Electrocoagulation treatment of automobile wastewater: optimization by RSM

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Abstract. In this study automobile, wastewater treatment was carried out using the batch mode electrocoagulation process. The Electrocoagulation process was optimized using response surface methodology. The central composite design was applied on four variable parameters were selected pH, electrolysis time (ET), the distance between electrodes (DE), and current (C) over depended response variable COD. The experiment was conducted as per the experimental run generated by the software. At optimum condition pH= 5.84, ET= 71.40 min, DE= 0.62 cm and C= 3.50 A COD removal was 91.53%. Applied model design is shown significance in terms of p-value less than 0.05 with a higher F value. ANOVA results show adequacy between predicted and observed experimental data. The correlation coefficient between predicted data and observed data was more than 0.90.

1. Introduction
Water is a necessity in commercial and domestic activities and all industrial processes, so the effluent generated from these different activities contains contaminants harmful both for flora and fauna existing on the planet [1]. The pollution control board had instructed automobile service stations to provide necessary effluent treatment before discharging [2]. Professional automobile systems generate wastewater that can greatly impact the environment if not properly managed and discharged. Contaminants in automobile wastewater include detergents, oil, and grease, hydrofluoric acid, phosphates, ammonium bifluoride products (ABF), etc [3-4]. Detergent and oil and grease, including biodegradable detergents, can be poisonous to aquatic life [4]. On the other hand, phosphates, which are plant nutrients, can cause excessive growth of nuisance plants in water bodies. Hydrofluoric acid, ammonium bifluoride products are harmful to living organisms [4]. Electrocoagulation is a simple and efficient electrochemical process that uses flocculating agents produced by oxidation of sacrificial electrodes [5-6]. Electrocoagulation has been successfully used to treat different kinds of wastewater, such as acid mine drainage discharge and industrial effluent, as well as natural water [7-10]. The electrocoagulation process is applied to remove a wide range of pollutants, such as arsenic, chromium, phosphate, nutrients, color, fluoride, and chemical oxygen demand [9-12]. Treatment using EC involves a confluence of effects from various parameters such as initial pH, time of operation, distance between the electrodes, and current [13]. Keeping in mind the interaction between these parameters in the treatment of wastewater using EC is a challenge. Experiments are performed in conventional methods by varying one process parameter by keeping other parameters as constant [14]. To avoid this procedure for all parameters and to reduce the total number of experimental runs, response surface methodology (RSM) involving a suitable design of experiments (DOE) may be employed. This
approach not only minimizes the number of experiments to be performed but also permits exploration of nonlinear (quadratic) interaction effects between various process parameters [15]. This study aims to perform a batch process of electrocoagulation using aluminum electrodes by using central composite design (CCD) to find the optimum process condition and determine individual, interactive and quadratic effects of process parameters on electrocoagulation treatment.

2. Material and methods

2.1 Wastewater collection

The wastewater sample was collected from various automobile service stations and garages at Raipur city and mixed for further analysis. Water is stored at 4°C. The parameters considered for automobile wastewater are hardness, pH, chemical oxygen demand (COD), total dissolved solid is determined as per standard method given in APHA [16].

| Sr No. | Parameters                          | Value BT* | Value AT* |
|-------|------------------------------------|-----------|-----------|
| 1     | pH                                 | 6.44-7.50 | 8.0       |
| 2     | Chemical Oxygen Demand (COD) (mg/L)| 750-860   | 70        |
| 3     | Total Solid (TS) (mg/L)            | 266       | 160       |
| 4     | Total Suspended Solid (TSS) (mg/L) | 56        | 40        |
| 5     | Total Dissolved Solid (TDS) (mg/L) | 210       | 120       |
| 6     | Hardness (mg/L)                    | 100-120   | 90        |
| 7     | Conductivity (µS/cm)               | 384       | 285       |
| 8     | Surfactant (mg/L)                  | 2.33-2.40 | 0.7       |
| 9     | Color (PCU)                        | 118       | 75        |

