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Evaluation and Optimization of Various Ozone – Based Advanced Oxidation Processes in the Treatment of Stabilized Landfill Leachate

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ABSTRACT

Background: Leachate pollution is one of the main problems in landfilling. Among the most problematic parameters in stabilized leachate are COD, ammonia, and color. The treatment technology that can be used may differ based on the type of leachate produced. Even after treatment, the effluent characteristics are always hard to comply with the discharge standard. **Objective:** The current study aimed to evaluate and compare the performance of the three treatment processes, namely ozone, ozone/Fenton and ozone/persulfate in treating stabilized leachate separately at different experimental conditions. **Results:** A central composite design (CCD) with response surface methodology (RSM) was applied to evaluate the relationships between operating variables. Based on statistical analysis, quadratic models for the four responses (COD, NH₃-N, Color, and ozone consumption (OC)) proved to be significant with very low probability values (<0.0001). For the three optimization designs; the predicted results fitted well with the results of the laboratory experiment. Regarding to the leachate biodegradability, initial BOD₅/COD ratio was 0.034, and it is improved to 0.05, 0.14 and 0.29 by applying O₃, O₃/Fenton and O₃/persulfate, respectively. The fraction of biodegradable COD (bi) increased from 24 to 28, 36 and 30% after applying O₃, O₃/H₂O₂/Fe⁺² and O₃/S₂O₈²⁻, respectively. Soluble COD (S) increased from 59 to 59% after O₃, 72% after ozone/Fenton and ozone/persulfate, respectively. COD (bsi) increased from ...to 38, 51 and 55% after O₃, O₃/H₂O₂/Fe⁺² and O₃/S₂O₈²⁻, respectively, whereas the PCOD reduced from 41 to 35 after O₃ and 28% after ozone/Fenton and ozone/persulfate, respectively. Accordingly, ozone/persulfate is an efficient method for enhanced biodegradability. **Conclusion:** Ozone/Fenton process has higher performance in COD and color removal, while, ozone/persulfate is an efficient method for enhanced biodegradability. Furthermore, ozone/persulfate process has higher performance in ammonia removal as well as it has good removal efficiency of COD and color from stabilized leachate.

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INTRODUCTION

Sanitary landfill is recognized as the most common and desirable method of urban solid waste management and as the most economical and environmentally acceptable method of municipal and industrial solid wastes disposal (Tengrui *et al.*, 2007). However, sanitary landfill generates a large volume of heavily polluted leachate (Zazouil and Yousefi, 2008). Leachate is mainly released from wastes deposited in a landfill due to successive biological, chemical, and physical processes. The quality and quantity of the water formed at landfills depend on several factors, including seasonal weather variations, land filling technique, phase sequencing, piling, and compaction method (Amonkrane *et al.*, 1997; Trebouet *et al.*, 2001).

Landfill leachate is a high-strength wastewater that is very difficult to manage. The leachate generated from mature landfills (age >10 years) is typically characterized by large amounts of organic contaminants measured as chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), ammonia, halogenated hydrocarbons suspended solid, significant concentration of heavy metals, and many other hazardous chemicals identified as potential sources of ground and surface

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water contamination (Schrab *et al.*, 1993; Christensen *et al.*, 2001; Renou *et al.*, 2008; Aziz *et al.*, 2009; Foul *et al.*, 2009). Moreover, the subsequent migration of leachate away from the landfill and its release into the environment are serious environmental pollution concerns that threaten public safety and health (Read *et al.*, 2001). Accordingly, many environmental specialists are determined to discover efficient treatments for large quantities of polluted leachate.

The application of a number of leachate treatment techniques, including biological, physical, and chemical processes, has been investigated (Abu Amr *et al.*, 2013 a,b&c; Baig *et al.*, 2001; Goi *et al.*, 2009). Given its oxidation efficiency, ozone has been suggested as one of the chemical processes for use in the treatment of stabilized landfill leachate to reduce the risk of leachate strength and non-biodegradable organics (Abu Amr *et al.*, 2014; Beaman *et al.*, 1998). Several applications of ozone on landfill leachate treatment have been conducted using ozone oxidation alone (Tizaoui *et al.* 2007; Hagman *et al.* 2008; Rivas *et al.*, 2003), a combination of ozone and coagulation, Fenton reaction and biological treatments as pre- or post-treatment process (Tatsi *et al.*, 2003; Amokranecet *et al.*, 1997; Cortez *et al.*, 2010; Goi *et al.*, 2009; Di Iaconi *et al.*, 2006; Vilar *et al.*, 2006), and ozone in the advanced oxidation processes (AOPs; Tizaoui *et al.*, 2007; Abu Amr and Aziz, 2012; Abu Amr *et al.*, 2013a, b &c). Nevertheless, the previous studies were carried out using various types of leachate, different experimental setting and aims which makes Ozone based processes evaluation and comparison inaccurate. Consequently, in this study, landfill leachate treatability and biodegradability enhancement using ozone alone, Ozon/fenton, and ozone/persulfate were carried out, simultaneously, to provide clear and adequate evolution.

