Electrochemical destruction of \textit{p}-chlorophenol and \textit{p}-nitrophenol – Influence of surfactants and anode materials

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Abstract

The electrochemical oxidative removal of \textit{p}-chlorophenol and \textit{p}-nitrophenol was studied by cyclic voltammetry (CV) and constant current electrolysis on commercially available graphite and titanium substrate insoluble anodes (TSIA). The effect of cationic cetyl trimethylammonium bromide (CTAB), anionic sodium dodecyl sulphate (SDS) and non-ionic polyoxyethylene(23)lauryl ether (Brij-35) surfactants, which prevent adherent film formation on the electrode surface were also studied. CV experiments indicate that \textit{p}-chlorophenol exhibits a relatively higher tendency for film formation on graphite and that sodium chloride is a better medium for the destruction of phenols. The electrochemical oxidation of phenols under galvanostatic conditions in chloride medium with CTAB enhanced the detoxification process with significantly lower fouling effects on TSIA. The surfactants, however, did not improve phenol removal on graphite under identical experimental conditions. A charge of 2.5 F per mol was found to be sufficient to achieve 44–48% removal of phenol on both the electrodes in the absence of the surfactants. A 55–65% removal was achieved in the presence of the cationic surfactant on the TSIA electrode. Phenol was removed as a low molecular weight polymer (MW \textit{C21}11000).

Keywords: Phenols; Surfactants; Electrochemical destruction; Graphite; Oxide-coated electrode

1. Introduction

Detoxification of phenols using electrochemical (EC) methods (Rajeshwar and Ibanez, 1997) is an active area of current interest. Recent work in this area is centered on the choice of suitable experimental conditions to avoid fouling and passivation effects of anodes. A variety of electrode materials including platinum (Ezerskis and Jusys, 2001; Torres et al., 2003), lead – dioxide (Wu and Zhou, 2001; Borras et al., 2004), graphite (Korbahti et al., 2002; Ortiz et al., 2003), glassy carbon (Ureta-Zanartu et al., 2002), boron-doped diamond-BDD (Hagans et al., 2001; Iniesta et al., 2001), gold (Ureta-Zanartu et al., 2001) stainless steel (Canizares et al., 2002) and oxide-coated titanium (Polcaro et al., 1999; Chozhan et al., 2004) have been investigated as anodes. The fouling and passivation of electrode materials is normally not observed at very low concentrations of phenols whereas it is a major challenge at higher concentrations.

Though some initial reports suggested BDD as a potential non-fouling electrode (Hagans et al., 2001), further studies did not confirm this (Iniesta et al., 2001). Chemically modified electrodes involving aluminosilicate and other complexes (Mohan et al., 2004; Obirai et al., 2005) have also been tried, although with limited success. Photo-electrochemical degradation on platinum (Davies et al., 2002) and TiO2 particulate systems (Pandiyan et al., 2002) has also been reported recently.

Besides anode fouling effect, energy consumption in EC processes is a serious issue. Complete EC oxidation of phenols to CO2 is a multi-electron, energy-intensive process.
Some studies do claim such exhaustive EC oxidation (Sathish and Viswanath, 2005). However removal of phenol probably occurs via oligomerization and coagulation (Canizares et al., 2002). Further efforts to minimize energy consumption using electrofloationation (Murugananthan et al., 2005) and EC oxidation followed by bio-degradation (Szpyrkoicz et al., 2005) have also been reported recently. Surfactants have been employed in the preparation of polymer-coated electrodes for the determination of phenols (Aranzazu et al., 2005). However, the influence of surfactants on detoxification of phenols has not been reported so far.

A study of the literature indicates that the EC detoxification of phenols is brought with the following challenges: (i) removal of phenols in significantly high concentrations; (ii) avoidance of electrode fouling and (iii) reduction in the energy or faradic charge for removal of phenols. Hence, surfactants can adsorb on the electrode surface and influence the fouling. They may also influence oligomerization and coagulation processes initiated by electrogenerated cation radicals of phenols. The present investigation was initiated to evaluate the role of surfactants in addressing the above challenges.

