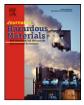
Contents lists available at SciVerse ScienceDirect



Journal of Hazardous Materials



journal homepage: www.elsevier.com/locate/jhazmat

Cavitationally induced biodegradability enhancement of a distillery wastewater

K.V. Padoley^a, Virendra Kumar Saharan^b, S.N. Mudliar^a, R.A. Pandey^a, Aniruddha B. Pandit^{b,*}

^a National Environmental Engineering Research Institute. Nagpur 440020. India

^b Chemical Engineering Department, Institute of Chemical Technology, Mumbai 400019, India

ARTICLE INFO

Article history: Received 14 October 2011 Received in revised form 21 February 2012 Accepted 17 March 2012 Available online 27 March 2012

Keywords: Hydrodynamic cavitation Biomethanated distillery wastewater Biodegradability index (BOD₅:COD ratio) Color

ABSTRACT

Hydrodynamic cavitation (HC) was evaluated as a pretreatment option for the complex/recalcitrant biomethanated distillery wastewater (B-DWW). The effect of various process parameters such as inlet pressure, dilution and reaction time on reduction of COD/TOC and enhancement of biodegradability index (BI:BOD₅:COD ratio) of the B-DWW was studied with an aim to maximize the biodegradability index and reducing the toxicity of the distillery wastewater. It was observed that higher operating pressure (13 bar) yielded the maximum BI whereas the lower pressure (5 bar) is suitable for the reduction in the toxicity of B-DWW. The toxicity of the distillery wastewater was analyzed by measuring the COD, TOC and color of the wastewater sample. The HC pretreatment under optimized conditions leads to a BI of 0.32, COD and TOC reduction of 32.24% and 31.43%, respectively along with a color reduction by 48%. These results indicate the potential of HC as a pretreatment option for enhancing the biodegradability index of the recalcitrant wastewater such as B-DWW along with reduced toxicity of wastewater as observed from COD, TOC and color reduction profile under optimized conditions.

© 2012 Published by Elsevier B.V.

1. Introduction

Distilleries are one of the highly polluting industries worldwide [1] and are rated as one of the 17 most polluting industries listed by the Central Pollution Control Board (CPCB), Govt. of India [2]. The Indian distilleries use sugarcane molasses as a preferred raw material for fermentation of sugar because of its easy and large scale availability. There are about 579 sugar mills and 295 distilleries in India [3]. Currently, about 40.72 million m³ of spent wash (wastewater) is generated annually from all these distilleries alone in India [4-8]. Significant volume of water is consumed for molasses preparation (dilution), yeast propagation (fermentation), etc. in the range of 14–22 LL⁻¹ of alcohol production. After the conventional anaerobic digestion the biomethanated wastewater retains around 40,000 mg/L of COD and significant color and becomes recalcitrant $(BI:BOD_5/COD \approx 0.14)$ to further treatment by conventional biological methods. This problem has emphasized the need for further research on effective treatment/pretreatment methods for safe disposal of anaerobically digested distillery wastewater.

Various researchers have reported several biological, physicochemical and phytoremediation approaches for the treatment of distillery wastewater [9–20]. However, all these studies have only concentrated on the removal of color/melanoidin from distillery wastewater and not on the holistic issue of biodegradability enhancement.

A recent technology such as cavitation which has found several applications [21] can be effectively utilized as a pretreatment option for refractory/recalcitrant wastes. 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 [22]. 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 operating frequencies [23], 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 [23,24].

In hydrodynamic cavitation, cavities are formed by passing the liquid through the constriction/geometry provided in line such as venturi and orifice plate. When the pressure at the throat or vena-contracta of the constriction falls below the vapor pressure of the liquid, the liquid flashes, generating number of vaporous cavities that subsequently collapse when the pressure recovers downstream of the mechanical constriction. The effects of cavity collapse are in terms of the creation of hot spots, releasing

Abbreviations: B-DWW, biomethanated distillery wastewater; HC, hydrodynamic cavitation; VFA, volatile fatty acid; COD, chemical oxygen demand; BOD, biochemical oxygen demand; BI, biodegradability index (BOD₅:COD ratio); BMP, biochemical methane potential; TOC, total organic carbon; AOP's, advanced oxidation processes; ND, non detectable.

