International Journal of Environmental Science and Technology
https://doi.org/10.1007/s13762-020-02837-3

ORIGINAL PAPER

Augmentation with Ozone-Assisted Electrochemical degradation of distillery spent wash for the removal of color and chemical oxygen demand

M. P. Wagh[1] · P. D. Nemade[2] · A. Sengupta[1]

Received: 26 October 2019 / Revised: 7 June 2020 / Accepted: 1 July 2020

Abstract
Distillery spent wash (DSW) is an extremely cumbersome and recalcitrant effluent. The present technologies are implemented for the industry to remove certain pollutants like chemical oxygen demand 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 view of this above condition various methods such as Electrochemical (EC) and ozone-assisted EC processes are implemented. Pair of aluminum (Al–Al) electrodes are more effective than other electrodes such as iron (Fe), copper (Cu), and graphite (Gr). Pair of Al–Al electrodes eliminate the chemical oxygen demand by 54.45% and color by 52.35%. Punched Al–Al electrodes minimize the chemical oxygen demand by 61.75% and color by 58.45%, respectively. Continuous electrochemical process reduces the chemical oxygen demand by 94.88% and color by 78.65%, respectively. Ozone-assisted electrochemical process using conventional plain electrodes removes chemical oxygen demand by 72% and color by 92%, respectively. Ozone-assisted punched electrodes enhance the degradation rate of chemical oxygen demand and color by 87.2% and 92%, respectively. Continuous ozone-assisted EC process with punched electrode removes chemical oxygen demand and color by 97.27% and 98.72%, respectively. Ozone-assisted EC was found more beneficial as compared to conventional plain EC. A pilot plant is designed to treat the intensive, recalcitrant, caramelized distillery spent wash, hence augmenting with ozone assisted EC method helps in achieving the desired satisfactory result.

Keywords Ozone-assisted electrochemical · Electrochemical (EC) · Punch electrodes · Distillery spent wash (DSW) · Chromophoric groups · Molasses

Introduction

Sugar is the major industrial sector after textiles in India with an annual turnover of Rs 41,000 crores. India is among the top five sugar producing countries in the world and ranks second after Brazil with an annual production of 321 lakh tons of sugar. The latter is the primary feedstock for alcohol manufacture by 285 distillery units (capacity 10 to 300 KLD) producing 27,00,000 m^3 of ethanol (250 L alcohol per ton of molasses) (Mohana et al. 2009; Santal and Singh 2013; Premalatha et al. 2014; Ghosh Ray and Ghangrekar 2019). Sugarcane molasses comprise 50% fermentable sugar and around 4–10 kg of molasses which are essential for the manufacture of 1 L of alcohol (Ozyonar and Karagozoglu 2012; Sahu et al. 2019); Davis 2001; Biradar 2003; David et al. 2015; Santal et al. 2016; Ravindra et al. 2017a, b; Wagh et al. 2019). In the manufacture of alcohol, fermentation and distillation are the principal steps and the spent wash released in the distillation section is the key source of wastewater generated from the distillery (Chandraraj and Gunasekaran 2004; Mohana et al. 2007; Asaithambi et al. 2012; Wagh and Nemade 2017). Distillery operations lead to the generation of about 15 L of spent wash for every liter of alcohol produced, and the spent wash is classified as a high strength process effluent with a high concentration of

Editorial responsibility: Samareh Mirkia.

✉ M. P. Wagh
profmpwagh@gmail.com

[1] Department of Civil Engineering, Dr. Vithalrao Vikhe Patil College of Engineering Ahmednagar, Ahmednagar, Maharashtra, India

[2] Department of Civil Engineering, S. B. Patil College of Engineering, Indapur Savitribai Phule Pune University, Pune, Maharashtra, India

Published online: 15 July 2020

dissolved organic and inorganic compounds (Zafar et al. 2019; Yadav 2012). In addition, a raw spent wash is characterized by its dark color, high temperature, and low pH (4.2–4.5). The typical characteristics of the DSW are presented in Fig. 1.

Indian distilleries produce 27,00,000 m^3 alcohol generating about 4, 05,00,000 m^3 of spent wash annually (15–20 L per liter of alcohol) (Kobya and Gengec 2012; Kobya and Demirbas 2015). The population equivalent of distillery spent wash based on BOD_5 is in 6.2 billion which means that the contribution of distilleries in India to organic pollution is approximately six times the current population of India. Other wastewaters generated from distillery include yeast sludge, cooling water, boiler blowdown, bottling plant waste, floor washings, and other miscellaneous sources like leakages and spillages (Biradar 2003). Distillery spent wash poses a serious threat to water quality in several regions of the country—lowering of pH value of the stream, higher organic load (BOD, COD), depletion of dissolved oxygen content, destruction of aquatic life, and bad smell are some of the major pollution problems. Groundwater contamination by effluent with high BOD and salt content near the lagoon sites, in most of the distilleries, has been reported widely (Wagh and Nemade 2015a).

There are several methods available for handling distillery spent wash, which include aerobic, anaerobic, physicochemical, composting, incineration, and wet air oxidation processes (Karri et al. 2017; Ravindra et al. 2017a, b; Fu et al. 2019; Rashidi et al. 2019; Hairuddin et al. 2019). Each of these technologies has different levels of acceptability and techno-economic viability based on the characteristic merits and limitations. Anaerobic digestion exploits the ability of various populations of bacteria to perform different steps in a degradation process to break down large organic molecules to water, carbon dioxide, and methane (Erhan et al. 2012; Wagh and Nemade 2018a). This process provides chemical building blocks for the growth and maintenance of the bacterial population. Anaerobic treatment is now a well-established primary treatment methodology for handling distillery spent wash based on different types of reactors (conventional digester, fluidized bed reactor, fixed film reactor, and UASB) (Biradar 2003). Several full-scale operating installations for anaerobic treatment of spent wash based on various techniques have demonstrated 70–85% BOD removal efficiency. In view of the high strength of spent wash, these efficiencies result in 15–30% of BOD and 30–40% of COD remaining as residual pollutants. Spent wash after anaerobic treatment will still be a strong effluent with a high

