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Oxidation of chlorophenols on Pt electrode in alkaline solution studied by cyclic voltammetry, galvanostatic electrolysis, and gas chromatography–mass spectrometry*

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Abstract: Potentiodynamic investigations on a platinum electrode show that oxidation of phenol, monochlorophenols, dichlorophenols, 2,3,6-, 2,4,5-, 2,4,6-trichlorophenols, and pentachlorophenol in 1 M NaOH solution, containing 1 mM of phenols, proceeds in the potential region of Pt oxide formation. The oxidation rate of phenols decreases with the increase in the number of chlorine atoms in the benzene ring in the row: phenol > monochlorophenols > dichlorophenols > trichlorophenols > pentachlorophenol. The electrochemical stability of phenols, as studied using a cyclic voltammetry, depends on their chlorination degree and isomerism.

Galvanostatic oxidation of 1 M NaOH solutions containing 1 mM of phenol, monochlorophenols, dichlorophenols, 2,3,6-, 2,4,5-, 2,4,6-trichlorophenols, and pentachlorophenol were carried out on a platinum electrode using 30 mA cm^{-2} current density. The electrolysis of the solutions was performed in the course of 10 h, and concentration of phenols in the anolytes was monitored during oxidation. The concentration of phenolic compounds diminishes from 1 mM to 10–50 μM during 4–5 h of electrooxidation and does not change during further galvanostatic oxidation.

A decrease in concentration of phenols during galvanostatic electrolysis weakly depends on the isomerism and a chlorination degree of the compounds. A rapid decrease in concentration of studied phenols during the first 4–5 h of electrolysis and a nonselective oxidation of different chlorophenols suggest that the oxidation proceeds via electrochemically generated oxidants. Further decrease in concentration of phenols is rather small due to deactivation of the electrode as a result of polymerization of corresponding phenols and diffusion limitations.

INTRODUCTION

Chlorinated phenols being widely used constitute a major class of organic pollutants that contaminate the ecosystem and accumulate in the food chain [1]. Various industrial effluents contain up to 18 mg/l of chlorophenols, while the municipal wastewater contains from 1 to 21 mg/ml of these compounds [1]. There are 19 different congeners among them. Several chlorinated phenols such as 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol have been classified as the priority pollutants [1]. Monitoring and detection of chlorophenols are of particular importance in environmental control and food analysis for the investigation of human and animal exposure [1].

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The remediation of polluted objects is also of major importance. Several methods of the treatment are known, such as: incineration, absorption, biological, chemical, and electrochemical methods [2]. The most widely used methods are incineration and biological treatment, especially, the latter, in wastewater remediation. A biological method is used for the treatment of readily degradable organic pollutants. The situation is completely different when the wastewater contains toxic, non-biocompatible organic pollutants [3]. Then, electrochemical method [4,5] can help to convert these pollutants into biocompatible organics before biological treatment [3]. Electrooxidation of most organic compounds, including phenols, theoretically is possible in the potential region before oxygen evolution, but practically, oxidation reactions are slow, and their rate is limited more by kinetic than thermodynamic factors [3]. The main problem in the case of oxidation of phenolic compounds is deactivation of the electrodes due to the formation of polymeric tars on their surfaces.

Passivation of the electrode may be reduced by a decrease in phenolic compound concentration, increase in the temperature of reaction medium, or using the electrodes, which have large overpotential for oxygen evolution. Using this kind of electrodes, it is possible to increase concentration of hydroxyl radicals on the electrode surface, which participate in oxidation reactions with phenols following hydroxylation or dehydrogenation mechanisms [6]. The main reaction products according to these pathways are carbon dioxide and water. Formation of hydroxyl radicals on various electrodes: Pt, Ti/IrO_2, Ti/SnO_2 was trapped using *N*,*N*-dimethyl-p-nitrosoaniline [3]. It was shown that the highest concentration of hydroxyl radicals is reached on the surface of Ti/SnO_2 electrode, while the concentration of these radicals on the surfaces of Ti/IrO_2 and Pt is almost equal to zero [3]. The most suitable electrodes for a removal of phenolic compounds are PbO_2 [7–11], SnO_2 [3,11–15], Ti/IrO_2, Ti/RuO_2, Ti/PbO_2, Ti/SnO_2 [2], and Bi/PbO_2 [16], platinum coated with quartery metal oxide film, containing Ti, Ru, Sn, and Sb oxides [17], and synthetic diamond electrodes [18–22]. The latter electrodes are the most advanced and most promising in this respect—they have very large oxygen evolution overpotential, and using them it is possible to mineralize completely a lot of organic compounds with almost 100% current efficiency [18–22].

