Continuous treatment of paper mill effluent by electrocoagulation for holding time analysis

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Abstract. This paper presents the potential of continuous electrocoagulation operation for the treatment of paper mill effluent. The electrocoagulation experiments were carried out based on the batch study for holding time analysis. Process performance was assessed in terms of chemical oxygen demand, color, total dissolved solids, and total organic carbon. Continuous electrocoagulation experiments were performed at constant pH 7.45, conductivity 7.72 mS/cm², electrode distance 1.5 cm and current density 10.35 mA/cm² with flow rate varied between 0.1 to 0.6 L/min. Flow rate 0.2 L/min with 120 min of holding time was an optimum condition in which removal efficiencies were 82.5%, 90%, 92.5%, and 84% for COD, Color, TDS, and TOC, respectively.

1. Introduction

Nowadays, paper mill industries use recycled fibers like waste paper, office waste, scrap newspapers, etc. as raw material for paper production. Every stage involved in this production consumes water and chemicals, which generates wastewater. Generated wastewater contains organic and inorganic pollutants. It is necessary to reduce this pollutant from wastewater for reuse and proper discharge in water bodies. Various methods are available for the treatment of wastewater, such as biological treatment [1], adsorption [2], oxidation [3], wet oxidation [4], and electrochemical [5-8]. These technologies are usually uneconomical for high flow rate treatments. In the past few decades, research has shown that electrocoagulation is a versatile treatment technique and successfully potential to treat wastewaters from the olive mill, dairy, petroleum, textile, and paper mill [9-12]. Most of the reported studies on electrocoagulation used batch mode of operation with paper mill effluent. The continuous operation provides process control and low variability of the process, while batch operation often blends segregation [13-14]. In addition, an appropriately designed continuous system handles small portions of effluent at the minimum time provided and increasing process monitoring. This is unfeasible for large-scale batch processes with a similar throughput [15-16]. Regardless of these advantages, the continuous operation also has some difficulties, and whenever not executed properly, the continuous operation has a chance to be failed. Uniform flow throughout the operation is one of the challenges in continuous operation with maintained quality of outlet flow. In the wastewater treatment process, the holding time analysis describes how the effluent flows inside the reactor in continuous mode and provides quality assurance and control. A few researchers reported continuous electrocoagulation operation with
different electrode material for the dairy industry [17], Papermill [14, 19, 22]. These continuous electrocoagulation treatments present the electrolysis time and flow rate as the variable parameters. But none of them used Stainless steel electrode with ongoing electrocoagulation treatment for paper mill wastewater.

Moreover, utilization of continuous electrocoagulation permits another degree of adaptability since the utilization has control not just on the flow boundaries and the nature of the electrochemical reaction estimation itself but also to the measurement or nature of the electrodes. Stainless steel was used as electrode materials for paper mill wastewater treatment because it is cheaper than other materials for electrodes to be commercialized and used in large scale plants. As shown in Table 1, stainless steel electrodes give better results with higher COD value. Stainless steel was also corrosion resistance metal compared to aluminum and iron, making stainless steel a better choice than other metals. The stainless steel electrodes used in monopolar arrangement require a low voltage and a higher current, contrary to the arrangements available that operate under a high voltage and a lower current. Monopolar arrangement electrodes might be considered because this arrangement offers a high pollutant removal with lower energy consumption. Thus, the present study’s objective was to assess the feasibility of continuous electrocoagulation operation for paper mill effluent. A previous survey of batch mode shows satisfactory results obtain on paper mill effluent. The present study’s main concern is to measure the effect of holding time based on the inlet flow rate of effluent. Effect of holding time was seen on parameters like Chemical oxygen demand (COD), Color, Total dissolved solids (TDS), and Total organic carbon (TOC).

