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Enhancing color and chemical oxygen demand degradation in distillery spent wash by electrocoagulation and ozone assisted electrocoagulation

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ABSTRACT

Distillery spent wash (DSW) is a highly complex, cumbersome, and recalcitrant effluent. Treatment for these DSW's is very difficult and expensive. The present technologies implemented for the industry to remove certain pollutants like COD and color, to safe and acceptable limits for final disposal into surface water or on land and to meet the requirements of regulatory standards. In this context, various methods such as electrocoagulation, ozone assisted electrocoagulation treatments were studied. Pair of Al–Al electrodes degrade the COD by 54.45%, color by 52.35%. Punched aluminum electrodes minimize the COD and color 61.75% and 58.45%, respectively. Continuous EC process degrades the COD and color 94.88% and 78.65%, respectively. Ozone assisted EC Process using conventional electrodes to removes COD and color 72% and 92%, respectively. Ozone assisted punched electrodes enhance the degradation rate of COD and color by 87.2% and 92%, respectively. Continuous ozone assisted EC process with punched electrode remove COD and color 97.27% and 98.72%, respectively. Ozone assisted EC was found more beneficial as compared to plain EC. A pilot plant was designed to treat the complex, cumbersome, recalcitrant, caramelized distillery spent wash, and satisfactory results were obtained which are discussed in result and discussion of this manuscript.

Keywords: Distillery spent wash (DSW); Punch electrodes; Electrocoagulation (EC); Ozone assisted electrocoagulation; Molasses

1. Introduction

In India, there were 285 alcohol manufacturing distilleries in the year 1999, producing 2.7×10^9 L of alcohol and generating 4×10^{10} L of wastewater (distillery spent wash (DSW)) annually [1]. In today's context there are 319 alcohol manufacturing distilleries producing 3.25×10^9 L of alcohol and 40.4×10^{10} L of wastewater annually [2–4]. The intense dark brown color of DSW produced by distillery industries have a very high chemical oxygen demand (COD), high biochemical oxygen demand (BOD), acidic pH, and toxic substances such as phenols [5,6]. In DSW 2% melanoidin and a dark brown recalcitrant pigment is the main crisis in its treatment. Melanoidin is only produced by the application of heat at high brix and low purity. Melanoidin is sensitive to pH [7]. Agro-based industries release a huge amount of melanoidin which is further widely distributed in foods and drinks. Cane molasses-based distilleries and fermentation industries are the main cause of environmental pollution. The structure of melanoidin is complex and is still not completely understood. It is assumed that melanoidin does not have a specific structure as its basic composition

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and chemical structures mainly depends on nature and molar concentration of reacting compounds and reaction circumstance as temperature, heating time, pH, and solvent used [7,8].

Sugar cane is the major crop in Ahmednagar district so it is called as sugar bowl of Maharashtra. In Ahmednagar district, there are 30 sugar factories that operates at full capacity and 20 distilleries which produces nearly 1,000 KL of alcohol and generates 11,168 m^3 of wastewater daily [9]. This enormous quantity of DSW if disposed of unprocessed that can create substantial stress on the watercourses from primary to widespread damage in aquatic life. Most of the nearby distilleries in Ahmednagar, Kolhapur, Pune, and Nashik districts of Maharashtra state have been reported to contaminate the groundwater by effluent having high BOD and salt content near the lagoon sites [1,10]. DSW causes a serious threat to water quality in several regions of the country-like lowering of pH value of the stream, high organic load (BOD, COD), depletion of dissolved oxygen content, destruction of aquatic life, and bad smell are some of the major pollution problems. Dark brown color present in melanoidin has hampered the photosynthesis process by blocking sunlight and hence the aquatic plant and animals are highly affected. DSW generated from the distillery industry depends upon the quality of molasses and fermentation processes (indirectly culture used for the fermentation process). Sugar molasses-based distillery industries expel a tremendous quantity of high strength wastewater. These are highly hazardous to the environment and ecosystem. DSW generated from the distillery industries is one of the most terrific risk that needs to be tackled by humankind carefully [11,12]. These industries produce recalcitrant organic compound that causes malignant color, odor complication to terrestrial, aquatic environment, and ecosystem [13]. DSW is highly complex wastewater that also contains high total solids (TS), nitrogen, phenolics, sulfate, and several heavy metals (Mn, Fe, Zn, Cd, Ni, and Pb) [14–16].

The present manuscript is trying to minimize the limitations associated with the inherent inability of the conventional technologies like aerobic oxidation, oxidation pond, etc. It also deals with high cost of the treatment for DSW. In this paper electrocoagulation and ozone assisted EC process has been suggested to treat the DSW as these methods provide solutions to conventional techniques mentioned.

