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# Indirect Electrochemical Oxidation of Phenol Using Rotating Cylinder Reactor

**Ammar S. Abbas[1], Mohammad H. Hafiz[2] and Rasha H. Salman[3]**
1,3Chemical Engineering Department - College of Engineering – University of Baghdad
2Engineering College – Iraqia University

## Abstract

Indirect electrochemical oxidation of phenol and its derivatives was investigated by using $MnO_2$ rotating cylinder electrode. Taguchi experimental design method was employed to find the best conditions for the removal efficiency of phenol and its derivatives generated during the process. Two main parameters were investigated, current density (C.D.) and electrolysis time. The removal efficiency was considered as a response for the phenol and other organics removal. An orthogonal array $L_{16}$, the signal to noise (S/N) ratio, and the analysis of variance were used to test the effect of designated process factors and their levels on the performance of phenol and other organics removal efficiency. The results showed that the current density has the higher influence on performance of organics removal while the electrolysis time has the lower impact on the removal performance. Multiple regressions was utilized to acquire the equation that describes the process and the predicted equation has a correlation coefficient ($R^2$) equal to 98.77%. The best conditions were found to get higher removal efficiency. Removal efficiency higher than 95% can be obtained in the range of C.D. of 96-100 $mA/cm^2$ and electrolysis time of 3.2 to 5 h. The behavior of the chemical oxygen demand (COD) mineralization denotes to a zero order reaction and the rate of reaction controlled by active chlorine reaction not by mass transfer of phenol towards the anode.

**Key words:** Phenol removal, COD removal, manganese dioxide, rotating cylindrical electrode, Taguchi method.

## Introduction

Petroleum refining is the physical, chemical, and thermal separation of crude oil into its main fractions and obtaining finished petroleum products through a series of separation and conversion steps. Petroleum refinery industry transforms crude oil into more than 2500 refined products, and large quantities of water are required for the purpose of attaining these products; about 80-90 % of the supplied water comes out as wastewater [1, 2].

The petroleum refinery wastewater is one of the worst contaminators of surface and ground waters and can cause detrimental environmental problems and tends to increase toxicity and creates the major environmental impact. In general, the effluent generated in the exploitation, production and refining of oil contains high concentrations of organic compounds with COD levels of approximately (300–600 ppm) and inorganic pollutants, sulphides, ammonia, chloride, 20–200 ppm of phenol, 1–100 ppm of benzene, heavy metals (0.1–100 ppm of chrome and 0.2–10 ppm of lead), suspended solids, grease and chemical additives. Consequently, these effluents need to be treated prior to discharge or reuse [3, 4].

Major consideration is paid to pollutants with an aromatic structure because they tend to be more toxic than their aliphatic complements. Aromatic compounds arise in many segments of the process industry, such as petroleum refineries, textiles, synthetic chemical plants, pulp and paper, detergent, plastics, pharmaceutical factories, pesticide, and herbicide. Water effluents containing aromatic chemicals are refractories, and are often toxic to biological treatment processes. Phenols are aromatic compounds enclosing one or more hydroxyl groups attached to the aromatic ring. Phenols are one of the widely distributed toxic substances and have been classified as one of the 65 priority pollutants which are considered to be harmful to humans and the environment and their presence must be limited to 0.1 mg/L [5– 7].

Conventional wastewater treatment involves a series of mechanical, physical, chemical, and biological operations and processes, but these processes are not always preferred and have many limitations. Electrochemical technologies for removal of organics from petroleum refinery wastewater and wastewater of other industries have a great attention hence they offer many distinctive advantages relative to the other technologies such as; Compatibility with Environment, Adaptability, Energy efficiency, Selectivity, Safety, Flexibility to automation, and Cost effectiveness [8, 9].

In electrochemical process, the destruction of organic pollutants may take place by either direct or indirect oxidation process. In the direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then removed by the anodic electron transfer reaction. It is well known that removal of phenol by direct electrochemical oxidation process causes a rapid fouling to the surface of employed electrode (such as graphite, platinum, ruthenium dioxide, lead dioxide, and tin dioxide) due to formation of a blocking polymer layer created by the polymerization of the phenoxy radicals produced in the initial stages of the reaction. This results in decreasing the active surface area of the electrode and a termination of the reaction within minutes [10].

In indirect oxidation process, strong oxidants such as hypochlorite/chlorine, hydrogen peroxide, ozone are electrochemically produced. The pollutants are then removed in the bulk solution by oxidation reaction of the produced oxidant. The effectiveness of the electrochemical oxidation process and its performance enhanced by the addition of high concentrations of chloride ions in water; beside it can decrease its energy consumption. All the oxidants are produced in situ and are utilized immediately. The electrochemical method is one of the methods of oxidizing phenols which making it possible to attain an oxidant at the site of consumption and rapidly regulate the parameters of electrolysis. Since oxidation of phenol in the absence of mineral salts continues gently, the oxidizing process is conducted against the background of chlorides. The chief oxidizing agent in electro-oxidation in chloride solutions was activated chlorine formed in the water being treated as a result of anodic oxidation of chloride ions and subsequent chlorine hydrolysis. Activated chlorine presence speeds up the treatment process.

