Treatment of Distillery Wastewater by Continuous Electrocoagulation Process

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Abstract: Effluent from distilleries, known as spent wash, leads to extensive soil and water pollution. Removal of pollutants and color from distillery effluent is becoming increasingly important from environmental and aesthetic point of view. Effluent from distilleries contains certain recalcitrant compounds. The present research deals with the treatment of distillery wastewater by continuous electrocoagulation (CEC) process using iron (Fe) as an electrode material. Effects of flow rates ($dm^3 h^{-1}$): 0.5–4.0 and residence time (τ): 0.5–4.0 h was investigated on degradation of chemical oxygen demand (COD), color, total solid (TS), and turbidity. At flow rates of 1.0 and 0.5 $dm^3 h^{-1}$, COD removal efficiency of 78.20 and 82.15%; and color removal efficiency of 79 and 90%, respectively, was achieved. TS concentration of wastewater slurry was also reduced by 65% after 3 h residence time with flow rate of 1 $dm^3 h^{-1}$.

Introduction

Distillery effluent or spent wash is generated after molasses fermentation to ethyl alcohol and its recovery by distillation. Normally the process produces about 15 liters of the spent wash per liter of the alcohol. This discharged effluent has obnoxious odor, dark brown color, acid pH and COD of about 1,20,000 and is difficult to treat to satisfy the environmental norms. Biomethanation is the first treatment, wherein some organics are converted into methane rich gas, which is used as fuel for boiler. Biomethanation of the effluent reduces the COD upto 60 to 80% and the wastewater after biomethanation needs further treatment. This effluent still has COD about 25,000 to 30,000 mgl"1. Activated sludge is the secondary treatment, which generates the bacterial sludge using organic matter as a carbon source to give an effluent with COD ranging from 6,000- 8,000 mgl"1 and has a dark brown color. To meet the environmental compliance the dark brown colour has to be reduced before discharge of the effluent. Conventionally, the coloured effluent is passed over active charcoal where the coloured material is adsorbed [1]. Therefore, these industries are facing the problem of a shortage of water. This problem can be resolved by reducing the consumption of water or by recycling of treated wastewater. However, wastewater or effluent generated in distillery exhibits high chemical oxygen demand (COD), suspended solids (SS), color, etc. and contains a number of other recalcitrant compounds.[5] The discharge of high COD and colored wastewater into the environment causes loss of environmental aesthetics, death of aquatic animals as well as profoundly affecting the terrestrial ecosystem. Distillery industries are one the highly polluting industries as they use organic raw material and generate toxic waste. The ministry of environment, forest, and climate change (MOEFCC) and central pollution control board (CPCB) have listed the Distillery wastewater in the "red category", which provide a serious pollution threat. Therefore, the treatment of Distillery industry wastewater requires the utmost attention today [2].

Various technologies such as adsorption, chemical coagulation, aerobic and anaerobic biological processes, advanced oxidation, electrocoagulation (EC), and membrane separation process are available for treatment wastewater. Although, treatment of wastewater is easy in large paper producing mills, since they can afford modern facilities and expensive equipments however, small industries are unable to treat their wastewater properly due to financial constraints. Some of the small paper mills do not have any chemical recovery units (CRU) even now [3].

EC process is the one of the most promising technologies in the area of wastewater treatment because of the requirement of simple equipment with ease of automation, no requirement of any addition of chemicals, formation of O_2 and H_2 bubbles during the process which enhances the efficiency of separation via electroflotation (EF) and the capability of handling wide variety of pollutants. The basic steps of EC process are: (i) electrolytic reactions at electrode surfaces, (ii) formation of OH^- ions and H_2 at the cathode, (iii) oxidation of generated metal ions and subsequent precipitation of metal hydroxides in aqueous phase, (iv) adsorption of pollutants at metal hydroxide surface and charge neutralization, and (v) removal of pollutants by settling [4].