2. Material and methods

DSW was collected from Shri Dnyaneshwar Sahakari sakhar Karkhana At-post Bhenda, taluka; Newasa, district-Ahmednagar, Maharashtra state, India. DSW sample was collected by adopting a random selection method. Out of these, 2 L volume was taken for analysis purpose. Polythene bottles were used for sample collection, that were thoroughly washed with distilled water. At the time of collection, the bottles were rinsed with collected sample for 3–4 times and then collected. Fig. 1 illustrates the basic structure of melanoidin. The initial characteristics of DSW COD 110,000 mg L^{-1}, BOD 50,000 mg L^{-1}, total solids (TS) 110,000 mg L^{-1}, total volatile solids (TVS) 80,000 mg L^{-1}, total suspended solids (TSS) 13,000 mg L^{-1}, chlorides 5,000 mg L^{-1}, phenols 2,500 mg L^{-1}, sulfate 7,500 mg L^{-1}, total nitrogen 8,000 mg L^{-1}, phosphate 2,500 mg L^{-1}. The initial temperature at the time of collection of wastewaters was checked and noted by using the thermometer and is found in the range of 27°C–33°C. To avoid the changes due to temperature and light, the sample was protected from direct sunlight exposure. Initial parameters of DSW are listed as: COD 3,875 mg L^{-1}, color on cobalt scale 16,656, pH –3.1, current density 1.2–3.5 A cm^{-2}, spacing between electrodes is 3 cm; agitation speed 100 rpm. Submerges area of electrodes 50.45 cm^2. Different pair of electrodes (Al–Al, Fe–Fe, Cu–Cu, and Gr–Gr) were implemented to carry out EC process. Electrodes were purchased from Vimal Iron Private Limited, MIDC, Ahmednagar, Maharashtra, India.

3. Experimental plan

The EC cell is made up of acrylic material. To study the effect of *in situ* coagulant dose generated due to current passing through electrodes applied to the DSW and electron transition can be studied thoroughly. The electrode used for the experimental work is a thin aluminum sheet of 3 mm thickness having a purity of 97%. The desired shape and dimensions are achieved by cutting the sheet of aluminum purchased locally from MIDC, Ahmednagar. The basic consideration is kept in mind, for deciding the shape of the electrode maximum submergence of the plate should be achieved to apply the optimum dose of *in situ* coagulants. Therefore, the size of the electrode is taken as 210 mm × 150 mm × 100 mm. The contact area of the single electrode is 12.5 cm^2 that is (5 cm × 2.5 cm) hence there are total four pairs of electrodes used in the arrangement and the total contact area of electrodes is 100 cm^2. The treatment technology consists of applying direct current (DC) or alternate current (AC) from an outside source among the cathode and sacrifices anode electrodes to improve the contact between the discrete particles in the effluent and endorse the *in situ* coagulants (Fig. 2). In the EC process as per the Faradays law, hydrogen gas is evolved at the cathode electrode and simultaneously dissolution of sacrificial

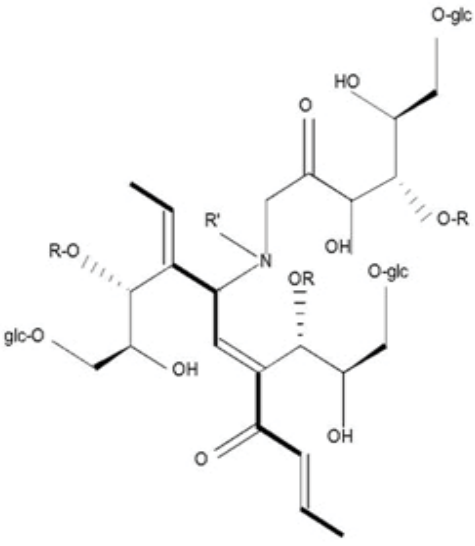

Fig. 1. Structure of melanoidin.

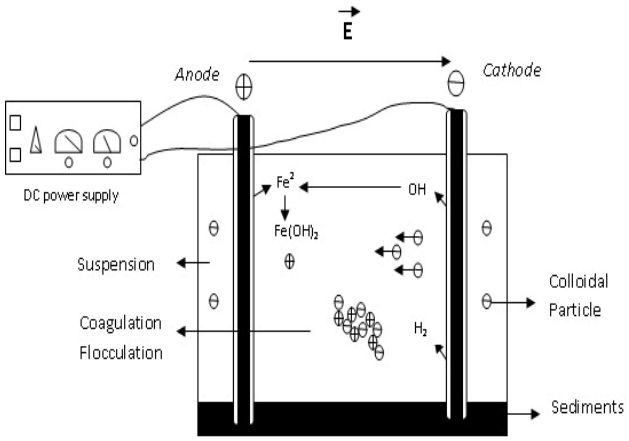

Fig. 2. EC process in the batch mode.

anode electrodes [17,18]. Sacrificial electrode utilizes DC to generate ions, which eliminates objectionable contaminants either by chemical reactions and precipitation or by causing colloidal materials to unite and then be removed by electrolytic flotation. This method leads to direct introduction of Al^{3+} or Fe^{3+} ions into the water by anodic reactions. The mechanism of EC is dependent upon the chemistry of effluent taking place, the conductivity of effluent. As the electric current is passed through electrodes, the production of chlorine, and hypo chloride ions occur as DSW contains chlorides. The reaction takes place among organic matter present in the DSW, and oxidation initiates. Hypochlorous acid and hypo chloride ions formation decompose the organic matter because of their high oxidative potential. Reactions taking place during EC with the use of Al electrodes can be described by the equations listed below:

For aluminum electrodes:
At anode:

$$Al \rightarrow Al^{3+} + 3e^{-} \quad (1)$$

At cathode:

$$Al + 3H_2O \rightarrow Al(OH)_3 + 3H^{+} + 3e^{-} \quad (2)$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^{+} + 6e^{-} \quad (3)$$

The COD of DSW has been carried out by using the dichromate reflux method (APHA – 2008). The initial COD found to be 3,875 mg L^{-1}. Initial color of DSW was carried out by using Pt. Cobalt scale and found to be 16,656. Composition of various electrodes were tested by using optical emission spectrometer. The ozone integrated electrocoagulation process was carried out to degrade the basic parameters of DSW. Fig. 3 elaborates the experimental setup. Ozone generator (Eltech ozone generator (Model el-Oz-O-3 g m h^{-1})), was used to generate the ozone gas in the laboratory using commercial grade oxygen as feed. The detailed specifications of the ozone generator is as followed:

- Operating pressure: 1.5 bar (abs),
- Operating temperature: 0°C–25°C,
- Ozone output: 3 gm h^{-1},
- Electrical supply: 220 V, 50 Hz,
- Ozone concentration: 30–70 mg L^{-1},
- Oxygen flow rate: 2 L^{-m} (L min^{-1}).