Table 1. Electrocoagulation treatment for pulp and paper mill wastewater.

| Mode | Electrode Material | Initial COD (mg/L) | Results | References |
|------|-------------------|-------------------|---------|------------|
| C    | Fe/Al             | 657               | COD> 81% | [18]       |
| B    | Al/SS, MS/SS      | 32000             | CODAl= 89%, CODMS= 95% | [19] |
| C    | Fe/Fe             | 24-136            | COD=76.47% | [20] |
| C    | Fe/Fe, Al/Al      | 2950              | COD=82%  | [21] |
| B    | MS/MS             | 925 ± 65          | COD= 55% | [22] |
| C    | Fe/Fe             | 2000              | COD=82.2% | [23] |
| B    | Fe/Fe             | 1537 ± 50         | COD=61%  | [3] |
| B    | Fe/Fe             | 285               | COD=32-68% | [24] |
| B    | graphite, Fe, Al  | 591.54            | COD=58.8% | [25] |
| B    | SS/SS             | 18600             | COD= 40.8% | [26] |
| C    | SS/SS             | 6500              | COD= 84% | [27] |
| B    | Fe/Fe, Fe/Al, Al/Fe | 1700         | COD>90%  | [28] |
| B    | Fe/Fe             | 800-1500          | sulphides removal= 88%, phosphorus removal= 40% | [29] |
| B    | Al/Al             | 7000              | COD= 77% | [30] |
| B    | Fe/Fe, Al/Al      | 1068.7            | COD=41.23% | [31] |

C=Continuous, B=Batch

2. Material and methods

2.1. Paper mill effluent collection and characterization

The paper mill effluent used in present investigation was obtained from a recycled fiber-based paper mill located in Chhattisgarh, India. The characteristics of effluent are presented in Table 2.
Characterization of the effluent was performed as per standard methods given in APHA [32]. All the chemicals used in the present study were of analytical grade and acquired from Merck, India. The standard discharge permissible limit for paper mill wastewater is presented in Table 3 [33].

Table 2. Characterization of recycled fiber-based paper mill effluent before and after treatment.

| Sr.No | Parameters                        | Before          | After         |
|-------|-----------------------------------|-----------------|---------------|
| 1     | Chemical Oxygen Demand (mg/L)     | 2700-3200       | 200-400       |
| 2     | Total Organic Carbon (mg/L)       | 1200-1300       | 140-200       |
| 3     | Color (CU)                        | 2500-2800       | 200-275       |
| 4     | Total Dissolved solid (mg/L)      | 2650-3000       | 400-600       |
| 5     | Total Suspended solid (mg/L)      | 100-150         | 40-60         |
| 6     | Total solid (mg/L)                | 2750-3150       | 440-660       |
| 7     | pH                                | 7.18-7.55       | 7.67-8.00     |
| 8     | Temperature (°C)                  | 26-32           | 38-40         |
| 9     | Salinity (PSU)                    | 2.09            | 2.00          |
| 10    | Conductivity (mS/cm)              | 3.40-4.00       | 4.58-5.04     |
| 11    | Hardness (mg/L)                   | 2000-2145       | 500-560       |
| 12    | Phosphates (mg/L)                 | 5.8-7.6         | 1.78-2.00     |

Table 3. The discharge capacity of paper mill wastewater for the small and large mill.

| Parameter/Flow                        | Concentration not to exceed |
|---------------------------------------|-----------------------------|
| 1. Large pulp & paper mill            | 200 cum/tone of paper       |
| 2. Large rayon grade/ new print       | 175 cum/tone of paper       |
| pH                                    | 6.5 to 8.5                  |
| Suspended Solid                       | 100 mg/L                    |
| Biological Oxygen Demand              | 30 mg/L                     |
| Chemical Oxygen Demand                | 350 mg/L                    |
| Total organic chloride                | 2.0 kg/tone of paper produces|
| 3. Small scale paper industry         |                             |
| Inland surface water                  |                             |
| pH                                    | 5.5 to 9.0                  |
| Suspended Solid                       | 100 mg/L                    |
| Biological Oxygen Demand              | 30 mg/L                     |
| Land                                  |                             |
| pH                                    | 5.5 to 9.0                  |
| Suspended Solid                       | 100 mg/L                    |
| BOD                                   | 100 mg/L                    |