Nitrophenols and chlorophenols are rated as priority pollutants (Keith and Telliard, 1979). Nitrophenols are mainly used in the production of pesticides, herbicides, explosives, dyes and plasticizers (Spain, 1995) and they cause severe environmental contamination. Chlorophenols are used in plastics, pesticides and wood preservatives. They contaminate the eco-system by bio-accumulation (Ezerskis and Jusys, 2001). Hence in the present work p-chlorophenol (PCP) and p-nitrophenol (PNP) were chosen for the EC destruction studies. Titanium substrate insoluble anodes (TSIA) with an RuO$_2$-IrO$_2$-TiO$_2$ coating (Subbiah et al., 1990) and graphite anodes were employed since these electrodes are commercially available and are well known anode materials for use in neutral chloride media. A fairly high concentration of phenols, around 50 mM was taken for detoxification. The influence of cationic, anionic and non-ionic surfactants was assessed using cyclic voltammetry (CV) and constant current electrolysis.

2. Experimental

2.1. Reagents

PNP and PCP were obtained from SRL. Cationic surfactant cetyl trimethylammonium bromide (CTAB), anionic surfactant sodium dodecyl sulphate (SDS), non-ionic surfactant polyoxyethylene(23)lauryl ether (Brij-35) were purchased from BDH. Potassium ferrocyanide was obtained from Merck. All the chemicals were of reagent grade. Double distilled water was used for the preparation of solutions.

2.2. Voltammetric measurements

Voltammetric measurements were carried out using an Autolab model PGSTAT 30 potentiostat/galvanostat controlled with a General Purpose Electrochemical System, software version 4.9 (Eco Chemie B.V., The Netherlands). An H-type glass cell was used for the voltammetric studies. A dry cell grade graphite electrode (Graphite India) of 7 mm diameter and a plate of TSIA of geometric area 0.45 cm$^2$ were used as working electrodes. A platinum foil was used as the counter electrode. All potentials were recorded against a saturated calomel electrode (SCE). Prior to the experiments the graphite electrode was polished with 1/0 to 4/0 emery sheets and washed with water, trichloroethylene (Chandrakekaran et al., 1991). The TSIA electrode was cleaned with isopropanol.

2.3. Constant current electrolysis

Galvanostatic experiments were carried out in an undivided glass cell of 75 ml capacity. A graphite sheet (area 16 cm$^2$) and a TSIA mesh (area 11.2 cm$^2$) were employed as anodes. A stainless steel sheet served as the cathode. Electrolysis was carried out in 0.1 M NaCl and 0.1 M NaOH solutions. The pH of the solutions was 6.3 for NaCl and 10.4 for NaOH. Experiments were conducted at 30 ± 1°C. The pH of the electrolyte remained constant before and after electrolysis. Throughout the electrolysis, the electrolyte was constantly stirred using a mechanical stirrer. A constant current equivalent to 2.5 A dm$^{-2}$ was passed using a home-made galvanostat. The solutions before and after electrolysis were analyzed to monitor the concentration of phenol using high performance liquid chromatography (HPLC). An LC-10AT pump and an SPD-10A UV-detector (Shimadzu, Japan) were used. A 70:30 (v/v) mixture of methanol/water was used as the mobile phase. The flow rate was 1.0 ml min$^{-1}$. The brown solid or the resinous mass formed during electrolysis was analyzed by FTIR (Perkin Elmer, Paragon-500). The molecular weight of the polymer was determined by gel permeation chromatography (GPC). An LC 6A pump and an RID 6A Detector (Shimadzu, Japan) were used. Tetrahydrofuran was used as an eluent.

3. Results and discussion

3.1. Cyclic voltammetric studies

A convenient method for the removal of phenolic compounds would be electrooxidative polymerization involving a small number of electrons per reactant molecule without fouling the electrode surface. Thus, the oligomerization/polymerization should preferably occur in the bulk of the solution. CV studies were carried out to arrive at the optimal experimental conditions.