MATERIALS AND METHODS

1.1 Leachate sampling and characteristics:

Leachate samples were collected from an aeration pond at PulauBurung Landfill Site (PBLs), at the Byram Forest Reserve in Penang, Malaysia.. The PBLs is classified as a semi-aerobic stabilized landfill and has an area of 62.4 ha, of which 33 ha are currently operational, receiving approximately 2200 t of municipal solid waste daily. The site is equipped with a natural marine clay liner and three leachate collection ponds (Huling and Pivets, 2004). A semi-aerobic landfill is an effective system for early stabilization of landfill sites and improvement of waste decomposition. Leachate from a semi-aerobic system is characterized by slightly lower organics compared with that in an anaerobic landfill, although still not subjected to biological treatment (Japan International Cooperation Agency, JAICA). In this study, the leachate samples were collected 9 times manually from March 2011 to July 2012 and placed in 20 L plastic containers. The samples were immediately transported to the laboratory, characterized, and cooled to 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 performed in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

Table 1: Characteristics of semi-aerobic landfill leachate from PBLs.

Parameters	Min.	Max.	Value (average)
COD (mg/L)	1780	2530	2025
BOD ₅ (mg/L)	90	107	93
NH ₃ -N (mg/L)	780	1090	810
Color (PT Co.)	3390	4100	3550
TOC	650	1010	860
pH	8.3	9.2	8.5
Suspended solids (mg/L)	197	220	212
Conductivity, (µS/cm)	17,480	18,920	18,670
Iron as Fe ²⁺ (mg/L)	6.5	12	9
Sulfate (mg/L)	154	207	187

2.2 Experimental Procedures:

2.2.1 Ozone oxidation:

Ozone experiments were conducted in a 2 L sample using an ozone reactor with a height of 65 cm and an inner diameter of 16.5 cm. The reactor was supported by a cross column ozone chamber to enhance the ozone gas diffusion (Figure 1). The water bath and cooling system supported the ozone reactor in keeping the internal reaction temperature at <15 °C as an optimal half-life of the dissolved ozone (30 min) in water (Lenntech, Water treatment solution, 2012). Ozone was produced by a BMT 803 generator (BMT Messtechnik, Germany) fed with pure dry oxygen with recommended gas flow rate of 200–1000 ml/min ± 10% under 1 bar pressure. The recommended

input ozone gas concentration (30 – 80 in g/m^3 non-thermal plasma (NTP) $\pm 0.5\%$) was measured by an ultraviolet gas ozone analyzer (BMT 964). The initial pH of leachate samples was adjusted at different pH values ranges between 3 and 11, in order to investigate an optimal initial pH in treating stabilized leachate by ozone. Response surface methodology (RSM) with central composite design (CCD) was used to optimize the ozonation process. The reaction time was varied between 10 and 120 min to determine an optimal ozonation time (Tizaoui *et al.*, 2007).

2.2.2 Ozone/Fenton based advanced oxidation process:

Fenton reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) was employed in the advanced oxidation during the ozonation of stabilized leachate. H_2O_2 (30%) and ferrous sulfate heptahydrate ($\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, 278.02 g/mol) were used in preparing the Fenton reagent, which was then added to the leachate sample in the ozone reactor as one reaction process. Different Fenton dosages, ozone dosage, pH and reaction time were performed.

2.2.3 Ozone/persulfate in the advanced oxidation process:

Persulfate ($\text{S}_2\text{O}_8^{2-}$) as sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, $M = 238$ g/mol) was employed in the advanced oxidation during the ozonation of stabilized leachate, which was added to the sample in the ozone reactor as one reaction process. Different Persulfate dosages, ozone dosage, pH and reaction time were performed.

RSM with CCD was utilized to optimize operational conditions for leachate treatment used ozone, ozone/Fenton and ozone/persulfate oxidation.

2.2.4 Biodegradable and soluble COD fractions:

The effects of the three ozonation treatment processes such as ozone alone, ozone/Fenton and ozone/persulfate on biodegradable and soluble characteristics of stabilized solid waste leachate were investigated. The fractions of biodegradable and non-biodegradable COD were determined through the initial COD of 1000 ml aerated sample; an air pump was used and COD was gradually measured until a constant value that serves as the final COD concentration was reached. The sample size was maintained at 1000 ml during aeration. Water loss in the sample was compensated by adding distilled water. Biodegradability was calculated using the following equation:

$$\text{COD (bi)} = (\text{COD}_i) - (\text{COD}_f) \quad (1)$$

where COD(bi) represents biodegradability, COD_i represents the initial total COD in the sample, and COD_f denotes the constant amount of COD after optimal aeration.

Soluble $\text{COD}_{(s)}$ and particulate COD were determined using the ZnSO_4 coagulant

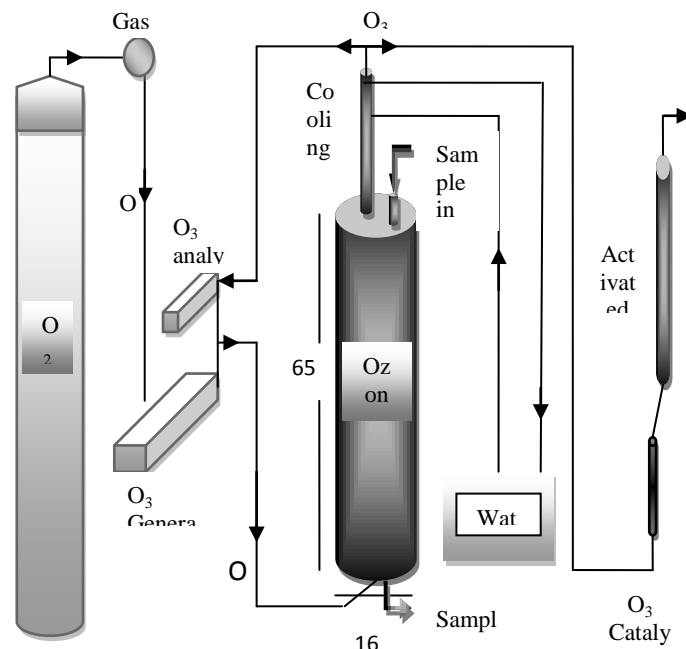


Fig. 1: Schematic diagram of ozone equipment and experiments procedures.

