TREATMENT OF DISTILLERY WASTEWATER USING COMBINATIONS OF ADVANCED OXIDATION PROCESSES: UV/O₃, UV/H₂O₂ & H₂O₂/O₃

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ABSTRACT

Molasses-based ethanol distillery plants generate large volume of wastewater containing high levels of organic matter and refractory color. In view of this problem, the feasibility of using advanced oxidation processes (AOPs), namely ultraviolet light – ozonation process (UV/O₃), ultravioletlight- hydrogen peroxide (UV/H₂O₂) and hydrohen peroxide – ozonation (H₂O₂/O₃), to treat distillery wastewater from molasses-based alcohol fermentation and distillation system was explored in this study. The efficiency of the AOPs in the degradation of COD and color at varying pH, H₂O₂ dosage and initial wastewater concentration was investigated at constant ozone supply of 606 mg for two hours of experimental batch run. In all runs, the COD and color removal were highest at 1,000 mg/L hydrogen peroxide, the highest applied dose in the experiment. At the natural pH of the wastewater (pH 4.6~4.9) the effectiveness of each AOP followed the sequence: H₂O₂/O₃ > UV/H₂O₂ > UV/O₃ > O₃ > UV-C. Color removal is best at the natural pH (4.6~4.9) for all AOP experimental runs. In H₂O₂/O₃ and UV/H₂O₂, COD removal is fastest at pH 4.6. UV/O₃ process is enhanced by operation at alkaline pH (10). H₂O₂/O₃ process is the most effective AOP. It removed 91% color and 60% COD (initial COD level of 1,000 mg/L). It also removed 32%, 27%, and 35% TKN, NH₄-N and DON, respectively. The COD removal in all AOPs tested follow second-order reaction rate equation while the color removal rate is first-order. The highest COD removal rate constant and color removal rate constant were in the H₂O₂/O₃ process at the highest oxidant concentration used (COD/H₂O₂ ratio of 1 and H₂O₂/O₃ ratio of 1.7).

Keywords: AOPs, COD, color, melanoidin, ozonation, peroxide, UV, recalcitrant

1. Introduction

Molasses based production of ethanol is among the main industries in the Philippines. Ethanol distillery plants generate large volume of wastewater, i.e., 13-15 m3 per m3 of product ethanol. The latter contains high levels of organic matter, i.e., 80-160 kg COD/m3, including complex substances such as hemicelluloses, dextrin, phenolics and lignin. It has a dark brown color, which cannot be removed by common biological treatment processes. The brown color of distillery wastewater has been attributed to recalcitrant polymeric pigments called melanoidin (Alfafara *et al.*, 2000). They are products of Maillard reaction of amino acids and carbohydrates. The reaction interaction of amino acids with reducing sugars, sugar dehydration and fragmentation of the reducing sugar with the formation of aldehydes, ketones, furans, pyrroles, quinolines and indoles. In the final stages of the reaction, brown pigments are formed through aldol condensation and polymerization of carbonyl compounds. Melanoidins formed in amino acid reducing sugar system have molecular weights of 290 -14200 (Kitts *et al.*, 1993).

Because of its relatively high temperature and COD levels, ethanol distillery wastewater is usually treated through one- or two-stage thermophilic anaerobic digestion process followed by aerobic process. However, these biological processes are not sufficient in removing color to acceptable levels. Color removal achieved in previous studies was up to about 7% only (Kalavati *et al.*, 2001). Several AOPs have been shown to be effective in degrading recalcitrant stable, inhibitory, or toxic substances (Legrini *et al.*, 1993), such as those present in wastewater from textile (Al-kdasi *et al.*,

2004; Kalra, *et al*., 2011), wine (Lucas *et al*., 2010) and distillery (Beltran *et al*., 2001) industries. In AOPs, generated hydroxyl radicals attack large organic molecules producing smaller intermediates, which may be easier to degrade, without generation of sludge (Atasi *et al*., 2009). Hydroxyl radicals are generated by means of oxidizing agents such as ultraviolet (UV) radiation, hydrogen peroxide (H_2O_2) or ozone (O_3). The latter can directly attack parts of molecules of high electron density or indirectly via hydroxyl radical. The latter is highly reactive and non-selective (Ref?/). Thus, combinations of AOPs for both COD and color removal in distillery wastewater may be more effective than single AOP alone. Moreover, most of the AOP studies used synthetic wastewater or model melanoidin. Thus, this study aimed to determine the efficiency of different combinations of AOPs, namely UV/O_3, UV/H_2O_2 and H_2O_2/O_3, for organic matter and color removal from molasses-based ethanol distillery wastewater at different pH levels, initial COD levels and H2O2 dosage. Further, this study aimed to determine the rate equation that best describes the AOP combinations.