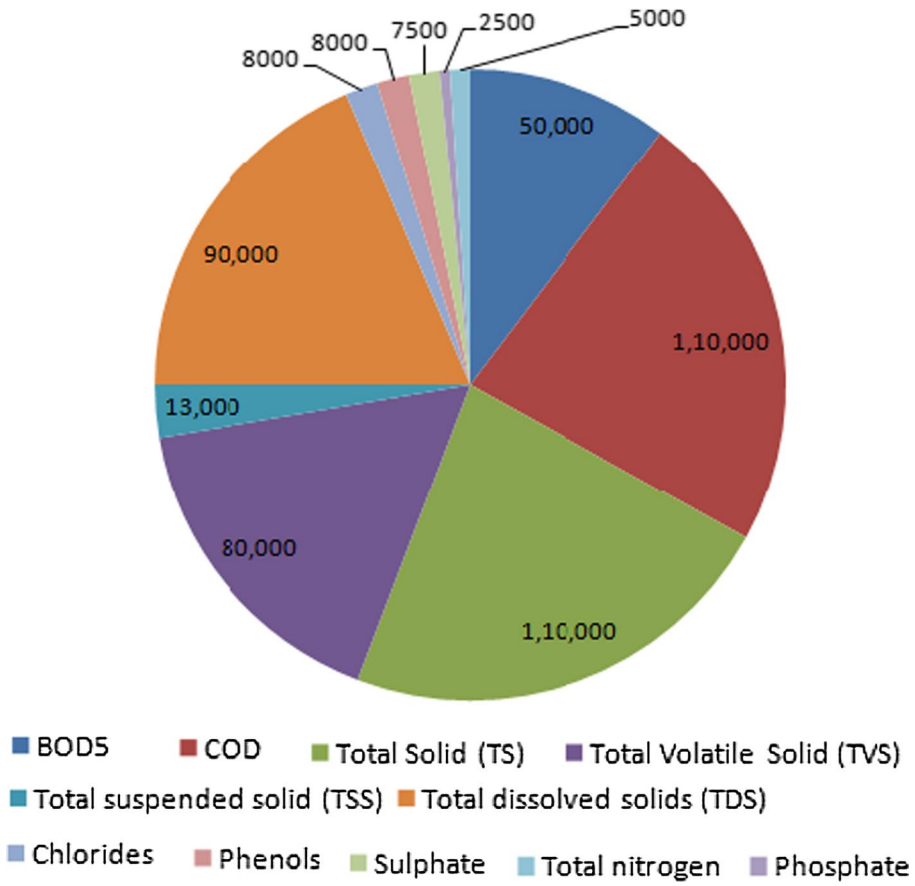

Fig. 1 Pie chart showing the typical characteristics of the distillery spent wash

residual BOD, COD and also dark color with a significant concentration of dissolved inorganic and organic salts (David et al. 2015; Wagh and Nemade 2018a).

The objective of the present study is to minimize the limitations associated with the inherent inability of the current technology and the high cost of the treatment. To dispose of these impurities (COD, color), electrochemical (EC), ozone, and ozone-assisted electrochemical process have been implemented. Day-by-day rules and legislation are mandatory to dispose of the distillery effluent. So, there is an urgent need to develop new technology to handle the intensive unwanted residual effluent generated during ethanol manufacturing.

Materials and methods

Distillery spent wash (DSW) was collected from Vikhe Patil distillery industry At-post Pravara Loni, taluka; Rahata, district- Ahmednagar, Maharashtra state, India. DSW was collected in polythene bottle, which was carefully cleaned with distilled water. To avoid the contamination, polythene bottle with samples was washed 3–4 times and then the sample was collected. The collected DSW was immediately brought to the research laboratory and stored in the refrigerator at 4 °C in order to avoid any deterioration in the physicochemical property of the spent wash until further use. Initial characteristics of the sample were carried out to confirm the concentration and parameters such as COD, BOD, TDS, and pH. Different pairs 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.

Experimental plan

As acrylic glass material is light in weight and DSW has less effect on it, the acrylic glass material was used to make EC cell. For the experimental work, a thin sheet of aluminum with thickness of 3 mm was used as an electrode and has purity of 97%. The aluminum sheet was purchased from Maharashtra Industrial Development Corporation (MIDC), Ahmednagar, locally. By cutting the sheet, desired shape and dimensions were achieved. To remove dust, dirt, and grease, sand polish stone was used. Electrode was washed thoroughly with 15% HCl and then rinsed with distilled water before each experiment. The maximum submergence of the electrode was kept to achieve the optimum dose of in situ coagulants. Thus, the dimensions of the electrode were taken 210 mm × 150 mm × 100 mm. Four pairs of electrodes having contact area 100 cm^2 were implemented. Electricity was supplied by connecting the electrodes to a direct current (DC) thus improving the contact between the discrete particles in the effluent and endorse the in situ coagulants (Fig. 2). During EC process, due to the application of direct current, corrosion of sacrificial anode electrodes occurs resulting in formation of coagulant corresponding to the anodic metal which eliminates objectionable contaminants either by chemical reactions or precipitation. Simultaneously, production of hydrogen at the cathode facilitates pollutant removal by electrolytic flotation (Wagh and Nemade 2017). The rate of dissolution of metal electrode in EC process enhances with an increase in current intensity. The amount of hydrogen peroxide (H_2O_2) generation increases as current intensity increased. Thus, producing more hydroxyl radicals in the electrolyte is extremely responsible for the degradation of recalcitrant pollutants. The effect of in situ coagulant dose applied to the DSW and

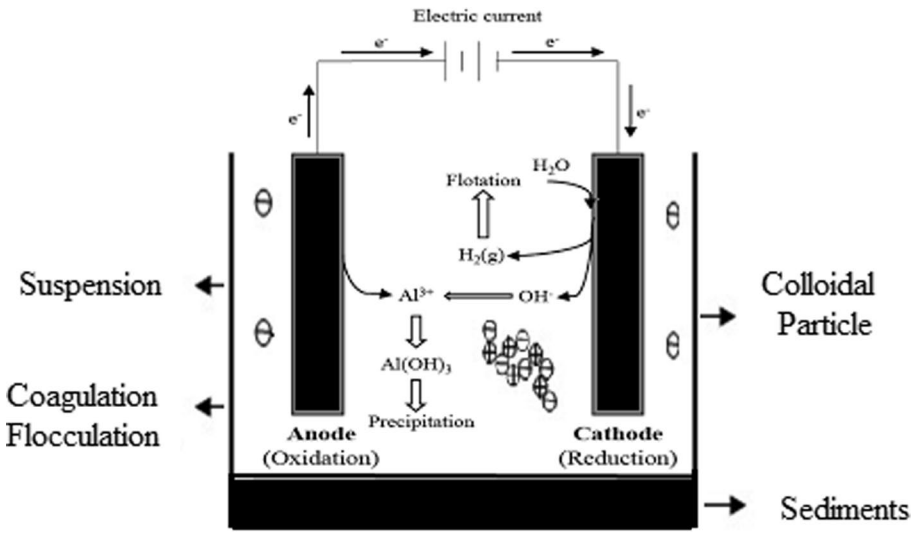

Fig. 2 EC process in the batch mode

electron transition can be studied thoroughly. The dichromate reflux method was used to find out chemical oxygen demand (COD) and found to be 3875 mg/L (APHA 2008). Initial color noted 16,656 Pt. Cobalt scale. Ozone-assisted electrochemical process was carried out to degrade the basic parameters of distillery spent wash (DSW). Figure 3 elaborates the experimental setup. Eltech ozone generator (Model el-oz-O–3 gm/h) was used to generate the ozone gas.

