

Application of a Continuous Bipolar Mode Electrocoagulation (CBME) system for polishing distillery wastewater

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Abstract. A continuous bipolar mode electrocoagulation (CBME) unit was used in this study for polishing a biologically treated distillery wastewater at laboratory scale. This study focuses on optimizing the process for removal of Total Organic Carbon (TOC) from an anaerobically-treated distillery wastewater. Response surface methodology (RSM) was used for optimizing the process. The study was conducted by varying three operating parameters: Initial pH (2-10), reaction time (0.5-15 min), and current density (13-40 A/sqm). High R-square values, above 0.9, were obtained with ANOVA. Optimal point was observed to be at pH-6.04, Reaction time-11.63 min, current density-39.2 A/sqm. Experimental values of TOC removal at optimal point were found to be 73% against maximum predicted value of 79%. Color removal efficiency was observed to be 85% at the optimal points. It can be concluded that CBME system can be a suitable alternative for removal of recalcitrant carbon and color post-biological treatment in distillery wastewaters.

1 Introduction

The wastewater released from distilleries is highly acidic in nature and highly colored. Distillery Wastewater (DWW) is commonly called spent wash. The characteristics of DWW is highly varied because of various feedstocks used and the type of ethanol production process adopted by the industry. DWW is generated in huge volumes in the distilleries. Wastewater is characterized by the presence of recalcitrant organic compound called melanoidins, which contributes to color. Biological treatment is usually adopted for treatment of DWW, however color compounds cannot be removed, even after the biological treatment. Discharge of improperly treated DWW in surface waters leads to obstruction of photosynthetic activity due to its highly colored nature [1-2]. Physico chemical treatment methods like ozonation [3], membrane processes, fenton oxidation process have been studied as tertiary treatment for DWW, after biological treatment [4]. Distillery industries in India adopt reverse osmosis (RO) membrane system or evaporator technique for achieving the zero liquid discharge (ZLD) criteria, set by Government of India [5]. However, there is a pressing need for a technology before RO systems for efficient removal of recalcitrant carbon present after biological treatment. Electrochemical methods are gaining prominence in present situation due to their ease in operation, lower cost of treatment and higher treatment efficiencies. Electrochemical methods have been used for control of sulfides from sewers [6], sludge dewaterability [7] etc. Electrocoagulation is a complex process involving simultaneous oxidation and

reduction happening on anode and cathode respectively. Oxidation causes the formation of adsorbent whereas evolution of hydrogen gas is a results of reduction [8]. Electrochemical methods have been studied for DWW for decolorization of melanoidins [9], removal of COD and color [10-11]. Electrocoagulation technique has been used for removal of organics [12-13]. Organic pollutants can be removed by surface complexation, where pollutants act as ligand to bind a hydrous ion. The hydroxides or poly-hydroxide particles formed as a result of release of metal ions from anodes are more active than conventional coagulants [14-15].

There exist two types of configurations for electrocoagulation system, monopolar and bipolar modes. Monopolar mode is the more studied electrocoagulation system. In monopolar mode electrocoagulation, all the electrodes are connected to a DC power supply. Table 1 summarizes literature on operating parameters, removal efficiencies and pollutant removal using monopolar mode electrocoagulation system for distillery wastewaters. Reaction times and current densities were found to be higher for monopolar mode electrocoagulation, which leads to higher cost and bigger footprint when applied at industrial scale.

The bipolar-mode electrocoagulation system consists of sacrificial electrodes placed in between two electrically connected electrodes. The central electrodes are not connected to the electrical power supply. The neutral plates will be charged, with opposite charges on either sides when electrical current is passed into the system. This kind of arrangement, has the advantage of

increasing the surface area for the reaction without any additional electrical connection [16].

Table 1. Literature on Monopolar mode Electrocoagulation system for DWW

| Electrode type | Operating parameters | Pollutant removal and efficiency | Reference |
|------------------------------|--|----------------------------------|-----------|
| Iron | Reaction time-120 min; Current density-44.65A/sqm | COD: 50.25% | [11] |
| Iron | Reaction time-130 min; Current density-145.67A/sqm | COD: 63.14% | [17] |
| Iron | Reaction time-60 min; Current density-800A/sqm | COD - 53.1% | [18] |
| Aluminium | Reaction time-60 min; Current density-300A/sqm | COD-72% | [19] |
| Iron cathode Aluminium anode | Reaction time-60min | COD-75% | [20] |

This study attempts to develop a design for a continuous bipolar mode electrocoagulation (CBME) system for polishing a distillery wastewater with the objective of attaining higher treatment efficiency, lesser operating cost, and simplification of operation. The study optimizes the process variables such as initial pH, reaction time and current density for achieving high removal of residual Total Organic Carbon (TOC), which corresponds to removal of recalcitrant organic compound called melanoidins in DWW. The color removal efficiency was analyzed at the optimized parameters. Optimization study has been carried out using a statistical method called response surface methodology (RSM). Full quadratic models were developed for predicting removal efficiencies.