Ozone gas was continuously purged into the bottom of the reactor cell with a constant flow rate of 3 gm h^{-1}. Detailed experimental procedure has been carried as as per author Wagh and Nemade [19]).

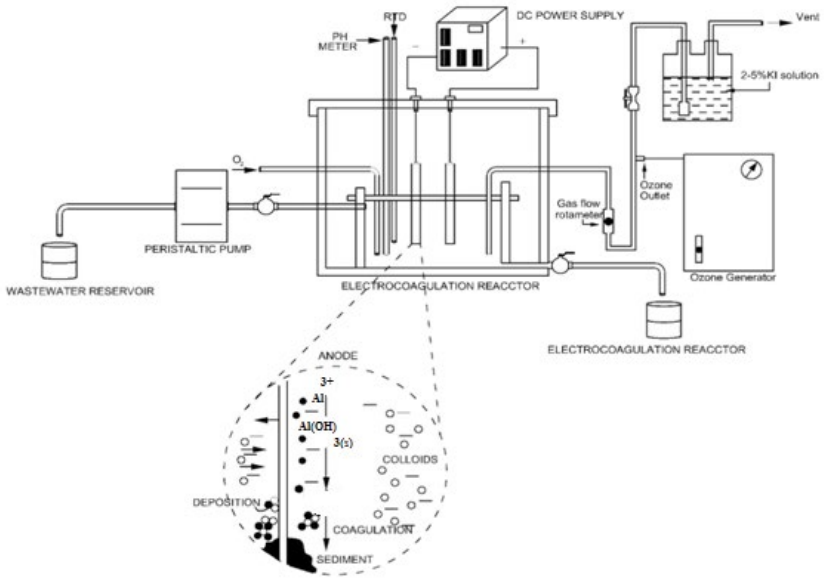

Fig. 3. Experimental setup.

4. Result and discussion

4.1. EC treatment by using different electrodes

This section represents the experimental results of different runs using different electrodes such as aluminum, iron, copper, and graphite electrodes. The experimental run was carried out to compare the efficiency of different electrodes. The selection of electrode material is based upon the purity of electrodes and a literature survey. From the literature survey, the optimum size of electrodes, optimal spacing between the electrodes, the most favorable current density, ideal electrolysis duration, and pH of DSW have been considered [9,18,19].

4.1.1. Electrocoagulation treatment using aluminum electrodes

Aluminum electrodes having dimensions 210 mm × 150 mm × 100 mm were implemented in the EC process. The composition of Aluminum electrodes is Al – 99.3%. Si – 0.340%, Cu – 0.250%, Mn – 0.017%, Zn – 0.072, Fe – 0.180%, Ti – 0.027%, Zr – 0.04%, Mg – 0.210, Cr – 0.018%. During the EC process, the pH of the DSW was increased as aluminum anode electrode was dissolved in DSW. The maximum removal efficiency was found within pH (4.1–5.8). This result is consistent with the result obtained in the literature survey [18–20]. During the EC process, two distinct mechanism processes takes place – precipitation and adsorption. For both processes' pH of DSW is more effective and plays a key role in decolorization and degradation of COD. Precipitation process takes place when pH is acidic and during this Al^{3+} is generated at anode electrodes by neutralizing the charge and reduces their solubility. With increase in pH adsorption mechanism gets into account due to amorphous aluminum hydroxides $[Al(OH)_3](s)$. Primarily colloidal particles formed during the EC process have acidic pH that are positively charged and stable. Amorphous aluminum hydroxides $Al(OH)_3(s)$ sweep flocs had the least solubility in the pH range 6.5–6.9 and a huge precise surface area that could absorb a few soluble organic compounds onto its surface (Kobya and Gengec [37]). As per Eq. (4) the monomeric $Al(OH)_4^-$ anion concentration was increased and solid $Al(OH)_3(s)$ was significantly reduced when the pH of DSW was greater than 6.5. Thus, the removal efficiency of the COD was lowered owing to the formation of soluble $Al(OH)_4^-$ at higher pH values. The efficiency of decolorization and degradation was reduced as hydrogen gas (H_2) was liberated and the formation of $(OH)^{\bullet-}$ ions takes place at the cathode [9,19,21]. Electrodes are chemically corroded by $(OH)^{\bullet-}$ ions generated with alkaline pH [21]. During the EC process, the pH of the medium increased, probably owing to the liberation of $H_2(g)$ at the cathode [22]. In EC treatment, as per the Ohmic heating effect, the temperature enhanced with respect to time.