^{*} Corresponding author. Tel.: +91 22 3361 2012; fax: +91 22 3361 1020. E-mail address: ab.pandit@ictmumbai.edu.in (A.B. Pandit).

^{0304-3894/\$ –} see front matter © 2012 Published by Elsevier B.V. doi:10.1016/j.jhazmat.2012.03.054

highly reactive free radicals, surface cleaning and/or erosion, and enhancement in local transport (heat, mass and momentum) rates. The collapse of bubbles, generates localized "hot spots" with transient temperature of the order of 10,000 K, and pressures of about 1000 atm [25]. 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 at the cavity-water interface. In the case of non volatile 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 only specific pollutants such as textile dyes, pharmaceutical drugs and pesticides [23-28]. Use of hydrodynamic cavitation reactor in real industrial wastewater treatment applications has been rarely investigated. Chakinala et al. [23] 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 best and most practical utilization of cavitation in an energy efficient manner can be made by using it as a pretreatment in combination with any other advanced oxidation system or conventional biological treatment systems. In the present investigation, hydrodynamic cavitation (HC) was evaluated as a pretreatment for the complex wastewater such as biomethanated distillery wastewater (B-DWW). The biomethanated distillery wastewater was subjected to HC reactor and the effect of various process parameters was assessed and optimized for maximizing COD/TOC reduction and enhancing biodegradability index (BOD₅:COD ratio) of the wastewater. The associated color reduction has also been studied.

2. Experimental methods

2.1. Experimental setup

The experimental setup for hydrodynamic cavitation experiment is shown in Fig. 1. 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, a 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 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. Fig. 2 shows the details of the cavitating device (venturi) used in this work.

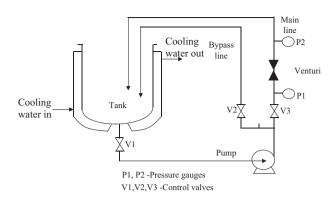


Fig. 1. Schematic representation of hydrodynamic cavitation reactor set-up.

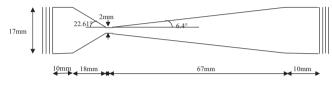


Fig. 2. Schematic of venturi.

2.2. Experimental protocol

2.2.1. Biomethanated distillery wastewater (B-DWW)

Distillery wastewater treated in a conventional anaerobic digester from a distillery near Nagpur, India (source not given due to confidentiality issues) was collected as a grab sample and transported to the laboratory in 25 L carboys. The wastewater was characterized for its physico-chemical composition and the results are presented in Table 1.

2.2.2. Preparation of the wastewater

The biomethanated distillery wastewater (B-DWW) stored at 4-5 °C was allowed to attain room temperature before experiments. The wastewater was then used as such for pretreatment using hydrodynamic cavitation.

2.2.3. Chemicals

All the chemicals used in the study were analytical or reagent grade. The chemicals used in the COD analysis viz. ferrous ammonium sulfate heptahydrate, potassium dichromate, mercuric sulfate, silver sulfate, concentrated sulfuric acid and ferroin indicator were analytical grade reagents (Ranbaxy Fine Chemicals India Ltd.). The BOD analysis was carried out using sodium thiosulfate, alkali iodide azide, manganous sulfate, starch, potassium dihydrogen phosphate, dipotassium hydrogen orthophosphate, disodium hydrogen phosphate, ammonium chloride, calcium chloride, magnesium sulfate and ferric chloride and were all analytical grade reagents (S.D. Fine Chemicals, Mumbai, India).

