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Wet air oxidation induced enhanced biodegradability of distillery effluent

S.N. Malik [a], T. Saratchandra [a], P.D. Tembhekar [a], K.V. Padoley [a], S.L. Mudliar [a], S.N. Mudliar [a,b,*]

[a] CSIR – National Environmental Engineering Research Institute, Nehru Marg, Nagpur, Maharashtra, India
[b] CSIR – Central Food Technological Research Institute, Mysore, Karnataka, India

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ABSTRACT

The present study reports the feasibility of Wet Air Oxidation (WAO) as a pretreatment option for enhanced biodegradation of complex distillery effluent. Initially, the distillery effluent was pretreated by WAO at different process conditions (pressure, temperature and time) to facilitate enhancement in the biodegradability index (BI = BOD_5: COD ratio). The biodegradability of WAO pretreated effluent was evaluated by subjecting it to aerobic biodegradation and anaerobic followed by aerobic biodegradation. Aerobic biodegradation of pretreated effluent with enhanced biodegradability index (BI = 0.4–0.8) showed enhanced COD reduction of up to 67.7%, whereas the untreated effluent (BI = 0.17) indicated poor COD reduction of only 22.5%. Anaerobic followed by aerobic biodegradation of pretreated effluent has shown up to 87.9% COD reduction, while the untreated effluent has shown only 43.1% COD reduction. Bio-kinetic parameters also confirmed the increased rate of bio-oxidation at enhanced BIs. The results indicate that the WAO pretreatment facilitates enhanced bio-oxidation/bio-degradation of complex effluents like the distillery spent wash.

1. Introduction

Complex organic wastewaters with dark colour, high COD, limited biodegradability along with huge volume that are known to cause serious problems are generated from molasses-based distilleries. For every 1 L of ethanol produced, about 8–15 L of distillery wastewater known as raw spent wash are generated (Lele et al., 2000) based on the process technology used for ethanol manufacture. In the year 1999, there were 285 distilleries in India producing 2.7×10^9 L of alcohol and generating 4×10^{10} L of wastewater each year (Joshi, 1999). This number has gone up to 319, with annual production of 3.25×10^9 L of alcohol thereby generating 40.4×10^{10} L of wastewater (Uppal, 2004). The distillery effluent is highly complex with biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) ranging between 35,000–50,000 mgL^{-1} and 100,000–150,000 mgL^{-1}, respectively (Nandy et al., 2002). After conventional anaerobic digestion, the biomethanated distillery wastewater still retains up to 40,000 mg L^{-1} COD along with intensified colour and becomes recalcitrant (biodegradability index < 0.2) to further effective treatment by biological methods. Biomethanation, followed by aerobic treatment or composting is widely practiced by majority of distilleries for beneficial utilization of distillery effluent. It has been widely reported that a single biological approach is inadequate for complete biodegradation of distillery spent wash due to its complex chemical nature. Also the anaerobic–aerobic treatment is ineffective due to high retention times and lower biodegradation rates along with limited COD removal (Sangave et al., 2007) and the treatment fails to meet the stipulated discharge norms. Therefore, the use of hybrid methods involving combination of advanced oxidation processes and biological processes are required for efficient treatment and management of this complex wastewater (Sheehan and Greenfield, 1980). Wet air oxidation (WAO) refers to the aqueous phase oxidation of organics and oxidisable inorganic compounds at elevated temperature and pressure using a pure oxygen gas or air. Elevated temperatures are used to increase the oxidation rate by enhancing the solubility of oxygen in the aqueous

Abbreviations: AD, aerobic degradation; AnD, anaerobic degradation; WAO, wet air oxidation; B-DWW, biomethenated distillery wastewater; MLSS, mixed liquor suspended solids (mg L^{-1}); COD, chemical oxygen demand (mg L^{-1}); BOD, biological oxygen demand (mg L^{-1}); BI, biodegradability index; Control, B-DWW; qmax, maximum rate of substrate utilization; q, specific substrate degradation rate; Kc, saturation constant; Y X/S, growth yield; K, rate constant of COD removal.

* Corresponding author. Environmental Biotechnology Division, CSIR – National Environmental Engineering Research Institute (NEERI), Nehru Marg, Nagpur 440020, India. Tel.: +91 712 2240097; fax: +91 712 2249900.
E-mail address: sn_mudliar@neeri.res.in (S.N. Mudliar).

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solution whereas elevated pressures are required to keep the water in liquid form (Thampi, 2000). WAO can potentially breaks the long polymeric chain compounds and converts them to highly biodegradable low molecular weight compounds. In the present work, the potential of wet air oxidation pretreatment to enhance the biodegradability of the bio-methanated distillery effluent has been investigated along with insights into enhancement in bio-kinetics of COD removal and biomass growth during anaerobic and aerobic biodegradation.

2. Materials and methods

2.1. Distillery effluent

The distillery effluent (known as bio-methanated spent wash) was procured from a molasses-based distillery located in Nagpur, India. The physico–chemical characteristics of distillery effluent is presented in Table 1. The wastewater was first filtered to remove the suspended solids and then used for further study. The wet air oxidation (WAO) pretreated and untreated (control) effluent were not diluted for aerobic degradation (AD) and anaerobic followed by aerobic degradation (AnD + AD) studies. For batch studies of WAO followed by AD at equivalent COD, the untreated effluent and WAO pretreated effluent were diluted with distill water to obtain the equivalent initial COD. The effluent samples were stored at 4 °C and brought to room temperature prior to experiments.

