World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:2, 2016

Hybrid Advanced Oxidative Pretreatment of Complex Industrial Effluent for Biodegradability Enhancement

K. Paradkar, S. N. Mudliar, A. Sharma, A. B. Pandit, R. A. Pandey

***Abstract*—**The study explores the hybrid combination of Hydrodynamic Cavitation (HC) and Subcritical Wet Air Oxidation-based pretreatment of complex industrial effluent to enhance the biodegradability selectively (without major COD destruction) to facilitate subsequent enhanced downstream processing via anaerobic or aerobic biological treatment. Advanced oxidation based techniques can be less efficient as standalone options and a hybrid approach by combining Hydrodynamic Cavitation (HC), and Wet Air Oxidation (WAO) can lead to a synergistic effect since both the options are based on common free radical mechanism. The HC can be used for initial turbulence and generation of hotspots which can begin the free radical attack and this agitating mixture then can be subjected to less intense WAO since initial heat (to raise the activation energy) can be taken care by HC alone. Lab-scale venturi-based hydrodynamic cavitation and wet air oxidation reactor with biomethanated distillery wastewater (BMDWW) as a model effluent was examined for establishing the proof-of-concept. The results indicated that for a desirable biodegradability index (BOD: COD - BI) enhancement (up to 0.4), the Cavitation (standalone) pretreatment condition was: 5 bar and 88 min reaction time with a COD reduction of 36 % and BI enhancement of up to 0.27 (initial BI - 0.17). The optimum WAO condition (standalone) was: 150oC, 6 bar and 30 minutes with 31% COD reduction and 0.33 BI. The hybrid pretreatment (combined Cavitation + WAO) worked out to be 23.18 min HC (at 5 bar) followed by 30 min WAO at 150oC, 6 bar, at which around 50% COD was retained yielding a BI of 0.55. FTIR & NMR analysis of pretreated effluent indicated dissociation and/or reorientation of complex organic compounds in untreated effluent to simpler organic compounds post-pretreatment.

***Keywords*—**BI, hybrid, hydrodynamic cavitation, wet air oxidation.

I. 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 are 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) [1] [2]. 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 number of treatment methods and strategies for thermal pretreatment, wet air oxidation, concentration-incineration, anaerobic treatment, etc. have been suggested/tested for the treatment of distillery wastewater. However, all these schemes on their own are either incomplete, unviable or unsustainable [1]-[3]. The literature reports advanced oxidation processes (AOP's) to be highly efficient for oxidation of a vast number of complex/recalcitrant organics via the hydroxyl radical mechanism [4]. Oxidative Processes such as Cavitation (acoustic and hydrodynamic), photocatalytic oxidation, Fenton oxidation, wet air oxidation works on the common principle of hydroxyl radical attack for oxidative removal of organics [5]-[8] and offer a new area of partial/complete treatment for recalcitrant wastes.

The WAO of the organic substrates in the liquid medium involves a free radical mechanism. The steps involved in 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 [9]. Unlike other AOPs, WAO is effective for effluents with high organic loading and high flow rates can partially cover the application range of incineration and biological methods, in particular 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 [10].

Most of the reported work concerning WAO is targeted mainly for complete destruction [11]-[13] or only concentrated on the removal of color/melanoidin from distillery wastewater and not on the holistic issue of biodegradability enhancement. 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).

Cavitation is defined as formation, growth and subsequent collapse of microbubbles or cavities in extremely small time intervals as micro to milliseconds, releasing large magnitudes of energy over a small region but at multiple locations in the reactor. Although ultrasonic cavitation is a costly option owing to its ineffective spatial distribution of cavities on a large scale and less effective transducer outputs at higher

K. Paradkar, A. Sharma and R. A. Pandey are with Environmental Biotechnology Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur-40020, India (phone: 0712-2240097; fax: 0712-2249900; e-mail: paradkarkiran@hotmail.com. a1_sharma@neeri.res.in, ra_pandey@neeri.res.in).

S. N. Mudliar is with 2 Plant Cell Biotechnology Division, CSIR-CFTRI, Mysore-570020, India (e-mail: snmudliar@gmail.com).

A. B. Pandit is with 3Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai- 40019, India (phone: 022-33612101; e-mail: ab.pandit@ictmumbai.edu. in).

operating frequencies [14], an alternative cavitation phenomena generated by manipulating the liquid flow pattern termed as hydrodynamic cavitation, is reported to be more energy efficient over acoustic cavitation for some application and even can find large scale applications [14],[15].

