A study on electrochemical oxidation of phenol for wastewater remediation

N Divya¹, A V Sreerag¹,³, Yadukrishna¹, Tiwin Joseph¹ and P A Solomon²

¹Department of Chemical Engineering, Government Engineering College Trichur, Thrissur, Kerala, India-680009
²Professor, Department of Chemical Engineering, Government Engineering College Trichur, Thrissur, Kerala, India-680009
³E-mail: sreeragav1997@gmail.com

Abstract. This era having been driven by the industrial revolution caused a major outbreak of pollutant quantity in water. Phenol is one of the most toxic chemicals and electrochemical oxidation is undoubtedly one of the attractive alternatives for the degradation of phenol available in wastewater. The present study aims at finding the best combination of operating parameters maximizing the phenol removal by electrochemical treatment of phenolic wastewater. Synthetically prepared phenol solution of various concentrations was electrochemically oxidized using a cylindrical flow cell. It was found that initial phenol concentration, time, current density, and salt concentration have a strong influence on the removal of phenol. Furthermore, based on the results obtained, a second-order regression model was proposed to predict the responses. Analysis of variance (ANOVA) result and the $R^2$ value of the model shows that the model could very well predict the realistic situation. According to the prediction by the model, the best set of operating conditions giving the complete removal of phenol is Time: 9.27 min, Current density: 3.58 A/dm², supporting Electrolyte concentration: 3.29 g/L, and Initial Concentration: 13.64 ppm.

1. Introduction

It is a fact that pollution is obviously the most common by-product of industrialization. Pollution caused by toxic chemical compounds in the aquatic environment has now become a major issue encountered by the present generation. There has recently been heightened concern among scientists on the effects of human and wildlife exposure to phenolic compounds in the environment, particularly the aquatic environment. High levels of phenol in the environment can disrupt the biological ecosystem and nutrient cycling[1]. Phenol is one of the 129 top priority chemicals that are toxic under the 1977 Amendments to the Clean Water Act and the US Environmental Protection Agency (EPA) has issued water quality criteria[3]. It is understood as poisonous to fish even at a concentration of 2 ppm and based on a 96-hour exposure, 10-100 ppm is fatal to aquatic life[7]. It is observed and found that long exposure to phenol may irritate the gastrointestinal, central nervous system, liver, kidney, and cardiovascular tissues in animals. It can also cause diarrhea and dark colouration of urine [9]. The acceptable range for phenol toxicity is 13-26 mg/L[13].

In its pure state, phenol is a colourless solid which is an organic aromatic compound with a hydroxyl group attached to the benzene ring. The reason behind high reactivity of phenolic compounds is due to its reaction at the benzene ring or the hydroxyl group[4]. Phenol is highly soluble in water and is quite flammable. Phenol is involved in the production of chemicals such as xylanols,
oils, plastics, aspirin, antiseptics, pharmaceuticals, oil refining, explosives, dyes, the reagent in chemical analysis and leather and wood preservatives[1]. The removal of phenol from wastewater is of great importance in environmental protection because of its high toxicity (COD)[2]. When the concentration in the wastewater is above 2000-4000 mg/L, phenol can be recovered economically; but below this concentration, phenol destruction is the best method[5]. Various methods for the removal of phenol are: polymerization, electro-coagulation, extraction, photo-decomposition, biological method, electro-Fenton method, Advanced Oxidation Process (AOP), adsorption and ion exchange, membrane based separation[6], photochemical oxidation and wet oxidation.

The electrochemical treatment of phenol has no reagent requirement[12]. Phenol oxidation is generally initiated by electron transfer that leads to phenoxy radical reaction, which then can undergo radical–radical coupling, radical disproportionation, radical elimination, and radical oxidation of cations. The radical reaction can lead to the formation of benzoquinone, an important intermediate of phenol oxidation. Benzoquinone can be degraded with ring breakage to various carboxylic acids like maleic acid and other organic compounds (ether). The intermediate maleic acid undergoes reduction to form succinic acid at the cathode and then oxidized to malonic acid, then to acetic acid, and finally to CO2 and water[13,14]. AOP generates a powerful oxidizing agent, hydroxyl radical that can react with most of the pollutants[8]. Electrochemical oxidation is amenable to automation and compatible with the environment because the main reagent involved is the electron, which is clean and eco-friendly. The main characteristics of electrochemical oxidation are versatility, energy efficiency, safety, selectivity, cost-effectiveness[10]. Electrode materials should be electrochemically stable, economically feasible, and should effectively remove organic pollutants[5].

