

Electrochemical Degradation of Aqueous Phenols Using Graphite Electrode in a Divided Electrolytic Cell

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Abstract—Untreated industrial effluents invariably contain large amounts of heavy metals and organics. This paper reports the electrochemical oxidation of synthetic water containing 200 ppm of phenol. Studies have been carried out in a compartmentalized cell using platinum (cathode) and graphite (anode). Electrolysis has been done for 40 h at constant applied potential of 5 V in different electrolytes, such as, NaCl (aq), NaOH (aq) and a mixture containing both NaCl (aq) and NaOH (aq) as the anolyte and acid as the catholyte. Phenol concentration decreased from the initial value of 200 to about 10 ppm.; the corresponding COD values, respectively, are ~400 to ~100 ppm. The reaction goes through chloro-compounds as intermediates before being mineralized. The carbon anode seems to be passivated with a thin layer of poly-phenol. A concomitant amount of hydrogen is generated during the electrolytic degradation of phenol.

Key words: Electrochemical Oxidation, Phenol Decomposition, Hydrogen Generation, Phenol Mineralization, Waste Water Treatment, Compartmentalized Electrolytic Cell

INTRODUCTION

The concern for environmental pollution from the industrial waste water is so high that it is but natural that many groups worldwide are engaged in this area. One of the methods for the removal of organic pollutants is by electrochemical oxidation of the organic pollutants. Researchers have reviewed the work in this area with a special emphasis on the merits of the electrochemical methods over the other processes [Rajeshwar et al., 1994; Juttner et al., 2000]. Different anodes like graphitic carbon electrode [Kannan et al., 1995; Liu and McCreey, 1995; DuVall, and McCreey, 1999, 2000], metal oxide electrodes [Tahar and Savall, 1998; Wu and Zhou, 2001; Azzam et al., 2000] and metal electrodes [Canizares et al., 2002] have been employed. The major problem in the electrochemical oxidation of phenol is formation of polymer film on the electrode surface; as a result, the current density decreases. For characterization of these polymeric films, Fourier Transform Infrared Spectroscopy (FTIR) has been widely used [Ezerskis and Jusys, 2002; Zareie et al., 2001]. The formation of these films mainly depends on the nature of the electrode, the ions in the electrolyte and the pH of the medium. It is reported that the formation of polymeric film on the electrode surface is favored by the alkaline medium in many cases [Comminellis and Pulgarin, 1991; Canizares et al., 1999]. Scanning tunneling microscopy has been used to study the morphology of the film formed during the electro-oxidation of phenol [Wang et al., 1991].

The electro-oxidation of phenol on various experimental factors like the nature of the electrode, pH, temperature and the nature of medium have been reported [Pulgarin et al., 1999; Ribordy et al., 1997; Iniesta et al., 2001]. Recently, attempts have been made to study the relationship between the structure and reactivity of p-substituted phenols for electrochemical oxidation at Pt anodes [Torres

et al., 2003]. They suggest that compounds with electron donor substituents will readily undergo electro-oxidation on Pt electrodes. When nickel or stainless steel is used as the anode, the efficiency has been found to be perceptibly slow due to the electro coagulation of the metal in the organic polymer matrix. Platinum metal anode has been reported to be efficient during electrolysis for the removal of organic wastes [Ezerskis and Jusys, 2001]. But the stability of the electrode in saline medium is a point to be kept in mind in addition to prohibitive cost of platinum. Photochemical decomposition of hazardous wastes like phenol and chlorophenols is another parallel way to clean up the environment [Peiro et al., 2001]. The removal of phenolic compounds by electro-assisted process, a combination of photoelectrocatalysis has been reported [Wu et al., 2002]. In this work a combined process of electrocatalysis and photocatalysis has significant synergistic effect at the suitable applied potential 3 V.

With this in view, an effort has been made in this paper to investigate the electro-oxidation of aqueous phenol as a test pollutant in a divided electrolytic cell. The advantage of the compartmentalization is the use of anolyte and catholyte with different composition. This in turn will open up new avenues, to employ much more stable electrodes involving chemically biased electrolytic cells. This setup further enables one to use a milder condition (5 V which is less than the literature reported values). It has been shown by FTIR technique that phenolic species are strongly adsorbed on the carbon anode (especially in alkaline medium) which inhibits the rate of mineralization of phenol.