Method (Hu *et al.*, 2002). A total of 1 ml of 0.6M ZnSO₄ solution was added to 100 ml of the sample; pH was adjusted at approximately 10.5 ± 0.3 using 5 M sodium hydroxide and sulfuric acid before adding the coagulant material. The sample was mixed using a magnetic stirrer for 1 min at high speed (approximately 200 rpm) followed by 5 min at low speed (30 rpm). Subsequently, the sample was allowed to settle for 1 h. A total of 30 ml of the sample was withdrawn and filtered through a pre-rinsed 0.45 μm mixed cellulose ester membrane filter (Milipore, MA). COD was then measured as COD_(s), and the difference between COD_(s) and COD_i was determined as particulate COD (PCOD). The value of COD_(bi) is considered as the soluble biodegradable COD_(sbi), whereas the soluble non-biodegradable COD_(subi) was determined by the difference between COD_(sbi) and COD_(s).

2.3 Analytical Methods:

Initial concentration of COD, color, NH₃-N, and pH were immediately tested before and after each run in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA 2005). The NH₃-N concentration was measured by the Nessler method using an HACH DR 2800 spectrophotometer. The pH was measured by a portable digital pH/mv meter. The COD concentration was determined by the closed-reflux colorimetric method using a DR2800 HACH spectrophotometer. The color concentration was measured using a DR 2800 HACH spectrophotometer. Test values are presented as the average of three measurements, and the difference between measurements was less than 3%. The removal efficiency of COD, color, and ammonia were obtained using Equation 1:

$$\text{Removal(\%)} = \left[C_i - \frac{C_f}{C_i} \right] \times 100 \quad (2)$$

Where C_i and C_f respectively refer to the initial and final COD, color, and ammonia concentration. Ozone consumption (OC) is calculated by the following equation:

$$OC = \frac{Q_G}{V} \times \frac{\int_0^t \left(1 - \frac{C_{AG}}{C_{AG0}} \right) dt}{(COD_0 - COD)} \quad (3)$$

Where Q_G is the gas flow rate, V is the sample volume, C_{AG} is the off-gas ozone concentration, C_{AG0} is the input ozone concentration, t is the time, and COD_0 and COD correspond to the initial and final COD, respectively.

RESULTS AND DISCUSSION

3.1 Comparison of the three oxidation processes:

The comparison of different ozone oxidation processes is of interest to determine the best removal performance of COD, colour and ammonia, as well as enhancing of biodegradability and their effects on COD fractions of stabilized leachate. The aim of this study was to evaluate the above mentioned approaches in terms of reduced organic load and ammonia, decreases colour, and enhances the biodegradable characteristics of stabilized leachate. To investigate the performance of combined ozone application and two advanced oxidant reagents, stabilized leachate was treated with ozone oxidation alone, ozone/Fenton and ozone/persulfate in the AOPs, respectively.

2.2.2 Ozone oxidation:

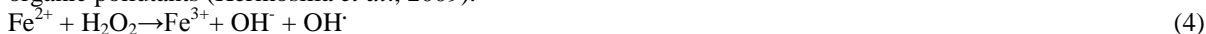
Three significant independent variables considered in this study were ozon dosage (A), initial COD concentration (B) and reaction time (C) which are presented in Table 2. There were a total of 20 runs of the CCD experimental design, and the results are shown in Table 2. The observed percentage removal efficiencies varied between 4% and 27.2% for COD, 0–8.5% for NH₃-N, and 11–90% for colour. Several researchers have conducted studies on the treatment of mature landfill leachate using ozone. Tizaoui *et al.* (2007) obtained 27% and 87% removal for COD and colour, respectively, after 60 min ozonation of raw leachate. In the same tendency, Hagman *et al.* (2008) obtained 22% COD reduction. Rivas *et al.* (2003) obtained a 30% depletion of COD. Accordingly, the efficiency of ozone technique for solely removing organics and ammonia from leachate is relatively weak; the technique is more efficient for colour removal, which may be attributed to the strength of organic components in leachate, improving the removal efficiency in lower initial COD concentration as shown in Table 2. Thus, many researchers have employed several advanced oxidation agents and techniques to improve the efficiency of ozone for leachate treatment, such as hydrogen peroxide (H₂O₂) and UV (Wu *et al.*, 2004; Tizaoui *et al.*, 2007)

Table 2: response values for different experimental conditions (ozone oxidation).