There are three main oxidation methods for oxidation of organic compounds: direct anodic oxidation at the electrode, non-direct electrooxidation, using oxidation-reduction pairs of some metals, e.g., Ce(III)/Ce(IV) and Co(II)/Co(III) [6], and mineralization by strong oxidants, e.g., ClO^- [2] or H_2O_2 [6], which are produced during electrolysis. Using Ti/IrO_2 anode, it was shown that ClO^- is produced in the anodic compartment during oxidation of Cl^- ions, and this oxidant itself effectively mineralizes phenol in alkaline solution [2]. Also, strong oxidants could be produced in the cathodic compartment [6]. It was shown that hydrogen peroxide is formed in the cathodic compartment using a graphite electrode, and this oxidant participates in oxidation of 4-chlorophenol [6]. The oxidation capability of H_2O_2 is increased in acidic solution by adding Fe(II) salts, known as a Fenton's reagent [6]. For detoxication of 4-chlorophenol using Fe(II) salts, three methods were proposed: electrochemical, photoelectrochemical, and peroxycoagulation method [6].

It was also shown that for removal of some phenolic compounds from the wastewater, a rather effective way is electrochemical adsorption of these compounds in the form of oligomeric and polymeric compounds on a high-surface-area carbon electrode [23]. The main advantage of this method is that the polymerization process can be performed at the potentials below oxygen evolution, and, therefore, by this way it is possible to reach a high current efficiency.

The present study aimed at (i) a comparative cyclic voltammetry study of the electrochemical behavior of phenol and chlorinated phenol in a model system on Pt electrode in alkaline solution; (ii) a constant current (galvanostatic) electrolysis of corresponding phenols on Pt electrode under anodic evolution of oxygen. Due to a fast electrode fouling by polymeric species derived upon electrooxidation of the phenols at higher concentrations [24–27], the initial concentration of the phenolic species of 1 mM was used. A concentration decrease during electrolysis of phenols was monitored by the gas chromatography–mass spectrometry (GC–MS). A dependence of the electrochemical stability of chlorophenols on their chlorination degree and isomerism in cyclic voltammetry and galvanostatic electrolysis experiments was studied and compared. The results are discussed in terms of electrochemical degradation (electrooxidation/mineralization) of hazardous phenolic species.

EXPERIMENTAL DETAILS

A potentiostat PI-50-1 and a function generator PR-8 with the computerized current-voltage data acquisition system were used to conduct cyclic voltammetry measurements. A constant current electrolysis was carried out under galvanostatic conditions at anodic current densities ca. 90 mA (30 mA cm^{-2}) for 10 h. The experiments were performed using an electrochemical three-compartment glass cell in which cathodic and anodic sections were separated by a glass frit. Working volume of the cell for the CV measurements was ca. 50 ml and about 5 ml for the constant current electrolysis. A Pt foil (1 × 1 cm) was used as a working electrode. $Ag/AgCl/KCl_{sat.}$ electrode was used as the reference (all potentials are quoted against the standard hydrogen electrode, SHE), attached to the working electrode through the Luggin capillary connected to the reference electrode compartment through a wetted valve. The current densities are reported for 1 cm^2 of the real electrode area found from the hydrogen monolayer adsorption charge on platinum in 0.5 M H_2SO_4 solution [28,29]. The potential sweep rate was 0.2 V/s in CV experiments.

Concentrations of the phenolic compounds during electrochemical oxidation were monitored using a Varian 3400 gas chromatograph equipped with a mass selective Saturn 3 ion trap detector in a full scan mode (10 to 650 m/z). Quantitation ions: m/z = 94 (for phenol), m/z = 128 (for monochlorophenols), m/z = 162 (for dichlorophenols), m/z = 196 (for trichlorophenols), and m/z = 266 (for pentachlorophenol) were used for evaluation of concentrations of the phenolic compounds. The samples of each anolyte ca. 50 µl, taken during electrolysis, were acidified by adding acetic acid, extracted with chloroform (1 ml), dried with Na_2SO_4, and after that the aliquots were used for the direct GC–MS analyses. Quantitative evaluation was performed against the calibration curves for standard solutions of phenols in 1 M NaOH, containing corresponding phenolic compounds at concentrations from 1mM to 1 µM, prepared the same way as described above. For the screening intermediate products the total chromatograms as well as specific ion chromatograms of the possible compounds, which could be formed during the electrolysis, for the phenols of a higher chlorination degree, and intermediate species for phenol and monochlorophenols [11,17,22], were analyzed by the computer software.

1 M NaOH solutions, containing 1 mM of corresponding phenolic compound, were used for both cyclic voltammetry (CV) and galvanostatic electrolysis experiments at room temperature. The solutions were constantly purged with Ar before and during the measurements. Analytical grade chemicals (Fluka, Aldrich, Riedel-de-Häen) and triply distilled water were used to prepare the solutions.

RESULTS AND DISCUSSION

CV studies of phenol and chlorinated phenols on a Pt electrode

CV experiments on a Pt electrode in 1 M NaOH solutions containing 1 mM of phenol and monochloro- (Figs. 1a–d), dichloro- (Figs. 2a–f), trichloro- (Figs. 3a–e) and pentachloro- (Fig. 3f) phenols were carried out to study the influence of the chlorine substituent(s) on the electrochemical activity of corresponding phenols.