The multi-sweep cyclic voltammograms of PCP in 0.1 M NaOH and 0.1 M NaCl solutions are shown in Figs. 1a2 and b2 respectively. The corresponding background currents for the two media are shown in Fig. 1a1 and b1 for comparison. In the absence of any surfactant, multi-sweep CV responses exhibit a gradual decrease in anodic current.
consistent with an increase in the number of cycles in both the media. After 7–8 cycles the voltammetric response turns out to be similar to that of the background CV response (Fig. 1 a1 and a2 and also Fig. 1 b1 and b2). It should be noted that the substantial decrease in the oxidation peak currents is due to passive polymer film formation, which is quite different from the slight decrease in peak currents normally noticed in conventional diffusion-controlled voltammetric responses.

The oxidation potential for PNP on graphite is higher by 200–300 mV as compared to that for PCP. The oxidation peak for PNP occurs closer to the oxygen evolution potential region (Fig. 2 a and b). Hence, distinct anodic peaks are not observed in these media. However, the passivation effect leading to substantial decrease in the peak current during the second and subsequent sweeps is clearly noticed in the CV responses (Fig. 2a and b).

Electrode fouling after the multi-sweep cycling for both the compounds was found to be substantial. This effect was further confirmed by recording the CV response of potassium ferrocyanide before and after multi-sweep cycling in phenolic solutions. A CV reversible response for potassium ferrocyanide on a freshly polished graphite electrode at a sweep rate 40 mV s\(^{-1}\) is shown in Fig. 3 a1. After multi-sweep cycling in NaOH solution containing PCP (as seen in Fig. 1 a2) both anodic and cathodic peak currents decreased. The film-covered electrode surfaces seem to block even the background surface redox processes (Fig. 3a2 and a3). The electrode fouling effect after multi-sweep cycling of graphite in NaOH containing PNP (as seen in Fig. 2a) appears to be similar (Fig. 3a3). These results indicate that in the absence of surfactants both PCP and PNP form insulating polymer films on the electrode surface, which inhibit further electron transfer.

CV responses obtained for PCP during multi-sweep experiments in the presence of cationic, anionic and non-ionic surfactants in 0.1 M NaCl are shown in Fig. 4 a2, b2, and c2 respectively. The peak currents during multi-sweep cycling decreased significantly in the presence of surfactants, suggesting film formation on the electrode surface even in the presence of surfactants. Similar surfactant effects were noticed also for PNP in NaCl. It is clear that polymeric film formation occurs in the presence of the surfactants for both PCP and PNP. Quite interestingly, however, these polymer layers were not adherent or passivating. This is evident from the voltammogram recorded for potassium ferrocyanide on the electrodes subjected to multi-sweep cycling (Fig. 4a2, b2 and c2), without polishing or cleaning the electrode surface. The CV recorded
for potassium ferrocyanide are shown in Fig. 3b1, b2 and b3; both the anodic and cathodic peaks can distinctly be seen. The voltammograms are also similar to that recorded in pure 0.1 M KCl solution on a freshly polished electrode (Fig. 3a1). These results suggest that the surfactants prevent the formation of adherent passive films on the graphite electrode.

Similar trends could be noticed for the phenolic compounds in NaOH medium as well. In alkaline media, the background currents are significantly higher even below 1 V in the presence of the cationic, anionic and non-ionic surfactants as given in Fig. 5a1, b1 and c1 respectively. The oxidation of phenols occurs as a competitive process in this region as may be seen from Fig. 5a2, b2, and c2 for PNP. In multi-sweep cycling experiments the anodic peak currents continuously decreased and retraced the background current after 5–6 cycles. Even after multiple cycling, the electrode surface doesn’t get passivated as may be noticed from CV responses recorded for ferrocyanide (Fig. 3c1, c2 and c3). The electrode activity in the alkaline medium remained unaffected, which may either be due to unstable polymer film formation or due to poor efficiency of phenol oxidation as compared to oxygen evolution.