In Kerala, Hindustan Organic Chemicals Limited (HOCL), Ambalamugal, Ernakulum produces phenol at a rate of 40,000 TPA. The existing technology in treating phenol is by the biological method. Because of its recalcitrant nature, the treatment is very slow (HRT in the order of 96 hrs.), ending up with the requirement of huge capital investment for the construction of treatment steps such as aeration tank and clarifier. Being one of the Advanced Oxidation Processes (AOP), electrochemical treatment of the effluent can increase the biodegradability of phenol.

The present investigation mainly focuses on obtaining the best set of operating conditions that give the most effective removal of phenol from the wastewater. The study also aims at developing a quadratic model for the removal of phenol from the wastewater.

2. Materials and Methods

2.1. Materials Used
All the chemicals used in the study were pure.

2.2. Sample Solution Preparation
The sample solutions of phenol of concentration 10, 20, 30 ppm in double distilled water were synthetically prepared from a stock solution of 200 ppm initially made.

2.3. Experimental Setup
The exact representation of the experimental setup used for the study is shown in Figure 1. The experimental setup consists of a cylindrical flow cell, DC power supply, peristaltic pump, and a beaker containing the feed solution. Mesh type electrode made of Ruthenium oxide coated on titanium and stainless steel were used as the anode and cathode respectively. The available area of the cell is 40 cm².
2.4. Experimental Procedure
Phenol solutions of the desired concentration (10, 20, 30 ppm) were made in 1 litre of double distilled water. The required amount of NaCl (1, 2, 3, 4 g/L) is being added and dissolved. The prepared sample solution is taken in a beaker and all connections were made. Then the peristaltic pump is switched on and the DC power supply is set to the required current density (1, 2, 3, 4 A/dm$^2$) by galvanostatic method (changing the voltage to get the desired current density). The stopwatch is started simultaneously. The treated solution is recycled back and the process is continued up to the desired time (10, 15, 20 minutes). The treated solution is analyzed on a fluorescence spectrophotometer from which the concentration of the treated sample is obtained. The fractional removal, indicating the efficiency of the process was calculated using the following equation:

$$Z = \frac{z_0 - z}{z_0}$$  \hspace{1cm} (1)

where $Z$ is the fractional removal efficiency of phenol and $z_0$ and $z$ are the initial and final phenol concentrations of sample.

2.5. Analytical approach- Calibration and analysis
The efficiency of electro-oxidation to treat the sample was evaluated by fluorescence spectrophotometry. The HITACHI F-4600 fluorescence spectrophotometer is used for the fluorescence analysis. For the fluorescence analysis, separate extraction is not required. It was calibrated using phenol solutions of various concentrations such as 1, 2, 3, 4, 5, 10, 20, 30 ppm. Fluorescence spectrometry is a fast, simple, and inexpensive method to determine the concentration of an analyte in solution based on its fluorescent properties. The concentration of the analyte is directly proportional to the intensity of the emission. The working parameters for fluorescence spectra analysis were an excitation wavelength of the range 240-360 nm and an emission range from 260-500 nm. The fluorescence emission spectra are obtained from the various samples taken from various concentrations of sample solution. The calibration curve is obtained from the fluorescence emission spectra.
3. Results and Discussion

3.1. Calibration
A set of known concentrations of phenol in water solution is prepared and the corresponding absorbances are measured using Fluorescence Spectrophotometer. The calibration curve obtained from the Fluorescence Spectrophotometer is obtained whose equation is:

\[-0.02X^2 + 2.1539X - 0.6229\]  \( (2) \)

3.2. Preliminary Investigations
The phenol solution of various concentrations (10, 20, 30 ppm) has been treated electrochemically using the electrochemical flow cell. The effect of operating time on the fractional removal of phenol was such that as the time proceeds phenol removal completion increases. When the time changes from 10 – 30min for 10 ppm phenol the removal rate increases from 93.31 - 95.11%. Similarly, for 20 and 30 ppm of initial concentration, the percentage removal changes from 86.59 - 88.47% and 44.94 - 67.31% respectively.

