original article

Advanced oxidation treatment of composting leachate of municipal solid waste by ozone-hydrogen peroxide

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ABSTRACT

Aims: This research was conducted to investigate the efficacy and feasibility of ozone-hydrogen peroxide advanced oxidation process as a post-treatment step of composting leachate treated by an anaerobic migrating blanket reactor biological treatment system.

Materials and Methods: Leachate samples was collected from the effluent of the biological treatment system and used in an ozone reactor after dilution. The effectiveness of the pH values (4.5-11.5), H_2O_2 concentrations (0.5-4 g/L), ozone doses (0.2-1 g/h) and reaction times (5-270 min) were evaluated to determine optimum operational conditions.

Results: The highest removal efficiencies were achieved 72% and 79% for chemical oxygen demand (COD) and biochemical oxygen demand$_5$ (BOD_5), respectively, at pH 8.5, 2.5 g/L H_2O_2 concentration, and 1 g/h ozone dose, during 270 min reaction time. Furthermore, results indicated that the BOD_5/COD ratio was decreased from 0.53 to 0.4 after 270 min reaction time.

Conclusions: The O_3/H_2O_2 was found to oxidize preferably COD and BOD_5 of the leachate samples. In consequence, a decrease in the biodegradability of leachate was observed after oxidation treatment. The O_3/H_2O_2 reaction proved to be a feasible technique for the oxidation of the leachate under study, and it can be considered a suitable treatment for this type of wastewater.

Key words: Biochemical oxygen demand$_5$ removal, chemical oxygen demand removal, composting leachate, O_3/H_2O_2 reaction

INTRODUCTION

Solid waste management has become one of the most significant problems in developed countries. In recent years, the international policy on management of organic wastes has been increasingly directed toward recycling.[1,2] The main goal of solid waste management is to divert the greatest amount of solid waste from landfills through source reduction, material reuse, recycling, business development, and composting.[3] Composting is increasingly used world-wide as a means of waste management to convert organic wastes to an organic

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fertilizer known as compost.[4,5] In Europe, huge amounts of organic municipal solid wastes and sludge are managed in composting facilities where these materials are processed.[1] One of the main problems associated with composting is the formation of leachate which contains any material that was extracted, suspended or dissolved in the compost pile.[6] Among chemical processes the advanced oxidation processes (AOPs) have been considered an attractive means to eliminate color, reduce the organic load or toxicity of different waters and wastewaters.[7,8] AOPs are based on the generation of hydroxyl free radicals to enhance a high degradation rate of organics in an aqueous system. Among AOPs the O_3/H_2O_2 process has been efficiently used as a chemical process for wastewater treatment and pre-treatment.[9] A wide variety of O_3/H_2O_2 applications have been reported, such as degradation of persistent organic pollutant in water,[10] oxidation of pharmaceuticals in wastewater,[11] de-colorization of textile dye in water,[12] removal of organic matter from water,[9] or degradation of pesticides from aqueous solutions.[13] Among them, applications of O_3/H_2O_2 for the treatment of leachates have been recently reported and different conditions for these processes have been studied.[8] Tizaoui *et al*. obtained 27% and 87% removal rates for COD and color, respectively, during the ozonation of leachate.[14] Hagman *et al*. obtained a 22% COD reduction.[15] Rivas *et al*. achieved a 30% reduction in COD.[16] Using hydrogen peroxide (H_2O_2) in advanced oxidation during the ozonation process, Tizaoui *et al*. reported 27% COD removal, whereas Hagman *et al*. achieved a COD removal rate ranging from 22% (ozone alone) to 50%.[14,15] Goi *et al*. achieved a COD removal rate ranging from 24% to 41% at varying pH values of 4.5-11, respectively.[17] Cassano *et al*. applied the biological pre-treatment of medium-age leachate with and without ozone, followed by photo-Fenton treatment, to reduce the operation cost and toxicity to the effluent.[18] However, these results have been obtained with landfill leachate, which are inherently different from composting leachate due to the aerobic conditions of the process and the use of "fresh" and "young" wastes. As we know, there are few studies published on the use of the O_3/H_2O_2 for the treatment of leachates from composting processes. Therefore, the objective of this paper is to study the utilization of the O_3/H_2O_2 for the treatment of leachate from the municipal solid waste composting site after treating by a biological process. The efficiency of this process is evaluated in terms of variations of the COD, BOD_5 and BOD_5/COD ratio after O_3/H_2O_2 treatment.

