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Anodic oxidation of chlorophenols in micelles and microemulsions on glassy carbon electrode: the medium effect on electroanalysis and electrochemical detoxification

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Abstract The voltammetric behavior of 2, 4-dichlorophenol (DCP), 2, 4, 6-trichlorophenol (TCP) and pentachlorophenol (PCP) in aqueous sodium hydroxide (NaOH), aqueous NaOH–sodium dodecylsulphate (SDS) micellar solution and SDS/n-hexane/n-butanol/water microemulsion on glassy carbon electrode (GC) is reported. In aqueous alkaline medium, the electrode fouling is significant. Among the three media, the electrode fouling is the minimum in aqueous microemulsion. The fouling effect also depends on the nature of the phenolic compound. DCP exhibits the maximum fouling effect, and PCP exhibits the minimum fouling effect. During oxidation of the TCP in the microemulsion, quinone–hydroquinone-like redox couples were formed on the electrode surface. Reproducible voltammetric responses without electrode fouling could be obtained for all the three phenolic compounds up to 20 mM concentrations in microemulsion. In the galvanostatic oxidation in NaOH media, DCP and TCP led to formation of polymeric films on the glassy carbon surface. The Average molecular weight of the polymer obtained is in the range of 7,500–9,500. Even 2.5% by weight of chlorophenols could be oxidized under galvanostatic conditions in microemulsions without significant fouling.

Keywords Chlorophenols · Electroanalysis · Electrochemical detoxification · Glassy carbon electrode · Micelles · Microemulsion

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1 Introduction

Detection and destruction of chlorophenols, which are common effluents in agrochemical, pulp and paper, pharmaceutical, and dyestuff industries, is an important environmental issue. In addition to biodegradation [1] and photo degradation methods [2], many electrochemical studies have also been reported in the past decade. Ezerkis and co-workers have studied the electro-polymerization behavior of chlorophenols using voltammetry [3], galvanostatic oxidation [4], GC–MS [5], and other spectroscopic techniques [6] using platinum anode. Glassy carbon electrode (GC) [7], iron oxide [8], and nickel phthalocyanine modified electrodes [9] have also been employed for a more detailed surface analysis using cyclic voltammetry, XPS, AFM, and impedance techniques [10]. In recent times, boron-doped diamond electrode has also been successfully employed for the removal of p-chlorophenol [11], dichlorophenol [12], and several other chlorophenols [13]. The determination and detoxification of pentachlorophenol was also achieved using square wave voltammetry and constant potential electrolysis on GCs [14].

A wide variety of electrodes such as platinum [15, 16] modified platinum [17], gold [18], modified GC [19], tin-dioxide-coated titanium electrode [20], and modified aerosol carbon electrode [21] have been used for oxidative removal of chlorophenols. Chlorophenols usually undergo oxidative polymerization on many electrodes even at low concentrations. Simultaneous dechlorination at the cathode and the oxidative polymerization at the anode in alkaline solution have also been reported recently [22, 23].

Many new modified electrode materials have been developed for the estimation of chlorophenols in alkaline solutions. These include modified gold [24], modified GC [25], and modified carbon paste electrodes [26]. Carbon

nanotubes coated on GCs have also been studied for the analysis of chlorophenols [27, 28]. Electroanalysis under hydrodynamic flow conditions have been reported recently [29]. Despite such attempts, chlorophenolic solutions containing more than 1–2 mM concentrations normally leads to irreproducible results in electroanalysis.

Micelles and microemulsion media containing surfactants can solubilize the phenolic compounds and their intermediates. The surfactant can also form adsorbed layers on the electrode surface and hence, prevent reactant adsorption and electrode fouling. Hence, voltammetric analysis and electrochemical detoxification of phenols in micelles and microemulsions offer considerable scope. In a recent study from this laboratory, micellar solution containing cationic surfactant cetyl trimethylammonium bromide (CTAB) was found to be effective for the electrochemical detoxification of *p*-chlorophenol and *p*-nitro phenol [30].

In this study, electrochemical oxidation of three chlorophenols namely 2, 4-dichlorophenol (DCP), 2, 4, 6-trichlorophenol (TCP), and pentachlorophenol (PCP) are reported. Three-electrolyte media, namely, alkaline solution, micellar solution containing 1% SDS, and microemulsion containing SDS, hexane, and butanol were chosen for this study. In addition to voltammetry on GC electrode, a few galvanostatic experiments were also carried out to study the influence of microemulsion medium on electrode passivation.