Results and discussion

Electrochemical treatment by using various electrodes

Aluminum (Al), iron (Fe), copper (Cu), and graphite (Gr) electrodes were implemented for experimentation. To find out the efficacy of electrodes, various runs were carried out.

Electrochemical (EC) treatment using aluminum (Al) electrodes

Aluminum electrodes having dimension 210 mm × 150 mm × 100 mm were executed in the EC process. The composition of aluminum electrodes is Al—97.596%, Si 0.51%, Fe—1.26%, Cu—0.35%, Mn—0.27%, and Ti—0.014%. During the EC process, as aluminum anode electrode was dissolved in DSW the pH of the DSW was enhanced. The maximum elimination efficacy occurred at pH (4.1–5.8). The result found is consistent with the literature survey (Merzouk et al. 2011; Erhan et al. 2012; Kobya and Demirbas 2015). In electrochemical process, precipitation and adsorption are the key mechanism, which play main role in elimination of color and chemical oxygen demand degradation. In acidic pH at anode electrode, Al^{3+} is generated and reduces the solubility by neutralizing the charge. The amorphous aluminum hydroxides Al $(OH)_3$ (s) formed due to adsorption at higher pH. In EC process, primarily colloidal particles formed were positively charged and stable. In the pH range 6.5–6.9 Al $(OH)_3$(s), sweep flocs have minimum solubility with an enormous precise surface area that could absorb a few soluble organic compounds onto its surface (Kobya and Gengec 2012). Literature survey recognized that the electrolysis process brings the pH of the electrolysis to neutral and resulting in maximum coagulation. Anode electrode did not get oxidized completely, and hence, plenty amount of H^+ ions are not produced in acidic pH. As per Eq. (1), 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

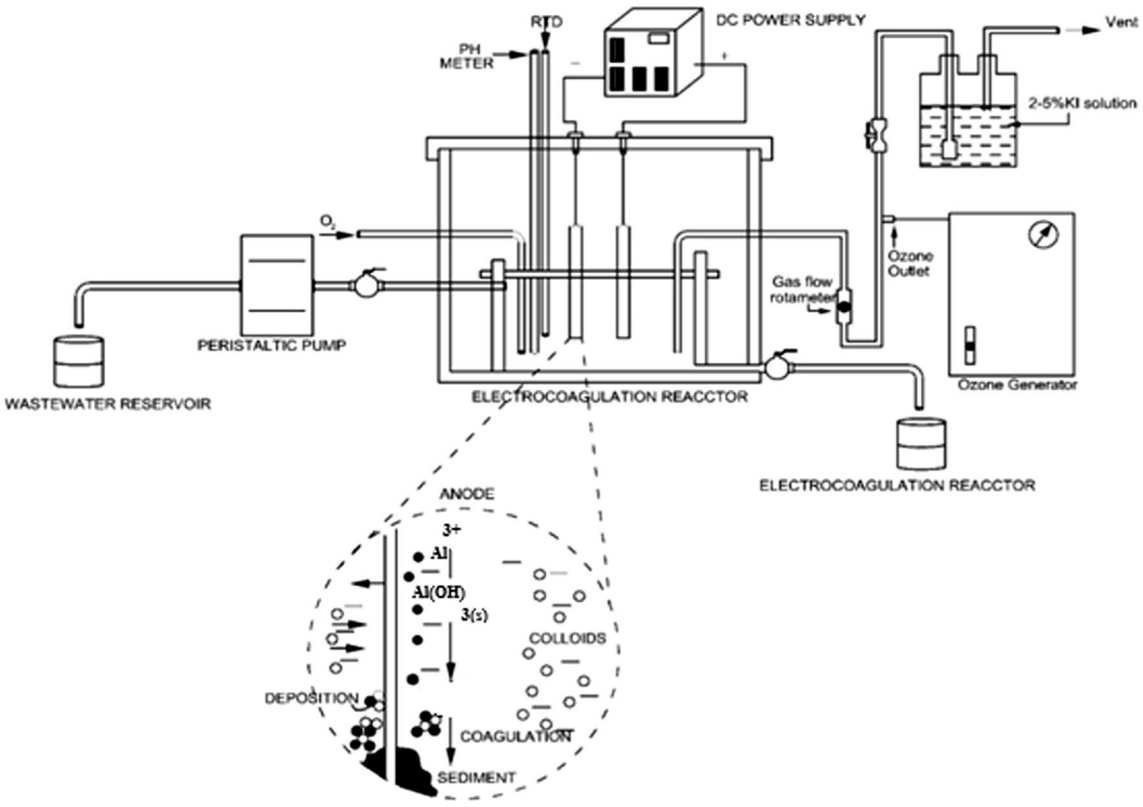

Fig. 3 Experimental setup

(Chen et al. 2000; Haldar and Gupta 2020). In EC process, the pH of the effluent enhanced, possibly due to the release of H_2 (g) at the cathode (Holt et al. 2002; Wagh and Nemade 2015a). In electrochemical process, as per the ohmic heating effect, the temperature increased with regard to time (Wagh and Nemade 2017):

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \quad (1)$$

Table 1 illustrates color and chemical oxygen demand elimination efficacy of aluminum electrodes. The chemical oxygen demand removal efficacy increased with an increase in time up to optimum time. The rate of chemical oxygen demand removal decreases and the reason may be more mixing of colloidal particles generated during the EC process. % chemical oxygen demand removed is around 54.45% and color 52.35%, respectively. Decolorization rate is enhanced as Al (OH)3(s) flocs are having a large specific surface area which absorbs soluble organic compounds (Kobya and Gengec 2012). The efficacy of color removal and chemical oxygen demand 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 (Shadmehr et al. 2019; Wagh et al. 2019).

