Effect of Chlorine Substitute on Phenols Electrooxidation Studied by Cyclic Voltammetry

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The electro-oxidation of chlorophenols (CPs) with one to three chlorine atoms on platinum, gold and glassy carbon electrodes was studied by cyclic voltammetry. The results obtained indicate that the electro-oxidation of CPs on all electrodes depends on the pH, number of chlorine atoms in the aromatic ring and position of the Cl atoms with respect to the phenolic OH group. From a comparative study of the electro-oxidation of several CPs in aqueous solution at different pH, it is concluded that for the same number of chlorine atoms the ortho isomer is oxidized at a more negative potential than the para isomer. The anodic potential of the electro-oxidation of the chlorophenols (CPs) increases with increasing pKa

Keywords: chlorophenols, electro-oxidation, gold electrode, platinum electrode, cyclic voltammetry

The removal of chlorophenols (CPs) from wastewater is of environmental interest because the CPs has a negative effect on a number of aquatic life forms.

In general, the resistance of CPs to microbiological degradation, their environmental persistence and toxicity increase with increasing Cl^- substitution [1]. It has also been reported that the position of the Cl atom in the aromatic ring determines the rate of microbial degradation. The CPs with two chlorine atoms in equivalent position in the aromatic ring present a lower degradation rate than those with a Cl atom in each of the ortho-, meta-, and para-positions. Therefore, the degradation and analytical detection of CPs is of great interest in the environmental protection field as well as in industrial process control [2].

Chlorophenols are slightly soluble in water, showing their acidity in aqueous solutions:

$$PhOH + H_2O \leftrightarrow PhO^- + H_3O^+ \qquad (1)$$

Their pKa extends from 5.5 to 9.4 and decreases with the increase in the number of chlorine atoms in the molecule.

Gattrell and Kirk [3] reported that phenol electro-oxidation produces electrode fouling and the tars formed on the electrode by polymerization show a low rate of oxidation, low permeability and strong adhesion to the electrode. 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 electro-oxidation of phenols and chlorophenols [4].

In the present paper we have focused on a comparative study of electrochemical oxidation of phenol and chlorophenols in acid and alkaline media on gold, platinum and glassy carbon electrodes in order to investigate the degree of the electrode fouling during electro-oxidation processes taking in account their chlorination degree and the isomerism. Similarly, the cyclic voltammetry measurements provide important information on the electrochemical stability of the species under study and are suitable for screening the processes occurring in a wide potential range.

Experimental part

All electrochemical measurements were performed in a typical three-electrode glass cell. The stationary and rotating disk electrodes of glassy carbon, platinum, and gold were used as working electrodes. A platinum foil served as a counter electrode. All potentials were measured versus satured calomel reference electrode. All solutions were deaerated with nitrogen for 10 min before each experiment.

Cyclic voltammetry measurements were performed in unstirred solution using a GAMRY PC3 potentiostat and the PHE200 standard techniques. The investigation has been done in anodic direction from -0.2 to 1.2 V. The scan rate was 100mV/sec. The PHE200's standard techniques use the analytical convention for current, thus for all recorded voltammograms the negative currents are anodic.

Before each scan the disk electrode that had become fouled during oxidation process of CPs was prepared to ensure a reproducible surface by polishing with 1 μm, 0.05 mm aluminum powder and rinsing with high purity water.

The studied phenols were phenol (Ph), 2 chlorophenol (2CP), 3 chlorophenol (3CP), 4 chlorophenol (4CP), as Aldrich p.a. reagents, which were used as received. As background electrolyte a 0.5M Na_2SO_4 solution was used. For adjusting the *p*H of solution, the concentrated NaOH and H_2SO_4 solutions were added. All the solutions were freshly prepared with distillate water. The experiments were carried out at room temperature.

Results and discussions

The experiments were performed using solutions of Ph, 2-CP, 3-CP, 4-CP at the same *p*H.

The influence of the position of the chlorine atom in the aromatic ring on the reactivity of the CPs, was studied by cyclic voltammetry of chlorophenols (2CP, 3CP and 4CP).