A comparison of the CV in presence of phenol—the parent molecule in the family of chlorinated phenols—on Pt in 1 M NaOH solution (Fig. 1a, solid line) and the CV in the blank (phenol-free) 1 M NaOH solution (Fig. 1a, dotted line) shows that: (1) electrosorption of hydrogen atoms (in the potential region from –0.4 to –0.7 V) is hindered in the solution containing phenol; (2) adsorption of hydroxyl anions (at the electrode potential about –0.1 V) is retarded in the solution containing phenol; and (3) anodic current increases considerably at the potentials more positive than 0.3 V in phenol-containing solution. These results suggest that: (i) phenol is adsorbed on Pt electrode in alkaline solution; (ii)

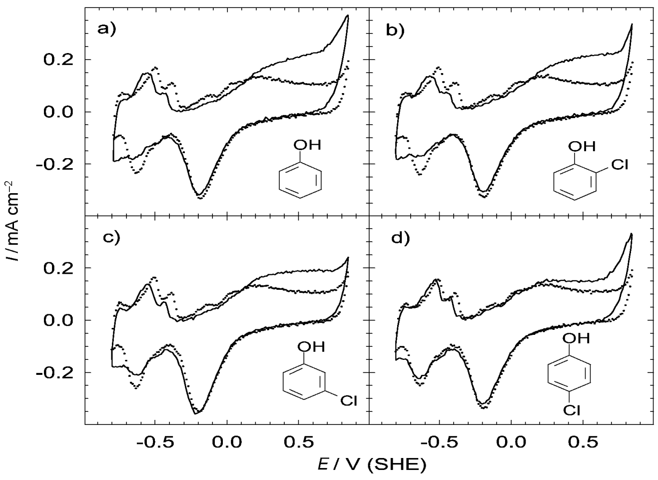

Fig. 1 The CV curves of Pt electrode in 1 M NaOH solution containing 1 mM of phenol (a), 2-chlorophenol (b), 3-chlorophenol (c), 4-chlorophenol (d), (solid lines) and in background 1 M NaOH solution (dotted lines). Potential sweep rate 200 mV/s, room temperature.

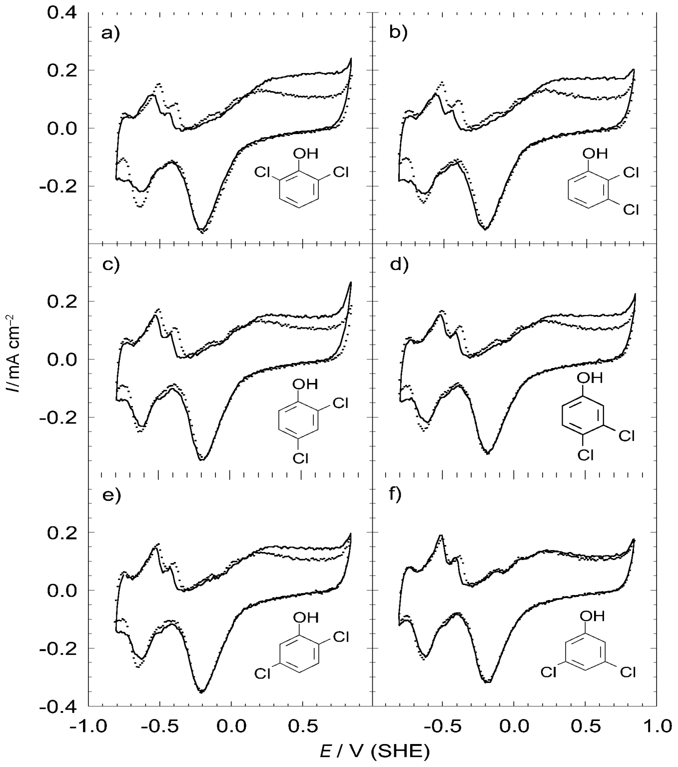

Fig. 2 The CV curves of Pt electrode in 1 M NaOH solution containing 1 mM of 2,6-dichlorophenol (a), 2,3-dichlorophenol (b), 2,4-dichlorophenol (c), 3,4-dichlorophenol (d), 2,5-dichlorophenol (e), 3,5-dichlorophenol (f), (solid lines) and in background 1 M NaOH solution (dotted lines). Potential sweep rate 200 mV/s, room temperature.

