures through ether-type links. The least favoured route is a

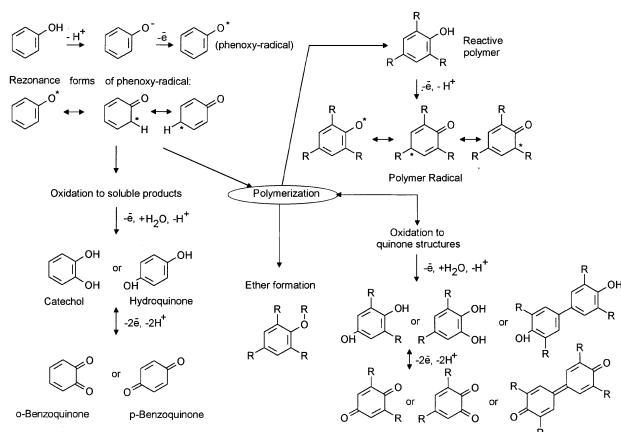


Fig. 1. Polymerization reaction pathways of phenol (where R = hydrogen or an adjacent ring in the polymer structure).

planar coupling leading to *para-para* or other carbon-carbon coupled dimers [18, 35].

However, deviations from the general polymerization routes can occur for phenol derivatives where the 2-, 4- and 6-positions are occupied by groups or atoms other than hydrogen, especially, by bulky substituents. It was reported that 4-bromo-2,6-di-*t*-butylphenol and pentabromophenol cannot be oxidatively polymerized [24, 36]. Halogen-substituted phenols are the starting materials for the synthesis of polyoxyphenylenes by oxidative displacement of halogens [31, 37, 38]. The ability of halide elimination from *ortho* and *para* positions of halogenated phenols in the course of their electropolymerization decreases in the group:  $I > Br > Cl \gg F$  [39].

The electropolymerization of phenol [17, 19–22], methyl-substituted [18, 23, 30] and some chloro-substituted phenols [23, 24] was investigated by means of cyclic voltammetry (CV) [17–22, 25, 26], gel permeation chromatography (GPC) [17, 30], Fourier transformed infrared (FTIR) spectroscopy [18, 20, 30], electrochemical quartz crystal microbalance (EQCM) [21], scanning tunneling microscopy (STM) [27, 29], polarographic [23].

The polymeric tars formed exhibit a low permeability and a strong adhesion to the electrode [17, 20]. These factors as well as the formation of less reactive ether- and quinone-type structures are postulated to be the main reasons of electrode deactivation during electrooxidation of phenols [18].

In the present paper we have focused on a comparative CV study of phenol and its chlorinated derivatives in alkaline medium on a Pt electrode in order to investigate the degree of the electrode fouling in the course of electrooxidation of phenols (depending on their chlorination degree and the isomerism). Due to a high stability in the large potential window, reproducibility in preparation and a high activity towards electrooxidation of many organic species, Pt is a convenient electrode material for such model studies, though a practical application of noble metal anodes is often limited. Similarly, potentiodynamic cyclic voltammetry measurements provide important information on

the electrochemical stability of the species under study and is a simple method for screening the processes occurring in a wide potential range, though a constant-current (potential) electrolysis is used more often for the practical purposes.

In the following papers we will present results of the kinetics for a constant-potential electropolymerization of chlorinated phenols studied by the EQCM [41] and characterization of the polymeric and oligomeric species formed by FTIR [42] and GC-MS [43]. The possible mechanisms of electropolymerization of chlorophenols will be discussed in the light of these experimental data.

## 2. Experimental details

Both a potentiostat PI-50-1 and a function generator PR-8 (Russia) were used to conduct electrochemical measurements. Two digital voltmeters V7-43 (Russia) were connected to an IBM-PC through a IEEE-488 interface for current-voltage data acquisition.

Pt foil (1 cm × 1 cm, geometric area 2 cm<sup>2</sup>, real surface area 3 cm<sup>2</sup>) was used as a working electrode. A Pt foil counter electrode (geometric area 2 cm<sup>2</sup>) and an Ag/AgCl/KCl<sub>sat.</sub> reference electrode (all potentials are referred to the standard hydrogen electrode, SHE) were used. The working electrode was immersed at a controlled potential of –0.8 V and the electrode potential was repetitively scanned to 0.85 V and back to –0.8 V. The current densities are reported based on the real 1 cm<sup>2</sup> electrode area found from hydrogen monolayer adsorption charge on platinum in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution [44, 45]. The potential sweep rate was 200 mV s<sup>–1</sup>. The experiments were performed at 20 ± 1 °C.

