



Challenges in the treatment of biomethanated spent wash by electro-Fenton process

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In distilleries, ethanol production by fermentation results in generation of concentrated wastewater stream, called as spent wash (SW). It contains high total solids (TS), and chemical oxygen demand (COD). Unscientific disposal of SW in aquatic or terrestrial ecosystems poses high risk to the surrounding environment. In India, biomethanation is the preferred treatment option for SW. However, the by-product, i.e., biomethanated SW (BMSW) contains dark brown color, high COD and low biodegradability. The present study reports the performance of electro-Fenton (EF) process for the treatment of SW (COD = 135 g/L) and BMSW (COD = 65.5 g/L) in a laboratory scale reactor (capacity = 250 mL). A COD reduction of upto 60% and 50% could be obtained with diluted SW and BMSW, respectively. However, electrode fouling and foaming were observed during EF runs. Lower voltage, use of AC supply and adequate stirring could reduce the above problems significantly.

Keywords: Biomethanated spent wash, electro-Fenton oxidation, iron electrode.

Introduction

Due to stringent effluent discharge regulations in India, alcohol distilleries are facing challenges in terms of their wastewater treatment. During alcohol production, spent wash (SW) is produced as the main waste stream which is highly polluted (chemical oxygen demand (COD) = 80–190 g/L). SW wastewater mainly contains reduced sugars, polysaccharides, long chain fatty acids, lignin, humic substances, caramels and melanoidins (produced from Maillard's reaction). The recalcitrant melanoidins impart most of the color and toxicity to SW¹. Anaerobic treatment of SW is a widely adopted method as it reduces COD of wastewater significantly accompanied with biogas generation. However, biomethanated SW (BMSW) still has high COD (COD = 45–65 g/L) and poor biodegradability. Current practices for BMSW handling include dilution, aerobic treatment, land disposal, ferti-irrigation, evaporation and composting². But each practice has its own disadvantages and limitations such as need for fresh water, space and high amount of energy.

Electrochemical oxidation and wet oxidation processes are suggested as potential treatment methods for such a high strength wastewater³. In these processes, the oxidation of pollutants takes place due to formation of free radi-

cals. In the present study, efficacy of electro-Fenton (EF) treatment was investigated for the treatment of SW and BMSW. In EF process, hydroxyl ($\bullet\text{OH}$) radicals are generated via *in situ* electro-generated Fenton's reaction. Based on mode of incorporation of the Fenton's reagent ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$), EF process can be categorised in four different types. In type 1, Fe^{2+} and H_2O_2 are electro-generated using an iron anode and gas diffusion cathode, respectively. In types 2 and 3, either hydrogen peroxide or ferrous iron is added externally and the other is electro-generated *in situ* into the system. In type 4, Fenton's reagent is added externally in the reactor and ferrous ions are regenerated through the reduction of ferric ions on the cathode⁴.

Efficiency of EF process depends on several reaction/operating parameters such as electrical conductivity (EC), H_2O_2 concentration, inter-electrode gap, stirring speed, potential difference (V) between electrodes and temperature⁵. In a study reported by Asaithambi *et al.*⁶, hybrid electrocoagulation process was assessed for the treatment of diluted distillery wastewater (COD = 2500 mg/L) using iron electrode. Effects of different operating parameters such as initial pH of the effluent (3–11), current density (0.03–0.23 A/dm²) and concentration of H_2O_2 (58.5–585 mg/L) on color and COD

removals along with electrical energy consumption were studied. An overall COD removal efficiency of 85% was observed at optimum conditions. The effect of operating parameters such as applied voltage, H_2O_2 dosage and reaction time on decolorization of molasses wastewater (COD = 87200 mg/L) using EF was observed in another study⁷. The color removal was 88.5% under the following optimal conditions: 2.86 V, 15.8% H_2O_2 /wastewater ratio and 90.7 min reaction. Moreover, single step addition of H_2O_2 was found to be more effective for color removal rather than stepwise addition.

In the present study, the performance of EF process was investigated for SW and BMSW at laboratory scale. The problems encountered during the process are also observed and reported in the paper.