The voltammetric studies on graphite presented so far indicate the following:

(a) Oligomerization/polymerization process is generally favourable in NaCl medium as compared to that in NaOH medium. In NaOH medium oxygen evolution reaction occurs competitively in the same potential region.

(b) Polymerization leading to fouling of the electrode surface is more significant for the more easily oxidizable PCP as compared to PNP. It appears that the cation (Ar–OH)/C5+ radical generated from PCP undergoes a more facile radical–substrate coupling leading to oligomerization/polymerization. Another cause may be the closeness of the PNP oxidation region to the background oxygen evolution region. Oxygen bubbles may inhibit film formation and thereby prevent fouling of electrode surface to some extent.

CV responses were also recorded on the TSIA working electrode. However, the background currents due to chlorine evolution in NaCl medium and oxygen evolution in NaOH medium were found to be substantially higher on this electrode. Hence the voltammetric peaks for PCP and PNP, the surfactant effect on the background current and the relative influence of graphite and TSIA electrodes could not be quantified from voltammetric studies. However, the possibility of oxidative polymerization of phenols through electrogenerated species such as Cl2, Cl' and OH' does exist. Hence, this electrode was also selected for constant current electrolysis.

3.2. Constant current electrolysis

Constant current electrolysis was carried out to further evaluate the influence of surfactants on the removal of PCP and PNP. As mentioned in the introductory section, it is essential to achieve detoxification with a minimum electric charge. In this work, 2.5 F per mol of phenol (2 F per mol + 25% excess current) was chosen as the amount of charge passed during a single batch of electrolysis. Around 40–50 mM of PCP and PNP were initially dissolved in the electrolyte medium, and subjected to constant current electrolysis. During electrolysis the average cell voltage was found to vary between 1.8 and 3.1 V. In general, the electrolyte solution turned yellow to brown in colour depending on the nature of the compound and operating conditions. After electrolysis the solution was filtered to remove the insoluble coloured polymer. The amount of phenol present in the clear solution and thus the percentage of phenol removed during constant current electrolysis was obtained from HPLC analysis. Data
showing the influence of medium, electrode material and surfactant are summarized in Table 1.

### 3.3. Effect of medium and anode material

In the absence of surfactants only a very low quantity of PCP was removed from NaOH (run 1) and NaCl (run 2) on the TSIA electrode. However a higher level of phenol removal could be realized in neutral NaCl medium. Comparatively better results were obtained for the removal of PNP in NaOH (run 3) as well as in NaCl medium (run 4). NaCl was found to be a better medium for PNP as well. On the TSIA electrode as much as 48% PNP could be removed in the first batch itself from the NaCl solution (run 4). Although phenols undergo oxidation in both NaOH and NaCl media, the background oxidation processes are different in these two media. In NaOH, oxygen evolution is the parallel process, while in NaCl it is chlorine evolution. The chlorine generated at the anode is also likely to assist in the oxidative polymerization of phenol. This probably accounts for the higher efficiency in NaCl as compared to that in NaOH. Hence, all further constant current electrolysis experiments were confined to the NaCl medium.

Similar results were obtained for the removal of PCP and PNP on graphite electrode in NaCl solution. The removal of PNP was substantially higher in this case (run 6) as compared to that of PCP (run 5). Quite interestingly in the absence of surfactants PNP removal was found to be around 48% on TSIA (run 4) and graphite electrodes (run 6). This, despite the fact that TSIA assists the oxidation of phenol predominantly through chlorine evolution, while graphite directly oxidizes the phenols, as suggested by the voltammetric behavior.

### 3.4. Effect of surfactants

On graphite both cationic and anionic surfactants are found to exhibit a negative influence on the removal of PCP (runs 7 and 8) and PNP (runs 9 and 10). The negative influence of the anionic surfactant is relatively higher than that of the cationic surfactant. For example in the case of PNP the removal efficiencies in the absence of surfactant and in the presence of cationic and anionic surfactants were found to be 48%, 44% and 26% respectively (runs 6, 9 and 10). It appears that surfactants adsorbed on graphite electrodes prevent oxidation of organic compounds significantly through a blocking effect, as may be inferred from our CV results (Figs. 4 and 5).