EXPERIMENTAL

1. Apparatus

A divided electrolytic cell (Fig. 1) has been designed using a carbon coated disc as a separator [Viswanath, 2004]. (The design and details of application of the cell has been submitted for patenting.) The separator prevented the mixing of the anolyte and catholyte but at the same time ensured the passage of current for electrolysis.

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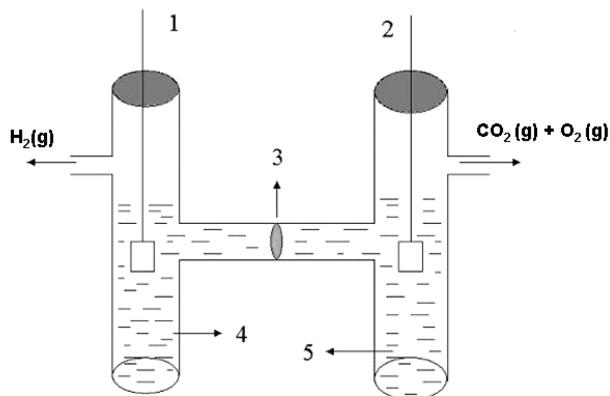


Fig. 1. Divided electrolytic cell for phenol decomposition.

1. Pt-cathode	4. Aq. acid
2. Carbon-anode	5. Phenol in solution
3. Separator disk	

A smooth platinum sheet (1 cm^2 area) dipped into a 1 M H^+ (aq.) solution acted as the cathodic part of the half cell. The volume of the acid taken was 50 mL . The anode compartment consisted of graphitic carbon (1 cm^2 area) as the electrode dipped into a solution of phenol along with a supporting electrolyte. A 50 mL solution of aq. phenol (with initial concentration of the phenol $\sim 200 \text{ ppm}$) was taken for electrolysis. Either NaCl (0.1 M , aq.), NaOH (0.5 M , aq.) or a mixture of NaOH (0.25 M in the mixture) and NaCl (0.05 M in the mixture) have been used as the supporting electrolytes. The decomposition of phenol was carried out under potentiostatic condition using an APLAB-7122 regulated DC power supply. The applied potential (DC) was kept constant at 5 V during the entire time of electrolysis. The anode potential was measured by using the saturated calomel electrode (SCE) as the reference electrode.

2. Analysis

Concentration of phenol was monitored as a function of time by UV-Vis spectrophotometry, by two different procedures. In the first method phenol as such was estimated spectrophotometrically by monitoring at λ_{max} 267 nm and in the second procedure 4-aminophenol method was employed and concentration of phenol was estimated colourimetrically by monitoring at λ_{max} 500 nm . The formation of p-chlorophenol intermediate was identified by Gas chromatography (nucon-5765) using FID and SC-30 column. The intermediate species was extracted after 5 hours of electrolysis with diethyl ether solvent from the electrolyte solution after saturating the electrolyte with NaCl . The Chemical Oxygen Demand (COD) was calculated by open reflux method [Clesceri et al., 1998]. The FTIR for different samples were recorded with a JASCO FT-IR Spectrometer.

RESULTS AND DISCUSSION

1. Removal of Phenols from Water

The concentration profile of phenol as a function of electrolysis time is shown in Fig. 2. The initial rate of degradation of phenol is almost independent of the supporting electrolyte. Nevertheless, after 4 hours of electrolysis, one finds that in the neutral chloride medium decomposition of phenol is faster than in the alkaline medium. In Fig. 3, the corresponding variation in the anode potential and the