2. Materials and methods

Batch AOP experiments (UV/O_3, UV/H_2O_2 and H_2O_2/O_3) were carried out using the experimental setup shown in fig. 1. The reactor was a 3-L plexiglass column having (i) a submersible UV lamp (23-in. length, 1.75 in. diameter, 253.7 nm, 15-W UV-C output) mounted in vertical axial position; (ii) ozone supplied through a diffuser at the bottom of the reactor; and (iii) magnetic stirrer at the bottom. The gases from the reactor were bubbled through two flasks of 2% KI solutions to destroy and measure residual ozone.
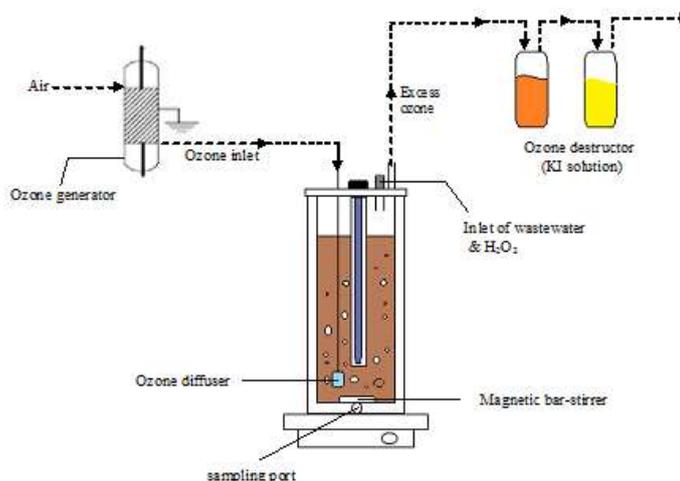

Figure 1: Schematic diagram of the experimental setup

The wastewater used in the experiment was taken from a local distillery plant, where wastewater comes from the sugarcane molasses based fermentation broth, bottom product spillages and equipment washings. It has 90,875 mg/L average total COD, 582 mg/L total N, 400 mg/L dissolved organic N, 181 mg/L ammonium-N, 127,630 PCU color level and 4.3 – 4.5 pH level.

Several runs were done at varying initial wastewater COD level (500, 100, 20 times dilution of distillery wastewater), H2O2 dosage (250, 500 and 1000 ppm) and pH levels (7 and 10). The H2O2 used was 33% (Sigma-Aldrich). The initial pH level was set using either 0.1 M NaOH or 0.1M H_2SO_4. The volume of the wastewater was 2 L per batch. During 120 minutes oxidation, samples of the wastewater were taken for pH, COD and color monitoring. The amount of residual ozone was measured using iodometric titration of the KI solution before and after a set time interval.

The COD of the samples were analyzed using the standard closed reflux method (APHA, 1998). Dissolved chemical oxygen demand (DCOD) was determined using filtered (0.45 µm) samples. To address interference by excess H_2O_2, the latter was determined through iodometric titration (Kingzett method). The COD values corresponding to the amount of excess H_2O_2 were

determined from the generated H_2O_2-COD curve, which is then subtracted from the measured COD of the samples from H_2O_2 – treated wastewater. The characteristic color intensity was recorded in platinum cobalt units (pcu). Color intensity of the wastewater was measured at 420 nm. Total kjeldahl nitrogen (TKN), dissolved organic-N (DON) and total ammonium-nitrogen (NH_4-N) levels were determined using standard methods (APHA, 1998). The amount of residual ozone in the effluent gas mixture was measured iodometrically according to standard methods. The reactor system was connected with two consecutive flasks where each contains 2% KI solution. Samples from each flasks were acidified using 0.1N sulfuric acid and was then titrated using 0.1 N of sodium thiosulfate solution.

