

Simultaneous removal of COD and color from municipal landfill leachate using Ozone/Zinc Sulphate oxidation process

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Abstract

Municipal landfill leachate generated from aged sites requires an efficient treatment to minimize the high level of refractory organic matters prior to final discharge. In the current study, the performance of combined ozonation and Zinc sulfate (ZnSO₄) for anaerobic stabilized leachate treatment was investigated. The efficiency of Zn dosage [COD₀/Zn ratio (g/g)], pH, and ozonation time was evaluated. The optimal removal efficiencies for COD and color were 90% and 99%, respectively at 1 g/6 g ZnSO₄ dosage (COD₀/Zn), pH 4, and 180 min reaction time. However, the performance of O_3/Zn oxidation process in removing ammoniacal nitrogen from leachate was not efficient as less than 5% removal for ammonia was obtained. The results revealed that the performance of the new catalytic ozone method (i.e., O₃/Zn) in removing removal organic substances from leachate was higher than another related oxidation process such as O₃/Fenton and O₃/persulfate.

Keywords: Ozonation, Zinc sulfate, Anaerobic stabilized leachate, Removal, Treatment

1. Introduction

There is increasing environmental pollution concerns on the safe disposal of Municipal solid waste (MSW). The percolation of rainfall in combination with the decomposition of landfilled solid waste generates highly contaminated liquid, called "leachate" (Aziz *et al.*, 2010). The high quantity of polluted leachate produced from landfilling MSW is causing high potential hazard on the surrounding soil, surface water and public health. Leachate contains large amounts of dissolve organic matter, inorganic ions like ammonia; heavy metals and other biological substances (Ghafari *et al.*, 2010; Shehzad *et al.*, 2015). The leachate characterization depends on various factors including amount of leachate generation, physicochemical compositions, age of the landfill, seasonal weather variations and climate of the site (Aziz *et al.*, 2010). However, age and type of landfill are among the most important factors that affect leachate characterization. Studies reported that the stabilized leachate from old landfills (>10 years) contains extremely high organic content, high ammonia and low biodegradability (BOD₅/COD < 0.1) (Schiopu and Gavrilescu, 2010; Bashir *et al.*, 2015).

Leachate requires an efficient treatment to minimize the high level of pollutants prior to final discharge (Aziz et al., 2010; Azmi et al., 2016). In recent years, several technologies have utilized to minimize the hazards of mature landfill leachate like coagulation/flocculation, adsorption using activated carbon, ion exchange, and advance oxidation techniques (Abu Amr and Aziz, 2012; Abu Amr et al., 2013; Bashir et al., 2011). Biological treatment is low cost and environmental friendly method for landfill leachate, when compare with the others treatment options (Bila et al., 2005). However, the biological treatment process shows inefficient treatment of landfill leachate such as incomplete mineralization. In recent years, the advance oxidation process (AOP) is extensively utilizing leachate treatment because of its effectiveness against complex organic matter (Li et al., 2010). Among various advance oxidation processes, Ozonation is one of the chemical processes, which involves the utilization of ozone to treat water and wastewater for the removal pollutants (Tizaoui et al., 2007). Ozone is a powerful oxidizing agent at an oxidizing potential of 2.08 eV, react with organic matter either directly or indirectly through OH^{*} radical (Goi *et al.*, 2009; Hagman *et al.*, 2008; Tizaoui et al., 2007). The application of ozone in wastewater treatment has recently received attention due to its potential advantages (Goi et al., 2009; Bila et al., 2005; Baig and Liechti 2001; Huang et al., 1993). These advantages are including high efficiency on removing color and the degradation of the organic matter, easy installation, no chemical residue and sludge generation (Abu Amr et al., 2013).