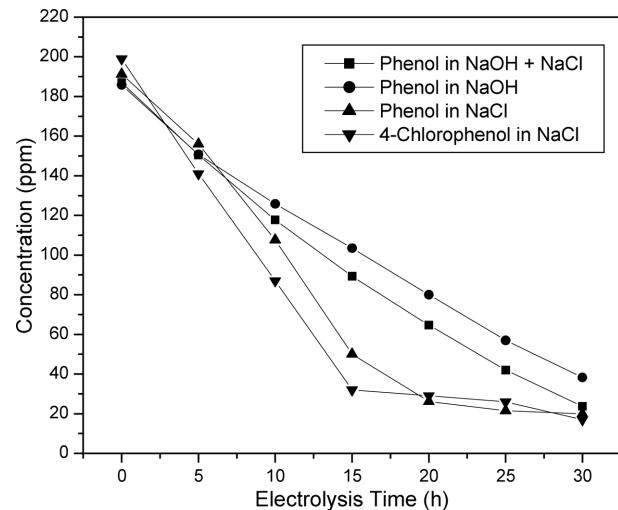


Fig. 2. Concentration profile of phenol and p-chlorophenol as a function of electrolysis time in different media at an applied cell potential of 5 V .

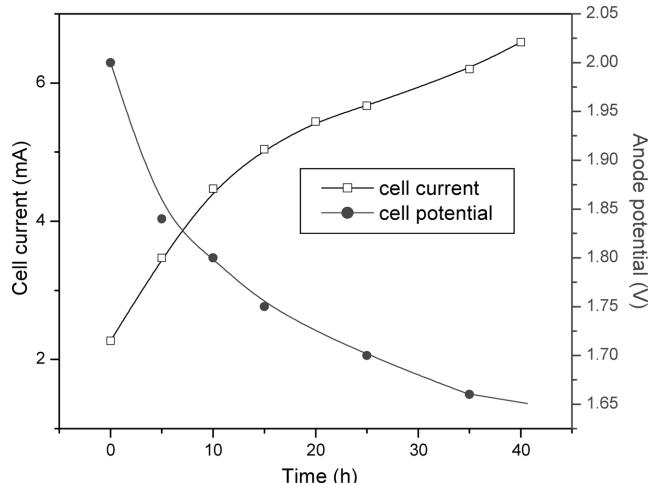


Fig. 3. Variation of anode potential and cell current as a function of electrolysis time at an applied cell potential of 5 V (in NaCl medium).

cell current are plotted as a function of time when NaCl alone is used as the supporting electrolyte. The experiments have been carried out at a constant cell potential of 5.0 V . At the start of the experiment the anode potential constitutes around 2 V . When NaCl is used as the supporting electrolyte, while the cell potential is maintained at a constant value of 5.0 V , the anode potential is found to decrease as electrolysis proceeds, while the cell current is observed to increase, indicating greater electrolysis as the time progresses. But when NaOH is present in the anolyte, the anode potential has been observed to be more or less constant at $1.5 \pm 0.2 \text{ V}$. The cell current on the contrary shows a decreasing trend (shown in Fig. 4). This shows that the electrolytic degradation is dependent on the electrolyte medium. The presence of alkali favours polymeric products to be coated on carbon electrode. This film can hinder or slow down the electrolytic process. Recently, in NaCl medium, formation of non-passivating polymer film on carbon electrode surface has been

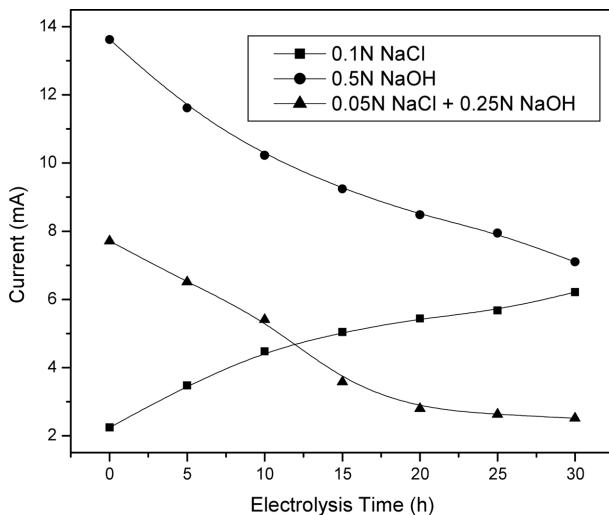


Fig. 4. Cell current Vs time in different media at an applied cell potential of 5 V.

reported during the electrolysis of phenol at high initial concentration [Zareie et al., 2001], but in this present study, in presence of NaCl electrolyte, the non-passive film formation has not been observed. This may be due to lesser concentration of phenol taken. When NaCl is present as the electrolyte the chlorine generated in situ will form hypochlorite or hypochlorous acid, a powerful oxidizing agent. In addition to this, the formation of p-chlorophenol will also assist the rate of decomposition of phenol, since the decomposition rate of p-chlorophenol is found to be faster than phenol. In Fig. 2, the concentration profile of phenol and p-chlorophenol in the NaCl medium shows that the decomposition rate of p-chlorophenol is higher than the phenol in the NaCl medium. In Table 1, electrolysis time, concentration of phenol and p-chlorophenol and COD are tabulated for electrolysis experiment with NaCl alone as the supporting electrolyte.