$$Al(OH)_3 + OH^{\bullet-} \rightarrow Al(OH)^{-4} \quad (4)$$

COD removal efficiency increased with an increase in time up to optimum time, then after that, the rate of COD removal decreases due to more mixing of colloidal particles generated during the EC process. Decolorization rate is enhanced as Al(OH)3(s) flocs having a large specific surface area that absorbs soluble organic compounds [23]. The efficiency of color removal and COD degradation has been curtailed because of the prolonged process of the attraction of heterogeneous electron present into electrolyte attracted toward the cathode. Hence, the adhesion of such species increased with time and a thick layer of material stops the electron transition from anode to cathode. Hence the overall process speed reduces with time and excess electron mobility [21,23]. Fig. 4 indicates the initial concentration of COD is 3,875 mg L^{-1} and color concertation 16,656 pt. Cobalt scale. It also illustrates % COD removed is around 54.45% and color 52.35%, respectively. Reaction conditions: aluminum electrodes (Al–Al); initial pH of sample 3.1; HRT 180 min; submerges area of electrodes 50.45 cm^2; current density 1.2–3.5 A cm^{-2}; spacing between electrodes is 3 cm; agitation 100 rpm.

4.1.2. Electrocoagulation treatment using iron electrodes

Iron electrodes having composition Fe 98.428%, Si 0.30%, C 0.23%, S 0.05%, and Mn 0.94% were implemented in EC process. During the EC process, Fe(II) ions or ferrous oxides are generated. Fe electrode has more solubility at acidic conditions and is easily corroded into Fe(III) or hematite [21,23,24]. The COD removal efficiency of iron electrodes reduces as hematite is difficult to settle. For alkaline pH protons present in the solution get reduced to hydrogen (H_2). Consequently, COD removal efficiency will be retarded at acidic pH since the proportion of hydroxide ion produced is less. Reaction conditions: iron electrodes (Fe–Fe); initial pH of sample 3.1; HRT 180 min; submerges area of electrodes 50.45 cm^2, current density 1.2–3.5 A cm^{-2}; spacing between electrodes is 3 cm; agitation speed 100 rpm. Fig. 5 shows maximum COD removal as 44.52% and decolorization as 41.08%. Initial COD is 3,875 mg L^{-1} and color is 16,656 Pt-Co units.

4.1.3. Electrocoagulation treatment using copper electrodes

Copper electrodes having a size of 15.2 cm × 5 cm × 1 cm were used in the EC process. Copper electrodes having composition Cu – 91.30%, Zn 8.43%, others 0.0856%. In EC

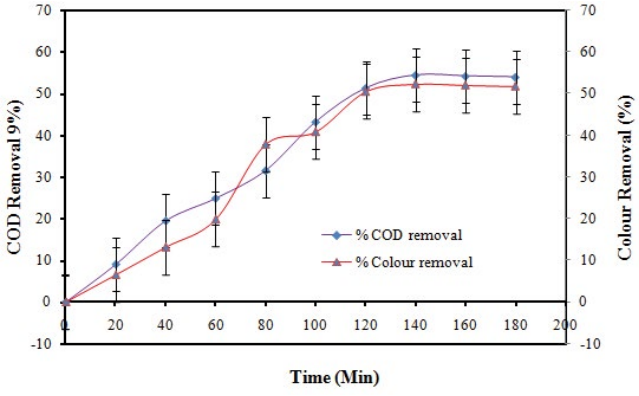

Fig. 4. Electrocoagulation treatment to DSW using aluminum electrodes.

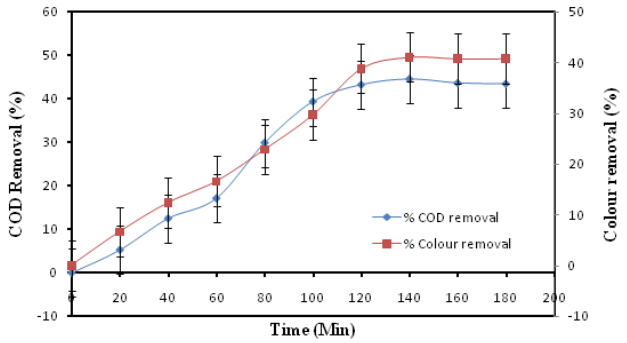

Fig. 5. Electrocoagulation treatment on DSW using iron electrodes.

process, copper electrodes get dissolved on a large scale and form copper oxides. As the color of copper oxide was dark brown hence removal efficiency is less than other electrodes. In EC process electro-oxidation and reduction process occurred instantaneously, as copper electrodes generate Cu cations and $Cu(OH)_2$ *in situ* which reasonably remove the pollutants [25,26]. During the EC process, brown reddish color was formed due to which COD and color removal rate was decreased. Copper electrodes are more costly than other electrodes. Reaction conditions: copper electrodes (Cu–Cu); initial pH of sample 3.1; HRT 180 min; submerges area of electrodes 50.45 cm^2, current density 1.2–3.5 A cm^{-2}; spacing between electrodes is 3 cm; agitation speed 100 rpm. Fig. 6 shows maximum COD removal is 39.35% and decolorization is 39.88%. Initial COD is 3,875 mg L^{-1} and color 16,656 Pt-Co units.

