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Colour removal and biodegradability enhancement of biomethanated spent wash from distillery using wet oxidation treatment

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In India, high strength spent wash (SW) produced from alcohol distilleries is preferably treated by biomethanation process. However, biomethanated SW (BMSW) still contains intensified dark brown colour, high chemical oxygen demand (COD) and poor biodegradability which requires further treatment before disposal. Wet oxidation (WO) is considered an effective treatment for high strength non-biodegradable wastewaters (COD > 10 g/L). Hence, the present study explored WO of BMSW (pH = 5.7, COD = 65.5 g/L, and total organic carbon (TOC) = 23.5 g/L) in a high pressure batch reactor (0.7 L capacity) at temperatures ranging from 160-220°C and oxygen pressure of 1.1 MPa. At 220°C temperature, TOC, COD and color removals of 39%, 59% and 90%, respectively, were observed after 3 h of reaction period. Meanwhile, biodegradability index (BI) was enhanced from 0.27 to 0.81. Carbon balance calculations showed that the oxidation reaction contribution in TOC removal was enhanced with increase in temperature (64 – 92% of total carbon removal). Fourier transform infrared (FTIR) analysis suggested the precipitation of carbonyl group and nitrogen containing compounds. During the reaction, volatile fatty acids (oxalic acid, malonic acid and acetic acid) formation was also confirmed in the treated wastewater.

Keywords: Biomethanated spent wash, Carbon balance, Solids characterisation, Wet oxidation

India is second largest sugar producer and fourth largest alcohol producing country in the world[1]. Currently, there are ~356 distilleries with annual alcohol production of 4.23 billion litres. Distilleries are agro-based industries utilizing molasses as raw material which is a waste by-product from sugar industries. These are considered among the most polluting industrial sectors worldwide[2]. During alcohol production, a high strength waste stream called as spent wash (SW), is generated. Depending upon the type of processes used for alcohol production, 5-day biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) of SW maybe 40-60 g/L and 80-190 g/L, respectively[2,3]. Biomethanation of SW is a common practice in most of the Indian distilleries which results in ~85% and ~60% reductions in BOD and COD, respectively[1]. However, biomethanated spent wash (BMSW) is difficult to dispose due to its high strength and poor biodegradability which restricts the applicability of aerobic biological treatment and physico-chemical processes (e.g., adsorption, coagulation etc). Hence, the present study explores wet oxidation (WO) process for BMSW treatment to reduce its COD and colour so that the treated BMSW could further be utilized for resource recovery and treated by other biological process.

WO is a potential treatment method for such high strength waste streams[4]. Some studies are available in the literature on WO or catalytic WO (CWO) of BMSW[5-8]. Dhale and Mahajani[6] carried out WO and catalytic WO (CWO) (using homogeneous $FeSO_4$ catalyst) of pre-treated BMSW (COD = 600-800 mg/L) at different temperatures (180-225°C) and oxygen pressures (0.69-1.38 MPa). The authors reported 60% COD reduction after CWO (catalyst dose = 150 mg/L) at 210°C temperature and 0.69 MPa pressure with formation of acetic acid in small concentration (= 40 mg/L). In recent past, Bhoite and Vaidya[8] carried out homogeneous CWO of BMSW (COD = 40 g/L) using same catalyst (dose = 16-48 mg/L) in similar conditions (temperature = 150-225°C and oxygen pressure = 0.69-2.07 MPa). Biomethanation potential (BMP) test on the treated BMSW (CWO followed by activated carbon adsorption) showed 1.1 m^3 of biogas (69% methane) generation per cubic meter of BMSW. In another study, Malik *et al.*[7] investigated performance of WO on filtered BMSW (*p*H = 7.5, and COD=40 g/L) at temperatures and pressures of 150-200°C and 0.6-1.2 MPa, respectively. The authors observed enhancement in biodegradability index (BI) (=BOD_5/COD) and COD removal from BMSW with increase in severity of oxidation conditions.

The results clearly show the effectiveness of WO/CWO process. However, most of the previous studies reported only BOD and COD removals. Moreover, pre- and post-treatment methods were also used before WO of BMSW which may affect economic feasibility of overall treatment. In CWO, use of catalysts (particularly homogeneous catalyst) necessitates a need for additional step for catalyst separation. The generation of solid residue during WO/CWO has not been reported so far up to the best of our knowledge.