Run no.	Factors			Response			
	A	B	C	1	2	3	4
	Ozone dosage (g/m ³)	COD concentration (mg/l)	Reaction time (min)	COD removal (%)	NH ₃ -N removal (%)	Colour removal (%)	OC (Kg O ₃ /Kg COD)
1	80	250	60	27.2	8.5	90	19.40
2	55	1125	35	18.8	1.1	31.8	3.62
3	30	250	10	16	0.0	25	3.44
4	55	2000	35	21	0.0	24	1.80
5	80	2000	10	10	0.0	18.5	2.04
6	55	250	35	24	6.5	72	7.72
7	55	1125	35	17.5	1.2	32.5	3.41
8	80	2000	60	15	0.0	27.3	6.96
9	55	1125	35	18	1.1	33	3.33
10	55	1125	35	18.5	1.2	32	3.41
11	30	2000	10	4	0.0	11	1.80
12	55	1125	35	17.6	0.9	31	3.70
13	30	2000	60	11	0.0	23	2.09
14	55	1125	10	15.5	0.0	16	1.60
15	30	1125	35	12.5	1.0	38	5.15
16	80	250	10	15	4.7	45	9.47
17	55	1125	35	17.5	1.2	33.6	4.50
18	30	250	60	20.8	2.0	88	4.72
19	55	1125	60	22	1.4	58	3.18
20	80	1125	35	19	2.2	31	6.09

3.2 Ozone/Fenton oxidation:

A total of 50 runs were executed using the CCD experimental design; interactions between the five independent variables were considered for each run to investigate the performance of treating semi-aerobic stabilized leachate using ozone and Fenton reagent in advanced oxidation. Fenton reagent was used to improve oxidation efficiency during ozonation of the stabilized leachate (Table 3). The removal efficiencies ranged from 10% to 79.3% for COD, 19% to 99% for color, and 0 to 41% for ammonia. In the O₃/H₂O₂/ Fe²⁺ system, Fenton ions reacted with H₂O₂ to form hydroxyl radicals (•OH) (Eq. 2); •OH has the potential to destroy and degrade organic pollutants (Hermosilla *et al.*, 2009).



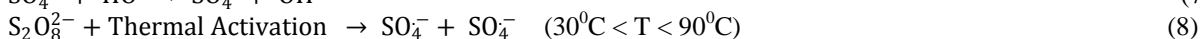
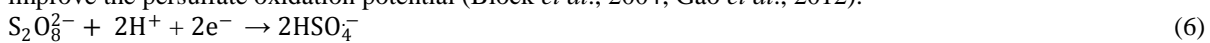
The reaction of ozone with H₂O₂ also generates •OH radicals. H₂O₂ is dissolved in water and dissociates into the hydroperoxide ion (HO₂⁻), which rapidly reacts with ozone to initiate a radical chain mechanism that generates hydroxyl radicals (Stahelin and Hoigne 1982; Glaze *et al.*, 1987), as demonstrated in Equations 4 and 5:



Several works have been conducted on leachate treatment using ozone-based advanced oxidation processes (AOPs). Tizaoui *et al.*, (2007) used H₂O₂ to improve ozone efficiency in landfill leachate treatments for COD (from 27% to 50%) and color (from 87% to 94%). Wu, *et al.*, (2004) performed O₃/UV to enhance the biodegradability of and color elimination in leachate. Cortez *et al.*, (2011) improved COD removal from 46% to 72% using O₃/OH⁻ and H₂O₂ after Fenton as pre-treatment process. In comparing the optimal conditions for the ozone/Fenton process (90 min in one treatment stage with 78% COD removal) with those of Fenton oxidation followed by ozonation, the results showed that around 50% of the reaction time was reduced, and removal efficiency increased from 58% and 95% to 78% and 98.5% for COD and colour, respectively. Goi *et al.* (2009) obtained a 77% COD removal efficiency at 240 min of ozonation after Fenton oxidation.

3.2.3 Ozone/persulfate oxidation:

The Na₂S₂O₈ dosage was determined as a COD/S₂O₈²⁻ ratio (g/g), namely, 1/1 to 1/10 during 60 min ozonation of leachate, to evaluate the role of ozone to initiate sulfite radical from S₂O₈²⁻ during ozonation process. Persulfate oxidation can be enhanced by the release of sulfate radicals, which have powerful effects on the oxidation of organics (Deng and Ezyske, 2011). The formation of sulfate radicals during oxidation can be significantly improved by catalysts, such as heat and UV radiation (Equations 5 – 7), which were found to improve the persulfate oxidation potential (Block *et al.*, 2004; Gao *et al.*, 2012).



Shiyong *et al.* (2009) activated persulfate oxidation using Microwave (MW) and 83% to 95% of COD removal from wastewater was obtained.

Four significant independent variables considered in this study were Ozone dosage (A), Persulfate dosage as COD/S₂O₈²⁻ ratio (g/g) (B) pH variance (C) and reaction time (D) which are presents in Table 4. A total of 30 runs were executed using the CCD experimental design; interactions between the five independent variables were considered for each run to investigate the performance of treating semi-aerobic stabilized leachate using ozone and persulfate reagent in advanced oxidation process.

Table 3: response values for different experimental conditions (ozone/fenton).

