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The Effect of Ozonation Pre-treatment in Enhancing the Biodegradability of Effluent from Distillery of Ethanol Fermented from Molasses

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Abstract— The effect of ozonation on the biodegradability of distillery wastewater in a batch anaerobic digester was investigated in semi-batch pilot-scale experiments. The organic matter and color reductions as well as gas production were monitored. The total COD and color reduction during the 30 minute ozonation were 24 ± 11% and 51 ± 7 %, respectively. Further anaerobic treatment resulted in average total COD reduction of 57 ± 7 % compared to 38 ± 14% for wastewater similarly treated by batch anaerobic digester and without prior ozonation. Without ozonation pre-treatment, there was no color removal in the anaerobically treated wastewater. While with ozonation pre-treatment 44 ± 12% color removal was achieved. Gas production for wastewater with and without ozonation pre-treatment was 27 L and 28 L, respectively. The biogas production in the anaerobic digester was more stable when the influent is pretreated with ozonation than without prior ozonation pre-treatment.

Keywords: ***anaerobic, biodegradability, ozonation***

I. INTRODUCTION

Distillery wastewater is a high strength liquid waste generally referred to as stillage's, distillery slops or vinasses. Its disposal to aquatic bodies presents serious environmental problems due to its high pollution load, low pH, high temperature and persistent color [6]. The characteristics vary considerably according to the fermentation feed stock, location and fermentation process adopted [4]. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD), which are the indices of its polluting character, are typically in the ranges 35,000 – 50,000 and 10,000 – 150,000 mg/L, respectively [9].

Current methods of treatment of this type of wastewater include biological treatments such as aerobic or anaerobic biological processes, trickling filters and lagoons and physicochemical treatment methods such as adsorption using activated charcoal, flocculation and coagulation. The high bio-recalcitrance and toxicity of phenolic contaminants in the wastewater cause difficulties in biological treatment [7]. Moreover, distillery slops contain persistent dark brown color pigments that remain even after biological processes known as melanoidins. While the chemical methods are quite disadvantageous in terms of their high operation cost and consumption of chemical agents as well as variations in color removal efficiency and high volume of solid waste produced [6].

A physicochemical step can be applied as pretreatment process when high concentration organic or toxic compounds are present. Example of an oxidant is ozone (O_3) with which organic compounds react rapidly because of its high oxidizing potential. The ozonation of aromatic compounds usually increases the biodegradability of the wastewater [10].

When ozonation was used as a pre-treatment, an improved biodegradability of the distillery spent wash was achieved. This may be the result of the reaction of ozone with the pollutant molecules present in the distillery spent wash that converted them into biologically degradable, more amenable products. Evolution in pH was also observed during the pre-treatment step indicating formation of organic acids, which were easily biodegradable [9]. The reaction of ozone with natural organic matter results in the formation of highly reactive hydroxyl radicals which have higher oxidation potential than ozone itself [7]. This powerful oxidant is soluble in water, readily available and do not produce by-products that need to be remove [4].

The combination of chemical and biological treatment is often the way to optimize the overall process of treating wastewaters [2]. Four cases in which real advantages could be obtained by a two-step process such as: (1) waste containing recalcitrant compounds; (2) presence of small

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amounts of recalcitrant compounds requiring a subsequent chemical refining; (3) presence of inhibitory compounds in main polluting load of biodegradable compounds and; (4) formation of recalcitrant biological or chemical products. Each waste should be considered separately to decide which chemical and biological treatments are more suitable [8].

In this study the effect of ozonation pre-treatment on the biodegradability of distillery was investigated using an anaerobic digester. Anaerobic treatment is suitable for treating high concentration wastewater. One of its advantage is the biogas produced that can be used as a source of energy. Thus, the effect of ozonation treatment in biogas production in the anaerobic digester was also determined.

II. MATERIALS AND METHODS

The raw untreated distillery wastewater was collected from Absolute Chemicals, a distillery plant located in Lian, Batangas, Philippines. The characteristics of the wastewater were as follows: pH= 4 - 4.5, COD = 52,000 – 71,900 mg/L, color = dark brown and TSS = 3,000 – 4,000 mg/L.