The anodic oxidation of phenol and chlorophenols occurs during a positive-going scan in the potential range 0.0 to 1.0V (fig. 1). The decrease of anodic current occurs after the first cycle, whereas the oxidation peak potential

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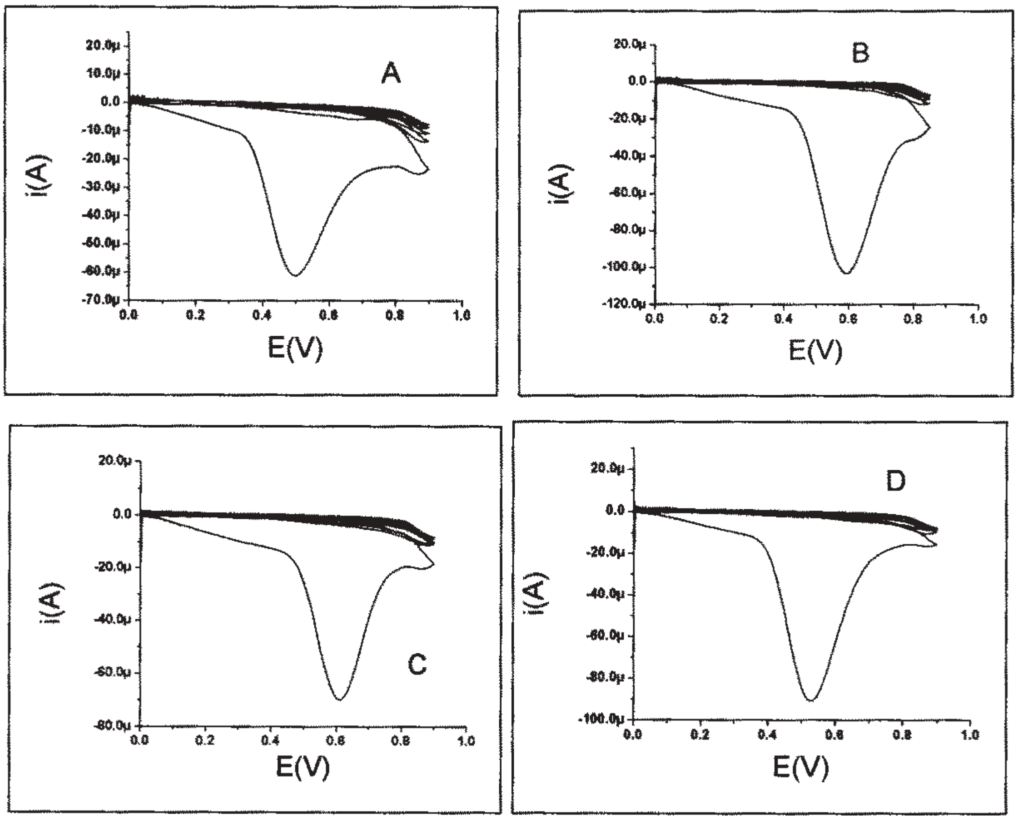


Fig. 1. Cyclic voltammograms at the platinum electrode, A=0.6 cm^2 , for (A), phenol, (B), 2CP, (C), 3CP, (D), 4CP; all concentrations were10mM, in 0.1M Na_2SO_4; *p*H=12, scan rate 100mV/s

shifts slightly to more negative potentials after each cycle. The decrease of the oxidation current peak is due to diminishing of the electrode surface area (blocked by the polymer film) and the hindrance of phenoxide ion diffusion [5].

A higher oxidation current for 2CP species in the first cycle might be due to a stronger 2-chlorophenoxide-ion interaction with the platinum electrode in comparation with that of phenoxide ion. The structural features of the polymer might explain the different electrode-fouling rate for phenol and 2CP, because the 2CP has either one ortho and one para Cl-unsubstituted positions. Thus, due to the blocking effect of one ortho position by a Cl-substitutuent, the polymer structure is more asymmetric and more permeable comparative with of phenol.