Run No.	Factor					Response			
	A: Ozone (g/m ³)	B: H ₂ O ₂ (mol L ⁻¹)	C: Fe ²⁺ (mol L ⁻¹)	D:pH	E:Reaction time (min)	1:COD removal (%)	2:colour removal (%)	3:NH ₃ -N removal (%)	4:OC (Kg O ₃ /Kg COD)
1	30	0.005	0.005	3	10	17.0	43	2	0.44
2	80	0.05	0.005	7	90	39.5	71	11	2.75
3	55	0.0275	0.0275	5	50	72.4	95.5	11.3	0.5
4	80	0.005	0.05	3	90	69.5	93	23	1.56
5	80	0.05	0.005	7	10	10.0	32	1	2.19
6	55	0.0275	0.0275	5	50	72.8	96	10.6	0.45
7	30	0.005	0.005	7	90	37	61	9	0.47
8	30	0.0275	0.0275	5	50	79	98	26	0.19
9	80	0.05	0.05	3	90	55	71	14	2.16
10	30	0.005	0.005	7	10	10.2	29	1	0.68
11	30	0.05	0.05	7	10	46	76	5	0.16
12	80	0.005	0.05	7	90	56.5	96	21	2.15
13	30	0.05	0.005	7	10	22.5	44	1	0.32
14	55	0.0275	0.0275	5	50	73	96	11	0.61
15	80	0.005	0.005	3	90	29	63	8.5	3.6
16	80	0.05	0.05	3	10	39	53	2	0.64
17	80	0.05	0.005	3	10	16	49	1	1.23
18	55	0.0275	0.005	5	50	42	74	9	0.51
19	55	0.0275	0.0275	5	50	72.4	95	10.3	0.58
20	55	0.0275	0.05	5	50	68	92	8	0.67
21	30	0.005	0.05	7	10	42	73	5.5	0.21
22	80	0.05	0.05	7	10	44	75	4	0.59
23	80	0.0275	0.0275	5	50	65.2	90.7	17	0.92
24	30	0.05	0.005	3	90	53	68	12	0.32
25	30	0.05	0.005	7	90	42.5	72	11	0.36
26	30	0.005	0.05	3	90	75.2	91	19	0.38
27	55	0.005	0.0275	5	50	70	95	9.5	0.57
28	55	0.0275	0.0275	5	50	73	96	10.8	0.45
29	55	0.0275	0.0275	5	50	73	96	11	0.42
30	55	0.0275	0.0275	5	50	73.1	96.2	10.5	0.51
31	30	0.05	0.05	3	90	76	97	12	0.19
32	80	0.005	0.005	3	10	9.5	23	2	0.21
33	55	0.0275	0.0275	3	50	70	95	8	0.46
34	55	0.0275	0.0275	5	50	72.8	95.5	11.5	0.38
35	30	0.005	0.005	3	90	48	77	7	0.29
36	55	0.0275	0.0275	5	10	68.6	73	10.8	0.07
37	30	0.05	0.005	3	10	14.5	25	1	0.5
38	55	0.05	0.0275	5	50	63	97	11.8	0.39
39	80	0.005	0.05	3	10	49	69	5	0.43
40	80	0.005	0.005	7	90	32	74	14	3.47
41	80	0.005	0.05	7	10	42.6	62	7	0.51
42	30	0.05	0.05	3	10	65.7	71	5	0.1
43	55	0.0275	0.0275	7	50	51	72.5	13	0.64
44	80	0.05	0.05	7	90	65	90	22	1.16
45	80	0.05	0.005	3	90	48	89	9	2.2
46	30	0.005	0.05	7	90	52.5	91	19	0.29
47	30	0.005	0.05	3	10	53	74	9	0.15
48	55	0.0275	0.0275	5	90	79.3	97	17	0.55
49	30	0.05	0.05	7	90	56	94	19	0.41
50	80	0.005	0.005	7	10	11	27	3	1.99

Persulfate reagent was used to improve oxidation efficiency during ozonation of the stabilized leachate; the results are presented in Table 4. The removal efficiencies were varied between 29 and 75.8% for COD, 63 and 96 for colour and between 29 and 81% for ammonia, respectively at different operational conditions (Table 4),

whereas the maximum values obtained at high pH (10), ozone (80 g/m^3), maximum reaction time (210 min) and higher persulfate dosage ($1 \text{ g/7gCOD/S}_2\text{O}_8^{2-}$).

Although persulfate is more efficient in removing organics and ammonia at high pH under the effects to initiate sulfate radicals (Huling *et al.*, 2006; Deng and Ezyske., 2011), however, persulfate can be tack place in oxidizing organics at low pH. Deng and Ezyske (2011) obtained specific removal for COD and ammonia at pH 4.

Table 4: Response value for different experimental conditions (ozone/persulfate oxidation).