In hydrodynamic cavitation, cavities are formed by passing the liquid through the constriction (venturi/orifice) provided in lines such as venturi and orifice plate. The collapse of bubbles generates localized "hot spots" with a transient temperature of the order of 10,000 K, and pressures of about 1000 atm. Under such extreme conditions, water molecules are dissociated into OH• and H• radicals. These OH• radicals then diffuse into the bulk liquid medium where they react with organic pollutants and oxidize/mineralize them. The two main mechanisms for the degradation of pollutants using hydrodynamic cavitation are the thermal decomposition/pyrolysis of the volatile pollutant molecules entrapped inside the cavity during the collapse of the cavity and secondly, the reaction of OH• radicals with the pollutant occurring in the cavity–water interface. In the case of nonvolatile pollutant, the main mechanism for the degradation of pollutants will be the attack of hydroxyl radicals on the pollutant molecules at the cavity–water interface and in the bulk fluid medium. The mechanical effects are also significant. In some cases, the intensity of shockwaves generated by the collapsing cavity can break molecular bonds, especially the complex large molecular weight compounds. The broken down intermediates are more amenable to OH• attack as well as biological oxidation, which can further enhance the rate of oxidation/mineralization of the pollutants in subsequent biological treatment (increase in BI).

The literature reports on the application of Hydrodynamic Cavitation are very scanty and limited only to synthetic wastewater containing specific pollutants such as textile dyes, pharmaceutical drugs, and pesticides [14]-[16]. Use of hydrodynamic cavitation reactor in real industrial wastewater treatment applications has been rarely investigated. Chakinala et al. [14] have tried Hydrodynamic Cavitation (HC) in conjunction with the advanced Fenton process for the treatment of real industrial wastewater and reported that Hydrodynamic Cavitation is very effective as a pre-treatment to biological oxidation for the effluent samples considered in their work.

The Cavitation process can be used in an energy efficient manner as a pretreatment in combination with any other advanced oxidation system or conventional biological treatment systems.

The SONIDO is a recent hybrid method of applying ultrasonic radiation followed by wet air oxidation [15], which can be effectively explored for the degradation of recalcitrant organics with increased efficiency and at comparatively less severe conditions of temperatures and pressures as compared to wet air oxidation (WAO) alone. When used alone these techniques can become less efficient when considered for large scale operations and hence a hybrid approach by combining both Cavitation & Wet Air Oxidation can lead to a synergistic effect since both the mechanisms are based on common free radical mechanism, it would be of much benefit to combining these for additional benefits. The HC can be used for initial turbulence and generation of hotspots which can just begin the free radical attack and this agitating mixture then can be subjected to less intense WAO since initial heat (to raise the activation energy) can be taken care by HC alone. The combined effect will be spectacular as compared to individual pretreatments. Keeping this view under consideration, some cavitationally pretreated samples were subjected to WAO to evaluate the synergy of combined hybrid "Soniwo- effect" or "Cavox-effect". The results obtained are presented and discussed in this section

The Biomethanated distillery wastewater was selected as a model complex effluent and hybrid cavitation followed by wet air oxidation was evaluated as a pretreatment option for enhancing biodegradability index. The results obtained individually and for the hybrid option are presented and discussed in this paper.

II. Materials and Methods

A. Hydrodynamic Cavitation Reactor and Operation

The experimental setup for hydrodynamic cavitation experiment is shown in Fig. 1.

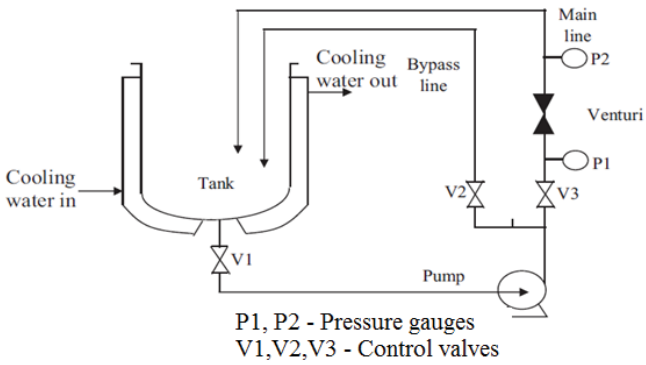

Fig. 1 Schematic representation of hydrodynamic cavitation reactor set-up

The setup includes a holding tank (15 L), a positive displacement pump (power rating 1.1 kW), control valves (V1–V3), flanges to accommodate the cavitating device, the main line, and a bypass line. The suction side of the pump is connected to the bottom of the tank and discharge from the pump branches into two lines: the main line and a bypass line. The main line consists of a flange which houses the cavitating device which can be an orifice, venturi or any other mechanical constriction. The bypass line is provided to control the liquid flow through the main line. Both the mainline and bypass line terminate well inside the tank below the Liquid level to avoid any induction of air into the liquid. The details of the cavitating device (venturi) are presented in Fig. 2.

The B-DWW was subjected to HC pretreatment for which, 6 L of wastewater was treated in cavitation reactor (Section II), and the cavitation was achieved using a venturi (shown in Fig. 2). The experiments were conducted at two different inlet pressures (low as well as high) and at different dilutions of the biomethanated distillery wastewater in the time range of 50–150 min. At the end of each defined time, interval the samples were withdrawn from the reactor through a sampling port, centrifuged and analyzed for pH, COD, BOD, TOC and color as per the standard procedures, specified earlier.