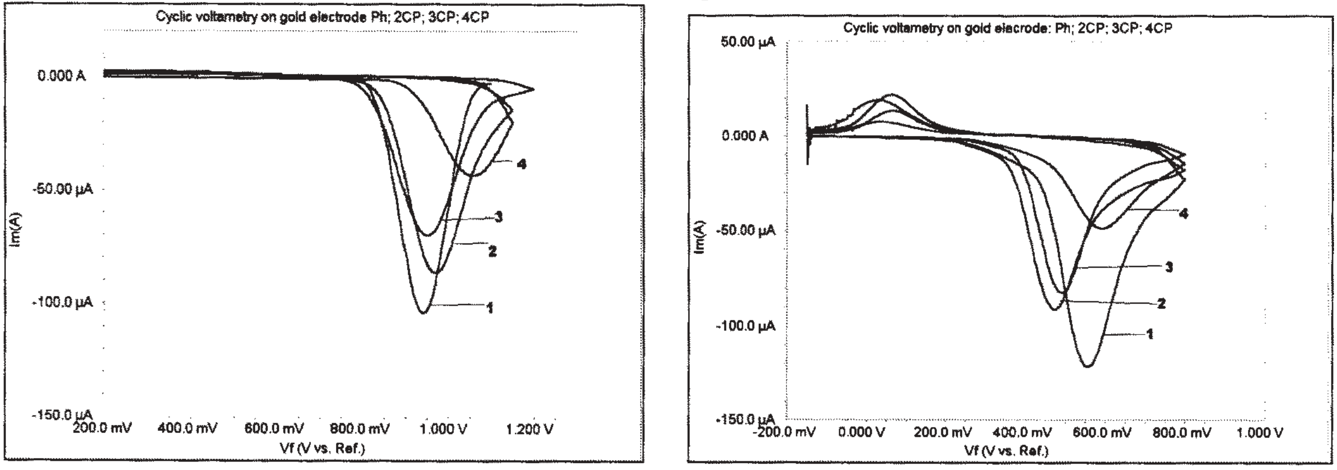
Deactivation of the electrode that occurs during 3CP oxidation is similar with that of phenol.

The molecule of 3CP has two ortho and one para Cl-unsubstituted positions via which the formed radical can be stabilized.

The CV plots for 4CP are similar with 2CP plots. In the 4CP molecule there are two ortho Cl-unsubstituted positions through which 4-chlorophenoxy radical could be stabilized. The elimination of chloride from the para position of 4CP is possible, in a greater extent compared with 2CP. 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 [6].

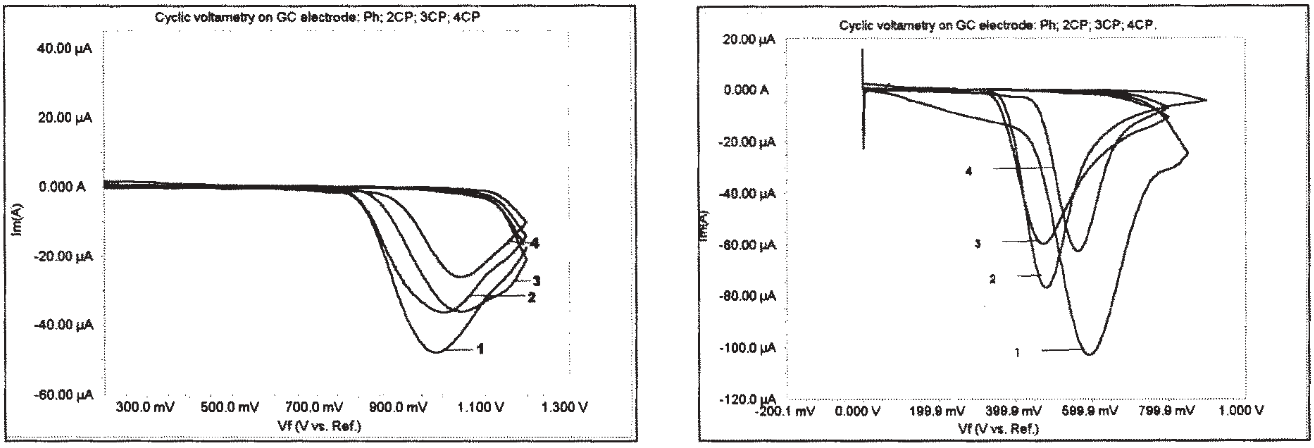
The effect on the CVs of the Cl atom position in the benzene ring was studied using a series of solutions of phenol, 2CP, 3CP and 4CP at the same pH (pH 1 and 12) at platinum, gold and glassy carbon electrodes.

Figure 2 shows the first cycle for all chlorophenols studied on gold electrode in acid (pH=1) and alkaline (pH=12) media.