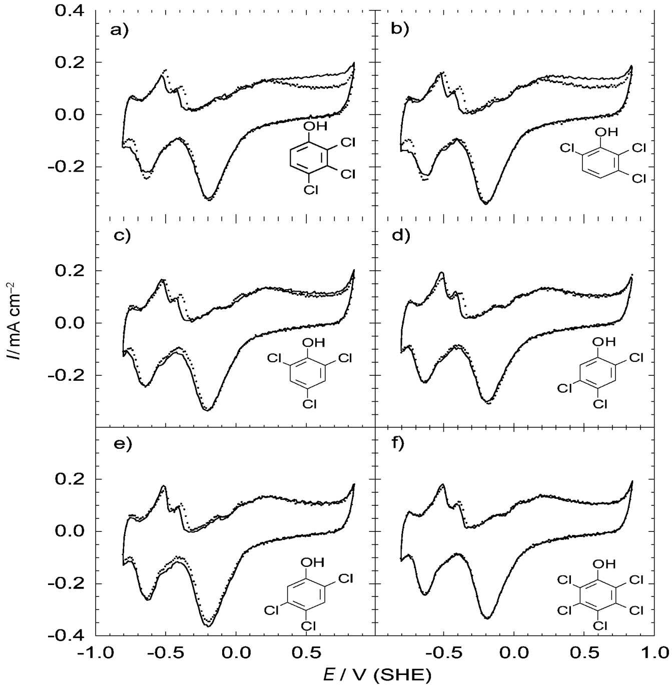

Fig. 3 The CV curves of Pt electrode in 1 M NaOH solution containing 1 mM of 2,3,4-dichlorophenol (a), 2,3,6-dichlorophenol (b), 2,4,6-dichlorophenol (c), 2,3,5-dichlorophenol (d), 2,4,5-dichlorophenol (e), pentachlorophenol (f), (solid lines) and in background 1 M NaOH solution (dotted lines). Potential sweep rate 200 mV/s, room temperature.

adsorption of phenol hinders adsorption of hydrogen atoms and hydroxyl ions; and (iii) oxidation of phenol proceeds at the potentials of PtO formation.

Phenol is a weak acid (pK_a = 9.99), and in 1 M NaOH solution it mainly exists in the form of phenoxide anion. Phenoxide anion can be adsorbed on Pt electrode either due to electrostatic interaction of the negatively charged oxygen and Pt atoms at more positive potentials, leading to a vertical (tilted) orientation of the molecule with respect to the electrode surface, or flat due to π-electron interaction between the benzene ring and the electrode, resulting in parallel orientation respect to the Pt surface. As a result of these two effects, phenoxide anions are oriented parallel or at a certain angle to the electrode surface [30]. The latter orientation reduces the interaction of the benzene ring with the electrode and hinders anodic oxidation of phenol, which can be oxidized to CO_2 (complete oxidation), ether and quinone-type structures (incomplete oxidation), or more saturated species (ring opening) [31].

A comparison of the CV curves of 2-chlorophenol (Fig. 1b), 3-chlorophenol (Fig. 1c), and 4-chlorophenol (Fig. 1d) shows that the electrochemical behavior of these isomers on Pt electrode markedly differs. The inhibiting effect of monochlorophenols on adsorption of hydrogen atoms in the potential region from –0.4 V to –0.7 V and adsorption of hydroxyl ions at the potential of –0.1 V (Figs. 1b–d) decreases in the row phenol ≥ 2-chlorophenol > 3-chlorophenol > 4-chlorophenol. This suggests that the adsorption interaction of corresponding molecules with the Pt electrode surface decreases. The oxidation rate of monochlorophenols decreases in the same row. The rate of anodic oxidation of phenol, 2- and 4-monochlorophenols (Figs. 1a,b,d) increases in the potential region more positive than 0.8 V when bulk oxygen evolution starts to a greater extent compared to 3-chlorophenol (Fig. 1c).

The difference in the electrochemical reactivity of monochlorophenols cannot be explained by a simple steric hindrance of the π-electron interaction of the benzene ring with the electrode due to the chlorine atoms. The steric hindrance can be expected to be approximately the same for all isomers of monochlorophenol. In contrast, 2-chlorophenol has a similar electrochemical activity as phenol despite the presence of chlorine atom in the ring. Moreover, the rate of anodic oxidation of monochlorophenols depends on the proximity of the Cl substituent to the hydroxyl group (Figs. 1b–d). Therefore, the difference in the electrochemical reactivity of monochlorophenols is determined, apparently, by the electronic effects: chlorine atoms are electron-withdrawing substituents and decrease the negative charge on the oxygen atom of phenol molecule [32]. This effect is more pronounced for chlorine atom neighboring to the OH group in 2-chlorophenol and becomes weaker in 3- and 4-chlorophenols, respectively. This is in accordance with corresponding increase in the pK_a values from 8.48 (2-chlorophenol), 9.1 (3-chlorophenol), to 9.38 (4-chlorophenol) [33,34]. Apparently, this causes a predominant flat orientation of 2-chlorophenol molecule on the electrode and therefore enables a similar rate of anodic oxidation to that found for non-substituted phenol. A gradual increase in the negative charge of phenoxide anion in 3-chlorophenol and 4-chlorophenol molecules, possibly, enables a vertical (tilted) orientation of the molecules, especially at more positive potentials, owings to electrostatic interaction between the anion and the electrode. The Cl substituents in 2- and 4- positions also increase the partial electron density in these positions, while in 3-chlorophenol, the partial electron density decreases in 2- and 4- positions and stabilizes intermediate phenoxy radicals [31]. This can be the reason of a lower oxidation rate of 3-chlorophenol at more positive potentials.