*BT=Before Treatment; AT=After Treatment

2.2. Experiment procedure

The EC treatment was conducted in a batch operation using a cuboidal reactor made up of acrylic sheets, as shown in Figure 1. For each experiment, 1.5 L wastewater was used. Four aluminum electrodes with dimensions 100 x 100 x 150 cm assembled parallel to each other with varied electrode spaces. Electrodes were connected to negative and positive DC power supply terminal (0-5A, 0-30V). A magnetic stirrer was used for the uniform mixing of wastewater during the experimental run. The solution pH was adjusted by the dropwise addition of 1N H₂SO₄ and 1N NaOH solutions for the experimental runs. Experiments were performed by varying the four factors viz. applied current, pH, electrode space, and reaction time. For analysis, 50 mL samples were taken before and after treatment of each experimental run.

![Figure 1. Experimental set up utilize for electrocoagulation experiment.](image)
2.3. Experimental design

The experimental run order was design using Central composite design (CCD) models of Design-Expert Software. In this design, four independent variable applied current, distance between the electrode, pH and electrolysis time were chosen since they are directly related to operational preference. The CCD with four factors is applied using the limits of the independent variables presented in Table 2. The limit of the variables was decided based on a few preliminary runs. A total number of 30 experiments were considered as standard DOE. To ensure the reliability of the collected data, each trial in Table 3 was replicated three times. The response was obtained in terms of percentage removal of the COD.

**Table 2.** Chosen variables levels and coded values for a set of experiments

| Factor | Name | Unit | Minimum | Maximum | Coded Low | Coded High | Mean | Std. Dev. |
|--------|------|------|---------|---------|-----------|-----------|------|-----------|
| A      | pH   | -    | 3.00    | 10.00   | -1 ↔ 3.00 | +1 ↔ 10.00 | 6.50 | 2.76      |
| B      | ET   | Min  | 20.00   | 75.00   | -1 ↔ 20.00 | +1 ↔ 75.00 | 44.50 | 21.99     |
| C      | DE   | Cm   | 0.50    | 5.00    | -1 ↔ 0.50 | +1 ↔ 5.00  | 1.35 | 0.60      |
| D      | C    | A    | 1.00    | 5.00    | -1 ↔ 1.00 | +1 ↔ 5.00  | 3.00 | 1.58      |

**Table 3.** Design of experiments generated by central composite design.

| pH     | Electrolysis | Distance b/w electrodes(cm) | Current | O | COD (%) | P |
|--------|--------------|------------------------------|---------|---|---------|---|
| 3.00   | 20.00        | 0.50                         | 5.00    | 60.43 | 56.55   |
| 10.00  | 20.00        | 2.00                         | 5.00    | 64.33 | 68.63   |
| 6.50   | 40.00        | 0.50                         | 3.00    | 72.25 | 85.04   |
| 6.50   | 40.00        | 1.50                         | 3.00    | 96.54 | 92.43   |
| 3.00   | 20.00        | 2.00                         | 1.00    | 45.32 | 46.32   |
| 6.50   | 40.00        | 1.50                         | 3.00    | 96.54 | 92.43   |
| 10.00  | 75.00        | 0.50                         | 5.00    | 86.45 | 82.49   |
| 6.50   | 40.00        | 1.50                         | 3.00    | 96.54 | 92.43   |
| 10.00  | 75.00        | 2.00                         | 5.00    | 83.22 | 82.05   |
| 6.50   | 40.00        | 1.50                         | 1.00    | 78.98 | 83.31   |
| 3.00   | 75.00        | 0.50                         | 1.00    | 68.67 | 61.44   |
| 10.00  | 20.00        | 0.50                         | 5.00    | 66.62 | 65.46   |
| 6.50   | 75.00        | 1.50                         | 3.00    | 96.00 | 93.55   |
| 6.50   | 40.00        | 2.00                         | 3.00    | 90.32 | 85.75   |
| 3.00   | 75.00        | 2.00                         | 5.00    | 72.55 | 76.30   |
| 6.50   | 20.00        | 1.50                         | 3.00    | 68.78 | 79.44   |
| 6.50   | 40.00        | 1.50                         | 5.00    | 95.56 | 99.45   |
| 3.00   | 40.00        | 1.50                         | 3.00    | 69.98 | 73.98   |
| 10.00  | 75.00        | 0.50                         | 1.00    | 58.54 | 64.21   |
| 6.50   | 40.00        | 1.50                         | 3.00    | 96.54 | 92.43   |
| 3.00   | 20.00        | 0.50                         | 1.00    | 43.38 | 45.44   |
| 10.00  | 20.00        | 2.00                         | 1.00    | 52.59 | 51.03   |
| 6.50   | 40.00        | 1.50                         | 1.00    | 57.73 | 50.76   |
| 3.00   | 75.00        | 0.50                         | 3.00    | 96.54 | 92.43   |
| 6.50   | 40.00        | 1.50                         | 3.00    | 73.45 | 76.13   |
| 3.00   | 75.00        | 2.00                         | 1.00    | 56.65 | 58.71   |
| 10.00  | 75.00        | 2.00                         | 1.00    | 60.22 | 60.87   |
| 3.00   | 20.00        | 2.00                         | 5.00    | 64.78 | 60.33   |
| 10.00  | 40.00        | 1.50                         | 3.00    | 75.54 | 79.76   |