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In spite of several advantages offers by the ozonation of wastewater, there are some disadvantages which limits the application of ozone in large scale wastewater treatment. The distinct disadvantages are low solubility in water e.g., 0.57 gL⁻¹ at ambient temperature, low stability with a halflife of about 20 min at neutral pH and ambient temperature, high energy requirement for ozone production which is about 12 to 18 kWh⁻¹, and the partial oxidation of the organic matters present in the wastewater either directly or by molecular ozone (Langlais et al., 1991; Lenntech, 2016). To overcome existing limitation of advance oxidation processes, environmentalists have promoted various methods for in-situ oxidization via indirect action of ozone on the organic materials with an elevated oxidation potential. For instance, Mehrjouei et al. (2015) summarized the performance of photocatalytic ozonation for the treatment of waste and wastewater. Cong et al., (2015) enhanced ozonation of parachlorobenzoic acid in liquid medium by using peroxymonosulfate. Recently, ozonation received attention for stabilized leachate treatment. Several application using ozone based advanced oxidation processes have been conducted for stabilized leachate treatment. Abu Amr et al. (2012, 2013 and 2016) used Fenton, persulfate and zirconium tetrachloride (ZrCl₄) to improve ozonation in stabilized leachate treatment, respectively. Tizaoui et al., (2007) employed H₂O₂ to enhanced ozonation of old landfill leachate. Rivas et al 2003 employed ozone and activated carbon for stabilized leachate treatment. Several oxidation processes have been applied on stabilized leachate treatment using factorial design and optimization to optimize the experimental conditions and asses the statistical relationship between factors and responses (Table 2). Studies have also utilized various transition metal compounds and determined catalytic activities on the oxidation (catalytic ozonation) of organic matter in wastewater (Chen and Wang; 2014; Sun et al.,2014; Zhu et al., 2014; Mehrjouei et al., 2015). Chen and Wang, (2014) determined the catalytic activity of TiO_2/α -Al₂O catalysts towards the in ozonation of natural organic matter. Sun et al., (2014) utilized MnOx/SBA-15 to improve the ozonation of oxalic acid in aqueous solution. Zhu et al. (2014) employed a catalytic chip containing CuO, ZnO, Al₂O₃, and ZrO₂ in the catalytic ozonation of basic yellow 87 removals in wastewater. However, it was observed that catalytic ozonation attains elevated rates of organic materials mineralization, particularly, in an acid medium. Catalytic ozonation is considered as a homogeneous treatment process due to the activation of the ozone by the metallic ion (s) presents in aqueous solution.

Among the various metallic compounds, Zinc sulfate $(ZnSO_4.7H_2O)$ has been investigated as a coagulant and found very effective in various wastewater treatments (Ho *et al.*, 2002). The performance of zinc sulfate in impoving ozone oxidation of organic materials in wastewater was not investigated. It is thereofore, the present sudy was undertaken to determine the influences of zinc sulfate in

ozonation of organic matter in anaerobic stabilized leachate. Wherein, the influences of zinc sulfate in ozonation of organic matter were evaluated based on the removal of COD and color with varying ZnSO₄.7H2O dosages, pH and reaction time.

2. Materials and methods

2.1. Leachate sampling and characteristics

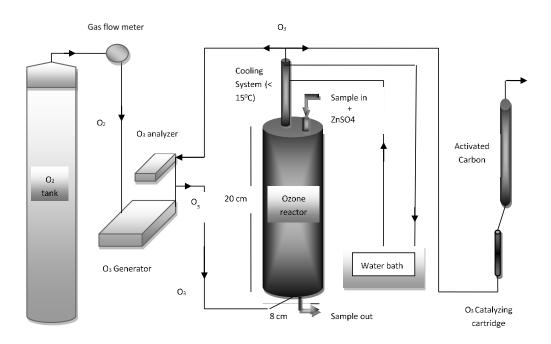
Leachate samples that used in this study were collected from Alor Pongsu Landfill Site (APLS), Alor Pongsu, Perak, Malaysia. APLS is classified as an anaerobic stabilized landfill for municipal waste disposal. The landfill is located at 5°04' N, 100°35' E coordinates. APLS started receiving waste in 2000. Since then the landfill received around 660,000 metrics tons of domestic waste, which is approximately 200 metric tons per day (Zawawi et al., 2011) and still working until the current date. In this study, the leachate was manually collected for five times using 20 L plastic containers within September 2014 to March 2015. The samples collected were immediately brought to the laboratory for the characterization. The samples were then stored in a refrigerator at 4 °C to minimize biological and chemical reactions. The physic-chemical compositions of the leachate are summarized in Table 1.