3.   Results and discussion
Single vs. Combined AOPs for distillery wastewater treatment
At initial COD (COD_0) of 1000 mg/L and initial pH 4.8, UV alone showed no significant decrease in color and COD, no change in pH. Ozone alone at the same COD_0 and pH conditions, 49% color and 12% total COD was removed. pH level from 4.8 to 4.5. Of the ozone supplied to the system, 65% was consumed in the reactor and about 5.6 mg of COD is removed per mg of ozone consumed.

UV/O_3 Treatment
At ca. 1000 mg/L COD_0 but varying initial pH (4.8, 7 and 10). The slowest DCOD and TCOD decrease are at pH 7. At the first 50 minutes, fastest TCOD decrease (ca. 15%) at pH 4.8 while fastest DCOD decrease (ca. 22%) at pH 10. About the same 75% color decreased in 50 minutes for pH 4.8, 7 and 10. UV/O3 treatment is better than UV or ozone treatment alone. The g ozone consumed/g ozone supplied was highest at pH 4.8 (0.822) but the g COD removed/g ozone consumed was highest at pH 10 (0.996). In effect, the g COD removed per g O3 supplied was a bit higher at pH 10 than at pH 4.8 (0.759 vs. 0.693). There were slower percent TCOD, DCOD and color removal rates at higher concentrations. Both the g ozone consumed/g ozone supplied and the g COD removed/g ozone consumed were highest at initial COD of 4625 mg/L (0.869 and 1.569, respectively). The g COD removed per g O3 supplied was 1.364 at this initial COD level, which is much higher than those of lower initial COD levels.

UV/H_2O_2 Treatment
For COD_0 of 1000 mg/L and initial pH of ca. 4.9, COD/COD_0 decrease with time at different initial H_2O_2 levels were similar and the color/(initial color level) decreased at fastest rate at 1000 mg/L initial H_2O_2. At varying initial pH levels (1000 mg/L COD_0; 500 mg/L H_2O_2), the COD/COD_0 and the $(H_2O_2)/(H_2O_2)0$ had the similar decrease in time but the color/(initial color) decrease was fastest at pH 4.9 and 10 than at ca. 7. At varying initial COD levels (500 mg/L H_2O_2), the COD/COD_0 had a faster decrease at the lowest concentration in the series (270 mg/L) vs. those of 1048 and 8778 mg/L initial COD. The $(H_2O_2)/(H_2O_2)0$ had similar trend as COD and color. The g COD removed per g H_2O_2 supplied (3.926) was best at the highest COD level in the series (8778 mg/L).
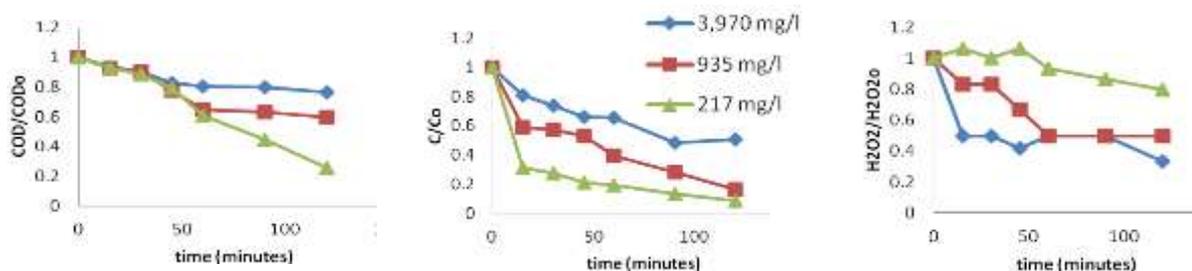
H_2O_2 /O3 Treatment

