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Treatment potential of EC towards bio-digester effluent: effects of process parameters, aeration, and adsorbent

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ABSTRACT

Present work deals with the decolorization and COD removal from the bio-digester effluent of a small-scale distillery unit through electrocoagulation (EC) in a batch reactor using aluminum (Al) as a sacrificial electrode. The effect of five independent factors namely, initial pH (pH_0: 2–11), contact time (t: 30–180 min), current density (j: 22.73–172.73 A m^{-2}), inter-electrode distance (d: 0.5–3 cm), and NaCl concentration (g: 0.5–3 g l^{-1}) has been studied to assess their effect on decolorization and COD removal. Most suitable conditions for the decolorization and COD removal was found to be pH 3, after a run time of 120 min, current density 113.63 A m^{-2}, inter-electrode distance 1 cm, and NaCl concentration 1.5 g l^{-1}at the initial value of color and COD as 10,000 Hazen and 5 g l^{-1}, respectively. Under optimum conditions, maximum decolorization and COD removal were 97.4 and 91.8%, respectively. It was found that application of aeration (air flow rate: 0.22 l min^{-1}) and activated carbon powder as adsorbent (dose: 0.5 g at every 30 min) in EC reactor containing 1.52 l waste water can further enhance the removal efficiency.

Keywords: Electrocoagulation; Decolorization; COD; Aluminum electrode; Bio-digester effluent; Distillery wastewater.

1. Introduction

In the twenty-first century, the energy security is a major issue due to rapid depletion of fossil fuels. Amongst various efforts to meet the energy demand the application of ethanol as a blending material with gasoline is very important. Although ethanol can be produced either from beet sugar or cane sugar, in India, it is produced from cane sugar in distillery. This process produces around 10–15 l of wastewater per liter of alcohol production, which is acidic (3.9–4.3) in nature and contains high amount of COD (80–1,040 g l^{-1}), BOD (46.1–96 g l^{-1}) and appears dark brown in color. An estimate shows that around 320 distilleries in India produce around 3.25 billion liters of alcohol and 40.4 billion liters of effluent per annum. Distillery wastewater contains high COD and BOD, which is conventionally converted to methane by anaerobic treatment in a bio-digester and approximately 60–65% of total COD is reduced [1–3]. However, bio-digester effluent (BDE) still contains high amount of COD (40.53–50 g l^{-1}), BOD (16.2–20 g l^{-1}), color, etc. which need further treatment before its discharge [4].

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Various treatment technologies are available for distillery wastewater treatment, such as (i) bio-methanation followed by solar evaporation, (ii) bio-methanation followed by aerobic treatment, (iii) bio-methanation followed by two-stage aerobic treatments followed by tertiary treatment for surface water discharge, and (iv) bio-methanation followed by evaporation and incineration followed by potassium recovery [5]. All the above processes are time consuming. Further, the BOD/COD ratio of BDE is very low in comparison to distillery wastewater and hence, biological treatment is not so effective. Thus, an alternate option for the treatment of BDE is required, electrocoagulation (EC) can be a suitable option for these processes.

In EC, the dissolved organic and inorganic compounds are removed as flocs with flow of electric current without the use of an external coagulant [6]. In this process, coagulants are produced *in situ*. Various electrochemical reactions occurring in EC reactor using aluminium (Al) as electrode can be summarized through Eqs. (1–3) as follows:

For Al electrodes:

$$\text{At anode}: \quad Al \rightarrow Al^{3+} + 3e^- \tag{1}$$

$$\text{At cathode}: \quad 3H_2O + 3e^- \rightarrow 3/2H_2 + 3OH^- \tag{2}$$

$$\text{Overall}: \quad Al^{3+} \rightarrow Al(OH)_n^{(3-n)} \rightarrow Al_2(OH)_2^{4+} \rightarrow Al_3(OH)_4^{5+} \rightarrow Al_{13\text{complex}} \rightarrow Al(OH)_3 \tag{3}$$

Two important mechanisms that favor decolorization and COD removal are; (i) *in situ* generation of coagulants ($Al(OH)_3$) during EC process and (ii) production of chlorine and hypochlorite ions on application of electric current to the electrodes. The later one exists when chlorides are present in wastewater (like distillery wastewater) and takes place through Eqs. (4–7).

$$\text{At anode}: \quad 2Cl^- \rightarrow Cl_2 + 2e^- \tag{4}$$

$$\text{At cathode}: \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{5}$$

$$\text{Mass solution}: \quad Cl_2 + H_2O^- \rightarrow HOCl + H^+ + Cl^- \tag{6}$$

$$HOCl^- \rightarrow H^+ + OCl^- \tag{7}$$

The removal of pollutants in EC process further can be accelerated by the addition of adsorbents and aeration [7,8]. Some literatures are available on the treatment of BDE using EC [9]. Some investigators have also explored the accelerating effect of adsorbent (activated carbon) on the removal of color and COD from wastewater [7,8]. However, hardly any literature is available which reports the effect of aeration in an EC reactor. Further, treatment of BDE and the detailed characterization of foam and sludge generated during the EC process are rare in the literature.

The present study focuses on the treatment of the BDE in a batch-scale EC reactor using Al as a sacrificial electrode. Effects of process parameters, such as initial pH (pH_0), time (t), current density (j), electrode distance (d), and NaCl concentration ($g\,l^{-1}$) on the decolorization and COD removal were investigated to identify the optimum process conditions. Characterization of foam and sludge generated during the EC at optimum conditions were done to assess their energy production capacity. Effects of addition of aeration and adsorbent dose with EC on the removal potential were also studied.