The presence of the second chlorine atom in the ring decreases the oxidation rate of dichlorophenols (Figs. 2a–f) compared to monochlorophenols (Figs. 1b–d). The rate of electrooxidation of dichlorophenols depends on the position of chlorine atoms in the ring and decreases in the row: 2,6-dichlorophenol > 2,3-dichlorophenol > 2,4-dichlorophenol > 3,4-dichlorophenol > 2,5-dichlorophenol > 3,5-dichlorophenol. This might be due to competitive electronic and steric effects. Withdrawal of the negative charge from the oxygen atom of phenoxide anion by two chlorine atoms makes chlorophenols stronger acids compared to monochlorophenols. The effect of the electron withdrawal is stronger for the dichlorophenol isomers with chlorine atoms neighboring (closer) to the OH group. This corresponds to the increase in the pK_a values [34] in the sequence 2,6-dichlorophenol (pK_a 6.8) > 2,5-dichlorophenol (pK_a 7.35) > 2,3-dichlorophenol (pK_a 7.45) > 2,4-dichlorophenol (pK_a 7.85) > 3,5-dichlorophenol (pK_a 8.13) > 3,4-dichlorophenol (pK_a 8.39). A stronger withdrawal of the negative charge at oxygen atom weakens electrostatic interaction between the phenoxide anion and the electrode and, therefore, maintains π-electron interaction and flat orientation of the molecule at the electrode. The latter, however, is hindered by the presence of chlorine atoms in the benzene ring depending on their position and leads to some deviations from the direct correlation of the electrochemical activity of dichlorophenols and their pK_a value. An electrostatic interaction between the phenoxide anion and the electrode causing a vertical (tilted) orientation of the molecule seems not to ensure oxidation (ring opening) of phenols in the potential region of PtO formation (compare, e.g., 2,6- and 3,5-dichlorophenol, Figs. 2a and 2f).

The electrochemical activity of phenols toward their oxidation on Pt electrode decreases with a further increase in the number of chlorine atoms in the benzene ring: the reactivity of trichlorophenols (Figs. 3a–e) is correspondingly lower than that of dichlorophenols (Figs. 2a–f). The rate of anodic oxidation of trichlorophenols on Pt electrode decreases in the row: 2,3,4-trichlorophenol (pK_a 7.6) > 2,3,6-trichlorophenol (pK_a 6.1) > 2,4,6-trichlorophenol (pK_a 7.7) > 2,3,5-trichlorophenol (pK_a 7.3) ≥ 2,4,5-trichlorophenol (pK_a 6.4). There is no direct correlation between the electrochemical reactivity of trichlorophenols and their pK_a values [34]. A steric hindrance of the π-electron interaction between the benzene ring and the electrode by chlorine substituents is more pronounced in the molecules with more symmetrically located chlorine atoms (2,4,5-, 2,3,5-, and 2,4,6-trichlorophenols). This leads to the decrease in the electrochemical activity of corresponding isomers. In contrast, four adjacent substituents along the edge of the aromatic ring in 2,3,4-trichlorophenol molecule force the adsorbed molecule into an edgewise orientation [35] and facilitate its oxidation.

The effect of the steric hindrance of π-electron interaction with Pt electrode, apparently, becomes critical with further increase in the number of chlorine atoms and, finally, this interaction is completely blocked in pentachlorophenol molecule (pK_a 5.26). In the case of 1 mM pentachlorophenol solution (Fig. 4f) the CV curve coincides with the CV of Pt electrode in 1 M NaOH solution (Fig. 2a).

The CV investigations of phenol and chlorinated phenols in alkaline medium (1 M NaOH) show that their oxidation rate on Pt electrode decreases in the row: phenol > monochlorophenols > dichlorophenols > trichlorophenols > pentachlorophenol. The main reasons for such a tendency, possibly, are:

i) A steric hindrance of π-electron interaction of the benzene ring with Pt atoms by the chlorine substituents in the ring. Molecules of monochlorophenols and dichlorophenol still have a possibility to adsorb on Pt through the edge of the benzene ring, which is not blocked by the chlorine atoms, and thus to enable at least partial interaction of π-electrons with Pt electrode. This interaction, however, is practically completely blocked by chlorine atoms of trichlorophenol and pentachlorophenol molecules.
ii) The rate of anodic oxidation can also be reduced due to weakening of the adsorption interaction of phenols with the electrode as a result of decrease in the electron density at the oxygen atom and π-electron system of the benzene ring (chlorine atoms are characteristic substituents for the negative induction effect in organic compounds—a withdrawal of π-electrons from the benzene ring by the chlorine atoms [32,36]).