2 Experimental

2.1 Reagents

DCP, TCP, and PCP were obtained from Acros Organics. Anionic surfactant sodium dodecyl sulphate (SDS) was purchased from Merck. The medium chain alcohol *n*-butanol (Merck) was used as co-surfactant, and the aliphatic oil phase *n*-hexane (Merck) was employed. All the chemicals were of reagent grade. Double distilled water was used for the preparation of solutions.

2.2 Cyclic voltammetry measurements

Cyclic voltammetry measurements were carried out in a Wenking LB 75L Potentiostat coupled with a Wenking VSG 72 Voltage Scan Generator. A Rikadenki 101T XY/T recorder was used to record the voltammograms. An undivided cell with stationary GC (Tokai GC-A 5-mm diameter) as working electrode and platinum foil as counter electrode were used. Saturated calomel electrode (SCE) served as the reference electrode. The GC was polished with sufficiently fine emery sheet, 1/0, 2/0, 3/0, and 4/0

(John oakey, England) washed with water and trichloroethylene prior to every experiment to get reproducible voltammograms.
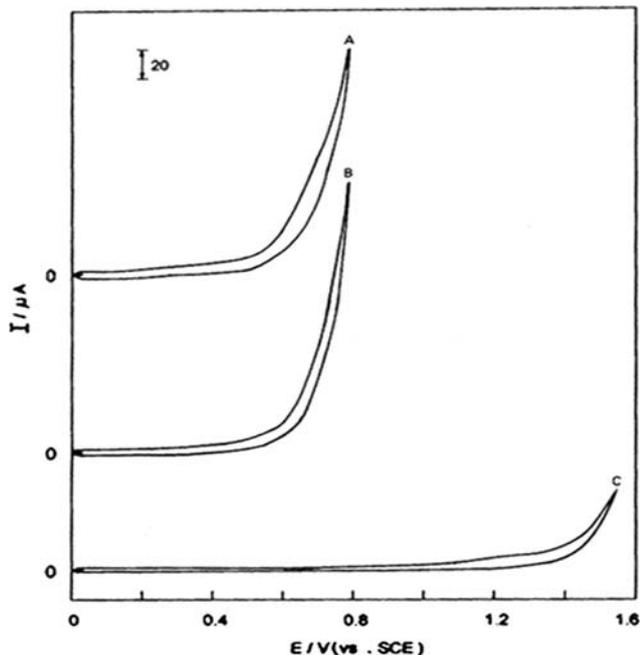
2.3 Constant current electrolysis

Galvanostatic experiments were carried out in an undivided glass cell of 50-mL capacity. A GC electrode (area 4.8 cm^2) was employed as the anode and the platinum foil served as the cathode. Electrolysis was carried out in SDS microemulsion solution. (SDS 8 wt%, *n*-hexane 13.3 wt%, *n*-butanol 26.7 wt%, and water 52 wt%.) The microemulsion was prepared by mixing the constituents and stirred vigorously until the clear solution is obtained. Experiments were conducted at 25 ± 1 °C. Throughout the electrolysis, the electrolyte was constantly stirred using a mechanical stirrer. A constant charge equivalent to 2.5 F per mole of phenolic compound at the rate of 0.2 A dm^{-2} was passed using a homemade galvanostat. The solution after electrolysis was analyzed to monitor residual concentration of chlorophenols using high performance liquid chromatography (HPLC). An LC-10 AT pump and an SPD-10A UV detector (Shimadzu, Japan) at 254 nm with a Shim pack CLC ODS-18 column were used. Methanol with a flow rate of 1.0 mL min^{-1} was used as eluent. In HPLC analysis, retention time and area of the chromatogram, which is a measure of concentration, were recorded. The solid or resinous mass formed during electrolysis was analyzed by gel permeation chromatography (GPC). An LC 6A pump and an RID 6A detector (Shimadzu, Japan) were used. Tetrahydrofuran was used as an eluent in GPC analysis. The retention time obtained was compared with the standard chromatogram to obtain the molecular weight range.

3 Results and discussion

3.1 Voltammetric studies

The background current obtained on GCE in 1.0 M NaOH solution (Fig. 1a) and that in the same solution containing 1% SDS (Fig. 1b) are quiet similar. The anodic background limit was found to be around 0.8 V versus SCE. A much wider potential window with the anodic limit beyond 1.5 V was obtained for microemulsion medium (Fig. 1c) employed in this study.