2. Experimental

2.1. Method

2.1.1. Properties of the industrial distillery wastewater

BDE for this study is collected from a local distillery in Bijnor, Uttar Pradesh. Random selection procedure was maintained for sampling point in above described site. Two plastic containers were used to collect the wastewater sample. For getting a homogenous sample they were thoroughly mixed after 24 h of collection of wastewater sample. Then, it was preserved in refrigerator at 4°C to conserve its

Table 1
Characteristics of BDE used in the present study

Parameters	Value
COD, $g\,l^{-1}$	5
BOD, $g\,l^{-1}$	1.9
COD/BOD	2.63
Color, Hazen	10,000 (Dark brown)
Total solids, $g\,l^{-1}$	32.40
Total suspended solids, $g\,l^{-1}$	30.42
Total dissolved solids, $g\,l^{-1}$	1.98
Cl^-, $g\,l^{-1}$	2.50
Conductivity, milli mho	5.28
pH	4.84
Turbidity, NTU	1,500

properties. BDE was characterized for various physico-chemical properties (Table 1), as per the standard method of analysis [10–12].

2.1.2. Experimental setup

Electrochemical treatment of BDE was done in a rectangular batch reactor, made of perspex of maximum/working volume of ~1.52 1 (108 × 108 × 130 mm). Four pieces of square-shaped Al electrodes of thickness 2 mm were used with dimensions of 8 × 8 cm whose total area was ~70.4 cm^2.

The active surface of the electrode was dipped in wastewater up to the neck. Both anodes and cathodes were positioned vertically and parallel to each other with a variation of inter-electrode distance of 0.5–3 cm. A gap of 5 cm was maintained between the Al electrodes and reactor's bottom surface to allow smooth mixing by magnetic stirrer (Remi-2MLH). Experimental studies were carried out in a galvanostatic regime. A precise DC power supply (REMI PS/0–30 V/0–5A) was used to maintain requisite current density in mono-polar mode. A schematic diagram of experimental setup used in this study is shown in Fig. 1.

2.1.3. Chemical reagents

The Al electrodes used in this study were purchased from a local market in Roorkee. All the chemicals, purchased from SD Fine-Chem. Limited and HiMedia Laboratories Pvt. Ltd., Mumbai, were of analytical grade (AR).

2.2. Procedure

2.2.1. Pretreatment of aluminum electrodes

Prior to each run, the Al electrodes were abraded manually with sand paper to remove scale, dirt, etc. then dipped in 15% HCl solution up to a depth of 8 cm for 15 min, and finally rinsed with distilled water. The electrodes were dried for half an hour in an oven at 105°C and weighed.

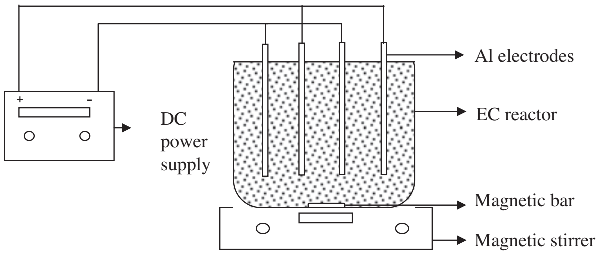

Fig. 1. Schematic diagram of EC unit.

2.2.2. Batch EC studies

1.52 l of screened (using 2 micron filter paper), homogeneous, and well-mixed distillery wastewater was added in the rectangular batch reactor. The real BDE sample was diluted suitably with distilled water to get the initial COD value as 5 g l^{-1}. The dilution was made to ensure that the BOD and COD value in the treated water were below the permissible limits [13]. The pH of the wastewater was adjusted using either 1 M H_2SO_4 or 1 M NaOH, and pH value was measured by a 5500 EUTECH pH meter. The pH, time, current density, inter-electrode distance, and NaCl concentration were adjusted at the desired value. The whole setup was placed on a magnetic stirrer (REMI-2MLH), and the stirrer speed was maintained at 100 rpm for providing fair mixing in the reactor without breaking the flocs formed during the EC process. Power supply was turned on at time $t = 0$ and the corresponding time was taken as the starting time of the EC process. A 5 ml of solution was taken at every interval of 30 min up to 120 min for analysis. After completion of each experiment, the sample was centrifuged (REMI-research centrifuge) for 15 min at 10,000 RPM to get the clear solution. Each experiment was repeated thrice and the average value is reported.

2.2.3. Analytical procedures

COD and color were chosen as the responses of the EC cell. Closed reflux-colorimetric method using COD analyzer (SN 09/17443 Lovibond Spectrophotometer) after addition of desired chemicals and providing digestion period of 2 h in COD reactor (ET 125 SC Lovibond, Germany) was used for the measurement of COD [14]. The % removal of COD was calculated according to the following relationship:

$$\% \text{ COD Removal} = \frac{(\text{COD}_i - \text{COD}_f)}{\text{COD}_i} \times 100 \tag{8}$$

UV–vis spectrophotometer (lambda 35, PerkinElmer instruments, Switzerland) was employed for measurement of color of BDE sample before and after electrolysis. Standard wavelength of 465 nm was used. The percentage decolorization was calculated by difference between the absorbance values before and after treatment.