0.1 M solutions of phenol and chlorophenols (from Aldrich, Riedel-de Hæn, Fluka) in 1 M NaOH were studied in a three-compartment electrochemical cell of 10 ml working volume. The compartments for the working electrode and the counter electrode were separated by a glass frit. The third compartment was for the reference electrode. The working electrode, prior electropolymerization measurements, was cleaned in a mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> (1:1) (caution: the mixture should be prepared and handled with an extreme care). Ar gas was bubbled through the solutions to remove oxygen. All the solutions were prepared using triply distilled water. Chemicals of ‘pure’ and ‘analytical’ grade were used.

## 3. Results and discussion

### 3.1. Cyclic voltammetry of a Pt electrode in alkaline solutions of phenol and monochlorophenols

The CV of the Pt electrode in 0.1 M solution of phenol, the parent molecule in the whole family of chlorinated phenols, is shown in Figure 2(a). Anodic oxidation of phenol occurs during a positive-going potential scan in

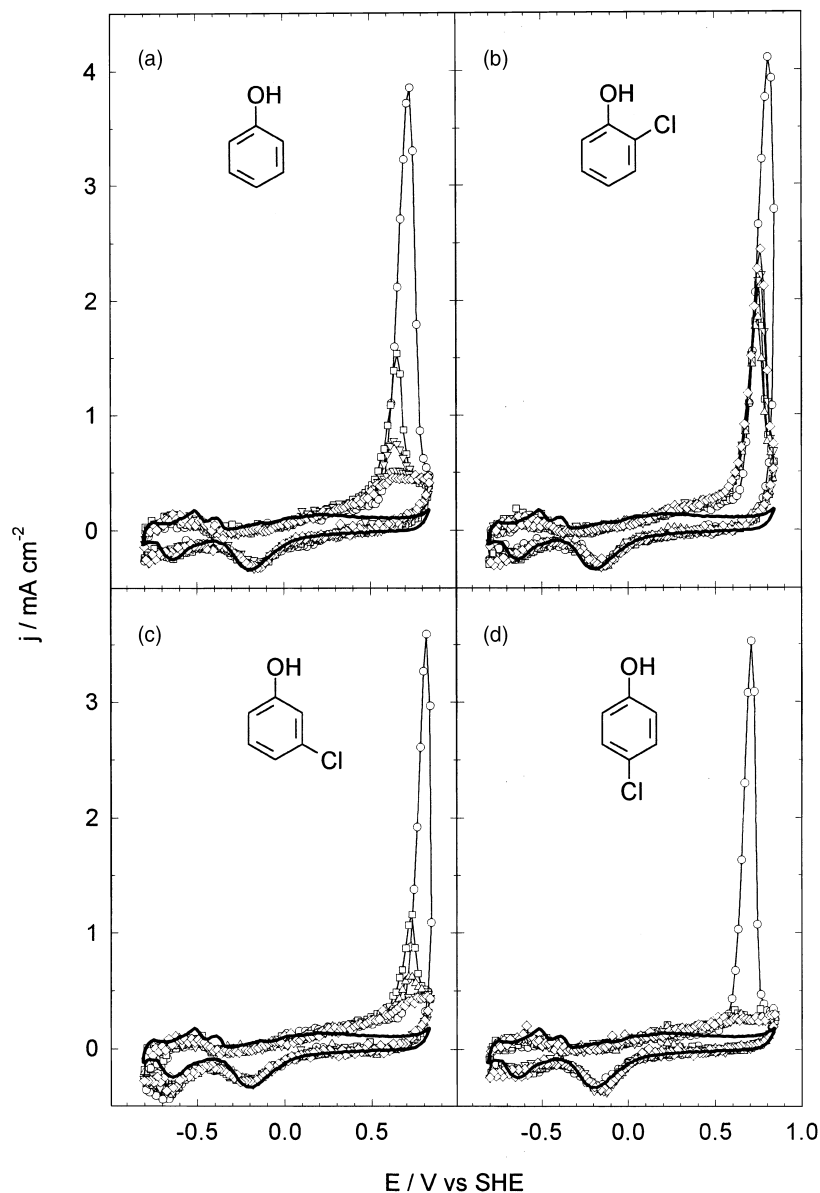


Fig. 2. CV curves of Pt electrode in 1 M NaOH solution, containing 0.1 M of (a) phenol, (b) 2-chlorophenol, (c) 3-chlorophenol and (d) 4-chlorophenol. Key: 1 cycle (○); 2 cycle (□); 3 cycle (△); 4 cycle (▽); 5 cycle (◇). CV curves of Pt electrode in background 1 M NaOH solution (—); potential sweep rate 200 mV s<sup>-1</sup>. *T* = 20 °C.