2. FTIR Studies

In order to find whether phenolic species are coated on carbon surface, FTIR spectra have been recorded for carbon powder under different environment. The spectra are shown in Figs. 5 and 6. Fig. 5 represents the conditions in the NaCl medium and Fig. 6 gives the details in the alkaline medium. Curve 'a' represents IR spectrum for carbon electrode powder material washed with distilled water and dried at 175 °C for 4 h in an air oven and pelletized with KBr. Curve 'b' is for the carbon powder, collected from the electrode immediately after electrolysis. The powder is washed and boiled with distilled water to remove traces of physically bound phenol, filtered and then dried at 175 °C for 4 h in an air oven. The dried

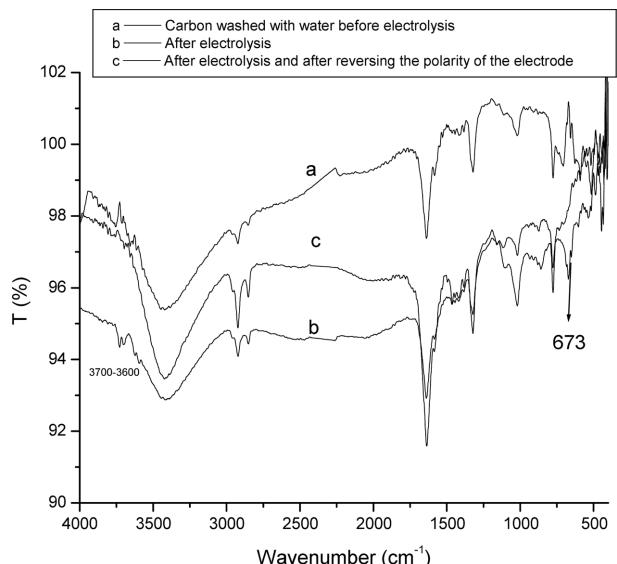


Fig. 5. IR spectrum of carbon electrode before and after the electrolysis in NaCl medium.

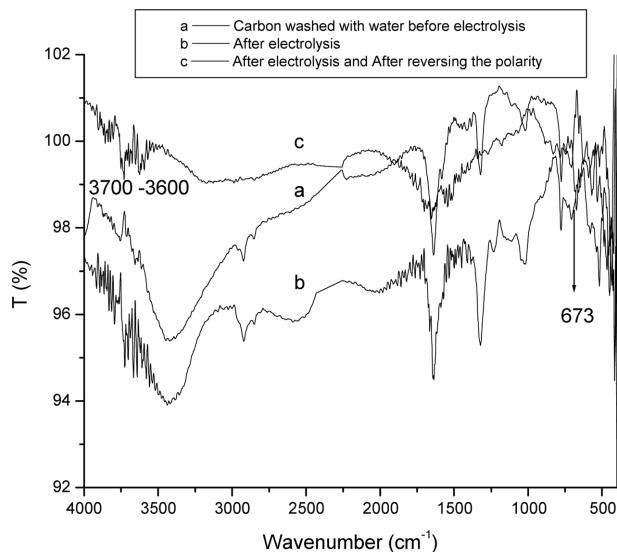


Fig. 6. IR spectrum of carbon electrode before and after the electrolysis in NaOH medium.

sample has been pelletized with KBr for recording the IR. Another sample of carbon has been collected from the electrode after the polarity of the carbon electrode had been reversed and employed as a cathode for a brief period (~5 minutes). During this process it

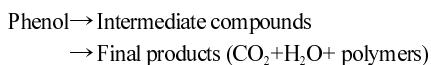
Table 1. Phenol and COD concentration as a function of electrolysis time at an applied cell potential of 5 V (in NaCl supporting electrolyte)