2.2.4. *Morphology of Al electrodes and physicochemical analysis of residues (foam and sludge)*

Electrodes and residues were analyzed by Scanning Electron Microscope (SEM) QUANTA, Model 200 FEG, USA, to study electrode morphology and distribution of elements in residue. To provide conductivity, the samples were first gold coated by a sputter coater, Edwards S150, England, and then SEMs images and energy dispersive X-ray (EDX) spectra (FE-SEM QUANTA 200 FEG, Netherlands) were taken. The types of functional group present in residues were analyzed by FTIR Model Nicolet Avatar 370 DTGS, USA. The thermal degradation characteristics of residues were studied by TGA/DTGA/DTA model SII 6300 EXSTAR, Japan. Thermo-gravimetric analysis (TGA) scans were recorded from 25 to 1,000°C using a scan rate of 200 ml min^{-1} under flow rate of air.

3. Results and discussion

The effect of various process parameters on the EC process was investigated and the results are discussed below.

3.1. *Effect of initial pH of the solution (pH_0)*

It was observed that pH of the BDE had an important effect on decolorization and COD removal (Fig. 2). Generally, pH of the BDE increases during the EC processes due to HO^- formation at cathode which normally depends on the characteristic of the electrode material used and on the initial pH of the effluent. From Fig. 2, it is evident that maximum removal efficiency was obtained at initial pH 3 after 120 min of operation. It is because, at low pH values ($pH < 6$), metal species like Al^{3+}, $Al(OH)_2^+$, etc. generated on the anode can bond with the anionic colloidal particles present in the BDE which neutralize the charge present on colloidal particles and reduce their solubility through coagulation and precipitation. Formation of larger flocs with larger surface area, permitting accelerated adsorption of organic matter and its entrapment of anionic colloidal particles contributes to the remarkable increase in removal efficiency [15] and at higher pH ($pH > 6$), Al takes the form $Al(OH)_4^-$, which predominantly unfavors adsorption for negatively charged organic matter. Hence, provides lesser removal.

In addition to this, it was found that removal efficiency decreases with increase in pH, probably due to the above reasons and lesser production of chlorine and hypochlorite in neutral or basic conditions [16]. Chlorine present in BDE takes the form of hypochlorous acid in low pH range which has higher oxidation potential than hypochlorite ion. Chlorine at alkaline condition remains as hypochlorite ion, which has low potential to oxidize organic matter [17].

Generation of hydrogen and oxygen bubbles at cathode and anode, respectively, and consecutive reactions of metal hydroxide with anions viz SO_4^{2-}, NO^{3-}, Cl^-, HCO^{3-} leads to rise in solution pH [18]. Thus, lower initial pH gradually increases to higher value during the EC process. It was noticed that pH increased to 7.53 and 8.12 after a period of 60 and 120 min without aeration and an adsorbent dose.

At higher initial COD concentration, the % removals of COD obtained through the EC process are low, thus, further treatment is required to achieve the permissible limit of COD value in treated water. Around ~50 and ~61% removal of COD from initial COD value of ~15.6 and ~9.3 g l^{-1}, respectively, for distillery wastewater has been reported recently [19,20]. However, at lower initial COD value, the % removal of COD is higher and can produce treated water with COD under permissible limit. Around ~93% COD removal has been reported at

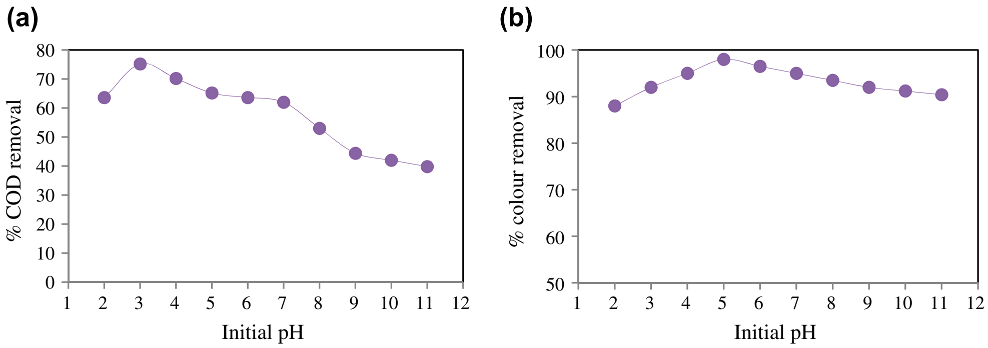

Fig. 2. Percent removal at different pH (time: 120 min, current density: 136.36 A m^{-2}, electrode distance: 1 cm, NaCl concentration: 0 g l^{-1}) for (a) COD and (b) color.

initial COD value of ~5 g l^{-1} for distillery wastewater [13]. Thus, in present study, initial COD of 5 g l^{-1} has been used for the BDE.

3.2. Effect of electrolysis time (t)

Variation of decolorization and COD removal with respect to time is shown in Fig. 3. Decolorization and % removal of COD depend on the amount of generation of metal and hydroxyl ion by the electrodes. The generation of Al^{3+} ions depends on the time of electrolysis process. An increase in generation of metal ion and their hydroxide flocs can be achievable when time prolongs, which accounts for increased removal efficiencies by co-precipitation and sweep coagulation [21]. From Faraday's law, the amount of metal ion (Al^{3+}) dissolved into the BDE solution can be computed by amount of electricity passed through it [22].

$$w = \frac{jtM}{nF} \tag{9}$$

Some amount of electrode material can also be dissolved in the solution through chemical processes in EC reactor [23–25]. The optimum time for decolorization and COD removal was found as 120 min, beyond which the decreasing trend was observed. This can be explained on the basis, that after prolonged time the adsorbed organic matter becomes saturated with metal ions, and after the optimum value of time, flocs degradation started and leaching from the adsorbed organic matter caused a lesser removal efficiency.