Table 1	l
---------	---

Characteristics of complex wastewater (biomethanated distillery wastewater).

Parameters	Value
рН	7.61
Color	Brown
COD (mg/L)	35,000
BOD (mg/L)	5000
TOC (mg/L)	10,000
Total solids (mg/L)	31,000
Total suspended solids (mg/L)	1600
Biomass (%)	1
BOD ₅ :COD ratio	0.168

The values given in the table are average of 3 sets of observations with S.D. < 5.

Table 2

Effect of inlet pressure on mineralization of biomethanated distillery wastewater.

Pressure	Time (min)	No. of passes	COD (mg/L)	TOC (mg/L)	%COD reduction	%TOC reduction
5 bar (<i>V</i> ₀ = 550LPH) ^a	0	0	34391.00	9523.00	0.00	0.00
	50	85	23723.00	6820.00	31.02	28.38
	100	180	23442.00	6790.00	31.84	28.70
	150	290	23302.00	6530.00	32.24	31.43
13 bar (V ₀ = 850LPH) ^b	0	0	33973.00	9540.00	0.00	0.00
	50	131	24128.00	7090.00	28.98	25.68
	100	279	22325.00	6490.00	34.29	31.97
	150	447	22325.00	6425.00	34.29	32.65

Where V_0 is the volumetric flow rate at corresponding pressure.

^a Absolute COD and TOC reduction is 11,089 mg/L and 2993 mg/L, respectively in 150 min of treatment.

^b Absolute COD and TOC reduction is 11,648 mg/L and 3115 mg/L, respectively in 150 min of treatment.

The chemicals used for TOC analysis included phosphoric acid, anhydrous potassium biphthalate, anhydrous sodium carbonate, anhydrous sodium bicarbonate were all analytical reagent grade chemicals (Qualigens Fine Chemicals (Division of Glaxo) India Ltd.). The distilled water used in the study for various purposes confirmed to pH: 5.5, conductivity: $140 \,\mu$ s/cm, Cl: 0, SO₄: 0. Tap water was used for the dilution of the B-DWW during cavitation pretreatment studies, having pH: 7.3, COD: ND, BOD: ND.

2.2.4. Analytical equipments and measurement protocols

The pretreated samples were centrifuged using a IEC centrifuge (Model PR-2) at $5000 \times g$ for 10 min at 20 °C and the supernatant was subjected to the physico-chemical analysis. The COD, BOD and TOC analysis was carried out as per the standard methods [29]. The degree of total oxidation to carbon dioxide (complete mineralization) that has occurred during cavitation was assessed by measuring total organic carbon using "Total Carbon Analyzer" (Model TOC 1200); supplied by Thermo Electron Corporation, USA and the methodology followed was as per standard methods [29]. Control dynamics, make pH meter was used for monitoring the pH of the samples during investigation. The estimation of color was carried out using Shimadzu UV-visible spectrophotometer, Model UV-1800, as per the method described by Naik et al. [30].

2.2.5. Biodegradability – post pretreatment

Biodegradability index (BI) is expressed as the ratio of BOD₅:COD and is a parameter for evaluating biodegradability (amenability to biological treatment) of a wastewater. This parameter is generally referred as biodegradability index (BI) with reference to suitability of wastewater for biological treatment [31]. The COD and BOD of the wastewater and hence the BI were

Table 3

Effect of extent of dilution on mineralization of biomethanated distillery wastewater.

evaluated after the hydrodynamic cavitation pretreatment and compared with that of the untreated B-DWW.

2.3. Hydrodynamic cavitation pretreatment of B-DWW

The B-DWW was subjected to HC pretreatment for which, 6 L of wastewater was treated in cavitation reactor (Section 2), 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.

