**PERFORMANCE OF COMBINED OZONE AND FENTON PROCESS IN TREATING DIFFERENT LEACHATE CONCENTRATIONS**

Hamidi Abdul Aziz¹, Salem S. Abu Amr²

**Abstract.** **Background:** Leachate pollution is one of the main problems in landfilling, and researchers have yet to find an effective solution to this problem. The technology that can be used may differ based on the type of leachate produced. The most problematic parameters in leachate are chemical oxygen demand (COD), ammonia, and color. **Material and Methods:** The performance of ozone/Fenton in advanced oxidation process (AOPs) in treating stabilized leachate was investigated. The optimal dosages of Fenton reagent (0.05 mol L⁻¹ (1,700 mg/L) H₂O₂ and 0.05 mol L⁻¹ (2,800 mg/L) Fe²⁺) were determined through preliminary experiments and added to the leachate sample into the ozone reactor. The input ozone concentration in a 2 L leachate sample was 80 g/m³ NTP ± 0.5% under 1 bar pressure. The initial COD varied between 250 and 2360 mg/L, color varied between 470 Pt. Co. to 4530 Pt. Co., and NH₃-N varied between 150 mg/l to 1170 mg/L.

**Results:** The maximum removal efficiency was 87% for COD, 100% for color, and 22% for NH₃–N at lowest leachate concentration. The lowest amount of consumed ozone (1.28 KgO₃/Kg COD) corresponded to the initial concentration of COD (2000 mg/L) with 60% removal of COD during 1 h ozonation. The biodegradability (BOD5/COD) improved from 0.09 in raw leachate to 0.27 at 500 mg/L initial COD. **Conclusion:** The current study revealed that the use of ozone/Fenton (O₃/H₂O₂/Fe²⁺) in AOPs is more efficient in removing COD and color in low concentrations of semi-aerobic stabilized leachate and in improving biodegradability.

**Keywords:** Ozonation, Advanced oxidation, Initial concentration, Stabilized leachate, Biodegradability

1. Introduction

Sanitary landfilling is the most common and desirable method for controlling urban solid waste. It is also considered the most economical and environmentally acceptable method for eliminating and disposing municipal and industrial solid wastes (Tengrui et al. 2007). However, sanitary landfills are also prone to polluting the immediate environment. Landfill leachate is the liquid that has seeped through solid waste in a landfill, gaining extracted, dissolved, or suspended materials in the process (Christensen et al. 2001). Landfill leachate is a potentially polluting liquid unless returned to the environment in a carefully controlled manner (Scottish Environment Protection Agency, SEPA 2003). Leachate contains high amounts of organic compounds, ammonia, heavy metals, a complex variety of materials, and other hazardous chemicals, and is recognized as a potential source of ground and surface water contamination (Schrab et al.

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Old (Stabilized) leachate characterized as a very low biodegradability which is difficult to biologically proceeds. The variation of biodegradability (BOD5/COD) in leachate was attributed to the different types of leachate that were classified based on landfill age and leachate decomposition. The BOD5/COD ratio in young (<5 years), intermediate (5–10 years), and stabilized (>10 years) leachate was reported as >0.3, 0.1–0.3, and <0.1, respectively (Schiopu et al., 2010; Naumczyk et al. 2012).

Treatment of these leachates in classical wastewater treatment plants is rarely practiced due to the nature and high levels of pollutants present in them (i.e. high COD and ammonia and low biodegradability). Researchers throughout the world are still searching for a total solution to leachate problem. To date, multiple stage treatments are required to remove simultaneously pollution from leachate. In literatures, different physiochemical and biological treatment applications on leachate treatment have been reported such as; Fenton, photo-Fenton, electro-Fenton, coagulation, electro-coagulation, ozonation, adsorption, ion exchange, Persulfate and biological processes. (Aziz, et al., 2011; Bashir et al., 2011;Mohajeri et al., 2010a, b; Primo et al., 2008; Morravia et al., 2012;Ilhan et al., 2008; Tizaoui et al., 2007; Shabimam and Dikshit, 2012; Deng and Ezyske, 2011). There is no single method which could effectively remove all the pollutants simultaneously.

Ozone has recently received much attention in landfill leachate treatment technology due to its powerful chemical oxidant and high capacity for oxidation (Huang et al. 1993; Rice et al. 1997; SEPA 2003; Wu et al. 2004). Several applications of ozone on landfill leachate treatment have been conducted (Tizaoui et al. 2007), obtaining 27% and 87% removal for chemical oxygen demand (COD) and color, respectively, during the ozonation of leachate. Hagman et al. (2008) obtained 22% COD reduction. Rivas et al. (2003) conducted 30% depletion of COD.

