



An influence of experimental parameters in the treatment of anaerobically treated distillery spent wash by using ozone assisted electrocoagulation

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ABSTRACT

In the present study post treatment of anaerobically treated distillery spent wash having residual BOD (5000–15000 mg l⁻¹) and COD (6000–43000 mg l⁻¹) was further treated with electrocoagulation [EC] which was further investigated in the presence of aeration by using a pair of the aluminum plate. Ozone assisted electrocoagulation has been implemented to study the effect of different parameters such as pH, voltage, and electrolysis time on the COD and colour removal efficiency. Oxidation of organic components present in the effluent and sludge were analyzed by using Fourier transform infrared spectroscopy (FTIR). Ozone assisted electrocoagulation process achieved maximum decolourization 92% and COD removal 72% at current density 9.75 A cm⁻², initial COD concentration 3875 mg l⁻¹ having initial pH 7.4 and ozone gas flow rate 2 gm h⁻¹. Carbon-carbon double bond of melanoidin structure started to cleavage due to combined effect of oxidation and ozonolysis which result into reduction in organic compounds. During the process technology energy consumption increased from 0.31 to 8.39 kWh m⁻³ and electrode consumption increased from 0.0146 to 0.1503 kg Al m⁻³. The first-order kinetic was studied based up on COD removal and consumption of electrode.

Keywords: Distillery spent wash; Chemical oxidation demand (COD); Anaerobic treatment; Electrocoagulation [EC]; Ozonolysis; Melanoidin

1. Introduction

Distillery spent wash is the most complex, caramelized, highly polluted cumbersome, having very high COD, BOD, dark brown colour, extremely acidic, and contains organic and inorganic toxic constituents [1–3]. In India, there are currently 356 distillery industries which produce approximately 42.29 billion L of alcohol and generated the massive quantity of spent wash nearly 52.57 billion L of spent wash (SW) [4]. If this effluent is disposed without any proper treatment, it will increase the environmental load factor, as per green chemistry concern, environmental load factor should be minimized otherwise stress on water course will affect the aquatic life. Thus in order to supersede these effects and factors it is recommended to treat the spent wash

anaerobically as it is more effective and economical than direct aerobic treatment. As aerobic biodegradation process is energy intensive and COD value is far away to discharge the standard of COD 500 mg dm⁻³ for irrigation and 300 mg dm⁻³ to discharge in sewers as applicable in India [5], so bio-methanation process is investigated as the basic treatment to treat the distillery spent wash [6]. Biomethanation process removes the COD up to 70% and BOD 80% but still far away as per the standard so post-treatment is required for bio-digested effluent.

Several treatment methods are implemented to reduce the effect of spent wash which includes degradation of melanoidin (an intense dark brown colour pigment present in the effluent) such as flocculation [7], coagulation [8–10], oxidation of ozonation [11], UV [12], electro-chemical process [13], adsorption [14,15], electrocoagulation Fenton [16–18] air flotation [19]. These methods are not so

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much effective as these methods are having limitations in operating time, sludge generation, chemical requirements [20]. Hence the conventional biological anaerobic process is more effective in removing biochemical oxygen demand (BOD) [21,22]. Thus in today's context electro coagulation [EC] is more effective than any other conventional methods as EC has the great affinity to remove the pollutant present in wastewater [6,23].

Thus the purpose of this study is to illustrate the effect of experimental study on electrocoagulation, ozonation, and ozone assisted electro-coagulation to degrade the distillery spent wash. The effect of different operating parameters such as time, pH, voltage, and concentration of effluent on the degradation of effluent are explored on the basis of Fourier transform infrared spectroscopy (FTIR).

2. Material and methods

The biomethanated distillery spent wash was collected in sterile sampling bottles from Shri Dhyaneshwar distillery industry Ahmednagar, Maharashtra, India. It is stored in the refrigerator at temperature 4°C. The concentration of BDSW was diluted up to 20% by adding distilled water and its characteristics were measured as per the standard method of analysis [24], characteristics of effluent are dark brown colour, pH 7.4, COD 3875 mg l⁻¹, BOD 1760 mg l⁻¹, TDS 4732 mg l⁻¹, Total sulphate 695 mg l⁻¹, and chlorides 912 mg l⁻¹. To obtain the desired pH of sample 1 N NaOH or H₂SO₄ are added. Spectro analytical instrument (Handheld XRF Spectrometer, Germany made) was used to find the chemical composition of Aluminium electrodes and resulted with 99.3% Al. Eltech, India ozone generator was used to generate the ozone gas. The IR spectrum of the effluent sample was recorded in the range of 4000–400 cm⁻¹ on spectro model FTIR-4100 type A. Report was collected for the sample at a resolution of ± 4 cm⁻¹. FTIR test was carried out at Shraddha analytical services Mumbai, India.