Electrochemical (EC) treatment using iron electrodes (Fe)

Iron electrodes of dimension 15 cm × 10 cm × 1 cm and having composition Fe 98.43%, Mn 0.94%, C 0.23%, Si 0.30%, S 0.1% were used for electrochemical process. Electricity was supplied by connecting the electrodes to a direct current (DC). Fe(II) ions or ferrous oxides are generated during electrochemical process. Fe electrode had more solubility at acidic conditions and got easily corroded into Fe(III) or hematite (Eqs. 2–5) (Chen et al. 2000; Kobya et al. 2003; Modirshahla et al. 2007). The chemical oxygen demand removal efficiency of iron electrodes had reduced since hematite is difficult to settle. For alkaline pH, protons present in the solution get reduced to hydrogen (H_2). Consequently, chemical oxygen demand removal efficiency will be retarded at acidic pH as the proportion of hydroxide ion produced is less. Table 2 shows maximum chemical oxygen demand removal is 44.52% and decolorization is 41.08%. Initial chemical oxygen demand is 3875 mg/L and color 16,656 Pt–Co units:

$$\text{At anode: } Fe \rightarrow Fe^{2+} + 2e^- \quad (2)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)$$

$$\text{At cathode: } 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (4)$$

$$\text{Overall: } Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \quad (5)$$

Electrochemical (EC) treatment using copper electrodes (Cu)

Copper electrodes have dimension 152 mm × 50 mm × 10 mm and composition Cu 91.48%, Zn 8.43%, and other elements 0.09%. During electrochemical process, electrode dissolved on a large scale and formed

Table 1 Electrochemical treatment to DSW using aluminum electrodes

Time (min)	pH	Temp (°C)	% COD removal		% Color removal	
			(mg/L)	Removal	(Pt–Co units)	
Run EC1 Al–Al electrodes						
0	3.1	25	3875	–	16,656	–
20	3.3	28	3525	9.03 ± 0.4	15,565	6.55 ± 0.33
40	3.7	38	3120	19.48 ± 0.5	14,457	13.20 ± 0.35
60	4.1	46	2911	24.87 ± 0.23	13,345	19.87 ± 0.27
80	4.3	52	2652	31.56 ± 0.32	11,345	37.89 ± 0.34
100	4.5	57	2200	43.22 ± 0.18	9845	40.89 ± 0.21
120	4.8	59	1888	51.27 ± 0.22	8237	50.54 ± 0.24
140	5.5	62	1761	54.45 ± 0.19	7935	52.35 ± 0.23
160	6.1	62	1774	54.22 ± 0.24	7980	52.08 ± 0.21
180	6.9	62	1783	53.98 ± 0.3	8025	51.82 ± 0.27

Reaction conditions

Aluminum electrodes (Al–Al); dilution 1:2; initial pH of sample 3.1; HRT 180 min; submerges area of electrodes 50.45 cm^2; current density 1.2–3.5A/cm^2; spacing between electrodes 3 cm; agitation 100 rpm

Table 2 Electrochemical treatment on DSW using iron electrodes

Time (min)	pH	Temp (°C)	% COD removal		% Color removal	
			(mg/L)	Removal	(Pt–Co units)	
Run EC2 Fe–Fe electrodes						
0	3.1	25	3875	–	16,656	–
20	3.4	29	3670	5.29 ± 1.45	15,543	6.68 ± 1.07
40	3.9	34	3390	12.52 ± 1.87	14,590	12.40 ± 1.34
60	4.3	42	3211	17.13 ± 2.10	13,888	16.62 ± 2.18
80	4.9	47	2717	29.88 ± 2.11	12,840	22.91 ± 2.11
100	5.2	53	2350	39.35 ± 1.78	11,700	29.75 ± 1.87
120	5.5	55	2200	43.22 ± 0.75	10,187	38.83 ± 1.56
140	5.8	59	2150	44.52 ± 0.69	9813	41.08 ± 1.45
160	6.5	60	2185	43.61 ± 0.98	9865	40.77 ± 2.56
180	7.2	60	2192	43.43 ± 1.15	9867	40.76 ± 1.34

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 3 cm; agitation speed 100 rpm

copper oxides which reasonably remove recalcitrant pollutants (Danial et al. 2017; Ali et al. 2013; Shadmehr et al. 2019). As the color of copper oxide is dark brown, color removal efficiency is less than other electrodes. Also, copper electrodes are more costly than other electrodes. During the electrochemical process, copper oxide was formed due to which COD and color removal rate has been decreased. Table 3 shows optimum chemical oxygen demand degradation is 39.35% and decolorization is 39.88%. Initial chemical oxygen demand is 3875 mg/L and color 16,656 Pt–Co units.

Electrochemical (EC) treatment using graphite electrodes (Gr)

Graphite electrodes having dimension 15 cm × 3 cm × 1 cm were implemented in the electrochemical process to find out the efficacy of electrodes. The disintegration of graphite electrodes took place during electrochemical process as oxidation of electrodes occurs. When the disintegration of the graphite electrode starts, it will start releasing fine particles of carbon in the solution. It will also try to interfere with the spectrophotometric measurement of chemical oxygen demand and color. After 2–3 batch tests, the electrodes need to be replaced. Graphite was unsuitable as an anodic material for the continued electrochemical process because it tended to be oxidized to carbon dioxide (Gonder et al. 2019).

Table 3 Electrochemical treatment to DSW using copper electrodes

Time (min)	pH	Temp (°C)	% COD removal		% Color removal	
			(mg/L)	Removal	(Pt–Co units)	
Run EC3 Cu–Cu electrodes						
0	3.1	26	3875	–	16,656	–
20	3.4	26	3700	4.51 ± 1.45	15,500	6.94 ± 1.56
40	4.1	33	3410	12 ± 2.67	14,990	10 ± 2.45
60	4.4	41	3295	14.96 ± 1.56	13,988	16.01 ± 1.22
80	4.7	46	2997	22.65 ± 2.15	13,040	21.71 ± 2.32
100	5.1	52	2750	29.03 ± 1.78	12,700	23.75 ± 1.67
120	5.3	53	2400	38.06 ± 2.20	11,157	33.01 ± 1.23
140	5.9	58	2350	39.35 ± 1.56	10,013	39.88 ± 2.11
160	6.4	59	2375	38.71 ± 2.52	10,053	39.64 ± 1.34
180	6.9	59	2378	38.63 ± 1.55	10,065	39.57 ± 0.73

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 3 cm; agitation speed 100 rpm

Table 4 Electrochemical treatment to DSW using graphite electrodes

Time (min)	pH	Temp (°C)	% COD removal		% Color removal	
			(mg/L)	Removal	(Pt–Co units)	
Run EC4 Gr–Gr electrodes						
0	3.1	24	3875	–	16,656	–
20	3.4	29	3680	5.03 ± 2.12	15,872	4.7 ± 2.5
40	3.7	33	3220	16.90 ± 2.07	14,497	12.96 ± 1.45
60	4.2	41	3011	22.29 ± 1.75	13,395	19.58 ± 2.76
80	4.7	46	2752	28.98 ± 1.56	12,445	25.28 ± 1.89
100	5.1	52	2500	35.48 ± 2.34	11,245	32.48 ± 3.23
120	5.4	53	2270	41.42 ± 0.79	10,837	34.94 ± 2.65
140	5.7	58	2151	44.49 ± 1.11	9935	40.35 ± 2.76
160	6.3	59	2164	44.15 ± 1.34	9950	40.26 ± 2.72
180	6.9	59	2173	43.92 ± 1.56	9945	40.25 ± 1.58

Reaction conditions

Graphite electrodes (Gr–Gr); agitation speed 100 rpm; initial pH of sample 3.1; HRT 180 min; spacing between electrodes 3 cm; submerges area of electrodes 50.45 cm^2; current density 1.2–3.5A/cm^2

Table 4 shows graphite electrode removes chemical oxygen demand 44.49% and maximum color removal 40.35%. The initial chemical oxygen demand and color of DSW are 3875 mg/L and 16,656 Pt. Cobalt scale, respectively.