Sodium chloride (NaCl) is a very good choice hence it is easily available at reasonable cost, it is able to increase the electrical conductivity of the wastewater to a suitable level [11– 13].

During the process of electrochemical oxidation of phenol, several aromatic and aliphatic intermediates are generated which they are more poisonous than phenol. Consequently, COD removal is very difficult in comparison with phenol removal because of the complex nature of COD and hence there are some intermediates can form, it is better to take the COD as a response as an alternative of phenol concentration. Moreover, longer electrolysis time is required for COD reduction compared to phenol removal. The energy consumption can be increased due to the extension of electrolysis time. So, the removal of organic contaminants in a very short time period makes the electrochemical method satisfactory for the industrial wastewater treatment applications. It can be concluded that an electrochemical method is successful for COD removal if it is successful for phenol removal, and vice versa [3, 14].

Most common anode materials used in wastewater treatment are graphite, lead/lead dioxide, nickel, platinum, $SnO_2$-Sb, and boron doped diamond (BDD). These electrodes have some disadvantages, graphite is unstable or it could be oxidized to CO or $CO_2$. Using $PbO_2$ electrode is not favorable due to the need for lead removal from the treated solution. $SnO_2$-Sb electrode has problems with deactivation and short service life. High anodic stability and a wide potential window for water discharge are one of the most advantages of BDD; however, the limitation of using it efficiently for wastewater treatment is still restricted by its high cost, mechanical resistance problems and difficulties in finding a suitable substrate on which to deposit the thin diamond layer. The investigation of cheaper materials with analogous performances have attracted a great effort among these, manganese oxides ($MnO_x$) materials represent an attractive family for electrode manufacture, this is due to their unique structures, good electrochemical properties, good electrocatalytic properties, the relatively low cost, low toxicity, environmentally friendly character in comparison with other transition metal oxides, the natural abundance, and chemical stability [10, 13, 15].

The aim of the present study are applying galvanostatic conditions in the process of indirect electrochemical oxidation of phenol and its derivatives from a simulated wastewater and examining the performance of this batch electrochemical reactor by using the Taguchi method. The purposes of Taguchi approach were studying the effect of two parameters (C.D., and electrolysis time) on the removal efficiency using $L_{16}$ orthogonal array experimental design, and determining the degree of significance of the studied factors on the removal efficiency using analysis of variance (ANOVA).

## Experimental Work

### 1. Materials and System

150 mg of phenol was dissolved in 1 L of distilled water for the preparation of simulated wastewater (which is equivalent to 315 mg/l of COD), and 1 g/l of NaCl, 0.1 M $H_2SO_4$ (as a supporting electrolyte) added also, all chemicals used in experiments

were of the reagent grade. The electrochemical cell consists of (2 liters) capacity glass reservoir fixed on a hot plate magnetic stirrer (LABINCO, model L-81), DC power supply (UNI-T: UTP3315TF-L) was used with outlet voltage (0-30 V) and output current (0-5 A). A cylindrical $MnO_2$ on graphite substrate (with 30 $cm^2$ as the effective area) was used as the anode. The cathode was a graphite hollow cylinder with an inside diameter of 8 cm and an outside diameter of 10 cm and 15 cm length fixed in the glass electrolytic bath. The electrical connection of the rod was achieved by a cylindrical brass ring, and the rod insulated from the holder by a piece of Teflon. To rotate the anode with the required rotation speed, an electrical gear box stirrer (Heidolph) was used with electronic tachometer and the speed of rotation was 200 rpm. A schematic diagram of the electrochemical process is shown in Figure 1.