2 Materials & Methods

2.1. Effluent & its characterization

A biologically treated DWW was used in this study. The wastewater was sampled at the outlet of the wastewater treatment plant (WWTP) of a distillery plant located in Andhra Pradesh, India. The WWTP has adopted anaerobic process for treating the DWW. The wastewater was collected from a tank that was placed after anaerobic reactor and preserved at 4°C until use. The characterization of Total organic carbon (TOC) was determined by a total organic carbon analyzer TOC (Shimadzu-TOCL-CPN). Color was analyzed using UV-Visible spectrophotometer at 475nm [9]. pH of anaerobically treated DWW was found to be 8.54±1,

TOC was 4600±10 and the wastewater was dark brown in colour.

2.2 Experimental set-up

A 1-L (effective volume: 765 mL) bipolar continuous flow electrocoagulation setup was fabricated using poly-acrylic sheet. Iron electrodes, each having a dimensions 15cm x 3.4cm x 0.3cm, were used as central sacrificial electrodes for the study. A total of 15 electrodes were used. The two end electrodes were connected to a electrical supply. The raw DWW enters the reactor from the bottom. A DC power supply pack was used, with a variable output of 0–220V. Experimental set-up is shown in Fig. 1. Removal efficiencies of total organic carbon and colour were determined using Eq-1. Colour removal efficiency was calculated using the absorbance values.

$$\text{Removal Efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i & C_f are initial and final concentrations of TOC.

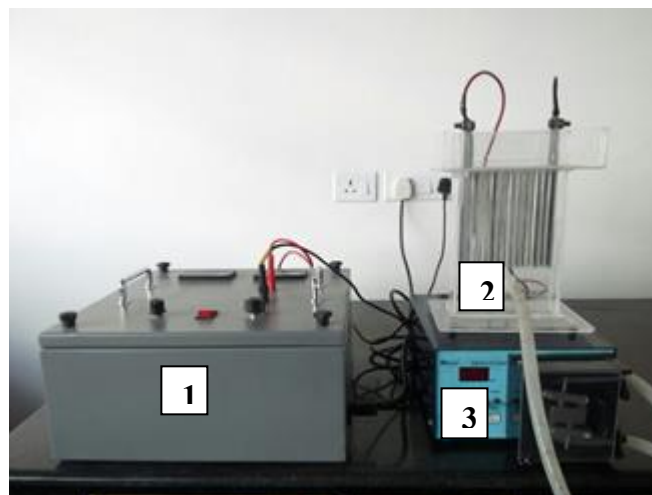


Fig. 1. Electrocoagulation set-up (1. DC power supply 2. CBME chamber 3. Peristaltic pump)

2.3 Experimental Design & Modelling

An experimental design, Central Composite Design (CCD), in Response Surface Methodology (RSM) was used for this study. Minitab software (version 17) was used for creating experimental design. Initial pH (pH), Retention time (RT), and current density (CD) were selected as independent variables for CBME system. Five levels were created for each independent variable in CCD to investigate the main effects and interaction effects. Table 2 represents the various independent process variables and levels created for the design. Removal efficiency of Total Organic Carbon (TOC) was chosen as dependent variable. Experimental design resulted in 20 experimental runs. The experimental data was fitted by a full quadratic model which describes the relationship between independent variables and dependent variable using multiple regression analysis. Experiments were conducted as per the design and removal efficiencies

were found out and compared with the predicted values of the responses [21].

Table 2. Independent variables and levels for CCD

| Independent variables | -2(α) | -1 | 0 | +1 | +2(α) |
|------------------------|----------------|------|------|------|----------------|
| pH | 2 | 3.6 | 6 | 8.3 | 10 |
| Retention time (min) | 0.5 | 3.4 | 7.7 | 12.0 | 15 |
| Current density(A/sqm) | 13 | 18.3 | 26.1 | 33.9 | 40 |

The model analysis was carried out with Fisher’s statistical test for Analysis of Variance (ANOVA). R-square values and lack of fit was used for validating the model. Response optimization was carried out by instantaneously solving equations for maximizing removal of TOC using RSM. Experimental validation runs were carried out at optimal settings of variables for the model. Response surfaces were plotted.