To find the efficiency of color and chemical oxygen demand removal, different pairs of electrodes (Al–Al, Fe–Fe, Cu–Cu, and Gr–Gr) were implemented. From all the experiments, it is found that the pair of aluminum electrodes are more effective than all other electrodes. Optimum chemical oxygen demand removed by Al, Fe, Cu, and graphite electrodes is 54.45%, 44.52%, 39.35% and 44.49%, respectively. Similar results were reported by Manisankar et al. (2004), Krishna et al. (2010), Khandegar and Saroha (2012), and Wagh and Nemade (2015a). For continuous EC process, a pair of aluminum electrode were implanted since it gave the highest efficacy as compared to other electrodes.

Continuous Electrochemical Process

In the presence of NaCl, continuous electrochemical processes were carried out by using aluminum electrodes to minimize the passivation of electrodes on a large scale. The total submerged area was 71.50 cm^2. Initial chemical oxygen demand is 5803 mg/L, color 21,191 Pt–Co units and pH 3.1. The continuous EC process seems to be more effective than the conventional EC process. The efficacy of degradation may be enhanced by replacing anode and cathode electrodes continuously in each run (Wagh et al. 2019). Figure 4 shows effect of electrolysis time on color and chemical oxygen

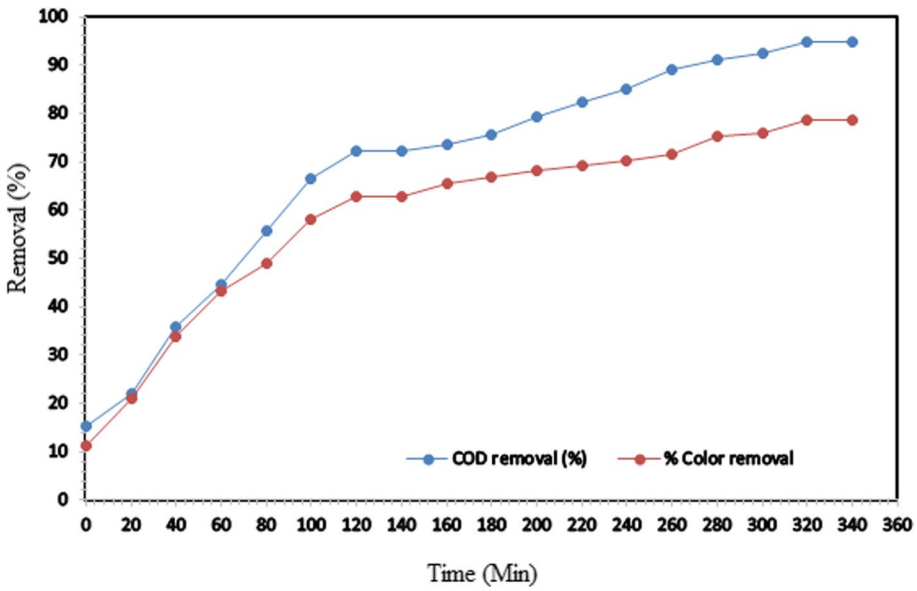

Fig. 4 Effect of electrolysis time on COD and color removal

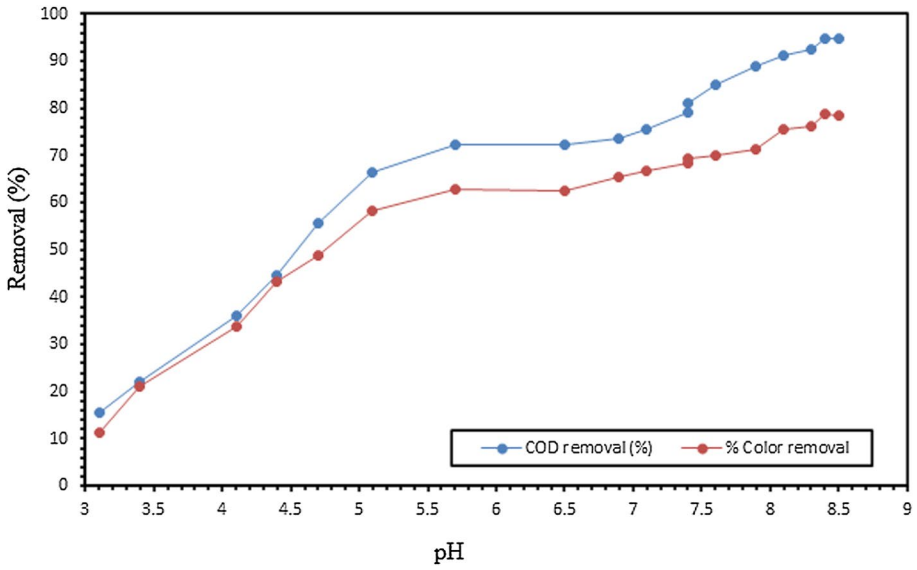

Fig. 5 Influence of pH in degradation of COD and color

demand removal. Figure 5 indicates the influence of pH on chemical oxygen demand and color removal.

Ozone treatment

Experiments were conducted within the range of pH 7–7.4, and the Ozone supply rate was constant at 3 gm/h. During the experimentation, the pH of samples had decreased from 7.4 to 7.7. This shows that during ozonation, the probable development of acidic by-products was generated. Distillery spent wash contains alcohol (-OH) and aldehyde (-CHO) groups, which were oxidized by Ozone to Carboxylic acids. Ozonation of melanoidin decreases in pH from 8.4 to 7.4 and the degradation of by-products were identified to consist mainly of acid fractions (Biradar 2003; Wagh and Nemade 2017). The chemical oxygen demand removal was 11% during the first 15 min. The decrease in chemical oxygen demand during the first 15 min may be due to the oxidation of simple organic compounds to CO_2, and the overall chemical oxygen demand reduction after an hour was 30%. There was no significant change in chemical oxygen demand and color removal in the distillery spent wash sample. The removal of organic matter was much slower as compared to the color removal which 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 efficacy was above 85%. The results obtained are summarized in Table 5.

