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Research article

# Iron-catalyzed wet air oxidation of biomethanated distillery wastewater for enhanced biogas recovery

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ABSTRACT

In the present work, catalytic wet air oxidation (WAO) technique was applied to biomethanated spent wash from a local sugar factory. This wash water exhibited high biological oxygen demand ($BOD_5 = 8100$ mg/L) and chemical oxygen demand (COD = 40,000 mg/L). The objectives of oxidative pre-treatment were two-fold, viz. efficient treatment of wash water and enhanced biogas recovery. For the catalytic oxidation process, two iron-based heterogeneous catalysts were employed, viz. $Fe_2O_3$ and Fe/C. To synthesize the Fe/C catalyst, activated carbon (AC) support was modified either by thermal treatment or chemical treatment with nitric acid; accordingly, the catalyst was named as Fe/AC-T or Fe/AC-N. In a batch slurry reactor, catalyst performance was investigated at T = 175 °C, $P_{O_2} = 0.69$ MPa and $\omega = 33$ mg/L (here, T, $P_{O_2}$ and $\omega$ denote temperature, oxygen partial pressure and catalyst loading) for 1 h. Based on the conversions of COD and total organic carbon (TOC) and the improvement in biodegradability index (BI), it was found that the activity of the catalysts reduced in the order: Fe/AC-N > Fe/AC-T > $Fe_2O_3$. The results were more encouraging (COD conversion = 87%, color reduction = 88% and BI value = 0.71) when carbon adsorption (5% w/v) followed WAO over Fe/AC-N. Clearly, our novel hybrid process for pre-treatment, viz. wet oxidation-carbon adsorption showed potential. Post biomethanation, around 1.2 $Nm^3$ biogas ($CH_4$ 72%) was formed per cubic meter of the wastewater; without pre-treatment by catalytic WAO and carbon adsorption, the yield of biogas ($CH_4$ 11%) was just 1 $Nm^3$ for every cubic meter of wastewater. After a last aerobic treatment step, 97% COD was removed and BI value was 0.84. Finally, a kinetic model was proposed to describe kinetics of COD reduction. In this way, a promising method was suggested for treating a complex wastewater.

## 1. Introduction

Indian distillers face the daunting task of effectively treating high volume of concentrated spent wash (Central Pollution Control Board, 2006). This liquid effluent has many unwanted features, viz. high acidity, dark brown color and high chemical oxygen demand (COD). The recovery of precious biogas via biomethanation of the spent wash is most prevalent; besides, a final polishing step by aerobic oxidation is often employed (Thakur et al., 2009; Kumar, 2003). According to Tembhekar et al. (2015), the biomethanated spent wash however resists aerobic treatment, due to its low biodegradability index (BI < 0.2) and high COD (30000-40000 mg/L). Thus, it is crucial to develop methods for efficiently treating biomethanated wash water.

The controlled wet air oxidation (WAO) of biomethanated spent wash at mild conditions is a useful option. In this process, COD is not entirely destroyed whereas biodegradability is much improved. As a result, additional biogas can be recovered before aerobic oxidation. Using such oxidative pre-treatment at 175 °C and 0.6 MPa air pressure, Padoley et al. (2012) reduced COD of distillery effluent (by 40%) and improved BI value (from 0.17 to 0.4) within 30 min. Further, Tembhekar et al. (2015) investigated the kinetics of COD destruction and BI improvement during the oxidation process. It is now known that oxidation also reduces toxicity and color of the effluent and accelerates aerobic treatment (Saratchandra et al., 2014; Malik et al., 2014). In this work, we applied this WAO technique to the washwater collected from a sugar factory in Maharashtra state.