Materials and methods

(A) Materials:

NaCl (purity = 99%), H_2O_2 (50% w/w) and NaOH (purity = 99%) were purchased from Merck chemicals, Mumbai. Iron and stainless steel (SS) electrodes were purchased from the local market. The DC power supply unit has current and voltage supply ranges of 0–2 A and 0–32 V. The SW and BMSW samples were collected from a distillery located in Pune, India. The distillery uses molasses as raw material, a by-product from sugar factory. The collected effluent was stored in the refrigerator at 4°C temperature to avoid any deterioration in its physico-chemical properties.

(B) Analytical methods:

Total organic carbon (TOC) of liquid samples was determined using a TOC analyser (TOC-VCSH, Shimadzu, Kyoto, Japan). pH of the samples was measured by Eutech Cyberscan pH Tutor (Singapore) equipped with glass electrode. EC of wastewater samples was determined with conductivity probe (HACH CDC-401, USA). BOD_5 , COD, total Kjeldhal nitrogen (TKN), alkalinity and total solids (TS) were obtained using standard methods described in American Public Health Association (APHA) handbook⁸. For BOD_5 measurement, airtight BOD bottles (~300 ml) were filled with appropriate sample volume and dilution water. The mixture was then kept in an incubator at 20°C temperature for 5 days. Initial and final dissolved oxygen (after incubation) concentrations were measured in the sample using dissolved meter (HQ30d, HACH, USA) which were used to compute BOD_5 of the sample. COD was measured according to closed reflux

dichromate titrimetric method⁸ in which sample digestion was carried out in a block digester (HACH, DRB 200) preheated to 150°C and refluxed for 2 h. The digested solution was titrated with ferrous ammonium sulfate (FAS) in the presence of Ferroin indicator to determine the end point. The amount and concentration of FAS were used to calculate COD of a sample. Residual H_2O_2 in aqueous samples was determined by spectrophotometric analysis using potassium titanium oxalate method⁹. For determination of total volatile solids (TVS), the oven-dried solids (at 103°C temperature) were ignited to constant weight at 550°C in a weighed crucible. Inorganic elements in BMSW samples was performed with inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (HORIBA Jobin Yvon-Ultima 2000, France). CHN analysis of the solids recovered after EF oxidation process was carried out using CHNS analyser (Flash EA1112 series, Thermo Finnigan, Italy).

(C) Experimental studies:

Batch EF oxidation runs were carried out in 250 mL glass reactor by passing constant voltage through Fe/SS electrodes immersed in BMSW wastewater. The schematic diagram of the reactor is shown in Fig. 1. The ferrous ions were leached from iron electrode whereas H_2O_2 was added externally. The oxidation reaction was performed for 90 min duration with 200 ml sample of SW/BMSW. The effective surface area of iron electrodes immersed in the wastewater was 55 cm². EC of wastewater was adjusted using NaCl solution. Before the oxidation reaction, H_2O_2 was added and the reactor contents were stirred using magnetic stirrer. The treated samples were

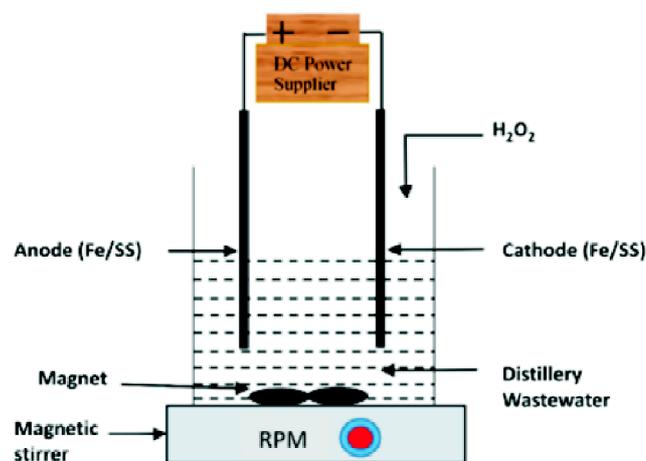


Fig. 1. Setup of the electro-Fenton reactor.

quenched immediately using 1 M NaOH solution as reported in previous studies^{5,10}. The samples were analysed for COD, TOC and residual H₂O₂ concentration. pH and EC of the treated wastewater were also measured. All the runs were conducted in duplicates.