Typical cyclic voltammograms of 2–20 mM DCP, TCP, and PCP at a sweep rate of 20 mV s^{-1} are presented in Fig. 2a, b, and c, respectively. In NaOH medium, the anodic peak current for DCP decreases significantly when the concentration is increased from 2 to 10 mM (see Fig. 2a curves a–c). Beyond 10 mM, the anodic peak current becomes independent of concentration (Fig. 2a

Fig. 1 Cyclic voltammogram of background electrolyte: *a* NaOH, *b* NaOH + 1% SDS (micelle), and *c* SDS microemulsion on GCE at a sweep rate of 20 mV s^{-1}

increase in the anodic peak current is noticed even up to 20-mM concentrations for this compound (Fig. 2c curves a–e). At higher concentrations, all the three compounds exhibit passivation effect in NaOH medium. In order to overcome this problem, earlier researchers have evaluated the influence of different electrode materials [6, 7] and modified electrodes [17–21] without changing the electrolyte medium. In this study, the electrochemical behavior of these compounds was further investigated in micellar and microemulsion medium on the same GC electrode.
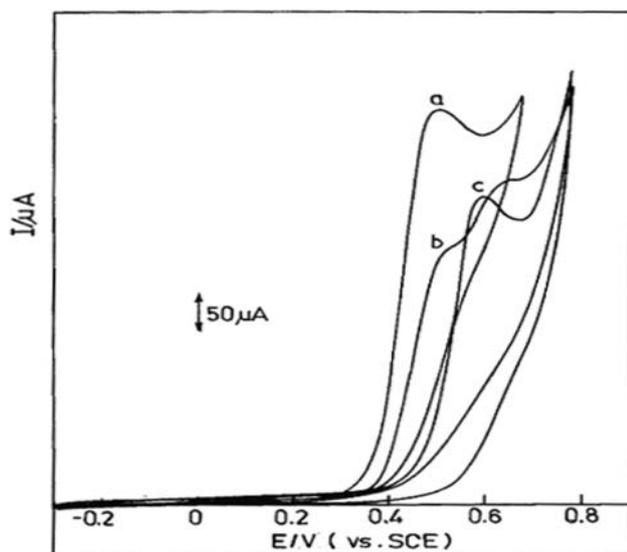
Typical cyclic voltammograms in 1 M NaOH containing 1% SDS for 10 mM DCP, TCP, and PCP at a constant sweep rate of 20 mV s^{-1} are presented in Fig. 3. Up to this concentration, no significant passivation effect was noticed in this SDS micellar system. The higher peak current at low peak potential was noticed for DCP (Fig. 3 curve a). Two closely spaced oxidation peaks were observed for TCP (Fig. 3 curve b). The anodic peak current was slightly lower for PCP (Fig. 3 curve c). Beyond 10 mM concentration, however, oxidative polymerization of phenols slowly sets in. Significant decrease in peak current with increasing concentration is noticed in this medium as well. This passivation effect is once again higher for DCP when compared to TCP and PCP.

Typical multi-sweep cyclic voltammograms for 10 mM DCP in 1 M NaOH containing 1% SDS are shown in Fig. 4a. The anodic peak current decreased gradually with increasing sweep number. In the tenth cycle, the anodic peak current decreased to 25% of the peak current value obtained in the first sweep, indicating gradual polymer film build-up on the electrode surface in the micellar medium.

The multi-sweep cyclic voltammograms obtained for 10 mM DCP in SDS microemulsion at the same sweep rate

curves d, e). The decrease in peak current with increasing DCP concentration is probably due to the formation of polymeric film on the electrode surface. Similar electrode passivation during the electro-oxidation of many chlorophenols has been reported by earlier researchers [5, 15]. The anodic peak current decreases slightly with increasing concentration in the case of TCP between 10 and 20 mM (Fig. 2b curves a–e). PCP exhibits significantly lower passivation effect in NaOH medium (Fig. 2c). Significant