the potential range of platinum oxide formation (from 0.55 to 0.8 V). In the first positive-going potential sweep the maximum current density of 3.9 mA cm<sup>-2</sup> is achieved at 0.73 V (Figure 2(a)). In the second cycle the maximum current drastically drops to the value 1.7 mA cm<sup>-2</sup>. The potential value, corresponding to the current density maximum in the second oxidation cycle, is equal to 0.65 V. The decrease in current also occurs in the third, fourth and fifth cycles (Figure 2(a)). In the fifth cycle the current density reaches only 0.5 mA cm<sup>-2</sup>. The oxidation peak potential shifts slightly to more negative potentials after each cycle (Figure 2(a)).

The decrease in current may be explained by deactivation of the Pt electrode [19] due to the polymerization process according the scheme shown in Figure 1. The high molecular weight substances (directly linked, ether linked and cross-linked) formed on the electrode surface

prevent phenoxide ion entry to the electrode due to a low permeability of such a film [20, 46, 47]. The residual currents after inhibition of the electrode are due to the inner Helmholtz layer reactions (full oxidation of organic species to CO<sub>2</sub>) which are slower than the outer Helmholtz layer reactions (partial oxidation to ether and quinone structures, Figure 1) [19]. Therefore, a decrease in the oxidation current is due to diminishing of the electrode surface area (blocking by the polymer film) and the hindrance of phenoxide ion diffusion towards the electrode surface within the film [17–19]. The shift of the oxidation current peak to more negative potentials with each cycle (Figure 2(a)) may be explained by the effect of the ionic species incorporated in the polymer on the electrode surface. For example, electron withdrawing groups and atoms (phenyl rings and ether linked oxygen atoms) can reduce the potential of further oxidation of

the polymer radical as compared to that of monomeric phenoxide ion [18, 19].

The CV curves of the Pt electrode in alkaline 2-chlorophenol solution are shown in Figure 2(b). The oxidation of 2-chlorophenol during the positive-going potential sweep occurs in the potential range from 0.63 to 0.85 V with a maximum current density ( $4.1 \text{ mA cm}^{-2}$ ) in the first cycle at 0.8 V (Figure 2(b)). A higher current density in the first cycle might be due to a stronger 2-chlorophenoxide ion interaction with the Pt electrode in comparison with that of phenoxide ion. This correlates to a negative inductive effect ( $-I$ ) of the Cl-substituent and a withdrawal of the electrons from the benzene ring. As a result, the electron density on the oxygen atom of phenoxide anion diminishes, which leads to a decrease in the  $pK_a$  value of 2-chlorophenol ( $pK_a$  8.5) as compared to that of phenol ( $pK_a$  10). Possibly, this results in causing a flat initial orientation of 2-chlorophenoxide on the electrode surface, compared to a tilted orientation of phenoxide on the Pt electrode surface [48]. Alternatively, the electrode passivation might be faster in the case of phenol (Figure 2(a)) (compared to the Pt fouling rate in the 2-chlorophenol solution (Figure 2(b))).

The oxidation peak potential diminishes to 0.75 V in the second cycle at the maximum current density similarly to phenol (Figure 2(b)). The current does not drop so fast in the following cycles compared to phenol (Figure 2(a)). The currents even increase slightly in the fourth and the fifth cycles (Figure 2(b)). The different electrode fouling rates for phenol and 2-chlorophenol might be explained by the structural features of the polymer, defined by the difference in composition and structure of corresponding monomers. 2-chlorophenol has one *ortho* and one *para* Cl-unsubstituted positions. The radical formed during monomeric ion oxidation is stabilized via these positions and presumably leads to the formation of ether and carbon-carbon linked 1,2,4-, 1,2,6-, 1,2,4,6-substituted polymer structures. Due to blocking of one *ortho* position by a Cl-substituent, the polymer structure is more asymmetric (possibly) and, therefore, more permeable compared to phenol. Elimination of chloride from the active *ortho* position of 2-chlorophenol is also possible to some extent as shown by the GC-MS analysis of the polymerization mixture [43]. An alternative explanation could be the formation of shorter, soluble oligomeric species in the case of 2-chlorophenol oxidation as compared to phenol.