2.2. Wet air oxidation setup and operation

The effluent was pretreated in a WAO reactor having 1.8 L gross volume capacity made of SS-316 (Model-4857, Floor Stand HP/HT Reactor, Parr Instruments, IL, USA). The reactor (I.D. 95 mm) contents were stirred by means of a four bladed turbine type impeller (I.D. 50 mm) at a stirring speed of 200 rpm and was equipped with a pressure indicator and a gas sparging tube. Impeller speed was maintained at 200 rpm ensuring the good mass transfer from the gas to the liquid phase. A rupture disc as well as non-return valve at the gas inlet was also provided to the reactor. Reactor controller consisted of a packaged temperature control unit assembled with appropriate power and safety relays, switches and pilot lights. The Reactor was properly sealed, ensuring the absence of any leakage. 2 KW electric heater was used to heat the reaction mixture to a desired temperature and air was sparged into the reactor to the predetermined level (Fig. 1).

No pH adjustments were made during the WAO pretreatment and the original effluent pH was considered as the initial pH for the pretreatment. The distillery effluent (1.2 L) with known initial COD was first charged to the reactor. All the lines were closed. The reactor was kept at the agitation speed of 200 rpm. Oxygen (air) was supplied at a predetermined level during reactor operation.

Table 1
Characteristics of complex wastewater studied.

Characteristics	Value
Colour	Brown
pH	7.5
COD (mgL^{-1})	40,000
BOD (mgL^{-1})	6744
Biomass (%)	1
TOC (mgL^{-1})	18700
Total solids (mgL^{-1})	31000
Total suspended solids (mgL^{-1})	1600
VFA (mgL^{-1})	180
BOD_5: COD ratio	0.17

Average of 3 sets of observation with SD < 5%.

Table 2
Calculated values of maximum specific growth rate of microorganism, growth yield and saturation constant under different WAO pretreatment conditions.

Batch	q_{max}, per day	Y, mg MLSS/mg of COD	K_s, mg COD/mg MLSS
AO			
0.4 BI	0.584	0.124	0.532
0.6 BI	0.212	0.196	0.0031
0.8 BI	0.285	0.145	0.549
B-DWW	0.156	0.102	1.039
AO (equivalent COD)			
0.4 BI	0.144	0.475	0.268
0.6 BI	0.147	0.076	0.275
0.8 BI	0.182	0.403	0.269
B-DWW	0.089	1.045	0.333
AnD + AO			
0.4 BI	0.204	0.28	0.139
0.6 BI	0.237	0.32	0.241
0.8 BI	0.226	0.31	0.337
B-DWW	0.132	0.22	0.619

The system was tightly sealed to ensure no leakage. The effluent was subjected to various WAO pretreatment conditions with respect to temperature (150–200 °C), pressure (6–12 bar) and time (15–120 min). After every run, the heater was turned off to allow the cooling of the reactor contents. The pretreated samples were then analysed for various physical–chemical parameters viz. pH, COD and BOD_5. It was further evaluated for the biodegradability (aerobic/anaerobic–aerobic) in suitable batch scale bioreactors.

2.3. Microbial culture for aerobic biodegradation

Aerobic mixed microbial culture (activated sludge of an effluent treatment plant treating dairy wastewater located at, Nagpur, India) was acclimatized and used in the present study. The culture was grown in 500 ml Erlenmeyer flask with 100 ml of mineral salt medium (MSM) containing (mg L^{-1}): $(NH_4)_2SO_4$, 230; $CaCl_2$, 7.5; $FeCl_3$, 1.0; $MnSO_4$. H_2O, 100; $MgSO_4$. $7H_2O$, 100; K_2HPO_4, 500; KH_2PO_4,250; (pH 7.5) under the agitating condition (200 rpm) to ensure contact of biomass with the flask contents. The acclimatization was continued for a period of one month, with periodic

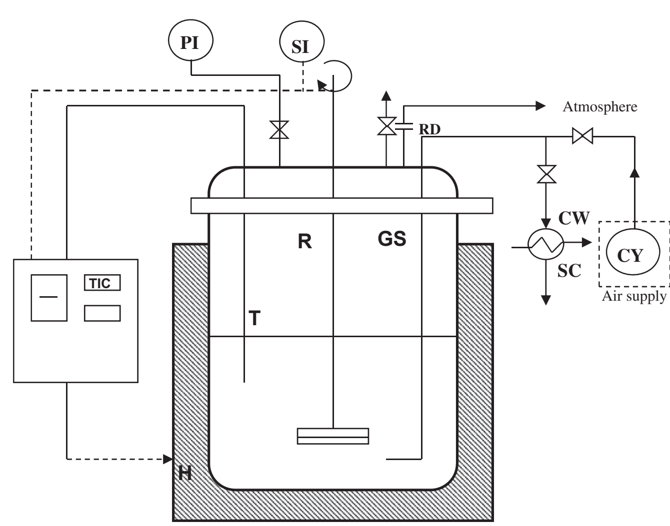

Fig. 1. Schematic diagram of experimental set up for wet air oxidation reactor. The schematic represents the actual reactor set up used in present study. (TIC, SIC, temperature, speed indicator and controller; PI, pressure indicator; SI, speed indicator; RD, rupture disc; GS, gas sparger; H, electric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