3.3. Effect of current density (j)

According to Faraday's law, metal dissolution rate is directly proportional to the applied current density (j).

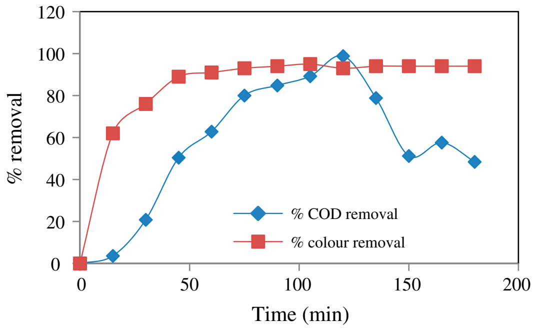

Fig. 3. Percent removal with respect to time at optimized initial COD concentration: 5 g l^{-1} (initial pH 3, current density: 113.64 A m^{-2}, electrode distance: 1 cm, NaCl concentration: 0 g l^{-1}).

At higher j values the rate of formation of metal and hydroxyl ion enhances, the production rate of hydrogen and oxygen bubbles at cathode and anode also increases with less size. These high-density bubbles attract flocculated particles under the influence of natural buoyancy, and enhance the rate of floating of flocculated particles, which increase the removal efficiency (Fig. 4). Co-precipitation is the responsible factor for higher decolorization and COD removal when Al electrode material dissolves more and forms more Al hydroxides, when j advances [26]. In addition, sludge production also gets momentum with j, and removal efficiency increases via sweep coagulation [27].

In this study, the optimum value of current density was 113.64 A m^{-2}. The removal efficiency declines at ≥ 136.36 A m^{-2}. This might be due to the increased solubility of precipitate on account of increased pH and temperature. As per the first law of thermodynamics, the partial electric current applied to the electrode got converted into heat energy, which is responsible for increased temperature effect. In the present case, the temperature was found to increase from 30 to 50°C.

3.4. Effect of inter-electrode distance (d)

In the present study, the inter-electrode distance was varied in the range 0.5–3 cm. It was found that there is increase in decolorization and COD removal values with increase in inter-electrode distance up to 2 cm, however the increase in % removal was not substantial. This might be due to the fact that due to less space, the electrostatic attraction between generated metal ions remains more and they go on colliding with each other, interrupting the formation of flocs necessary to coagulate the organic matter by precipitation and sweep coagulation. Reduction in removal efficiency is also observed on extra increase in inter-electrode distance from 2.5 to 3 cm (Fig. 5). This can be explained on the basis that it actually increases the resistance or hindrance effect which in turn offsets the generation of metal ions at a constant current density. Due to this, the metal ions have to travel a longer distance for flocs formation. The less formation of flocs might be responsible for less efficiency towards decolorization and COD removal [28].

As inter-electrode distance is not a dominant factor, to minimize the over potential caused by solution hindrance, the optimum value of inter-electrode distance was set at 1.0 cm to compensate the energy loss [29].

3.5. Effect of NaCl (electrolyte) concentration (g)

Removal efficiency of the wastewater also depends upon the specific conductivity of the solution. In

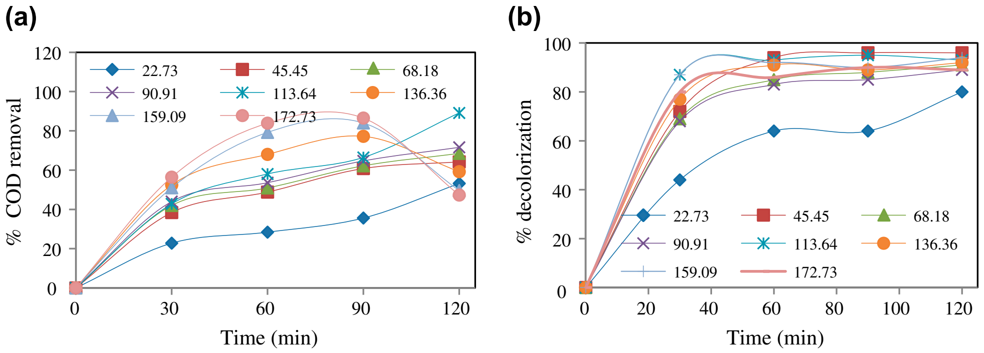

Fig. 4. Percent removal at different current densities with respect to time (time: 120 min, initial pH: 3, electrode distance: 1 cm, NaCl concentration: 0 g l^{-1}) for (a) COD and (b) color.

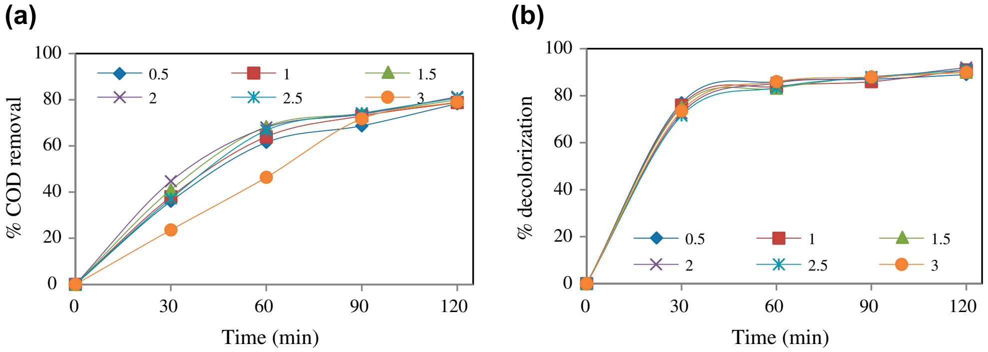

Fig. 5. Percent removal at different electrode distance with respect to time (time: 120 min, initial pH: 3, current density: 113.64 A m^{-2}, NaCl concentration: 0 g l^{-1}) for (a) COD and (b) color.