2.4. Experimental protocol for conducting biochemical methane potential (BMP)

A 2.5 L amber colored anaerobic (nitrogen purged) bottle reactor was used for conducting lab scale experiment for the evaluation of BMP. The bottle was filled with 2 L of pretreated (13 bar, 25% dilution, 50 min of pretreatment) B-DWW along with 10% acclimatized biomass from a distillery anaerobic digester treating raw spent wash. The temperature during cavitation was maintained at $35 \pm 2 \circ$ C with the aid of a water circulating in the jacket. The total gas evolution (i.e. CH₄ and CO₂) was monitored volumetrically using water displacement method [31]. The control sample consisted of B-DWW without hydrodynamic cavitation pretreatment and with 10% acclimatized biomass (the COD of this wastewater without pretreatment was appropriately diluted to get the same starting COD as that of pretreated B-DWW). The samples were

% Dilution	Time (min)	COD (mg/L)	TOC (mg/L)	%COD reduction	%TOC reduction
No dilution ^a	0	34391.00	9523.00	0.00	0.00
	50	23723.00	6820.00	31.02	28.38
	100	23442.00	6790.00	31.84	28.70
	150	23302.00	6530.00	32.24	31.43
25% dilution ^b	0	28208.00	7940.00	0.00	0.00
	50	19539.00	5710.00	30.73	28.09
	100	18300.00	5500.00	35.12	30.73
	150	18163.00	5430.00	35.61	31.61
50% dilution ^c	0	21280.00	6044.00	0.00	0.00
	50	13193.00	3725.00	38.00	38.37
	100	11916.00	3610.00	44.00	40.27
	150	11207.00	3445.00	47.34	43.00

^a Absolute COD and TOC reduction is 11,089 mg/L and 2993 mg/L, respectively in 150 min of treatment.

^b Absolute COD and TOC reduction is 10,045 mg/L and 2510 mg/L, respectively in 150 min of treatment.

^c Absolute COD and TOC reduction is 10,073 mg/L and 2599 mg/L, respectively in 150 min of treatment.

removed periodically during the 40-day experiments and were centrifuged at 5000 rpm for 10 min for various analyses.

3. Results and discussion

3.1. 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 mg/L (avg.). The samples were collected at different time intervals and analyzed for COD and TOC. The results are presented in Table 2. 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 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. This seems to be practical since a higher pressure (13 bar) raises feasibility issues for large scale operations and also increasing operating pressure from 5 bar to 13 bar, increases the operating cost by (13/5) times without any significant enhancement in the COD reduction. Saharan et al. [27] have carried out degradation of Reactive Red 120 dye using hydrodynamic cavitation and venturi (used in our study) as a cavitating device. They have found out that the degradation rate increases with an increase in the inlet pressure (3-10 bar) reaching to a maximum at 5 bar inlet pressure and then decreases. The results obtained in the present investigation are also in accordance with the conclusion found out by them earlier.

3.2. Effect of dilution on mineralization of B-DWW

The original wastewater (34,000 mg/L COD) was diluted 25% and 50% concentration (%, V/V) using tap water and was treated using HC maintaining inlet pressure at the selected optimum (5 bar). The values of COD and TOC observed at different treatment times are presented in Table 3. It can be observed from the values of COD and TOC that the dilution has no significant effect on the mineralization of distillery wastewater. Although the percentage reduction is marginally higher at 50% dilution, the total quantum (mg of COD/TOC/L) of COD and TOC reduction is lower at 25% and 50% dilution as compared to undiluted wastewater. These results are contrary to the literature reports [23] that increasing dilution leads to enhanced mineralization using a chemically added oxidant (Fenton agent), which does not hold true for the present system. This may be attributed to the inherent recalcitrance and complex nature of the B-DWW.

3.3. Effect of cavitation on color reduction of B-DWW

The dark brown color of the distillery wastewater is not only due to the presence of a complex biopolymer called melanoidins, which are Maillard reaction products but also due to 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 [32] for the recovery of absolute alcohol. The hydrodynamic cavitation pretreatment in the present study has not only resulted in

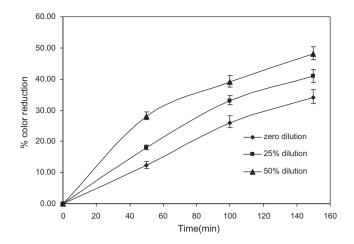


Fig. 3. Effect of inlet pressure (5 bar) on color reduction on biomethanated distillery wastewater.