Hence, thepresent study planned non-catalytic WO of BMSW at different temperatures (160-220°C) with sub-stoichiometric oxygen supply with an aim to improve biodegradability of wastewater. Furthermore, mass balance and solids characterisation were also performed for improved understanding about WO process.

Experimental Section

Chemicals and distillery wastewater

The chemicals used for COD, BOD5 and total kjeldahl nitrogen (TKN) analyses were purchased from Merck Chemicals, Mumbai, India. The standard *p*H buffer solutions (pH = 4, 7 and 10) used for *p*H meter calibration were also supplied bythe same vendor. Oxygen cylinder required for WO runswas procured from Alchemie Gases & Chemicals Pvt. Ltd., Mumbai, India.

The BMSW samples were collected from a local molasses baseddistillery situated near Pune, Maharashtra. The collected effluent was stored in the refrigerator at 4°C temperature to avoid any deterioration in its physico-chemical properties.

Wet air oxidation setup and operation

WO experiments on BMSW were performed in a 0.7 L stainless steel (SS-316) high pressure reactor (Fig. 1)[9]. In the experiments, 150 mL of BMSW was taken in the reactor vessel which was then sealed and heated to increase the reactor temperature upto the set value under mildagitation (stirring speed= 200 rpm). After achieving thedesired temperature after ~40 min, a sample (referred as ‘zero time’) was withdrawn before adding oxygen pressure of 1.1 MPa (60% of the stoichiometric oxygen requirement). Subsequently, the stirrer speed was increased to 1000 rpm for ensuring elimination of mass transfer. All the runs were performed in batch mode for 180 min duration. The treated samples were analysed for *p*H, COD, total organic carbon (TOC), BOD_5, colour number (CN). All the runs were conducted in duplicates.

Analytical methods

TOC measurements were made using a TOC analyser (TOC-VCSH, Shimadzu, Kyoto, Japan). The *p*H of the samples was measured by Eutech Cyber scan *p*H Tutor (Singapore) equipped with glass electrode. The *p*H meter was calibrated using buffer solutions 4, 7 and 10 before the analysis. Electrical conductivity (EC) of wastewater samples were measured with conductivity probe (HACH CDC-401, USA). BOD_5, COD and total solids (TS) concentration were measured using standard methods described in American Public Health Association (APHA) handbook[10]. 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. Alkalinity was estimated using potentiometric titration to end point *p*H of 4.3 while chloride concentration was measured using Argent metric method[10]. TKN in the aqueous samples was measured using macro-Kjeldahl method[10].

Elemental analysis of BMSW was carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (HORIBA JobinYvon-Ultima 2000, France). CHN analysis of the solids recovered after WO process was carried out using CHNS analyser (Flash EA1112 series, ThermaFinnigan, Italy). In order to determine the functional groups present in the solids, Fourier transform infrared (FTIR) analysis was performed on FTIR machine (Burker, 3000 Hyperion Microscope Vertex 80, Germany). The analysis was performed at resolution of 0.2 cm^{-1} and spectral range of 4000-400 cm^{-1}.

Organic acids in treated wastewater samples were detected and quantified using high performance liquid chromatography (HPLC) (Infinity-1200, Agilent) connected with UV detector. Synergi Hydro-RP column (250 mm x 4.6 mm, particle size = 4 µm, pore size = 80Å) purchased from Phenomenex, India was

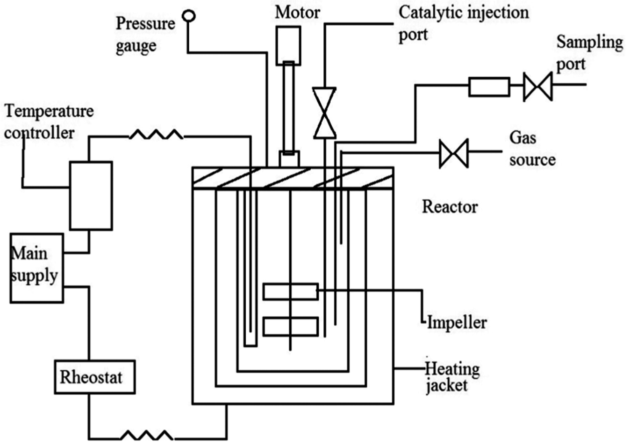


Fig. 1—Schematic diagram of high pressure batch reactor of (capacity = 0.7 L)