S. No	Time (h)	Phenol concentration (ppm)	p-Chlorophenol concentration (ppm)	Phenol COD (ppm)	p-Chlorophenol COD (ppm)
1	0	191	199	399	341
2	20	26	29	134	147
3	30	20	17	125	132
4	40	12	-	93	-

is expected to remove any of the weakly bound phenol. The powder is collected and washed with distilled water. Then it is boiled with distilled water to remove traces of physically bound phenol washed and filtered, dried at 175 °C for 4 h in an air oven and pelletized with KBr. This is shown in curve 'c' of Figs. 5 and 6.

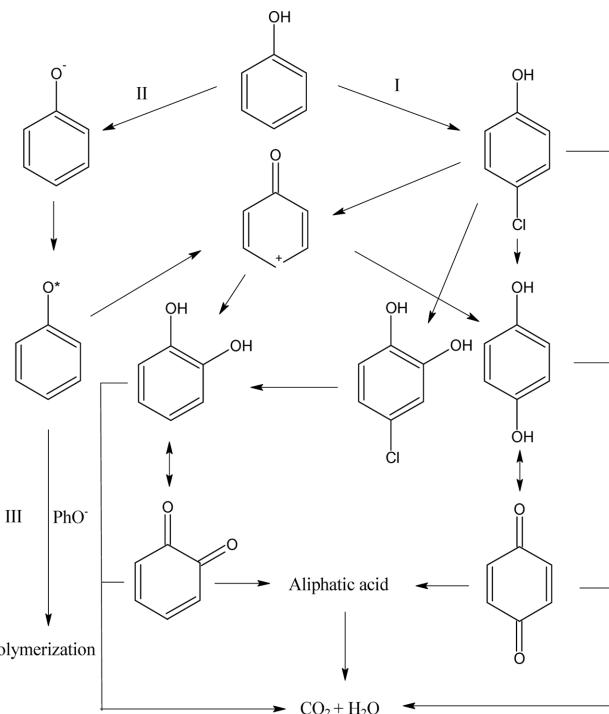
In the experiment with NaCl as the supporting electrolyte, an O-H stretching frequency $\sim 3,600-3,700 \text{ cm}^{-1}$ and a C-H bending frequency $\sim 650-700 \text{ cm}^{-1}$ can be seen on the electrode surface after the electrolysis. These absorption frequencies disappear on reversing the electrode potential. This proves that the phenol is adsorbed on the electrode surface during electrolysis. At the same time this is not strongly bound, as these frequencies disappear when the potential has been reversed. Similar experiments carried out in the alkaline medium show that the species adsorbed on the surface are still retained even after the reversal of potential. This clearly indicates that the surface is coated with phenolic species (may be polymeric). It is worthwhile to keep in mind that the phenate ion eliminates the bridging through hydrogen bond as shown in curve 'c' in Fig. 6.

Generally, the reaction sequence for phenol decomposition is as follows:



In order to check whether any chlorinated phenol is formed as intermediates, λ_{\max} for phenol and chlorophenols have been recorded and the values are given in Table 2. The phenol and o-chlorophenol have λ_{\max} 268-272 nm, respectively. Whereas, the p-chlorophenol has a value around 278 nm and the phenoxide has a value around 286 nm. The λ_{\max} value of samples electrolyzed in NaCl is also included. The sample has initial λ_{\max} pertaining to phenol. On electrolysis there is a shift in the λ_{\max} value to 276-278 nm. At the end of electrolysis the λ_{\max} shifts back to the original. From this it may be concluded that p-chlorophenol has been formed as an intermediate species during the initial stages of electrolysis. The formation of p-chlorophenol intermediate has also been confirmed by gas chromatography by taking the electrolysed solution (after 5 hours of electrolysis). The disappearance of p-chlorophenol at the end of the electrolysis is observed.

Based on the results of our study, the possible pathway for the decomposition of phenol is shown in the Scheme 1, which is similar to the one reported in the literature [Torres et al., 2003; Gattrell and Kirk, 1990]. In presence of NaCl, pathways I and II are favoured and III is restricted; but in alkaline medium, pathway I is completely restricted due to the absence of chloride ion in the medium and II & III are favoured. Particularly, polymerization of phenol



Scheme 1. Proposed pathway for the decomposition of phenol.