The CV curves of the Pt electrode in 3-chlorophenol solution are shown in Figure 2(c). Deactivation of the electrode that occurs during 3-chlorophenol oxidation is similar to phenol (Figure 2(a)) and 2-chlorophenol (Figure 2(b)). The oxidation peak potential values are almost the same as in the case of 2-chlorophenol (Figure 2(b)). The current decay, with cycling, is slightly faster compared to that of phenol (Figure 2(a)). The molecule of 3-chlorophenol has two *ortho* and one *para* Cl-unsubstituted positions via which the radical formed can be stabilized. Therefore, the polymer structures

formed are presumably 1,3,4-, 1,3,6-, 1,3,4,6-substituted, ether linked with some quinone groups, analogous to that of phenol polymer. Chloride elimination, most likely, does not occur from the inactive *meta* position. Apparently, chloro-substituent remaining in *meta* position tends to decrease the permeability of the polymer film compared to polyphenol. A decrease in the acidity of 3-chlorophenol ( $pK_a$  9.1) compared to 2-chlorophenol suggests a weaker withdrawal of the electrons from the benzene ring and an increase in the negative charge on the oxygen atom of 3-chlorophenoxide anion. This possibly results in a weakening of the 3-chlorophenoxide interaction with Pt electrode and a preferred tilted initial orientation of the molecule.

The CV curves of the Pt electrode in 4-chlorophenol solution (Figure 2(d)) considerably differ from those in phenol (Figure 2(a)), 2-chlorophenol (Figure 2(b)) and 3-chlorophenol solutions (Figure 2(c)). The current reaches a maximum value of  $3.6 \text{ mA cm}^{-2}$  in the first positive-going potential scan at 0.7 V (Figure 2(d)). After the first cycle the current quickly drops in subsequent cycles to values which are nearly equal to those of the background currents of the Pt electrode in 1 M NaOH solution (Figure 2(d)). Such a current drop may be explained by the compact structure of the polymers formed which efficiently block the electrode. There are two *ortho* Cl-unsubstituted positions in 4-chlorophenol molecule through which 4-chlorophenoxy radical could be stabilized. Presumably, 1,2,4- and 1,2,4,6-substituted ether linked structures with some quinone groups are formed which are more linear compared with the polymers formed from phenol and other monochlorophenol isomers. Also the elimination of chloride from the *para* position of 4-chlorophenol is possible, and to a greater extent compared to that of 2-chlorophenol as evidenced by the GC-MS analysis [43]. Possibly, the more regular (compact) structure of the polymer film prevents the monomer interaction with the electrode and leads to a rapid deactivation of the electrode. The highest  $pK_a$  value among the monochlorophenols, for 4-chlorophenol (9.4), suggests the highest negative charge on the oxygen atom of the corresponding phenoxide anion (due to the weak electron withdrawal by the chlorine substituent located in *para* position). Possibly, this leads to a preferred vertical initial orientation of 4-chlorophenoxide anion and the formation of a dense polymer film. Due to some elimination of chloride, *para* ether linked (poly-phenyl-ether) type polymers might be formed which may be very unreactive for further oxidation compared to carbon-linked (poly-phenol type) polymers that have a number of sites for further oxidation. This might partially explain the very rapid loss of electrode activity in the case of 4-chlorophenol polymerization.