4.1.4. Electrocoagulation treatment using graphite electrodes

Graphite electrodes were implemented in the EC process to find out the efficiency of electrodes. Graphite electrodes are effective to oxides the pollutant at very low current densities, as *in situ* oxidizing agents are generated by indirect oxidation [27]. Due to the acidic DSW and oxidation process, the disintegration of graphite electrodes takes place. The disintegration of the graphite electrode starts, then it will continue to release fine particles of carbon in suspension and tend to interfere with spectrophotometric estimation of COD and color. The graphite electrodes require replacement after two to three batch tests. Therefore, graphite electrodes were not suitable as an anodic material for prolonged electrocoagulation because of its tendency to get oxidized to carbon dioxide [28]. Fig. 7 shows that graphite electrodes remove COD up to 44.49% and optimum color up to 40.35%. The initial COD of DSW is 3,875 mg L^{-1}. Different pair of electrodes (Al–Al, Fe–Fe, and Cu–Cu) were implemented to find the efficiency of color and COD removal. From all the experimental work, it was found that the pair of aluminum electrodes provides more effective results than all other electrodes. Maximum COD removal efficiency by Al (54.45%), Fe (44.52%), Cu (39.35%), and graphite electrodes (44.49%), respectively. Similar results have been reported by [19,28–31]. Reaction conditions: graphite electrodes (Gr–Gr); agitation speed 100 rpm. Initial pH of sample 3.1; HRT 180 min; spacing between electrodes is 3 cm, submerges area of electrodes 50.45 cm^2; current density 1.2–3.5 A cm^{-2}.

For continuous EC process pair of aluminum, electrodes were implanted as it gives the highest efficiency as compared to other electrodes.

4.1.5. Continuous electrocoagulation process

Continuous EC processes were carried out in a series of three tanks by using aluminum electrodes and in the presence of NaCl to minimize the corrosion (passivation) of electrodes on a large scale. The total submerged area of both the electrode was 71.50 cm^2. To perform the experiment 500 mL of DSW was taken. Initial parameters of the DSW were (COD 5,803 mg L^{-1}, color 21,191 Pt-Co units, and pH 3.1). The continuous EC process is more effective than the simple EC process. As in the EC process, the same effluent has been treated. During continuous EC process anode and cathode electrodes were replaced continuously in each run efficiency of degradation has been enhanced. The temperature of DSW was increasing gradually up to optimum 72°C then after it becomes constant.

4.2. Ozone treatment

Ozone treatment was carried out at pH 7–7.4 at 28°C and the ozone supply rate was maintained at 3 gm h^{-1} for

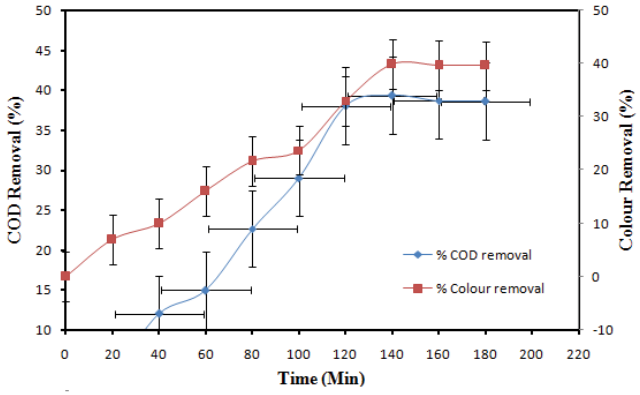

Fig. 6. Electrocoagulation treatment to DSW using copper electrodes.

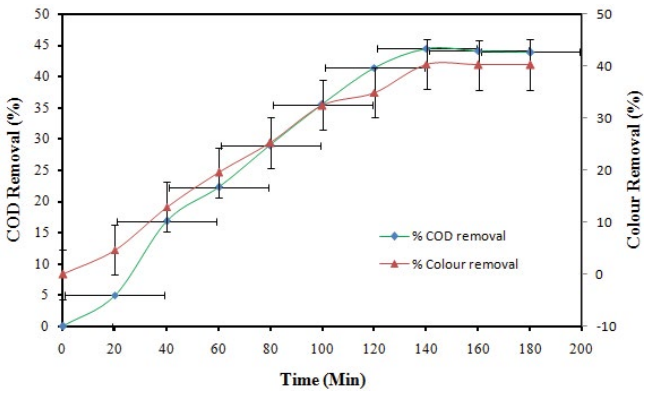

Fig. 7. Electrocoagulation treatment to DSW using graphite electrodes.

Table 1
Continuous EC treatment to DSW using aluminum electrodes [9]

Time (min)	pH	Temperature (°C)	% COD removal		% Color removal	
			(mg L^{-1})	removal	(Pt-Co units)	
Tank 1						
0	3.1	24	5,803	–	21,191	–
20	3.4	29	4,910	15.38 ± 2.35	18,815	11.21 ± 2.35
40	4.1	33	4,520	22.11 ± 3.54	16,757	20.92 ± 2.87
60	4.4	41	3,715	35.98 ± 1.57	14,015	33.86 ± 3.28
80	4.7	46	3,220	44.51 ± 4.24	12,045	43.16 ± 3.73
100	5.1	52	2,110	63.64 ± 3.87	10,845	48.82 ± 3.27
120	5.7	58	1,770	69.4 ± 1.87	8,850	58.23 ± 2.57
140	6.5	62	1,610	72.25 ± 1.56	7,910	62.67 ± 1.77
160	6.7	62	1,614	72.18 ± 2.05	7,915	62.65 ± 1.82
180	6.9	62	1,620	72.13 ± 2.35	7,921	62.62 ± 2.34
Tank 2 (same electrode used)						
180	6.9	43	1,620	72.13 ± 2.13	7,921	62.05 ± 2.35
200	7.1	51	1,537	73.51 ± 2.35	7,302	65.54 ± 1.28
220	7.4	63	1,411	75.68 ± 3.63	7,021	66.88 ± 1.64
240	7.4	69	1,203	79.26 ± 3.29	6,712	68.33 ± 2.47
260	7.4	69	1,207	79.20 ± 2.22	6,718	68.03 ± 2.49
Tank 3 (exchange of anode and cathode)						
260	7.4	49	1,207	79.20 ± 1.23	6,718	68.03 ± 2.45
280	7.6	55	1,035	82.16 ± 1.67	6,500	69.35 ± 4.23
300	7.9	61	875	84.92 ± 2.47	6,341	70.07 ± 3.98
320	8.1	69	635	89.06 ± 2.56	5,965	71.385 ± 3.19
340	8.3	71	515	91.12 ± 2.33	5,211	75.41 ± 3.28
360	8.4	71.5	435	92.50 ± 2.18	5,075	76.05 ± 3.19
380	8.5	72	297	94.88 ± 2.11	4,523	78.65 ± 4.23
400	8.7	72	303	94.77 ± 1.78	4,541	78.57 ± 2.11