2.1. Kinetics of Ozone assisted EC

Ozone assisted EC is the complex cumbersome process in which temperature can influence EC reaction in a number of ways like thermodynamics of hydrogen gas bubble liberation, kinetics of chemical reaction inclusive to solution physiochemical properties such as the electrical conductivity, the size of colloidal particles and the solubility of metal hydroxides [25,26]. As per the existing studies, it should remember that the kinetic mechanism for pollutant removal using ozone assisted EC technique is absolutely cumbersome. The nature of pollutants and their characteristics are totally complicated and mechanisms of removal of pollutants are different from pollutant to pollutant. Due to this in the present study, a simple integral approach has been implemented. To elaborate the basic concept of depletion of COD from anaerobically treated distillery spent wash by using ozone assisted EC process the following first order kinetic model was tested [Eq. (1)]:

$$-d \frac{(COD)}{dt} = k(COD) \quad (1)$$

where COD was the residual COD concentration in the effluent, mg l⁻¹, and k was the first order rate constant. Integrating Eq. (1) gives the liberalized Eq. (2).

$$\ln \left[\frac{(COD_0)}{(CODF)} \right] = kt \quad (2)$$

To verify the validity of Eq. (2), the graph of $\ln [(COD_0)/(CODF)]$ vs. time at various current densities are plotted. From Fig. 1a it is clear that the residual COD concentration data fit a straight line for all current densities considered. Fig. 1b elaborates the consumption of electrodes for different current density with respect to EC time which fits a nature of straight line equation. To evaluate the relation between the kinetic parameter and DC current density, the corresponding values of the kinetic parameter, k , obtained from the slope of each plot, the squared correlation coefficient, R^2 , are close to one, which shows the virtue of first order kinetics to describe the COD reduction adequately (Fig. 1c).

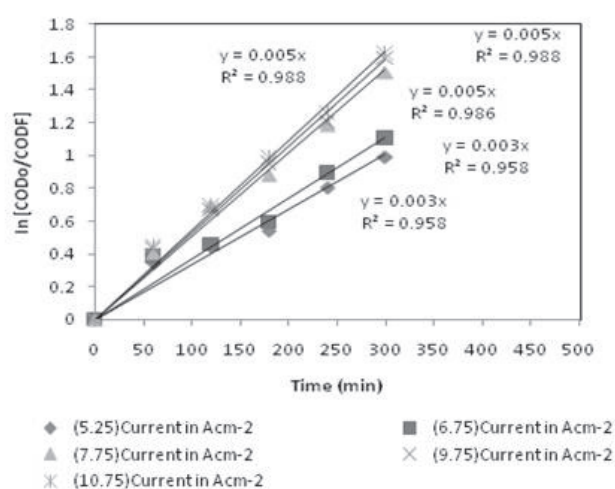


Fig. 1. (a) First order kinetic model at different current density, for ozone assisted EC.

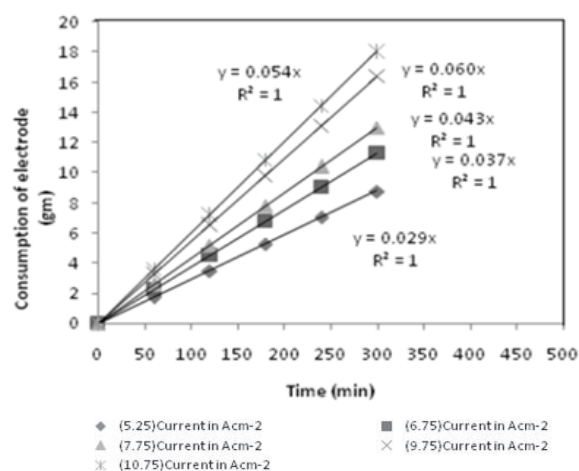


Fig. 1. (b) Electrode consumption at different current density, for ozone assisted EC.

3. Experimental plan

A schematic diagram of the experimental setup used for electrocoagulation, ozonation, and ozone assisted electrocoagulation is shown in Fig. 2. A lab scale batch mode made up of acrylic glass having reactor volume of 4.284 m³ (204 mm × 100 mm × 210 mm) was used for the experiment. For each experimentation process, spent wash of capacity 2000 L was placed in an electrolytic cell. Aluminum plates of thickness 10 mm and having dimensions of 100 mm ×

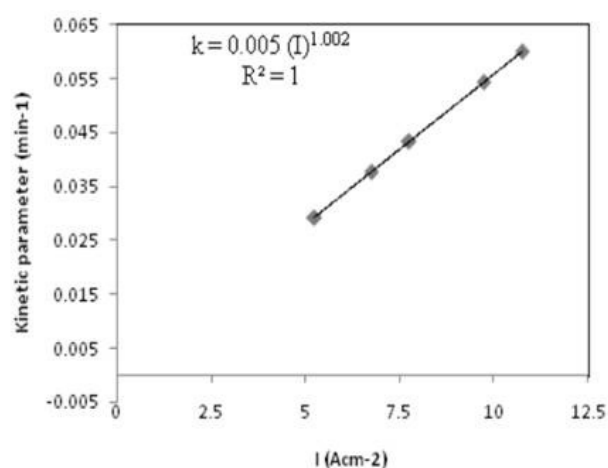


Fig. 1. (c) Variation of first order kinetic constant, k , with DC current density, I .