Results and discussion

(A) Wastewater characteristics:

Various wastewater characteristics of the distillery wastewater sample are given in Table 1. Initially pH and EC of SW were found to be 3.4 and ~36 mS/cm compared to 5.7 and ~51 mS/cm for BMSW, respectively. COD and BOD₅ of SW were about twice to that of BMSW. BOD₅ to COD ratio (i.e. biodegradability index) for SW and BMSW was 0.52 and 0.27, respectively.

Table 1. Characteristics of SW and BMSW samples

Parameters	SW	BMSW
Color	Dark brown	Blackish
pH	3.4	5.7
EC (mS/cm)	36±2.3	51±1.4
BOD ₅ (g/L)	70.6±1.3	18±1.6
COD (g/L)	135±0.4	65.5±0.2
TOC (g/L)	36.5±0.5	23.3±0.2
TS (g/L)	124±0.6	55±0.3
TVS (g/L)	74	26.8
TKN (g/L)	–	3
Alkalinity (g CaCO ₃ /L)	–	12.2
Cl ⁻ (g/L)	–	9.5
Mg (g/L)	–	1.93
Na (g/L)	–	0.5
S (g/L)	–	3.8

(B) Performance of EF oxidation for SW and BMSW:

EF oxidation experiments were carried out to examine the effect of applied potential difference, electrode inter-change, stirring speed, electrode material and EC on SW and BMSW degradation. Details of all the experiments conducted is summarized in Table 2. For this study, optimum conditions for COD removal reported by Thanapimmetha *et al.*⁷ for EF oxidation of molasses wastewater were followed. EF runs were carried out with 200 mL of raw SW and BMSW wastewater using iron electrodes at following reaction conditions: inter-electrode gap = 2 cm, H₂O₂ dosage = 422 mM and reaction time = 90 min. The parameters are highlighted in bold to show their effect on the EF oxidation performance.

Table 2. Details of EF experiments carried out for SW and BMSW wastewater treatment

Experiment No.	Reaction parameters
	SW
1	pH = 3.9; EC = 16.9 mS/cm; DF = 1.55; V = 2.8; [H ₂ O ₂] = 422 mM
	BMSW
2	pH = 5.7; EC = 51 mS/cm; V = 2.8; [H ₂ O ₂] = 422 mM; stirring speed = 150 rpm
3	pH = 5.7; EC = 51 mS/cm; V = 2.8; [H₂O₂] = 0 mM ; stirring speed = 150 rpm
4	pH = 5.7; EC = 7.3 mS/cm; dilution = 10 times ; V = 2.8; [H ₂ O ₂] = 42.2 mM; stirring speed = 150 rpm
5	pH = 5.7; EC = 51 mS/cm; V = 1 ; [H ₂ O ₂] = 422 mM; stirring speed = 150 rpm
6	pH = 5.7; EC = 51 mS/cm; V = 1.2 ; [H ₂ O ₂] = 422 mM; stirring speed = 150 rpm
7	pH = 5.7; EC = 51 mS/cm; V = 1.2; [H ₂ O ₂] = 422 mM; stirring speed = 300 rpm
8	pH = 5.7; EC = 51 mS/cm; V = 1.2; [H ₂ O ₂] = 422 mM; interchanging electrode (after every 15 min interval) ; stirring speed = 150 rpm
9	pH = 5.7; EC = 77.1 mS/cm ; V = 1.2; [H ₂ O ₂] = 422 mM; stirring speed = 150 rpm
10	pH = 5.7; EC = 51.4 mS/cm; V = 1.2; [H ₂ O ₂] = 422 mM; SS electrodes ; stirring speed = 150 rpm

The TOC and COD removals during various experimental runs are illustrated in Fig. 2 while final pH and EC of the treated wastewater are presented in Fig. 3. Residual H₂O₂ concentration in treated wastewater is shown in Fig. 4.