Although ozone is effective in stabilized leachate treatment, its effectiveness will be improved using advance oxidant materials and techniques. By employing hydrogen peroxide in advanced oxidation during the ozonation process, Tizaoui et al. (2007) obtained a COD removal of 50%, whereas Hagman et al. (2008) obtained a COD removal from 22% (ozone alone) to 50%. Goi et al. (2009) obtained a COD removal from 24% to 41% at varying pH from 4.5 to 11, respectively. Ozonation and Fenton are now being used increasingly in landfill leachate treatment. These processes are generally applied as pre-treatment (Gau and Chang 1996; Geenens et al. 2000; Haapea et al. 2002; Kamenev et al. 2002; Fang et al. 2005; Goi et al. 2009; Cortez et al. 2010) or post-treatment (Iaconi et al. 2006; Vilar et al. 2006; Goi et al. 2009) stages in the consequence of improving the efficiency of the treatment. Recently, Abu Amr and Hamidi (2012) improved COD removal efficiency from 15% used ozone alone to 65% used Ozone/Fenton in AOPs. However, the performance of this new process in different initial leachate concentrations has not been investigated. Furthermore, the effectiveness of Ozone/Fenton process in enhance biodegradability of stabilized leachate was not well documented. In the present study, a new treatment process (O₃/H₂O₂/Fe²⁺) was introduced by employing the Fenton reagent in the advanced oxidation process for the treatment of stabilized solid waste leachate by ozone as one treatment stage. The main objective of the present study is to investigate the performance of employing Ozone/Fenton reagent in advanced oxidation in treating different concentrations of semi-aerobic stabilized leachate.
2. Materials and methods

2.1. Leachate sampling and characteristics

Leachate samples were collected from a leachate aeration pond of a semi-aerobic stabilized landfill leachate at Pulau Burun Landfill Site (PBLS), Byram Forest Reserve in Penang, Malaysia. PBLS has an area of 62.4 ha, of which 33 ha are currently operational and receive about 2200 t of municipal solid waste daily. It is equipped with a natural marine clay liner and three leachate collection ponds (Bashir et al. 2011). On March 14 and June 17, 2011, approximately 20 L of leachate was collected manually and placed in plastic containers. The samples were transported immediately to the laboratory, characterized, and cooled at 4 °C to minimize the biological and chemical reactions. The average characteristics of the leachate used in the experiments are summarized in Table 1. Sample collection and preservation were done in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA), 2005.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>2360</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>70</td>
</tr>
<tr>
<td>NH₃-N (mg/L)</td>
<td>1170</td>
</tr>
<tr>
<td>Color (PT Co.)</td>
<td>4530</td>
</tr>
<tr>
<td>pH</td>
<td>8.5</td>
</tr>
<tr>
<td>Suspended solids (mg/L)</td>
<td>197</td>
</tr>
<tr>
<td>Conductivity, μS/cm</td>
<td>17,880</td>
</tr>
</tbody>
</table>

2.2. Experimental procedures

All experiments were carried out in a 2 L sample using an ozone reactor with height of 65 cm and inner diameter of 16.5 cm, supported by a cross column ozone chamber for enhancing ozone gas diffusion (Figure 1). Ozone was produced by a BMT 803 generator (BMT Messtechnik, Germany) fed with pure dry oxygen with the recommended gas flow rate of 200 ml/min ±10%. Input ozone concentration was 80 g/m³ NTP ± 0.5% under 1 bar pressure. Gas ozone concentration (in g/m³ NTP) was measured by an ultraviolet gas ozone analyzer (BMT 964). The water bath and cooling system <15 °C supported the ozone reactor. Fenton reagent (H₂O₂/Fe²⁺) was employed in advanced oxidation during the ozonation of stabilized leachate. Hydrogen peroxide (H₂O₂, 30%) and ferrous sulfate heptahydrate (Fe₂SO₄·7H₂O, 278.02 g/mol) were used in preparing the Fenton reagent, and then added to the leachate sample into the ozone reactor. The optimal dosage of Fenton reagent (0.05 mol L⁻¹ (1,700 mg/L) H₂O₂ and 0.05 mol L⁻¹ (2,800 mg/L) Fe²⁺) and 60 min ozonation at pH 7 were obtained through a set of preliminary experiments as follow: Fenton reagent (H₂O₂/Fe²⁺; with molar ratios of 0.5, 1, 2, 3, 4, 5, and 6) and 0.01 mol ferrous sulfate (Mohajeri et al., 2010) were immediately added into an ozone reactor before each run to achieve the highest performance ratio for the treatment of stabilized leachate. Molar dosages of Fenton reagent were gradually added while maintaining the optimal molar ratio (1:1 obtained from previous step) to determine the optimum dosage for the efficiencies of COD, color, and NH₃–N removal. Based on the optimum molar dosage of Fenton reagent, the initial pH of the leachate was gradually adjusted from 2 to 11 using 5 M sulfuric acid solution and 5 M...
sodium hydroxide solution. The reaction time was examined from 10 min to 180 min at the optimal pH value (7) Abu Amr and Aziz, (2012). Four each run, pH was adjusted after added Fenton reagent in to the sample immediately.