On TSIA electrode, the cationic surfactant has a favourable impact on the removal of PCP (run 11) and PNP (run 14). In the case of PCP the oxidative removal efficiency increases remarkably from 14% to 57% while with PNP it
improves moderately from 48% to 64%. However for both PCP and PNP the anionic and non-ionic surfactants exhibit an either insignificant positive effect (run 13) or a negative effect (runs 12, 15 and 16).

Since no distinct oxidation peak was observed for phenol oxidation on TSIA electrode, chlorine evolution followed by chemical oxidation is probably an important parallel pathway for the oxidative removal of phenols on these electrodes. The cationic species CTA$^+$ builds up the surface concentration of chloride ions through formation of CTACl, facilitating the chlorine evolution reaction. The cation radical generated during phenol oxidation may also be prevented by the cationic surfactant from adsorbing on to the electrode surface. This may prevent electrode fouling, thereby contributing to a higher rate of removal of phenols. This type of catalytic influence is possible only in the case of cationic surfactants.

3.5. Recycling and product characterization

The results summarized in Table 1 correspond to single batch constant current electrolysis. The electrolyte after filtering the polymeric material can be subjected to a subsequent constant current electrolysis under the same experimental conditions. A further removal of phenol was achieved after passing charge of 2.5 F per mol for the remaining concentration. In a typical experiment involving PNP on TSIA in 0.1 M NaCl solution [conditions similar to run 4], 98% removal could be achieved in three successive stages. This removal may be achieved in two stages in the presence of surfactants. Essentially, a
continuous EC oxidative removal involving electrolysis, simultaneous filtration and recycling may be a feasible approach for a large-scale EC removal of these phenols. The polymeric products isolated during constant current electrolysis were subjected to FTIR analysis and GPC. The polymer formed is aromatic in nature (−C=O− stretching vibrations at 1450–1600 cm\(^{-1}\)) they also have an ether linkage (−C−O−C− stretching vibrations at 1100–1300 cm\(^{-1}\)) (Ezerskis and Jusys, 2002). The C–Cl bond is retained as such in the polymer (C–Cl bond at 1100 cm\(^{-1}\)). The intensity of the hydroxy bands is weak and broad. This proves the presence of polymeric stretched –OH groups in the polymer. The molecular weight \(M_n\) and \(M_w\) were determined as 4390 and 4492, respectively. It is inferred from the molecular weight data that the polymer formed is monodispersed. The molecular weight obtained in the present work is close to the value reported in the literature (Zhang et al., 2006).

The electrolyte solution after the filtration of polymeric material was ether extracted and analyzed for other organic constituents, especially chlorinated products. At least in the case of PNP this ether phase did not contain any compound with aromatic C–Cl bond. Recent investigations on phenol degradation also indicate the absence of new nuclear chlorinated carcinogenic molecules (Comninellis and Nerini, 1995; Polcaro et al., 1999). However, this aspect may require further confirmation in scale-up investigations.

4. Conclusions

Significant amounts of substituted phenols (PCP and PNP) can be removed from effluents by simple galvanostatic electrolysis with commercially available graphite or TSIA in chloride media using cationic surfactants such as CTAB. In the absence of surfactants, the behavior at both the electrodes are similar. In the presence of CTAB, the TSIA electrode performs much more efficiently. The phenols are removed mainly through oxidative polymerization. Cationic surfactants favor polymerization in the liquid phase by blocking the adsorption of electro generated cation radical of phenol on the electrode surface. About 55–65% reduction in phenolic content may be achieved in a single batch by passing electric charge of 2.5 F per mol. Complete removal is possible through recycling the same solution after filtration of the polymeric product. The experiments also suggest the feasibility of a flow cell operation with a filtration step for the removal of solid polymer.

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References