150 mm were used as electrodes. The submerged area for both electrodes were 7150 mm² having dimension of 55 mm × 65 mm. Electrodes were kept 5 cm above the bottom of the cell for easy stirring. The weight of electrode was measured before conducting the experiment. The spacing between the electrodes was kept constant and current was applied to both anode and cathode electrode. Electrocoagulation was started by dissolving electrodes and generation of metals in the effluent. Before the experiment each electrode was washed with acetone to remove the impurities present on aluminum electrodes. Each electrode was scrubbed by using sand paper to remove grease. Electrodes were dipped in freshly prepared HCl solution. At the end of each experiment, electrodes were washed to remove the sludge and solid residues on the surfaces and weighted. DC power supply having a capacity 7V–30V and 5.25–10.75 Amp was used. For each and every run the voltage applied was assorted to measure the efficiency of the treatment at different voltage ranges, agitation of the solution has been carried out by the magnetic stirrer. Ozonation, electrocoagulation, and ozone assisted electrocoagulation techniques were applied in the experimental work, ozone gas was continuously purged into the bottom of reactor cell with a constant flow rate of 2 gm h⁻¹. Sobo Aquarium Air pump (India) was used for aeration purpose with aeration rate 10 gallons per minute. The concentration of ozonation was determined by using iodometric method [27,28]. The sample was collected during the experiment at a regular interval of time and filtered using Whatmann 42 filter paper. Analysis of sample was strictly carried out as per standard procedure to determine the colour removal and COD reduction [24].

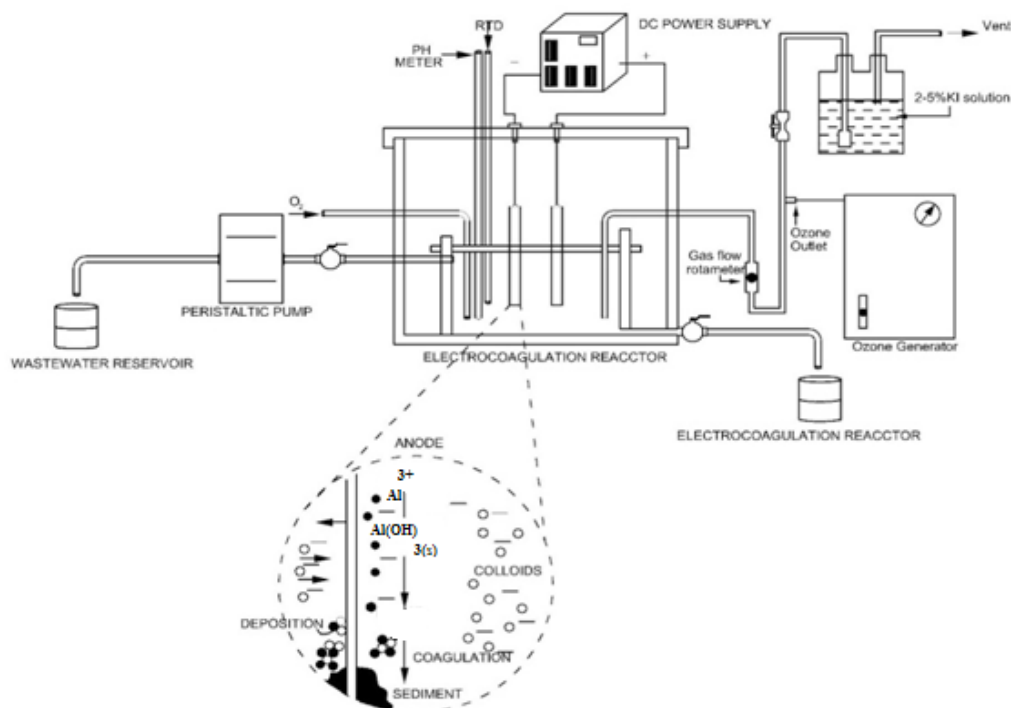


Fig. 2. Ozone assisted electrocoagulation process.