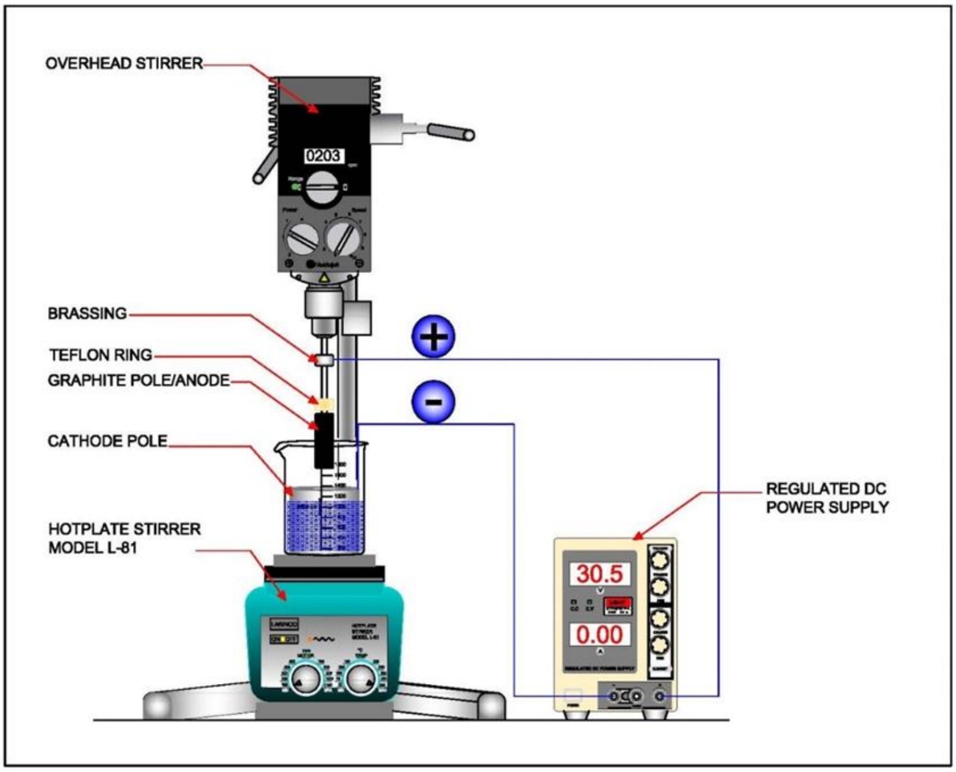

Fig. 1: schematic diagram of the electrochemical system

## 2. Procedure

- After the preparation of electrolytic solution, the cathode electrode which was the hallow cylinder graphite was dipped into the electrolytic solution, and the $MnO_2$ anode electrode was fixed to the agitator and dipped into the electrolytic solution.
- The electrodes were connected to the DC power supply and a constant current density was applied to the electrolytic cell for a specified time and rotation speed of the electrical stirrer.
- The samples were collected during the electrolysis process, and the temperature of the electrolyte was maintained about 25°C ±1.

Taguchi design approach was used to study the effect of the two parameters on the removal efficiency of phenol and any other by products which was measured by the COD at the end of each experiment by using a COD reactor (Lovibond Water Testing, RD 125 model) where 2 ml of the sample was added to a vial containing a standard amount of a potassium dichromate oxidizing mixture. The phenol and any other organics exist in the sample would be oxidized for 2h at 150 °C. The vial was allowed to cool to room temperature and then a Photometer- System MD200 (Lovibond Water Testing) was used to measure the COD.

## 3. Taguchi Design

Full factorial design is a traditional optimization approach which involves a large number of experiments because it would take all possible combinations for studied variables. This approach is not useful because of time consuming and high operational cost [16].

Another method in the experimental design is called Taguchi method. Taguchi method can be used to determine the effect of factors on distinctive properties and the optimal conditions of the studied parameters. The determination of the possible combinations of factors and identification of best combinations can be easily achieved by this method [17, 18].

The Taguchi method uses a distinct design of orthogonal arrays. The Orthogonality means that factors can be evaluated individually from one another; the effect of one factor cannot be affected with the evaluation of the influence of another factor [19].

The variables considered for the study are time (t), and C.D. since they have a powerful effect on the performance of electro-oxidation process [20, 21], these variables and their levels are illustrated in Table 1, where four levels of each parameter were chosen. The suitable orthogonal array which allows the investigating of the effect of the considered parameters and the interaction between them for these levels would be $L_{16}$; either ($4^2$), and the experiments under the same conditions were carried out as shown in Table 1. Each row in this table represents one experimental run. The four values of time and C.D. were studied at four values (2, 3, 4, and 5 h) and (25, 50, 75, and 100 mA/cm$^2$), respectively, corresponding to levels 1, 2, 3, and 4.

Table 1: Coded & real values of $L_{16}$ orthogonal array

| **Exp. No.** | **Coded Values** | | **Real Values** | |
|---|---|---|---|---|
| | **A** | **B** | **C.D. (mA/cm$^2$)** | **Time (h)** |
| 1 | 1 | 1 | 25 | 2 |
| 2 | 1 | 2 | 25 | 3 |
| 3 | 1 | 3 | 25 | 4 |
| 4 | 1 | 4 | 25 | 5 |
| 5 | 2 | 1 | 50 | 2 |
| 6 | 2 | 2 | 50 | 3 |
| 7 | 2 | 3 | 50 | 4 |
| 8 | 2 | 4 | 50 | 5 |
| 9 | 3 | 1 | 75 | 2 |
| 10 | 3 | 2 | 75 | 3 |
| 11 | 3 | 3 | 75 | 4 |
| 12 | 3 | 4 | 75 | 5 |
| 13 | 4 | 1 | 100 | 2 |
| 14 | 4 | 2 | 100 | 3 |
| 15 | 4 | 3 | 100 | 4 |
| 16 | 4 | 4 | 100 | 5 |