*O=Observed Value; P=Predicted Value*
3. Result and discussion
A second-order polynomial equation was successfully used for describing automobile wastewater COD percentage removal. The equation was reduced due to the presence of a statistical insignificant term polynomial equation. The equation in terms of coded variables can be presented in the following:

\[ \text{COD(\%)} = 95.82 + 2.77A + 7.36B + 6.1093C + 8.07D - 0.6369AB - 0.1514AC \\
+ 0.8969AD - 0.9025BC + 0.8957BD + 0.7260CD - 15.56A^2 - 8.49B^2 - 7.79C^2 - 1.05D^2 \]

3.1. Fit analysis
The coefficient of regression (R\(^2\)) is an important parameter to check the quality of the model and its prediction capacity. For the best model, fit R\(^2\) should be greater than 0.80 [17]. In the present study values, R\(^2\) for COD removal is greater than 0.80, as shown in Table 4. This shows the good adequacy of the model. Adj. R\(^2\) value greater than 0.80 indicates that the model terms are significant. R\(^2\) value verification similar data graph was plotted between the observed and predicted data shown in Figure 2.

| Std. Dev. | Mean  | R\(^2\)  | Adj. R\(^2\) |
|----------|-------|----------|--------------|
| 6.89     | 74.72 | 0.9135   | 0.8328       |

Table 4. Fit statistics summary for chosen quadratic model design.

Figure 2. Regression plot between observed and predicted data.
3.2. ANOVA Analysis
The ANOVA, Table 5, allows analyzing the significance and interaction between variables. The variables chosen for this investigation are pH, electrolysis time (ET), the distance between the electrodes (DE), and current (C).

Table 5. ANOVA analysis results for COD removal.

| Source | Sum of Squares | df | Mean Square | F-value | p-value |
|--------|----------------|----|-------------|---------|---------|
| Model  | 7511.44        | 14 | 536.53      | 11.31   | < 0.0001 significant |
| A-pH   | 137.34         | 1  | 137.34      | 2.90    | 0.1094  |
| B-ET   | 972.28         | 8  | 121.53      | 20.50   | 0.0004  |
| C-DE   | 0.2149         | 1  | 0.2149      | 0.0045  | 0.0947  |
| D-C    | 1170.17        | 1  | 1170.17     | 24.68   | 0.0002  |
| AB     | 6.54           | 1  | 6.54        | 0.1380  | 0.7155  |
| AC     | 0.3713         | 1  | 0.3713      | 0.0078  | 0.0930  |
| AD     | 12.87          | 1  | 12.87       | 0.2714  | 0.6100  |
| BC     | 13.30          | 1  | 13.30       | 0.2806  | 0.0604  |
| BD     | 12.94          | 1  | 12.94       | 0.2729  | 0.0609  |
| CD     | 8.54           | 1  | 8.54        | 0.1800  | 0.6774  |
| A²     | 627.63         | 1  | 627.63      | 13.24   | 0.0024  |
| B²     | 158.25         | 1  | 158.25      | 3.34    | 0.0877  |
| C²     | 122.11         | 1  | 122.11      | 2.58    | 0.1294  |
| D²     | 2.88           | 1  | 2.88        | 0.0608  | 0.0808  |