### 3.2. Cyclic voltammetry of a Pt electrode in alkaline solutions of dichlorophenols

The Pt electrode CV curves in 1 M NaOH solutions containing 0.1 M of dichlorophenols are shown in

Figure 3. The maximum current value reaches  $3.2 \text{ mA cm}^{-2}$  in the case of 2,3-dichlorophenol and 2,6-dichlorophenol in the positive-going potential scan at potential 0.82 V (Figure 3(a) and (b)). After the first cycle the oxidation peak maximum for these isomers slightly shifts towards more negative potentials due to a lower oxidation potential of the polymeric structures formed. The polymerization route of 2,3-dichlorophenol could be compared to that of the 2-chlorophenol. One *ortho* and one *para* Cl-unsubstituted position is available in both isomers. Therefore, the 2,3-chlorophenoxy radical is stabilized via these positions. This leads to the formation of 1,2,3,4-, 1,2,3,6- and 1,2,3,4,6-substituted derivatives during anodic oxidation of these

monomers. These structures, due to a remaining Cl-substituent in the *meta* position, are presumably less permeable compared to the polymers formed from 2-chlorophenol (Figure 2(b)). However, the polymer films derived from 2,3-dichlorophenol are most likely more asymmetric and, therefore, do not cover the electrode so densely as in the case of 4-chlorophenol (Figure 2(d)). As a result full inhibition of the electrode does not occur under the same conditions (Figure 3(a)).

In the case of 2,6-dichlorophenol (Figure 3(b)) only one *para* Cl-unsubstituted position is available in the monomer. Presumably, 1,2,4,6-substituted linear head-to-tail linked polymer is formed under anodic oxidation of 2,6-dichlorophenol (Figure 3(b)). This is in agreement