Run no.	Factors				Response			
	A	B	C	D	1	2	3	4
	Ozone dosage (g/m^3)	COD/ $\text{S}_2\text{O}_8^{2-}$ ratio (g/g)	pH	Reaction time (min)	COD removal (%)	Colour removal (%)	$\text{NH}_3\text{-N}$ removal (%)	OC (Kg O_3 /Kg COD)
1	30	1/4	6.5	120	54	86	59	0.146
2	80	1/4	6.5	120	61	83	52.8	1.55
3	55	1/4	6.5	120	56	64	37	1.2
4	80	1/7	10	30	31	91	61	1.6
5	30	1/7	10	210	58	63	38	0.23
6	80	1/1	10	30	40.5	95	57.5	1.5
7	55	1/4	6.5	210	59.6	65	41	0.64
8	30	1/1	3	30	37.5	65	34	0.76
9	80	1/7	10	210	75.8	96	81	2.09
10	30	1/7	10	30	32	83.5	52.9	0.46
11	55	1/4	6.5	120	55.3	95.5	65.2	1.2
12	30	1/7	3	210	67	96	65.3	0.2
13	80	1/7	3	210	73	83	53	1.22
14	55	1/4	6.5	120	55.6	93	78	1.2
15	30	1/1	10	210	71	80	61.5	0.58
16	80	1/7	3	30	47.5	83	54.4	1.2
17	30	1/7	3	30	45	83	53.3	0.3
18	55	1/4	6.5	120	56	81	65.5	1.33
19	55	1/4	10	120	59	93	59	1.53
20	30	1/1	3	210	62	92	59	0.44
21	80	1/1	3	210	61	70.7	31	0.56
22	80	1/1	3	30	36	71	33	1.28
23	30	1/1	10	30	34	87	62	0.58
24	55	1/7	6.5	120	63.7	72	29	1.3
25	55	1/4	6.5	30	34	81	44	1.07
26	55	1/1	6.5	120	51	83.5	53.5	1.62
27	55	1/4	6.5	120	56.7	94	69	1.25
28	80	1/1	10	210	68	89	60	1.83
29	55	1/4	3	120	65	83	52.5	1.01
30	55	1/4	6.5	120	55	82	52.5	1.15

3.3 Analysis of variance (ANOVA):

Table 5 presents the analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic models and other statistical parameters for COD, $\text{NH}_3\text{-N}$, colour removal and OC for the three oxidation processes.

Data given in this table demonstrate that all the models were significant at the 5% confidence level, given that P values were less than 0.05. The values of the coefficient of determination obtained in the present study for COD, $\text{NH}_3\text{-N}$, colour removal, and OC were higher than 0.80. For a good fit of model, the coefficient of determination should be at a minimum of 0.80. A high R^2 value close to 1 illustrates good agreement between the calculated and predicted results within the range of experiment, and shows that a desirable and reasonable agreement with adjusted R^2 is necessary (Joglekar and May, 1987; Nordin *et al.*, 2004).

The Adequate Precision (AP) ratio of the models varies between 14.388 and 28.772, which is an adequate signal for the model. AP values higher than 4 are desirable, and confirm that the predicted models can be used to navigate the space defined by the CCD.

Four quadratic models are significant model terms (Table 5). Insignificant model terms, which have limited influence, were excluded from the study to improve the models. Based on the results, the response surface models constructed for predicting COD, $\text{NH}_3\text{-N}$, colour removal efficiency, and OC were considered reasonable. Summary of the final equations in term of coded models for the responses of the three oxidation processes (Ozone, Ozone/Fenton and Ozone/persulfate oxidation) is presented in Table 6.

Table 5: Summary ANOVA for analysis of variance and adequacy of the quadratic model.

		Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	Prob> F	
ozone oxidation	COD Removal (%)	Model	427.61	4	106.90	20.73	< 0.0001	
		X	47.96	1	47.96	9.30	0.0081	
		Residual	77.35	15	5.16			
		Pure Error	2.31	5	0.46			
	SD=2.27, R ² =0.8468, Adj R ² = 0.8060, Pred. R ² = 0.7068, Adeq Precision = 17.508.							
	NH ₃ -N Removal (%)	Model	95.79	7	13.68	28.82	< 0.0001	
		Residual	5.70	12	0.47			
		Pure Error	0.068	5	0.014			
	SD=0.69, R ² =0.9439, Adj R ² = 0.9111, Pred. R ² = 0.7623, Adeq Precision=19.710.							
	colour Removal (%)	Model	8919.57	4	2229.89	77.04	< 0.0001	
		Residual	434.20	15	28.95			
		Pure Error	4.25	5	0.85			
	SD=5.38, R ² =0.9536, Adj R ² = 0.9412, Pred. R ² = 0.8874, Adeq Precision=28.772.							
	OC	Model	161.97	2	80.99	9.54	< 0.0017	
		Residual	144.27	17	8.49			
Pure Error		0.94	5	0.19				
SD=2.91, R ² = 0.8352, Adj R ² = 0.7763, Adeq Precision= 14.388.								
Ozone/Fenton oxidation	COD Removal (%)	Model	2.064E+004	7	2948.	90.15	< 0.0001	
		Residual	1374.	42	32.70			
		Pure Error	0.5287	7	0.07554			
		Mean = 51.31, R ² = 0.9376, SD = 5.719, Adj R ² = 0.9272, Pred. R ² = 0.9162, Adeq. Precision = 32.87						
	Colour Removal (%)	Model	2.184E+004	9	2426.	42.69	< 0.0001	
		Residual	2273.	40	56.83			
		Pure Error	1.135	7	0.1621			
	Mean = 75.47, R ² = 0.9042, SD = 7.41, Adj R ² = 0.8883, Pred. R ² = 0.7352, Adeq. Precision = 23.323							
	NH ₃ -N Removal (%)	Model	1642.	10	164.2	24.57	< 0.0001	
		Residual	260.6	39	6.683			
		Pure Error	1.155	7	0.1650			
	Mean = 10.24, R ² = 0.8661, SD = 2.52, Adj R ² = 0.8360, Pred. R ² = 0.8522, Adeq. Precision = 17.582							
	OC (Kg O ₂ /Kg COD)	Model	39.37	6	6.561	27.03	< 0.0001	
		Residual	10.44	43	0.2427			
		Pure Error	0.02240	7	0.003200			
Mean = 0.9584, R ² = 0.8713, SD = 0.34, Adj R ² = 0.8423, Pred. R ² = 0.7758, Adeq. Precision = 22148								
Ozone/persulfate oxidation	COD Removal (%)	Model	4478.49	9	497.61	48.44	< 0.0001	
		Residual	205.44	20	10.27			
		Pure Error	1.81	5	0.36			
		Mean = 55.04, R ² = 0.9561, SD = 3.20, Adj R ² = 0.9182, Pred. R ² = 0.8742, Adeq. Precision = 26.135						
	Colour Removal (%)	Model	2778.95	5	555.79	66.10	< 0.0001	
		Residual	201.79	24	8.41			
		Pure Error	0.33	5	0.067			
	Mean = 82.51, R ² = 0.9323, SD = 2.90, Adj R ² = 0.8845, Pred. R ² = 0.7997, Adeq. Precision = 20.19							
	NH ₃ -N Removal (%)	Model	4717.96	10	471.80	22.97	< 0.0001	
		Residual	390.25	19	20.54			
		Pure Error	0.64	5	0.13			
	Mean = 53.56, R ² = 0.9134, SD = 4.59, Adj R ² = 0.8808, Pred. R ² = 0.8595, Adeq. Precision = 18.751							
	OC (Kg O ₂ /Kg COD)	Model	6.91	9	0.77	21.48	< 0.0001	
		Residual	0.71	20	0.036			
		Pure Error	0.019	5	3.817E-003			
Mean = 1.03, R ² = 0.9251, SD = 0.19, Adj R ² = 0.8641, Pred. R ² = 0.7885, Adeq. Precision = 16.011								