The high efficacy of iron catalyst for WAO of distillery spent wash is well-known. Using homogeneous $FeSO_4$ catalyst, Dhale and Mahajani (2000) reported high reduction in COD (60%) and color (95%) at 210 °C in 2 h. More recently, we employed the same catalyst for WAO and reported superior biogas yield from the oxidized spent wash (Bhoite and Vaidya, 2018). Due to the ease in separation and reuse, employing heterogeneous iron-based catalysts for WAO appears beneficial. For example, Quintanilla et al. (2007) investigated oxidative

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destruction of phenol over Fe/AC catalyst (AC denotes activated carbon). This carbonaceous support had high specific area, thermal resistance, adsorption capacity and the presence of functional groups on the surface. Upon promotion with Fe, its surface acidity increased and phenol oxidation was made easy. This catalyst was stable and capable of reducing toxicity. Zazo et al. (2009) reported that Fe promotes the oxidation of the surface of AC by increasing oxidation surface groups such as carboxylic acids. They reported high removal of toxicity and total organic carbon (TOC) during oxidation over Fe/AC.

In this work, two heterogeneous WAO catalysts were chosen, viz. $Fe_2O_3$ and Fe/AC. Especially for Fe/AC, the role of the synthesis procedure on its performance was investigated. Up to now, detailed work on these iron catalysts is missing. Here, the effects of temperature (range 175–225 °C) and oxygen ($O_2$) partial pressure (range 0.69–2.07 MPa) on the conversion of COD and TOC and the improvement in BI values were investigated. Besides, the role of toxic and refractory ingredients and intermediates in the oxidation pathway was elucidated. After controlled oxidation, the use of adsorption over AC for color reduction and further improvement in biogas generation potential was also explored. To the best of our knowledge, there is no such systematic study reported in past works.

## 2. Experimental

### 2.1. Materials

A sugar factory in Maharashtra state provided the biomethanated spent wash. Some salient features of this effluent were so: biological oxygen demand $BOD_5 = 8100$ mg/L, COD = 40,000 mg/L, TOC = 7800 mg/L, total solids = 35,000 mg/L and pH = 8.6. Ferric oxide ($Fe_2O_3$), ferric nitrate $Fe(NO_3)_3$ and powdered activated carbon (Cabot Corporation) were purchased from S. D. Fine Chemicals Ltd., Mumbai. A local vendor (HANNA Instruments, Mumbai) provided COD reagents of middle range (0–1500 mg/L). Another seller (Lovibond Aqualytic, Mumbai) provided BOD reagents, nitrification inhibitor and KOH solution (45%). Gas cylinders containing $O_2$ and nitrogen (purity 99.5%) were purchased from Inox Air Products Ltd., Mumbai. For doing TOC analysis, $TiO_2$ was purchased from SGE International Pvt. Ltd., Australia. Perchloric acid (70%, analytical reagent grade) was purchased from Qualigens Fine Chemicals, Mumbai.

### 2.2. Synthesis of Fe/AC

AC support was modified, either by thermal treatment (denoted by AC-T) by heating at 700 °C for 1 h in a muffle furnace, or chemical treatment (denoted by AC-N) by boiling with 6 M nitric acid until evaporation was complete. The modified supports were washed with deionized water until pH of the filtrate was neutral. Subsequently, they were dried overnight at 100 °C and impregnated with aqueous Fe $(NO_3)_3$ at ambient temperature to prepare Fe/AC-T and Fe/AC-N (metal 2.5%). Both catalysts were then dried at room temperature for 2 h, heated overnight at 60 °C and finally heated at 200 °C for 6 h, according to the procedure reported by Quintanilla et al. (2007).