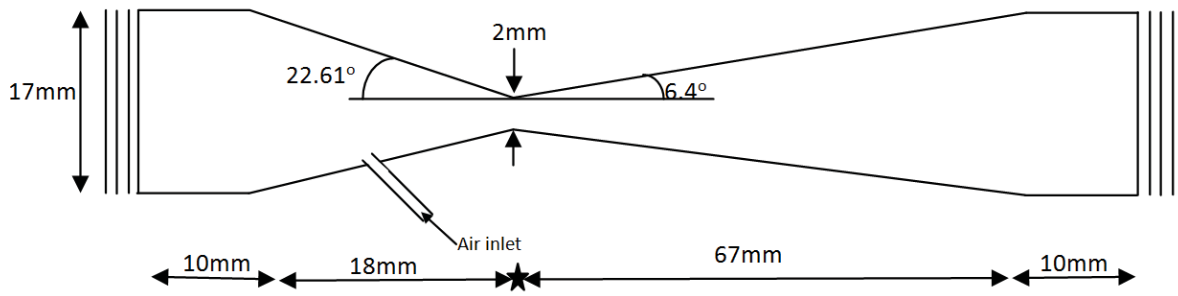

Fig. 2 Schematic of venturi

B. Wet Air Oxidation Reactor and Operation

The B-DWW was pre-treated 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. 3. The impeller speed was maintained at 200 rpm. The reactor was also provided with a rupture disc as well as a non-return valve at the gas inlet. Five hundred millilitre of the wastewater was used for pretreatment. The reactor was properly sealed, ensuring the 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 schematic of the reactor set up is presented in Fig. 3.

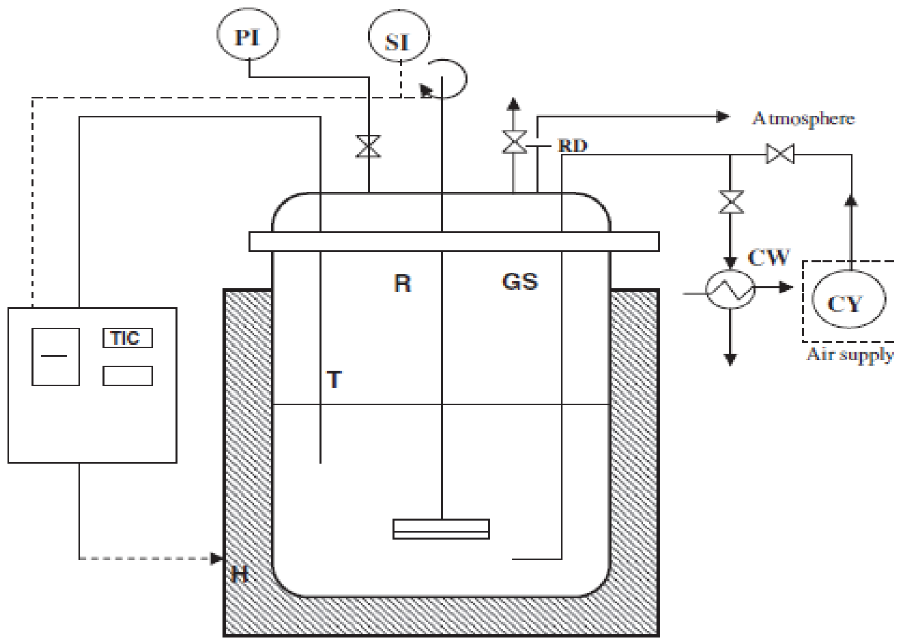

Fig. 3 Schematic diagram of experimental setup for wet air oxidation reactor

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 (specially to cover the less severe range of WAO). After every run, the reactor was put in a cooling mode. The pre-treated samples were analyzed for pH, COD, BOD, VFA, and BOD5: COD ratio. The total volume (0.5 L) did not vary since the system was tightly sealed.

C. Analysis

The COD, BOD, TOC and VFA analysis was carried out as per the standard methods [17]. A Control dynamics make pH meter was used for monitoring pH of the samples during the investigation. To avoid the complexity of standards, each run was conducted three times for both WAO, and HC and samples were analyzed. The error in analytical measurements was always observed to be less than 5%. The estimation of color in cavitationally pretreated samples was carried out using Shimadzu UV–visible spectrophotometer, 170 Model UV-1800. All the chemicals used in the study were analytical reagent grade.

FTIR analysis of WAO and cavitationally pretreated sample were performed using Fourier Transform Infrared Spectrometer (FTIR, Model: Vertex 70-BRUKER).

III. Results and Discussion

A. Effect of Inlet Pressure on Mineralization of B-DWW

The effect of the venturi inlet pressure on COD/TOC reduction was evaluated at a lower (5 bar) and higher (13 bar) inlet pressure. The B-DWW was used as such at an inlet COD of 34,000 mgL^{-1} (avg.). The samples were collected at different time intervals and analyzed for COD and TOC. The results are presented in Table I which are the average values of 3 sets of observations.