COD/TOC reduction but also has reduced the concentration of total color of B-DWW. The hydrodynamic cavitation studies at 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. 3.

The results presented in Fig. 3 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.

The hydrodynamic cavitation pretreatment seems to reorient the complex molecules of distillery waste leading to breaking down of the constituents (chromophores) imparting color to the wastewater. The chemical structure of melanoidins is still not completely known, and it is assumed that they do not possess a definite structure as their elemental/chemical structure depends largely on the nature and molar concentration of parent reacting compounds including pH, temperature, heating time and solvent system use [32,33]. Bhargava and Chandra [32] have reported the bacterial degradation of major color causing compounds in distillery wastewater using Bacillus sp. and Alcaligenes sp. They reported 70% color degradation by using a microbial consortium prepared using Bacillus and Alcaligenes sp., and have reported that an increase in the temperature from 30 to 37 °C lead to an increased degradation of color causing compounds.

Sreethawong and Chavadej [34] have reported color removal from diluted (20% concentration) distillery wastewater using ozonation in presence and absence of ironoxide catalyst, and their findings suggest that in the presence of ironoxide catalyst the reduction in color and COD of the diluted distillery wastewater was more. In the present investigation, the dilution of the wastewater has lead to an enhanced color removal from B-DWW; however, the reduction is only incremental by a margin of 7% at 25% concentration and 14% at 50% concentration for a treatment time of 150 min as compared to 34% at zero dilution. These findings suggest that dilution is helping only marginally to alter the color of the wastewater and the same can be seen from the BOD values (data discussed in later section), since they are also increasing only slightly with dilution. The dilution also requires the treatment of higher volume and the additional consumption of water. Hence this strategy of dilution is not recommended.

Table 4

Effect of cavitation pretreatment on biodegradability index of biomethanated distillery wastewater.

Reaction condition	Time (min)	COD (mg/L)	BOD (mg/L)	BOD/COD
	0	34391.00	4853.00	0.14
Pressure = 5 bar, no	50	23723.00	5120.00	0.22
dilution	100	23442.00	5500.00	0.23
	150	23302.00	5500.00	0.24
	0	28208.00	3666.00	0.13
Pressure = 5 bar, 25%	50	19539.00	4170.00	0.21
dilution	100	18300.00	4250.00	0.23
	150	18163.00	4500.00	0.25
	0	33973.00	4756.00	0.14
Pressure = 13 bar, no	50	24128.00	5830.00	0.24
dilution	100	22325.00	6400.00	0.29
	150	22325.00	6400.00	0.29
Pressure = 13 bar, 25% dilution	0	28754.00	3738.00	0.13
	50	18795.00	6000.00	0.32
	100	18374.00	5910.00	0.32
	150	18363.00	5800.00	0.32

3.4. 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 [31]. 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 4. 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. It was also observed that at lower pressure (5 bar) and zero dilution the ratio increases to the tune of 0.24 becoming 0.25 when the sample dilution is 25%, thus dilution is again not aiding in BOD enhancement significantly. At higher pressure (13 bar) the ratio enhances to a value of 0.29 at zero dilution and enhances to 0.32 at spent wash concentration of 25%, thus as compared to lower pressure higher pressure yields slightly better BOD/COD ratio on treatment. From the obtained results, it can be inferred that lower inlet pressure (5 bar) is suitable for the reduction in toxicity (COD/TOC reduction), whereas for enhanced biodegradability (higher BI), higher inlet pressure operation would be preferred. Thus, it is shown that hydrodynamic cavitation is capable of reducing the toxicity of distillery wastewater as well as the pretreatment increases the biodegradability of the B-DWW. Hence, depending on the final objective of the pretreatment, hydrodynamic cavitation can be effectively utilized for the treatment of complex wastewater such as B-DWW.