Configuration of electrodes in EC reactor is very important and can be arranged in series or parallel in monopolar or bipolar system. In the monopolar parallel mode, all anodes are connected to each other, and similarly all cathodes connected to each other. In the monopolar series system, the outermost electrodes are connected to a power source and the current passes through the other electrodes, thus polarizing them. Since higher resistance is encountered in the electrodes connected in a series mode, higher potential is required for a given current. In bipolar parallel connection, where two parallel electrodes are connected to the electric power source with no power connection to the sacrificial electrodes, maintenance of system becomes easier due to the simpler set-up [5].

Few studies have been reported for the treatment of pulp and paper mill wastewater by batch EC process and by continuous EC (CEC) process. However, in the reported CEC studies, no information has been given regarding the analysis of sludge, rate of dissolution and consumption of electrodes and operating cost of CEC process. For the application of the EC process on industrial scale, studies on CEC process are of utmost im-

portance. It is necessary to study the effect of various operating parameters such as pH, flow rate, residence time, etc. All these aspects have been covered in the present study [6].

The aim of the present study is to investigate the CEC process for the treatment of paper mill wastewater using parallel plate electrodes arrangement. The effects of the residence time (hydraulic retention time, τ) and flow rates were studied on the removal of COD, color, TS, and turbidity; specific energy consumption (SEC), and instantaneous current efficiency (ICE).

Experimental

Wastewater and chemicals

The wastewater as obtained from Symbhaoli Distillery was used in the experiments. The wastewater had a very low transparency and was dark yellow-brown in color due to presence of melanoidin forming pigments chromophores. The characteristics of wastewater are given in the Table 1.

Table 1 Characteristics of Distillery wastewater

Parameter	Range
pH	6.86–7.12
BOD (mg dm^{-3})	625–679
COD (mg dm^{-3})	2500
Total solids (mg dm^{-3})	2280
Color (platinum cobalt unit)	1758
Turbidity (NTU)	189
Chlorides (mg dm^{-3})	48–69
Adsorbable organic halogens (AOX) ($\mu g\, dm^{-3}$)	560
Total alkalinity (mg dm^{-3})	390–410

All the chemicals used in the study were of analytical reagent grade. Ammonium ferrous sulphate, 1–10 phenanthroline, mercuric sulphate, and silver sulphate were obtained from HiMedia Laboratories, Mumbai (India). Potassium dichromate was obtained from Ranbaxy Chemicals Ltd, New Delhi (India). Potassium chloroplatinate and cobalt chloride were obtained from Qualigen Fine Chemicals, Mumbai.

Experimental procedure

The schematic diagram of the laboratory scale experimental set-up used in the CEC treatment of pulp and paper mill wastewater is shown in Fig. 1. The CEC reactor and electrodes configuration details are given in Table 2. CEC experiments were performed at optimum operating conditions obtained in batch study of present wastewater with different flow rates and residence times (Table 2). The feed tank and the CEC reactor were stirred continuously by a magnetic stirrers to maintain uniform concentration of the feed. The flow rate of

the feed to the reactor was maintained through a peristaltic pump (Miclins-20 PP, India). The voltage across the cell was measured using a digital multi meter (Keithley, Germany). Samples were collected at regular time intervals from the CEC reactor outlet, filtered, and analyzed for color and COD.

Analytical procedure

pH was measured using a digital pH meter (NIG 333, Toshniwal, Delhi). The color intensity was measured as per standard methods given by American Public Health Association (APHA) using a spectrophotometer (Perkin Elmer, Switzerland).[48] Adsorbable organic halides (AOX) was measured using a Thermo-Scientific AOX analyzer. COD of the solution was determined as per standard methods given by APHA.[48] The decolorization of the samples was determined by monitoring the decrease in absorbance of the visible spectrum from 190–480 nm. The percent decolorization was estimated by following equation:

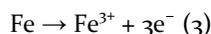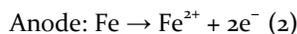$$D = \frac{100\left(A_{\text{initial}} - A_{\text{observed}}\right)}{A_{\text{initial}}} \quad (1)$$

where, D is the decolorization in%, A_{initial} and A_{observed} is the area under the curve of the absorption spectrum before and after time t.[49]
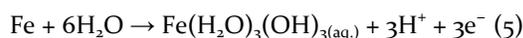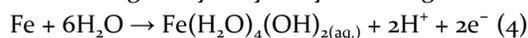
Reaction mechanism

The sacrificial Fe electrodes generate Fe^{2+} and OH^- ions according to the Faraday's law. Electrochemical
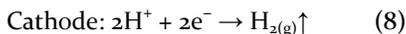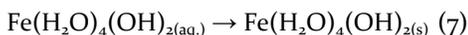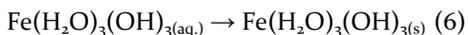
degradation is a complicated time-dependent process, which completed in steps i.e. hydrolysis, polymerization, and precipitation.[50–52] During these steps, three classes of products of different species are involved, i.e. (a) low molecular weight iron hydroxides $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(OH_2)^{4+}$ etc.; (b) hydrolytic iron polymer $(Fe_n(OH)_m(H_2O)_x^{(3n-m)+})$, or $Fe_mO_n(OH)_x^{(3m-2n-x)+}$; and (c) precipitated oxides (amorphous(am)-$Fe(OH)_3$), FeOOH and Fe_2O_3). Fe^{3+} ions may undergo hydration depending on the pH of the solution.

In fact, for pH $\leq$ 5, at least four different Fe(III) ions coexist: Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$. In the range of pH $\geq$ 5, $Fe(OH)_6^-$, $Fe(OH)_4^-$ and other species may also be formed.[40,43,44,53] Following anodic and cathodic reactions take place in an EC reactor having iron electrodes, over a pH range of 6–9:[54]

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (2)

$Fe \rightarrow Fe^{3+} + 3e^-$ (3)

Iron undergoes hydrolysis by following reactions:

$Fe + 6H_2O \rightarrow Fe(H_2O)_4(OH)_{2(aq.)} + 2H^+ + 2e^-$ (4)

$Fe + 6H_2O \rightarrow Fe(H_2O)_3(OH)_{3(aq.)} + 3H^+ + 3e^-$ (5)

$Fe(H_2O)_3(OH)_{3(aq.)} \rightarrow Fe(H_2O)_3(OH)_{3(s)}$ (6)

$Fe(H_2O)_4(OH)_{2(aq.)} \rightarrow Fe(H_2O)_4(OH)_{2(s)}$ (7)

Cathode: $2H^+ + 2e^- \rightarrow H_{2(g)}\uparrow$ (8)

The pH for minimum solubility of $Fe(OH)_n$ is in the range of 7–8. More hydrogen is evolved due to iron hydrolysis.

RESULTS AND DISCUSSION

EFFECT OF FLOW RATES AND RESIDENCE TIME

Removal of COD and color. Degradation of COD as a function of electrolysis time (ET) at the residence time τ (0.5–4 h) and flow rate (0.5–4 dm^3 h^{-1}) is shown in Fig. 2a. Percentage removal of COD was 78.2, 80 and 82.2% at τ = 1, 2 and 4 h, respectively. As the residence time in the CEC reactor decreases, a slow but prolonged (30 and 75 min at τ = 4 h and 0.67 h, respectively) formation of flocs takes place. At τ < 1 h, large scale flake (golden yellow color on drying-due to rusting) start to deposit over the anode plates which results in the current drop by ~0.05A.