MATERIALS AND METHODS

Leachate samples

In this study, the leachate samples were collected from the effluent of an anaerobic migrating blanket reactor (AMBR) treatment system that was operating in pilot scale for treatment of the composting leachate from the Isfahan municipal solid waste composting site, a central province in Iran. Samples were used to apply into the O_3/H_2O_2 process after dilution. Characterizations of the leachate used in the O_3/H_2O_2 process are shown in Table 1.

Experimental setup and procedures

The ozone reactor was a closed cylindrical plexiglass vessel with a height of 100 cm and an inner diameter of 8 cm. Ozone was generated using an ozone generator (O & W (OWA-1000) — China) and was continuously introduced into a column through a diffuser placed at the bottom. In the each experimental run, 1 l of diluted leachate was treated in batch system. A stirrer (Labinco-90-402) was used during the process to provide adequate mixing. Ozone in the off-gas was converted to oxygen using the KI solution. The gas flow rate was 6.4 L/min and the input ozone concentration was about 1 g/h.

In the ozone experiments, the leachate samples from the effluent of AMBR process was used in the ozone reactor. To determine the optimum conditions, four-stage experiments were applied:

1. In the constant concentration of the H_2O_2 (1 g/L), ozone dose (1 g/h) and reaction time (30 min), the initial pH of the leachate was gradually adjusted from 4.511.5 using 1 N sulfuric acid and sodium hydroxide solution.
2. Based on the optimum value of pH, several concentrations of H_2O_2 (0.5-4 g/L) were immediately added into the ozone reactor before each run to achieve the highest performance concentration for the treatment. Reaction time and ozone dose was constant as before.
3. At the next stage and based on the optimum pH value and H_2O_2 concentration, the ozone dose was variable from 0.2 to 1 g/h to determine the optimum dosage.
4. Finally, ozonation was done in the optimum conditions of the whole variables (pH, H_2O_2 and ozone) at 10 times (5-270 min) for the efficiencies of COD and BOD_5 removal.

Material and analysis

Hydrogen peroxide (30%, w/w) had analytical reagent grade (Merck, Germany). The double distilled water was used to prepare experimental solution. The pH was adjusted to desired values with 1 N H_2SO_4 and 1 N NaOH and was measured by a pH-meter (Metrohm Herisau-E520). Also, COD and other analysis were conducted in accordance with the standard methods.[19] BOD_5 was measured using the respirometric method by measuring oxygen pressure

Table 1: Characterization of leachate from AMBR process effluent

Parameter	AMBR process effluent
COD (g/L)	40.1 ± 7.1
BOD_5 (g/L)	22.2 ± 3.7
Ratio BOD_5/COD	0.55
pH	7.57 ± 0.28
Electrical conductivity (mS/cm)	14.85 ± 1.65
Color	Black

AMBR: Anaerobic migrating blanket reactor, COD: Chemical oxygen demand, BOD: Biochemical oxygen demand

decrease using Oxitop bottles (WTW IS 6). It is important to note that during this work, since acidic and alkaline pH can affect microbial activity, BOD_5 measurements were done after neutralizing the pH of the sample, as recommended in standard methods.[19] All experiments were carried out at room temperature in triplicate and the results were reported as average ± standard deviation.

RESULTS

Leachate characterization

The characterization of leachate from the effluent of AMBR processes is shown in Table 1. As shown, the leachate from the AMBR presented a very high level of COD and BOD_5, whereas the ratio of BOD_5/COD was around 0.55, which corresponded to a high level of biodegradability of the organic matter.

Effect of pH

In the current study, the effect of initial pH variation was examined to determine the optimal pH during the O_3/H_2O_2. By increasing pH value to 8.5, maximum removal of COD and BOD_5 was observed 28% and 35%, respectively. The removal efficiencies of the target parameters were decreased and remained almost unchanged at pH values exceeding 8.5 [Figure 1]. Pearson correlation test showed a direct linear relationship between pH values and efficiency of COD ($P < 0.05, r = 0.729$) and BOD_5 ($P < 0.05, r = 0.783$) removal.