Different concentrations of leachate were used during the ozonation experiments. The initial COD varied between 250 and 2360 mg/L, the color varied between 470 Pt. Co. to 4530 Pt. Co., and NH$_3$-N varied between 150 mg/l to 1170 mg/l. The leachate concentrations were adjusted using the following equation (1):

$$C_1V_1 = C_2V_2$$  \hspace{1cm} (1)

where $C_1$ is the original concentration of COD before it was watered down or diluted, $C_2$ denotes the final COD concentration after dilution, $V_1$ is the volume to be diluted, and $V_2$ represents the final sample volume after dilution.

**Figure 1.** Schematic diagram of ozone equipment and experiments procedures.

### 2.3. Analytical Methods

COD, color, NH$_3$-N, and pH were tested immediately before and after each run of the experiments in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA 2005). The concentration of NH$_3$-N was measured by the Nessler Method using HACH DR 2500 spectrophotometer, whereas pH was measured by a portable digital pH/Mv meter. COD concentration was determined by the closed reflux colorimetric method using DR2800 HACH spectrophotometer. Color concentration was measured using DR 2800 HACH spectrophotometer. BOD$_5$ was measured according to Standard Methods (APHA 2005). The removal efficiency of COD, color, and ammonia were obtained using the following equation:
Removal (%) = \left[ \frac{C_i - C_f}{C_i} \right] \times 100 \quad (2)

where \( C_i \) and \( C_f \) are the initial and final COD, color and ammonia concentrations, respectively.

3. Results and Discussion

3.1. Treatment efficiency

To investigate the efficiency of employing ozone/Fenton in the advanced oxidation process for different concentrations of stabilized leachate treatment, a set of experiments with different initial COD concentrations were achieved in the ozone reactor by adding optimal Fenton dosage (0.05 mol L\(^{-1}\) (1,700 mg/L) \( \text{H}_2\text{O}_2 \) and 0.05 mol L\(^{-1}\) (2,800 mg/L) \( \text{Fe}^{2+} \)) at pH 7. Fenton is used for improving the oxidation potential during ozonation. The initial COD varies between 250 and 2360 mg/l. Figure 2 illustrates the removal efficiency of COD at different initial COD of stabilized leachate.

\[
\text{Figure 2. Effects of Initial COD concentration on removal of COD by Ozone/Fenton in the advanced oxidation process (O}_3 = 80, \text{H}_2\text{O}_2 = 1700 \text{mg/l, Fe}^{2+} = 2800 \text{mg/l, pH= 8.3, RT= 60 min).}
\]

In the \( \text{O}_3/\text{H}_2\text{O}_2/\text{Fe}^{2+} \) system, the Fenton ions reacted with \( \text{H}_2\text{O}_2 \), resulting in the formation of hydroxyl radicals (\( \cdot\text{OH} \)) (Equation 3). \( \cdot\text{OH} \) has the potential to destroy and degrade organic pollutants (Hermosilla et al. 2009).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \quad (3)
\]

