Removal of COD from Textile Mill Wastewater by Electro-Coagulation Process Using SS/Al as Composite Hydrogel Electrode

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ABSTRACT: Textile industry, is a major consumer of water for different wet processes of operations. It is concern owing to significant organic matter and dyeing agents which produce color, inturn contributes high Chemical Oxygen Demand (COD). The Electrocoagulation (EC) process is considered as an effective treatment in the removal of dye and COD from textile mill wastewater. This paper focuses on, the performance of an EC process by incorporating titanium plates (Electro-oxidation) for the treatment of textile mill wastewater. The wastewater was characterized for COD, Biochemical Oxygen Demand (BOD), pH, conductivity, chlorides, turbidity and color. The effect of operating parameters such as current density, electrolysis time, and initial COD concentration was studied. Furthermore, energy and electrode consumption was also examined. The optimum electrolysis time and voltage for Stainless Steel–Titanium (SS-Ti) and Aluminium–Titanium (Al-Ti) was found to be 60 min at 14 V and 45 min at 16 V respectively. The COD removal efficiency of SS coated with sodium alginate hydrogel in combination with Ti was found to be 90% and Al coated with sodium alginate hydrogel in combination with Ti was observed 87%. The electrode dissolution of SS was 0.62 mg/L and Al was 0.125 mg/L at 16 V at 60 mins and 14 V at 45 mins respectively. The power consumption of SS and Al was found to be 9.6 kWh/m³ and 5.25 kWh/m³, respectively. The most suitable EC–EO performance was achieved using Al–Ti electrode in economical terms when compared to SS–Ti electrode.

KEYWORDS: Electrocoagulation, Electro-oxidation, COD, sodium alginate hydrogel, Monopolar, Bipolar

I. INTRODUCTION

The textile production industry uses large amount of water intensive chemical operations. This industry produces massive levels of wastewater and therefore creates environmental and economic challenges [19,21]. The effluent from textile dyeing process contains dye formulations, sequestering agents, surface active agents, inorganic salts etc., which not only causes aesthetic problems but also interfere with photosynthetic activities in receiving water bodies if not treated properly [3,24,26]. There are many conventional processes to treat textile mill effluents such as, adsorption, chemical degradation, photo degradation, chemical coagulation and biodegradation [8,28]. Hence, Electrocoagulation is an electrochemical method developed to overcome the drawbacks of conventional wastewater treatment technologies. Electrocoagulation process provides a simple, reliable and cost effective method for the treatment of wastewater without any need for additional chemicals and it also reduces the generation of sludge during treatment process [8,13,21]. EC process has been applied for the removal of various types of pollutants such as dyes, heavy metals and organic based substances [1,14,25]. Electrochemical system comprises the in-situ generation of coagulants with the dissolution of sacrificial anode. The anode is commonly made of aluminium or iron [7,21]. The metal ions react with the cathode generating hydroxyl ions (OH⁻) and gaseous H₂. In this process insoluble hydroxides will be produced that adsorb the pollutants and eliminate them from the solution [22].

Many researchers have conducted EC treatment on Textile Mill wastewater to remove color and COD. Zhang and Ma (2016) have conducted studies on the removal of alizarin red S by Fe/Al composite hydrogel electrode. The experimental results showed the COD removal efficiency of 83.8% with an initial alizarin red S dye concentration of...
300 mg/L [31]. Naje et al. (2015) have carried out studies on the performance of EC process by adopting titanium plates as cathode, which helps in oxidizing the dissolved dye(s) present in the textile mill wastewaters [21]. Seema et al. (2016) have investigated the direct and indirect electrochemical oxidation of Malachite Green (MG) dye in acidic and basic medium using RuO$_2$-TiO$_2$ and Pt coated Ti mesh as electrodes [27]. The removal efficiency of COD and color was more efficient in Al-Al and Fe-Fe combination, rather than Al-Fe or Fe-Al combinations [15]. Naje and Abbas (2013) have performed the combination of EC-EO processes to treat the textile mill wastewaters and the better results were observed when Al and Ti coated with iridium oxide plates with an alternate electrode pack were used [22]. However, the EC process is limited by sacrificial anodes, easy passivation and also the process is not feasible to treat large volume of dye wastewater and thereby the research and development of Fe/Al composite hydrogel electrode can solve the problems [6,31]. Hence, in the present investigation, it is proposed to conduct laboratory bench-scale electrocoagulation studies using the sodium alginate hydrogel, a novel electrode on the removal of COD from textile mill wastewaters.

