Application of Continuous Electrocoagulation Process for Distillery Wastewater Treatment

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The present study deals with the treatment of distillery wastewater by continuous electrocoagulation (CEC) method utilizing iron (Fe) as an electrode material. Impacts of flow rates (L/h) and retention time (τ) were investigated on reduction of different physicochemical parameters (TS, colour, COD). COD reduction of 80.10% and 83.1%; and color reduction of 83.2% and 91.5%, separately was accomplished at retention time of 2 and 4h. In addition to this, after 200 minutes electrolysis time (ET), 71% of TS in wastewater was diminished at flow rate of 1 L/h. SEC was found to be from 14.1 to 11.6 kWh/kg COD eliminated with change in flow rate from 3 to 1 L/h at 160 minutes ET. Dissolution of electrodes was likewise explored with an alteration of flow rates.

Keywords: Chemical Oxygen Demand, Distillery wastewater, Effluent treatment, Flow rate

Introduction

Distilleries are the exceptionally high polluting point sources as they utilize natural crude material and produce contaminated water.¹ The Central Pollution Control Board (CPCB) has recorded the distillery wastewater in the "red category", which implies it represents a real pollution threat.¹ Distillery effluent is created after fermentation of molasses to ethyl liquor and its retrieval by distillation. Ordinarily the process produces around 15 liters of the spent wash per liter of the liquor. Nonetheless, distillery wastewater displays low pH, dark brown colour, contains high percentage of suspended solids, dissolved organic content which results in exceptionally high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) values. The release of this highly polluted and toxic spent wash on the land and in water bodies significantly affects the terrestrial ecosystem and causes loss of aquatic life.² To meet the environmental norms, the dark brown colour must be decreased before release to the environment. Consequently, the treatment of distillery wastewater requires the most extreme consideration today.

Current treatment strategies used for distillery effluent include physical (surface-assimilation, nano-filtration, electrodialysis, etc), chemical (sedimentation assisted with coagulants and flocculants, conventional oxidation, electro-floatation, electro-coagulation) and biological (aerobic or anaerobic or combination of both) treatment.³ ⁴ Nevertheless, Electrocoagulation (EC) method is quite possibly the most able advances in the field of wastewater treatment since it manages wide range of contaminants, requires basic equipment with simple mechanization, no need of any coagulants, generation of oxygen (at anode) and hydrogen (at cathode) as gases throughout this mode of treatment that upgrades efficacy through electroflotation.⁵ ⁶ The five stages of EC are as the following: (i) Oxidation of metal into cations at anode (ii) reduction of water into hydrogen gas and OH⁻ ions at cathode (iii) precipitation of metal hydroxides in solution, which acts as coagulants (iv) surface assimilation of contaminants, toxins on metal hydroxides, and (v) aggregation of contaminants to form flocs which either settles or gets entrapped in the bubbles of oxygen and hydrogen and float on surface.⁷

Arrangement of electrodes in EC reactor is extremely important. The electrode connected to the positive end of the DC source act as anode where oxidation takes place while the other electrode which is connected to the negative terminal acts as cathode where reduction reaction takes place throughout the electrolysis process. Since large surface area is required for the treatment of wastewater, arrangement of EC reactor comprises of numerous cathodes and anodes.

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associated in various ways. In the Monopolar mode of parallel connection, a low potential difference is required as compared with monopolar series connections. In the bipolar mode of parallel connection, sacrificial electrodes are placed between the two parallel electrodes without any electrical connection. When an electric current is passed through the outer electrodes, the uncharged sites of sacrificial electrodes get charged oppositely with respect to the parallel electrode alongside it. Upkeep of framework gets simpler in bipolar parallel connection due to the easier set-up.5,8

EC process (Batch as well as Continuous) has been utilized for the reduction of pollution load of pulp and paper mill effluent.9 Though, no such data has been found with respect to the treatment of distillery wastewater. The present research explores the continuous electrocoagulation method for the treatment of distillery effluent by means of parallel electrodes framework. It is important to contemplate the impact of different flow rates and electrolysis time on the physic-chemical parameters of distillery effluent. In the current examination, impacts of the residence time and flow rates were investigated for the reduction of COD, colour, total solids (TS) and turbidity. The rate of disintegration of anodes as a function of electrolysis time has also been evaluated. Since specific energy consumption (SEC) is considered as an important tool in assessing the energy efficiency of any process, it has also been estimated at different residence times.

Materials and Methods
The wastewater sample for the study was obtained from Symbhaoli distillery, Gajraulla, (U.P) India. The wastewater was translucent, dark yellow-brown in color (due to melanoidins). AR (analytical reagent) grade chemicals were used in the present research work.