present study, NaCl (0.5–3 g l^{-1}) was used as an electrolyte because of its cheap price and low toxicity. Moreover, it resists the organic matter to attach on the surface of anode which can cause suppression. It was observed that decolorization and COD removal enhances with increase in NaCl concentration up to 1.5 g l^{-1}, after that increased dose of electrolyte can result in over exhaustion of sacrificial anode material. Similar optimum dose of NaCl was also observed while removing indigo carmine from aqueous solution by EC, which supports the present study [30]. This can be explained on the basis of Eq. (10) [31].

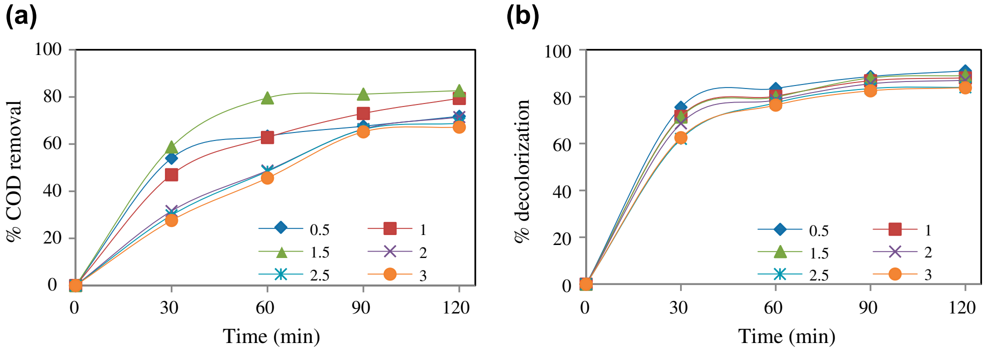

Fig. 6. Percent removal at different NaCl conc. with respect to time (time: 120 min, initial pH: 3, current density: 113.64 A m^{-2}, electrode distance: 1 cm) for (a) COD and (b) color.

Table 2
Decolorization and COD removal from BDE through EC with and without aeration and adsorbent

Parameters	Values before treatment ↓ Time (min) →	Removal after EC treatment (average value of triplicate runs for each experiment has been reported) (optimized conditions)															
		Without aeration** and adsorbent*				With aeration**				With adsorbent*				With aeration** and adsorbent*			
		30	60	90	120	30	60	90	120	30	60	90	120	30	60	90	120
Color (Hazen)		% Decolorization															
	10,000[a]	67.5	77.2	87.6	*97.4*	59.2	75.3	80.25	*98.3*	71	80.2	*97.3*	70.8	74.7	78.7	*98.2*	87.8
	20,000[b]	62.1	73.5	83.6	*92.7*	65	75	84.6	*96.1*	45	69.6	*95.3*	62.5	47	79.7	*97.9*	65
COD ($g\,l^{-1}$)		% COD removal															
	5[a]	36.6	59.8	76.8	*91.8*	39.3	63.7	78.8	*92.7*	40.5	59.6	*89.3*	77.4	43.3	64.7	*91*	84.3
	10[b]	31	47.5	61.7	*79.4*	30.7	51.4	68.4	*81.3*	29	53.3	*78.1*	69.2	33.5	59.7	*82.7*	68.3
Initial pH		Final pH values															
	3[a]	5.79	7.53	7.90	8.12	5.82	7.70	8.00	8.19	6.13	8.37	8.93	9.34	6.36	8.75	9.00	9.48
	3[b]	5.12	7.30	7.72	7.90	5.17	7.83	7.98	8.24	5.38	7.98	8.41	8.57	6.10	8.00	8.13	8.74

**Aeration using aquarium pump (flow rate = 0.22 l min^{-1}).

*Adsorbent (activated charcoal) (doses: 0.5 g at every 30 min).

[a,b] At COD value of 5 and 10 $g\,l^{-1}$ respectively.

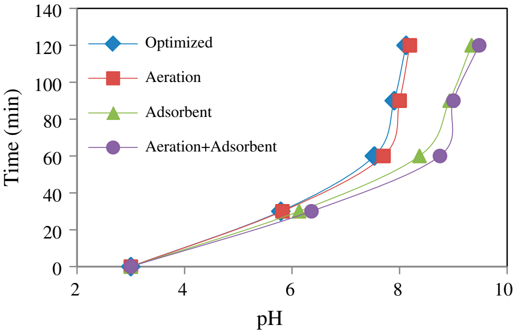

Fig. 7. Variation of pH with time at various conditions for $5\,\mathrm{g\,l^{-1}}$ initial COD (time: 120 min, initial pH: 3, current density: $113.64\,\mathrm{A\,m^{-2}}$, electrode distance: 1 cm, NaCl concentration: $1.5\,\mathrm{g\,l^{-1}}$).

$$R = \frac{id}{Ak} \tag{10}$$

As cell resistance is related to conductivity in reverse fashion, increasing specific conductance can lead to decreased cell resistance. In accordance to the Faraday's law (Eq. (11)):

$$\text{Current} = \frac{\text{Voltage}}{\text{Resistance}} \tag{11}$$

Current can be less prone to cell resistance. Hence, elevated oxidation of Al greatly helps in fair efficiencies. The optimum value for NaCl dose was found as $1.5\,\mathrm{g\,l^{-1}}$. Effect of addition of electrolyte concentration in EC process is shown in Fig. 6.