Table 5 Ozone treatment to distillery spent wash

Time (min)	pH	COD removal (%)	Color removal (%)
Run O1			
15	7.1	11	43
30	7.5	16	73
45	7.5	23	83
60	7.4	30	88
75	7.3	29.55	87.5
Run O2			
15	7.1	15	44
30	7.5	18	75
45	7.5	26	84
60	7.4	30.5	86.5
75	7.3	31.23	87.5
Run O3			
15	8.4	14	47
30	8.2	15	75
45	8.1	22	84
60	8.0	28	85
75	7.7	29	85

Ozone-Assisted Electrochemical process

A pair of punched aluminum electrode were implemented to carry out the EC process, and Eltech ozone generator (3 g/h) was implemented to purge the ozone gas from the bottom of the experimental tank. Table 6 indicates the variation of chemical oxygen demand and color with respect to time. During the process of Ozone-Assisted EC, the pH of the DSW changes due to Ozonolysis

Table 6 Ozone-assisted electrochemical treatment to DSW

Time (min)	pH	% COD removal		% Color removal	
		(mg/L)	Removal	(Pt–Co units)	
Run OA1					
0	3.1	3875	–	16,656	–
20	3.5	3111	19.71 ± 2.08	13,000	21.95 ± 1.25
40	4.0	2656	31.45 ± 2.35	11,257	32.41 ± 2.33
60	4.3	2025	47.74 ± 2.12	9615	42.27 ± 2.87
80	4.7	1723	55.53 ± 2.86	7605	54.34 ± 2.37
100	5.2	1303	66.37 ± 2.35	5510	66.91 ± 2.34
120	5.7	887	77.10 ± 1.40	3434	79.38 ± 2.68
140	6.5	493	87.2 ± 1.83	1331	92.00 ± 2.19
160	6.7	512	86.78 ± 1.48	1345	91.92 ± 1.76
180	6.9	517	86.65 ± 1.86	1362	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/hr

and Oxidation process (Wagh et al. 2019). The Ozone-Assisted Electrochemical process enhances the characteristics of distillery spent wash by breaking the carbon–carbon double bond present in the melanoidin (Fig. 6) (Wagh and Nemade 2017; Asaithambi et al. 2016).

Continuous ozone-assisted EC process

Continuous ozone-assisted EC process had been carried out for 360 min and chemical oxygen demand and color disintegration was then checked. As Ozone is a powerful oxidizing reagent it breaks the carbon–carbon double bond of melanoidin structure hence the molecular weight of melanoidin is decreased on a large scale. The efficiency of color removal and chemical oxygen demand removal depends upon different parameters such as the initial pH of the DSW, current density applied to the electrodes, the spacing between the electrodes and the concentration of DSW. Table 7 shows the maximum chemical oxygen demand removal achieved up to 97.27% and color removal up to 98.72%.

Table 7 Continuous ozone integrated electrochemical treatment to DSW

Time (min)	pH	% COD removal		% Color removal	
		(mg/L)	Removal	(Pt–Co units)	
Run OA3					
0	3.1	7022	0	21,147	0
20	3.5	5968	15.1 ± 1.13	19,455	8 ± 2.02
40	4.0	5407	23 ± 1.34	16,494	22 ± 2.23
60	4.3	4862	30.7 ± 2.27	12,688	40 ± 2.72
80	4.7	4494	36 ± 2.07	11,207	47 ± 2.13
100	5.2	3721	47 ± 2.21	9347	55.8 ± 2.12
120	5.7	3376	52 ± 2.46	8438	60.1 ± 2.02
140	6.5	2768	60 ± 1.32	7216	65.9 ± 2.42
160	6.7	2457	65 ± 1.45	6074	71.3 ± 1.26
180	6.9	2228	68 ± .1.76	5034	76.2 ± 1.26
200	7.3	1966	72 ± .1.23	4017	81 ± .1.13
Electrodes polarity changed and added NaCl (200gm)					
220	7.7	1724	75.4 ± .1.11	3121	85.2 ± .1.27
240	8.1	1411	79.9 ± .1.06	2114	90 ± .1.21
260	8.3	1143	83.7 ± .1.24	1203	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/hr