3.5. Evaluation of biochemical methane potential (biogas) for cavitationally pretreated B-DWW

Preliminary experiments were conducted to assess the BMP of the cavitationally pretreated B-DWW as against untreated B-DWW as a control. The experiment was set up as per the method discussed in Section 2. The results (Fig. 4) indicate that in the cavitationally pretreated B-DWW (13 bar, 25% dilution, 50 min, BI: 0.32), 400 mL of gas volume was generated after a total duration of 40 days (including the lag period of 6 days), along with net 70% COD reduction, whereas in the control system (BI: 0.168), the gas volume was observed to be only 60 mL with around net 12% COD

reduction under similar experimental conditions. Biochemical methane potential has been reported for model organic containing wastewaters [35], where in 45 mL cumulative gas volume was observed after 34 days incubation of p-coumaric acid solution (740 mg/L, 50 mL + 50 mL biomass) and non acclimatized anaerobic seed inclusive of a lag period of 2 weeks, whereas in current study the lag phase was only around a week (6 days precisely). This reduction in lag phase can be attributed to the efficient hydrodynamic cavitation pretreatment of the waste constituents to more biodegradable constituents and also due to the use of acclimatized biomass (inoculum). This reduction in the lag period can significantly reduce the digester volume. The preliminary cost estimate for the unoptimized hydrodynamic cavitation as a pretreatment method to get the enhanced biogas formation is about US\$0.12/L of effluent treated. Though, the cost of this treatment is significantly higher than the quantum of the gas, which is generated, this method offers a possible solution to eliminate/reduce the bio-calcitrant nature of the B-DWW. The preliminary economical analysis of hydrodynamic cavitation pretreatment is presented in Appendix A. Hence, it can be concluded that the hydrodynamic cavitation is capable of enhancing the efficiency of conventional biological processes in terms of reduction of toxicity as well as increase in biogas generation, along with a significantly net higher reduction in COD and color. Due to hydrodynamic cavitation pretreatment, the efficiency of the conventional biological process is increased by almost 6 fold in terms of COD removal and biogas formation. Sangve and Pandit [8] have studied the efficacy of the ultrasonic irradiation as a

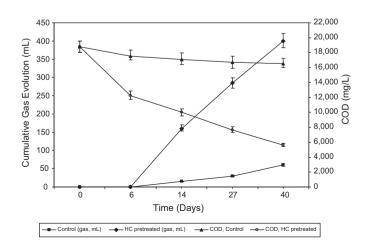


Fig. 4. Cumulative gas evolution during BMP analysis.

pretreatment step for the treatment of one of the polluting industrial effluent samples, the distillery spentwash. They have found out that the ultrasound pretreatment enhanced the biodegradability of the untreated effluent and the extent of degradation achieved in the case of ultrasound pretreated sample is almost double as compared to the untreated sample. Further optimization and the advantage of the scale of operation can be explored using a full scale system.

4. Conclusions

The hydrodynamic cavitation can be effectively utilized for enhancing the biodegradability of complex wastewater such as B-DWW along with reduced toxicity (lower COD/TOC and color). The lower inlet pressure (5 bar) is suitable for the reduction in toxicity of distillery wastewater and higher pressure have no additional benefits on the reduction of toxicity. The higher pressure (13 bar) seems to be effective for enhancement of the biodegradability index and biochemical methane potential.

Acknowledgments

KVP is thankful to Department of Science and Technology (DST) for the Woman Scientist Fellowship. VKS would like to thank DIISR, Australia and DST, GOI for providing financial support under the India–Australia Strategic Research Funding Program.

Appendix A.

Sample calculation for the cost estimation of hydrodynamic cavitation pretreatment.