The colour of the sample was measured by using spectrophotometer and COD is determined by using dichromatic closed reflux method. RTD (resistance temperature detector) sensor was used to measure the temperature of the sample. Aluminum electrodes were used to check the performance of materials. Experimental work was conducted to study the effect of electrocoagulation, ozonation and ozone assisted electrocoagulation.

The percentage of colour removal was calculated by using the following equation

$$\% \text{ Colour removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (3)$$

where C_i and C_f are initial and final color removal efficiency at a time t sample for the corresponding wavelength $\lambda_{\max}$.

The percentage COD removal was calculated by using the following equation

$$\% \text{ COD removal} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100 \quad (4)$$

where COD_i and COD_f are the initial and final values with time t .

4. Result and discussion

4.1. Comparison of ozone, EC and ozone assisted electrocoagulation process

The colour and COD removal efficiency of three processes are as shown in Fig. 3, which illustrates the percentage of maximum colour removal efficiency by ozonation, electrocoagulation [EC] and ozone assisted electro coagulation are 46, 83 and 92 respectively. For completion of the process a time period of 5 h is required. Similar results were obtained by [27]. The COD removal efficiency of ozone assisted electrocoagulation was more than the individual

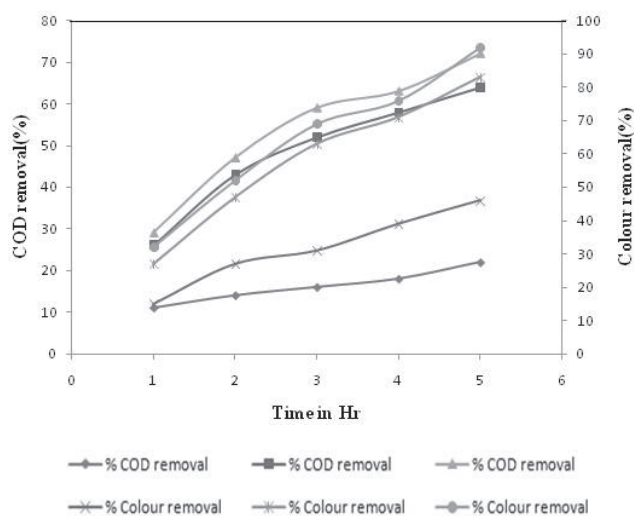


Fig. 3. Comparison of ozone, EC and ozone assisted electrocoagulation process.

process of ozonation and EC due to cleavage of carbon-carbon double bond of melanoidin. During the ozonation process, decolourization rate was much faster than the removal of organic matter as there was preferential attack of chromophoric groups [29]. Since ozone is assisted to treat melanoidin, as a result, this combination gave rise to an electrophilic reaction which made an electron reach π system by breaking carbon-carbon double bond. The molecular weight of melanoidin also decreased due to ozonolysis [30]. Pretreatment of ozonation followed by aerobic degradation reduced COD by 21.4% which is higher than untreated effluent [31]. It was found that at 4 h ozonation pretreatment process it gives enhanced result of aerobic biodegradation of distillery spent wash [32]. During the ozonation process, low molecular organic acids and oxygenated products were produced. These elements decrease effluents quite easily and help in degenerating the same [33,34]. Ozone directly attacks the carbon-carbon bond and forms bleached products like aliphatic acids, ketones, and aldehydes [32]. Figs 4a, 4b and 4c elaborate the structure of melanoidin which contains carbon-carbon double bonds in molecules, and rupture of carbon-carbon double bond due to oxidation and structure of melanoidin get separated.

4.2. Decolourization process of melanoidin molecules

Melanoidin present in spent wash conspicuously contains alcohol ($-\text{OH}$) and aldehyde ($-\text{CHO}$) groups which may get oxidized by ozone to carboxylic acids. Melanoidin molecules (MMs) are highly acidic, polymeric, hugely dispersed colloids, which are negatively charged due to the separation of carboxylic, hydroxyl and phenolic groups, MMs consist of hydroxyl and hydrophilic components such as $-\text{OH}$, $-\text{NH}_2$, $>\text{C}=\text{O}$, $-\text{COOH}$ and $-\text{NH}-\text{CH}=\text{O}$ [16,23,35]. Carboxyl and phenolic groups are most active and dominating groups and separation of H^+ is concerned to the pH of the solution. $-\text{COO}^-$ and $-\text{O}^-$ forms exists when pH is alkaline, also carboxyl and hydroxyl ions exist in $-\text{COOH}$ and $-\text{OH}$ forms when pH is acidic [15,36].

