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Wet air oxidation as a pretreatment option for selective biodegradability enhancement and biogas generation potential from complex effluent

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HIGHLIGHTS

- ▶ Wet oxidation pretreatment for biodegradability enhancement of complex waste.
- ▶ Biogas generation potential from pretreated effluent is reported.
- ▶ Concept illustrated using biomethanated distillery waste as a case study.
- ▶ Sensitivity analysis of wet-ox conditions on BI enhancement is reported.

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ABSTRACT

This study looks at the possibility of wet air oxidation (WAO) based pretreatment of complex effluent to selectively enhance the biodegradability (without substantial COD destruction) and facilitate biogas generation potential. A lab-scale wet air oxidation reactor with biomethanated distillery wastewater (B-DWW) as a model complex effluent (COD 40,000 mg L^{-1}) was used to demonstrate the proof-of-concept. The studies were conducted using a designed set of experiments and reaction temperature (150–200 °C), air pressure (6–12 bar) and reaction time (15–120 min) were the main process variables of concern for WAO process optimization. WAO pretreatment of B-DWW enhanced the biodegradability of the complex wastewater by the virtue of enhancing its biodegradability index (BI) from 0.2 to 0.88, which indicate favorable Biochemical Methane Potential (BMP) for biogas generation. The kinetics of COD destruction and BI enhancement has also been reported.

1. Introduction

Complex industrial effluents with high COD and color are generated from various industries such as distillery, heterocyclic chemical manufacturing etc. The cane molasses-based distilleries is one such source generating complex, troublesome and strongest industrial organic effluents with high COD (90000–110000 mg L^{-1}), dark brown color and huge volume (8–15 L L^{-1} of alcohol produced) (Kumar, 2003; Sangve and Pandit, 2004). After conventional anaerobic digestion, the distillery wastewater still retains up to 40,000 mg L^{-1} COD and substantial color and becomes recalcitrant (biodegradability index < 0.2) to further effective treatment by biological methods. This problem provides an opportunity for the development of effective pretreatment methods to enable the biogas generation potential from such complex effluent.

A variety of treatment methods and strategies like thermal pretreatment, wet air oxidation, concentration-incineration, anaerobic treatment etc. have been suggested or tested for the treatment of distillery wastewater, however, all these schemes on their own are either incomplete, unviable or unsustainable (Kumar, 2003; Pant and Adholeya, 2006; Sangve and Pandit, 2004).

Recently, wet air oxidation has found great attention in the area of wastewater treatment, and involves the liquid phase oxidation of organics or oxidizable inorganic components at elevated temperature (125–320 °C) and pressure (1–60 bar) using a gaseous

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Abbreviations: B-DWW, biomethanated distillery wastewater; VFA, volatile fatty acids (mg L^{-1}); COD, chemical oxygen demand (mg L^{-1}); BOD, biochemical oxygen demand (mg L^{-1}); BI, biodegradability index (BOD_5: COD ratio); BMP, biochemical methane potential; WAO, wet air oxidation; AOPs, advanced oxidation processes; APHA, American Public Health Association; AWWA, American Water Works Association; ANOVA, Analysis of variance; WPCF, Water Pollution Control Federation; SD, standard deviation; rA, rate of reaction (mg L^{-1} min^{-1}); rA (COD), rate of COD destruction (mg L^{-1} min^{-1}); rA (BI), rate of BI enhancement (mg L^{-1} min^{-1}); α, proportionality constant; T, temperature (K for kinetic purpose and °C for other purpose); PO_2, oxygen partial pressure (bar).

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source of oxygen (usually air). The degree of oxidation is mainly a function of temperature, oxygen partial pressure, residence time and the oxidizability of the pollutants under consideration (Mishra et al., 1995).

The WAO of the organic substrates in the liquid medium involves a free radical mechanism. The steps involved during the process are mainly (a) destruction of the organic molecules (COD reduction) into lower molecular weight compounds or (b) complete mineralization into CO_2 and H_2O (Gunale and Mahajani, 2007; Tufano, 1993; Li et al., 1991).

Unlike other AOPs, WAO is effective for high organic loading at high flow rate and can partially cover the application range of incineration and biological methods, especially for the treatment of effluents containing COD of 10000–100000 mg L^{-1} and/or toxic contaminants for which the biological treatment is not feasible (Kim and Ihm, 2010).

Most of the reported work with reference to WAO is targeted mainly for complete destruction (Belkacemi et al., 2000; Daga et al., 1986; Debellefontaine et al., 1996). However, it has also been reported that none of the advanced oxidation methods (sonication, photo-catalytic, Fenton, ozonation, wet oxidation etc.) can be used individually in wastewater treatment applications with good economics and high degree of energy efficiency (Adewuyi, 2001, 2005; Gogate and Pandit, 2004). Therefore, there is a need to lower the energy requirement of such pretreatment systems by targeting only limited and selective treatment to enhance the biodegradability and facilitate subsequent biogas generation (resource recovery).

In the present investigation, WAO was investigated as a pretreatment option for complex effluent using a lab-scale reactor and biomethanated distillery wastewater as a model effluent, with emphasis on selectively enhancing the biodegradability and retaining sufficient residual COD for biogas production potential. The kinetics of oxidation has also been expressed in terms of COD destruction and BI enhancement.

2. Methods

2.1. Complex model wastewater (biomethanated distillery wastewater) and reagents

The biomethanated distillery wastewater (B-DWW) was procured from the molasses-based distillery near Nagpur located in Central India (details not provided due to confidentiality issues). The wastewater was transported to the laboratory and was stored in tightly capped car buoys in cold storage (at 4 °C) for further use. The collected wastewater was analyzed for its physico-chemical characteristics and the results are presented in Table 1. All the reagents and chemicals used in the study were of analytical grade.