Effect of H_2O_2

Effect of different H_2O_2 concentrations at eight values from 0.5 to 4 g/L was evaluated on ozonation efficiency. Figure 2 shows the dependence of COD and BOD_5 degradation on H_2O_2 concentration with 1 g/h O_3 and 30 min reaction time at pH 8.5. Results obviously indicated that removal efficiency was significantly influenced by H_2O_2 concentration. The maximum degradation of COD and BOD_5 were 37 and 48% in H_2O_2 concentration of 2.5 g/L, respectively. The further increase of the H_2O_2 concentration from 2.5 g/L slowed down the degradation rate of both COD and BOD_5. Furthermore, Pearson correlation test showed a direct linear relationship between H_2O_2 concentrations and efficiency of BOD_5 removal ($P < 0.05$, $r = 0.667$). This test also showed an inverse relationship between H_2O_2 concentrations and COD removal that was not significant ($P > 0.05$, $r = -0.517$).

Ozone dose and reaction time

The effect of O_3 dose on COD and BOD_5 degradation was also investigated in the presence of optimum H_2O_2, pH 8.5 and constant reaction time. As shown in Figure 3, the removal percent of COD increased from 10, 13, 18, 25 and 35% when ozone dosage increased to 0.2, 0.4, 0.6, 0.8 and 1 g/h, respectively. BOD_5 also showed the same result and its removal efficiency increased from 11 to 46% when ozone increased from 0.2 to 1 g/h.

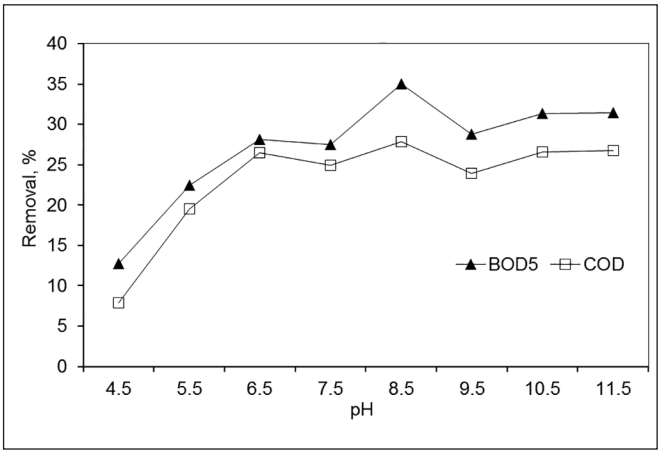

Figure 1: Effect of the initial pH on COD and BOD_5 removal during the ozonation processes. (H_2O_2 [1 g/L], O_3 [1 g/h] and reaction time [30 min])

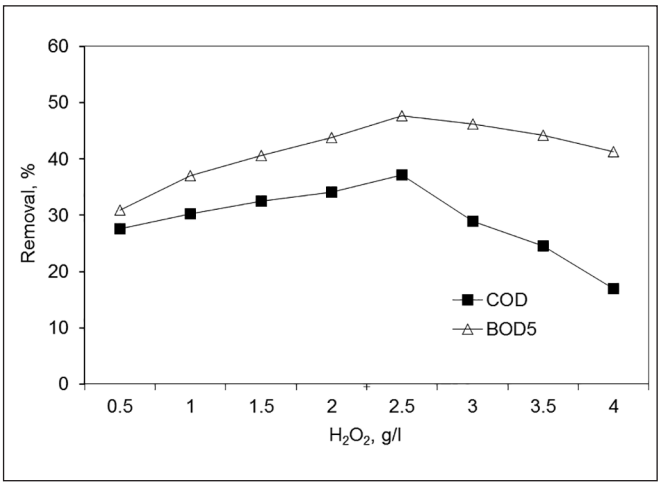

Figure 2: Effect of the initial H_2O_2 on COD and BOD_5 removal during the ozonation processes. (Solution pH [8.5], O_3 [1 g/h] and reaction time [30 min])

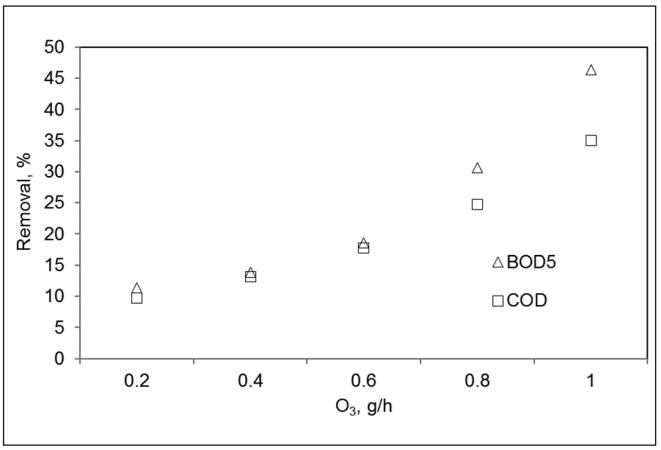

Figure 3: Effect of the O_3 dose on COD and BOD_5 removal during the ozonation processes. (Solution pH [8.5], H_2O_2 [2.5 g/L] and reaction time [30 min])