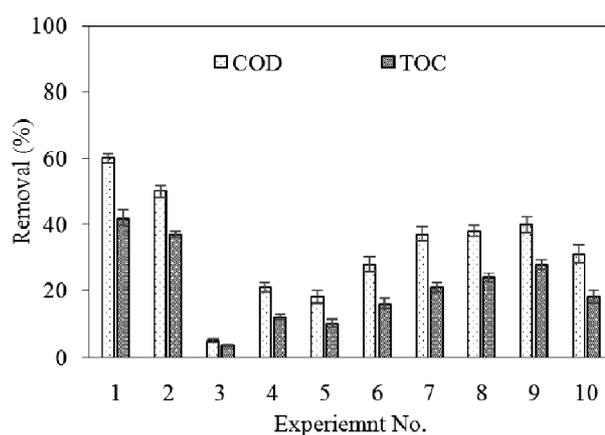


Fig. 2. TOC and COD removal during EF oxidation of SW and BMSW at different conditions with wastewater volume = 200 mL, inter-electrode gap = 2 cm, [H₂O₂] = 422 mM and EC_{SW} = 36 mS/cm and EC_{BMSW} = 51 mS/cm.

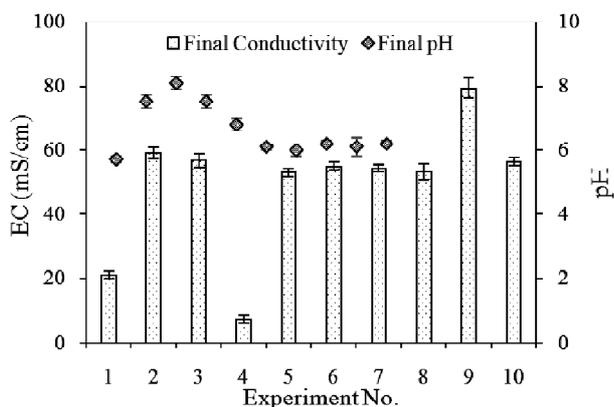


Fig. 3. Change in EC and pH during EF oxidation of SW and BMSW at different conditions with wastewater volume = 200 mL, inter-electrode gap = 2 cm, $[H_2O_2] = 422$ mM and $EC_{SW} = 36$ mS/cm and $EC_{BMSW} = 51$ mS/cm.

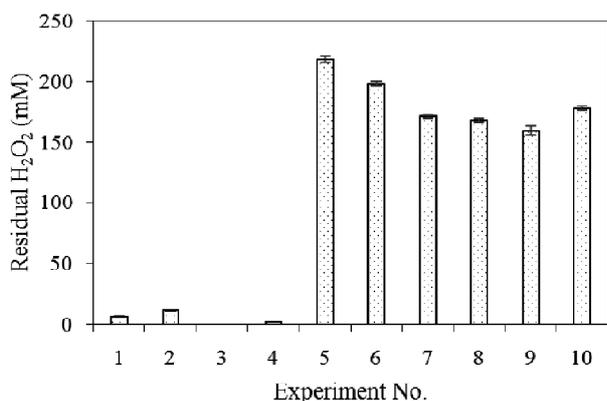
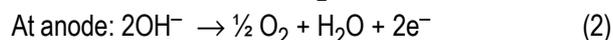
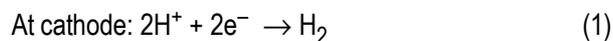


Fig. 4. Residual H_2O_2 concentration during EF oxidation of distillery wastewater at different experimental conditions (Wastewater volume = 200 mL, inter-electrode gap = 2 cm, $[H_2O_2] = 422$ mM and $EC = 36$ mS/cm (SW) and 51 mS/cm (BMSW)).

The study was started with oxidation of SW. In order to have desired COD of 87200 mg/L as used by Thanapimmetha *et al.*⁷, appropriate dilution of SW (dilution factor (DF) = 1.55) was done. The other reaction parameters were as follows: pH = 3.9, EC = 16.9 mS/cm, $V = 2.8$ and stirring rate = 150 rpm. After 90 min, 42% TOC and 60% COD removal for SW was observed after 90 min of the run (Experiment 1). Similar run was carried out using BMSW for which 37% and 50% TOC and COD removals were observed (Experiment 2).

Electrode fouling and foaming in the reactor were observed during EF oxidation. The foaming problem could be suppressed at low voltage ($V < 1.2$ V). At potential higher

than 1.23 V, water electrolysis may take place which lead to release of gases from electrodes via reactions 1 and 2 (H_2 at cathode and O_2 at anode)¹¹ due to which foaming is caused.