The use of the experimental design was the central composite design (CCD) to optimize a process with the chemical oxygen demand (COD) response parameter. In order to see the effect of variables and their significance on the automobile wastewater treatment process, the analysis of variance (ANOVA) was performed. ANOVA analyses validate the factorial models. Validation of ANOVA is done based on the F-Value and P-Value, which is shown in Table 5. The F-value is simply the ratio of mean squared deviations and mean square error of each process variable. Value of P <0.05 suggest that model is significant, if P-value > 0.10 then the terms are not significant [18-20].

3.3. Effect of variables
COD removal efficiency decreases with acidic pH value and alkaline pH value beyond the optimum pH value. At acidic pH of less than 5, COD removal decrease since metal ions generated during the electrocoagulation by Al electrode subsequently hydrolyzes to form polymeric species as Al(OH)²⁺, Al₂(OH)₃²⁺ and Al(OH)⁴⁺ etc. At acidic pH, pollutants connect with metal cations to form insoluble charged neutral species. Therefore, neutralized organics form bigger flocs by van der wall forces. However, pH increases to optimum, the OH- ions compete with organics for metal adsorption sites and precipitation of metal hydroxides occurs. At alkaline pH, an attraction between metal ions and pollutants decreases due to precipitation of hydroxides decreases, resulting in a decrease in COD removal. COD removal efficiency increases with increasing value of electrolysis time as shown in contour plots Figure 3. AS ET increases the formation of metal hydroxides floc, thereby increasing a large number of pollutants connected with metal ions resulting in the removal of COD. Beyond the optimum value of ET metal, ions are in the form of complexes Al(OH)⁴⁺ flocs remaining in dissolved form; thereby, removal efficiency does not increase further. Experimental results show that when the distance between the electrodes increases beyond the optimum value, COD removal efficiency decreases. This is because increases in ohmic resistances between electrodes when DE was increased because the electric potential between the electrodes decreases while increasing DE. When the current
value increases, COD removal was also maximized, as presented in Figure 3. Current in electrocoagulation determines the dissolution rate of metal ions, and the generation of bubble formation affects the generation of flocs. Metal ion generation increases with increases in current. Therefore, larger numbers of pollutant molecules get neutralize at flocs surface, increasing COD removal efficiency. Beyond optimum value, metal hydroxides are found in dissolve form; therefore, fewer pollutant molecules neutralize, and COD removal efficiency decreases.

3.4. Optimization
The optimization of variables was completed for maximum removal of COD. Optimum variables conditions are presented in Table 6. An electrocoagulation experiment was performed in repeat mode at the optimum condition to confirm the removal efficiency and the same given in Table 6.

Table 6. Optimum operating variables conditions for response parameter COD removal efficiency.

| pH       | ET, min | DE, cm | C, A  | COD, % |
|----------|---------|--------|-------|--------|
| 5.84196  | 71.4071 | 0.627797 | 3.50651 | 91.53  |

Figure 3. Three-dimensional contour plots for different variables effect on response COD

4. Conclusion
The present study shows the suitability of the electrocoagulation method for the treatment of automobile service station wastewater. Statistical analysis suggested the optimum operating condition, pH 5.84, Electrolysis time 71.40 min, the distance between the electrodes 0.62 cm, and Current 3.50 A. At this optimum condition, COD removal efficiency was found 91.53 percentages. The adequacy of R², F-Value, and P-Value proves that the analyzed parameters are significant and influence the EC process. This study shows that aluminum electrodes are capable of removing more than 90 percent of COD from automobile wastewater. Optimization of the process is possible by using CCD design for variables, and the model was well fitted. In the future, this system can be integrated with the adsorption process.

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