## Results and Discussion

Taguchi design of experiment (DOE) technique was applied at the present study to examine the most manipulating factors on COD removal efficiency, to find the best conditions of C.D., and time of electrolysis for organic pollutants removal. The $L_{16}$ orthogonal array results illustrated in Table 2; the experimental data were analyzed using MINITAB 17 software.

Table 2: Results of experimental design for organics removal, *COD initial value= 315 ppm

| Exp. No. | Real values | | Response | | |
|---|---|---|---|---|---|
| | **C.D.(mA/cm$^2$)** | **Time(h)** | **COD(ppm)** | **Removal efficiency (%)** | **S/N** |
| 1 | 25 | 2 | 290 | 7.9365 | 23.5461 |
| 2 | 25 | 3 | 246 | 21.9048 | 27.3517 |
| 3 | 25 | 4 | 188 | 40.3175 | 30.1682 |
| 4 | 25 | 5 | 115 | 63.4921 | 31.9016 |
| 5 | 50 | 2 | 236 | 25.0794 | 28.4772 |
| 6 | 50 | 3 | 199 | 36.8254 | 32.2829 |
| 7 | 50 | 4 | 122 | 61.2698 | 35.0994 |
| 8 | 50 | 5 | 75 | 76.1905 | 36.8327 |
| 9 | 75 | 2 | 154 | 51.1111 | 31.6877 |
| 10 | 75 | 3 | 116 | 63.1746 | 35.4933 |
| 11 | 75 | 4 | 88 | 72.0635 | 38.3098 |
| 12 | 75 | 5 | 59 | 81.2698 | 40.0432 |
| 13 | 100 | 2 | 58 | 81.5873 | 34.6706 |
| 14 | 100 | 3 | 19 | 93.9683 | 38.4763 |
| 15 | 100 | 4 | 5 | 98.4127 | 41.2928 |
| 16 | 100 | 5 | 3.15 | 99.0000 | 43.0261 |

## 1. Main Effect Plots

The relationship between the studied parameters and output response can be visualized by main effect plot. Figure 2 represents the Main effect plot for the COD removal efficiency (%) using indirect electrochemical oxidation process (i.e., electro-oxidation of organics in the presence of NaCl), where 1 g/l of NaCl was added to the electrolytic solution. It is well-known that the phenol removal is achieved by the reactive chlorine species such as chlorine and hypochlorous acid or hypochlorite ion ($Cl_2$, HOCl and $OCl^-$) that react very fast with organics chiefly by the reactions in solution. Free chlorine is the dominant oxidizing agent in acidic conditions, while in slightly alkaline conditions hypochlorite, chloride ions and hydroxyl radicals are all produced in appropriate concentrations [22]. The HOCl generation increases as the C.D. also increases, therefore the organic removal efficiency increased. The organic removal also governed by the electrolysis time, the generation of HOCl increases with time increasing.

## 2. Signal –to- Noise

A basic signal- to-noise (S/N) ratio is a quantitative measure that employed by Taguchi method to determine the optimum removal conditions, besides it used for the evaluation of the variation of the response around the mean value due to experimental noise, so an optimal response with smaller variations can be obtained. The terms ‘signal’ to ‘noise’ ratio signify the desirable (mean for the output characteristic) and undesirable values (standard deviation (SD) for the output characteristic) for the output response, respectively. The analysis of means and S/N ratio that recommended by Taguchi uses a theoretical approach that includes plotting the effects and visually recognizing the factors that appear to be significant, without the need for ANOVA analysis, so the analysis would be very simple [23, 24] .

The choice principles of S/N ratio depend on the objective of the design; The S/N ratios are different according to the type of output response. Generally, a better signal attained when the noise is smaller, so that a larger S/N ratio yields better results. Therefore, the optimal level of process parameters is the level with the highest S/N ratio. Usually, there are three types of S/N ratios, higher is best (HB), nominal-is-best (NB), and lower is best (LB) to choose from. For each level of the process parameters, the S/N ratio computed based on the S/N analysis [25].