A. Two-phase Anaerobic Digester

Wastewater from the ethanol distillery plant was treated in a two-phase batch anaerobic digester system. The schematic diagram of the reactors was shown in **Fig.1**. The anaerobic digesters were filled with seed sludge (volatile suspended solids (VS) content = 3,500 ± 150 mg/L). The seed sludge was taken from a full-scale UASB reactor treating distillery wastewater facility of Absolute Chemicals Inc. To stabilize and enhance the sludge, the anaerobic digesters were fed with water containing 500 mg/L urea and potassium hydrogen orthophosphate with trace elements. Prior to loading in the digester, the pH of the distillery wastewater was adjusted to 7 - 7.5 by adding sodium hydroxide solution. The first anaerobic digester was fed with distillery wastewater at 20 L /3 days by using a centrifugal pump. The effluent from this anaerobic digester (AD 1) was then stored in a 40 L plastic storage tank. The valve connecting the storage tank and the second anaerobic digester (AD II) was opened until 10 L of effluent from AD 1 was fed into AD 2. The rest of the volume was discarded to a separate storage tank. The retention time was set to 3 days for both reactors. The biogas produced for the first and second anaerobic digesters was measured using a wet gas meter and a 10 L Marriot flask with 5% sodium hydroxide, respectively. As an indication of performance of the two-phase anaerobic digesters, the reduction in COD level for influent and effluent was determined.

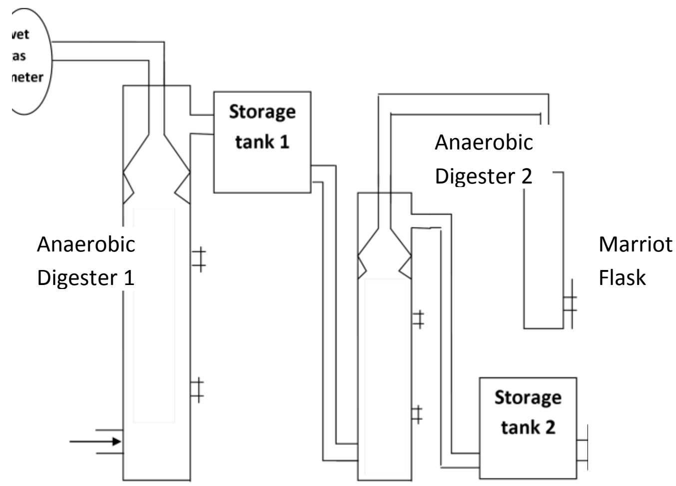

Figure 1. Schematic Diagram for two-phase Anaerobic Digester

In this study, there were two runs performed in the span of 36 days. Each run was completed in 18 days. The first run was done by subjecting the diluted raw wastewater to a two-phase anaerobic digester. While in the second run, the raw diluted wastewater was subjected to a 30 minute ozonation pre-treatment and two-phase anaerobic treatment. The composition and gas production of the wastewater with and without ozonation pre-treatment were compared after anaerobic treatment.

B. Ozonation Pre-Treatment

Ozonation as a pre-treatment was carried out on raw diluted distillery wastewater with concentration of 6063 ± 806 mg/L. Ozone gas was generated using a laboratory-scale ozone generator from Ozone Solutions. Oxygen was used as feed gas to this unit and supplied from an oxygen cylinder. The generator has a built-in flow

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meter that can be adjusted using the regulator valve of the oxygen cylinder. The experiments were performed at room temperature and semi-batch mode by sparking ozone into the wastewater sample. The ozone generated was bubbled through glass tubing inserted through a rectangular column. The ozone gas was allowed to react with the sample for 30 minutes.

The excess ozone flows through a silicon tubing connected to two one litre- Erlenmeyer flask with potassium iodide solution. The reactor used was made of plexi-glass having a height and square base area of 121.9 cm. and 82 cm^2, respectively, and an effective internal volume of approximately 10 L.

At every ozonation pre-treatment run, the reactor was filled with 10 L of wastewater. The experiments were performed at room temperature and at oxygen gas flow rate of 2L/min generating approximately 4 g/h of ozone. Samples were taken before and after 30 minutes ozonation pre-treatment and analyzed for pH, color and COD using standard methods for water and wastewater analysis. The COD and color removal analysis was performed using HACH 8900 Colorimeter. The ozone pre-treated wastewater was further treated in a two phase anaerobic digester.

III. Results And Discussion

A. Effect of Ozonation as pre-treatment on color and organic matter content

The effect of ozonation was studied for the anaerobic treatment. The average total COD fed to the ozonation step was 6063 ± 806 mg/L mg/L for 18 days of operation. The COD concentrations in the influent and effluent wastewater and the percent COD reduction are shown in **Table 1**. Ozonation was carried out for 30 minutes at the natural pH of the distillery wastewater which was at 4.5. There was a decrease in pH from 4.5 in the influent to 3.5 in the effluent. This decrease was probably due to the formation of dicarboxylic acids and small molecule organic acids [7].