The results indicate that there is no significant increase in the percentage reduction of COD and TOC with an increase in the inlet pressure (34% reduction in COD and 33% reduction in TOC were obtained at 13 bar pressure as compared to 32% and 31% respectively at 5 bar inlet pressure). The results also yielded the fact that maximum mineralization of the distillery wastewater at any selected pretreatment operating conditions occurs in the first 50 min of circulation (85 passes) through the HC and after which there is no significant reduction of COD and TOC, thus indicating optimum treatment time to be 50 min. The results obtained at a higher inlet pressure (13 bar) did not lead to any further mineralization of the distillery wastewater as that observed at 5 bar operating pressure. Therefore, further experiments were conducted at 5 bar operating pressure.

TABLE I
Physico-Chemical Characteristics of Biomethanated Distillery Wastewater

Parameters	Value
pH	7.61
Color	Brown
COD (mg L^{-1})	40,000
BOD (mg L^{-1})	6744
TOC (mg L^{-1})	18,700
Total Solids (mg L^{-1})	31000
Total Suspended Solids (mg L^{-1})	1600
Biomass (%)	1
BOD:COD ratio	0.168

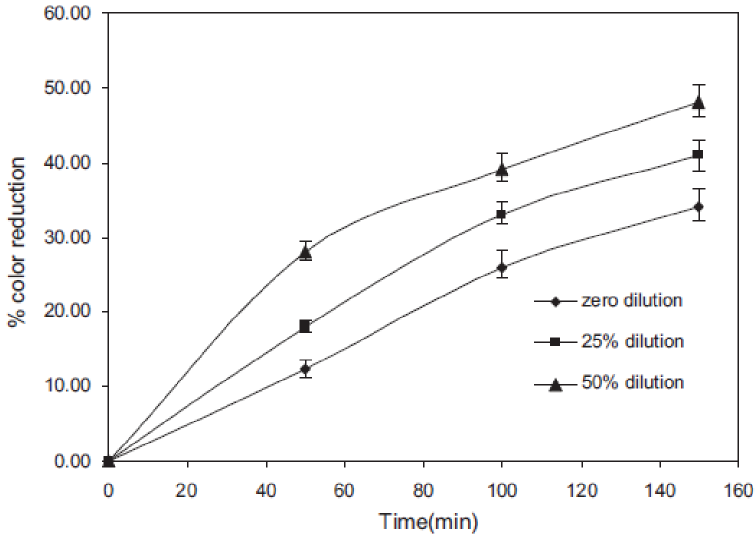

Fig. 4 Effect of inlet pressure (5 bar) on color reduction on biomethanated distillery wastewater

B. Effect of Cavitation on Color Reduction of B-DWW

The dark brown color of the distillery wastewater can be attributed to the presence of bioplymers such as melanoidins, which are Maillard reaction products along with the caramel colorants, which are generated during the processing (concentration, evaporation) of sugarcane juice at higher temperatures in sugar industries as also during the distillation of sugarcane molasses for the recovery of absolute alcohol. The hydrodynamic cavitation pretreatment in the present study has not only resulted in COD/TOC reduction but also aided in reducing the concentration of total color of B-DWW. The hydrodynamic cavitation studies at an optimal inlet pressure (5 bar) indicate that a maximum 36% color could be removed from undiluted B-DWW at 5 bar operating pressure in 150 min of treatment. The color reduction profile is presented in Fig. 4. The results presented in Fig. 4 indicate that HC pretreatment not only results in COD/TOC removal but also reduces the color content (indirectly toxicity) of the wastewater system. For undiluted wastewater, a maximum of 34% color reduction is observed while for 25% and 50% concentration of diluted wastewater, a maximum color reduction of 41% and 48% are observed respectively.

C. Effect of Cavitation on Biodegradability of B-DWW

The biodegradability index (BI) is a measure of the extent to which a waste is amenable to biodegradation. BI can be expressed as a ratio of BOD5:COD. For good biodegradability of any wastewater, a minimum BOD: COD ratio (BI) of 0.3–0.4 is considered to be ideal, with a ratio of ≥0.3 desirable for coupling with aerobic treatment and ≥0.4 for anaerobic treatment [18]. In the present study, the pretreatment with hydrodynamic cavitation has lead to an enhancement of BI under all the experimental conditions. The values of BOD and BI are shown in Table II.

TABLE II
EFFECT OF EXTENT OF DILUTION ON MINERALIZATION OF BIOMETHANATED DISTILLERY WASTEWATER

% Dilution	Time (min)	COD (mg/L)	TOC (mg/L)	% COD reduction	%TOC reduction
No dilution[a]	0	34391	9523	0.00	0.00
	50	23723	6820	31.02	28.38
	100	23442	6790	31.84	28.70
	150	23302	6530	32.24	31.43
25% dilution[b]	0	28208	7940	0.00	0.00
	50	19539	5710	30.73	28.09
	100	18300	5500	35.12	30.73
	150	18163	5430	35.61	31.61
50% dilution[c]	0	21280	6044	0.00	0.00
	50	13193	3725	38.00	38.37
	100	11916	3610	44.00	40.27
	150	11207	3445	47.34	43.00

a, b, c: indicate zero, 25% and 50% dilution of wastewater with tap water respectively.