At lower residence times (t ≤ 0.67 h), the suspended solid particles tend to cling and deposit at the rim of the dents on the anode plate surface and as the electrolysis proceeds, these particles act as the nucleus for further particle deposition, leading to the spread of the flake formation over the entire plate area. The COD degradation rate decreased in accordance with the increased residence time at a steady state. The increase in residence time improved the COD and color removal; however, the degradation byproducts tend to accumulate gradually atop the reactor as a foamy green gel. Fig. 2b demonstrates the change in color intensity of the reactor effluents at different τ. At any τ, an abrupt increase in color intensity from 1750 to ~3750–4300 PCU was observed during the initial 30 min ET. This occurred due to the oxidative polymerization of wastewater, which yields dark colored organic compounds. After 30 min, the color removal depends on the flow rate. The decolorization reaches a constant value at ~135 min ET for 1 ≤ τ ≤ 4 h and maximum 89.9% removal (183 PCU) at τ = 4 h. It was 78.7% removal at τ = 0.67 h. The iron levels of 200–500 mg dm^{-3} in the CEC reactor can remove color by ~90%. As seen from the Fig. 2, the color removal begins to "bottom off" and further treatment produces no color reduction. In contrast, for τ = 0.5 h, the color intensity reached a value of 2450 PCU at the end of ET with a concomitant COD reduction of <14%. A decrease in turbidity from 182 NTU to 3–7.2 NTU was observed for flow rates of 0.5–1 dm^3 h^{-1} (τ = 2 to 4 h) at 150 min ET. At a flow rate of 4 dm^3 h^{-1} (τ = 0.5 h), the treated wastewater had a turbidity of ~418 NTU.

Fig. 2c shows color intensity of the wastewater before and after CEC process. At the beginning of each run, the wastewater solution was translucent, dark brown in color. The solution first became darker and more opaque as the reaction proceeded. A head of creamy foam was formed on the top of the

solution due to the production of hydrogen gas. As the electrolytic reactions progress, a forest green viscous gel like flocs start accumulating at the top of the CEC reactor which gradually turns to pleasing dark brown color. As can be seen, the intensity of the wastewater is brought down from an initial value of 1750 PCU to <175 PCU.

pH of wastewater, cell voltage and percentage variation in COD removal. Fig. 3a shows the variation in the pH of the CEC reactor treated effluent as a function of ET at different flow rates and residence times.

At all the flow rates and up to ~40–60 min ET, a quick increase in the pH was observed after which the change in the pH was marginal. The initial increase in the pH during electrolysis is attributed to the production of hydroxyl ions in the solution. As the EC process proceeds (at τ < 1 h) the bubble coalescence is inhibited probably because of the alkaline pH of the solution. Therefore, a reduction in COD/color removal occurs and the active nucleation sites of the anode plates, which produce bubbles, tend to be blocked by micro-flocs, which gradually spread over the anode plates [7]. In addition, the chemical dissolution of Fe consumes H^+ resulting in the pH increase. Short residence time ended up with lower final pH values. Long residence time caused increased final pH values. Since pH is a logarithmic function, the pH change is less at higher pH values. A slight drop in the pH at flow rates > 2 dm^3 h^{-1} was observed, particularly after 60–75 min ET [8]. This was because of the gradual consumption of hydroxyl anions as well as the production of hydrogen cations in the dissociation reactions of HOCl and OCl^- along with the formation reaction of HOCl in the treated waste stream [9].

Fig. 3b shows the variation in cell voltage during electrolysis and Fig. 3c shows the corresponding COD removal for flow rates in the range of 0.5–4 dm^3 h^{-1}. With a starting cell voltage of ~3.1–3.2 V and ET up to 45–60 min, a decline in cell voltage was observed irrespective of the flow rate. Up to this time, flake deposition occurs over the anode plates simultaneously adding to the increase in color intensity along with a small amount of COD removal (Fig. 3c). At this time, for flow rates <2 dm^3 h^{-1}, the cell voltage again begins to increase gradually and reaches the near starting value at the end of the ET. During this period, flocs start forming in the reactor, degrading COD, color, turbidity and other organic constituents. Flakes that were deposited along the edges of the anode plates are released back to the solution with an increase in cell voltage. In contrast, at flow rates >3 dm^3 h^{-1}, the cell voltage continues to decline and do not recoup back to the starting value with large scale flake deposits all over the anode causing reduced removal efficiencies. At any flow rate, the voltage across the cell gradually decreases to a minimum and then increases to its initial value. The degradation starts when the cell voltage begins to increase gradually. The color and turbidity show an increase with ET, reach the maxima and then decrease.[10]