II. RELATED WORK

Characteristics of wastewater

The raw wastewater characterization of a textile mill wastewater has been carried out for COD, Color, Conductivity, Sulphates, Turbidity, Alkalinity, pH, Temperature, Chlorides, Total solids and Total Dissolved Solids. The results of the wastewater characteristics are presented in Table 1. Characterization of textile mill wastewater indicate that, wastewater is categorized under low strength wastewater. The electro-coagulation process proves to be economical for the treatment of low/medium strength wastewaters. The conductivity plays a vital role as it is a measure of water’s capability to pass electrical flow. If the conductivity of the wastewater is low, then certain amount of ionic salts are added to enhance the conductivity and thereby, reducing the electrical energy cost and increasing the efficiency of the process. In the present study, the conductivity of the wastewater sample was found to be 4.1 m mho. Further, the COD value was found to be in the range of 2000–3000 mg/L. The dyes, salts and chemicals used in the textile mill have contributed high COD to the wastewaters. The chloride content in the wastewater helps in the conductance and also if the chloride to sulphate ratio is less than 1, then passivation of the electrodes occurs. From Table 1 the ratio of chloride to sulphate found to be less than 1, indicated the deposition of the metal hydroxides on the surface of the electrodes which results in the reduction of the efficiency of EC process.

Preparation of Sodium Alginate hydrogel electrode

SS/Al composite alginate electrodes were prepared by adding sodium alginate solution of 2.0% (w/v) with SS and Al to the gelling solution composed of 5.0% (w/v) CaCl$_2$ (CaCl$_2$·2H$_2$O). SS and Al electrodes were put in the gelling solution at 60°C for 2 hours, then washed repeatedly with distilled water and finally stored in 3% (w/v) AlCl$_3$ for dye degradation [31].

Mechanism of EC Process

When SS/Al composite hydrogel anode is used, Al and SS dissolve at the anode (Eqns. 1, 2 and 3) and hydrogen gas is released at the cathode (Eq. 4). The Al and Fe ions are consumed in water and react to form Al(OH)$_3$ and Fe(OH)$_3$ precipitates, (Eqns. 5 and 6) which are effective coagulants for the removal of pollutants from wastewater [31]. Hydrogel is a natural polymeric material with advantages such as, high adsorption ability [23] and large porosity and specific surface areas, and cost effectiveness. It is widely used to adsorb heavy metals [12,20] and organic pollutant [9].

**At Anode:**

\[
\begin{align*}
\text{Al}^{3+} (aq) - 3e^- & \rightarrow \text{Al}^{3+} (aq) \\
\text{Fe}^{3+} (aq) - 2e^- & \rightarrow \text{Fe}^{2+} (aq) \\
\text{Fe}^{3+} (aq) - 3e^- & \rightarrow \text{Fe}^{3+} (aq)
\end{align*}
\]

**At Cathode:**

\[
2\text{H}_2\text{O} (l) + 2e^- \rightarrow 2\text{OH}^- (aq) + \text{H}_2 (g)
\]

**SS and Al reactions**

\[
\text{Al}^{3+} (aq) + 3\text{H}_2\text{O} (l) \rightarrow \text{Al(OH)}_3 (s) + 3\text{H}^+ (aq)
\]
Al^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Al(OH)_3(s) \quad (5)

Fe^{2+}_{(aq)} + O_2(g) + 2H_2O(l) \rightarrow 4Fe^{3+}_{(aq)} + 4OH^{-}_{(aq)} \quad (6)

Fe^{3+}_{(aq)} + 3H_2O(l) \rightarrow Fe(OH)_3(s) + 3H^+_{(aq)}

Electrode Consumption and Energy Consumption

The theoretical value of any metal dissolution is calculated using Faraday’s law [11,29].

C_{theoretical} = \frac{M_i \times I \times RT}{(Z \times F \times V)} \quad (7)

C_{theoretical} indicates Faraday’s theoretical amount of Fe or Al in solution (mg/L), M_i = Molecular mass (g/mol), I = Current (A), RT = Reaction time (s), Z = electron moles, F = Faraday’s constant, V = wastewater volume

The energy intake for the EC process may be computed from the equation [10,18].

C = \frac{U \times I \times RT}{V} \quad (8)

C = Energy consumption (KWh/m^3), U = Voltage (V), RT = Reaction time (s), V = Volume of textile wastewater (m^3)

Table 1: General Characteristics of Textile Mill Wastewater.