Table 1
Characteristics of complex wastewater (biomethanated distillery wastewater).

Parameters	Value
pH	7.61
Color	Brown
COD (mg L^{-1})	40000
BOD (mg L^{-1})	6744
TOC (mg L^{-1})	18700
Total solids (mg L^{-1})	31000
Total suspended solids (mg L^{-1})	1600
VFA (mg L^{-1})	180
BOD:COD ratio	0.17

Values are average of three set of observations with SD < 5%.

2.2. Wet air oxidation reactor and operation

The B-DWW was pretreated in a Wet Air Oxidation Reactor, having 1.8 L gross volume (Model-4578, Floor Stand HP/HT Reactor, Parr Instruments, USA) made of SS-316. The reactor (I.D. 95 mm) had a four bladed turbine type impeller (I.D. 50 mm) and was equipped with a pressure indicator and a gas sparging tube. The experimental set up is presented in Fig. 1. The impeller speed was maintained at 200 rpm. The reactor was also provided with a rupture disc as well as non-return valve at the gas inlet. Five hundred milliliter of the wastewater was used for pretreatment. The reactor was properly sealed, ensuring absence of any leakage. The reaction mixture was then heated to a desired temperature and air was sparged into the reactor to the predetermined level (6–12 bar). The biomethanated distillery wastewater (B-DWW) stored at 4 °C was allowed to attain the room temperature before pretreatment.

The B-DWW was subjected to WAO for pretreatment in batch experiments. The reaction volume of each batch experiment was 0.5 L. No pH adjustment was made during the pretreatment; therefore the original wastewater pH was the initial pH for the pretreatment step. Wet air oxidation was carried out using designed experiments in the temperature range of 150–200 °C, pressure 6–12 bar and time 15–120 min (especially to cover the less severe range of WAO). After every run, the reactor was put in a cooling mode. The pretreated samples were analyzed for pH, COD, BOD, VFA and BOD: COD ratio. The total volume (0.5 L) did not vary since the system was tightly sealed.

2.3. Analysis

The COD, BOD, TOC and VFA analysis was carried out as per the standard methods (APHA, AWWA, WPCF, 1998). Control dynamics make pH meter was used for monitoring pH of the samples during investigation. To avoid the complexity of standards each WAO run was conducted three times and sample was analyzed. The error in analytical measurements was always observed to be less than 5%. FTIR analysis of WAO untreated and treated sample was performed using Fourier Transform Infra-red Spectrometer (FTIR, Model: Vertex 70-BRUKER). Similarly, the sample preparation for protonic nuclear magnetic resonances (H^1 NMR) spectrum was done by extracting with D_2O under nitrogen atmosphere and further transferred to a 5-mm NMR tube. The samples were analyzed at 25 °C with a BRUKER AV III 500 MHz FT NMR Spectrometer and chemical shifts were recorded in ppm (δ) with TMS at 0.0 as an internal standard.

2.4. Biodegradability–post pretreatment

The biodegradability index (BI) is a measure of the extent to which a waste is amenable to biodegradation. BI can be expressed as ratio of BOD_5: COD (Momani et al., 2002). The COD and BOD of the wastewater were evaluated after the WAO pretreatment as per the Standard Methods (APHA, AWWA, WPCF, 1998) and compared with the B-DWW without WAO pretreatment.

2.5. Biochemical methane potential (BMP)

Assessment of anaerobic biodegradability of WAO pretreated biomethanated distillery wastewater was performed using the BMP measurement. A 2.5 L amber colored anaerobic (Nitrogen purged) bottle reactor was used for the lab scale experiment for evaluation of BMP. The bottle was filled with 2 L of WAO pretreated (optimized) B-DWW along with 10% acclimatized biomass from a distillery anaerobic digester treating raw spent wash. The experiment was conducted at room temperature (35 ± 2 °C). The total gas evolution (i.e. CH_4 and CO_2) was monitored volumetrically

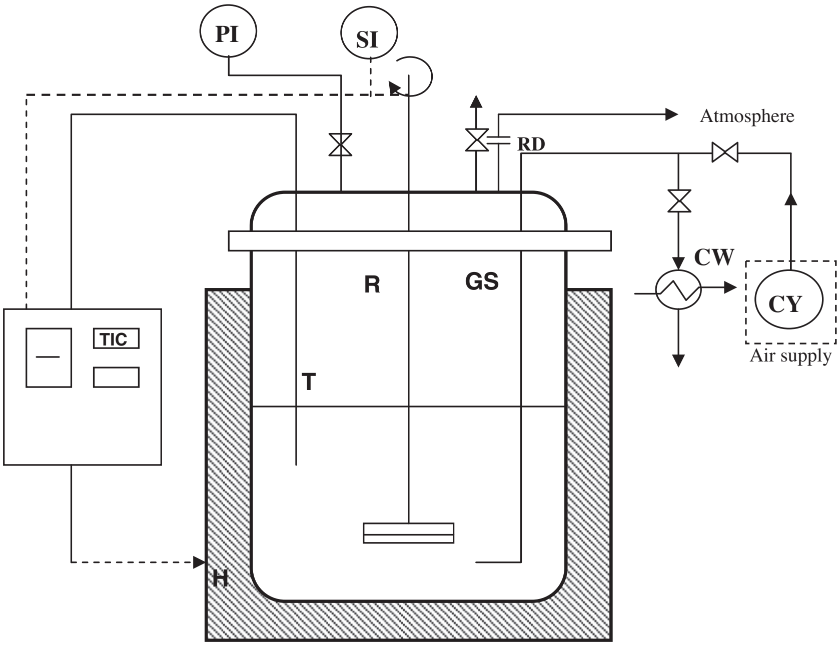

Fig. 1. Schematic diagram of experimental set up for wet air oxidation reactor. The schematic represents the actual reactor set up used in present study. (TIC, SIC, temperature, speed indicator and controller; PI, pressure indicator; SI, speed indicator; RD, rupture disc; GS, gas sparger; H, electric heater; T, thermo well; R, reaction vessel; CW, cooling water; CY, gas cylinder).