(pathway I) occurs only in the alkaline medium where the phenoxide ion is more stable.

3. Efficiency of Phenol Removal

The rate of production of hydrogen at the cathode compartment, during the electro-decomposition of phenol with NaCl as supporting electrolyte is shown in Fig. 7. The amount of hydrogen generated indicates a current efficiency of >97%. Thus with the present cell one gets a value added by-product in the form of hydrogen. The chemical reaction for the phenol mineralization is,

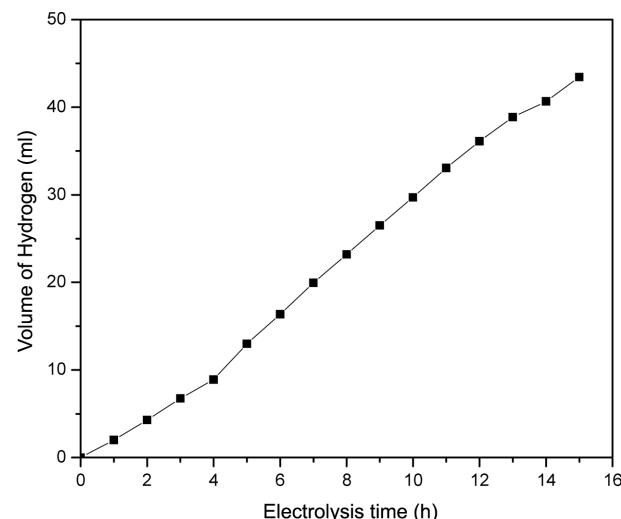
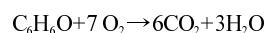


Fig. 7. Rate of hydrogen evolution at the cathode during the decomposition of phenol at an applied cell potential of 5 V.

Theoretically 7 moles of oxygen is needed for each mole of phenol. This will be equivalent to 14 moles of hydrogen at the cathode. In our experiments, the anolyte contained 8 mg of phenol, which is equivalent to 0.085 mmole of phenol. This will liberate 1.19 mmole of hydrogen. The hydrogen gas volume at 300 K for this amount will be around 30 mL. The fact that more hydrogen is liberated indicates that either side reactions are accompanying phenol degradation or not all the liberated oxygen is used in the phenol degradation. Thus, it can be seen as added advantages of using a divided cell. The generation of hydrogen, a value added by-product and fuel of the future, will be a valuable by-product. The average current efficiency (ACE) for phenol removal has also been calculated by using the following formula.

$$\text{ACE} = \frac{\text{Experimental change in number of moles of phenol}}{\text{Theoretical change in number of moles of phenol}}$$

The experimental change in the number of moles of phenol was calculated by taking the difference between the initial and final COD values. For this calculation, the cell current was taken as average between 0 to 40 h for every 5 h from the Fig. 3. It was observed that the Average Current Efficiency for the removal of phenols in the NaCl medium were 63% for phenol and 85% for chlorophenol, respectively.

CONCLUSIONS

In the present study a relatively lower voltage of 5 V has been found to be sufficient to degrade phenol. This has been possible due to the compartmentalisation of the cell. As a consequence, *in situ* generated nascent oxygen at the anode compartment is providing an additional route for the degradation process. The electrochemical decomposition of phenol is dependent on the medium in which it is present. Among the alkaline and NaCl medium, the decomposition was faster in the second case. In the NaCl medium, the formation of p-chlorophenol intermediate and absence of non-passive film formation on the electrode surface has been identified and confirmed by using UV-Visible, IR and Gas chromatography. The formation of passive film (polymer) on the carbon electrode surface in alkaline medium leads to slower degradation of phenol. The IR study confirms that the polymer is strongly adsorbed on the electrode surface. This indicates that the polymerization of phenol is favoured only in the alkaline medium. The major advantage of the divided electrolytic cell is the production of a valuable co-byproduct of pure hydrogen with >97% efficiency, and it enables one to employ lesser voltage; hence, the energy consumed will be concomitantly less than the literature reported values.

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