3.3.4 Comparison on biodegradability:

The variation of biodegradability (BOD₅/COD) in leachate is attributed to the different types of leachate according to landfill age and leachate decomposition. The BOD₅/COD ratio in young (<5 years), intermediate (5 to 10 years), and stabilized (>10 years) leachate is >0.3, 0.1 to 0.3, and <0.1, respectively (Schiopu *et al.* 2010). Stabilized leachate with very low biodegradability (BOD₅/COD=0.034 to 0.05) and very strong organics made the biological treatment difficult. Different ozone applications have been used to enhance the biodegradability of landfill leachate (Tizaoui *et al.*, 2007; Bila *et al.*, 2004; Cortez *et al.*, 2011b; Cortez *et al.*, 2011a). However, the performance of ozone alone in improving the ratio was still very low. Based on the results, the ozone/persulfate process is an efficient method for enhancing the biodegradability of stabilized leachate (Table 7).

3.5 Comparison the effect of COD fractions:

COD fractionation is the most important parameter for leachate quality. However, the effects of ozone applications on these fractions have not been evaluated. The effects of the three ozone applications on COD fractions in stabilized leachate are compared in this section (Table 8). Based on outcome of the optimum condition obtained by RSM; The residual effluent after each three treatment

processes (ozone, ozone/Fenton and ozone/persulfate) were used to evaluate the effects of the three treatment processes on biodegradable and soluble characteristics of stabilized solid waste leachate were investigated in this research. The fractions of biodegradable COD_(bi), non-biodegradable COD_(ubi), soluble COD_(s), biodegradable soluble COD_(bsi), non-biodegradable soluble COD_(ubsi), and particulate COD (PCOD) were examined and calculated before and after each ozonation treatment processes.

Table 6: Summary of the final equations in term of coded models for the responses of the three oxidation processes (Ozone, Ozone/Fenton and Ozone/persulfate oxidation).