using water displacement method (APHA, AWWA, WPCF, 1998). The Methane percentage was analyzed using Perkin–Elmer Auto System GC. The Porapak Q 80/100 packed column (6 feet, 2 mm I.D.) with thermal conductivity detector, hydrogen as carrier gas (at 50 mL min^{-1}) and injector, oven and detector all at 100 °C was used for methane analysis. The control sample consisted of B-DWW without WAO pretreatment and with 10% acclimatized biomass, the COD of this wastewater without WAO pretreatment was appropriately diluted to get the same starting COD as that of WAO pretreated B-DWW. The sample was removed everyday during the 6-day experiment. The samples were centrifuged at 5000 rpm for 10 min and then used for the analysis of pH, COD, BOD. The analysis was carried out in triplicates and the mean values are presented as results.

3. Results and discussion

3.1. Effect of WAO conditions on complex wastewater pretreatment

3.1.1. Effect of pressure

The effect of pressure on COD reduction vis-à-vis BI enhancement was studied in the range of 6–12 bar at three different temperatures (150–200 °C) and at various time intervals (15–120 min) and for initial COD of 40,000 mg L^{-1} (Fig. 2). In order to ascertain the true kinetics of the reaction it is necessary to eliminate diffusion resistance for which the effect of agitation was also accounted for in this investigation, studies were conducted in the range of 150–500 rpm (data not shown). It was observed that the liquid side mass transfer resistance was completely eliminated at 200 rpm. Therefore to ascertain true kinetics all the further experiments were conducted at this rpm in a kinetically controlled regime.

The COD concentration reduces in the range of 16–36% at 6 bar pressure (150–200 °C, 15 min), yielding BI values of 0.2–0.32. Similarly 50–70% COD reduction and BI enhancement in the range of 0.55–0.88 was observed at 120 min. When the pressure was increased to 12 bar, the COD reduction from 17% to 36% (150–200 °C, 15 min), with BI enhancing in the range of 0.3–0.4 was observed. Similarly a reduction in the COD was observed in the range of 55–70% (150–200 °C, 120 min), with enhanced BI in the range of 0.63–0.86. In the range of pressure considered in this study, the system behavior indicates that the pretreatment can be operated at lower range (6 bar) to get the minimum desirable BI (0.4 indicated by dotted horizontal line in the Fig. 2).

This trend indicates that as pressure increases (in the range studied) there is a slight increase in the COD reduction (5–7%) for all the experimental runs.

From the results, it can be concluded that an experimental condition yielding around 40% COD reduction and a BI around 0.4 (175 °C, 30 min and 6 bar) would be suitable for present setup where the main objective is pretreatment (and not COD destruction) along with reorientation of complex waste molecules to become more amenable to enhance biodegradation (BI).

The WAO reaction in the present study is most likely to proceed via the free radical mechanism and in number of studies have been reported earlier by various authors (Li et al., 1991; Tufano, 1993; Collado et al., 2010). The WAO mechanism for salicylic acid solutions have been studied resulting in 98% removal of salicylic acid (1000 mg L^{-1}) at 41 bar in 60 min, whereas when pressure was reduced to 25 bar, the same removal could be achieved in 140 min (Collado et al., 2010). Gunale and Mahajani, 2008, have reported WAO of aqueous morpholine over rubidium–titanium dioxide catalyst in the pressure range of 3.4–13.8 bar, wherein the rate of COD reduction (9000 mg L^{-1}) increased with increasing pressure up to 6.9 bar during 120 min reaction and then reduced with increasing pressure. The literature reports the oxygen reaction orders for WAO in the range of 0–1.5 for various organic compounds (Collado et al., 2010; Li et al., 1991; Mishra et al., 1995). However, these reports cannot be directly correlated with present data, since the pressure range reported was much higher, as also the reaction time was very high and more so the reported literature deals mostly with single known compounds and the present investigation involves a complex effluent with the main aim of enhancing its biodegradability.