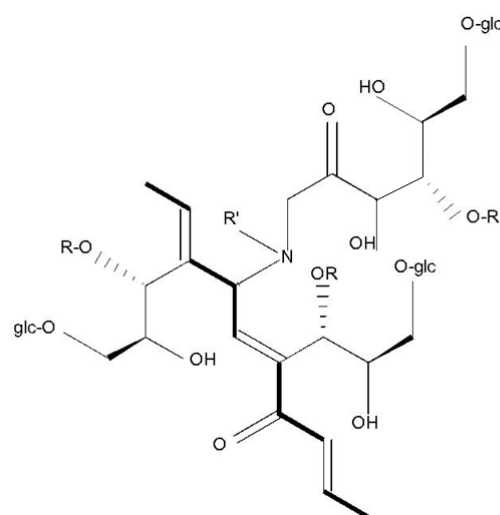


Fig. 4. (a) Structure of Melanoidin.

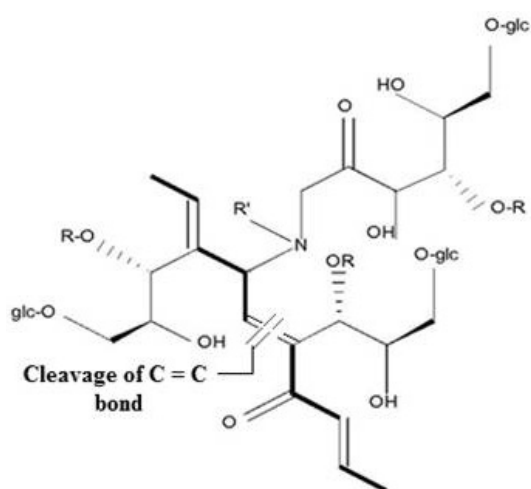


Fig. 4. (b) Cleavage of C=C bond in Melanoidin structure.

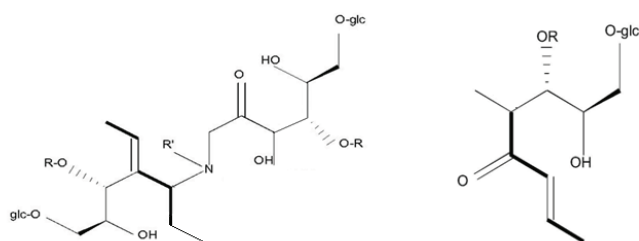


Fig. 4. (c) Ozonolysis of Melanoidin (oxidation of melanoidin structure).

4.3. Effect of pH on decolourization and COD removal

To learn the sequel of pH on decolourization of distillery spent wash test were conducted at different pH [37–40]. The efficiency of COD removal depends on the pH (3–6) of the effluent, acidic pH (3–4.5) having more influence for removing the COD, the reason may be a number of hydroxide ions was less in a solution for acidic pH, and at higher pH condition decrease in production of chlorine/ hypochlorite [27,35]. Colour degradation capacity goes on decreasing with increase in pH 7–10 as polymerization degree of the melanoidin varies with pH (3–10), decolourization rate not only depends on the pH but also depends on important factor time. Initially decolourization rate is faster as lower pH led to faster reaction [23,27]. Fig. 5a illustrates the maximum COD removal is 72% at pH 3 and initial concentration of melanoidin is 3,875 mg l⁻¹. Optimum decolourization has been achieved 92% at pH 3 (Fig. 5b), similar results were achieved by the different researcher as summarized in Table 1. Ozonation treatment was found to be probable pretreatment to accelerate the biodegradability of biomethanated distillery effluent with decolourization [41]. Figs. 5a, 5b indicate ozone assisted electrocoagulation process was more effective than individual ozonation and EC process, colour removal for ozonation process was 42% and COD removal 22%. For EC process colour and COD removal was 83% and 64% respectively.

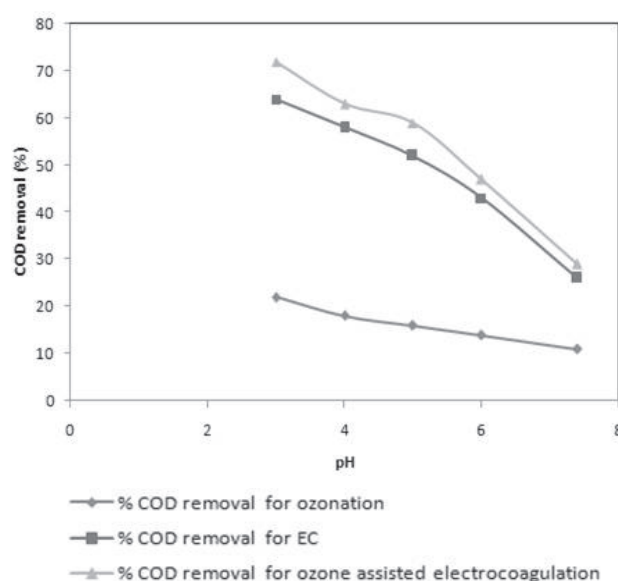


Fig. 5 (a) Effect of pH on COD removal.