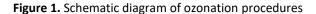
Table 1. General characteristics of leachate from APLS
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Parameters	Min.	Max.	Value (average)
COD (mg/L)	2180	4250	3350± 96
BOD₅ (mg/L)	199	348	274±3
NH ₃ -N (mg/L)	1450	1897	1674±24
Color (Pt Co.)	4650	20300	11400±187
рН	7.93	8.64	8.29±0.04
Conductivity, (µS/cm)	8208	13367	10788±256
Temperature (°C)	28.1	30.2	29.2±1
Dissolved Oxygen (%)	1.1	8.5	4.8±0.2
Dissolved Oxygen (mg/L)	0.09	0.64	0.37±0.06
Total Dissolved Solid (mg/L)	4855	8110	6483±112
Salinity (ppt)	4.08	7.11	5.60±0.5

2.2. Experimental procedures

The experiments in this study were performed using leachate sample volume of 500 mL. The ozone reactor used in this study designed with 20 cm height and 8 cm inner diameter (Fig. 1). A cross-column ozone chamber was placed in the reactor to enhance the ozone gas diffusion. Using a water bath and cooling system, the internal reaction temperature of the reactor was maintained at below 15 °C, which is the optimal condition to maintain the half-life of dissolved O₃ (30 min) in water (Block and Brown, 2004). BMT 803 generator (BMT Messtechnik, Germany) was utilized to generate ozone gaze using pure dry oxygen. The follow rate of the generated ozone gas was adjusted at 1,000 mL/min ± 10% to generate O₃ concentration with 27 g/m^3 at 1 bar of pressure. The concentration of ozone gaze was measured using an ultraviolet gas ozone analyzer (BMT 964). Zinc sulfate (ZnSO₄.7H₂O) (M = 287.54 g/mol) was used to improve ozonation during the oxidation of leachate (Fig. 1).





A set of experiments were performed to obtain the optimal operation conditions of the variables, such as ZnSO₄.7H₂O dosages, pH and reaction time on the recovery of COD and color from stabilized landfill leachate. At first, the influences of ZnSO₄.7H₂O dosage was determined with varying COD/Zn²⁺ (COD/Zn²⁺, g/g) ratios. Desired amount of ZnSO₄.7H₂O and 500 mL of leachate was taken into the ozone reactor and allowed to react for 60 min at natural leachate pH of 8.05. Subsequently, the effect of the initial pH on COD and color removal was determined by varying pH from pH 3 to pH 11 at optimal ZnSO₄.7H₂O dosages (i.e., 1g/2g COD/ ZnSO₄.7H₂O) for the ozonation time of 60 min. The pH of the leachate sample was adjusted 5 M of sulfuric acid and sodium hydroxide solutions. Finally, the influences of ozonation time on the removal of COD and color was optimized with varying reaction time from 30 min to 240 min at optimal ZnSO₄.7H₂O dosages (i.e., 1g/2g COD/ Zn²⁺) and pH (i.e., pH 4).

After each run, the sample was allowed to settle for 1 h at pH 6 prior to further analysis. In order to evaluate the performance of combined ZnSO4/ozonation process on the simultaneous removal of COD and color from anaerobic stabilized leachate, the leachate sample was treated by ZnSO4.7H₂O and ozone separately, zinc sulphate coagulation was performed in a 500 mL sample volume reactor, using (1g/6g COD₀/ Zn²⁺) ZnSO₄ dosage, at pH 6, rapid mixing with 250 rpm during 5 min followed by 60 rpm for 30 min (slow mixing) then, the sample was settled for 25 min (Gafari *et al.*, 2005).