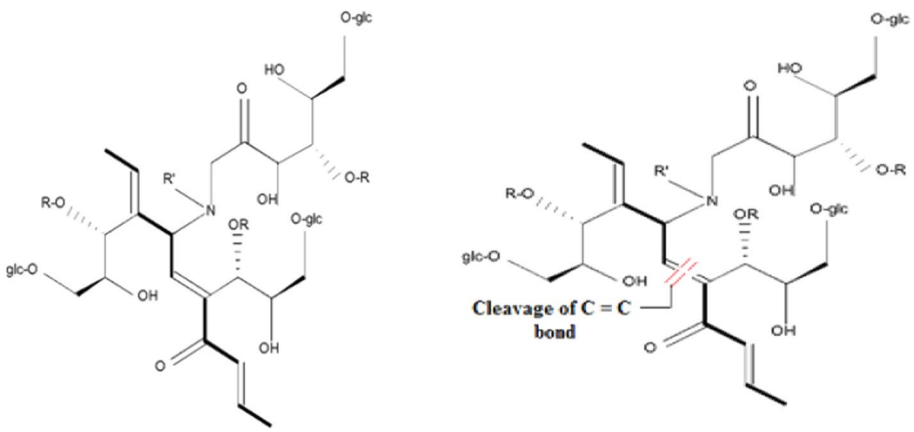

Fig. 6 Cleavage of C = C bond in melanoidin

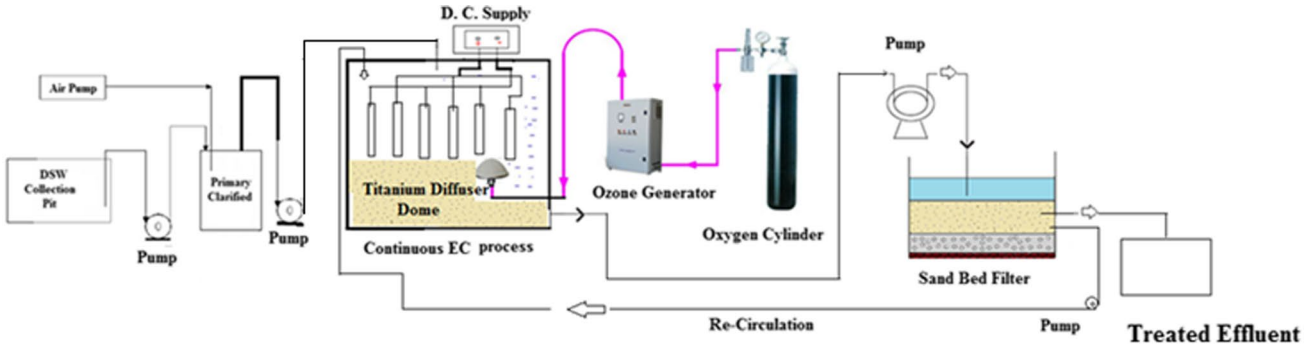

Fig. 7 Pilot plant to treat cumbersome distillery spent wash

Design of pilot plant to treat recalcitrant pollutants

Distillery spent wash needs hybrid methods to minimize the parameters of chemical oxygen demand and biochemical oxygen demand. In reality, an ample amount of literature survey is available but cannot be calculated in advance exact efficiency of the EC process prior to the design effluent treatment plant. In this section, small-scale pilot plants were designed to test chemical oxygen demand and color. Setup of the pilot plant is shown in Fig. 7. The various constraints of distillery effluent differs from industry to industry, and it depends upon the manufacturing process and molasses feed. Therefore, the efficiency of the EC process changes dramatically. The pilot plant consists of different units such as distillery spent wash collection tank having dimensions of 4.5 m × 2.10 m × 1.0 m. The total volume of the tank is 9. 45 m^3 (9450 L). The clarified unit was used to clarify the effluent. Sand filtration unit was used to filter the effluent. The dimension of the sand filtration unit was 3.1 m × 0.65 m × 0.55 m. Ozone-Assisted Electrochemical unit was installed with the dimension of tank having 1.8 m x 0.95 m × 0.95 m. The total volume of the tank was 1.71 m (1710 L). Total submerged area of electrodes were 11,250 cm^2. 8 pairs of aluminum electrodes were designed for the EC process, and each pair having a submerged area of 700 cm^2 (35 cm × 20.1 cm). According to different researchers (Kobya and Gengec 2012; Prajapati and Chaudhari 2015; Asaithambi et al. 2012; Wagh et al. 2019) the design of EC unit and electrodes were made. The design of a pilot plant was purely based upon trial-and-error method, and it removes chemical oxygen demand and color by 98.27% and 99.02%, respectively.

Conclusion

This study brings to notices the major findings of the different treatments like Electrochemical, Ozone, and Ozone-Assisted electrochemical technology for treatment of distillery spent wash (DSW). Experiments were conducted in laboratory with batch mode operation. In this research work, parameters like chemical oxygen demand and color were used to assess the removal efficiency of selected treatment methods. Maximum chemical oxygen demand is removed by Al, Fe, Cu, and graphite electrodes as 54.45%, 44.52%, 39.35%, and 44.49%, respectively. Ozone can degrade 31.23% chemical oxygen demand and 87.5% color of distillery spent wash. Ozone-Assisted Electrochemical proves to be more effective than individual ozonation and Electrochemical treatment. The rate of floc formation was enhanced in acidic condition and color removal mechanisms were controlled by adsorption and coagulation was eliminated. The optimal chemical oxygen demand and color removal by Ozone-Assisted Electrochemical process was 97.27% and 98.72%, respectively. It also proves that punched electrodes were more effective than conventional plain electrodes. Chemical oxygen demand and color removal rates are enhanced by 7.3% and 6.1%, respectively. Thus it can be said that the Hybrid treatment like Ozone-Assisted Electrochemical process enhances the degradation of the complex organic compound to simple biodegradable carboxylic acids. The development of carboxylic acids represents the degradation of melanoidin.Thus from the above experimental study it can be stated that augmentation with Ozone Assisted EC process gives more desirable and acceptable results.

Acknowledgment The authors would like to express sincere thanks to Principal, Dr. Uday Naik, Dr. Vithalrao Vikhe Patil College of Engineering, Ahmednagar, Maharashtra, India.

References

Ali I, Asim M, Khan TA (2013) Arsenite removal from water by electro-coagulation on zinc–zinc and copper–copper electrodes. Int J Environ Sci Technol 10:377–384

APHA (2008) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association Inc., New York

Asaithambi P, Susree M, Sarsvanathamizhan R, Matheswaram M (2012) Ozone assisted electrocoagulation for treatment of distillery effluent. Desalination 297:1–7

Asaithambi P, Aziz ARA, Daud WMABW (2016) Integrated ozone—electrocoagulation process for the removal of pollutant from industrial effluent: optimization through response surface methodology. Chem Eng Process Process intensif 105:92–102

Biradar A (2003) Physico-chemical and biological methods for the Treatment of post anaerobic distillery spent wash. Ph.D, thesis, center for environmental science and engineering. Indian Institute of Technology, Bombay

Chandraraj K, Gunasekaran P P (2004) Bacterial alcoholic fermentation. In: Pandey A (ed) Concise Encyclopedia of Bioresource Technology. Food Products press, New York, pp 327–333

Chen X, Chen G, Yue PL (2000) Separation of pollutants from restaurant wastewater by electrocoagulation. Sep Purif Technol 19:65–76

Danial R, Abdullah LC, Sobri S (2017) Potential of copper electrodes in electrocoagulation process for glyphosate herbicide removal. MATEC Web of Conferences. 103:06019

David C, Arivazhagan M, Ibrahim M (2015) Spent wash deolourization using nano Al_2O_3/kaolin photocatalyst, Taguchi and ANN approach. J Saudi Chem Soc 19:537–548

Davis SB (2001) The chemistry of colour removal a processing perspective Sugar Milling Research Institute, University of Natal, Durban, 4041. South Africa 75:328–336

Erhan G, Kobya M, Demirbas E, Akyol A, Oktor K (2012) Optimization of baker's yeast wastewater using response surface methodology by electrocoagulation. Desalination 286:200–209

Fu Y, Meng XJ, Lu NN (2019) Characteristics changes in banana peel coagulant during storage process. Int J Environ Sci Technol 16:7747–7756

Ghosh Ray S, Ghangrekar MM (2019) Comprehensive review on treatment of high-strength distillery wastewater in advanced physico-chemical and biological degradation pathways. Int J Environ Sci Technol 16:527–546. https://doi.org/10.1007/s13762-018-1786-8

Gonder ZB, Balcioglu G, Kaya Y, Vergili I (2019) Treatment of carwash wastewater by electrocoagulation using Ti electrode: optimization of the operating parameters. Int J Environ Sci Technol 16:8041–8052

Hairuddin MN, Mubarak NM, Khalid M, Abdullah EC, Walvekar R, Karri RR (2019) Magnetic palm kernel biochar potential route for phenol removal from wastewater. Environ Sci Poll Res 26:35183–35197