One of the important factors in the electrochemical oxidation of phenol is current density. On studying the variation of phenol degradation at different current densities ranging from 1 to 4A/dm² it was observed that the phenol removal completion was rapid at high current density and low initial phenol concentration. For 10 ppm of phenol concentration the removal rate increases from 88.82 to 94.98% with a current density of 1 and 4 A/dm² respectively.

On studying the effect of NaCl concentration on phenol removal it was observed that as the electrolyte (NaCl) concentration increases, the conductivity of the solution also increases. Under well-mixing condition NaCl electrolyses to form a dominant active substance (HClO) which was responsible for the fast degradation of phenol. Due to this the synergistic effect became predominant [11].

1. \( H_2O + MO_X \rightarrow MO_X[\cdot OH] + H^+ + e^- \)  \( (3) \)
2. \( 2Cl^- \rightarrow Cl_2 + 2e^- \)  \( (4) \)
3. \( Cl_2 + H_2O \rightarrow HClO + HCl \)  \( (5) \)

3.3. Detailed Investigation
The experimental domain, as shown in the table below has been decided from the results of preliminary investigation. The effect of current density, time, NaCl concentration and initial concentration on fractional removal of phenol was investigated using RSM.

| Table 1. Range of variables |
|---|---|---|
| Variables          | Range         |
| Time (minutes)     | -1 0 1        |
| Current density (A/dm²) | 2 3 4  |
| NaCl concentration (g/L) | 2 3 4  |
| Initial concentration (ppm) | 10 20 30 |

Using this domain and considering initial concentration, time, current density and NaCl concentration, 27 runs of the experiment were obtained from Response Surface Methodology. It is as shown below:
Table 2. Design of experiment and experimental response for electrochemical oxidation runs

| Sl No. | Time (minute) | Current density (A/dm²) | NaCl Conc. (g/L) | Initial Conc. (ppm) | Removal (%) |
|--------|---------------|-------------------------|------------------|---------------------|-------------|
| 1      | 5             | 2                       | 3                | 20                  | 29.25%      |
| 2      | 15            | 2                       | 3                | 20                  | 77.05%      |
| 3      | 5             | 4                       | 3                | 20                  | 73.95%      |
| 4      | 15            | 4                       | 3                | 20                  | 97.10%      |
| 5      | 10            | 3                       | 2                | 10                  | 75.10%      |
| 6      | 10            | 3                       | 4                | 10                  | 81.60%      |
| 7      | 10            | 3                       | 2                | 30                  | 37.23%      |
| 8      | 10            | 3                       | 4                | 30                  | 61.50%      |
| 9      | 5             | 3                       | 3                | 10                  | 38.40%      |
| 10     | 15            | 3                       | 3                | 10                  | 97.70%      |
| 11     | 5             | 3                       | 3                | 30                  | 43.23%      |
| 12     | 15            | 3                       | 3                | 30                  | 51.33%      |
| 13     | 10            | 2                       | 2                | 20                  | 39.50%      |
| 14     | 10            | 4                       | 2                | 20                  | 62.05%      |
| 15     | 10            | 2                       | 4                | 20                  | 52.35%      |
| 16     | 10            | 4                       | 4                | 20                  | 93.60%      |
| 17     | 5             | 3                       | 2                | 20                  | 30.80%      |
| 18     | 15            | 3                       | 3                | 20                  | 76.15%      |
| 19     | 5             | 3                       | 3                | 20                  | 53.00%      |
| 20     | 15            | 3                       | 4                | 20                  | 96.15%      |
| 21     | 10            | 2                       | 3                | 10                  | 51.40%      |
| 22     | 10            | 4                       | 3                | 10                  | 97.70%      |
| 23     | 10            | 2                       | 3                | 30                  | 34.50%      |
| 24     | 10            | 4                       | 3                | 30                  | 59.97%      |
| 25     | 10            | 3                       | 3                | 20                  | 97.70%      |
| 26     | 10            | 3                       | 3                | 20                  | 93.30%      |
| 27     | 10            | 3                       | 3                | 20                  | 95.50%      |

3.3.1. Model Development and Analysis. The response fractional removal of phenol under different combinations of electro-oxidation time, current density, supporting electrolyte (NaCl) concentration, and the initial concentration for the 27 sets of experimental conditions as proposed by the RSM design and are reported in Table 2.