2.3. Analytical methods

The concentration of COD and color were determined before and after each experiments by using a DR 2800 HACH spectrophotometer. Leachate sample was mixed well before analysis. pH of the sample was measured by using a portable digital pH/Mv meter. The removal

efficiencies of COD, and color were calculated by using the following Eq 1:

$$\% \text{Removal} = \frac{x_i - x_f}{x_i} \times 100 \tag{1}$$

where x_i and x_f refer to the initial and final COD and, color, respectively.

3. Results and discussion

3.1 Effect of ZnSO₄ dosages

The influences of zinc sulphate on improving the ozonation was determined with varying zinc sulphate dosages at pH 8.05 (natural leachate pH) for 60 min. The results obtained are present in Fig.2. It was observed that zinc sulphate played an effetive role on increasing the removal of COD and color from the stabilized anaerobic leachate. The percentange COD and color removal of 4% and 22%, resepectively, were gained at COD/Zn²⁺ ratio of 1/0 (only with O₃ and in absence of ZnSO4, 7H2O). However, the percentage removal of COD and color increased rapidly with increasing zinc sulphate dosages upto the COD/Zn²⁺ ratio of 1:2 (69% and 79%, respectively), thereafter the increased of percentage COD and color removal was negligiable with zinc sulpahte dosages. The maximum removal COD and color were obtanied about 74%, and 86%, respectively, at COD/ Zn^{2+} (g/g) ratio of 1:6.

3.3 Effect of pH

The effect of pH on the removal of COD and color from the stabilized anaerobic leachate using zinc sulphate assisted ozonation process was determined, as presented in Fig.3. The influence of pH was dtermined with varying pH 3 to pH 11 at COD/Zn²⁺ (g/g) ratio of 1:6 for 60 min. It was found the removal of COD and color was slightly increased with increasing pH from pH 3 to pH 4, thereafter the removal of COD and color was found to decrease with increasing pH

from pH 4 to pH 11. The romoval of COD and color was obtained at pH 3 were 75% and 93%, respectively, those were slightly increased to 77% and 94% at pH 4, respectively. Wherein, the romoval of COD and color was obtained at pH 11 were 60% and 73%. The highest COD and

color removal of 77% and 94% were gained at pH 4. Thus,. the pH 4 was determined to be the optimal pH for the zinc sulphate assisted ozonation process for the stabilized anaerobic leachate.

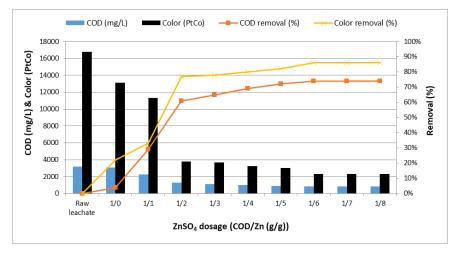


Figure 2. Effect of ZnSO4 dosage on COD and Color removal at 60 min ozonation of leachate, pH 8.05 and O3 dosage 27g/m^3

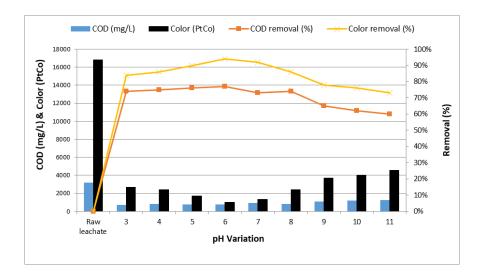


Figure 3. Effect of pH variation on COD and Color removal during 60 min ozonation of anaerobic stabilized leachate (RT: 60 min, ZnSO₄ dosage 1g/6g COD/Zn⁺² g/g), O₃ dosage 27g/m³)

3.3 Effect of reaction time

Fig. 4 shows the influence of the reaction time on COD and color removal from the stabilized anaerobic leachate at COD/Zn^{2+} (g/g) ratio of 1:6 and pH 4. As can see in Fig.4, both COD and color removal increased with increasing reaction time and reached to maximum about 90% and almost 100% at reaction time of 150 min and 180 min, respectively. However, the increase of the COD removal was negligiable with further increased of reaction time over 150 min.