TABLE I PERFORMANCE OF OZONATION PRE-TREATMENT

Time (day)	Initial COD concentration mg/L	Final COD concentration mg/L	% Total COD removal	% Color removal
3	6403	4323	33	53
6	5157	4477	13	56
9	6516	5457	16	53
12	7129	4671	34	57
15	5080	4460	12	46
18	6096	4071	33	40

The percent COD removal for all treatments applied was calculated using the eq. 1:

$$X_{COD} = \frac{COD_f - COD_o}{CODo} \times 100 \quad (1$$

(1)

where X_{COD} is the percent COD removal, COD_f is the final COD concentration and COD_o is the initial COD concentration.

The ozonation pre-treatment resulted in an average COD and color reductions of 24 ± 11% and 51 ± 7 %, respectively. The color reduction of the distillery wastewater has been attributed to ability of ozone to directly attack the C = C double bonds in aromatic and chomophoric molecules, leading to the formation of “bleached” products, like aliphatic acids, ketones and aldehydes [10]. At lower pH, the degradation of organic matter in distillery wastewater occurs by direct reaction with molecular ozone [9]. Compounds susceptible to ozonolysis are those containing C=C double bonds, specific functional groups (e.g.OH, CH_3, OCH_3) and atoms carrying a negative charge (N, P, O, S and nucleophile carbons). The ozonation of organic compounds in water usually produces oxygenated organic products and low molecular weight organic acids that are relatively easily biodegradable [9].

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Thus, apart from COD reduction, ozonation would also improve the biodegradability of the wastewater as would be discussed in the later section.

B. Effect of Ozonation Pre-treatment on Biodegradability of Distillery Wastewater

The percent total COD removal and COD concentrations for wastewater with and without ozone pre-treatment are shown in **Fig. 2 and Table II,** respectively. The wastewater with 30 minutes ozonation pre-treatment resulted to 57 ± 7% COD reduction compared to the wastewater without ozonation pre-treatment that resulted to 38 ± 14% after the two-phase anaerobic digester. These COD removal results show that ozonation prior to anaerobic treatment improved the biodegradability of the distillery wastewater.

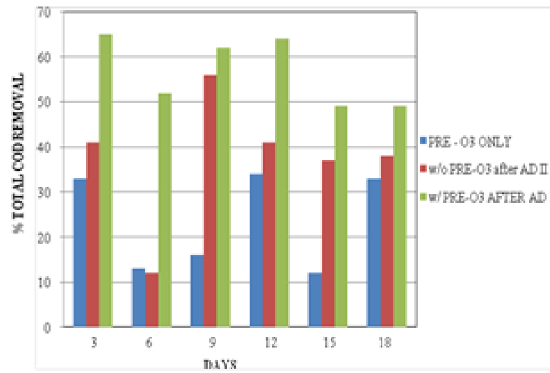

Figure 2 Comparison of the % total COD removal for wastewater treated in the anaerobic digester with and without ozonation

TABLE II COD CONCENTRATIONS FOR ANAEROBIC TREATMENT WITH AND WITHOUT OZONATION PRE-TREATMENT

DAYS	ANAEROBIC TREATMENT ONLY			COMBINED OZONATION AND ANAEROBIC TREATMENT			
	Influent COD (mg/L)	COD after AD I (mg/L)	COD after AD II (mg/L)	Influent COD (mg/L)	COD AFTER O3 (mg/L)	COD after AD I (mg/L)	COD after AD II (mg/L)
3	5450	2532	3216	6403	4323	3446	2254
6	4966	3138	4364	5157	4477	3610	2497
9	6050	3903	2632	6516	5457	3953	2493
12	4948	3524	2939	7129	4671	3501	2585
15	4726	2273	2998	5080	4460	3535	2594
18	5552	3924	3424	6096	4071	3507	3083

Ozone reaction with the organic matter present in the wastewater have resulted in the production of more biologically degradable compounds leading to a higher COD reduction in the ozone pre-treated wastewater.