<table>
<thead>
<tr>
<th>Parameter(s)</th>
<th>Unit</th>
<th>Observed Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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<td>7.5</td>
</tr>
<tr>
<td>Conductivity</td>
<td>m mho</td>
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</tr>
<tr>
<td>BOD5</td>
<td>mg/L</td>
<td>775</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>2148</td>
</tr>
<tr>
<td>TSS</td>
<td>mg/L</td>
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</tr>
<tr>
<td>TDS</td>
<td>mg/L</td>
<td>5324</td>
</tr>
<tr>
<td>TS</td>
<td>mg/L</td>
<td>9011</td>
</tr>
<tr>
<td>Sulphates</td>
<td>mg/L</td>
<td>395</td>
</tr>
<tr>
<td>Chlorides</td>
<td>mg/L</td>
<td>250</td>
</tr>
<tr>
<td>Alkalinity as CaCO_3</td>
<td>mg/L</td>
<td>802</td>
</tr>
</tbody>
</table>

Experimental Setup

The treatment of textile wastewater was performed using batch electrolytic cell that was made of Plexiglas with a length, width and height of 10, 10 and 17 cm, respectively (Figure 1). The sets of electrodes include 4 SS/Al electrode plates coated with sodium alginate hydrogel and 3 plates made of Ti, each with a surface area of 100 cm^2 (10 × 10 cm). The inter electrode distance was 1 cm. SS/Al and Ti plates were continuously exchanged within the electrode pack. The Ti electrodes were positioned in between 2 electrodes made up of SS/Al but not electrically connected. A total of 3 inner Ti electrodes were used in bipolar arrangement. The thickness of each electrode was 0.1 cm. The electrodes were placed in the reactor in a vertical manner with the help of grooves. A magnetic stirrer with a 500 rpm rotating velocity was used to stir the contents of the cell. The cathode and anode groups were connected to the negative and positive ports of a DC power supply (Testronix). Voltage was varied from 8 V to the maximum to find the optimum condition and current level was controlled at a constant value in every run using a variable resistor. Textile wastewater of 1 L volume was taken for every run. The reactor was run for 75 minutes and the samples were collected for every 15 minutes of interval. Approximately 10 ml of sample was withdrawn from the electrolytic cell for the sample analysis. The sample analysis was conducted according to standard methods [4,21].
III. EXPERIMENTAL RESULTS

COD REMOVAL EFFICIENCIES

Bipolar arrangements with SS-Ti and Al-Ti Electrodes

In electrolysis process, COD removal efficiency depends on the concentration of metal ions produced, electrode material, mode of electrical connection and reaction time [17,21,30]. The bipolar configurations in the EC treatment process of textile mill wastewater were carried out using Al and SS with Ti electrodes at various voltage values starting from 8 V to 16 V and electrolysis time from 0 min to 75 min. The variation of final COD concentration with electrolysis time at different voltage using SS-Ti electrodes have represented in Figures 2a-b. From Figures 2(a-b) it can be depicted that, COD values were decreasing with electrolysis time for the applied voltage from 8 to 16 V. This may be due to the adsorption of organic and inorganic constituents on the sodium alginate hydrogel electrode coated on SS. After 45 minutes, there was an increase in COD value in the reactor and it may be due to the maximum generation of the metal hydroxides such as Fe(OH)$_2$, Fe(OH)$_3$ and Al(OH)$_3$. After 45 minutes there was again decrease trend in the COD concentration which was due to the reaction between generated hydroxides with the pollutants present in the wastewater and later on the precipitation was formed, which is generally act as a scum. The increase in voltage enhances the dissolution of anode and thereby, the efficiency of the pollutant removal increases. It was also observed that, at 14 V, there was a decrease trend in COD concentration (60 mins). The initial concentration of COD was found to be 3500 mg/L and final COD concentration (60 mins) reduced to 350 mg/L, thereby the efficiency of COD removal was found to be 90%, which was the maximum removal efficiency when compared with the other applied voltages.
There was a drastic increase in COD concentration from 350 mg/L to 2650 mg/L. This may be due to the formation of complex metal hydroxide and also due to the presence of surfactants and other dyes which were inactive in the process [5]. The removal of COD was high at 60 minutes of electrolysis time at 14 V and hence, it is considered to be the optimum condition for the combination of SS and Ti electrodes for the removal of COD from textile mill wastewater. Akanksha et al. (2014) have conducted experiment on the removal of COD from textile mill wastewater using both SS and Al electrode at optimum conditions (14 V, 80 mins) was 92.97% and 87.23% respectively. Almost the same treatment efficiencies is reached in the present study using SS at 14 V at 60 mins and Al at 16 V at 45 mins.