Reaction conditions: initial pH of sample 3.1; submerges area of electrodes 71.50 cm^2; current density 9.75 A cm^{-2}, spacing between electrodes is 3 cm; NaCl = 2,000 mg L^{-1}

the removal of COD and color of biomethanated spent wash (sample diluted 1:2 and 1:4) and the results are summarized in Table 2. The pH of the samples increased from 7.4 to 7.7 which indicates the possible formation of some acidic by-products during ozonation. Natural melanoidin in spent wash contains alcohol (–OH) and aldehyde (–CHO) groups, which may have been oxidized by ozone to carboxylic acids. Ozonation of synthetic melanoidin decreases in pH from 8.4 to 7.4 and the degradation of by-products were identified to consist mainly of acid fractions [10,19,31]. COD removal efficiency was 11% during the first 15 min. The decrease in COD during the first 15 min may be attributed to the oxidation of simple organic compounds to CO_2, and the overall COD reduction in 1 h was 30%. There was no significant change in COD and color removal in the DSW sample. The reduction of color was observed to be much faster than the removal of organic matter and indicates the preferential attack of the chromophoric groups to complete oxidation. Decolorization rate was higher during the first 10–15 min and the overall decolorization efficiency was above 85%.

4.3. Ozone assisted electrocoagulation process

Pair of punched aluminum electrodes were implemented to carry out the EC process and Eltech ozone generated (3 gm h^{-1}) was used to purge the ozone gas from the bottom of the experimental tank. Table 3, indicates the variation of COD and color concerning time. During the process of ozone integrated EC, the pH of the DSW was changed because of ozonolysis and oxidation process [32,33].

4.4. Continuous ozone assisted EC process

Continuous ozone assisted EC process has been carried out for 360 min to check the further degradation of COD and color. As ozone is a powerful oxidizing reagent. Due to the ozonation process carbon–carbon double bond of melanoidin structure start to cleavage, also the molecular weight of melanoidin decreases on a large scale. The efficiency of color removal and COD removal depends upon different parameters such as the initial pH of the DSW, current density

Table 2
Ozone treatment to distillery spent wash

Time (min)	pH	COD removal (%)	Color removal (%)
Run O1			
15	7.1	11 ± 2.24	43 ± 2.39
30	7.5	16 ± 1.78	73 ± 2.74
45	7.5	23 ± 1.26	83 ± 2.91
60	7.4	30 ± 1.67	88 ± 2.82
75	7.3	29.55 ± 2.28	87.5 ± 2.74
Run O2			
15	7.1	15 ± 1.72	44 ± 2.75
30	7.5	18 ± 1.98	75 ± 2.16
45	7.5	26 ± 1.33	84 ± 1.38
60	7.4	30.5 ± 1.25	86.5 ± 1.45
75	7.3	31.23 ± 1.03	87.5 ± 2.34
Run O3			
15	8.4	14 ± 1.78	47 ± 1.43
30	8.2	15 ± 1.56	75 ± 1.46
45	8.1	18 ± 1.24	84 ± 2.13
60	8.0	28 ± 1.13	85 ± 1.89
75	7.7	29 ± 1.21	85 ± 1.47

Table 3
Ozone assisted electrocoagulation treatment to DSW

Time (min)	pH	% COD removal		% Color removal	
		(mg L^{-1})	removal	(Pt-Co units)	
Run OA1					
0	3.1	3,875	–	16,656	–
20	3.5	3,111	19.71 ± 2.08	13,000	21.95 ± 1.25
40	4.0	2,656	31.45 ± 2.35	11,257	32.41 ± 2.33
60	4.3	2,025	47.74 ± 2.12	9,615	42.27 ± 2.87
80	4.7	1,723	55.53 ± 2.86	7,605	54.34 ± 2.37
100	5.2	1,303	66.37 ± 2.35	5,510	66.91 ± 2.34
120	5.7	887	77.10 ± 1.40	3,434	79.38 ± 2.68
140	6.5	493	87.2 ± 1.83	1,331	92.00 ± 2.19
160	6.7	512	86.78 ± 1.48	1,345	91.92 ± 1.76
180	6.9	517	86.65 ± 1.86	1,362	91.82 ± 2.03

Reaction conditions: initial pH of sample 3.1; HRT 180 min, aluminum electrodes, submerges area of electrodes 71.50 cm^2; current density 9.75 A cm^{-2}, ozone flow rate 3 gm h^{-1}.

applied to the electrodes, the spacing between the electrodes, the concentration of DSW, etc. Table 4 shows maximum COD removal achieved up to 97.27% and color removal up to 98.72%.