Galvanostatic oxidation of phenol and chlorinated phenols on Pt electrode

The CV studies on Pt electrode in alkaline solution containing 1 mM of phenol or chlorinated phenols (previous paragraph) suggest that the electrochemical activity of phenols decreases with the degree of chlorination and depends on the isomerism of the molecules. Analogous CV experiments in alkaline solutions containing 0.1 M of corresponding phenol have shown [24] that the electrooxidation of these compounds at the potentials before oxygen evolution results in polymerization and subsequent passivation of the platinum electrode. A passivation ability for chlorophenols was found to be the highest for *p*-substituted isomers. In order to decrease retarding polymerization effects and to increase a mineralization rate, for the experiments described further comparatively small concentrations (1 mM) of phenols were used and oxidation experiments were performed under galvanostatic conditions at a current density 30 mA cm^{-2}.

A linear decrease in concentration of phenol and monochlorinated phenols during galvanostatic electrolysis in a semilogarithmic scale (Fig. 4) suggests a pseudo-first-order kinetics in agreement with [11]. The largest decrease in concentration of these phenols occurs within the first four hours of electrolysis and reaches the values 26 to 14 μM (Fig. 4). A rapid decrease in concentration of the phenols (by factor of 10) during the first hour of electrolysis suggests that their electrooxidation occurs: either complete oxidation to CO_2 or partial oxidation to intermediate compounds. Incomplete oxidation of phenols may result in formation of both soluble species and oligomeric and polymeric products, which are depositing on the electrode surface. A qualitative GC–MS analysis of the anolyte samples during and after electrolysis of phenol and monochlorophenols did not show any soluble products of incomplete oxidation of phenol and monochlorophenols (formation of the gaseous intermediates was not checked in the present study). Therefore, it could be concluded that the main oxidation products during electrolysis of phenol and monochlorophenols under these conditions are mainly insoluble polymeric/oligomeric compounds, formed on the electrode surface, and inorganic salts: carbonate, chloride, hypochlorite, chlorite, and chlorate, formed in alkaline solution as a result of electrolysis. Formation of insoluble polymeric species on Pt electrode during a constant potential electrolysis of phenol and monochlorophenols in alkaline solution was confirmed by *in situ* EQCM measurements [25]. An *ex situ* FTIR characterization of the electrodeposited polymeric films confirmed a presence of ether and quinone-

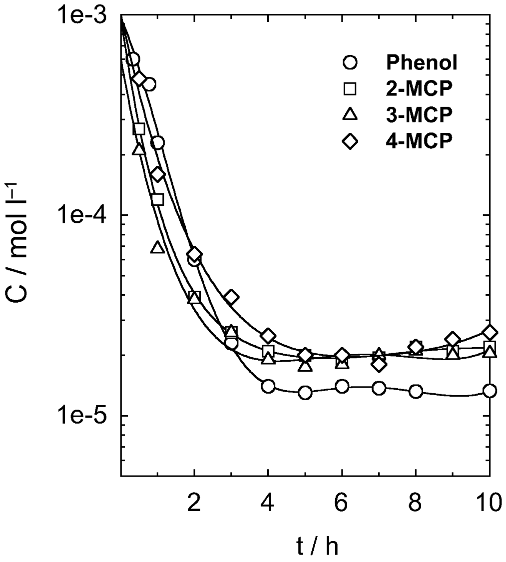

Fig. 4 Changes in concentration of phenol (circles), 2-monochlorophenol (squares), 3-monochlorophenol (triangles), and 4-monochlorophenol (diamonds) during galvanostatic oxidation on Pt electrode in 0.1 M NaOH solution containing 1 mM of corresponding phenol. Anodic current density 30 mA cm^{-2}, room temperature.

type species, as well as more saturated compounds formed due to the benzene ring opening at potentials of anodic oxygen evolution [26].

In the progress of the oxidation, a further decrease in concentration of phenol and monochlorophenols is negligible after 3–4 h of electrolysis (Fig. 4). This might be due to the electrode passivation as a result of polymeric tars formation on the electrode surface as confirmed by potentiostatic EQCM measurements [25]. It was shown by the FTIR analysis of the polymeric films that partially saturated compounds are formed on Pt electrode when the electrode potential reaches that of oxygen evolution [26]. The formation of the polymeric tars on the electrode after 3–4 h of electrolysis may result in diffusion limitations of phenoxide anions toward the electrode within the film. It is important to note that the CV studies on Pt electrode in 0.1 M solutions of monochlorophenols showed significant differences in the ability of the Pt electrode fouling within the potential region of PtO formation, with the increase in passivation rate in the row 2-chlorophenol < 3-chlorophenol < 4-chlorophenol [24]. In contrast, galvanostatic electrolysis experiments show no significant differences in the mineralization rate of monochlorophenols (Fig. 4). This might be rationalized in terms of a different permeability of the polymeric tars formed under mild anodic oxidation conditions (not reaching oxygen evolution) due to different structure of the films defined by the isomerism of the monomer molecules. Galvanostatic oxidation of phenols in the regime of anodic oxygen evolution apparently leads to the formation of heavily oxidized, disordered insoluble tars on the electrode surface with minor differences in the permeability of the film.