The experimental data obtained were fit with a full quadratic model with regression coefficients. In addition to the intercept, linear, and quadratic terms, the model also reflects the two-way interactions through the incorporated interaction terms. The model can be represented as:

\[ y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \]

(6)

where \( y \) = fractional removal of phenol; \( \beta_0 \) = constant; \( \beta_1, \beta_2, \) and \( \beta_3 \) are the regression coefficients for linear effects; \( \beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}, \) and \( \beta_{34} \) are interaction coefficients. The coefficients of the model are as shown in Table 3. \( X_1 \) represents time, \( X_2 \) represents current density, \( X_3 \) represents NaCl concentration and \( X_4 \) represents initial phenol concentration.
Table 3. Estimated regression coefficients and corresponding t- and p-values for fractional removal of phenol

| Factors | Coefficients of model (uncoded factors) | t-value | p-value | Significance (%) |
|---------|-----------------------------------------|---------|---------|------------------|
| $\beta_0$ | -4.62759 | -7.96 | 0 | > 99% |
| $\beta_1$ | 0.25071 | 8.077 | 0 | > 99% |
| $\beta_2$ | 1.13246 | 6.422 | 0 | > 99% |
| $\beta_3$ | 0.825808 | 4.698 | 0.001 | > 99% |
| $\beta_4$ | 0.0929883 | 5.992 | 0 | > 99% |
| $\beta_{11}$ | -0.0060713 | -6.62 | 0 | > 99% |
| $\beta_{22}$ | -0.146396 | -6.38 | 0 | > 99% |
| $\beta_{33}$ | -0.158133 | -6.89 | 0 | > 99% |
| $\beta_{44}$ | -0.0019485 | -8.5 | 0 | > 99% |
| $\beta_{12}$ | -0.012325 | -2.33 | 0.038 | 96.20% |
| $\beta_{13}$ | -0.0011 | -0.21 | 0.839 | 16.10% |
| $\beta_{14}$ | -0.00256 | -4.83 | 0 | > 99% |
| $\beta_{23}$ | -0.04675 | 1.765 | 0.103 | 89.70% |
| $\beta_{24}$ | -0.0052075 | -1.97 | 0.073 | 92.7 |
| $\beta_{34}$ | 0.0044425 | 1.677 | 0.119 | 88.10% |

With the help of the foregoing model for fractional removal of phenol suggested by RSM, it was possible to forecast the fractional phenol removal for any combination of the four parameters into consideration within the experimental sphere of influence. The significance of the regression coefficients for fractional removal of phenol was analysed using p- and t-tests. The p, t and significance level (1 - p) are given in Table 3. It can be observed from the tables that all terms except some interaction terms significantly influence the response. The interaction term of time–salt concentration was the least influential terms in the model. The model equations obtained for the response (fractional removal of phenol) can be represented in terms of uncoded variables as:

$$ y = -4.62759 + 0.25071X_1 + 1.13246X_2 + 0.825808X_3 + 0.0929883X_4 - 0.0060713X_1^2 - 0.146396X_2^2 - 0.158133X_3^2 - 0.0019485X_4^2 - 0.012325X_1X_2 - 0.0011X_1X_3 - 0.00256X_1X_4 + 0.04675X_2X_3 - 0.0052075X_2X_4 + 0.0044425X_3X_4 $$ (7)

where $y$ represents fractional removal of phenol in uncoded units. Finally, graphical analyses of the data were done using ANOVA using Minitab 16 statistical analysis software. The model terms were evaluated by the p-value (probability) with a 95% confidence level and the statistical significance was checked by the Fisher F-test. The quality of the fit was expressed by the coefficient of determination, $R^2$ and adjusted $R^2$. The significance of the regression coefficients of the parameters on phenol removal was tested using Fisher’s F-test.