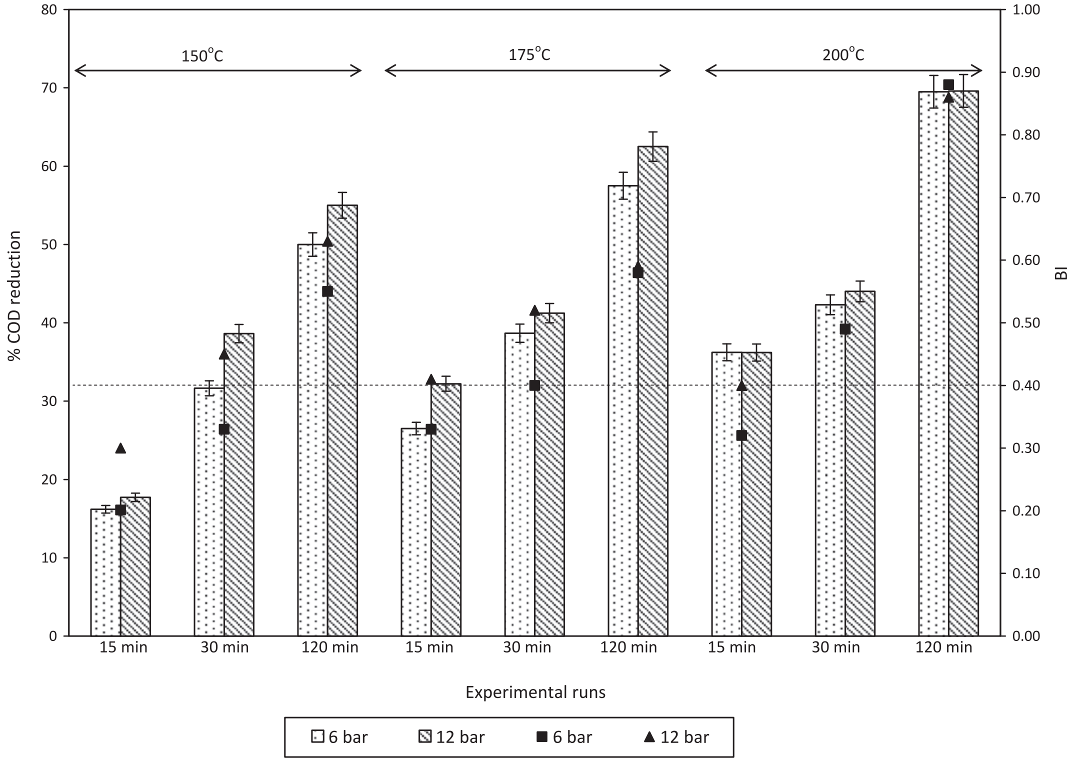

Fig. 2. Effect of pressure and temperature of wet oxidation process on % COD reduction and BI profile in pretreated biomethanated wastewater. The figure represents the % COD reduction and enhancement in biodegradability under various experimental conditions and effect of various process parameters on COD removal and BI enhancement. The dotted horizontal line represents the desirable BI value for coupling with biological treatment.

3.1.2. Effect of temperature

The effect of temperature (150–200 °C) was evaluated on the pretreatment of biomethanated distillery wastewater. The results were interpreted in terms of COD reduction and BI enhancement and are presented in Fig. 2.

As is generally observed in WAO systems, higher COD reduction was achieved at higher temperatures. The COD reduction was observed in the range of 16–69% for various experimental conditions and at minimum and maximum reaction time (15–120 min). The enhancement in BI was observed in the range of 0.2–0.88 (0.17 initial). In the present study, the effect of temperature is significant only up to 175 °C which means that temperature does not yield a linear effect on WAO efficiency after 175 °C (Fig. 2). For all practical purposes a BI of 0.4 is good enough to make a waste amenable to biodegradation (Metcalf and Eddy, 1979), which in this study is observed at an experimental condition of 175 °C, 6 bar and 30 min of reaction time.

Degradation of 10,000 mg L^{-1} Aniline has been reported to occur at 230 °C and oxygen partial pressure 0.345–1.380 MPa in a Fenton assisted WAO (Gunale and Mahajani, 2007). Ciba Geigy (1990) has developed its own WAO system for the treatment of various wastes from the chemical industry with two bubble column reactors; the conditions for operation are 295 °C, 160 bar and 180 min and COD 110000 mg L^{-1}.

Although literature reports are available for WAO, most of them deal with either complete treatment or else catalytic process and mostly all studies are based on single/pure compound (Collado et al., 2010; Gunale and Mahajani, 2008; Vaidya and Mahajani, 2002a, 2002b) (See Fig. 3).

3.1.3. Effect of initial COD

WAO studies at varying initial COD was also investigated at the observed optimum WAO condition (175 °C, 6 bar and 30 min), in order to evaluate its effect on overall process efficiency.

The results obtained indicate that at higher initial COD, the process efficiency (%) in terms of COD removal and BOD enhancement improves. Thus, maximum COD removal (33%) is observed at 40,000 mg L^{-1} initial COD (10828 mg L^{-1} BOD). Similarly minimum removal (17%) was observed at 15,000 mg L^{-1} initial COD (4672 mg L^{-1} BOD). This finding is in agreement with the observations of Mishra et al. (1995), wherein the authors claim that the efficiency of WAO increases with increasing COD and thus higher feed COD makes process self-sustaining. Several other literature reports (Collado et al., 2010; Pintar and Levec, 1992) available regarding single/pure compound indicate inhibition effect of the initial higher substrate concentration on the rate of WAO.

3.2. Sensitivity analysis of wet air oxidation pretreatment conditions on BI enhancement and COD reduction

The experimental wet air oxidation pretreatment data obtained was subjected to multiple regression analysis using MINITAB 14 software (details of methodology were as per that reported earlier by authors: Banerjee et al., 2009) (Mathews, 2005). The functional mathematical relationship between BI (Y_1) and % residual COD (Y_2) can be represented as:

$$\begin{aligned}Y_1 = {} & 0.3986 - 0.0076X_1 + 0.0536X_2 + 0.0045X_3 + (3.2 * 10^{-5}X_1^2) \\ & - (4.6737 * 10^{-5}X_3^2) - (2.2222 * 10^{-4}X_1X_2) + (3.2790 \\ & * 10^{-5}X_1X_3) - (6.5891 * 10^{-5}X_2X_3)\end{aligned}$$

$$\begin{aligned}Y_2 = {} & 289.78 - 1.7702X_1 - 3.72219X_2 - 1.3292X_3 + 0.00363X_1^2 \\ & + 0.00619X_3^2 + 0.0192X_1X_2 + 0.0009X_1X_3 - 0.00268X_2X_3\end{aligned}$$

Where Y_1 and Y_2 are the Biodegradability index and% residual COD, X_1 is reaction temperature, X_2 and X_3 are pressure and the reaction time respectively.