2.2. Experiment method

The electrocoagulation setup was shown in Figure 1. 2 L capacity reactor made up of acrylic sheet dimensions of 0.13×0.13×0.15 m connected to the peristaltic pump for effluent feeding. Four stainless-steel plate electrodes were arranged in a monopolar mode in the reactor. The electrodes dimensions were
0.085×0.090×0.002 m, with a total effective electrode area of 144 cm². Electrodes terminals are connected to DC power supply (0-30V, 0-5A). Working volume of 1.5 L and 250 rpm were maintained throughout EC experiments. Based on satisfactory results obtained by conducting batch EC treatment of paper mill effluent. Presented continuous EC experiments were carried out at optimum operating conditions obtained by batch experiment, which is pH 7.45, conductivity 7.72 mS/cm², electrode distance 1.5 cm and current density 10.35 mA/cm². Effect of flow rate in range of 0.1 L/min to 0.6 L/min was determined based on holding time analysis. Papermill effluent was fed into the reactor from the bottom using a peristaltic pump. Effluent samples from the reactor were taken at different intervals during the experiment, and the experiment proceeded until steady-state concentrations were achieved. Performance of EC was validated in terms of percentage COD, Color, TDS, and TOC.

3. Result and Discussion
Flow behavior changes with fluid properties, when flow rate varies the paper mill effluent flow patterns, directly affecting the removal efficiency of organic presents in the wastewater. Flow rate variation effect presented in this study with respect to holding time in the reactor and validated in terms of percentage removal of COD, Color, TDS and TOC. Optimum operating conditions obtained by batch experiment that is remained constant throughout all continuous experiments. Analytical readings of holding time were taken up to 360 min at a flow rate range of 0.1 L/min to 0.6 L/min.

3.1. Effect on COD
Figure 2 shows that COD's removal efficiency under the batch optimum conditions at the effluent flow rate varies between 0.1 L/min to 0.6 L/min. Generally, removal efficiencies were increasing when there was an increase in the holding time. At flow rate, 0.1 L/min removal efficiency was lower than 0.2 L/min. This is because a 0.1 L/min flow rate was not enough for rapid mixing to form metal hydroxide, which results in the decrement in COD removal efficiency [26-27]. At 0.2 L/min flow rate, organic pollutants have sufficient time in the reactor to form floc with metal oxides presented in the reactor due

![Figure 1. Schematic diagram of Continuous EC experimental setup.](image-url)
to anode dissociation. When the flow rate is 0.2 L/min in continuous electrocoagulation operation, the holding time maximized and vice versa. Reactor volume was constant as 1.5 L, so when increment in inlet flow rate, more than 0.2 L/min occurs, it results in a decrement in holding time of wastewater in the reactor. As flow rate increased, 0.2 to 0.6 L/min decrease in holding time was lead to a decrement in COD removal efficiency as present in Figure 2. The COD removal 82.5% at 0.2 L/min flow rate with 120 min of holding time was maximum after that COD removal reaches study state, and notable increment was not noticed.

![Figure 2](image_url)

**Figure 2.** Effect of flow rate with respect to holding time on the removal efficiency of COD (pH =7.45, conductivity=7.72 mS/cm, electrode distance=1.5 cm and current density 10.35 mA/cm²)

### 3.2. Effect on Color

The color is generally the primary contaminant to be perceived in paper effluent that influences the aesthetics, water lucidity, and oxygen level in water bodies. Papermill effluent is contaminated with lignins, lignin degradation products, and humic acids [26]. These contaminants make the effluent stream dark-colored and are often referred to as color bodies. The use of different types of dyes for printing of paper and coloring of paper makes effluent more toxic in color [23]. Since pulp mill produces large quantities of this densely-colored effluent, the discharge of this effluent into adjacent streams and water bodies can cause an objectionable discoloration of the water. Removal in color for continuous electrocoagulation study is presented in Figure 3 with flow rate variation. Same as COD removal, a 0.2 L/min flow rate was optimum. Effluent flow rate affects removal efficiencies because rapid mixing is required in the initial condition of the EC process to grow larger flocs and precipitate these enough in the solutions to reach the removal. Color removal was 90% at a flow rate of 0.2 L/min. After an increment in a flow rate of more than 0.2 L/min, results hindered the reactor, destroying the floc and electrostatic force between the particles. They were not enough to form a metal hydroxide. Holding time for formed floc was reduced at the maximum flow rate, leading to a reduction in color removal at a higher flow rate.
Figure 3. Effect of holding time on the removal efficiency of Color (pH = 7.45, conductivity = 7.72 mS/cm², electrode distance = 1.5 cm and current density = 10.35 mA/cm²)