For investigation of the reaction time effectiveness on degradation efficiency during the O_3/H_2O_2 process, the experiment was conducted with different reaction times between 5 and 270 min at the optimum conditions of other parameters. Results showed that increase in reaction time could raise the removal efficiency. The maximum removals of COD and BOD_5 were 72% and 79% at 270 min, respectively, although increasing in the removal efficiency after 210 min was negligible [Figure 4]. The results from Pearson correlation test showed a direct linear relationship between reaction times and efficiency of BOD_5 ($P < 0.05$, $r = 0.972$) and COD removal ($P < 0.05$, $r = 0.974$).

BOD_5/COD ratio during ozonation

For untreated samples, BOD_5/COD ratio attains value of about 0.53 while O_3/H_2O_2 causes to reduce it to value near 0.4, after 270 min [Figure 5]. This ratio is higher than found in leachates from landfill, which usually present values of BOD_5/COD ratio around 0.1. Pearson correlation test also showed an inverse relationship between reaction times and BOD_5 to COD ratio that was not significant ($P > 0.05$, $r = -0.089$).

DISCUSSION

This study showed the O_3/H_2O_2 performance for treatment of municipal solid waste composting leachate. Our results demonstrated that the O_3/H_2O_2 process could adequately remove COD and BOD_5 from the leachate. In ozone treatment systems, the optimal pH values for the degradation of organic compounds have been revealed better results at elevated pH.[20,21] As shown in Figure 1, ozonation at high pH values is more efficient for leachate treatment. This phenomenon was also observed by Cortez *et al.*[20] The same study reported that increasing of pH could increase the COD removal during ozonation of leachate and COD removal was enhanced from 18 to 49% after ozonation at pH 5.5 and pH 11, respectively.[8]

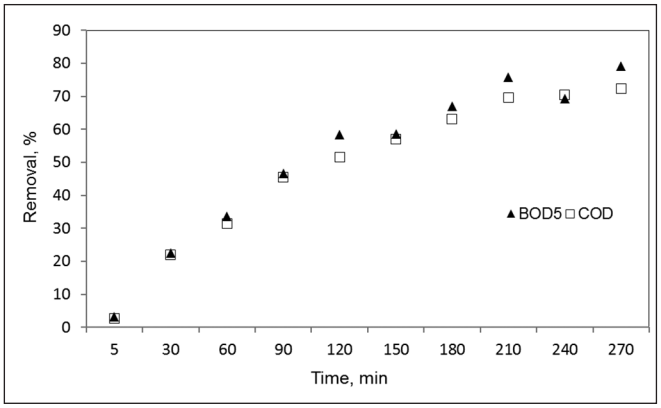

Figure 4: Effect of the reaction time on COD and BOD_5 removal during the ozonation processes. (Solution pH [8.5], H_2O_2 [2.5 g/L], O_3 [1 g/h])

Ozone decomposition into •OH radicals can be accelerated by H_2O_2 addition, which constitutes a beneficial factor.[11,21] Our results also showed that H_2O_2 could raise the removal rates although the further increase of the H_2O_2 concentration from 2.5 g/L showed lower degradation rate of both COD and BOD_5 [Figure 2]. Cortez *et al.*, have reported that the application of H_2O_2/O_3 enhanced the oxidation rate of the landfill leachate compared to ozone alone. their results showed that COD removal was enhanced from 27% with ozone only to 72% in the presence of ozone and 400 mg/L of hydrogen peroxide, at 5.6 g O_3/h and pH 7.[8] The initial increase in removal efficiency was due to the increased concentration of •OH formed by H_2O_2 and while when H_2O_2 concentration was too high, the excess amount of H_2O_2 will consume hydroxyl radical and inhibit the reaction followed equations 1, 2 and 3.[10]

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}OOH + H_2O \quad (1)$$

$$^{\bullet}OOH + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (2)$$

$$2{}^{\bullet}OH \rightarrow H_2O_2 \quad (3)$$

Some authors reported that when the applied hydrogen peroxide dose is above the optimum value, H_2O_2 acts as a radical scavenger and decreased the removal efficiency.[22,23] Results of Tizaoui *et al.*, suggested that concentrations of H_2O_2 at 2 g/L gave better performance than H_2O_2 at 6 g/L and COD removal was decreased from 46.6% to 40.1% when H_2O_2 increased to 6 g/L.[14]