Biogas formed in the cavitationally pretreated B-DWW (13 bar,

25% dilution, 50 min, BI: 0.32) = 400 mL in 2 L of pretreated B-DWW. Biogas formed in the control system = 60 mL.

Enhanced biogas formed due to hydrodynamic cavitation treatment = (400 - 60) mL = 340 mL in 2 L of pretreated B-DWW.

Total biogas formed in 6L of cavitationally pretreated B-DWW=340 (mL) \times (6/2)=1.02 L.

Total electrical energy consumed = pump power \times total treatment time = 1.1 kW \times (50/60) h = 0.92 kWh.

Biogas formed per unit energy consumed = 1.02 (L)/0.92 kWh = 1.11 L/kWh.

Electrical cost in India for heavy industry = 0.13 US\$/kWh.

Cost for the enhanced biogas formation = 1.11 (L/kWh)/0.13 (US\$/kWh) = 8.5 L/US\$ = 0.12 US\$/L.

References

- 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) 16–34.
- [2] CPCB, Annual Report, Central Pollution Control Board, New Delhi, 2003.
- [3] Z.V.P. Murthy, L.B. Chaudhari, Treatment of distillery spent wash by combined UF and RO processes, Global NEST J. 11 (2009) 235–240.
- [4] N.K. Saha, M. Balakrishnan, V.S. Batra, Improving industrial water use: case study for an Indian distillery, Resour. Conserv. Recy. 43 (2005) 163–174.
- [5] D. Pant, A. Adholeya, Biological approaches for treatment of distillery wastewater: a review. Bioresour. Technol. 98 (2006) 2321–2334.
- [6] K. Belkacemi, F. Larachi, S. Hamoudi, A. Sayari, Catalytic wet oxidation of highstrength alcohol-distillery liquors, Appl. Catal. A: Gen. 199 (2000) 199–209.
- [7] J. Dahiya, D. Singh, P. Nigam, Decolorisation of synthetic and spentwash melanoidins using the white-rot fungus Phanerochaete chrysosporium JAG-40, Bioresour. Technol. 78 (2001) 95–98.