Fig. 2 Cyclic voltammograms of **a** DCP (*a–e*, 2, 4, 6, 8, 10 mM), **b** TCP (10, 12, 14, 16, 18, 20 mM) and **c** PCP (*a–f*, 10, 12, 14, 16, 18, 20 mM) on GCE in NaOH medium at a sweep rate of 20 mV s^{-1}
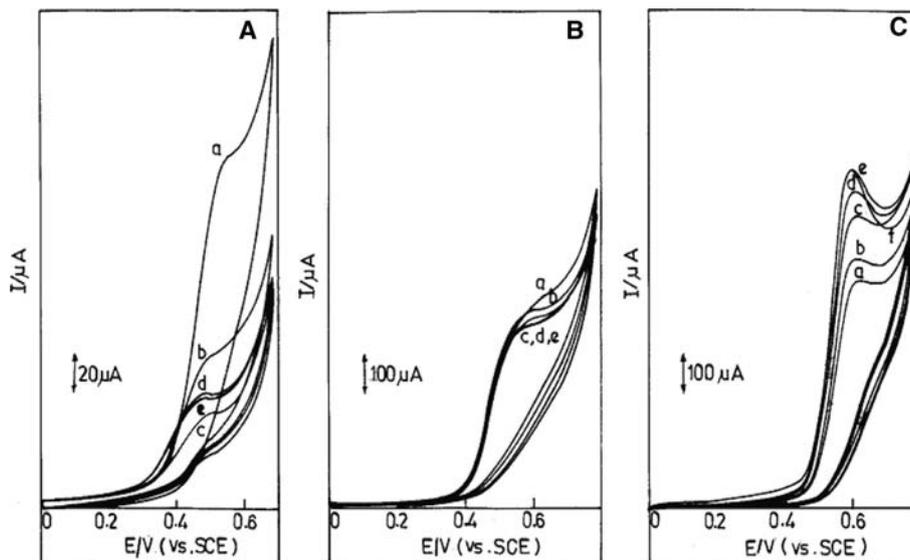
Fig. 3 Cyclic voltammograms of 10 mM *a* DCP, *b* TCP, and *c* PCP on GCE in 1 M NaOH containing 1% SDS at a sweep rate of 20 mV s^{-1}

are presented in Fig. 4b. The anodic oxidation peak occurs at a much higher potential of +0.9 V (Fig. 4b) when compared to around 0.5 V in micellar medium (Fig. 4a). The anodic peak potential also moves to more negative region with increasing sweep number. However, the anodic peak current reaches a steady value in multi-sweep experiments suggesting that the passivation effect is significantly lower even for DCP in SDS microemulsion. In microemulsion, two cathodic peaks are observed for DCP in the reverse sweeps. The first cathodic peak around

0.05 V increases with sweep number, and the second cathodic peak around 0.2 V decreases slightly with sweep number. No such cathodic peaks were observed in SDS micelles.

The anodic peak currents also increase systematically with increasing concentration of DCP, TCP, and PCP in microemulsion medium. A small prepeak is also noticed before the main anodic oxidation peak for all the three compounds. Typical cyclic voltammograms for 2–10 mM DCP in microemulsion medium are shown in Fig. 5a. The first anodic prepeak around 0.5 V does not increase significantly with reactant concentration. The second main anodic peak increases linearly with reactant concentration. The peak current of both the cathodic peaks in the reverse sweep also increases slightly with the concentration of DCP (Fig. 5a). Well-defined cyclic voltammograms were also obtained for 10–20 mM TCP at constant sweep rate (Fig. 5b). The anodic and cathodic peaks are well defined and sharp for this compound. The anodic prepeak is independent of reactant concentration. All other peak currents increase linearly with increasing concentrations.

Typical multi-sweep cyclic voltammograms in microemulsion medium for 20 mM TCP and 10 mM PCP are presented in Fig. 6a and b, respectively. In the case of PCP, only one broad cathodic peak is observed (Fig. 6b). The multi-sweep cyclic voltammograms for TCP exhibit some interesting voltammetric features in the second and subsequent sweeps. Two distinct new anodic peaks A3 and A4 corresponding to the cathodic peaks C3 and C4 are observed. The first anodic peak (A1) practically disappears in the second, and subsequent sweeps C3/A3 and C4/A4 indeed appear to the two well-defined redox couples.