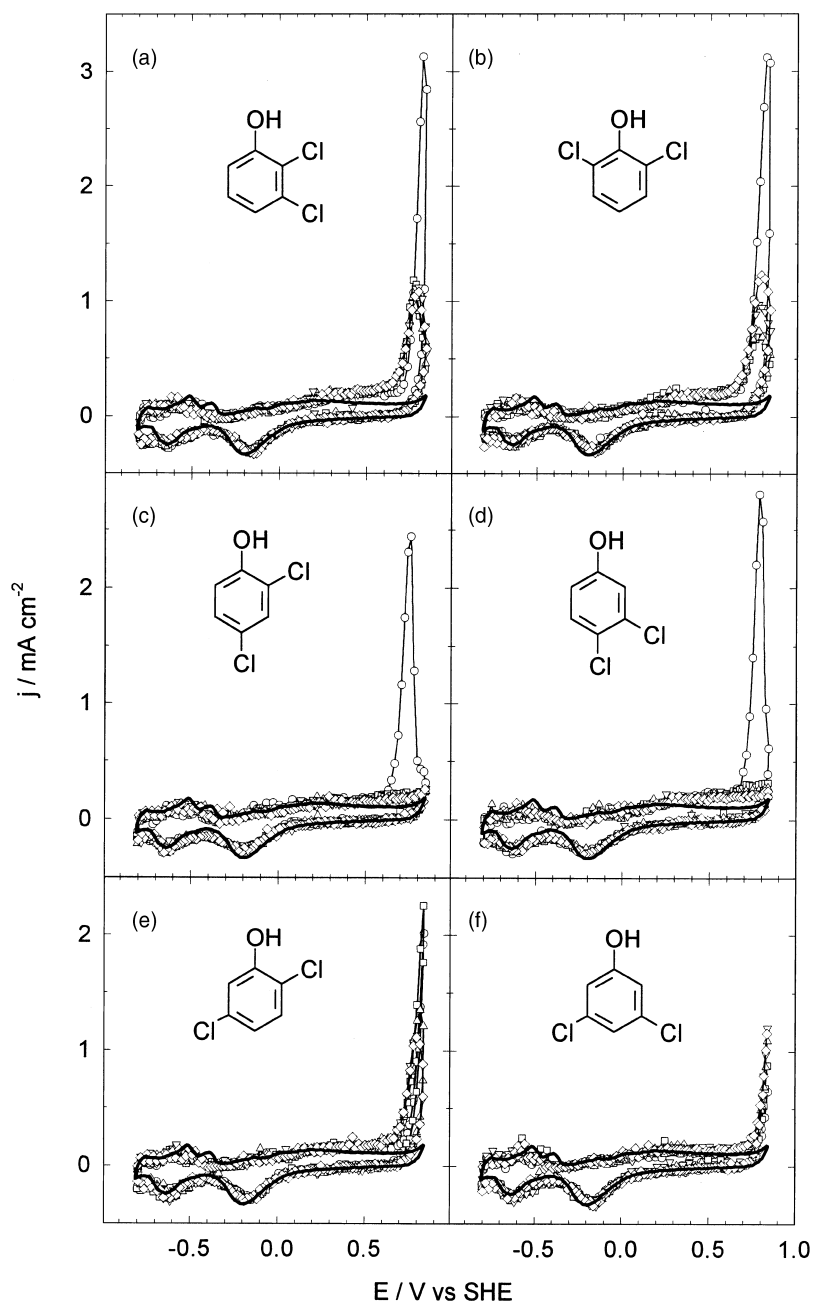


Fig. 3. CV curves of Pt electrode in 1 M NaOH solution, containing 0.1 M of (a) 2,3-dichlorophenol, (b) 2,6-dichlorophenol, (c) 2,4-dichlorophenol, (d) 3,4-dichlorophenol, (e) 2,5-dichlorophenol and (f) 3,5-dichlorophenol. Key: 1 cycle (O); 2 cycle (□); 3 cycle (Δ); 4 cycle (∇); 5 cycle (◇). CV curves of Pt electrode in background 1 M NaOH solution (—); potential sweep rate  $200 \text{ mV s}^{-1}$ .  $T = 20 \text{ }^\circ\text{C}$ .

with 2,6-dimethylphenol polymerization resulting in a linear polymeric structure formation with molecular weight ranging from 1000 to 4000 g mol<sup>-1</sup> [30]. Nevertheless, it is reported that a 19% loss of chloride occurs during oxidative polymerization of 2,6-dichlorophenol [24]. Moreover, a polymerization mixture of 2,6-dichlorophenol shows some amount of dimers and trimers with eliminated chloride [43]. Therefore, chloride elimination during electro-oxidation of this dichlorophenol isomer cannot be excluded either. Elimination of chloride results in polymerization via *para* as well as *ortho* positions forming the products similar to those forming in the case of 2-chlorophenol. The CV curve of the Pt electrode in 2,6-dichlorophenol solution (Figure 3(b)) can be interpreted as characteristic for the branched, more permeable polymers.

The CV curves of the Pt electrode in alkaline 2,4-dichlorophenol and 3,4-dichlorophenol solutions are shown in Figure 3(c) and (d). The maximum current values (2.4 and 2.8 mA cm<sup>-2</sup>, respectively) are reached in the first positive-going potential scan (Figure 3(c) and (d)). After the first cycle the currents drastically drop to the background values (Figure 3(c) and (d)). Such behaviour is similar to that of 4-chlorophenol (Figure 2(d)). 2,4-Dichlorophenol has one Cl-unsubstituted *ortho* position and 3,4-dichlorophenol has two Cl-unsubstituted positions. Presumably, 2,4-dichlorophenol under anodic oxidation conditions yields ether linked 1,2,4,6-substituted polymeric structures. However, chloride elimination from the active *ortho* and *para* positions during electropolymerization of these isomers also might occur leading to a variety of substitution products [43]. In the case of 3,4-dichlorophenol 1,3,4,6- and 1,2,3,4,6-substituted high molecular weight substances could be formed. Possibly, these polymers have a more dense structure, similar to that obtained in 4-chlorophenol electropolymerization (Figure 2(d)).

The anodic current maximum in 2,5-dichlorophenol and 3,5-dichlorophenol solutions occurs at more positive potentials in the first and the second cycles (Figure 3(e)). In the third cycle the oxidation peak becomes wider suggesting formation of polymeric structures with a lower oxidation potential than that of the monomer. One *ortho* and one *para* Cl-unsubstituted positions in the molecule of 2,5-dichlorophenol leads to a variety of 1,2,4,5-, 1,2,5,6- and 1,2,4,5,6-substituted structures, possibly, ether linked, carbon-carbon linked with some quinone groups. Such variety in the bonding possibilities during the polymerization process forms numerous reaction centres, which enable the formation of polymers of different size and structure. Cross-linking of the monomers is also possible, what leads to the formation of the 'net-like' rigid polymers. Corresponding interchain packing and mobility of such polymers could lead to a higher porosity of the film, which results in slower deactivation of the electrode (Figure 3(e)).