It was observed that there is two-fold increase in the ratio after 150 min treatment, however, individually the increase in the ratio with time is almost constant with a value of 0.22 at 50 min, 0.23 at 100 min and 0.24 at 150 min indicating that the effective reorientation of complex molecules to render them biodegradable is occurring during the first 50 min of the treatment.

D. Effect of WAO Conditions on Complex Wastewater Pretreatment

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 (150–200ºC) and at various time intervals (15–120 min) and for initial COD of 40,000 mg L^{-1} (Fig. 2). 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 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 (150–200ºC, 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% (150–200ºC, 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% (150–200ºC, 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 the horizontal dotted line in the Fig. 5). 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 (175ºC, 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 mechanism for salicylic acid solutions has been studied resulting in 98% removal of salicylic acid (1000 mg L^{-1}) at 41 bar in 60 min, whereas when the pressure was reduced to 25 bar, the same removal could be achieved in 140 min [19]. Gunale and Mahajani, [9] 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 [19], [20]. 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 involve a complex effluent with the main aim of enhancing its biodegradability.

2. Effect of Temperature

The effect of temperature (150–200ºC) 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. 5. As is generally observed in WAO systems, the 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. 5). For all practical purposes, a BI of 0.4 is good enough to make a waste amenable to biodegradation [18], which in this study is observed at an experimental condition of 175°C, 6 bar and 30 min of reaction time.

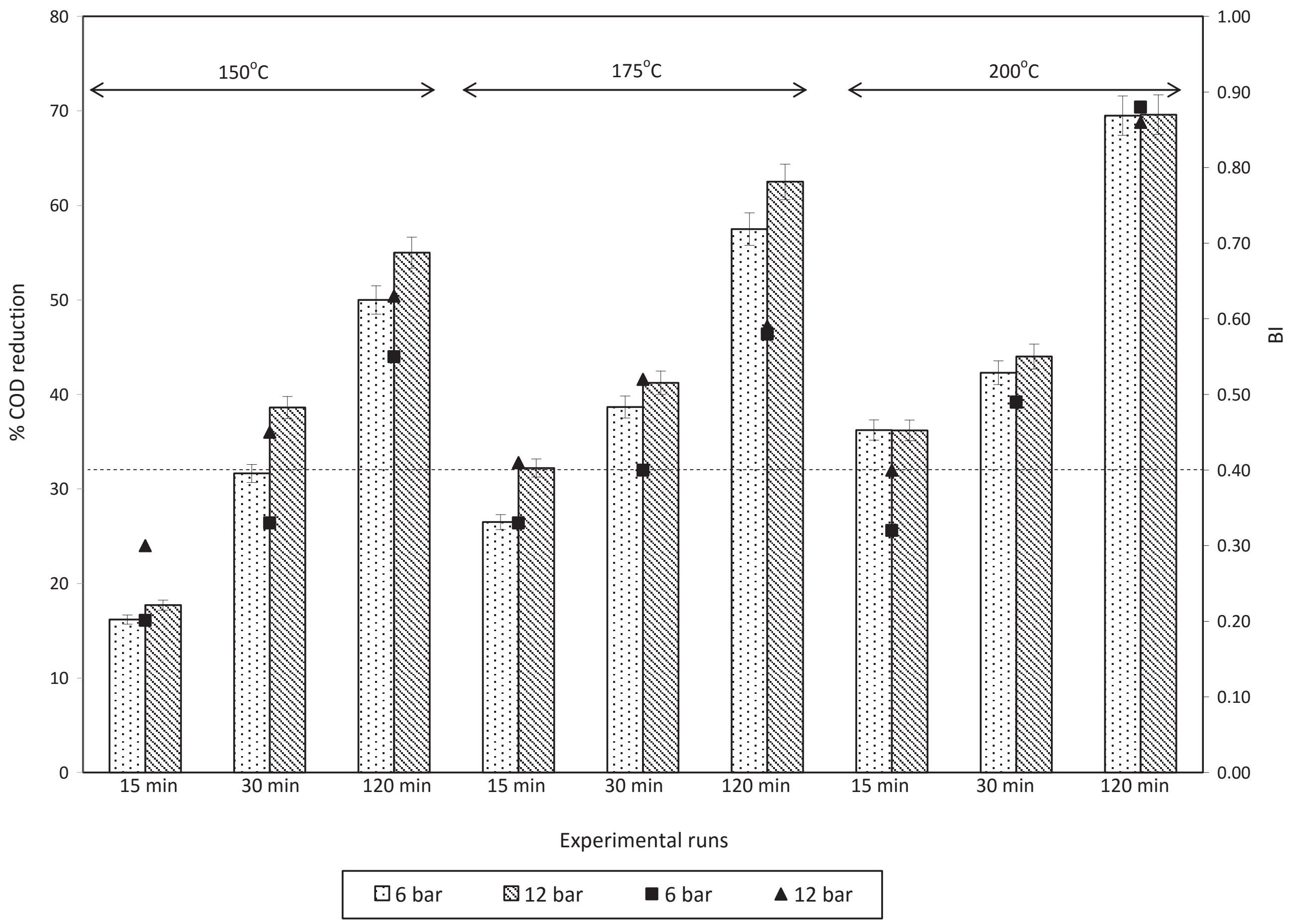

Fig. 5 Effect of pressure and temperature of wet oxidation process on % COD reduction and BI profile in pretreated biomethanated wastewater

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 [9]. 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 [19], [21].