Ozone oxidation	
COD removal (%)	$= 18.98 + 2.19 X_1 - 4.20 X_2 + 3.55 X_3 - 3.93 X^2$
NH ₃ -N removal (%)	$= 1.32 + 1.24 X_1 - 2.17 X_2 + 0.72 X_3 + 1.61 X_2^2 - 0.94 X_3^2$ $- 1.40 A B - 0.72 X_2 X_3$
Colour removal (%)	$= 33.69 - 21.62 X_2 + 17.08 X_3 + 8.69 X^2 - 10.90 X_1 X_2$
OC (Kg O ₃ /Kg COD)	$= + 4.87 + 2.68 X_1 3.01 X_2$
Ozone/Fenton oxidation	
COD removal (%)	$= 72.11 - 3.215 X_1 + 10.39 X_2 + 13.92 X_3 - 3.738 X_4 - 18.04 X_5^2 - 12.54 X_4^2 - 2.934 X_2 X_3$
NH ₃ -N removal (%)	$= 95.06 + 14.62 X_2 + 13.15 X_3 - 8.521 X_2^2 - 10.52 X_3^2 - 9.771 X_4^2 - 4.156 X_2 X_4 - 2.344 X_3 X_4$
Colour removal (%)	$= 12.28 + 5.359 X_2 + 2.853 X_4 + 0.7941 E 7.890 X_1^2 - 2.960 X_3^2 - 5.110 X_4^2 - 3.110 X_5^2 + 1.156$ $X_2 X_4 - 0.81 X_3 X_4$
OC (Kg O ₃ /Kg COD)	$= + 0.48 + 0.66 X_1 + 0.35 X_2 - 0.29 X_4 + 0.10 X_5 + 0.50 X_4^2$ $+ 0.35 X_1 X_2 - 0.22 X_1 X_4 - 0.12 X_2 X_3 - 0.11 X_4 X_5$
Ozone/persulfate oxidation	
COD removal (%)	$= 56.42 + 1.85 X_1 + 1.78 X_2 + 14.33 X_3 - 1.37 X_4 - 9.59 X_2^2 + 5.61 X_4^2 + 1.52 X_1 X_2 - 3.29 X_2 X_4 +$ $2.39 X_3 X_4$
NH ₃ -N removal (%)	(%) $= 82.51 + 1.77 X_2 + 11.60 X_3 - 2.73 X_4 - 2.61 B X_4$ $+ 1.89 X_3 X_4$
Colour removal (%)	$= + 52.67 + 3.86 X_2 + 13.12 X_1 - 9.00 X_3^2$ $+ 10.50 X_4^2 + 2.76 X_1 X_2 - 2.27 X_2 X_3 - 3.84 X_2 X_4 + 5.40 X_3 X_4$
OC (Kg O ₃ /Kg COD)	$= 1.21 + 0.50 X_1 - 0.035 + 0.19 X_4 - 0.30 X_1^2 + 0.31$ $X_2^2 - 0.30 X_3^2 + 0.13 X_1 X_2 + 0.16 X_1 X_4$
Where X ₁ , X ₂ and X ₃ are, ozone dosage g/m ³ , Initial COD concentration (mg/L) and reaction time (min), respectively.	

Table 7: Comparison the effect of the three ozone applications on biodegradability.

Process	BOD ₅ /COD
Raw leachate	0.034 – 0.05
Ozone alone	0.06
Ozone/Fenton	0.14
Ozone/Persulfate	0.29

The quantity of biodegradable and soluble COD fractions in raw leachate was relatively low, whereas that of non-biodegradable, non-soluble, and particulate fractions was high (Table 8). The biodegradable COD improved from 24% to 28%, 36% and 39% after ozone only, ozone/Fenton and ozone/persulfate, respectively. Therefore, biological processes were observed to be generally affected by fresh leachate, containing mainly volatile fatty acids, but were less effective for stabilized leachate (Trebouet *et al.*, 2001). Bilgili *et al.* (2008) obtained 40% and 30% removal of COD using the aerobic and anaerobic reactors of the leachate treatment system, respectively. The results revealed that ozone can improve the removal of COD via extended aeration. The fraction of soluble COD_(s) in stabilized leachate was 59%, whereas particulate COD was 41%; COD_(s) fraction increased to 65% after 60 min of ozonation, while reducing in particulate COD was obtained from 41% to 35%. The results revealed that ozonation of stabilized leachate can convert insoluble organics into soluble one. The most biodegradable organic material was produced after oxidation using ozone solely (Hagman *et al.*, 2008). The results obtained in the current study improved COD_(Sbi) fraction in stabilized leachate from 40% to 43%, 51% and 55 after ozone only, ozone/Fenton and ozone/persulfate, respectively. Meanwhile, COD_(Subi) fraction was reduced to 57%. The results reveal that ozonation converts non-biodegradable organics to biodegradable components, suggesting the enhanced availability of applying the biological treatment of stabilized leachate after ozonation.

As shown in Table 8, each treatment process improved the soluble and biodegradable soluble COD fractions but reduced the non-biodegradable, particulate, and non-biodegradable soluble fractions. Based on the results, ozone/persulfate is an efficient process to improve biodegradability and solubility of organics in stabilized leachate.

Table 8: Comparison the effect of the three ozone applications on COD fractions.

Process Fraction	Raw leachate	Ozone Only	Ozone/Fenton	Ozone/Persulfate
Biodegradable COD (%)	24	28	36	39
Non-biodegradable COD (%)	76	72	68	61
Soluble COD (%)	59	65	72	72
Particulate COD (%)	41	35	28	28
Biodegradable soluble COD (%)	40	43	51	55
Non-biodegradable soluble COD (%)	60	57	49	45

2. Conclusion:

The performance of the three ozonation techniques in AOPs, namely, ozone alone, ozone/Fenton, and ozone/persulfate in treating stabilized leachate was investigated and compared. According to the results, the performance of ozone alone was poor, and utilizing new advanced oxidation material during ozonation of such leachate was required to improve leachate treatability. Ozone/Fenton in AOP is a viable choice for degrading and decolorizing stabilized leachate. However, the performance of the ozone/persulfate process to improving biodegradable and soluble organic fractions in stabilized leachate was better than that of other processes. The process achieved high biodegradability (BOD_5/COD ; 0.29) compared with other treatment methods, which suggests further organic degradation via biological process as a post-treatment. The effect of the three ozonation processes on COD fractions in stabilized leachate was also documented. It can be concluded that ozone/persulfate process is the best choice for improving biodegradable and soluble fractions in stabilized leachate.

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Authors' Contribution:

Prof. Dr. Hamidi Abdul Aziz and Dr. Salem S. Abu Amr developed the idea and had an important role in the result and material section. Dr. Mohammed J.K. Bashir performed the statistical analysis, the discussion and the abstract submission.

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