Fig. 4 Multi-sweep cyclic voltammograms recorded on GCE in 10 mM DCP in **a** 1 M NaOH containing 1% SDS and **b** SDS microemulsion at a sweep rate of 20 mV s^{-1}
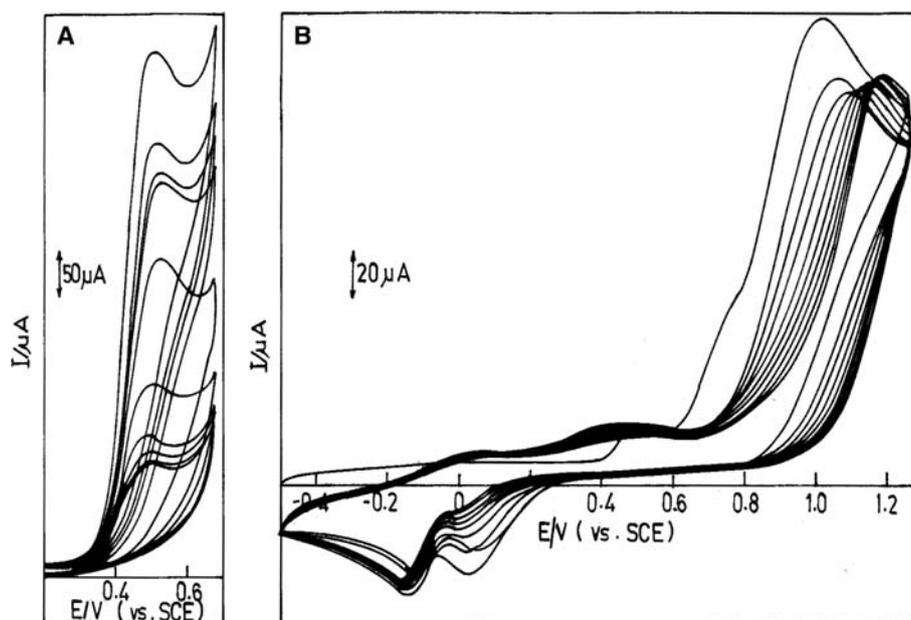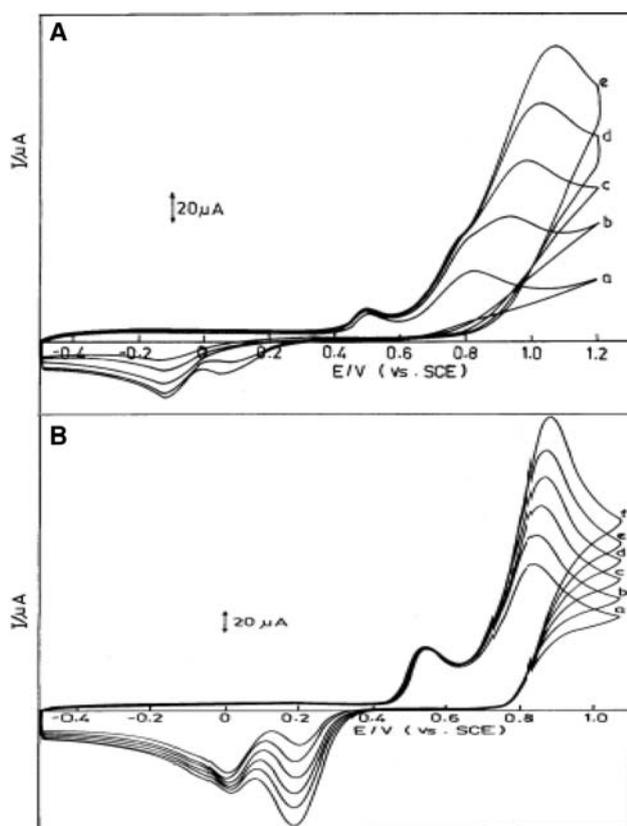
Fig. 5 Cyclic voltammograms of **a** DCP (*a–e*, 12, 14, 16, 18, 20 mM) and **b** TCP (*a–f*, 10, 12, 14, 16, 18, 20 mM) on GCE in SDS microemulsion at a sweep rate of 20 mV s^{-1}

The 2, 4, 6-TCPs possess C–Cl bonds in ortho- and the para-positions of the phenolic group. However, even in such cases, the phenolic radical can undergo further oxidation with chlorine removal through subsequent chemical

and electrochemical transformations to give different quinone–hydroquinone redox couples (Scheme 1). Such mechanistic schemes have been previously proposed for the oxidation of chlorophenols such as *p*-chlorophenol and pentachlorophenol [11, 12, 16] in alkaline medium.