3.6. Effect of aeration and adsorbent

The effect of individual and combined addition of aeration and adsorbent in the EC reactor on decolorization and COD removal is summarized in Table 2.

From Table 2, it is evident that addition of aeration and adsorbent increases the % removal of COD and color. However, combination of aeration and adsorbents gives maximum COD and color removal. Coagulation takes place through charge neutralization followed by precipitation (predominantly followed at lower pH), sweep coagulation and floatation (predominantly followed at neutral pH), and adsorption (predominantly followed at higher pH). Aeration increases

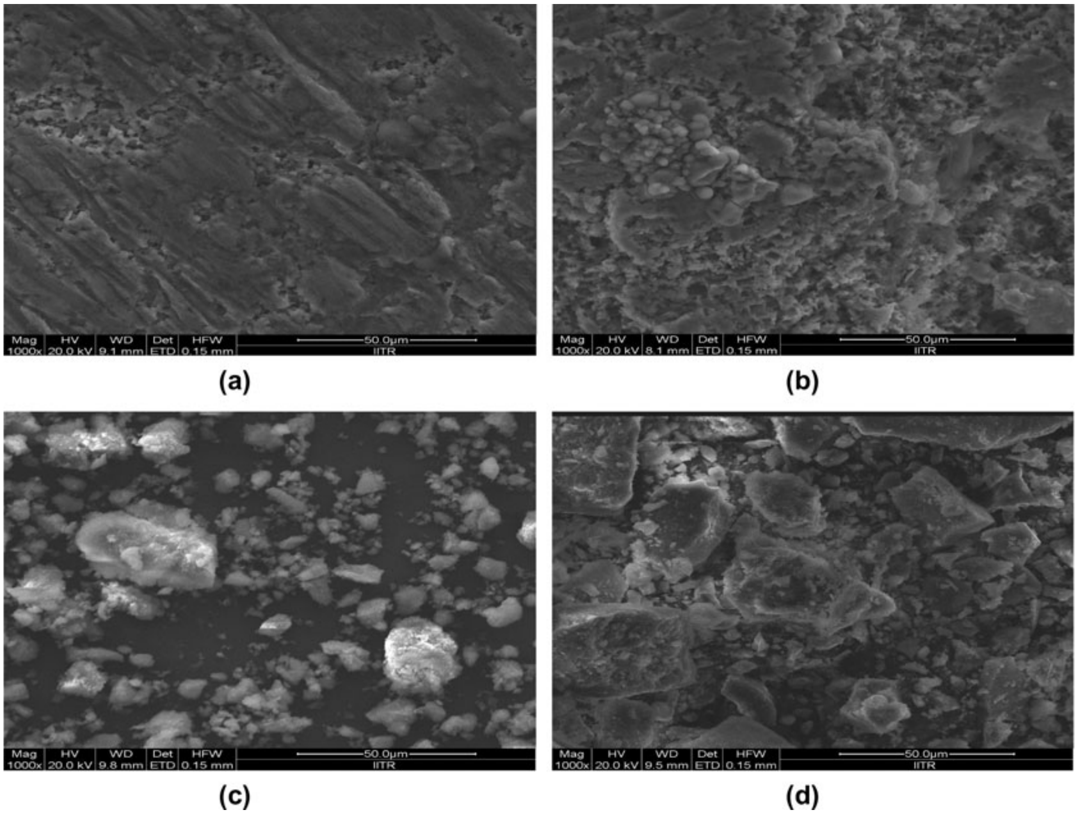

Fig. 8. SEM images of electrode and residues (a) unused electrode (1000×), (b) used electrode (1000×), (c) foam (1000×), and (d) sludge (1000×).