The reaction of ozone with \( \text{H}_2\text{O}_2 \) generates \( \cdot\text{OH} \) radicals. \( \text{H}_2\text{O}_2 \) is also dissolved in water and dissociates into the hydroperoxide ion (\( \text{HO}_2^- \)), which rapidly reacts with ozone to initiate a radical chain mechanism that generates hydroxyl radicals (Staehelin et al. 1982; Glaze et al. 1987), as demonstrated in Equations 4 and 5.
The removal efficiency ranged from 60% to 87%, whereas the maximum removal corresponded with the lowest initial COD concentration (250 mg/l). For color removal, the treatment efficiency was much better, which ranged between 95% and 100% (Figure 3). As shown in Figure 3, the total removal of color was obtained at less than 750 mg/l initial COD. However, the removal efficiencies of COD and color were more efficient at initial COD less than 1500 mg/l. The reaction of ozone with hydrogen peroxide gives rise to •OH radicals. H₂O₂ is also dissolved in water and dissociates into a hydro peroxide ion (HO₂⁻), which reacts rapidly with ozone to initiate a radical chain mechanism that leads to hydroxyl radicals (Staehelin et al., 1982; Glaze et al., 1987).

Several studies have been conducted on leachate treatment using ozone-based advanced oxidation processes (AOPs). Tizaoui et al. (2007) obtained 50% and 87% removal efficiency of COD and color, respectively, using H₂O₂ as advanced oxidation during the ozonation of stabilized leachate. Nevertheless, the removal efficiency of ammonia by system O₃/H₂O₂/Fe²⁺ is relatively low, which ranged from 12% to 22% at different initial concentrations of ammonia (150 mg/l to 1170 mg/l) (Figure 4).

Ammonia removal has become an important concern in leachate treatment, the latest development regarding the pollution control from solid waste transfer station and landfill in Malaysia reported NH₃–N as one of the parameters included in the standard discharge limits for pollutants in landfill leachate. The existence of high level of NH₃–N in landfill leachate over a long period of time is one of the most important problems routinely faced by landfill operators. The acceptable discharge limit according to Regulations 2009, Malaysian Environmental Quality Act 1974 [Act 127] was 5 mg/L. Nevertheless, the removal efficiency of ammonia by the O₃/H₂O₂/Fe²⁺ system was relatively low. The removal of ammonia is attributed to the contribution of sulfate at high pH (8–9) during the reaction process, given that ferrous sulfate (Fe₂SO₄) is a part of the Fenton reagent. Deng and Ezyske (2011) achieved 100% ammonia removal using a sulfate radical in the advanced oxidation of mature leachate at pH 8.3.
Figure 3. Effects of Initial Color concentration on removal of Color by Ozone/Fenton in the advanced oxidation process (O$_3$ = 80, H$_2$O$_2$ = 1700 mg/l, Fe$^{2+}$ = 2800 mg/l, pH= 8.3, RT= 60 min).

Figure 4. Effects of Initial NH$_3$-N concentration on removal of NH$_3$-N by Ozone/Fenton in the advanced oxidation process (O$_3$ = 80, H$_2$O$_2$ = 1700 mg/l, Fe$^{2+}$ = 2800 mg/l, pH= 8.3, RT= 60 min).

To evaluate the treatment efficiency of the combined ozone/Fenton system (Simultaneously) with other applications, three treatment processes for stabilized landfill leachate were performed, namely, ozone alone, Fenton alone (separately), and Fenton as pretreatment followed by ozone as post-treatment (sequentially). Figure 5 shows that the efficiency of ozone alone is insufficient for the removal of COD, colour, and ammonia (15%, 44%, and 0%, respectively). Compared with that of other processes, these lower values are attributed to the high concentration of organics in leachate containing a considerable amount of dissolved ozone in the aqueous phase from the beginning of the reaction (Rivas et al., 2003). Thus, the Fenton reagent is more efficient for leachate treatment than O$_3$ alone. The performance of ozone after Fenton treatment is very low,
which is consistent with the results reported by Goi et al. (2009). The removal efficiency is also improved by the advanced oxidation system (O$_3$/H$_2$O$_2$/Fe$^{2+}$) to 78%, 98 %, and 22 % for COD, colour, and ammonia, respectively, under optimal conditions.

![Figure 5](image-url)

**Figure 5.** Comparing the performance of Fenton in advanced oxidation of ozone with other applications for the treatment of stabilized leachate.