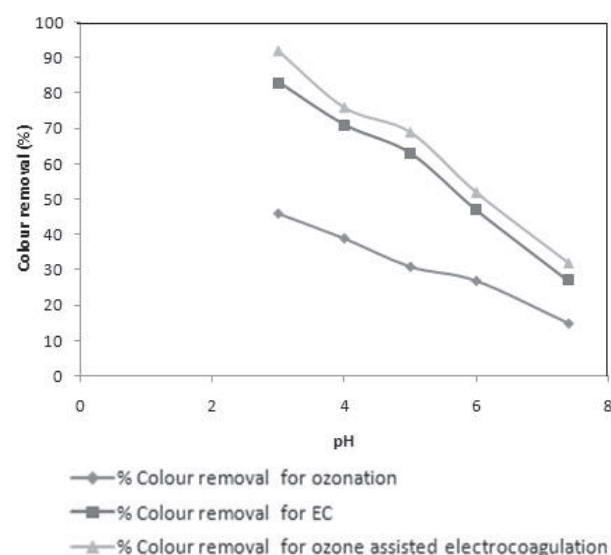


Fig. 5. (b) Effect of pH on decolourization.

4.4. Fourier transform IR spectrum analysis

The infrared spectra analysis of anaerobic digested spent wash which was post-treated by ozone assisted electrocoagulation resulting in further sludge formation from melanoidin were recorded in the 4000–450 cm⁻¹ range (Figs. 6a, 6b, 6c). The modified and reposition of functional groups of melanoidin before the treatment and after the treatment were especially important to learn the oxidation process of melanoidin due to ozone assisted electrocoagulation. Figs. 6a, 6b, and 6c show the structural characterization of sample analyzed by FTIR. The stretching frequencies at 3433.49, 2358.43, 1638.25, 1410.15, 1043.41 and 604.09 cm⁻¹ were similar to the existence of an alcoholic (–OH), –C–H stretching,

Table 1
Effect of pH on decolourization and COD removal

pH	Colour removal (%)	COD removal (%)	References
4.2	98	–	23
2	–	84.56	25
6	100	83	25
3	–	81.3	35
3	–	70	38

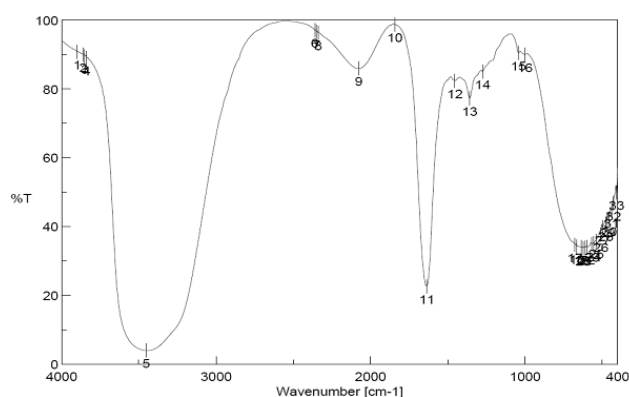


Fig. 6. (a) Fourier transform IR analysis of untreated spent wash.

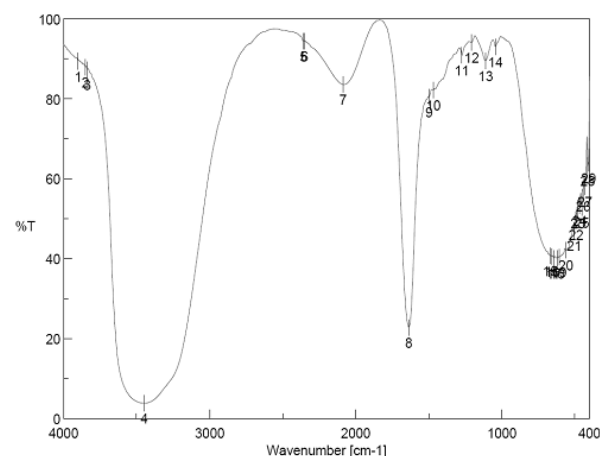


Fig. 6. (b) Fourier transform IR analysis of treated spent wash (Ozone + EC).

ketonic ($\text{C}=\text{O}$), aldehydic (-COH), carboxylic (-COOH), carbon-carbon double bond ($\text{-C}=\text{C-}$) respectively (Table 2). Similar results were obtained by [23,42].