3 Results & Discussions

3.1. Model formulation & Validation

Twenty experimental runs were conducted in duplicates based on the CCD design. Design matrix of independent variables are shown in Table 3. TOC removal percentages were calculated after each run. Second order quadratic model was fitted to the observed experimental responses.

Main effects, interaction effects and quadratic terms were considered in the quadratic model. P-value obtained in the ANOVA table was used for verification of the significance of each model term. A p-value less than 0.05 confirms that the parameters have strong significant effect on the removal efficiencies of TOC. Table 4 represents the ANOVA table for TOC removal. The linear, quadratic and interaction terms were found to be statistically significant having p-value <0.05.

Lack of fit was found to be non-significant, as the p-value >0.05, which proves that model to be statistically significant. Correlation between the observed and the predicted values was evaluated by R-square. High R-square values demonstrated good correlation. Predictability of the model for new responses was represented by $R^2_{\text{predicted}}$ values. Therefore, R^2 and $R^2_{\text{predicted}}$ values should be close enough to validate the model [22]. Table 5 represents the R^2 values for the model, which was found to be more than 90%. R^2 , $R^2_{\text{predicted}}$, R^2_{adj} are found to be in close agreement with each other proving the model to be significant.

Table 3. Design Matrix

| Std. Order. | Independent process variables | | |
|-------------|-------------------------------|-------|-------|
| | pH | RT | CD |
| 1 | -1 | -1 | -1 |
| 2 | 1 | -1 | -1 |
| 3 | -1 | 1 | -1 |
| 4 | 1 | 1 | -1 |
| 5 | -1 | -1 | 1 |
| 6 | 1 | -1 | 1 |
| 7 | -1 | 1 | 1 |
| 8 | 1 | 1 | 1 |
| 9 | -1.68 | 0 | 0 |
| 10 | 1.68 | 0 | 0 |
| 11 | 0 | -1.68 | 0 |
| 12 | 0 | 1.68 | 0 |
| 13 | 0 | 0 | -1.68 |
| 14 | 0 | 0 | 1.68 |
| 15 | 0 | 0 | 0 |
| 16 | 0 | 0 | 0 |
| 17 | 0 | 0 | 0 |
| 18 | 0 | 0 | 0 |
| 19 | 0 | 0 | 0 |
| 20 | 0 | 0 | 0 |

Table 4. ANOVA table for TOC

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|--------------------------|----|---------|---------|---------|---------|
| Model | 9 | 6107.78 | 678.64 | 23.16 | 0.00000 |
| Linear | 3 | 3995.60 | 1331.87 | 45.45 | 0.00000 |
| Square | 3 | 1601.56 | 533.85 | 18.22 | 0.00000 |
| 2-Way Interaction | 3 | 510.63 | 170.21 | 5.81 | 0.015 |
| Lack of fit | 5 | 88.77 | 17.75 | 0.43 | 0.809 |

Table 5. Model summary

| Parameter | R-sq | R-sq(adj) | R-sq(pred) |
|-----------------------------|-------|-----------|------------|
| Total Organic Carbon | 95.3% | 93.1% | 84.5% |

3.2. Significance of Process variables

The effects of the independent process variables on the removal efficiencies of TOC were investigated. A quadratic model was used to fit the data and multiple regression analysis was carried out. This resulted in a quadratic equation for the response (Eq-1). Fig. 2 displays the graphical representation of the effects of process variables on removal efficiencies of TOC. 2D-

surface plots are two dimensional illustration of a three dimensional plot.

Total organic carbon (TOC) removal, as a function of process variables was expressed using Eq-2. Various response terms, such as linear, quadratic and interactive were included in the model equation explaining the correlation.

$$TOC\ removal\ (\%) = 67 - 2.36\ pH + 3.42\ RT - 1.77\ CD - 1.1\ pH * pH - 0.48\ RT * RT + 0.0048\ CD * CD + 0.440\ pH * RT + 0.270\ pH * CD + 0.128\ RT * CD \quad (2)$$