5. Design of pilot plant to treat DSW

The efficiency of the electrocoagulation process depends upon the concentration of effluent, volume of sample, specification of electrodes. EC process also depends upon the key parameters such as electrolysis duration, pH of the effluent. In this section, small scale pilot plants were designed to test COD and color. Set up of the pilot plant has been shown in Fig. 8. Parameters of distillery effluent were varying from industry to industry, as it depends upon the manufacturing process and molasses feed. So, the efficiency of the EC process may change intensely. The pilot plant consists of different units such as DSW collection tank having dimension 4.5 m × 2.10 m × 1.0 m. The total volume of the tank is 9.45 m^3 (9,450 L). The clarified unit was used to clarify

Table 4
Continuous ozone integrated electrocoagulation treatment to DSW

Time (Min)	pH	% COD removal		% Color removal	
		(mg L^{-1})	removal	(Pt-Co units)	
Run OA2					
0	3.1	7,022	0	21,147	0
20	3.5	5,968	15.1 ± 1.13	19,455	8 ± 2.02
40	4.0	5,407	23 ± 1.34	16,494	22 ± 2.23
60	4.3	4,862	30.7 ± 2.27	12,688	40 ± 2.72
80	4.7	4,494	36 ± 2.07	11,207	47 ± 2.13
100	5.2	3,721	47 ± 2.21	9,347	55.8 ± 2.12
120	5.7	3,376	52 ± 2.46	8,438	60.1 ± 2.02
140	6.5	2,768	60 ± 1.32	7,216	65.9 ± 2.42
160	6.7	2,457	65 ± 1.45	6,074	71.3 ± 1.26
180	6.9	2,228	68 ± 1.76	5,034	76.2 ± 1.26
200	7.3	1,966	72 ± 1.23	4,017	81 ± 1.13
Electrodes polarity changed and added NaCl (200 g)					
220	7.7	1,724	75.4 ± 1.11	3,121	85.2 ± 1.27
240	8.1	1,411	79.9 ± 1.06	2,114	90 ± 1.21
260	8.3	1,143	83.7 ± 1.24	1,203	94.3 ± 1.56
280	8.5	823	88.3 ± 2.72	845	96 ± 1.91
300	8.7	610	91.3 ± 0.96	434	97.94 ± 1.88
320	8.8	192	97.27 ± 0.57	314	98.51 ± 1.46
340	8.9	191	97.27 ± 0.72	269	98.72 ± 0.86
360	8.9	191	97.27 ± 0.72	269	98.72 ± 0.86

Reaction conditions: initial pH of sample 3.1; HRT 360 min; aluminum electrodes; submerges area of electrodes 71.50 cm^2; current density 9.75 A cm^{-2}; ozone flow rate 3 gm h^{-1}.

Table 5
Design parameters for pilot plant

S. No	Unit	Dimension of tank/ flow rate
1	DSW collection tank (Pit)	4.5 m × 2.10 m × 1.0 m
2	Sand Filtration unit	3.1 m × 0.65 m × 0.55 m
3	EC unit	1.8 m × 0.95 m × 0.95 m
4	Submerged area of electrodes	35 cm × 20 cm
5	Ozone	3 gm h^{-1}
6	Current density	133 A cm^{-2}
Distillery spent wash parameter details		
7	Hydraulic retention time	24 h
8	Initial COD	12,000 mg L^{-1}
9	pH	6.5
10	Color	Light brown
11	Spacing between electrodes	2 cm

the effluent. Sand filtration unit has been implemented to filter the effluent. The dimension of the sand filtration unit is 3.1 m × 0.65 m × 0.55 m. Ozone assisted electrocoagulation unit was installed with the dimension of tank is 1.8 m × 0.95 m × 0.95 m. The total volume of the tank is 1.71 m (1,710 L). Total submerged areas of electrodes are 11,250 cm^2. Eight pairs of aluminum electrodes were designed for the EC process, each pair having submerged area 700 cm^2 (35 cm × 20.1 cm). The design of the EC unit and pair of electrodes are carried out as per different researchers [9,19,34–49]. Details of design parameters and effluent parameter characteristics are mentioned in Table 5. Design of pilot plant purely base upon trial and error basis and has been prepared for Sun flair industry Aurangabad, Maharashtra, India.

6. Conclusions

This study highlights the major findings of the present study based on different treatments like electrocoagulation, ozone, ozone assisted electrocoagulation, to treat DSW. Laboratory scale experiments were conducted in batch mode operation. In this research work, parameters like COD and color are used to assess the removal efficiency of selected treatment methods. Table 6, shows summary of result obtained by using EC process, ozone assisted EC process, and continuous EC process.

The major observations and conclusions of different treatment methods are presented subsequently.