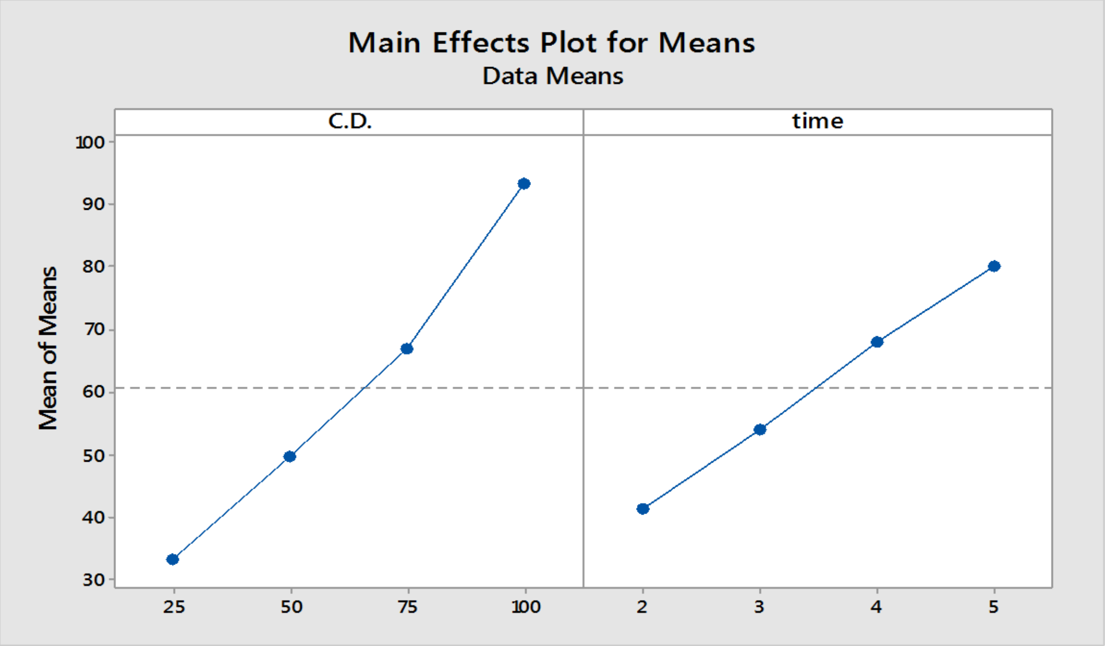

Fig. 2: Main effect plot for organics removal efficiency

In order to maximize the removal efficiency the bigger is better approach is implemented, in which the S/N ratio is calculated as presented in Equation 1 [26]:

$$S/_N = -10 \log\left[\frac{1}{n}\left(\sum_{i=1}^{n}\frac{1}{y_i^2}\right)\right] \quad \ldots(1)$$

Where $y_i$ is the response of each experiment, and n is the repetition number of each experiment.

S/N ratio can reflect both the average and the variation of the quality characteristics; so, it merges several repetitions into one value which reflects the amount of variation present [16].

Table 2 shows the S/N ratios calculated based on Equation 1 for all the responses of experiments.

The effect of each control parameter on the response obtained from the response Table 3 for S/N which represented graphically in Figure 3. This table contains ranks based on delta statistics, which compare the relative magnitude of effects. The highest average for each factor minus the lowest average for the same called the delta statistics. Rank 1 is assigned to the highest delta value, rank 2 to the second highest delta value; and so on, so ranks are assigned based on delta values [27]. Therefore, the values of delta in this table indicate that the current density has the greatest influence on the organic removal followed by time, and speed of rotation.

In the main effect plot of S/N ratio, the x-axis point to the value of each process parameter at three levels and the y-axis is the response S/N values. The main effect plots used to determine the optimum conditions of the design, so obtaining the optimal value of the responses.

According to the main effect plot of S/N ratio, the best conditions for the organic removal are current density of 100 mA/cm$^2$, and electrolysis time of 5 h. These conditions are the conditions of run (16), so no confirmation step is required in this analysis. The COD removal efficiency was 99 %.

Table 3: Response Table for Signal to Noise Ratios (bigger is better)

| Level | C.D. | Time |
|---|---|---|
| 1 | 28.24 | 29.60 |
| 2 | 33.17 | 33.40 |
| 3 | 36.38 | 36.22 |
| 4 | 39.37 | 37.95 |
| Delta | 11.12 | 8.36 |
| Rank | 1 | 2 |