Equation 1 shows all the significant terms in the model. Retention time was found to be more significant among the first and the second order coefficients and quadratic terms. Interaction coefficient term of initial pH and retention time had the highest effect among the interactions. Positive value in the main effects coefficients shows that TOC removal efficiency increased with increase in the respective main effect. Negative sign in quadratic term of pH and retention time indicate a downward curvature of surface plot and indicates maximum levels of response in the selected ranges of variables. Positive signs in interaction terms indicates that both factors together show a synergistic effect [23]. All the interaction terms were found to be positive which indicates a synergistic interactive effect for both the variables. Response surface plots of TOC removal efficiencies depicting the significant interaction terms are explained in Fig. 2. Fig. 2(a) corresponds to interaction between retention time and current density. This plot shows a deep curvature at retention time, depicting, higher removal efficiencies at higher current densities

and near central values of retention time. Current density above 30 A/sqm retention time of 5-10 min has shown higher TOC removal. Fig. 2 (b) represents the interaction between pH and current density. Removal efficiency was found to be higher at pH 2-7 and CD above 20 A/sqm. Fig. 2(c) represents the plot between pH and retention time, indicating higher TOC removal at pH-3-7 and retention time 5-10 min.

pH variation can change the surface charge of the particles. Progressive reaction changes the pH of the water, which, in turn, influences the removal of organics from the effluent [15]. At pH-4-5.5, charge neutralization of particles happen [21] and adsorption phenomenon is observed at pH range more than 6.5 [24] due to the formation of Fe(OH)₃ flocs. Dissolved organic contaminants were found to be removed in the range of pH 4-6 [9]. Current density was found to be a significant factor in electrocoagulation process. Increase in current density results in formation of metal species, by dissolution of sacrificial anode following Faraday's law. It can be ascertained from the plots obtained that, at lower pH, charge neutralization is favoured as the higher amount of metal is dissolved due to higher current density. Retention time allows the reaction to happen for a particular time. Treatment efficiency was found to be increased with retention time, to certain point, which then gradually have shown a declining trend, due to the adsorption and desorption mechanism. These interaction effects indicate that the removal of TOC can be enhanced at higher current density and higher retention time and pH < 7.

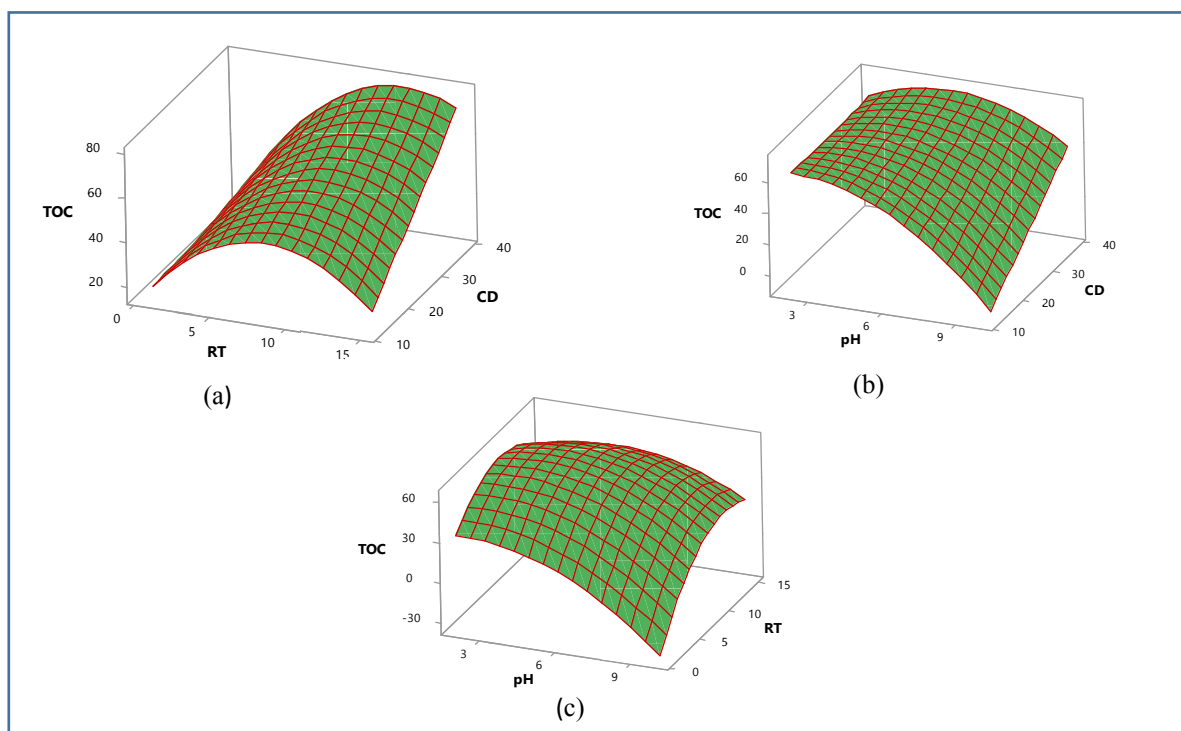


Fig. 2. Surface plots for TOC (a) Retention time (RT) vs Current density (CD) (b) pH & Current density (CD) (c) pH and retention time(RT)