Haldar A, Gupta A (2020) Application of electrocoagulation: issues with community-level defluoridation. Int J Environ Sci Technol 17:789–798. https://doi.org/10.1007/s13762-019-02323-5

Holt PK, Barton GW, Wark M, Mitchell CA (2002) A quantitative comparison between chemical dosing and electrocoagulation. Colloid Surfaces A Physicochem Eng Aspects 211:233–248

Karri RR, Sahu JN, Jayakumar NS (2017) Optimal isotherm parameters for phenol adsorption from aqueous solutions onto coconut shell based activated carbon: error analysis of linear and nonlinear methods. J Taiwan Inst Chem Eng 80:472–487

Khandegar V, Saroha AK (2012) Electrochemical treatment of distillery spent wash using aluminum and iron electrodes. Chin J Chem Eng 20(3):439–443

Kobya M, Demirbas E (2015) Evalutions of operating parameters on treatment of Can manufacturing wastewater by electrocoagulation, J Water Process Eng 64–74

Kobya M, Gengec E (2012) Decolourization of melanoidins by a electrocoagulation process using aluminium electrodes, Environ Technol 1–10

Kobya M, Can OT, Bayramoglu M (2003) Treatment of textile waste waters by electro-coagulation using iron and aluminum electrodes. J Hazard Mater 100:163–178

Krishna BM, Murthy UN, Kumar BM, Lokesh KS (2010) Electrochemical pretreatment of distillery waste water using aluminum electrode. J Appl Electrochem 40:663–667

Manisankar P, Rani C, Vishwanathan S (2004) Effect of Halides in the Electrochemical Treatment of Distillery Effluent. Chemosphere 57:961

Merzouk B, Gourich B, Madani K, Vial Ch, Sekki A (2011) Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation comparative study. Desalination 272:246–253

Modirshahla N, Behnajady MA, Kooshaiian S (2007) Investigation of the effect of different electrode connections on the removal efficiency of tartrazine from aqueous solutions by electrocoagulation. Dyes Pigment 74(2):249–257

Mohana S, Desai C, Madamwar D (2007) Biodegradation and decolorization of anaerobically treated distillery spent wash by a novel bacterial consortium. Biores Technol 98:333–339

Mohana S, Acharya BK, Madamwar D (2009) Review on Distillery Spent wash treatment technologies and potential applications. J Hazard Mater 163:12–25

Ozyonar F, Karagozoglu B (2012) Systematic assessment of electrocoagulation for the treatment of marble processing wastewater. Int J Environ Sci Technol 9:637–646. https://doi.org/10.1007/s13762-012-0093-z

Prajapati AK, Chaudhari PK (2015) Physicochemical Treatment of Distillery Wastewater—a review. Chem Eng Commun 202:1098–1117

Premalatha M, Sankaran K, Vijayasekaran M, Somasundaram VT (2014) DEPHY Project: distillery wastewater treatment through anaerobic digestion and phycoremediation—A green industry approach. Renew Susta Energy Rev 37:634–643

Rashidi R, Yousefinejad S, Mokarami H (2019) Catalytic ozonation process using CuO/clinoptilolite zeolite for the removal of formaldehyde from the air stream. Int J Environ Sci Technol 16:6629–6636

Ravindra k, Manoj W, Thakare SB (2017a) Post Treatment to Biomethanated distillery spent wash by using Chitosan Powder. Int J Sci Adv Res Technol 3(6):866–869

Ravindra k, Manoj W, Thakare SB (2017b) Application of Chitosan powder to enhance the properties of distillery spent wash. Int J Eng Res General Sci 5(3):249–257

Sahu O, Mazumdar B, Chaudhari PK (2019) Electrochemical treatment of sugar industry wastewater: process optimization by response surface methodology. Int J Environ Sci Technol 16:1527–1540. https://doi.org/10.1007/s13762-018-1765-0

Santal AR, Singh N (2013) biodegradation of melanoidin from distillery effluent: role of microbes and their potential enzymes. Biodegrad Hazard Special Prod 5:71–100

Santal AR, Singh NP, Saharan BS (2016) Anovel application of Paracoccus pantotrophus for the decolourization of melanoidins from distillery effluent under static conditions. J Environ Manag 169:78–83

Shadmehr J, Mirsoleimani-azizi SM, Zeinali S (2019) Electrocoagulation process for propiconazole elimination from wastewater: experimental design for correlative modeling and optimization. Int J Environ Sci Technol 16:5409–5420. https://doi.org/10.1007/s13762-018-1891-8

Wagh M (2019) Ozone assisted electrocoagulation and fungal treatment for distillery spent wash, Ph.D., Thesis Pune University

Wagh MP, Nemade PD (2015a) Color and COD removal of Distillery Spent wash by using electrocoagulation. Int J Eng Res General Sci 3(3):1159–1173

Wagh M, Nemade PD (2015b) Treatment processes and technologies for decolourization and COD removal of distillery spent wash: a review. Int J Innovat Res Adv Eng 7(2):30–40

Wagh M, Nemade PD (2015c) Treatment of distillery spent wash by using coagulation and electrocoagulation [EC]. Am J Environ Protect 3(5):159–162

Wagh M, Nemade PD (2016) Electro-Coagulation [EC] process to treat basic dye. Int J Develop Res 06(05):7858–7862

Wagh MP, Nemade PD (2017) An influence of experimental parameters in the treatment of anaerobically treated distillery spent wash by using ozone assisted electrocoagulation. Desalination Water Treatment 83:7–15

Wagh MP, Nemade PD (2018a) Biogas generation from distillery spent wash by using an OPUR western biotechnology process: a case study. Desalination Water Treatment 118:241–248

Wagh W, Nemade PD (2018b) Biodegradation of anaerobically treated distillery spent wash by Aspergillus species from a distillery effluent contaminated site. Desalination Water Treatment 104:234–240

Wagh M, Nemade P (2019) Remediation and decolourization of distillery spent wash by using advanced oxidation processes – a review. Indian J Environ Protect 39(7):651–658

Wagh MP, Nemade P, Jadhav P (2019) Continuous Electrocoagulation process for the distillery spent wash using Al electrodes. In: Proceedings of the 2nd international conference on advanced technologies for societal applications 2:41-49

Yadav S (2012) Degradation and decolourization of post methanated distillery effluent in biphasic treatment system of bacteria and wetland plant for environmental safety. Ph. D, thesis, school of life science, Pandit Ravi Shankar Shukla University

Zafar Z, Ayaz K, Nasir MH (2019) Electrochemical performance of biocathode microbial fuel cells using petroleum-contaminated soil and hot water spring. Int J Environ Sci Technol 16:1487–1500. https://doi.org/10.1007/s13762-018-1757-0