Maximum COD removed by Al, Fe, Cu, and graphite electrodes is 54.45%, 44.52%, 39.35%, and 44.49%, respectively. Ozone can degrade 31.23% COD and 87.5% color of DSW. Ozone assisted electrocoagulation proves to be more

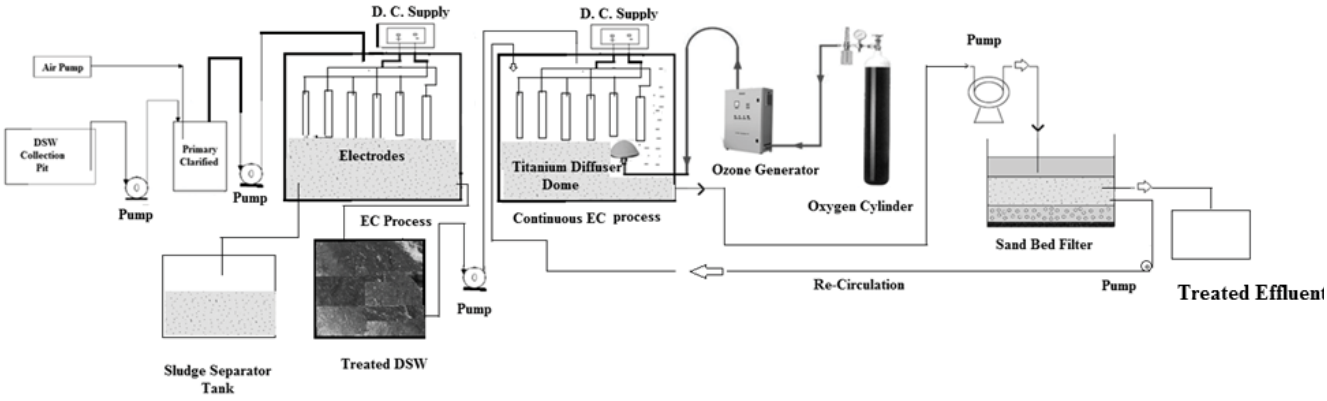

Fig. 8. Pilot plant to treat cumbersome distillery spent wash.

Table 6
Summary of electrocoagulation (EC) process, ozone treatment, ozone assisted electrocoagulation process to degrade the efficiency of COD and color

S No	Types of electrodes	Initial COD (mg L^{-1})	Initial color (Pt-Co units)	Spacing (cm)	Dimension (cm)	pH	Current density Acm^{-2}	COD removal (%)	Color removal (%)
Submerged area 50.45 cm^2, current density – 3 A cm^{-2}									
1	Al–Al	3,875	16,656	3	10 × 15 × 1	3.1	1.2	54.45	52.35
2	Fe–Fe	3,875	16,656	3	15 × 10 × 1	3.1	1.2	44.52	41.08
3	Cu–Cu	3,875	16,656	3	15.2 × 5 × 1	3.1	1.2	39.35	39.88
4	Gr–Gr	3,875	16,656	3	15 × 5 × 1	3.1	1.2	44.49	40.35
Submerged area 50.45 cm^2, current density – 5.25 – 10.75 A cm^{-2}									
Punched electrodes									
5	Al–Al	3,875	16,656	3	15 × 9.5 × 2	5.5	9.75	61.75	58.45
Punched electrodes with aeration									
6	Al–Al	5,803	21,191	3	15 × 9.5 × 2	5.8	9.75	72.25	63.55
Continuous EC process submerged area 71.50 cm^2, duration									
7	Al–Al	5,803	21,191	3	15 × 9.5 × 2	8.7	9.75	94.88	78.65
Ozone assisted EC process plane electrode									
8	Al–Al	3,875	16,656	3	10 × 15 × 1	3.1	9.75	72	92
Ozone assisted EC process punched electrode									
9	Al–Al	3,875	16,656	3	10 × 15 × 1	3.1	9.75	87.2	92
10	Al–Al	5,803	21,191	3.2	10 × 15 × 1	5.5	9.75	75.80	82.62
Continuous-ozone assisted EC process with punched electrode									
11	Al–Al	5,803	21,191	3	10 × 15 × 1	8.9	9.75	97.27%	98.72

effective than individual ozonation and EC process. Floc formation rate was enhanced in an acidic condition and color removal mechanisms were controlled by adsorption and eliminate coagulation. The optimum COD removal and color removal by ozone assisted electrocoagulation process was 97.27% and 98.72%, respectively. Punched electrodes are effective than plain electrodes. COD and color removal rates are enhanced by 7.3% and 6.1%, respectively. Hybrid treatment of ozone assisted electrocoagulation enhances the degradation of the cumbersome organic compound to simple biodegradable carboxylic acids. The development of carboxylic acids represents the degradation of melanoidin.

Recommendations

Electrocoagulation process, ozone treatment, and ozone assisted electrocoagulation treatment options can be adapted to treat different industrial wastewaters.

- As EC process is unable to degrade COD 100%. Therefore, it is essential to further treat them by ozone assisted EC process to safely dispose of DSW.
- Treated spent wash should be used preferably at the plant site to perform further studies of the effluent to eliminate the problems associated with variation in COD concentration during transporting the spent wash to the laboratories.
- Pilot plant investigation to develop baseline data and scale-up criteria to form a design basis may be done. This will help in finding the application at the plant scale.
- To enhance the efficiency of the treatment technology, after each run, electrodes may replace or change the polarity of electrodes to avoid the more corrosion of electrodes.
- Maintain the optimum temperature and pH of the effluent (DSW) to enhance the decolorization rate.

Future work

- Detailed sequential investigation to be carried out such as ozone assisted continuous EC process followed by fungal treatment.
- The relevance of this research to a full-scale industrial level would be feasible if further research in the continuous fungal culture set up is implemented. Also, the extraction of fungal biomass is essential.
- Treated spent wash should be used preferably at the plant site to perform further studies of the effluent to eliminate the problems associated with variation in COD concentration during transporting the DSW to the laboratories.
- Modifications in electrode configurations such as a rotating disk electrode or rotating cylindrical electrode may help in improving the EC process.

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