From Figures 3(a-b), it can be observed that there was a significant decrease in the COD concentration during the first 45 minutes of electrolysis time and beyond which no significant improvement was observed. The increase in the COD concentration at 15 minutes from the startup of reactor run was mainly due to release of metal ions into the wastewater. Further, the metal ion reacts with hydroxides and form metal hydroxides, which react with organic pollutants present the wastewater and reduces COD concentration at 45 minutes of electrolysis time. The COD removal efficiency was found to be 87% having a final COD concentration of 315 mg/L with 45 minutes of electrolysis time at 16 V. The COD removal efficiency was observed as 64% after 60 mins. It was also observed that, within 15 minutes of electrolysis time the removal efficiency has decreased by around 10-15%. Hence, 45 min of electrolysis time has been considered as optimum electrolysis time for COD removal.
Removal of COD using Al and SS electrodes

The bipolar configuration in the EC treatment process of textile wastewater was carried out using five Al electrodes at 14 V for 15 min interval of electrolysis time upto 75 minutes. The initial COD concentration of wastewater was found to be 2549 mg/L. A plot of electrolysis time vs. COD concentration are made is shown in Figure 4. The concentration of COD has been decreased with the increase in electrolysis time. At 45 minutes maximum removal efficiency of COD was obtained (61.4%). There was an increase in the amount of Aluminium cations in solution due to higher supply of current; simultaneously the rate of formation of Al(OH)₃ was also increased. Thereby the pollutant removal efficiency gradually increased. COD removal efficiency was increased during the start-up of the reactor upto 45 mins and thereafter decreased. This may be due to the formation of complex components which are formed in the reactor and these components contribute to COD as they are inactive to the oxidation and reduction reactions.

On the other hand, bipolar configuration in the EC treatment process of textile wastewater was carried out using five SS electrodes at 16 V for 15 min interval of electrolysis time upto 75 minutes. The initial COD concentration was found to be 2549 mg/L and a plot of electrolysis time against COD concentration is shown in Figure 4. The concentration of COD has been decreased with the increase in electrolysis time. Maximum COD removal efficiency of 64.7% was observed at 45 min of the reactor run. The COD removal efficiency depends on the quantity of iron hydroxide (Fe(OH)₂, Fe(OH)₃) generated, which is bound with potential electrolysis time. With the increase of OH⁻ ions, the
distribution of the coagulation agent density was found to be more effective, which can produce related coagulation and improve the pollutant removal efficiency.

Electrode and Energy Consumption

The theoretical value of Al and SS dissolution in mg/L and the energy consumption of Al and SS electrodes at different applied voltages are depicted in the Figures 5 and 6. The dissolution of the Al electrode was found to be 0.1254mg/L at 14 V and an optimum efficiency of 87% was achieved at a current intensity of 0.6 A at 45 minutes of electrolysis time. Due to the generation of metal hydroxides, wastewater in the reactor changes to acidic medium and thereby enhances the dissolution rate of iron metal [10] and the dissolution of SS metal at 16 V is 0.6244 mg/L. The energy consumption of SS electrode at 16 V was found to be 9.6 kWh/m$^3$ and for Al electrode at 14 V was found to be 5.25 kWh/m$^3$.

Fig. 5. Dissolution of Al and SS metal at varied voltages

Fig. 6. Energy Consumption of Al and SS metal at varied voltages
IV. CONCLUSIONS

The EC–EO process showed an effective treatment of textile mill wastewater. The Mp(Al)–Bp(Ti) electrodes were more effective in the removal of pollutants (COD) from the textile mill wastewater compared with the Mp(SS)–Bp(Ti) complex. The optimum conditions for Al–Ti were observed at 45 mins (14 V) and SS–Ti were observed at 60 mins (16 V). COD removal efficiency using Al–Ti and SS–Ti were found to be 90% and 87%, respectively. It was observed that oxidation of the pollutants was enhanced by the incorporation of Ti plates. The COD removal efficiency using Al and SS were found to be 61% and 64%, respectively. This clearly indicates that, the combination of metal electrodes with Ti plates increases the percentage removal of COD by direct and indirect oxidation. The energy consumption and electrode consumption of SS was found to be more when compared to Al and thereby Al electrode is considered to be more economical for EC treatment process.

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