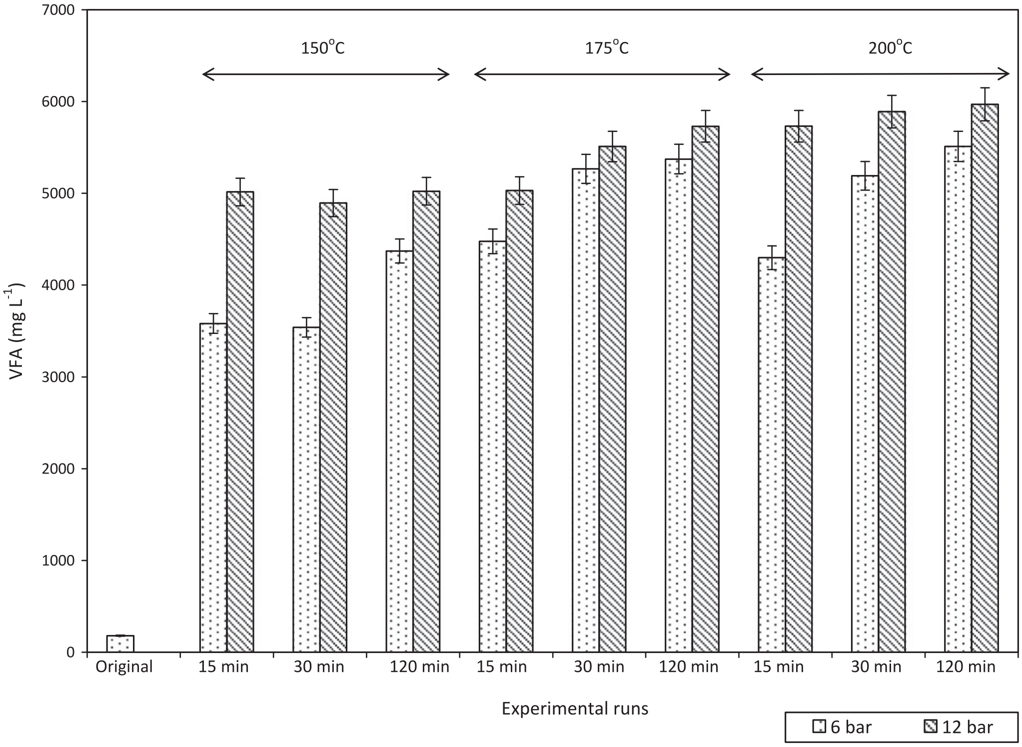

Fig. 3. Volatile fatty acid profile in wet air oxidation pretreated biomethanated distillery wastewater. The figure represents the concentration of volatile fatty acids generated as a by-product of WAO pretreatment under various experimental conditions and effect of process parameters on VFA generation.

The ANOVA model for the biodegradability index of spent wash as a function of different condition of WAO treatment is shown in Table 2. ANOVA of the regression model demonstrates that the model is highly significant at main effects ($P = <0.05$) (Mathews, 2005). Coefficient estimation for BI shows that coefficients of parameters for temperature and time are significant at 95% confidence interval (CI). The model variables shown in Table 2 imply that the linear negative effect of reaction temperature and linear positive effect of pressure and reaction time ($P < 0.05$) predominate over their interactive effects. Among the main effects, positive effect of reaction time (X_3) was observed to have profound effect on response followed by linear negative effect of temperature (X_1) and positive effect of pressure (X_2) ($P < 0.05$). From the full factorial fit regression analysis it was confirmed that the interaction effects between the variables were insignificant ($P > 0.05$). Similar analysis was carried out for % COD reduction (Table 2) implies that the linear negative effects of reaction temperature and reaction time ($P < 0.05$) predominate over their interactive effects and also these terms had found very significant influence on the% residual COD as ($P < 0.05$) at 95% CI. Time (X_3) has the maximum linear negative effect ($P < 0.01$) on Y_2 followed by linear negative effect of temperature (X_1). It was confirmed that the square effect of temperature had the highest effect on the Y_2 ($P < 0.05$) and other square and interaction effects were insignificant ($P > 0.05$).

Table 2
The estimation of coefficient and analysis of variance of the calculated model of process parameters for BI enhancement and % residual COD of biomethanated distillery waste.