It should be noted that the time, current density, salt concentration, and initial phenol concentration were highly influential parameters for the electro-oxidation of phenol all with an associated p-values less than 0.05. Among the interaction terms, the time-initial phenol concentration and time-current density were shown to be most influential with a p-value less than 0.05. Further, the model competency was checked by computing the coefficient of determination $R^2$. The $R^2$ value can reveal how well the
The model reproduces the observed outcomes of the experiments. A high $R^2$ value for the coefficient guaranteed satisfactory representation of the proposed model compared to the experimental observations. Here, the value of $R^2$ was 97.77% for the fractional removal of phenol.

3.3.2. Combined Effect of Variables. The variation of fractional removal of phenol with the four parameters follows the pattern shown in the figure below. Figures explain the response surface plots showing the combined effect of the parameters on fractional removal of phenol. In each plot, two factors were varied, while the others kept constant. The plots were obtained from the second-order models of Equation (7).

From figure 2 it is clear that the current density and reaction time are directly proportional to phenol removal and a better performance of the system can be achieved by increasing current density which would accelerate the phenol removal [15]. This was similar to the individual effects. Higher current density produces more hydroxyl radicals (•OH) which is responsible for phenol removal. Time plays a vital role in the effectiveness of the electrooxidation process. Electrooxidation method would be more effective with a longer processing time [17].

The supporting electrolyte allows a better ion transfer in the vicinity of the electrodes and increases electrical conductivity. This will ultimately result in reduction in cell voltage and higher current
density. From figure 3, NaCl concentration was found to be directly proportional to the strength of oxidation. The increase in phenol oxidized with the increase in NaCl concentration can be explained with the help of formation of oxidizing species as indicated by the reaction (3-5) [16]. At a higher NaCl concentration, the Cl generation at anode increases and this along with the Cl-, ClO- and HClO would contribute to the oxidation of phenol.

From figure 4 it can be concluded that higher concentration of salt when combined with high CD gives higher fractional removal. The reason behind such observation is described above. From the results obtained from figure 5, it was concluded that maximum removal occurs at lower initial phenol concentrations and high NaCl concentration. Mesh type anode made of Ruthenium oxide coated on Titanium, performs well for electrochemical degradation of high concentration of phenol solution with appropriate current density and NaCl as supporting electrolyte.

3.3.3. Optimization for maximum phenol removal. The optimum operating conditions as predicted by the response optimizer tool of Minitab 16 is presented in figure 6. According to the prediction by the model the best set of operating condition giving the complete removal of phenol is Time: 9.27 min, Current density: 3.58 A/dm², supporting Electrolyte concentration: 3.29 g/L and Initial Concentration: 13.64 ppm.

| D 1.0000 | High | Low |
|----------|------|-----|
| Time (mi) | 15.0 | 5.0 |
| Current | 4.0 | [3.5758] |
| NaCl con | 4.0 | [3.2929] |
| Initial | 30.0 | [13.6364] |

Figure 6. The optimum operating conditions as predicted by the response optimizer

4. Conclusion
There has recently been heightened concern among scientists with regard to the effects of human and wildlife exposure to phenolic compounds in the environment, particularly the aquatic environment. Even though conventional biological treatment is a suitable process of degrading phenol, the treatment is slow because of its recalcitrant nature. The proposed quadratic regression model predicts the effect of important operating parameters on the completion of electrochemical oxidation process for phenol in the wastewater and reasonably optimizes the operating conditions. It showed a high coefficient of determination value (phenol removal R² value of 0.9777) thus ensuring satisfactory conformity of the second-order regression model with the experimental data. According to the prediction by the model the best set of operating condition giving the complete removal of phenol is Time: 9.27 min, Current density: 3.58 A/dm², supporting Electrolyte concentration: 3.29 g/L and Initial Concentration: 13.64 ppm.
The experimental results indicate that electrochemical oxidation is effective in pollutant removal and successfully reduced phenol content.

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