The oxidation current of 3,5-dichlorophenol on a Pt electrode is the smallest in the family of monochlorinated and dichlorinated phenols in the potential range under

the study (Figure 3(f)). Such a tendency may be explained by the steric hindrance of the monomer molecule interaction with the Pt electrode. The molecule has two *ortho* and one *para* Cl-unsubstituted positions. The radicals formed can be stabilized via these positions. Presumably, the polymerization reactions proceed by attacking preferably *ortho* position, since *para* position is hindered by two adjacent Cl atoms. This is in accordance with the data of 3,5-dimethylphenol polymerization [23]. It is possible that polymerization of 3,5-dichlorophenol yields to 1,3,5,6- and 1,2,3,5,6-substituted products, mainly ether linked. Carbon-carbon coupling with formation of quinone species is also possible, however, it does not dominate due to a steric hindrance.

### 3.3. Cyclic voltammetry of a Pt electrode in alkaline solutions of trichlorophenols and pentachlorophenol

The CV curves of the Pt electrode in alkaline 2,4,5-trichlorophenol solutions are shown in Figure 4(a). The maximum current density of 2.4 mA cm<sup>-2</sup> is reached at 0.82 V in the first positive-going potential scan. After that, the currents drop drastically to the background values in the subsequent cycles (Figure 4(a)). Such behaviour is similar to that of 2,4-dichlorophenol (Figure 3(c)). The molecule of 2,4,5-trichlorophenol has only one *ortho* Cl-unsubstituted position via which radicals formed can be stabilized. However, positions (2) and (4) are also active in the electrochemical coupling as evidenced by chlorine elimination based on the GC-MS data [43]. It is possible that the polymerization occurs preferably through the chlorine-free *ortho* position leading to more regular polymer structure formation. Therefore, dominantly ether linked 1,2,4,5,6-substituted polymeric structures are formed. A few reaction centres enable the formation of more linear polymer which covers the electrode more densely and rapidly passivates it.

The CV curve of the Pt electrode 2,4,6-trichlorophenol has a characteristic increase in oxidation current in the first cycle reaching the highest value at a positive potential limit of 0.85 (Figure 4(b)). The current value exceeds 4 mA cm<sup>-2</sup>, and is the highest one as compared to other chlorophenols (Figures 2(a-d), 3(a-f), 4(a-d)). In the second cycle the current drops to a current density of 1 mA cm<sup>-2</sup> (Figure 4(b)). In this case the oxidation potential corresponding to the maximum oxidation currents shifts towards more positive values. Presumably, the polymer ions have less electron withdrawing groups and atoms (e.g., chlorine) as compared to the monomeric ion [18]. This implies that elimination of chloride occurs during polymerization of 2,4,6-trichlorophenol. Either *ortho* or *para* position of the monomer is attacked by the oxygen atom of 2,4,6-trichlorophenoxy radical. Apparently, mainly ether linked, 1,2,4,6-substituted structures with some quinone groups, similar to that of 2,6-dichlorophenol polymerization, are formed due to elimination of chloride. This is in accordance with the data for anodic oxidation of 2,4,6-trichlorophenol