Terms	BI		% Residual COD	
	Coefficients	P	Coefficients	P
Constant	0.3986	0.000	289.78	0.000
Linear effect	–	0.000	–	0.000
Temperature	−0.0076	0.001	−1.7702	0.001
Pressure	0.0536	0.083	−3.7221	0.641
Time	0.0045	0.000	−1.3292	0.000
Square	–	0.219	–	0.021
Temperature∗temperature	$3.2*10^{-5}$	0.553	0.0036	0.351
Time∗time	$-4.67*10^{-5}$	0.106	0.0061	0.008
Interaction	–	0.225	–	0.611
Temperature∗pressure	$-2.22*10^{-4}$	0.397	0.0192	0.307
Temperature∗time	$3.27*10^{-5}$	0.073	0.0009	0.452
Pressure∗time	$-6.58*10^{-5}$	0.564	0.0026	0.739

3.3. FTIR and NMR analysis

Fourier Transform Infrared Spectroscopy (FTIR) technique was used to investigate the presence of various functional groups pre- and post-WAO treatment of B-DWW. FTIR analysis indicated the dissociation and reorientation of complex organic compounds in the untreated B-DWW to new and simpler organic compounds. In comparison to the untreated sample, in the WAO treated sample, main absorptions were found approximately near 2935 and 2860 cm^{-1} and also at 1470 and 720 cm^{-1} (Table 3), which is indicative of the presence of longer linear aliphatic chain compounds in the WAO treated samples (Coates, 2000). In WAO treated sample, additionally intense bands were found in the ranges 1600–1300, 1200–1000 and 800–600 cm^{-1} which showed the presence of simple hydrogen bonded OH absorption of a hydroxyl (alcohol) function. Some sharp peaks occurred between 3670 and 3550 cm^{-1} which predicted non-hydrogen-bonded hydroxyl group. The absorption peaks between 1700–1650 cm^{-1} in WAO treated sample indicated the formation of carboxylate (carboxylic acid salt). From the IR spectra it can also be observed that strong OH bonds are produced in treated sample over control. The important structural feature of Melanoidin (major coloring compound in original sample) is the peak of C=N and C=C conjugated bonds. The WAO pretreatment aids in cleavage of the C=N (azomethane) and C=C (ethylinic) linkage producing more hydroxyl groups in (3400 cm^{-1}) pretreated sample over the control. This proves the

Table 3
FTIR analysis of WAO treated B-DWW.

Sample	Stretching frequencies (λ_{max})	Assignments
Original B-DWW	3586 2853 1610 1420 1358 1044 865 772 731 692 651 615 544 431	–OH, $-CH_3-O-$, NH, CN, C–F, C–Cl, C–Br, C–I, S–S
Pretreated 0.2 BI (150 °C, 6 bar, 15 min)	3614 3246 2850 2761 1612 1355 1043 690 654 613 508 432	OH, NH_4^+, $RCOO^-$, C–F, C–Br, S–S
Pretreated 0.4 BI (175 °C, 6 bar, 30 min)	3579 3314 3245 2850 2762 1612 1424 1359 1301 1213 1045 693 654 544 508 427	OH, $C_nH_{2n-2,}$ Polymeric OH, $-CH_3-O-$, NH_4^+, NO_3^-, $RCOO^-$, SO_4^{2-}, CN, C–Br, C–I, S–S
Pretreated 0.8 BI (200 °C, 6 bar, 120 min)	3617 2851 2760 1648 1611 1417 1363 1044 871 732 692 652	OH, CH_2, $R-NH_2$, C=C, SO_4^{2-}, $R-SO_2O-$, CN, C–O–O–, C–Cl, C–Br

conversion of complex molecules to simpler forms. The preliminary investigation on ^{1}H NMR spectrum of untreated and treated sample has shown signals at δ 7.4 ppm δ 8.0 ppm in only the untreated sample. This is indicative of the tentative presence of aromatic groups in the untreated sample whereas these signals were not observed in WAO treated samples, probably because of breakdown of aromatic compounds by wet oxidation into simpler aliphatic compounds (Jacobsen, 2007).

3.4. Effect of WAO on anaerobic biodegradation potential of B-DWW

The WAO of B-DWW in the present study not only leads to BI enhancement along with reduction in COD, but also generates substantial amount of volatile fatty acids (VFA) during the reaction. The VFA profile at various experimental conditions is presented in Fig. 4.

The obtained results indicate that higher temperature, pressure and reaction time favor higher VFA production. At lower pressure (6 bar), the VFA content is found to enhance 20–25-fold, 25–26-fold and 24–31-fold of the initial value (180 mg L^{-1}), for 150, 175 and 200 °C respectively during the 15–120 min reaction time. At higher pressure (12 bar) the minimum and maximum VFA production enhancement is in the range of 26–28-fold, 28–32 and 32–33-fold at 150, 175 and 200 °C respectively during the 15–120 min reaction time.

These results are indicative of the fact that higher VFA generation occurs at higher operating parameters. It may however, be noted that a BI of 0.4 is sufficient to facilitate biogas generation.VFA and alkalinity are good indicators for evaluating the process efficiency of anaerobic digestion since total alkalinity reflects VFA as well as bicarbonate profile. VFA: Alkalinity ratio of 0.4 obtained in the present study to achieve a desirable BI of 0.4 (Alkalinity data not presented) can be tolerated well by conventional anaerobic digesters (up to 0.8) (Deublein and Steinhauser, 2008; Zhao and Viraraghavan, 2004). These findings support the fact that the wastewater after WAO pretreatment has a potential for biogas generation and therefore the pretreatment condition 175 °C, 6 bar and 30 min can be considered as experimental optimum to get a minimum BI (optimum) for subsequent biogas generation.

Under all the circumstances, the pretreatment leads to the generation of sufficient quantities of VFA (3540–5970 mg L^{-1}) suggesting the role of the pretreatment step in transforming the parent pollutant molecules to simpler biodegradable form like acids.

It has been reported that during WAO, the longer molecules are oxidized to various intermediate products. Most of the initial intermediates formed (except the low molecular carboxylic acids) are unstable and are further oxidized to oxidation end products (CO_2, etc.) or to low molecular weight carboxylic acids (mainly acetic acid), which are reported to resist further oxidation (Mishra et al., 1995).