3.3. Effect on TDS
A total dissolved solids is a measure of the combined total of organic and inorganic substances contained in the wastewater. The solubilization of maximum chlorolignin compounds presented in paper mill results the high contamination of TDS in the effluent [23]. The TDS removal was investigated by varying at flow rate ranges of 0.1 L/min to 0.6 L/min with 360 min of holding time observation. Figure 4 shows that at 0.2 L/min flow rate, provide maximum TDS removal efficiency 92.5% at 120 min of holding time. The increases in flow rate more than 0.2 L/min could be attributed to the formation of insoluble metal hydroxide, which could not trap solid particles because of rapid mixing breaks the solid sludge formation. The predominant nature of amorphous hydroxides reduces removal efficiency after an increment in flow rate. This is due to the fact that aggregation of small particles persisted, forming flocs at slower flow rate. Flow rate at 0.1 L/min not provide better results than 0.2 L/min because of flow rate less than optimum not able to provide proper mixing in the rector, which results reduction in force between dissolved particles and metal hydroxides and it takes time to form flocs and settled as sludge.
Figure 4. Effect of holding time on the removal efficiency of TDS (pH = 7.45, conductivity = 7.72 mS/cm$^2$, electrode distance = 1.5 cm and current density = 10.35 mA/cm$^2$)

3.4. Effect on TOC
Total organic carbon becomes an important parameter used to monitor overall levels of organic compounds presented in wastewater. Compared to COD analysis TOC, carbon is presented at low level of contaminations concentration for precise and accurate analysis of water purity. TOC is a potential option in contrast to the COD test and has the upside of being both rapid and possibly more exact than the COD test. While it has recently been considered a potential replacement for COD test, increasingly precise testing techniques have emerged, making the test considerably more feasible and accurate, particularly for increasingly complex compounds presented in wastewater. Wastewater treatment at different flow rates with varying holding time was measured in terms of TOC removal efficiency. The flow rate varies between 0.1 to 0.6 L/min for 360 min of holding time observation, as presented in Figure 5. In TOC, flow rate 0.3 L/min gives better results than 0.2 L/min, holding time at 180 min to provide maximum removal efficiency compared to 120 min. So if target responses are COD, Color, TDS and TOC together, then 0.2 L/min with 120 min holding has been taken as an optimum condition because all target responses provide optimum results with TOC removal of 84%. If TOC is the only response that has been taken into account, then 0.3L/min with 180 min of holding time has been taken as an optimum condition because which is 88%, but due to an increase in flow rate and holding time increase cost of the process with only 4% of removal variation. Flow rate 0.2 L/min with 120 min of holding time has been taken as an optimum condition. The variation occurs only in TOC removal due to fact that high flow rate create turbulence in the continuous flow reactor and remove carbon presented in wastewater and because of high flow rate the wastewater presence in reactor was minimized which results increase in holding time up to 60 min increment to maximum removal of all carbon presented in wastewater.
Figure 5. Effect of holding time on the removal efficiency of TDS (pH = 7.45, conductivity = 7.72 mS/cm², electrode distance = 1.5 cm and current density = 10.35 mA/cm²)

4. Conclusion
Based on the presented study, it can be concluded that the continuous electrocoagulation technique provided enough evidence of being more precise and the potential to expand in industrial-scale paper mill effluent treatment. Electrocoagulation is found to be the most effective technology for the removal of multiple contaminations in one pass. In addition, an appropriately designed continuous system handles small portions of effluent at the minimum time provided and increasing process monitoring. Process performance was assessed in terms of chemical oxygen demand, color, total dissolved solids, and total organic carbon. Flow rate 0.2 L/min with 120 min of holding time was an optimum condition in which removal efficiencies were 82.5%, 90%, 92.5%, and 84% for COD, Color, TDS, and TOC, respectively.

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