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), 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 [19] available regarding single/pure compound indicates inhibition effect of the initial higher substrate concentration on the rate of WAO.

IV. Hybrid Pretreatment

The Biomethanated distillery wastewater was subjected to HC at a lower (5 bar) and a higher (13.3 bar) pressure. The wastewater was evaluated as such and was also diluted 25 times and 50 times (v/v) before pretreatment. The results obtained are presented in Fig. 6.

The results in Fig. 6 indicate that Higher initial pressure of Cavitation (13.3 bar) does not seem to favor COD removal as compared to lower pressure (5 bar). Maximum COD reduction of 54% is observed at 5 bar pressure, 50 D and 150 min. A comparison between 5 bar and 13.3 bar, 50 D, 150 min reaction indicates 50% and 53% COD reduction respectively. Thus, lower pressure can be preferred over higher pressure when COD removal is of concern. Higher dilution and higher pressure (13.3 bar, 50D) however aids in enhancing the BI (BOD) while marginally enhancing the COD reduction. At 5 bar pressure, significant COD reduction occurs within the first 50 min of reaction. Therefore, it seems appropriate to conduct the experiments in the time range of 0-50 min at 5 bar without dilution. Thus, it can be summarized that Hydrodynamic Cavitation (HC) at the low-pressure range without dilution leads to enhancement in BI up to 0.24 (from an initial of 0.17) while high pressure and dilution indicate an enhancement in BI up to 0.47. Lower pressure HC seems to be potential for integration with wet air oxidation (WAO) since a BI greater than 0.2 is desirable for coupling with aerobic treatment, while BI greater than 0.4 is desirable for coupling with anaerobic treatment [18]. Further, HC pretreated BDWW at 5 bar, 23.18 minutes and 5 bar, 88.09 minutes was subjected to WAO at 150°C, 6 bar and 30 min (the starting conditions for a WAO reaction). The results obtained are presented in Table.III. Indicate that this is the ideal condition of Cavitation for BDWW when COD removal is of concern when the objective is limited only to COD reduction, since max COD (20%) get removed within this period (23.18 min). The wastewater also, diluted 25 and 50 times, and pretreated Cavitationally for 150 minutes was also subjected to WAO in the same condition as above. The results (Table III) indicate that pretreatment at this condition yields maximum BOD (a highest BI) when BOD COD ratio is of concern and hence as per the requirement the Hybrid approach can be synergistically applied to various complex wastewaters.

TABLE III
SUMMARY OF HYBRID PRETREATMENT OF BIOMETHANATED DISTILLERY WASTEWATER

Sample Description	Initial	After Cavitation			After WAO		
		COD (mgL^{-1})	BOD (mgL^{1})	BI	COD (mgL^{1})	BOD (mgL^{1})	BI
5 bar, 23.2min	PH: 8.3	28011	6201	0.22	15160	5827	0.38
5 bar 88.09 min	COD: 37523	25562	6802	0.27	12295	6719	0.55
13.3 Bar, 25 D, 150 mins	BOD: 4875	18363	5896	0.31	10453	7403	0.71
13.3 Bar, 50 D, 150 mins	BI: 0.13	12960	6118	0.47	8583	7787	0.90