### 2.3. Methodology for WAO and carbon adsorption

A batch-operated high pressure reactor (make: Parr Instruments Company, USA, material: SS316, capacity: 300 mL) was used for WAO trials. To control the reaction temperature and the agitation speed in the liquid phase, Parr 4842 controller was used. Details of the setup and procedure are provided in our past works (Vaidya and Mahajani, 2002a; 2002b; Vaidya and Junghare, 2011; Bhoite and Vaidya, 2018). Typically, the reactor was loaded with 150 mL of the spent wash and the heterogeneous catalyst (range 16–48 mg/L) and purged with nitrogen to ensure an inert atmosphere. After releasing nitrogen, the reactor content was stirred at 1200 rpm and heated to the desired temperature (175, 200 or 225 °C). Then $O_2$ was charged at a chosen partial pressure (0.69, 1.38 or 2.07 MPa) and the reaction was continued for 1 h. Liquid samples (1–2 mL) were collected between times and analyzed. More $O_2$ was sometimes charged to maintain constant total pressure. After 1 h, the reactor was cooled and the reaction mixture was filtered. The filtrate was then treated with activated carbon (5% w/v) for 1 h at 30 °C under continuous stirring. After adsorption on carbon, the treated solution was filtered and analyzed for removal of color, COD and $BOD_5$ (see Ayub and Usmani, 2014).

### 2.4. Methodology for anaerobic and aerobic treatment

After WAO and carbon adsorption, the spent wash was biodigested using procedures reported in literature (Padoley et al., 2012; Malik et al., 2014). For instance, washwater oxidized with $Fe_2O_3$ catalyst and treated further with carbon was biodigested in a single anaerobic reactor. The procedure followed was so: at first, pH of washwater was adjusted to a value of 7.5 using 1 N NaOH solution. Next, nitrogen was bubbled into wash water (2 L) inside the glass reactor. After that, inoculation was carried out at T = 30 °C for 25 days with continuous stirring. Biomass sludge (1%) acclimatized in the anaerobic digester in a distillery was used. To measure the volume of the generated biogas, and thus, the biomethane potential, the amount of water displaced during the experiment was found. Gas chromatography (PerkinElmer) was used to determine the methane content of biogas every day. The reactor was operated in the batch mode for 25 days without any supernatant or sludge disposal. After 25 days, the washwater was centrifuged and suitably analyzed. Subsequently, aerobic digestion was performed inside another glass reactor by continuously bubbling air into biomethanated washwater at T = 30 °C for 15 days (see Uzal et al., 2003). Once again, activated sludge acclimatized in distillery digester was used. This reactor was also operated in the batch mode for 15 days. Finally, the effluent was centrifuged and filtrate was analyzed. The entire procedure of bio-digestion and aerobic treatment was then repeated using washwater oxidized over Fe/AC-T and Fe/AC-N (and then treated with activated carbon), and finally, using raw spent wash (without any pre-treatment).

### 2.5. Methods of analysis

Both raw and pre-treated washwater were characterized using suitable analyzers for measuring TOC (ANATOC series II, SGE International Pvt. Ltd., Australia), COD (HANNA Instruments, Mumbai) and $BOD_5$ (Analytical Laboratory, Mumbai). In all measurements, the accuracy was 1 mg/L. From the ratio of $BOD_5$ to COD, the value of BI was found. The initial BI value of washwater before oxidation was just 0.2. UV spectrophotometer was used to find the extent of color reduction of washwater after carbon adsorption. Fourier Transform Infra-red Spectrometer (FT-IR) analysis was performed to identify the washwater constituents and oxidized intermediates (FTIR Model: Bruker-VERTEX 80V instrument). The spectral range was 4000 to 400 $cm^{-1}$. Also, gas chromatography-mass spectroscopy (GC-MS, ThermoFisher Scientific, Mumbai) was used to ascertain some oxidation products; the details were so: DB-5 column MS, 95% non-polar; quadrupole detector; carrier gas Helium; ramp 17°/min, initial and final temperature 60 and 300 °C. Methane content of biogas was found by GC (thermal conductivity detector, 3 m long Hayesep-DB column, carrier gas hydrogen). The error in all experimental measurements was < 2%.

## 3. Results and discussion

### 3.1. Catalyst characterization

Electron microscopy techniques were used to characterize the Fe/AC-T and Fe/AC-N catalysts: JEOL-JSM 6380 LA instrument for scanning electron microscopy (SEM) and JEOL JEM 2100 instrument for