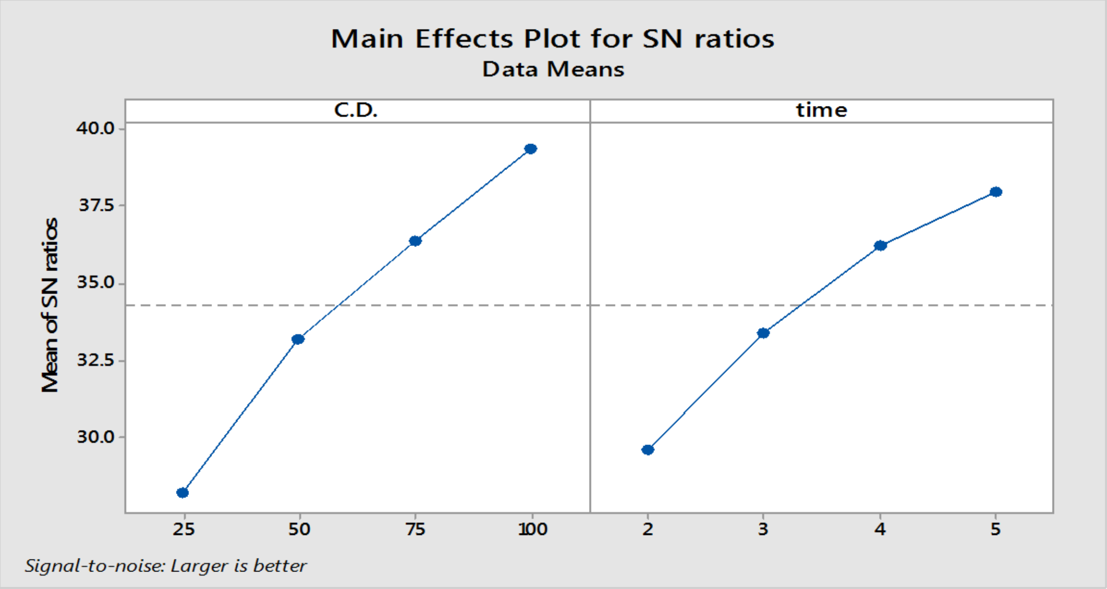

Fig. 3: Main effect plots of SN ratios for removal efficiency of phenol and other organics

## 3. Analysis of Variance (ANOVA)

The utilization of ANOVA by Taguchi method is a very good implement to find out which are statistically the most significant parameter and to find out the value of percentage contribution of each factor to a change in the dependent variable. Analysis of variance on the experimental results accomplished to determine the variation source during the process of indirect electrochemical oxidation of the organics; then the identification of the effect order of factors on the organics removal would relatively be easy [28].

The ANOVA was established based on the degree of freedom (DF), the sum of the square (SS), the percentage contribution of each parameter, adjusted sum of squares (Adj SS), adjusted mean of square (Adj MS), F-value, and P-value. The statistical expressions of these terms can be defined in many books and studies dealing with experiments design and analysis [29].

Any factor has a high percent contribution; then a small variation in its magnitude will have a great influence on the performance. The percentage contribution for each parameter defied as the portion of a total observed variance in the experiment for each significant parameter. When the value of this percentage contribution is greater, then it contributes to the final results more than other factors [26].

The results of the ANOVA summarized in Table 4. As in the S/N ratio analysis, it is obvious that the significance of the factors succeeds in the following order of importance: C.D.> electrolysis time.

The data given in Table 4 showed that the contributions of the two factors i.e. C.D., and time of electrolysis were 66.03 and 28.37%, respectively. It is clear that current density has the greatest contribution on organic removal followed by electrolysis time.

Statistically, the F value for each studied parameter is the ratio of the mean of squared deviations to the mean of squared error. For the present condition, the value of $F_{(1,\ 15)}$ with 95% confidence level is 4.2417 [30]. Generally, when F>4, it means that the studied parameter is significant and the variation of it makes a big change on the performance [18].

It is obvious from the results of F value in Table 4 that all the two studied parameters are significant since all of them have F> 4.

The significance of each factor on response is determined by P-value. If p-value value < 0.05 (for a confidence level of 95%) indicates that the factor is significant. P-values in this study < 0.05 (for a confidence level of 95%); indicate that all model terms are significant.

Measuring the proportion of the total variability explained by the model is called the $R^2$ static, is close to (1) for our response. The same result acquired with respect to the adjusted $R^2$, which used for considering the model significance since it is convenient when comparing the model with different number of terms. The results illustrate that adj.$R^2$ is not suggestively different from the ordinary $R^2$.

Residual plots used to calculate the adequacy of the model. The residual plots for phenol and other organic removal are presented in Figure 4.

The descriptions of each residual plot for the present experiments known as followed:

- Normal probability plot point out that the data are normally distributed and the variables are manipulating the response. There are no Outliers existing in the data.
- Histogram proves that the data are not skewed and no outliers exist.
- Residuals versus fitted values indicate that the variance is constant and a non-linear relationship exists. Ideally, the points should fall randomly on both sides of zero.
- Residuals versus order of the data indicate that there are systematic effects in the data due to time or data collection order.