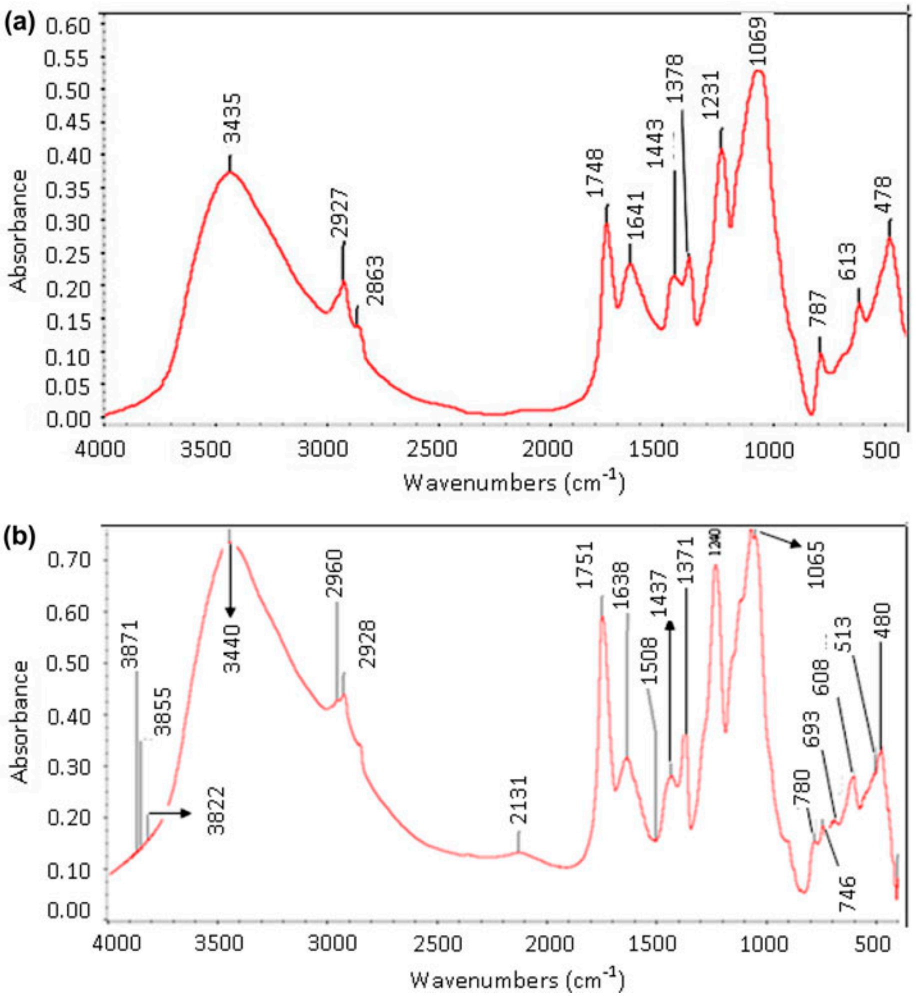

Fig. 9. FTIR of foam and sludge, (a) foam and (b) sludge.

floatation and addition of activated carbon increases adsorptive removal of COD and color. Since, the pH of the solution increases in EC process with respect to time as shown in Fig. 7, both the aeration and adsorption process can contribute to the removal of COD and color. Thus, % removals increase with the addition of aeration as well as adsorbents and maximum removal is achieved for the combined effects.

Under the effect of fast uplift and increased adsorbent dose, pH accelerated to 8.75 and 9.48 for a period of 60 and 120 min, respectively. In the present case, application of aeration and adsorbent gives ~2 and ~1% more removal of COD and color, respectively, only in 90 min instead of 120 min at optimized conditions.

3.7. *Morphology of Al electrodes and physico-chemical analysis of residues (foam and sludge)*

SEM images of electrode before and after use in EC are shown in Fig. 8(a) and (b), respectively. Unused Al electrode is rough, whose roughness is distributed throughout its surface without any dents. Due to exposure in EC cell, the Al electrode converted its roughness into many dents having size in the range 10–500 μm. Dents formation resulted due to the dissolution of Al electrode around the nucleus of active sites. Sludge particles, micro-flocs, and amorphous organic matter also adhere at the surface of used electrode. Sludge particles have bigger size than foam with crystalline nature as evident from Fig. 8(c) and (d).

3.7.1. *FTIR analysis*

Fig. 9(a) and (b) shows the FTIR image of foam and sludge, respectively. From Fig. 9(a) and (b), it is evident that the largest peak in the FTIR spectrum of foam and sludge is not showing too much difference in the wavelength, few small extra peaks were evident in the FTIR spectrum of sludge between 4,000–3,500 cm^{-1}

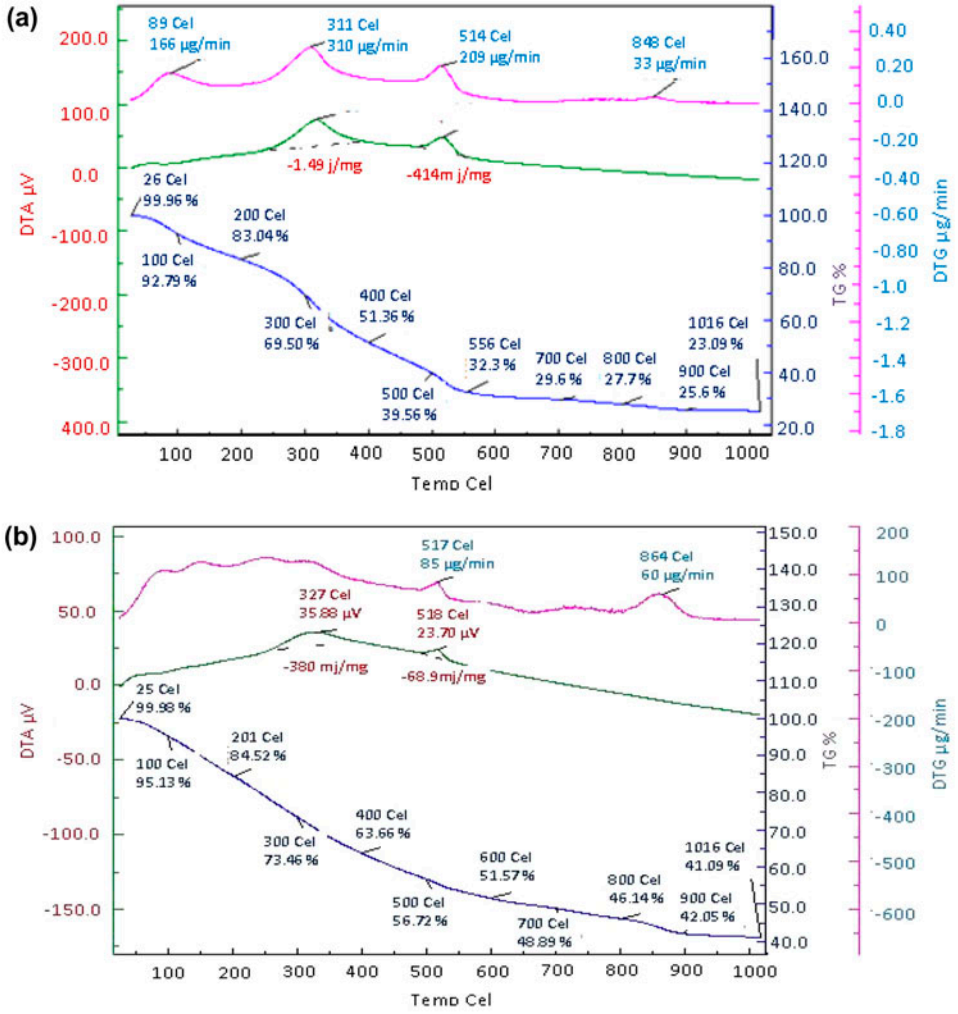

Fig. 10. Thermo-gravimetric analysis (TGA), differential thermo-gravimetric analysis (DTGA) and differential thermal analysis (DTA) curves; (a) foam and (b) sludge.