Table 1—Characteristics of untreated and treated BMSW

Parameters	Untreated BMSW	Treated BMSW				
		WO_160°C	WO_180°C	WO_200°C	WO_220°C	HT_220°C
Colour	Black	Dark brown	Brown	Yellow	Light yellow	Blackish
CN	4	2.9	2.1	1.1	0.4	4
*p*H	5.7	5.2	5.3	5.5	5.4	5.5
EC (mS/cm)	51	51.2	51.5	52.3	52.4	56.2
BOD$_5$ (g/L)	18 ± 1.6	12.5 ± 0.5	14.6 ± 1.2	18.7 ± 0.8	19.1 ± 0.2	12.9 ± 0.5
COD (g/L)	65.5 ± 0.2	41.9 ± 0.7	34.2 ± 0.8	28.5 ± 0.7	23.5 ± 0.3	47.8 ± 0.6
TOC (g/L)	23.3 ± 0.2	20.4 ± 0.1	19.1 ± 0.1	17.2 ± 0.3	14.4 ± 0.1	22.6 ± 0.1
BI (BOD$_5$/COD)	0.27	0.29	0.43	0.65	0.81	0.27

used for the analysis. For the analysis, dilute solutions of known concentration of compounds were injected individually as well as inmixture to determine retention time for various compounds. Colour of the wastewater samples was determined using UV spectrophotometer (UV-1800, Shimadzu, Japan). Absorbance of sample was taken at three different wavelengths (436, 525 and 620 nm) to calculate colour number (CN cm^{-1}) of a sample[11]. For darker samples, the CN should also be higher. Distilled water was taken as reference for absorbance.

Results and Discussion

The untreated and treated BMSW was analysed for various physico-chemical characteristics as shown in Table 1. BMSW wastewater received from distillery was dark black in color (CN = 4)and having high TOC (= 23.3 g/L) and COD (= 65.5 g/L) with poor biodegradability (BI = 0.27). The initial *p*H and EC of BMSW were 5.7 and 51 mS/cm, respectively.

The elemental analysis results showed higher concentrations of Mg, Na and S (1.93 g/L, 0.5 g/L and 0.4 g/L, respectively) while Fe, Zn and Mn were found in very low concentrations. Metals like Cu, Zn, Se, Pb and Ni were not detected in BMSW.

Wet oxidation of BMSW

In the beginning,'control'hydrothermal (HT) experiment was carried out at 220°C in absence of oxygen in which only ~4% TOC and ~17% COD removals were obtained with no change in colour and biodegradability index. Subsequently, WO batch runs were carried out using 150 mL of BMSW wastewater at different temperatures (160-220°C) for 3 h duration. COD and TOC removals enhanced with increase in temperature (Fig. 2a), which is also reported in previous studies[7,8]. Higher organics removal with increasing temperature can be attributed to the enhancement in oxygen solubility and higher reaction rate. The maximum TOC and COD removals of 39% and 59%, respectively were observed during the run carried out at 220°C temperature (Fig. 2a). Meanwhile, CN was reduced to 0.4 which is 10 times lower than that of untreated BMSW. Moreover, BIwas increased to 0.81 from an initial value of 0.27. The results suggest the breakdown of complex and colour imparting non-biodegradable organic compounds (such as melanoidins and caramels) into simpler biodegradable compounds. The above compounds are considered responsible for intense colour of the wastewater[12,13]. Decrease in final *p*H of the treated wastewater to 5.1 was possibly due to formationof low molecular weight fatty acids during oxidation process. Belkacemi*et al*.[5] reported the formation of acetic, malonic, tartaric, lactic, and phthalic acids after WO of BMSW. In the present work, the untreated and treated (at 220°C) wastewater samples were analysed for the presence of four carboxylic acids: oxalic, malonic, acetic and maleic (Table 2). The concentrations of these acids were observed in the treated BMSW concentrations of 1.9 g/L, 7.2 g/L, 13.5 g/L and 0.03 g/L, respectively. The concentrations of malonic and acetic acids in WO treated BMSW were more than five and nine times, respectively, to those in the untreated BMSW.