Potential redox couples and oligomeric intermediates that can be generated during the electrochemical oxidation of phenolic compounds have been well documented in the literature [10, 18]. Many anodic and cathodic peaks observed in this study may indeed be due to such redox processes.

From the electro-analytical angle, the sensitivity of the anodic peak currents in different electrolyte media was investigated in greater detail (Fig. 7). DCP gives a single anodic peak in NaOH (Fig. 2a) and micellar media (Fig. 3 curve a). The anodic peak current decreases with increasing concentration in NaOH medium (Fig. 7a line a), and hence, this medium cannot be employed for analytical purposes. The anodic current in SDS micelle, however, increases linearly with increasing reactant concentration (Fig. 7a line b). The pre-peak observed in microemulsion (Fig. 5a) is almost independent of reactant concentration (Fig. 7a line c). The anodic peak current for the main anodic peak increases linearly with concentration (Fig. 7a line d). The peak current value in microemulsion, however, is lower than the micellar medium.

In NaOH medium, the anodic peak current for TCP becomes almost independent of reactant concentration at higher reactant concentration (Fig. 7b curve a). Both the first and second anodic peak currents observed in micellar medium (Fig. 3 curve b) increase linearly with increasing reactant concentration (Fig. 7b line b and c). The first anodic peak current, however, is more sensitive. In

Fig. 6 Multi-sweep cyclic voltammograms recorded on GCE **a** 20 mM TCP and **b** 10 mM PCP in SDS microemulsion at a sweep rate of 20 mV s^{-1}
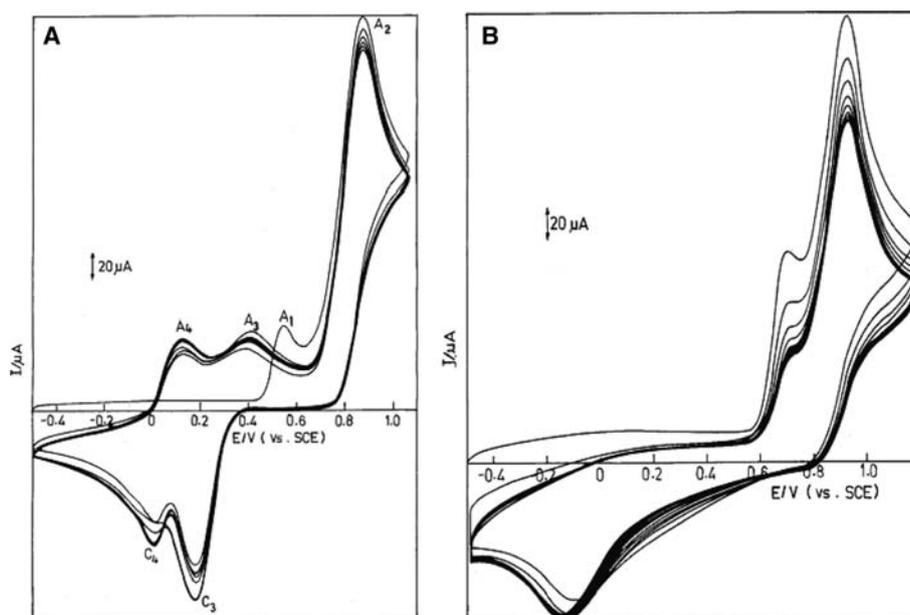
Scheme 1 Oxidation of chlorophenols leading to hydroquinones
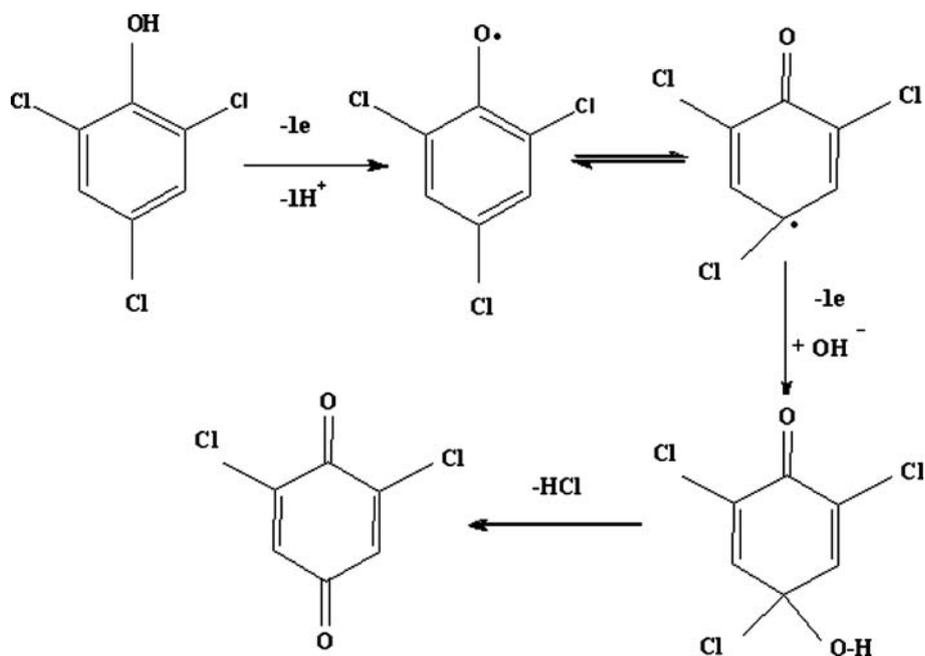
microemulsion, once again, only the second anodic peak is sensitive to reactant concentration (Fig. 7b line d and e).