In EF runs, electrode fouling was due to deposition of solids on the surface of electrode material. Ultimate analysis of the solids deposited on the electrode surface suggested that major fraction (~50%) of the solids was organic in nature. Residual H_2O_2 was reduced to 7 mM and 12 mM after treatment of SW and BMSW, respectively, from initial value of 422 mM. Solids precipitation was also observed at bottom of the reactor after treatment. Hence, TOC and COD removals were due to the combination of oxidation and precipitation. 'Control' run (Experiment 3) was conducted without H_2O_2 to find the effect of H_2O_2 on EF oxidation of BMSW. In this run, TOC and COD removals of 3.4% and 5.1%, respectively, were observed.

To avoid foaming and fouling problems, subsequent experiment (Experiment 4) was performed with ten times diluted BMSW with H_2O_2 concentration of 44.2 mM. TOC and COD removals of 12% and 21% were observed at the end of experiment but problems of electrode fouling and foaming were still observed. The decrease in TOC and COD removals in this experiment may be due to lowering of EC due to dilution.

For further experiment (Experiment 5), EF oxidation of BMSW was carried out at minimum potential ($V = 1$). TOC and COD removal of 10% and 18% were observed, respectively (Fig. 2). Lower TOC and COD removals could be attributed to the smaller current density. Foaming was not observed in this run though electrode fouling was still found.

To enhance organics removal efficiency of the process and to overcome the problem of electrode fouling, different experiments were carried out at enhanced potential of 1.2, higher stirring rate, electrode interchanging, increasing EC and using stainless steel electrodes. Increase in potential to 1.2 V (Experiment 6) enhanced the TOC and COD removals to 16% and 28%, respectively. Increasing stirring rate (300 rpm) also enhanced TOC and COD removal to 21% and 37%. With increase in stirring rate (Experiment 7), electrode fouling was lesser due to which removal could have enhanced.

Alternating current (AC) may also help in improving the

efficacy of EF process by minimizing the problem of electrode fouling⁷. In AC mode, the charge on electrodes changes within fraction of seconds due to which anode and cathode keeps on interchanging. An EF run (Experiment 8) was carried out by interchanging electrodes after 15 min time interval to determine the effect on TOC and COD removals from BMSW. Slightly enhanced TOC removal of 24% and COD removal of 38% were observed during this run. In order to have higher current density at lower potential, a run (Experiment 9) was carried out by adding electrolyte to increase EC (NaCl = 2.16 g/L). Experiment 10 was conducted using stainless steel electrodes to see the effect of electrode material. TOC and COD removals were found to enhance with increase in EC, however, no significant effect of using stainless steel electrode was observed on the removal efficiency.

To check whether foaming is due to electrolysis of water in EF oxidation, a Fenton's run was carried out at H₂O₂ dosage of 422 mM (10% of stoichiometric) and 2.1 M (50% of stoichiometric) with 200 mL of BMSW at following reaction conditions: Fe²⁺ = 285 mg/L and reaction time = 90 min. Fe²⁺ dosage was calculated according to the Faraday's formula in eq. (3).

$$m = \frac{M \times I \times t}{z \times F} \quad (3)$$

where, m = mass (g) of Fe liberated at electrode, M = atomic mass of Fe, I = current (A) passed through electrodes, z = number of electrons involved in redox reaction; $z = 2$, F = Faraday's constant; $F = 96485$ C.

The COD and TOC removals of 8.4% and 6.8%, respectively were observed with H₂O₂ dosage of 422 mM. In comparison, enhanced COD and TOC reductions of 21% and 18.5% were observed with H₂O₂ dose of 2.1 M. Foaming was not observed in Fenton run carried out at H₂O₂ dosage of 422 mM, though very less foaming was observed during initial 10–15 min of Fenton reaction at H₂O₂ dosage of 2.1 M, which could be due to release of CO₂ during the mineralization of organics in EF oxidation process.

Conclusion

The major problem faced by distilleries is disposal of BMSW because after biomethanation a huge amount of

blackish wastewater with high organic load is generated. During EF treatment of SW and BMSW, electrode fouling and foaming were the identified as the major problems. In EF runs, electrode fouling was found due to deposition of solids on the surface of electrode material. The preventive measures like change of applied potential (V), electrode material and stirring speed can suppress these problems to an extent and may improve treatment performance. The results showed that the foaming problems could be reduced at lower electrode potential (≤ 1.23 V) which may be due to inhibition of electrolysis of water at lower potential.

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