Table 4: Analysis of Variance for organic removal efficiency

| **Source** | **DF** | **Seq SS** | **Contribution** | **Adj SS** | **Adj MS** | **F-Value** | **P-Value** |
|---|---|---|---|---|---|---|---|
| **C.D.** | 3 | 7839.6 | 66.03% | 7839.6 | 2613.20 | 35.35 | 0.000 |
| **Time** | 3 | 3368.7 | 28.37% | 3368.7 | 1122.89 | 15.19 | 0.001 |
| **Error** | 9 | 665.3 | 5.60% | 665.3 | 73.92 | - | - |
| **Total** | 15 | 11873.6 | 100.00% | - | - | - | - |
| **General Linear Model** | S<br>8.59764 | R-sq<br>94.40% | R-sq(adj)<br>90.66% | PRESS<br>2102.60 | R-sq(pred)<br>89.29% | - | - |

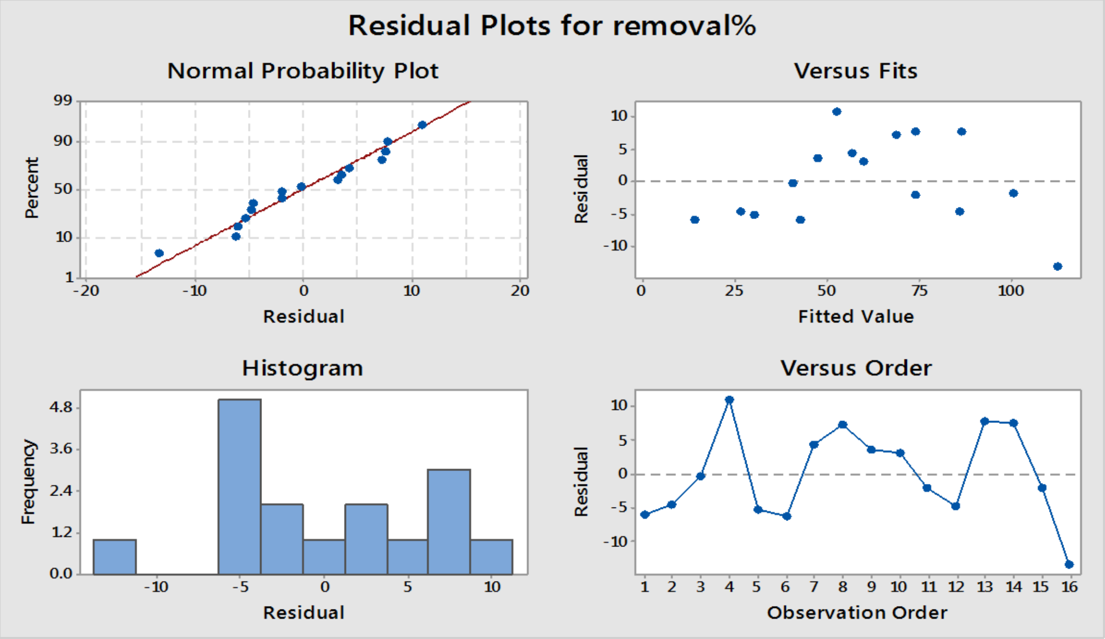

Fig. 4: Residual plots of organics removal efficiency

## 4. Multiple Regression Analysis

The multiple regression model for COD removal efficiency is as follows:

$$COD\ removal\% = -61.87 + 0.940\,X_1 + 24.56\,X_2 + 0.0039\,X_1^2 - 0.1854\,X_1.X_2 \quad \ldots(2)$$

Where $X_1$ is current density and $X_2$ is electrolysis time. The predicted equation had the squared value of the correlation coefficient ($R^2$) equal to 98.77% with error percentage equal to 2 %.

Contour plot presented in Figure 5 clarifies that the best conditions for getting removal efficiency > 95% are C.D. within the range 96-100 mA/cm$^2$, and time of 3.2-5 h. Using 100 mA/cm$^2$ gives removal efficiency > 95% within 3.2 h, while using 90 mA/cm$^2$ gives it within 5h.