It is reported that, O_3 can participate in the reaction process of •OH generation, therefore, more O_3 was added, more •OH radicals would be formed. As can be seen in Figure 3, both COD and BOD_5 degradation rate was enhanced when ozone dose increased. Since O_3 would not consume the generated •OH, thus the more O_3 introduced in the reaction solutions, the more •OH radicals would be generated, resulting in higher degradation.[24] Results demonstrated a phenomenal enhancement for COD and BOD_5 removal in maximum ozone dose of 1 g/h. In the study by Bila *et al.*,

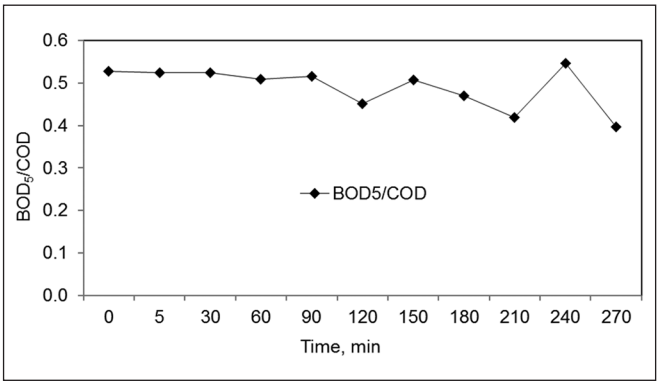

Figure 5: Variations in BOD_5/COD ratios during the ozonation processes. (Solution pH [8.5], H_2O_2 [2.5 g/L], O_3 [1 g/h])

on ozonation of a landfill leachate, results showed that the greater ozone concentration leaded to greater COD removal from the leachate and COD was decreased from 4000 mg/L to 1400 mg/L when the ozone dose was enhanced to 9 g/L.[25] In the other study by Cortez *et al.*, COD and TOC removal increased to 23% and 14%, respectively, after increasing O_3 concentration from 63 mg/L to 112 mg/L.[20]

Ozonation time is another critical factor to control of the oxidation. Increase of the ozonation time showed a better result on the COD and BOD_5 removal. This phenomenon can be related to more opportunity of the •OH radicals to practice. Many studies on leachate treatment with O_3/H_2O_2 have shown the same results.[8,20] Results from a study on landfill leachate treatment with ozone and O_3/H_2O_2 showed that COD removal increased from 25 to 40 and 45% after 20, 40 and 60 min reaction time, respectively.[14]

Leachate from the AMBR effluent presented a very high level of COD, BOD_5 and BOD_5/COD ratio which corresponded to a high level of biodegradability of the leachate. Figure 5 shows that O_3/H_2O_2 decreased this ratio to 0.4 after 270 min. Results from Trujillo *et al.*, showed that the BOD_5/COD ratio was decreased during the leachate composting treatment by Fenton reaction.[1] Most studies on landfill leachate treatment with AOPs have shown the invers results with our study. In these studies, BOD_5/COD ratios were enhanced after ozonation that indicate the oxidation processes can break down or rearrange molecular structures of organic matter and convert the non-biodegradable organics to more biodegradable forms.[8,23,26] One possible explanation for this fact is that composting leachates consist of particulate and dissolved organic matter from fresh and young wastes instead of landfill leachate that is a mixture of different aged materials.[1] The high level of BOD_5 (in the case of effluent from the AMBR process) indicates that a significant amount of particulate organic matter is also degradable.

CONCLUSIONS

The results of the present study have clearly delineated that ozonation combined with H_2O_2 provides a promising technique for the treatment of composting leachate. Results revealed that pH control was essential to obtain efficient COD and BOD_5 removal in the O_3/H_2O_2. The optimal pH for O_3/H_2O_2 was found at pH 8.5. Furthermore, the O_3/H_2O_2 system is significantly affected by H_2O_2 and O_3 concentration and it is necessary to obtain the optimal concentration. Ozonation was found to oxidize preferably COD and BOD_5 of the leachate, resulting in a significant reduction of the BOD_5/COD ratio. The use of O_3/H_2O_2 reaction, given the high biodegradability of composting leachate, can be proposed as a post-treatment after biological treatment to treat remained slowly biodegradable COD. The resulting effluent may be treated in a municipal wastewater treatment plant or by further treatment systems.

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