### 3.2. Biodegradability

One of the major environmental problems for solid waste landfill-stabilized leachate is low in biodegradability. The performance of a system (O$_3$/H$_2$O$_2$/Fe$^{2+}$) in the advanced oxidation process (APOs) on biodegradability of stabilized leachate was evaluated. COD is a measure of oxidizable organic matter, whereas BOD$_5$ is a measure of biodegradable organic matter. The BOD$_5$/COD ratio is considered as a measure of biodegradability of organic matter and shows the maturity of landfill leachate, which typically decreases over time (Tchobanoglous et al. 1993; Qasim and Chiang 1994). BOD$_5$ measurements were performed before and after each ozonation process to assess the effect of initial COD concentration on biodegradability of stabilized leachate, and the results are presented in Figure 5. As shown in Figure 5, the BOD$_5$/COD ratio varied from 0.09 to 0.27. Generally, the ratio becomes higher by reducing the initial COD, especially when it is lower than 1500 mg/l. However, the highest ratio corresponds to 500 mg/l initial concentration of COD. The results in the current study proved that the system (O$_3$/H$_2$O$_2$/Fe$^{2+}$) in AOPs becomes more efficient in improving biodegradability in lower concentrations of semi-aerobic stabilized leachate. Several studies have exhibited improvement of biodegradability following treatment of leachate by ozone based on the AOPs. Tezaoui et al. (2007) obtained 0.7 improvement using O$_3$/H$_2$O$_2$. Bila et al. (2005) reported 0.3 improvements by conjunction ozone with physiochemical treatment and biological process.
3.2. Ozone consumption

Ozone consumption (OC) during oxidation process was calculated using Equation (6). The result is given in Table 2.

\[
OC = \frac{Q_G}{V} \times \int_0^t \left( 1 - \frac{C_{AG}}{C_{AG0}} \right) dt 
\]

where \( Q_G \) is gas flow rate, \( V \) is sample volume, \( C_{AG} \) is off-gas ozone concentration, \( C_{AG0} \) is input ozone concentration, \( t \) is time, and \( COD_0 \) and \( COD \) correspond to the initial and final COD, respectively (Tezoui et al. 2007).

Table 2 illustrates the OC after 60 min ozonation for different initial concentrations of stabilized leachate compared with COD removal efficiency. As shown in Table 2, the lowest OC value (1.28 KgO\(_3\)/Kg COD) corresponds to 60% removal efficiency of COD. Previous studies have reported OC values. Tizaue et al. (2007) and Wang et al. (2003) reported 1.5 and 16 kgO\(_3\)/kg COD using hydrogen peroxide as advanced oxidation, whereas approximately less than 1 kgO\(_3\)/kg COD was reported by Ho et al. (1974), and Abu Amr and Aziz (2012) obtained 0.63 kgO\(_3\)/kg COD.

Table 2. Ozone consumption during ozonation of different leachate concentration by Ozone/Fenton in the advanced oxidation process.

<table>
<thead>
<tr>
<th>Initial COD (mg/l)</th>
<th>COD 250</th>
<th>500</th>
<th>750</th>
<th>1000</th>
<th>1250</th>
<th>1500</th>
<th>1750</th>
<th>2000</th>
<th>2360</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/l)</td>
<td>35</td>
<td>85</td>
<td>143</td>
<td>228</td>
<td>346</td>
<td>533</td>
<td>670</td>
<td>930</td>
<td>950</td>
</tr>
<tr>
<td>OC (kgO(_3)/kgCOD)</td>
<td>3.8</td>
<td>2.6</td>
<td>1.8</td>
<td>1.75</td>
<td>1.5</td>
<td>1.47</td>
<td>1.3</td>
<td>1.28</td>
<td>1.3</td>
</tr>
</tbody>
</table>
4. Conclusion

In the present study, the performance of system ($O_3/H_2O_2/Fe^{2+}$) in the advanced oxidation for removing COD, color, and ammonia from different concentrations of semi-aerobic stabilized leachate was investigated. The initial COD varied between 250 and 2360 mg/L, color varied between 470 Pt. Co. to 4530 Pt. Co., and NH$_3$-N varied between 150 mg/l to 1170 mg/l. Accordingly, the removal efficiencies varied between 60% and 87% for COD, 95% to 100% for color, and 12% to 22% for NH$_3$–N. Ozone consumption for COD removal was calculated, and the lowest amount of consumed ozone (1.3 KgO$_3$/Kg COD) corresponded to the highest initial concentration of COD (2360 mg/L), with 60% removal of COD during 1 h ozonation. Moreover, the biodegradability (BOD$_5$/COD) ratio improved from 0.09 in raw leachate to 0.27 at 500 mg/L initial COD. Ozone/Fenton is an efficient method for stabilized leachate treatment and for improving biodegradability at natural pH, which suggests enhancement of the availability of applying biological treatment of leachate without pH adjustment of the effluent after ozonation.

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