CONCLUSIONS

In the experimental study of batch mode electrocoagulation process for treatment of distillery wastewater it is observed that; process yields significant result as compared to the conventional treatment process by using aluminum electrodes. The effect different of pH, voltage and hydraulic retention time were studied clearly. From the experimental work it is clear that, the COD,Chlorides,Sulphates,Total hardness and Turbidity removal efficiency were increased by maintain the optimum voltage supplied to the electrode,HRT and the maintaining optimum charge density within the volume of electrolyte. The removal efficiency shows that the electrocoagulation proves a sustainable treatment process for treatment of Distillery wastewater.

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Table 2 Continuous EC reactor, electrode characteristics, and optimized operating conditions

| CEC reactor specification		Electrode characteristics		Optimized operating conditions	operating
Material	Material	Material and shape	Iron	Cell voltage	3.1–3.2
Dimensions (cm)	Dimensions (cm)	Shape	Rectangular	No. of electrodes and electrode gap	6 and 10 mm
Volume (dm³)	Volume (dm³)	Size of each plate	9 cm × 10 cm	Active electrode SA/V ratio (m^2 m^{-3})	54
Type	Type	Thickness (mm)	1.5	Current density (A m^{-2})	55.56
Stirring mechanism	Stirring mechanism	Plate arrangement	Parallel	pH	~7
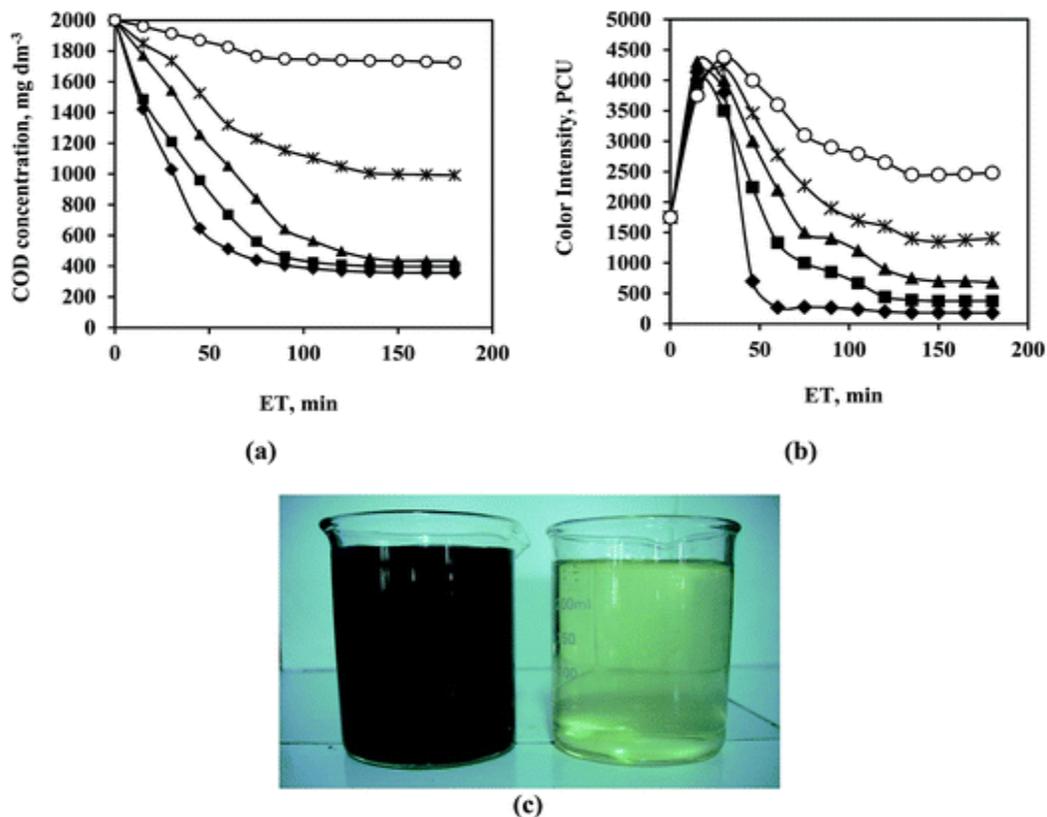
Fig. 2 (a and b) Degradation of COD and variation in color intensity at different flow rates (c) Color of wastewater before and after CEC treatment. Flow rate, dm³ h⁻¹; residence time, h: ◆(0.5 dm³ h⁻¹; 4 h), ■(1 dm³ h⁻¹; 2 h), ▲(2 dm³ h⁻¹; 1 h), ✳(3 dm³ h⁻¹; 0.67 h), ○(4 dm³ h⁻¹; 0.5 h).
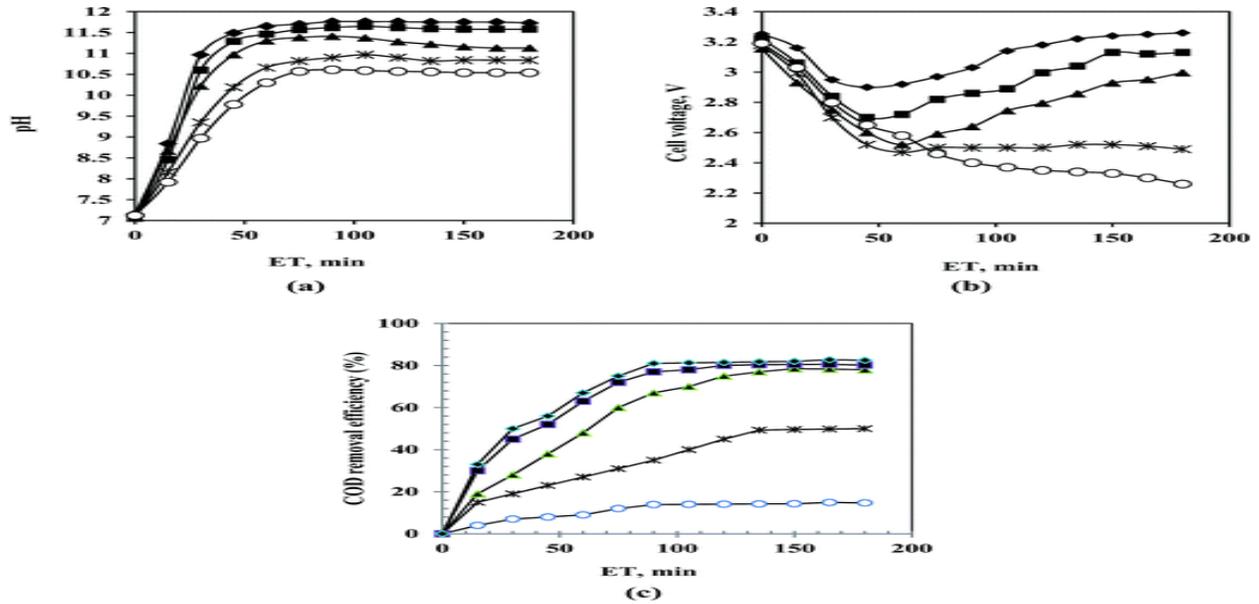
Fig. 3 (a) Change in pH of wastewater, (b) cell voltage and (c) COD removal efficiency at different flow rates. Flow rate, $dm^3\ h^{-1}$; residence time, h: ◆—($0.5\ dm^3\ h^{-1}$; 4 h), ■—($1\ dm^3\ h^{-1}$; 2 h), ▲—($2\ dm^3\ h^{-1}$; 1 h), ✶—($3\ dm^3\ h^{-1}$; 0.67 h), ◦—($4\ dm^3\ h^{-1}$; 0.5 h).