A B

Fig.2. Cyclic voltammograms at the gold electrode, A=0.6 cm^2 , for: (1), 4CP; (2), Ph; (3), 2CP; (4), 3CP, in acid (A) and alkaline medium (B)., all concentrations were 10mM, in 0.1M Na_2SO_4; scan rate 100mV/s



A

B

Fig.3. Cyclic voltammograms on glassy carbon electrode, A=0.6 cm^2, for: (1), 4CP; (2), 2CP; (3), Ph; (4), 3CP, in acid (A) and alkaline medium (B). all concentrations were 10mM, in 0.1M Na$_2$SO$_4$; scan rate 100mV/s

It is known that the electrooxidation of CPs starts with the formation of phenoxi radical, which for gold electrode occurs at the same potential, irrespective of the nature of CP species. Probably the oxidation of CP at gold begins with the interaction of the phenol molecule (at acidic *p*H) with an adsorbed OH group formed by electrooxidation of an Au-H$_2$O site, the process proceeding after the subsequent cleaning of a surface site [7]. The polymerization rate depends on CP structure, increasing in the order: 4CP<3CP<2CP, an order which reflects the general trends observed in additions of phenyl radicals to substituted benzenes [8]. Such additions take place mainly at the *ortho* and *para* position, irrespective of the nature of substituent. In the case of CPs, steric hindrance by the phenolic OH grup directs the radical attack towards the *para* position. The electronic delocalization in the phenoxy radical leads to bond formation in the polymers through the *ortho* and mainly *para* carbon atoms. These effects explain the poor reactivity of all CPs that have the *para* position blocked by a Cl atom; the reactivity of PCP is lower than of 2.4 CP or 4CP.

Figure 3 shows progressive CV curves of CPs studied at glassy carbon electrode.

The values of anodic currents are smaller than the anodic currents recorded at platinum and gold electrodes.

An estimation of the reactivity of the different CPs can be obtained by comparing values of peak potential (table1). From these data it is observed that with increasing number of Cl atoms the peak potential decreases, and for the same number of Cl atoms the *ortho* isomer has a peak at less positive potential than of the *para* isomer, indicating that the latter is more stable (less reactive).

Table 1

VALUES OF ANODIC PEAK POTENTIAL AND ACIDITY CONSTANT FOR DIFFERENT CPS ON GLASSY CARBON ELECTRODE

Compound	Ep (V) vs. SCE		pKa
	pH=1	pH=12	
Phenol	1.05	0.46	10
2CP	1.00	0.56	8.4
3CP	1.03	0.53	9.1
4CP	1.04	0.49	9.4
2,4 DCP	0.91	0.57	7.9

At higher pH, for pH>pKa only, the ionized CP is involved in the oxidation process and, consequently, no protons participate in the reaction.

A plot of anodic peak potential versus pKa obtained for five CPs is presented in figure 4.

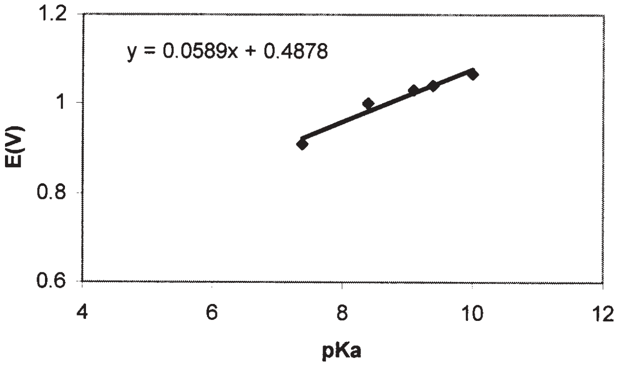


Fig. 4. Plot of anodic peak potentials for different CPs versus their pKa

A straight line with a slope of 0.058 V (pKa unit)$^{-1}$ was obtained which shows an increasing difficulty for electrooxidation with the increase of acidity constant [9]. Although the linear correlation coefficient is not too high (r=0.95) the tendency is important, because it is shown that the effect of substituents on the acidity can be evaluated using Hammett‘s equation, in which nucleophilic σ^- constant are correlated with the pKa [10].

The reactivity of the CPs towards their electro-oxidation on glassy carbon electrode decreased with increasing the acidity constant. In this case, it is possible to correlate one chemical parameter of the CPs, i.e. their acidity constant, with their electrochemical reactivity.

Conclusions

The results obtained in this work indicate that the electro-oxidation of CPs at platinum, gold and glassy carbon electrodes depends on the *p*H and position of the chlorine atoms as substitutes in the aromatic ring.

The electrode fouling is a result of surface blocking by the high molecular weight species produced during anodic oxidation of CPs. Both the polymerization degree and the electrode deactivation ability depend on the structure and the permeability of the polymer formed, determined by the degree of chlorination and the isomerism of the monomers.

The reactivity of the CPs depends on the number of chlorine atoms, but also on their position in the aromatic ring, *para* substitution yielding less reactive isomers than *ortho* substitution.

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