A report on WAO of anaerobically digested sludge suggests that during WAO, higher temperature leads to generation of more organic acids, especially acetic acid, however beyond 225 °C, the acetic acid itself was degraded (Wu et al., 1987). Further, it has also been reported that WAO becomes self-sustaining with no auxiliary fuel requirement when the COD is above 20,000 mg L^{-1} (Mishra et al., 1995). In the present study, the most severe condition of WAO operation was 200 °C, 12 bar and 120 min, which is far milder, as compared to the typical conditions of WAO used for total destruction of organics, which begin from 200 °C and 40 bar (Mantzavinos et al., 1999) and therefore the wet-ox system can be potentially self-sustaining pretreatment option for a complex effluent (such as distillery) containing a large spectrum of unknown compounds.

Preliminary experiments were conducted to assess the BMP of the WAO pretreated B-DWW as against untreated B-DWW as a control. The experiment was set up as per the method discussed in materials and methods section.

The biogas generation potential from WAO pretreated B-DWW (at 175 °C, 6 bar, 30 min), with enhanced BI of 0.4 vis-à-vis untreated B-DWW is illustrated in Fig. 5. The results show a total gas generation of 2064 mL, along with 34% COD reduction containing up to 49.56% methane. In untreated B-DWW the total gas volume equivalent to 2632 mL was observed, along with 6% COD reduction and up to 1.5% methane.

Biochemical methane potential has been reported by several workers. Lei et al. (2008) have reported BMP for model organic containing wastewaters, where in 45 mL cumulative gas volume was observed after 34 days incubation of p-coumaric acid solution. BMP for nonfarm biomass substrates have been reported by Gooch et al. (2010) in community scale digesters, wherein cumulative biogas generation was mapped for 30 days. Anaerobic digestion has also been reported for fungally pretreated wastewater, wherein 53% COD was removed using fungal pretreatment and 99.5% COD removal could be achieved in anaerobic digester (Melamane et al., 2007).

3.5. Kinetic model

The WAO reaction mechanism is hypothesized to involve two steps, an initial fast oxidation of organic substrate followed by a final slower oxidation of low molecular weight compounds formed, such as acetic acid and oxalic acid (Gunale and Mahajani, 2007). The same hypothesis holds true for the present study and therefore a COD based lumped parameter kinetic model can be proposed for the two step WAO treatment of B-DWW for COD destruction (Eq. (1) and (2)):

$$-r_{A1} = 0.455\exp(-1509.4/T)[COD]^1[P_{O2}]^{0.37}\ldots \quad \text{Fast step} \tag{1}$$

$$-r_{A2} = 0.499\exp(-2122.7/\mathrm{T}) \times [\mathrm{COD}]^1[P_{O2}]^{0.22}\ldots \quad \text{Slow step} \tag{2}$$

The kinetic model is valid in operating range: 150–200 °C, 6–12 bar, 150–200 rpm, 7–8 pH, initial COD 40,000 mg L^{-1}. The activation energy is observed to be 12.54 and 17.64 kJ mol^{-1}, while the kinetic rate constants are 0.455 and 0.499 min^{-1} for fast and slow step respectively.

Activation energy of 42.0 kJ mol^{-1} has been reported for WAO of 1000 mg L^{-1} of salicylic acid solution (Collado et al., 2010). Sim-