Table 2—Concentration of different acids in untreated and treated BMSW calculated form HPLC analysis

Acids	Concentration (g/L)	
	Untreated	WO_200°C
Oxalic acid	1.5	1.9
Malonic acid	1.3	7.2
Acetic acid	1.5	13.5
Maleic acid	0	0.03

Characterization of solids recovered after WO of BMSW

The filterability of BMSW was very poor and clogging of the nylon filter (0.45 µm) was observed during vacuum filtration. After WO treatment, the filterability was improved significantly as no clogging and resistance was observed during the test. The solids deposited on the filter were subjected to CHN

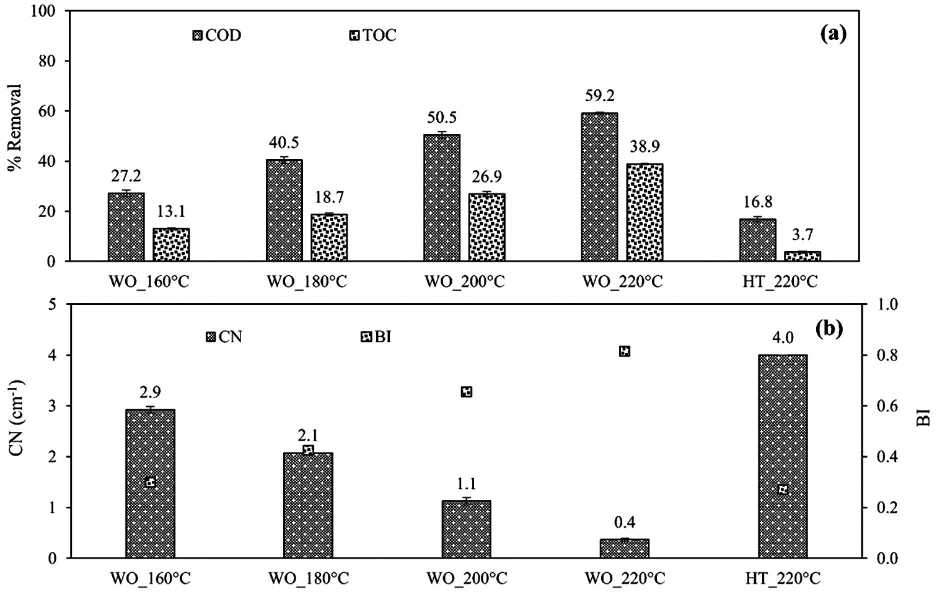


Fig. 2—WO of BMSW: (a) COD and TOC removals and (b) color number and BI (P_{O2} = 1.1 MPa, temperature = 160-220°C, stirring speed = 1000 rpm and run time = 3 h)

Table 3—CHN analysis of solids recovered after WO of BMSW

Parameter	Solids generated after WO/HT of BMSW				
	WO_160°C	WO_180°C	WO_200°C	WO_220°C	HT_220°C
Mass concentration (g/L)	3.8	4.5	5.3	5.1	4.7
Carbon (%)	25.2	22.5	19.5	11.2	47.5
Hydrogen (%)	3.1	2.9	2.1	1.1	4.1
Nitrogen (%)	3.4	3.8	2.9	2.3	3.9
Oxygen (%)	28.2	27.3	26.9	19.8	20.3
Ash (%)	40.1	42.6	48.6	65.6	24.2
Calorific Value (MJ/kg)	7.9	6.9	4.8	1.8	18.2

and FTIR analyses in order to get insight into organics removal mechanisms and their nature, respectively. During WO experiments, ~4-5 g/L of solids were generated (Table 3). Themass of solids was found to increase with rise in temperature which can be due to occurrence of polymerization reactions at higher temperature. On contrary, carbon content in the solids obtained after WO experiments was decreased with temperature due to enhanced oxidation of organic solids. High calorific value (HCV) of the recovered solids after WO treatment of BMSW was calculated using Dulong formula (Equation 1)[14].

$$\text{Calorific value (kJ/kg)} = 337C + 1419(H - 0.125O_2) + 93S + 23N \quad \text{... (1)}$$

where C, H, O, S and N are percentage by weight of carbon, hydrogen, oxygen, sulphur and nitrogen respectively, in recovered solids on dry basis.

HCV reduced with decrease in carbon content. The solids recovered after hydrothermal treatment (HT) without oxygen at 220°C contained the highest calorific value (18.2 MJ/kg) whereas it was in the range of 1.8-7.9 MJ/kg in the solids recovered after WO treatment (Table 3).

Carbon balance calculations

Carbon balance was also performed using TOC in wastewater and carbon content in solids before and after WO runs (Table 4). The results showed that the contribution of TOC reduction due to oxidation of organics was enhanced as the reaction temperature was increased. The ratio of TOC removed by oxidation to TOC in precipitated solids was increased from ~1.8 to ~13 with increase in WO reaction temperature from 160-220°C.