The increase the removal efficiency with increasing of zinc sulphate dosages at pH 8.05 due to the generation of

hydroxyl redical (Langlais *et al.*, 1991; Tizaoui *et al.*, 2007). Tizaoui *et al.*, (2007) reported that the increased of ozonation of landfill leachate with H_2O_2/O_3 in a alkaline medium might due to the effect of indirect oxidation caused by existing hydroxyl radicals (Tizaoui *et al.*, 2007). The formation of Hydroxyl radicals can be express as shown in Eq. 2 and Eq. 3.

$$H_2O_2 + 2O_3^{2-} \rightarrow OH^* + 3O_2$$
 (2)

$$HO_2^-+O_3 \rightarrow HO_2^-+O_3 \tag{3}$$

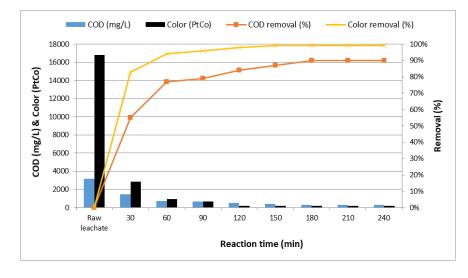


Figure 4. Effect of reaction time on COD and Color removal during ozonation of anaerobic stabilized leachate (ZnSO₄ dosage 1g/6g COD/Zn⁺² (g/g), pH (6), O₃ dosage 27g/m³)

The effectiveness of ozonation in removing COD and Color were impoved by increasing the dosage of Zinc sulfate. Zinc sulfate can be hydroyzed in aqueous solution to zinc hydroxide (Eq 4 and Eq. 5), which contrepute to enhance ozone oxidation under the effect of hydroxyl radicals. Tizaoui *et al.* 2007 improved the removal efficiency of COD by utilizing hydrogen peroxide combined with ozone for leachate treatment. Abu Amr and Aziz (2012) used Fenton reagent to enhance ozonation of stabilized leachate.

$$Zn^{2+}+H_2O \Leftrightarrow +ZnOH^++H^+$$
(4)

$$Zn^{2+} + 2H_2O \rightleftharpoons Zn \quad (OH)_n + 2H^+ \tag{5}$$

pH plays an important role in controlling the ozonation kinetics. Ozonation may have two different reaction mechanisms at alkaline and acidic pH levels. In alkaline pH level, ozone decomposes to hydroxyl radicals, those have redox potential and un-selective nature. Whereas, in acidic medium ozone act as a direct ozonation process which has lower oxidation potintial ($E^0 = 2.07$) than OH[.] ($E^0 = 2.80$). Studies reported that the performance of ozonation in oxidizing organics in nature and alkaline pH is higher than that in in acidic medium under the efffect of hydroxil radical (Tizaoui et al., 2007). In the present study, it was observed that the ozonation performance was higher at pH 6 and 7. Moreover, the formation of ZnOH led to improve the oxidation potintial by generate additional amount of hydroxyl radicals. Coca et al. (2005) argued that hydroxide anions competed for ozone with organic materials in alkaline medium, which results in relatively higher COD and color removal. However, the removal of COD and color was reduced at pH 8 and 9 (Figure 3). Tizaoui et al. (2007) reported that the effect of high hydroxyl group dosage led to inhibite the oxidation of ozone and reduced the removal effecincy of the organic materials in leachate. Another reason might inhibit the removal of COD and color from stabilized landfill leachate in alkaline medium is the increased of ozone decompositions into hydroxyl radicals in alkaline medium due to present of Zn²⁺. The decomposed hydroxyl radicals might generate oxygen or other less reactive species such as HO_2^* . The HO_2^* radicals less reactive than hydroxyl radicals and might decompose to hydroxyl radicals in few steps, which results in slower degradation of organic materials present in leachate and hence minimize the COD and color removal in alkaline medium (Tizaoui *et al.*, 2007; Rehman *et al.* 2012). The ozone deformation into oxygen and less reactive species in presence of Zn^{2+} in alkaline medium can be express as below:

$$O_3 + OH^- \xrightarrow{Zn^{2+}} HO_2^- + O_2$$
 (6)

$$HO_2^- + O_3 \xrightarrow{Zn^{--}} HO_2^* + O_3^- *$$
(7)

$$HO_2 * \xrightarrow{Zn^{2+}} H^+ + O_2^- *$$
(8)

$$O_2^- * + H^+ \xrightarrow{Zn^{2+}} HO_2^*$$
(9)

$$2HO_2^* + \xrightarrow{Zn^{2+}} H_2O_2 + O_2$$
(10)

$$H_2O_2 + O_2^- * \xrightarrow{Zn^{2+}} OH^* + OH^- + O_2$$
(11)

Maximum about 90% and almost 100% removal of COD and color were gained at COD/Zn²⁺ (g/g) ratio of 1:6 and pH 4 for reaction time of 150 min and 180 min, respectively. However, the decline of precentage COD removal over 150 min reaction time might due to the saturation of ozon at reaction time of 150 min. Since landfill lechate constitutes various organic materials, Thus, the optimal experimental conditions for the treatment of stabilized anaerobic landfill leachate on the removal of COD (90%) and color (almost 100%) could be determined as COD/ Zn^{2+} (g/g) ratio of 1:6, pH 4 and reaction time 180 min. Table 2 shows the removal of COD and color from stabilized anaerobic landfill leachate using various treatment process. Based on the data found in literature, it can be concluded that the O₃/ZnSO₄ is the most effective treatment process for the removal of COD and color from the stabilized anaerobic landfill leachate. Abu Amr et al. (2013) obtained 72% and 93% COD and color removal, respectively, using persulphate assisted ozonation process. Further, 65% and 98% COD and color

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removal were gained, respectively, using Fenton reagent assisted ozonation process. Abu Amr *et al.*, (2016) achieved 80% removal from COD using Ozone/ZrCl₄ process for leachate treatment. Wherein, about 90% and almost 100 removal of COD and color removal, respectively were gained in the present study using zinc sulphate assisted ozonation process. Thus, the performance of process (O₃/ZnSO₄ can be considered is one of the efficient process for treating stabilized leachate treatment. In order to evaluate the performance of combined ozone and ZnSO₄, additional experiments for ozone alone and ZnSO₄ alone

were perfumed at different pH levels (Table 2). The performance of ozone alone is week, although ZnSO₄ alone achieved significant removal compared to ozone alone, however, the performance of combined ozone and ZnSO4 was higher than ozonation and coagulation separately. Moreover, the current treatment process considered not efficient for NH₃-N removal from landfill leachate. Abu Amr *et al.*, (2013) reported that ozone alone is not efficient for ammonia removal from leachate, while the performance of both O₃/Fenton and O₃/Persulfate for ammonia removal was higher.

Table 2. Comparing the performance Zn/ozone oxidation of techniques with other advanced oxidation applications for the treatment of stabilized leachate