As discussed above, PCP does not show fouling effect on electrode surface even in NaOH medium. The anodic peak currents decreases in the order: $i_{p\ NaOH} > i_{p\ micelle} > i_{p2\ \mu E}$ (Fig. 7c line a, b, and d). The first anodic peak in microemulsion is once again insensitive to reactant concentration (Fig. 7c line c).

From an analytical point of view, it appears that micellar medium does not foul or passivate the electrode as NaOH medium. The micellar medium also shows greater sensitivity to reactant concentration when compared with the microemulsion medium. At higher phenolic concentration (15 mM), the main anodic peak in the microemulsion medium may be employed for analytical purposes.

3.2 Galvanostatic electrolysis

Galvanostatic electrolysis experiments for all the three compounds were carried out in NaOH and microemulsion. A total current of 2.5 F per mole of phenolic compound was passed; 1 g of chlorophenol dissolved in 40 mL of electrolyte was employed for each experiment. The cell voltage for all the three compounds during electrolysis in NaOH solution was found to increase from 3.3 to 3.8 V, suggesting an increase in the overall resistance during electrolysis probably due the polymer film formed on the anodic surface. On the other hand, the total cell voltage decreased from 10.4 to 6.8 V in microemulsion for these compounds. After electrolysis, the anode was found to be covered with a thick polymeric layer only in the case of DCP and TCP in NaOH solution. The polymeric layer was

dissolved in THF and subjected to GPC analysis. The approximate molecular weight for the polymer during DCP electrolysis was 7,257, and for TCP, the average molecular weight was 9,664.

After electrolysis, the alkaline electrolyte solution was neutralized and ether extracted to obtain organic mixture. In the case of microemulsion, the solution was vacuum distilled. The solid obtained was extracted with 3:7 mixtures of heptane and ethyl acetate. After removing the solvent mixture from the filtrate, the sample was once again extracted with ether to obtain the product mixture. The HPLC analysis in 100% methanol indicated formation of multiple products. The reactant concentration in the case DCP decreased by 84.7 and 74.9% in alkaline and microemulsion media, respectively. TCP reactant concentration also decreased by 84% during electrolysis in alkaline solution. In microemulsion, however, only 13% of TCP was consumed during electrolysis. The consumption of PCP from alkaline as well as microemulsion solutions was found to be less than 10%. The organic mixture was subjected to the FTIR analysis. The compound was aromatic in nature (C=C stretching vibrations at 1,450–1,600 cm^{-1}). They also have an ether linkage (C–O–C stretching vibrations at 1,100–1,300 cm^{-1}). The C–Cl bond is also present in the organic mixture (C–Cl bond at 1,100 cm^{-1}). The presence of hydroquinone–quinone group was also confirmed (C=O stretching vibrations at 1,715 cm^{-1}).