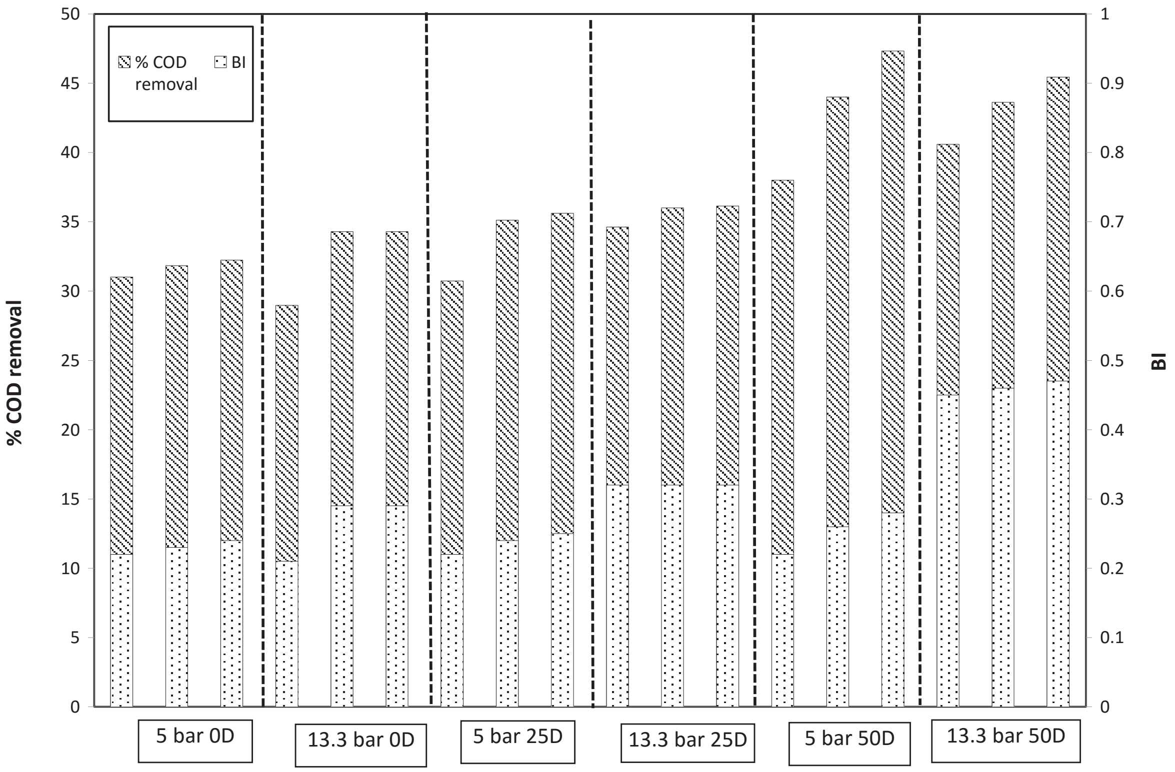

Fig. 6 Profile of COD & BI of BDWW at various venturi hydrodynamic cavitation conditions

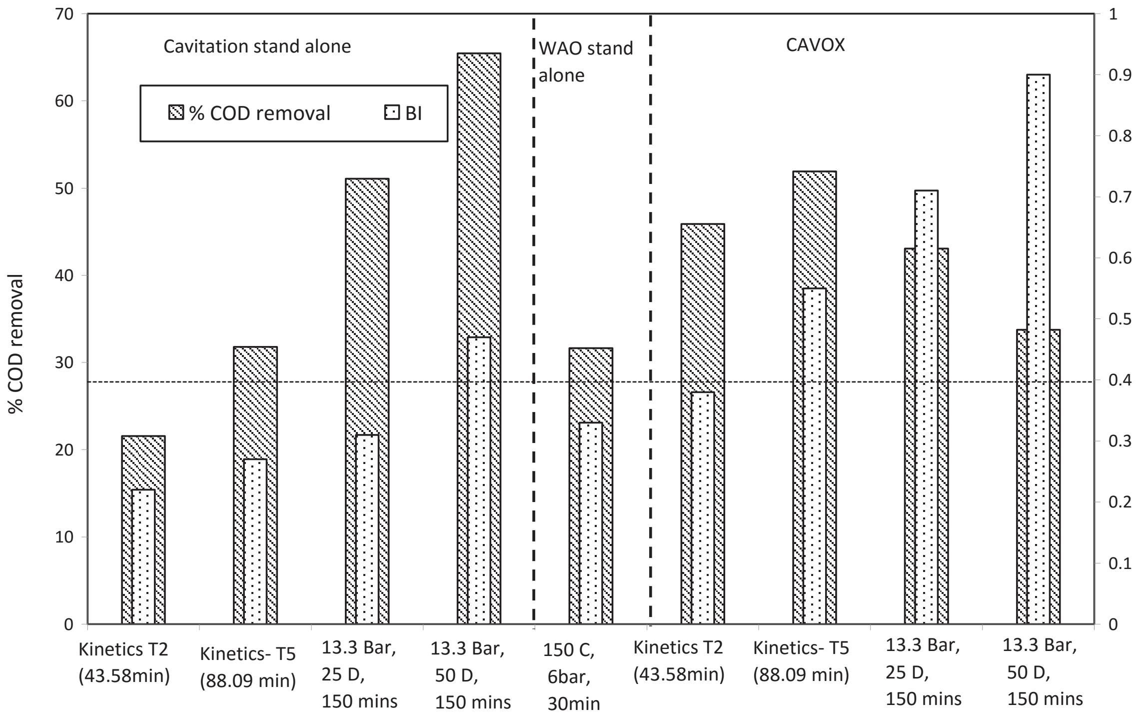

Fig. 7 Comparison of cavitation and WAO as stand-alone and hybrid pretreatment for biodegradability enhancement

V. Comparative Evaluation between Cavitation, WAO, and SONIWO

The results of individual Cavitation, Wet Air Oxidation, and Hybrid pretreatment are summarized in Fig. 7.