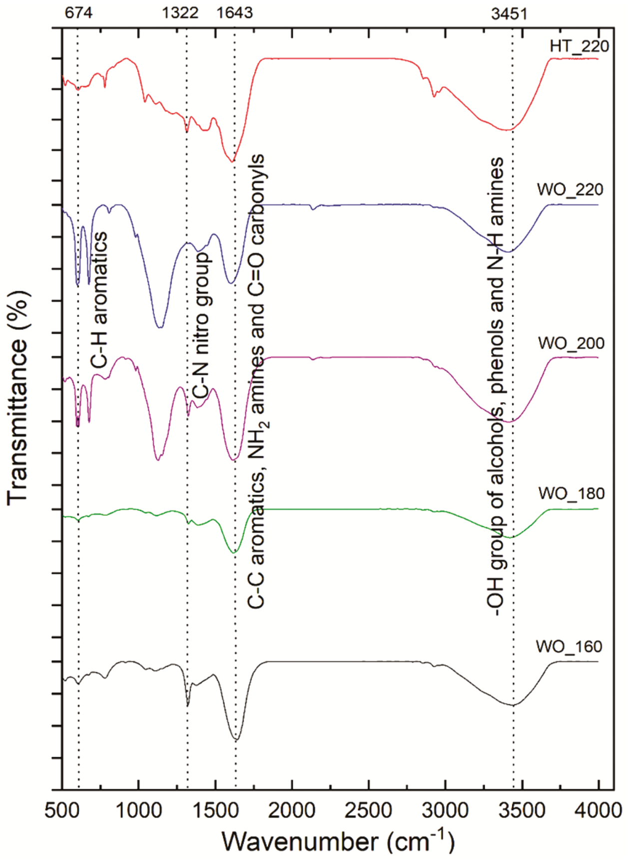
FTIR analysis of the recovered solids

FTIR analysis was carried out to predict the nature of solids precipitated during WO of BMSW (Fig. 3). The peaks obtained in FTIR spectra were compared with those reported in literature[15,16]. The peaks

Table 4—Carbon balance during WO of BMSW (initial TOC = 23500 mg/L)

Experiment	TOC_F (mg/L)	TOC_R (mg/L)	Recovered carbon in solids in 150 ml (mg)	TOC_S (mg/L)	TOC_O (mg/L)
WO_160	20433	3067	163	1089	1978
WO_180	19103	4397	172	1156	3241
WO_200	17184	6316	177	1182	5134
WO_220	14364	9136	98	655	8481

TOC_F = final TOC of treated BMSW; TOC_R = TOC removal from BMSW; TOC_s = Total organic carbon in solid phase and TOC_O = TOC oxidized.



Fig, 3—FTIR analysis of solids recovered after WO of BMSW

appearing at 3200-3500 cm^{-1} indicate the presence of O-H group of alcohols, phenols and N-H of amines while the peak between 2850-3000 cm^{-1} was assigned to O-H stretch of carboxylic acids. The presence of C=O group from carboxylic acids was predicted due to the peaks observed at 1640-1700 cm^{-1}as per literature[17]. The peak due to C-N bond was appeared at 1322 cm^{-1} according to study[16], whereasthe peaks observed between 670-900 cm^{-1}in FTIR spectra of only the solids obtained after WO at 200°C and 220°C show the presence of C-H bond of aromatic organic compounds. For comparison, only two prominent peaks could be identified (1640 cm^{-1} and 3450 cm^{-1}) in FTIR spectrum for the solids recovered after HT treatment at 220°C (without oxygen). From the above results, it can be suggested that low molecular weight organic compounds were formed due to oxidative breakdown of larger molecules some of which precipitated out and appeared in solids.

Conclusion

From the above study, it can be suggested thatnon-catalytic WO of BMSW at moderate temperatures and sub-stoichiometric oxygenwas very effective in TOC and COD removals (upto39% and ~59%, respectively). Colour removal and biodegradability index were significantly improved with increase in reaction temperature. Though the solids formation was more for the WO runs performed at higher reaction temperature but carbon content was significantly reduced and mostly it was comprised of inorganic substances as HCV was also very low. Moreover, the higher temperature favoured the oxidation of organics rather than their precipitationdue to polymerisation as evident from TOC_O to TOC_S ratio at different temperature conditions. Formation of maleic acid and increase in concentration of oxalic acid, malonic acid and acetic acid were observed during WO reaction.

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