Experimental Arrangement
The experimental arrangement of CEC treatment of distillery wastewater is shown in Fig 1. CEC trials were made on distillery effluent at different operational conditions (flow rates and residence times). To keep up even concentration of the feed, constant stirring of feed chamber and the CEC apparatus was done by magnetic stirrers. The flow rate of the feed to the CEC apparatus was established through a peristaltic siphon. The cell voltage was measured by using a digital multimeter (T-33). Treated samples were collected from the outlet of CEC apparatus at regular time intervals, filtered and examined for color and COD reduction.

Fig. 1 — Schematic diagram for the experimental arrangement of electrocoagulation process

Analytical Methods
Digital pH meter (model PR 8404) consisting of combined glass electrode was used to measure pH of samples. Reflux and titrimetric method was used to determine the COD of samples. The color intensity was evaluated by using a spectrophotometer (Perkin Elmer, Switzerland) as per standard methods given by (APHA).10

Chemistry of Electrocoagulation
The reactions taking place during electrocoagulation depends mainly upon the types of electrodes, pH, conductivity and total solids concentration of the effluent. Electrochemical degradation is a highly complex process and is completed in several steps: (i) Dissolution of iron as ferrous ions on anode (oxidation) (ii) Formation of hydroxide ions and hydrogen gas at cathode (reduction) depending upon the pH of effluent (iii) Formation of gelatinous precipitate of ferrous or ferric hydroxide in the solution (iv) Hydration of Fe(OH)n to various degrees depending upon the pH of solution (v) Electrostatic attraction (charge neutralization) or complexation of iron hydroxides with dissolved and suspended contaminants (vi) Removal of contaminants as ‘flocs’ which settles due to gravity (vii) Entrapment of suspended impurities in bubbles of H2 gas and removal from the top of reactor as froth. It is important to mention that three types of precipitates are formed during electrocoagulation viz. (a) low molecular weight iron hydroxides (b) hydrolytic iron polymer and (c) iron oxides.11

Results and Discussion
Physicochemical parameters viz., pH, TS, TSS, TDS, BOD, COD, etc. of distillery wastewater were measured and the readings are reported in Table 1.

On comparing the physicochemical characteristics of distillery waste water with paper and pulp mill effluent, it was found that pH of distillery waste water is acidic (pH = 4.5) whereas that of paper and pulp
mill is highly basic (pH = 10). The BOD and COD values of distillery waste water are considerably higher than that of paper and pulp mill waste water. The TDS of distillery waste water is higher than that of paper and pulp mill waste water whereas TSS of paper and pulp mill waste water is higher than distillery waste water.12

Effect of Electrocoagulation Process on COD

Rate of decrease of COD with electrolysis time was 76.4, 80.1 and 83.1% at \( \tau = 1, 2 \) and 4 h, correspondingly (Fig. 2). It has been seen that as the \( \tau \) in the CEC apparatus diminishes, there is slow formation of a thick precipitate. At \( \tau < 1 \) h, brilliant yellow-coloured flakes of iron oxides begin to deposit on anodes which cuts down the current by 0.08 A. At lower \( \tau \) (\( \leq 0.8 \) h), the suspended precipitate particles were found to stick on the edges of anode. As the process advances, the specs of precipitates tend to behave as the site for additional agglomeration, covering the entire plate region by flaky precipitates.9

Effect of Electrocoagulation Process on Colour Intensity

Reduction in color intensity of the distillery wastewater at various residence time is shown in Fig. 3. There was an unanticipated rise in color intensity from 6287 to about 10000 during the initial 30 minutes of electrolysis time. This phenomenon can be explained as initially there was oxidative polymerization of distillery effluent, which produces dark brown coloured organic species. After this time span, the color reduction initiates and which is straightforwardly related to the residence time. The maximum reduction in colour was 91.5% at \( \tau = 4 \) h while at \( \tau = 1 \) h it was just 78.7%. From Fig. 3, it can be observed that colour reduction starts to fall later and there is no more change in colour with additional treatment.