- [8] P.C. Sangve, A.B. Pandit, Ultrasound pretreatment for enhanced biodegradability of the distillery wastewater, Ultrason. Sonochem. 11 (2004) 197–203.
- [9] S. Mohana, C. Desai, D. Madamwar, Biodegrading and decolorization of anaerobically treated distillery spent wash by a novel bacterial consortium, Bioresour. Technol. 98 (2007) 333–339.
- [10] H.V. Adikane, M.N. Dange, K. Selvakumari, Optimization of anaerobically digested distillery molasses spent wash decolorization using soil as inoculum in the absence of additional carbon and nitrogen source, Bioresour. Technol. 97 (2006) 2131–2135.
- [11] J.S. Knapp, E.J. Vantoch-Wood, F. Zhang, Use of wood-rotting fungi for the decolorisation of dyes and industrial effluents, in: G.M. Gadd (Ed.), Fungi in Bioremediation, Cambridge University Press, Cambridge, 2001, pp. 242–304.
- [12] A.M. Jiménez, R. Borja, A. Martín, Aerobic-anaerobic biodegradation of beet molasses alcoholic fermentation wastewater, Process Biochem. 38 (2003) 1275–1284.
- [13] Y. Satyawali, M. Balakrishanan, Wastewater treatment in molasses-based alcohol distilleries for COD and color removal, J. Environ. Manage. 86 (2008) 481–497.
- [14] V.P. Migo, M. Matsumara, E.J.D. Rosaria, H. Kataoka, Decolorization of molasses wastewater using an inorganic flocculant, J. Ferment. Bioeng. 75 (1993) 438–442.
- [15] R. Sowmeyan, G. Swaminathan, Inverse anaerobic fluidized bed reactor for treating high strength organic wastewater, Bioresour. Technol. 99 (2008) 3877–3880.
- [16] A. Bes-Piá, J.A. Mendoza-Roca, M.I. Alcaina-Miranda, A. Iborra-Clar, M.I. Iborra-Clar, Combination of physico-chemical treatment and nanofiltration to reuse wastewater of printing, Desalination 157 (2003) 73–80.
- [17] M. Pena, M. Coca, G. Gonzalez, R. Rioja, M.T. Garcia, Chemical oxidation of wastewater from molasses fermentation with ozone, Chemosphere 51 (2003) 893–900.
- [18] A. Pala, G. Erden, Decolorization of a baker's yeast industry effluent by Fenton's oxidation, J. Hazard. Mater. 127 (2005) 141–148.
- [19] S. Mohana, K.B. Acharya, D. Madamwar, Treatment technologies and potential applications, J. Hazard. Mater. 163 (2009) 12–25.
- [20] N.K. Singh, G.C. Pandey, U.N. Rai, R.D. Tripathi, H.B. Singh, D.K. Gupta, Metal accumulation and ecophysiological effects of distillery effluent on *Potamogeton pectinatus* L., Bull. Environ. Contam. Toxicol. 74 (2005) 857–863.
- [21] P.R. Gogate, Cavitation: an auxiliary technique in wastewater treatment schemes, Adv. Environ. Res. 6 (2002) 335–358.
- [22] D.V. Pinjari, A.B. Pandit, Cavitation milling of cellulose to nanosize, Ultrason. Sonochem. 17 (2010) 845–852.
- [23] 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) 49–54.
- [24] P.R. Gogate, A.B. Pandit, Hydodynamic cavitation: a state of the art review, Rev. Chem. Eng. 17 (2001) 1–85.
- [25] V.K. Saharan, A.B. Pandit, P.S. SatishKumar, S. Anandan, Hydrodynamic cavitation as an advanced oxidation technique for the degradation of Acid Red 88 dye, Ind. Eng. Chem. Res. 51 (2012) 1981–1989.
- [26] M. Sivakumar, A.B. Pandit, Wastewater treatment: a novel energy efficient hydrodynamic cavitational technique, Ultrason. Sonochem. 9 (2002) 123-131.
- [27] V.K. Saharan, M.P. Badve, A.B. Pandit, Degradation of Reactive Red 120 dye using hydrodynamic cavitation, Chem. Eng. J. 178 (2011) 100–107.
- [28] R.K. Joshi, P.R. Gogate, Degradation of dichlorvos using hydrodynamic cavitation based treatment strategies, Ultrason. Sonochem. 19 (2012) 532–539.
- [29] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington DC, 1998.
- [30] N. Naik, K.S. Jagadeesh, M.N. Noolvi, Enhanced degradation of melanoidin and caramel in biomethanated distillery spent wash by microorganisms isolated from mangroves, Iran. J. Energy Environ. 1 (2010) 347–351.
- [31] Metcalf, I. Eddy, Wastewater Engineering Treatment Disposal Reuse, 2nd ed., Tata McGraw Hill, New Delhi, 1979.
- [32] R.N. Bhargava, R. Chandra, Biodegradation of the major color containing compounds in distillery wastewater by an aerobic bacterial culture and characterization of their metabolites, Biodegradation 21 (2010) 703–711.
- [33] V.A. Yaylayan, E. Kaminsky, Isolation and structural analysis of Maillard polymers: caramel and melanoidin formation in glycine/glucose model system, Food Chem. 63 (1998) 25–31.
- [34] T. Sreethawong, S. Chavadej, Color removal of distillery wastewater by ozonation in the absence and presence of immobilized iron oxide catalyst, J. Hazard. Mater. 155 (2008) 486–493.
- [35] D. Mantzavinos, M. Sahibzada, A.G. Livington, I.S. Metcalfe, K. Hellgardt, Wastewater treatment: wet air oxidation as a precursor to biological treatment, Catal. Today 53 (1999) 93–106.