		COD		Color		References
	Experimental conditions	Initial (mg/L)	Removal (%)	Initial (Pt.Co)	Removal (%)	
Persulfate (S ₂ O ₈ ²⁻)	RT: 240 min, pH= 8.5, COD/S ₂ O ₈ ^{2.} ratio (1g/7g), Rotation: 350 rpm, Temp. 28 °C	2480	39	3450	55	Abu Amr <i>et al.,</i> (2013)
Fenton	RT: 120 min, pH=3, 0.05 mol L ⁻¹ H ₂ O ₂ and 0.05 mol L ⁻¹ Fe ²⁺	2180	55	4100	71	Abu Amr and Aziz (2012)
Fenton+ Ozone	RT: 120 min, pH=3, 0.5 mol L ⁻¹ H ₂ O ₂ and 0.05 mol L ⁻¹ Fe ²⁺ + RT:60 min, pH=7, O ₃ : 80g/m ³	2180	58	4100	95	Abu Amr and Aziz (2012)
Persulfate + Ozone	RT: 240 min, pH= 8.5,COD ₀ /S ₂ O ₈ ²⁻ ratio (1g/7g), Rotation: 350 rpm, Temp. 28 °C)+ (RT: 60 min, O ₃ : 80g/m ³ pH= 8.5.	2480	55	3450	86	Abu Amr <i>et al.,</i> (2013)
Fenton / Ozone	05 mol L ⁻¹ H ₂ O ₂ and 0.05 mol L ⁻¹ Fe ²⁺ , RT: 90 min, pH=7, O ₃ : 80g/m ³	2180	65	4100	98	Abu Amr and Aziz (2012)
Ozone/Persulfate	RT: 210 min, pH=10,COD ₀ /S ₂ O ₈ ²⁻ ratio (1g/7g), O ₃ = 80g/m ³	2480	72	3450	93	Abu Amr <i>et al.,</i> (2013)
ZrCl ₄	1/2 g/g COD ₀ /ZrCl ₄ , pH 6. 250 rpm. Rapid mixing at 5 min, followed by 60 rpm for 30 min (slow mixing)	3125	22	12474	48	Abu Amr <i>et al.,</i> (2016)
ZrCl ₄ /Ozone	1/2 g zirconium tetrachloride dosage (COD ₀ /ZrCl4), pH 6, RT:90 min and O ₃ = 27g/m ³	3125	80	12474	99	
Ozone alone	RT: 60 min, O ₃ : 27g/m ³ pH= 8.5.	3200	15	16000	44	- Current
Ozone alone	RT: 60 min, O ₃ : 27g/m ³ pH= 7.	3200	13	16000	41	
Ozone alone	RT: 60 min, O ₃ : 27g/m ³ pH= 4.	3200	9	16000	27	
Zinc Sulphat	RT: 60 min, pH= 6, ZnSO ₄ dosage 1/6 g/g Zn/COD)	3200	55	16000	76	
Zinc Sulphat	RT: 60 min, pH= 4, ZnSO ₄ dosage 1/6 g/g Zn/COD)	3200	52	16000	73	
Zinc Sulphat	RT: 60 min, pH= 9, ZnSO₄ dosage 1/6 g/g Zn/COD)	3200	44	16000	63	treatment
ZnSO₄/Ozone	RT:60, pH=6, ZnSO₄ dosage 1/6 g/g Zn/COD O₃= 27g/m³	3200	90	16800	100	process
ZnSO₄/Ozone	RT:60, pH=4, ZnSO₄ dosage 1/6 g/g Zn/COD O₃= 27g/m³	3200	76	16800	87	
ZnSO₄/Ozone	RT:60, pH=9, ZnSO ₄ dosage $1/6 \text{ g/g Zn/COD O}_3=$ 27g/m^3	3200	68	16800	79	

*Reaction time

4. Conclusion

The study evaluated the performance of combined ozonation with ZnSO₄ for the landfill leachate treatment. The optimum conditions of $O_3/ZnSO_4$ oxidation was obtained at ZnSO₄ dosage, pH variation, and ozonation time. Ozone alone only achieved 4% and 22% removal for COD and color, respectively, which revealed that ozone alone is not sufficient for leachate treatment. The combined ozone and ZnSO₄ improved the removal of COD and color from 4% to 90% and from 22% to 99%, respectively. Although ZnSO₄ achieved better removal in COD (65%) and color (86%), however, the combined ($O_3/ZnSO_4$) treatment process improved the removal

efficiencies of organics during the ozonation of the leachate.

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