The results indicate that for a minimum acceptable BI (0.4) for good biodegradability of a wastewater Cavitation as a standalone pretreatment indicates 13.3 bar, 25D and 150 min to be an ideal condition for maximum COD reduction (65%) and for getting an ideal BI (0.47). The optimum WAO condition (standalone) indicated 31% COD reduction and 0.33 BI at 150^{o}C, 6 bar and 30 minutes. The hybrid pretreatment (combined Sonication + WAO) indicate 23.18 min to be ideal condition, since it retains around 50% residual COD and also yields a BI of 0.55, however if maximum BI (0.9) is concerned then 13.3 bar, 50D and 150 min (HC) followed by WAO (150^{o}C, 6 bar and 30 minutes) appears to be ideal with 33% residual COD and 0.9 BI.

Acknowledgment

KVP is thankful to Department of Science and Technology (DST), Government of India for the Woman Scientist Fellowship to conduct the research work. All the authors are thankful to Director CSIR-NEERI for his permission to present this work.

References

[1] A. Kumar, Handbook of waste management in sugar mills and distilleries. Somaiya Publication. 2003.
[2] P.C. Sangve, A.B. Pandit, Ultrasound pretreatment for enhanced biodegradability of the distillery wastewater, Ultrason. Sonochem. 11 (2004),pp. 197–203.
[3] D. Pant, A. Adholeya, Biological approaches for treatment of distillery wastewater: a review, Biores. Technol. 98 (2006),pp. 2321-2334.
[4] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions. Adv in Envtal Res., 8 (2004), pp.501.
[5] K. V. Padoley, P.D. Tembhekar, T. Sarathchandra, A.B. Pandit, R.A. Pandey, S.N. Mudliar, Wet Air Oxidation as a pretreatment option for selective Biodegradability Enhancement and Biogas generation potential from Complex Wastewater. Bioresource Technol, 120 (2012a), pp. 157-164.
[6] K. V. Padoley, S.N. Mudliar, S.K.Banerjee, S.C.Deshmukh and R.A. Pandey, Fenton oxidation: A pretreatment option for improved biological treatment of pyridine & 3-cyanopyridine-plant wastewater Chem Engg J. 166, 2011.
[7] K. V. Padoley, Virendra Kumar Saharan, S.N.Mudliar, R.A.Pandey, Aniruddha B.Pandit, Cavitationally Induced Biodegradability Enhancement of a Distillery Wastewater, J.Haz. Mat. 219-220, (2012b), pp. 69-74.
[8] H.-L. Wang, W.-Z. Liang, Q. Zhang, W.-F. Jiang, Solar-light-assisted Fenton oxidation of 2,4-dinitrophenol(DNP)using Al 2O3-supported Fe(III)-5- sulfosalicylic acid (ssal) complex as catalyst, Chem. Eng. J. 164 (2010),pp. 115–120.
[9] T.L. Gunale, V.V. Mahajani, Studies in mineralization of aqueous aniline using Fenton and wet oxidaation (FENTWO) as a hybrid process. J Chem Tech Biotechnol. 82, (2007), pp.108-115.
[10] K.-H. Kim, S.-K. Ihm, Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review, J. Hazard. Mater. 186 (2010),pp. 16-34.
[11] K. Belkacemi, F. Larachi, S. Hamoudi, A. Sayari, Catalytic wet oxidation of high- strength alcohol-distillery liquors, Appl. Catal. A: Gen. 199 (2000),pp. 199–209.
[12] N.S. Daga, C.V.S. Prasad, J.B. Joshi, Kinetics of hydrolysis and wet air oxidation of alcohol distillery waste. Ind Chem Eng. 28, (1986).
[13] H. Debellefontaine, M. Chakchouk, J.N. Foussard, J. N. D. Tissot, P. Striolo, Treatment of organic aqueous wastes: wet air oxidation and wet peroxide oxidation(R). Environ. Pollut. 92, (1996), pp.155–164.
[14] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process, Ultrason. Sonochem. 15 (2008),pp. 49-54.
[15] P.R. Gogate, A.B. Pandit, Hydodynamic cavitation: a state of the art review, Rev. Chem. Engg. 17 (2001) 1-85.
[16] M. Sivakumar, A.B. Pandit, Wastewater treatment: a novel energy efficient hydrodynamic cavitational technique, Ultrason. Sonochem. 9 (2002),pp. 123-131.

[17] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington DC, 1998.
[18] Metcalf, I. Eddy, Wastewater Engineering Treatment Disposal Reuse, 2nd ed.,Tata McGraw Hill, New Delhi, 1979
[19] S., Collado, L., Garrido, A., Laca, M., Diaz, Wet oxidation of salicylic acid solutions, Environ. Sci. Technol. 44, (2010), pp.8629-8635.
[20] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Wet air oxidation. Ind. Eng. Chem. Res. 34 (1995), pp.2–48.
[21] S. Mohana, C. Desai, D. Madamwar, Biodegrading and decolorization of anaerobically treated distillery spent wash by a novel bacterial consortium, Biores. Technol. 98 (2007), pp. 333-339.