The other reason for low oxidation rates during a long-term electrolysis might be diffusion limitations due to a considerable decrease in concentration of phenolic compounds in the solution (by two orders of magnitude) after 3–4 h of electrolysis. It might be presumed that a secondary (chemical) oxidation of the phenols occurs near the electrode surface by hydroxyl radicals and atomic oxygen formed. The secondary oxidation of phenols by the molecular oxygen formed in the solution could be excluded, because in this case, the concentration of phenolic compounds should continuously decrease due to their oxidation in the anolyte volume up to non-detectable concentrations contrary to the obtained results.

In the case of galvanostatic oxidation of dichlorophenols, the concentration decrease is similar (Fig. 5) to that of monochlorophenols (Fig. 4). A rapid decrease in concentration occurs within the period of 4 h (Fig. 5). After 10 h of electrolysis, the most pronounced decrease in concentrations are for 2,3-dichlorophenol and 2,4-dichlorophenol, which reach 6 μM and 9 μM, respectively (Fig. 5). Negligible changes in concentrations of dichlorophenols in the course of the electrolysis after 4 h (Fig. 5) indicate that the electrode passivation occurs due to the polymers formed on the electrode surface, as in the case of phenol and monochlorophenols (Fig. 4). On the other hand, the most pronounced deactivation of the electrode is in the case of 3,4-dichlorophenol (Fig. 5). It was shown that in 1 M NaOH solution, containing 0.1 M of this isomer during oxidation under potentiodynamic conditions, a most rapid deactivation of Pt electrode occurs [24], as well as under potentiostatic oxidation conditions as monitored using the EQCM [25]. Nevertheless, these differences in the mineralization rate of dichlorophenols are negligible compared to a complete hindrance of anodic oxidation rate occurring during potentiodynamic and potentiostatic oxidation of *para*-substituted isomers of dichlorophenol [24,25]. Similarly to the discussion above, it is most likely due to a higher permeability of the films formed under galvanostatic oxidation conditions. As in the case of phenol and monochlorophenols, the extracts of the anolyte during and after galvanostatic oxidation of all dichlorophenols do not show any soluble intermediate compounds. Therefore, the main oxidation products formed during galvanostatic oxidation of dichlorophenols are most likely insoluble compounds formed on the Pt electrode surface and inorganic salts, namely carbonates and chlorine oxy-anions, in the solution bulk.

Similar features occur during galvanostatic oxidation of trichlorophenols and pentachlorophenol as shown in Fig. 6. Significant decrease in concentration of phenols proceeds in the course of first 4 hours of electrolysis (Fig. 6). After that the rates of oxidation decrease and the maximum decrease of concentration after 10 hours of electrolysis is reached for 2,3,6-trichlorophenol (Fig. 6) suggesting a

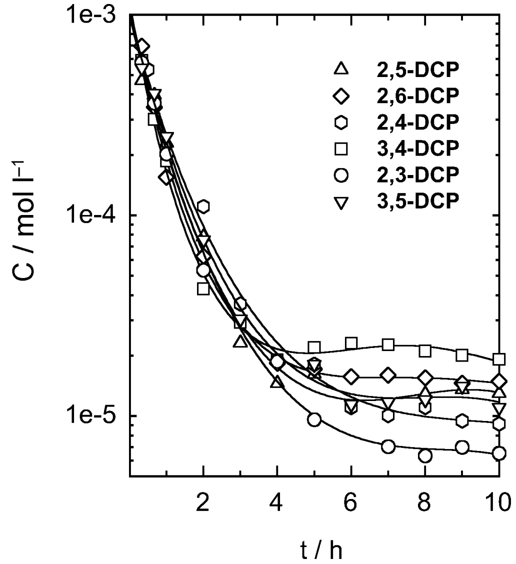

Fig. 5 Changes in concentration of 2,4-dichlorophenol (hexagons), 3,4-dichlorophenol (squares), 2,5-dichlorophenol (triangles up), 2,6-dichlorophenol (diamonds), 2,3-dichlorophenol (circles), and 3,5-dichlorophenol (triangles down), during galvanostatic oxidation on Pt electrode in 0.1 M NaOH solution containing 1 mM of corresponding phenol. Anodic current density 30 mA cm^{-2}, room temperature.