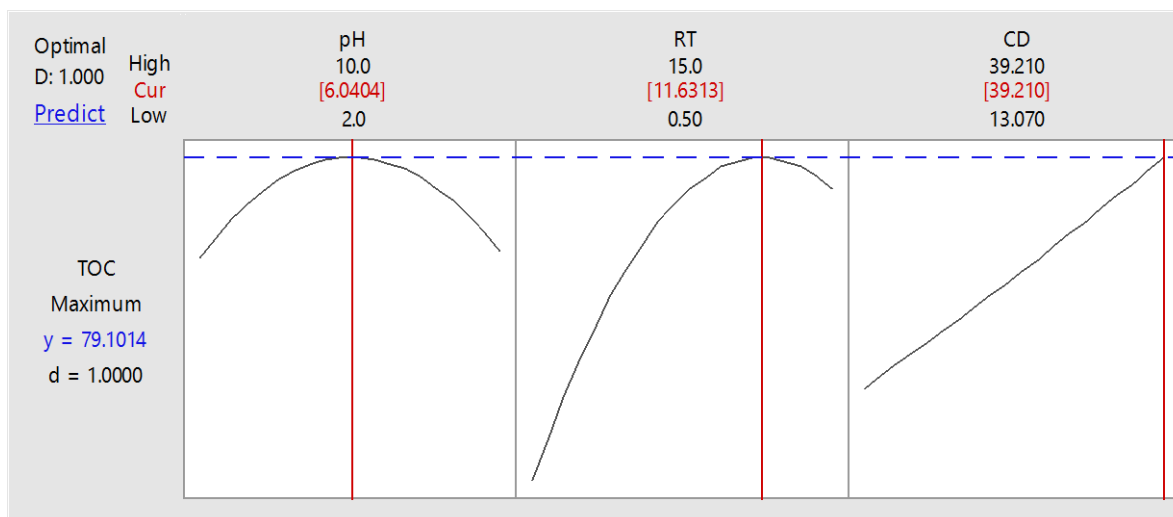


Fig. 3. Optimization plot for TOC

3.3 Optimization

Optimization was carried out for maximizing the removal of TOC. Local optima are located at diverse regions, which makes the optimization difficult. A desirability function was selected to solve the optimization problem. Desirability function was developed for the response, where the process variables will be transformed into a dimensionless desirability scale. Desirability scale ranges from 0-1, where 0 indicates undesirable response and 1 indicates desirable response [25].

Fig. 3 illustrates the optimization plot, indicating a pH-of 6.04, a reaction time of 11.63 min, and a current density of 39.2 A/sqm to be the optimal point for maximum removal of TOC. Under these conditions the predicted maximum removals of TOC was found to be 79.1%. Desirability function for TOC was found to be 1, validating the optimal values. Vertical red lines on the Fig. 3 indicates the optimal setting values for each variable. Horizontal blue dotted lines indicate current response values. The grey region indicate settings, where the response has zero desirability.

Conformational (experimental) runs were carried out with the optimized operating conditions predicted by the model. TOC removal was found to be 73%, showing a good correlation between observed and predicted responses at the optimized points. Decolourization efficiency at the optimal points was found to be 85%.

4 Conclusions

The current research was a study on the application of continuous bipolar mode Electrocoagulation (CBME) system for polishing an anaerobically treated distillery wastewater, for maximum removal of recalcitrant organic carbon.

➤ The results depicted highest TOC removal of 73% at optimized operating parameter of pH-6.04min, reaction time -11.63 min, reaction and current density-39.2A/sqm.

➤ CBME system being a continuous system and the operation time being less than 15 min adds an advantage at industrial scale applications. This kind of arrangement occupies lesser footprint when compared to monopolar mode electrocoagulation system, for which reaction time is higher than 30 min.

➤ Removal of organic compounds were found to be influenced by the initial pH value.

➤ Optimum current density of the system was found to 39.2 A/sqm, which was less compared to other monopolar mode systems used for distillery wastewater as shown in Table 1. This will reduce the cost of the system.

➤ CBME system can be applied for efficient removal of colour and TOC, contributed by recalcitrant organic pollutants from DWW with lesser reaction time, lesser current density, and near-neutral pH compared to monopolar systems.

➤ The future scope of study of CBME system will be application on various real wastewaters and removal of emerging pollutants.

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