Effect of Electrocoagulation Process on pH

Change in the pH of the distillery wastewater with respect to electrolysis time at various flow rates and residence times is shown in Fig 4. In the electrolysis

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Table 1 — Characteristics of Distillery wastewater

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
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<tr>
<td>Odour</td>
<td>Unpleasant</td>
</tr>
<tr>
<td>pH</td>
<td>4.5</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>32300</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>45164</td>
</tr>
<tr>
<td>Total Dissolved solids (mg/L)</td>
<td>38000</td>
</tr>
<tr>
<td>Total Suspended Solids (mg/L)</td>
<td>4200</td>
</tr>
<tr>
<td>EC (( \mu ) mho/cm)</td>
<td>16450</td>
</tr>
<tr>
<td>Color (platinum cobalt unit)</td>
<td>6287</td>
</tr>
<tr>
<td>Chlorides (mg/L)</td>
<td>8530</td>
</tr>
<tr>
<td>Hardness (mg/L)</td>
<td>2432</td>
</tr>
<tr>
<td>Total alkalinity (mg/L)</td>
<td>2864</td>
</tr>
<tr>
<td>Dissolved Oxygen (mg/L)</td>
<td>Nil</td>
</tr>
</tbody>
</table>

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Fig. 2 — Decrease in COD of distillery effluent during electrolysis at different flow rates

Fig. 3 — Change in color intensity of distillery effluent during electrolysis at different flow rates

Fig. 4 — Change in pH of distillery effluent during electrolysis at different flow rates
time range of 40–60 minutes (at all flow rates), a sharp rise in the pH was seen. It became constant after this time period. The production of hydroxyl ions in the solution during electrolysis process can be the reason for the preliminary rise in the pH. Further, there is consumption of H\(^+\) ions during the oxidation of iron, which consequently increases the pH of the reaction mixture. Longer the residence time, higher was the final pH of treated effluent.

**Effect of Electrocoagulation Process on Cell voltage**

Change in cell voltage during electrolysis for different flow rates is depicted in Fig. 5. The starting cell voltage is in the range of 3.0–3.5 V which begins to decline as the electrolysis process progresses irrespective of the flow rates. When the flow rate of effluent was kept below 2 L/h, the cell voltage once more starts rising slowly after 60 minutes of electrolysis and approaches close to the initial value after 200 minutes of the process. During this time interval, thin flake formation begins at anode which is in concurrence with reduction in color, COD and other organic species content. Interestingly when the flow rate of effluent was kept more than 3 L/h, the cell voltage keeps on decaying and doesn't return to the initial value. Large scales of precipitates are formed during this period, which covers the entire surface of anode causing reduced removal efficiencies.\(^{13}\)

In the current investigation, specific energy consumption (SEC) of the electrocoagulation process has also been determined by using Eq. 1.

\[
SEC = \frac{\text{Amount of energy consumed}}{\text{(COD)}_{\text{before treatment}} - \text{(COD)}_{\text{after treatment}}} \times \frac{P \times t \text{ (kWh)}}{\Delta \text{COD} \text{ (kg)}}
\]

...(1)

where \(P\) is power (kW), \(t\) denotes electrolysis time (h) and \(\Delta\text{COD}\) represents drop in COD. SEC is plotted against electrolysis time at different flow rates and residence times and is depicted in Fig. 6. At 160 minutes ET, for the flow rate of 1, 2 and 3 L/h, SEC quantities are obtained as 11.6, 12.4 and 14.1 kWh/kg COD removed respectively.

**Effect of Electrocoagulation Process on Anode Consumption and Total Solids Concentration**

The variation in the amount of anode consumption (g) and concentration of total solids (TS; g/L) is shown in Fig. 7 at flow rate of 1 L/h and residence time of 0.5 h for different electrolysis time. Amount of anode dissolution and the volume of sludge generation increased with increase in \(\tau\). In the beginning of the process (up to \(\sim 40\) minutes), there was a steady rise in TS concentration which could be attributed to disintegration of anodic iron into the distillery effluent. Later as electrolysis advances, precipitation of iron hydroxides and other organic species commences, bringing down the TS concentration. The reduction in TS of effluent was found to be \(\sim 29.4\) g/L (71%) after 200 minutes of electrolysis.
Conclusions
In the present investigation of continuous electrocoagulation of distillery effluent, it is observed that process yields significant results as compared to the conventional treatment processes such as chemical coagulation and electrocoagulation process using aluminum electrodes. The effect of different of flow rates, electrolysis time (ET) has been studied on the various parameters such colour, COD, pH, total solids (TS) of distillery wastewater. From the experimental work it is clear that there is significant reduction in colour (91%), COD (82%) and total solids (71%) of the wastewater. After electrocoagulation treatment, the complex organic compounds such as melanoidins, phenolics and metal sulphides present in distillery waste water are converted into simple inorganic compounds which bring down the colour, COD and total solids. There was an increase in the pH of the effluent from the acidic to neutral side which makes it acceptable to be discharged into the water bodies. The removal efficiencies show that the electrocoagulation proves to be a sustainable procedure for the treatment of distillery wastewater.

References