4.5. Effect of current density and hydraulic retention time

Current density and processing time are significant parameters for the removal of COD and decolourization of effluent [11]. As per the law of Faraday, current density and time are directly proportional to coagulation dosage. Deco-

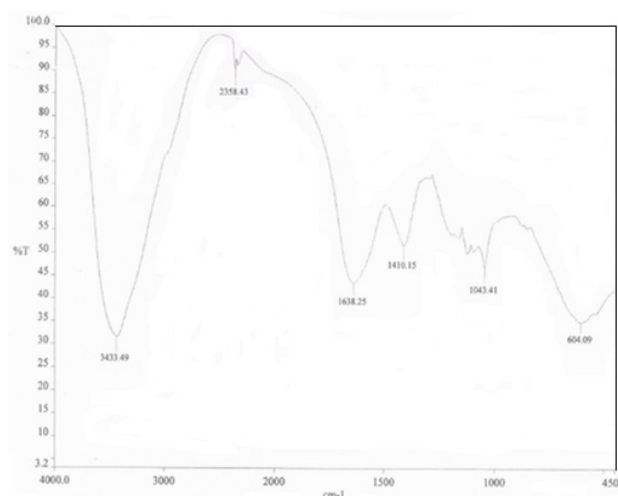


Fig. 6. (c) Fourier transform IR analysis of sludge.

Table 2
Fourier transform IR analysis of melanoidin and sludge generated during ozone assisted electrocoagulation

Wave length (cm^{-1})	Functional group
3600–3300	O–H alcohol strong bond, N–H
3400–3200	OH stretch form -COOH and -COH
2800–3100	C–H stretching from -CH , -CH_2 and -CH_3
3000–2900	C–H stretching
2000–2400	C–H
1850–1650	C=O stretching
1660–1600	N–H
1450	C–H
1410.5	C=O
1350–1330	C–H bond
1043.41	C–OH
604.09	Protein structure

lourization rate of effluent goes on increasing with increase in current density up to saturation level then decolourization rate decreases with increase in current density because the rate of cleavage of aluminum electrode increases and restabilization of colloids due to higher current density [43]. Colour removal efficiency gradually increases current density from 5.25 to 9.75 A cm^{-2} . Fig. 7 indicates effect of current density on colour and COD removal, the optimum colour removal efficiency was 92% at current density of 9.75 A cm^{-2} . Similar results reported by a number of researchers are represented in Table 3. The temperature of sample increases with current density. During EC the temperature increases due to the ohmic heating effect. Maximum 69°C temperatures were recorded during EC process. The effect of temperature increase might affect energy loss during EC process and may influence the kinetics of the process and enhance the reaction [44]. Hydraulic retention time mainly required for colloidal migration due to electrophoresis towards anodic surface and time required for actual coag-

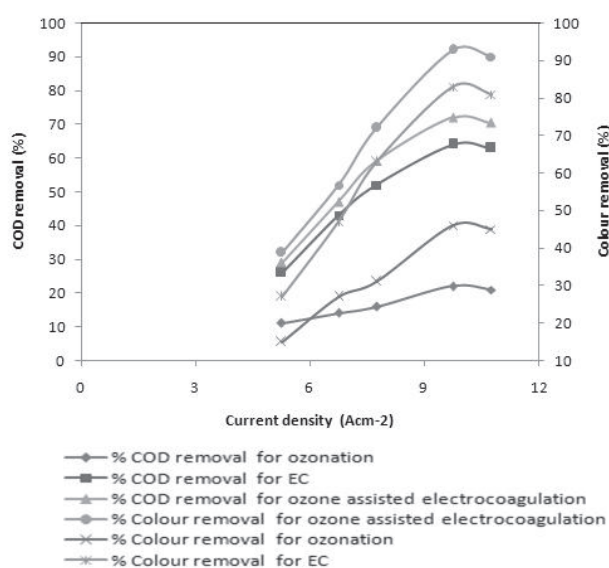


Fig. 7. Effect of current density on colour and COD removal.

Table 3
Effect of current density on removal of colour and COD

Current density	Colour removal (%)	COD removal (%)	References
20 A m ⁻²	–	72	18
7.5 A m ⁻²	98	–	23
3 A dm ⁻²	–	84	25
3 A dm ⁻²	100	83	25
0.187 A cm ⁻²	–	81.3	35
20 mA cm ⁻²	–	70	38

ulation. In the context of the experimental investigation, it can be seen that colloidal destabilization and accumulation mostly occur near the anodic surface due to the mass transport of the discharge ions was driven by diffusion [45].

4.6. Effect of pH on power consumption

Fig. 8 shows that with the increase in pH of melanoidin the efficiency of the power consumption increases. Concentration of melanoidin affects the consumption of electrodes in a proportional manner. The decolourization efficiency of melanoidin decreases with increase in concentration of melanoidin [23]. Similar results were reported by Asaithambi et al., [27]. Degradation of COD was more at higher concentration which decreases the power consumption from 25.23 to 13.7 kWh kg⁻¹ of COD. This may be due to lower concentration of oxidizing agents.