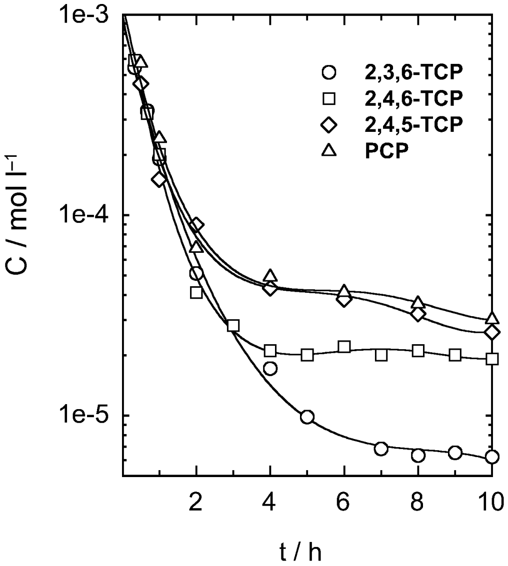

Fig. 6 Changes in concentration of 2,3,6-dichlorophenol (circles), 2,4,5-trichlorophenol (diamonds), 2,4,6-trichlorophenol (squares), and pentachlorophenol (triangles) during galvanostatic oxidation on Pt electrode in 0.1 M NaOH solution containing 1 mM of corresponding phenol. Anodic current density 30 mA cm^{-2}, room temperature.

weaker fouling. The same tendency was shown in CV [24] and EQCM [25] experiments for this isomer. However, trichlorophenol isomers and pentachlorophenol, being rather electrochemically inactive as follows from the CV studies (Fig. 3), can be mineralized during galvanostatic electrolysis by the electrochemically generated oxygen species to the same extent as other chlorophenols.

The EQCM data [25] show that the number of electrons during electropolymerization of chlorophenols on Pt electrode at 0.78 V SHE is close to 2 electrons per monomer in most cases, suggesting an ether-linked polymer formation as confirmed by the FTIR studies of electropolymerization products [26]. Higher values of the electron number per monomer electropolymerization can be due to (i) their deeper oxidation, especially, when reaching the potential of oxygen evolution (more positive 0.8 V) [26]; ii) anodic oxidation of chloride ions, eliminated from the active *ortho-* and *para-* positions due to electropolymerization, to oxy- anions, e.g., chlorate [25]. Assuming for simplicity, 2 electrons per monomer electropolymerization as the main oxidation route in alkaline solution, the charge, consumed for the decrease in concentration of chlorophenols from 10^{-3} M to ca. 10^{-4} M within the first 2 h of electrolysis, is about 170 C. From the ratio to the total charge passed during 2 h of galvanostatic electrolysis at 90 mA (650 C) the current efficiency ca. ~25% can be found. This suggests that during galvanostatic electrolysis of chlorophenols in alkaline solution, the electropolymerization occurs to a considerable extent. The latter results in immobilization of insoluble species on the electrode surface and corresponding decrease of phenolic species in the solution bulk. However, insoluble species formation leads to the electrode fouling and activity losses—an ineffective electrolysis of water occurs predominantly after ca. 4 h (Figs. 4–6). The effective electropolymerization during galvanostatic electrolysis on Pt electrode in alkaline solution even at low (1 mM) concentration might be rationalized as a preferred radical formation from phenoxide anions induced by electrochemically generated hydroxyl radicals in oxygen evolution reaction.

Apparently, the insoluble species formation is the main reason why no intermediate oxidation products are detected for the electrolysis in a strongly alkaline solution in contrast to a well-documented intermediate product formation during electrolysis of chlorophenols in the neutral [11,17] and acidic medium [22]. However, formation of some carboxylic acids e.g., formic, oxalic, maleic, fumaric, succinic, malonic, and some other chlorinated species [17], which are volatile or highly soluble in water, cannot be excluded due to the sample extraction procedure applied before the GC-MS analyses.

Therefore, despite a low current efficiency of galvanostatic electrolysis, the advantage of this approach is a low selectivity in oxidation rate of hazardous chlorinated phenolic species and a complete mineralization of organic molecules in the solution to inorganic anions and/or immobilization of insoluble organic species on the electrode surface.

CONCLUSIONS

CV investigations of phenol and chlorinated phenols in alkaline medium show that the oxidation rate of the phenolic compounds on Pt electrode decrease in the row: phenol > monochlorophenols > dichlorophenols > trichlorophenols > pentachlorophenol. The electrochemical stability of phenols in CV studies depends on the chlorination degree (number of chlorine atoms) and their isomerism (proximity of the Cl substituents to the OH group of phenol). The main reasons of different electrochemical activity of chlorophenols toward their electrooxidation most probably are a steric hindrance of π-electron interaction of the benzene ring with Pt atoms by chlorine substituents, and a decrease in the electron density on the oxygen atom and benzene ring due to withdrawal of electrons by the chlorine atoms.

The electrolysis in the galvanostatic mode at an anodic current density of 30 mA cm^2 for 10 h showed that the concentration of phenols is reduced about two orders of magnitude within the first 3–4 h of electrolysis weakly depending on their chlorination degree and the isomerism. This suggests that oxidation of phenols occurs by electrochemically generated oxidants at the electrode (hydoxyl radicals, atomic and molecular oxygen). The GC–MS analysis of the anolytes showed that no soluble intermediates are formed during electrooxidation while insoluble oxidation products are accumulated on the electrode surface after a long-term electrolysis. The deposits formed inhibit the electrode surface and prevent further effective oxidation of phenols.

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