wavelength and 1,000–500 cm^{-1} wavelength. The change in peaks at corresponding wavelength is probably due to the settling down of complex compounds in the sludge and fixing of lighter components with the foam. Comparing Fig. 9(a) and (b), it seems that both foam and sludge approximately contains the same types of functional groups. Broad bands in between 3,500 and 3,000 cm^{-1} are due to the O–H functional groups. Others are as follows: C=O stretching from 1,725 to 1,700 cm^{-1}, C–O stretching from 1,440 to 1,395 cm^{-1}, and 1,320 to 1,210 cm^{-1}. Small and sharp peaks observed at 478 cm^{-1} for foam and 480 cm^{-1} for sludge are probably due to the C–X stretching [32].

3.7.2. TGA–DTA

Decomposition temperature of numerous oxides and functional groups decides the thermal stability of foam and sludge. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) of foam and sludge are shown in Fig. 10(a) and (b), respectively.

Table 3
EDX analysis of foam and sludge

	Foam		Sludge	
Element	wt. %	at. %	wt. %	at. %
C	34.73	43.8	23.43	31.82
O	51.6	48.85	53.95	55.02
Na	0.21	0.14	0.02	0.01
Al	9.76	5.48	17.48	10.57
Si	0.17	0.09	0.08	0.05
S	3.12	1.47	2.6	1.32
Cl	0.41	0.18	0.33	0.15

Table 4
TGA analysis of foam and sludge

Sample	Heating rate (℃ min^{-1})	Transition zone	Temperature range (℃)	Weight loss (wt.%)
Foam	10	1st	25–200	21.37
		2nd	200–500	39.89
		3rd	500–1,000	18.32
Sludge	10	1st	25–200	17.75
		2nd	200–500	22.48
		3rd	500–1,000	18.76

In the temperature range of 25–200℃, TGA shows loss of weight due to moisture removal and some lighter compounds and weight loss increases due to evolution of CO_2 and CO in the temperature range of 200–500℃ for both foam and sludge. Weight loss is more in foam in comparison with sludge due to the presence of high carbon content in foam in comparison with sludge (Table 3). Approximately, 18% weight loss occurs in temperature range 500–1,000℃ for both foam and sludge. Maximum degradation rate was 310.63 μg min^{-1} at 310.19℃ and 137.57 μg min^{-1} at 250.8℃ for foam and sludge, respectively, and ash content was found to be ~25 and ~41% in foam and sludge, respectively. From Fig. 10(a) and (b), it seems that calorific value of foam (1.9 J/mg) is higher than the calorific value of sludge (450 mJ/mg) because of the presence of high carbon and less ash content in the foam in comparison to the sludge. Weight loss of foam and sludge at various temperature ranges is shown in Table 4.

3.7.3. EDX analysis

EDX analysis of foam and sludge is shown Table 3. It is evident that carbon content is higher in foam than sludge and Al content is high in sludge as compared to foam.

Foam and sludge generated during EC process contain high amount of carbon (~24–35%) which is similar to carbon content of low grade coal (peat), municipal solid wastes, etc. and thus can be used as an energy source [33]. Thus, the EC process is advantageous in extracting energy recovery from wastes. However, more investigations are required to assess the feasibility of the process for real fielded application. Further, as EC process improves the biodegradability of the wastewater [34], this may be helpful in adopting biological method as further treatment method, which is a cost-effective process.

4. Conclusion

Based on the results obtained in this study, the following conclusions can be derived:

1. The optimum conditions for decolorization and COD removal are pH: 3, electrolysis time: 120 min, current density: 113.64 A m^{-2}, inter-electrode distance: 1.0 cm, and NaCl concentration: 1.5 g l^{-1}.
2. At optimum conditions, maximum decolorization and COD removal were 97.4 and 91.8%, respectively, for initial COD value 5 g l^{-1} of BDE.
3. At optimum conditions, maximum decolorization and COD removal were 92.7 and 79.4%, respectively, for initial COD value 10 g l^{-1} of BDE.
4. Use of aeration and adsorbent further improves the effectiveness of the EC process. Time required for achieving similar removal of COD and color is reduced from 120 to 90 min due to addition of aeration and adsorption.
5. Calorific value of foam was found higher than the sludge due to its higher carbon content.

Nomenclature

$\text{COD}_{\text{i/f}}$ — initial/final chemical oxygen demand, g l^{-1}
w — amount of electrode material dissolved, g of Al m^{-2}
j — current density, A m^{-2}
t — electrolysis time, s
M — molecular mass of Al (26.98 amu)
n — number of electrons involved in redox reaction (3)
F — Faraday's constant (96,500 C mol^{-1})
i — current, A
d — inter-electrode distance, cm
A — surface area of aluminum electrode, m^2
k — specific conductivity of the solution, mS m^{-1}

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