Galvanostatic electrolysis, thus suggested that predominant mode of removal of chlorophenols is through oligomer and polymer formation. Simple alkaline media may be more effective for this purpose.
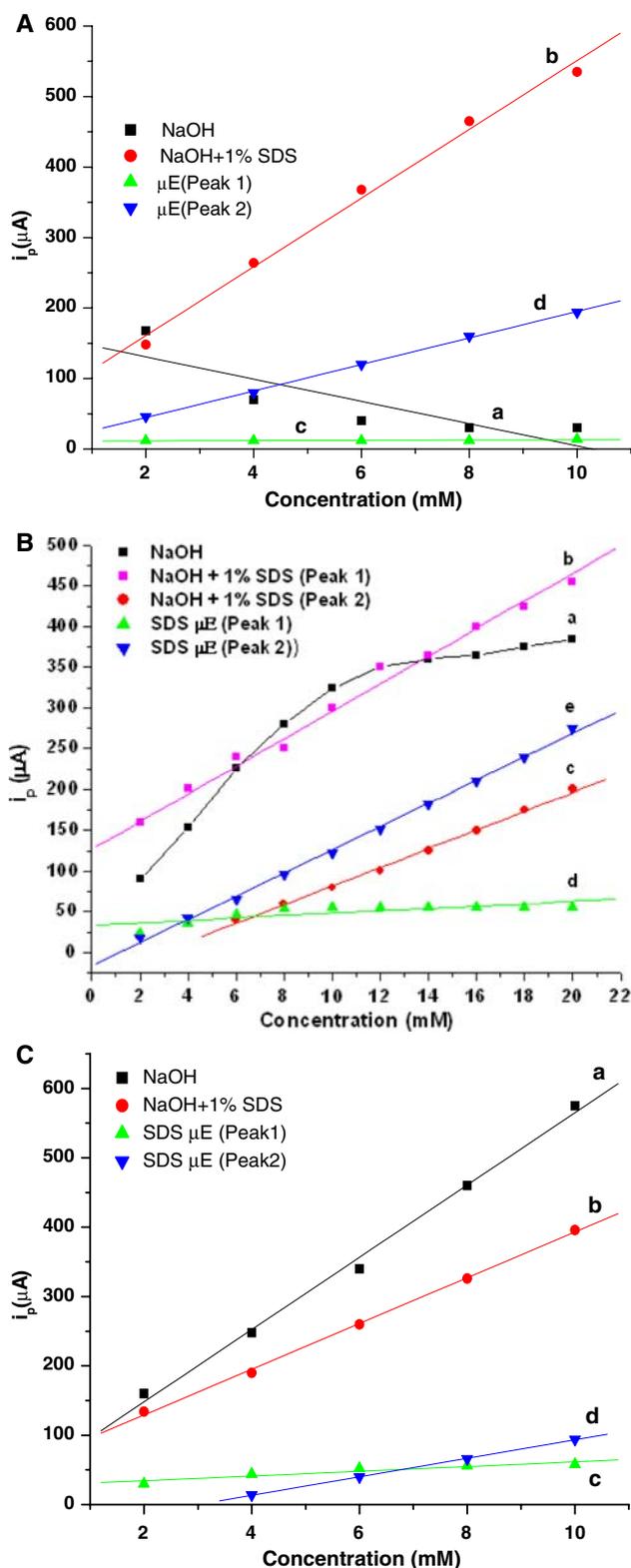
Fig. 7 **a** Effect of concentration on DCP in all the mediums at 20 mV s^{-1} in SDS microemulsion medium. **b** Effect of concentration on TCP in all the mediums at 20 mV s^{-1} in SDS microemulsion medium. **c** Effect of concentration on PCP in all the mediums at 20 mV s^{-1} in SDS microemulsion medium

4 Conclusions

Earlier attempts toward electroanalysis as well as oxidative detoxification of chlorophenols have generally focused on new types of anodes and chemical modifications of anodic surfaces. It appears that micellar and microemulsion media can be effectively used for these purposes. NaOH–SDS micelle is found to be suitable for voltammetric analysis of all the three compounds investigated at least up to 15 mM reactant concentrations. For analysis involving higher concentrations of these phenolic compounds, SDS microemulsions would be suitable. For phenolic removal through oxidative polymerization, simple NaOH medium appears to be suitable. The anodic behavior of chlorophenols also depends on the number of chlorosubstituents. The adsorption of chlorophenols probably decreases with increasing chlorine substituents on the aromatic ring. Further investigations on the oxidative behavior of halogenated and other substituted phenols in these media also would be worthwhile.

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