Color level increased after the anaerobic treatment for both samples with and without ozonation pre-treatment. The further increase in color level for the sample without ozonation pre-treatment may indicate that more pigmented compounds were formed after the anaerobic treatment. Biologically treated distillery wastewater are dark brown in color and contain a high COD due to the presence of recalcitrant compounds such as caramel, melanoids, a variety of sugar decomposition products, anthocyanins and tannins and other xenobiotic compounds formed during yeast growth and the processing of alcohols [1]. The biological treatment usually depends on the oxidative properties of microorganisms and most bacteria are not able to degrade the recalcitrant compounds mentioned above. The increase in color level after the two-phase anaerobic digester for the sample with ozonation pre-treatment may have resulted to the reformation of melanoidin pigments under autoclaving conditions [9]

A comparison of percent dissolved COD removal for wastewater after the anaerobic treatment with and without ozonation pre-treatment is shown in **Fig. 3**. Greater dissolved COD removal was achieved after the anaerobic digester for the wastewater with ozonation pre-treatment equivalent to an average of 63 ± 7% while 43 ± 15% for the wastewater without ozonation pre-treatment. This may be a result of ozone's high oxidizing property that it was able to render soluble organic matter more biodegradable in the anaerobic process. It can also be deduced from total and dissolved COD data that lower amount of suspended solids was present in the effluent treated with combined ozonation and anaerobic digester. This may indicate that ozone was able to induce hydrolysis resulting to lower molecular weight organics. Low sludge production in the digester was also noted which may be due to lower amount of suspended solids in the influent with ozonation pre-treatment.

The total dissolved and suspended COD and color removals for wastewater with ozonation pre-treatment show enhanced biodegradability of the distillery wastewater subjected to anaerobic treatment as shown in the high reductions achieved.

A slightly higher average gas production was observed for wastewater without ozonation pre-treatment compared with ozonation pre-treated wastewater equivalent to 9.5 L / day and 9 L / day, respectively. Although the first sample's gas production was slightly higher, a more stable gas production was observed for wastewater with ozonation pre-treatment. A slightly lower gas production for the latter may be the result of the elimination of some biodegradable organic compounds that could have been available for the anaerobic bacteria. This is because ozonation is known to be non-selective in terms of its oxidizing properties [11].

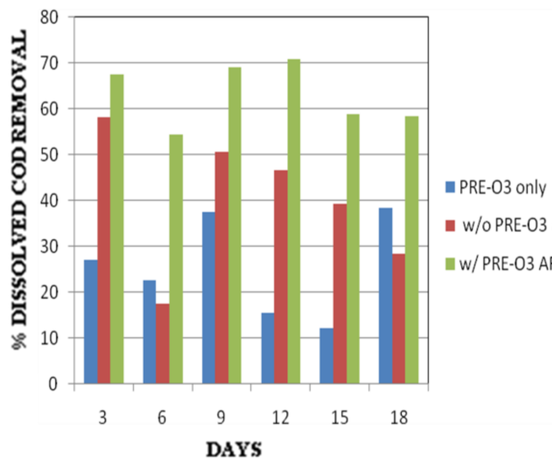

Figure 3. Comparison of the % Dissolved COD removal for wastewater treated in the anaerobic digester with and without ozonation pre-treatment

IV. CONCLUSIONS

The use of ozonation as a pre-treatment enhances the biodegradability of distillery wastewater in an anaerobic digester treatment. This was significantly indicated by the larger reduction in total, dissolved and suspended solid COD. An average of 57 ± 7% and 63 ± 7% total and dissolved COD reductions, respectively, were achieved for wastewater with ozonation pretreatment compared to 38 ± 14%. and 43 ± 15% total and dissolved COD, respectively for wastewater without ozonation pre-treatment. Large amount of suspended solids were removed during ozonation pre-treatment. The pre-treatment employed can easily reduced suspended solids due to its high oxidative properties that can induce hydrolysis.

Color was reduced at an average of 51 ± 7% after pre-ozonation and 44 ± 12% after the two-phase anaerobic digester treatment. No color reduction was observed after AD II for the wastewater without ozonation pre-treatment. The increase in color level after the anaerobic treatment may be a result of the reformation of pigmented compounds.

The wastewater with ozonation pre-treatment had slightly lower average gas production of 9L/day compared to 9.5 L/day for the wastewater without ozonation pre-treatment. This could be a result of the elimination of more biodegradable organic compounds that could have been available for the anaerobic bacteria. It is known that ozone is non-selective in terms of its reactivity.

This study showed that a short ozonation prior an anaerobic treatment demonstrated better performance compared to an anaerobic treatment alone as shown in higher removal efficiency achieved in the combined treatment.

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