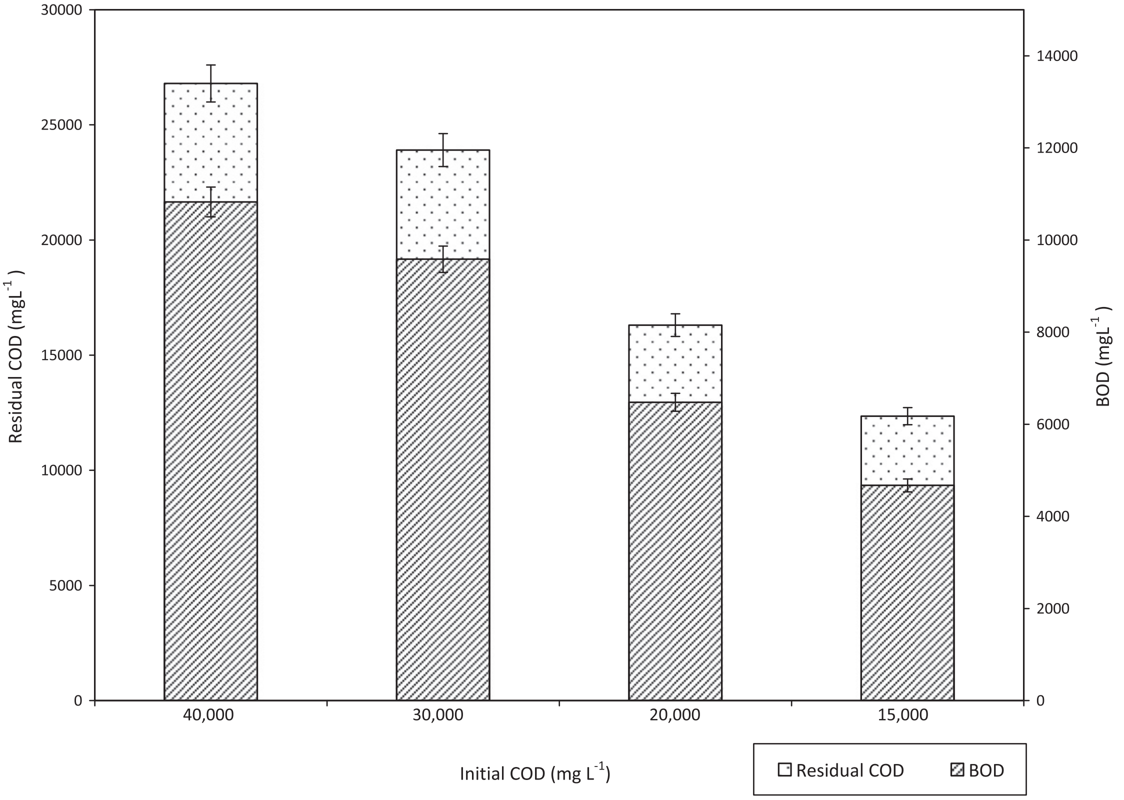

Fig. 4. Effect of Initial COD on wet air oxidation of biomethanated distillery wastewater (175 °C, 6 bar, 30 min). The figure represents the effect of initial organic loading (COD) on the efficiency of WAO vis-à-vis the pattern of BOD formation at the experimental optimum condition (175 °C, 6 bar, 30 min).

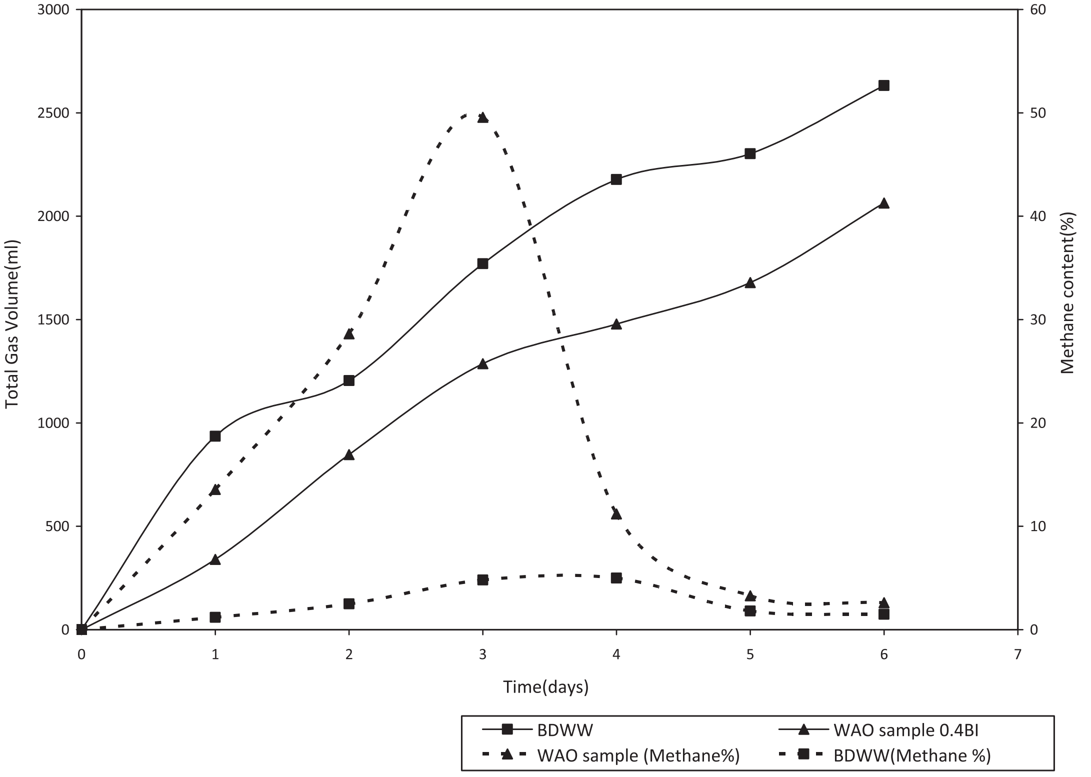

Fig. 5. Evaluation of biochemical methane potential for wet air oxidation pretreated biomethanated distillery wastewater (BI: 0.4). The figure illustrates the biogas production potential in terms of total gas volume generated vis-a vis% methane produced in untreated (control) and wet air oxidation pretreated biomethanated distillery wastewater having a BI 0.4 (175 °C, 6 bar, 30 min).

ilarly, Gunale and Mahajani (2007) have reported activation energy of 12.22 kJ mol^{-1} and 23.47 kJ mol^{-1} for WAO of aniline (9000 mg L^{-1} COD) in a two-step mechanism (fast and slow); however, they have used a hybrid approach (Fenton followed by WAO). The values of activation energies for phenols and their substitutes have been reported in the range of 12–200 kJ mol^{-1} in the temperature range of 150–180 °C (Joglekar et al., 1991).

The rate of BI enhancement can be correlated with rate of COD destruction as follows:

$$\ln r_{A(BI)} = \alpha^{*} \ln r_{A(COD)}$$

In both the steps (fast and slow) α was estimated to be 0.95 and 1.11 (data not shown). Thus the lumped kinetic approach appears to be appropriate for modeling the kinetics of COD destruction and BI enhancement.

4. Conclusions

- WAO pretreatment indicated BI enhancement in the range of 0.2–0.88 (original 0.17)
- An WAO condition of 175 °C, 6 bar and 30 min (BI of 0.4, residual COD 60%) can be the desired optimum pretreatment condition
- At optimum WAO condition a substantial amount of VFA formation indicates favorable potential for anaerobic biogas production
- The WAO reaction followed a two-step mechanism, first order for COD and 0.37 and 0.22 respectively with respect to oxygen

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