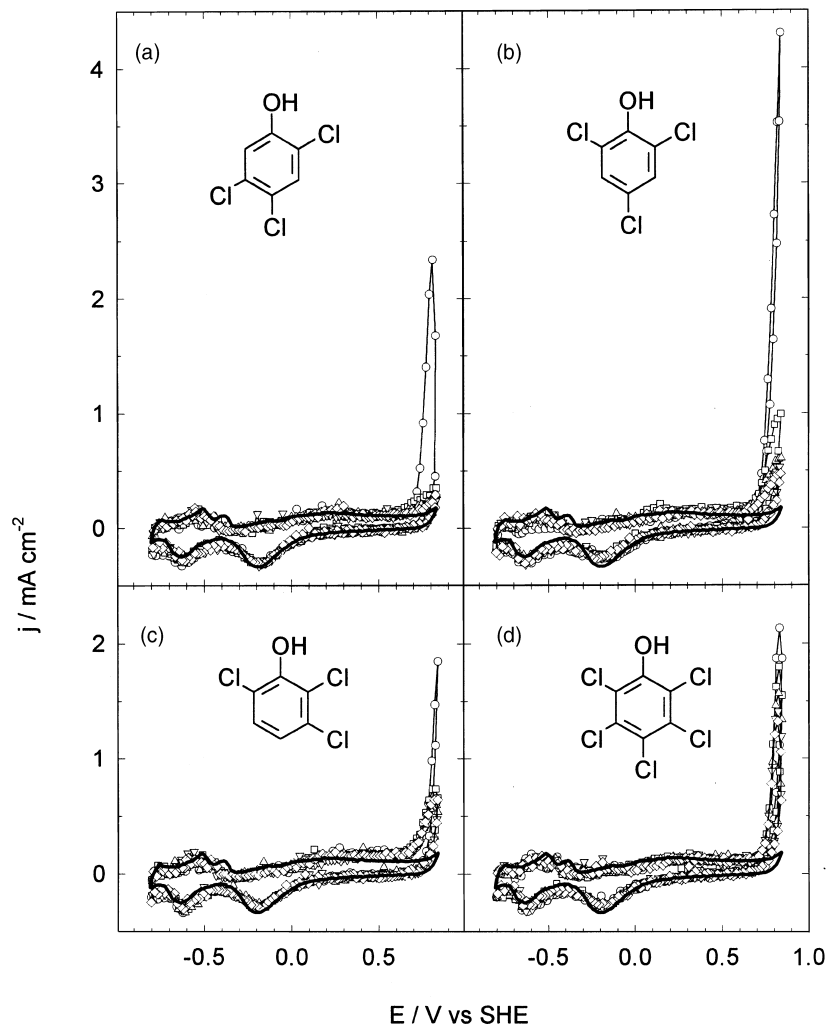


Fig. 4. CV curves of Pt electrode in 1 M NaOH solution, containing 0.1 M of (a) 2,4,5-dichlorophenol, (b) 2,4,6-dichlorophenol, (c) 2,3,6-trichlorophenol and (d) pentachlorophenol. Key: 1 cycle (○); 2 cycle (□); 3 cycle (△); 4 cycle (▽); 5 cycle (◇). CV curves of Pt electrode in background 1 M NaOH solution (—); potential sweep rate  $200 \text{ mV s}^{-1}$ .  $T = 20 \text{ }^\circ\text{C}$ .

[24]. Possibly, further chloride elimination in the polymeric structure formed could occur, as suggested for 2,6-dichlorophenol oxidation [24], resulting in formation of the ether linked structures.

The CV curves of the Pt electrode in 2,3,6-trichlorophenol solution are shown in Figure 4(c). Qualitatively the curves are similar to those of 2,4,6-trichlorophenol (Figure 4(b)) though quantitatively the maximum anodic current reached in the first positive-going scan is about half the size (Figure 4(c)). Assuming the polymerization via *para* Cl-unsubstituted position, a linear, ether linked, 1,2,3,4,6-substituted polymer is formed. Possibly, some elimination of chloride occurs from *ortho* position as in the case of 2,6-dichloro- and 2,4,6-trichlorophenols. In this case ether linked, 1,2,3,6-substituted and quinone type, 1,2,3,4,6-substituted structures are formed.

The CV of the Pt electrode in pentachlorophenol solution is shown in Figure 4(d). The oxidation current steadily reduces after each cycle; however, the electrode is not fully passivated. Since all five positions in the pentachlorophenol molecule are occupied by the

chlorine atoms, the polymerization occurs entirely through chloride elimination. It was reported that during the anodic oxidation of pentachlorophenol at lower potentials, the radicals have a sufficient lifetime for a chain reaction to occur, while at higher potentials the radicals quickly couple and the primary product is a dimer, 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone [24]. It is also possible that the mixture of ether linked, hexa-substituted oligomers with some quinone groups is formed.

#### 4. Conclusions

The potentiodynamic investigations on the platinum electrode in alkaline solutions of phenol and its chlorinated derivatives show that the fouling of the Pt electrode occurs during the electro-oxidation of all phenols. Full deactivation of the electrode occurs after the first cycle in the case of *para*-substituted chlorophenols: 4-monochlorophenol, 3,4-dichlorophenol, 2,4-dichlorophenol and 2,4,5-trichlorophenol. Partial

deactivation of the electrode occurs in the cases of phenol and *ortho*-substituted chlorophenols: 2-mono-chlorophenol, 2,3-dichlorophenol, 2,6-dichlorophenol, 2,5-dichlorophenol, 2,4,6-trichlorophenol and in the case of 3-chlorophenol polymerization. Weak fouling of the electrode occurs in the case of *meta*-substituted chlorophenols: 3,5-dichlorophenol, 2,3,6-trichlorophenol, and pentachlorophenol.

The electrode fouling is most likely a result of surface blocking by the high molecular weight species produced during anodic oxidation of phenols. 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.

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