Figure 2: H_2O_2/O_3 treatment of distillery wastewater at varying initial wastewater concentration (initial H_2O_2 concentration: 500 mg/L; $H_2O_2/O_3 = 0.8$; without initial pH adjustment): Significant differences for both Color and H_2O_2 consumption plot ($p<0.05$), none for COD.
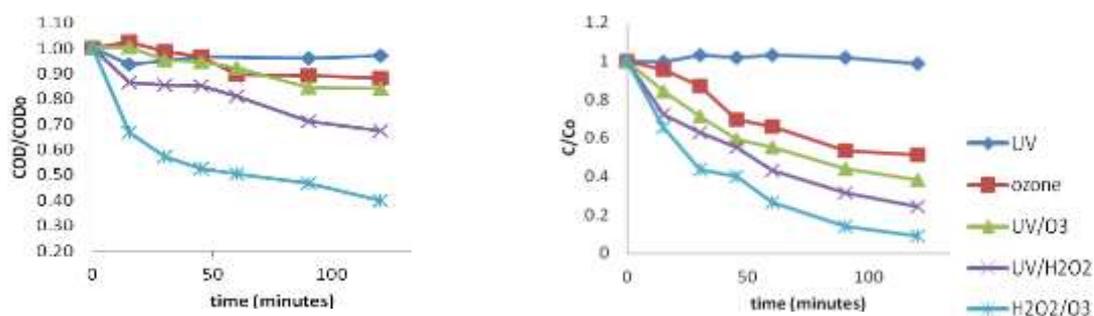
Figure 3: COD and color profile of various advanced oxidation treatment of distillery wastewater (initial COD ~1000 mg/L; initial H_2O_2 concentration ~1,000 mg/L; without initial pH adjustment)

Table 1: COD removed and H_2O_2 & ozone consumed after 2 h H_2O_2/O_3 treatment

Initial pH of wastewater	Initial COD (mg/L)	H_2O_2 level (mg/L)	g H_2O_2 consumed	g ozone consumed	mg COD removed	g COD removed /(g H2O2+O3)
4.6	800	500	0.510	0.308	385.5	0.471
7.7	800	500	0.170	0.366	152.0	0.284
10.9	800	500	0.850	0.472	167.4	0.127
5.7	217	500	0.255	0.0372	160.3	0.549
4.6	935	500	0.510	0.3084	385.47	0.471
4.8	3,970	500	1.914	0.4524	947.67	0.401
4.5	1000	250	0.340	0.377	210.8	0.311
4.6	1000	500	0.510	0.308	385.5	0.471
4.7	1000	1000	0.680	0.306	566.7	0.575

H_2O_2/O_3 Treatment

As in other AOP combinations, pH decreased with time during treatment indicating that acids are probably produced. The greatest pH decrease (4.7 to 4.4) was that at initial H_2O_2 of 1000 mg/L (same initial COD 1,000 mg/L). At the same COD_0 (1000 mg/L), the COD/COD_0 and the color/(initial color) (C/Co) both decreased faster at higher H_2O_2 dose (1000 mg/L) that at 500 and 250 initial H_2O_2 levels. At varying initial pH (800 mg/L COD_0; 500 mg/L initial H_2O_2), the COD/COD_0 decreased faster at pH 4.6 and 10.7 that at 7.7. There were no significant differences among C/Co at varying pH levels. At same initial H_2O_2 (500 mg/L) but varying COD_0, the C/Co and the decrease was faster at lower COD_0 (217 mg/L) than at 3970 mg/L COD_0 (Fig. 2) The COD/COD_0 vs. time trends were similar at varying COD_0. The g COD removed per g $H_2O_2 + O_3$ was best (0.575) at 1,000 mg/L H_2O_2 and 1000 mg/L COD_0. Next to this was at 500 mg/L H_2O_2 and 217 mg/L COD_0.

Kinetics of Combined AOPs

Overall, the COD decrease with time follows second order reaction, while the decrease In color level with time follows first order kinetics.

4. Conclusions

The percentage COD and color removal were better in combined AOPs (UV/H_2O_2 and H_2O_2/O_3) compared to single AOPs (Fig. 2). However the ratio of oxidant (H_2O_2 or O_3) to the COD level need to be optimized further in order o achieve the best COD and color removal per unit amount of oxidant. In some combinations of COD and oxidant dosage, color or COD decrease was better at pH 4 or ca. pH 10 that those of pH 7.

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