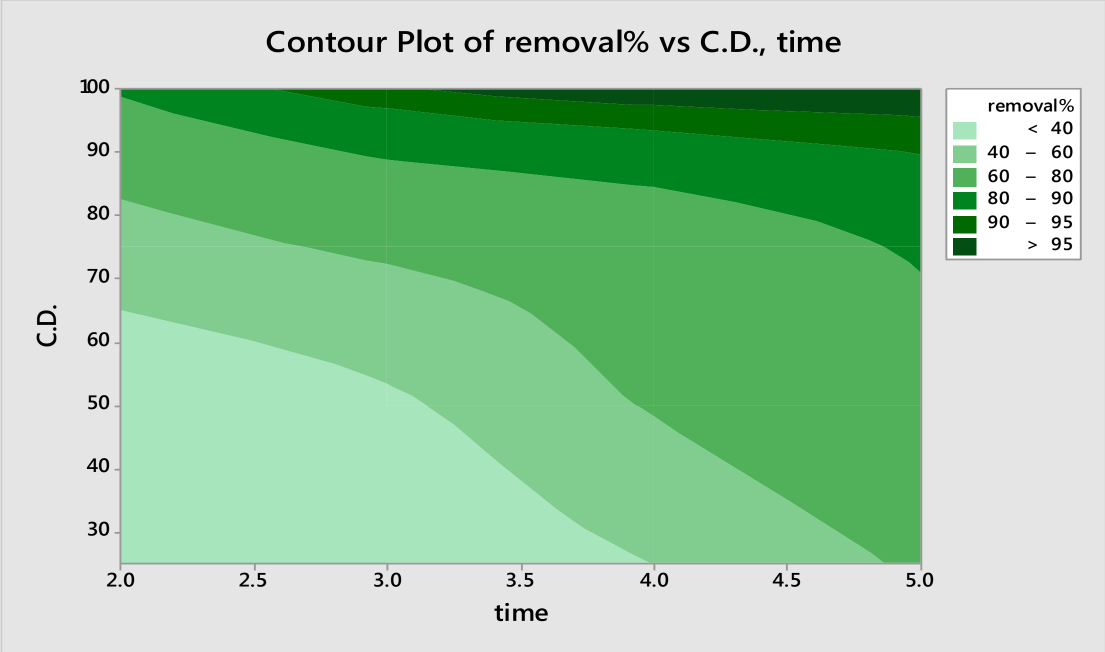

Fig. 5: Contour Plot of removal efficiency versus C.D. (mA/cm$^2$) and Time (h)

The decay in COD affected intensely by the concentration of chloride ion ($Cl^-$) and by the operational variables (current and voltage). The effects of current densities on COD are presented in Figure 6. Phenol removal succeeded by the reactive chlorine species (i.e., hypochlorous acid (HOCl)), which is the dominant oxidizing agent in acidic conditions. The COD decreased and removal percentage increased with the C.D. increasing. As the C.D. increases from 30 to 90 mA/cm$^2$, the COD decreases linearly from 315 to 110.61, and 18.34 ppm, respectively. While the removal efficiency increases from 64.88 to 94.17 % respectively. The linear behavior of the COD reduction under different current densities refers to a zero order reaction and the rate of reaction controlled by active chlorine reaction not by mass transfer of phenol towards the anode. These results are in agreement with previous studies done by other workers [15, 21, 31].

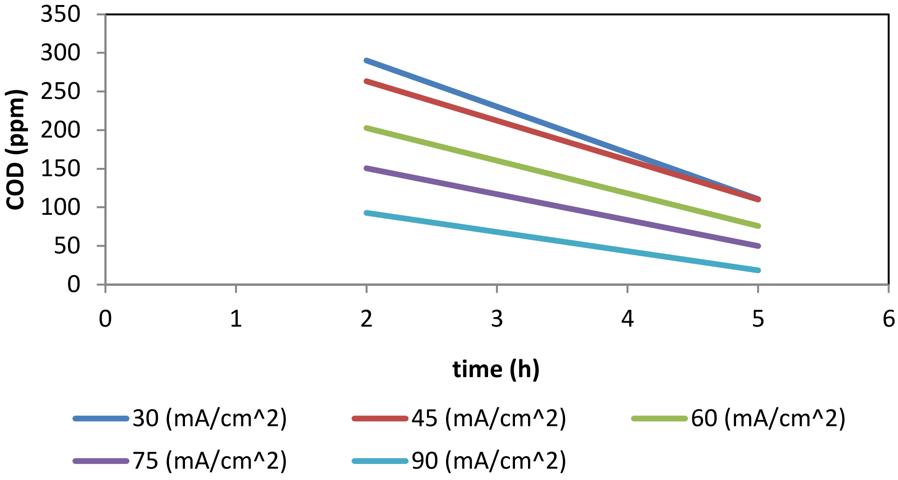

Fig. 6: COD vs. electrolysis time at different current densities for rotating $MnO_2$ cylinder electrode, $COD_o$=315 ppm

## Conclusion

Removal of phenol has been studied in the present work by indirect electrochemical oxidation and a DOEs (derived from the Taguchi approach technique) was applied to observe the best experimental conditions, C.D. and time designated as the studied parameters, and these factors varied at four levels with an orthogonal array of $L_{16}$, which could examined with the bigger is better as a quality character. Taguchi analysis suggested that C.D. has the largest influence on the performance of electrochemical removal of phenol and other organics. Based on The results of the ANOVA, it can be established that the significance of the factors has the following order of importance: C.D. followed by the electrolysis time. Based on Taguchi multiple regression model, the best conditions for removal efficiency of COD equal to 99%, were C.D. of 100 mA/cm$^2$ and electrolysis time of 5 h.

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