4.7. Operating cost of the system

Operating cost of ozone assisted EC process is one of the essential parameter, as it affects the application of treatment. Operating cost mainly consists of the cost of alumi-

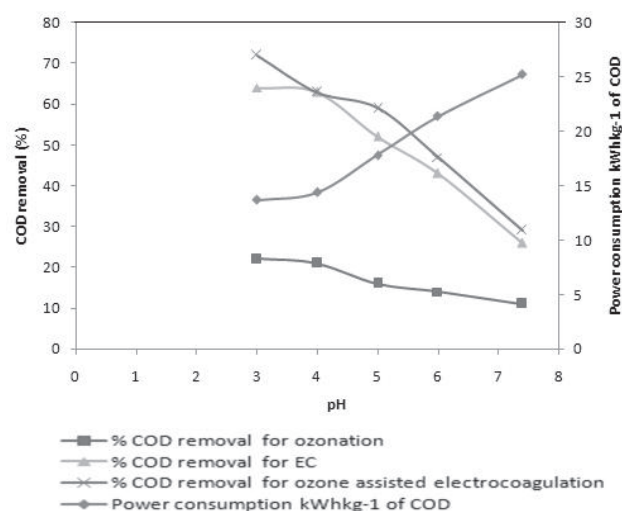


Fig. 8. Effect of pH on COD removal and power consumption.

num electrode, electrical energy consumption, labour cost, maintenance cost, etc [46].

$$\text{Operating cost} = a \text{ Energy Consumption} + b \text{ Electrode Consumption} \quad (5)$$

where a , b , are India's current market rates assessed as per March 2017. a = electrical energy cost is approximately 0.067 US \$ kWh⁻¹, b = electrode material cost is approximately 2.005 US \$ kg⁻¹ for aluminum.

Energy consumption is the consumed electrical energy used to remove COD and electrode consumption is the amount of the sacrificed electrode to remove COD. Consumption of electricity can be worked out by using Faraday's law:

$$\text{Energy consumption} = \frac{V \cdot I \cdot t}{v} \quad (6)$$

Terms included in the equation are V is voltage (V), I is current (A), t is the time in seconds and v the volume of the spent wash (m³).

As per the Faraday's law, electrode material consumption and amount of coagulant generated can be estimated by using following equation.

$$\text{Electrode consumption} = \frac{I \cdot t \cdot M_m}{Z \cdot F} \quad (7)$$

F - Faraday's constant (96,485 C mol⁻¹), M_m - The molar mass of aluminum (26.98 g mol⁻¹), and Z is the number of electron transfer (for Al electrode $Z = 3$). I = Current density in A cm⁻², t = time in second.

Table 4 shows the amount of aluminum electrode consumption (dissolved gm cm⁻²) during the process.

Electrode consumption is directly proportional to current density. When current density was increased from 5.25 to 10.75 A m⁻², Energy consumption increased from 0.31 to 8.39 kWh m⁻³ and electrode consumption increased from 0.0146 to 0.1503 kg Al m⁻³ similar result has been obtained by [47,48].

Table 4

Amount of electrode consumption (dissolved) during different current densities

Time in h	Amount of electrode Consumption (dissolved) in gm				
	Current in A cm ⁻² 5.25	Current in A cm ⁻² 6.75	Current in A cm ⁻² 7.75	Current in A cm ⁻² 9.75	Current in A cm ⁻² 10.75
1	1.756	2.265	2.600	3.271	3.607
2	3.5123	4.5299	5.201	6.543	7.214
3	5.284	6.795	7.802	9.813	10.821
4	7.045	9.060	10.402	13.084	14.428
5	8.78	11.325	13.003	16.358	18.036

5. Conclusion

The following conclusion has been summarized based on the results

1. Ozonation, electrocoagulation [EC] and ozone assisted electrocoagulation treatment was successfully treated for the distillery effluent.
2. Ozone assisted electrocoagulation is more effective than individual ozonation and EC process.
3. The different operating parameter has the influence on the degradation of distillery spent wash such as pH of effluent, current density, the time required for the process.
4. Floc formation rate was enhanced in an acidic condition and colour removal mechanism controlled by adsorption and eliminate coagulation.
5. The optimum COD removal and colour removal by ozone assisted electrocoagulation process was 72% and 92% respectively.
6. Hybrid treatment of ozone assisted electrocoagulation enhances the degradation of the cumbersome organic compound to uncomplicated biodegradable carboxylic acids. The development of carboxylic acids represents the degradation of melanoidin.
7. The ozone assisted EC process was analyzed using first order kinetic with power law dependency of its kinetic parameter upon the DC current density.

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