

The Effect of Persulfate Oxidation on the Biodegradability of Concentrated Anaerobic Stabilized Leachate

(Kesan Pengoksidaan Persulfat terhadap Keterbiodegradan Pekatan Larut Lesap Anaerob Stabil)

AHMED H. HILLES, SALEM S. ABU AMR, ABBAS F.M. ALKARKHI* & MD SOHRAB HOSSAIN

ABSTRACT

Anaerobic stabilized landfill leachate was treated by persulfate ($S_2O_8^{2-}$) oxidation. The effect of three factors namely; persulfate dosage, pH and reaction time on COD and NH_3-N removals; was studied. The results of analysis of variance (ANOVA) showed that the selected factors significantly affected the percentage of COD and NH_3-N removals. Furthermore, the maximum removal was achieved at 60 min of persulfate oxidation, a COD/ $S_2O_8^{2-}$ ratio (1 g/4.2 g), and pH7, the percentage of removals for COD and NH_3-N were 45% and 55%, respectively. The effect of persulfate oxidation on the biodegradability of leachate was also investigated. The results showed that the BOD_5/COD ratio improved from 0.09 to 0.1. The oxidation enhanced the biodegradable (COD_{bi}) from 36% to 57%. Hence, persulfate is suitable to pre-treat highly-concentrated stabilized leachate. This process should follow the organic degradation and ammonia removal followed by biological treatment processes.

Keywords: ANOVA; biodegradability; landfilling leachate; persulfate; Tukey's test

ABSTRAK

Larut lesap stabil anaerob telah dirawat secara pengoksidaan persulfat ($S_2O_8^{2-}$). Kesan tiga faktor iaitu dos persulfat, pH dan masa tindak balas terhadap penyingkiran COD dan NH_3-N telah dikaji. Ujian ANOVA menunjukkan faktor tersebut memberi kesan yang bererti terhadap peratusan penyingkiran COD dan NH_3-N . Seterusnya penyingkiran maksimum COD dan NH_3-N masing-masing sebanyak 45% dan 55% telah dicapai pada masa 60 minit, nisbah COD/ $S_2O_8^{2-}$ pada 1 g/4.2 g dan pada pH7. Kesan pengoksidaan persulfat terhadap keterbiodegradan larut lesapan juga dikaji. Hasil kajian menunjukkan nisbah BOD_5/COD meningkat daripada 0.9 kepada 1.0. Pengoksidaan telah meningkatkan biodegradasi (COD_{bi}) dari 36% kepada 57%. Dengan ini, persulfat sesuai merawat larut lesap stabil yang berkepekatan tinggi. Proses ini seharusnya diikuti dengan degradasi bahan organik dan penyingkiran ammonia melalui proses rawatan secara biologi.

Kata kunci: ANOVA; keterbiodegradan; larut lesapan; persulfat; ujian Tukey

INTRODUCTION

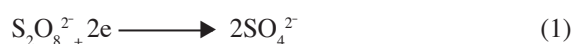
Solid waste landfilling is still considered as the most acceptable, economical and applicable technology for solid waste disposal, however, one of the landfilling disadvantages is generated leachate (Qasim & Chiang 1994). Leachate is produced during the decomposition process (US EPA 2005). Leachate is a liquid effluent generated from landfills as a consequence of rainwater percolation through wastes, biochemical decomposition of organics in solid waste and the moisture content of wastes themselves (Renou et al. 2008; Sabahi et al. 2009). The color of leachate depends on the rainfall conditions and varies from black to brown. The brownish color of the leachate is formed the high level of dissolved organic materials such as humic substances (Cameron & Koch 1980; Gasim et al. 2010; Jumaah et al. 2016). With the increasing age of a landfill, the characteristics of the leachate vary from one landfill site to another (Kjeldsen & Christophersen 2001).

Despite the evolution of landfill technology, from uncontrolled open dumps to highly engineered facilities

designed to eliminate or minimize the potential adverse impact of the waste on the surrounding environment, the generation of contaminated leachate remains an inevitable consequence of the practice of waste disposal in landfills (Alkassasbeh et al. 2009; Jeeva et al. 2012; Mohd et al. 2011; Poznyak et al. 2008).

Several factors can affect the composition of the leachate such as type and composition of the solid waste, the age of the landfill, climate and seasonal variations (Kesson & Nilsson 1997). Furthermore, the degree of the municipal solid waste (MSW) stabilization (Bookter & Ham 1982), hydrology and geology sites, landfill design and operation, conditions within the landfill such as its pH and moisture content (Kjeldsen et al. 1998). As water interacts with the refuse while seeping through a landfill, it becomes contaminated with waste components containing various organic and inorganic pollutants in dissolved or suspended forms (Paxeus 2000). According to numerous authors, three types of leachates can be classified by landfill age: Young, intermediate and stabilized (Alvarez-Vazquez et al. 2004; Kurniawan 2011). In general, young leachate is

highly contaminated with organic compounds, ammonia, halogenated hydrocarbons and heavy metals. The humic substances (HS) constitute an important group of leachate organic matter (Kang et al. 2002; O'man & Hynning 1993). Nevertheless, the principal components of organic compounds in landfill leachates do not vary significantly: only the composition of organics can be varied dependently on the landfill age (Mejbri et al. 1995; Nanny & Ratasuk 2002). Also, with increasing landfill age, the produced leachates are characterized by the presence of substantial quantities of recalcitrant, difficult-to-treat, 'hard' COD (the chemical oxygen demands) compounds. The degradation of organic matter, using various physiochemical treatment applications such as electrochemical oxidation (Bueno & Bertazzoli 2005), coagulation-flocculation, chemical precipitation and activated carbon adsorption, combination of coagulation, flocculation and chemical oxidation, advanced oxidation and ozonation (Abu Amr et al. 2014, 2013a, 2013b; Kurniawan et al. 2006; Lopes & Zamora 2005; Monje & Velasquez 2004; O'Melia et al. 1999; Rivas et al. 2004; Tatsi et al. 2003) were conducted and reported in literature. In the literature, it is reported that conventional biological treatment is not an effective in treating leachates with a high concentration of organics (Renou et al. 2008) and this type of leachate needs to be previously treated to become applicable for biological process. The most suitable way of doing this is to employ pre-treatment using physical and oxidative processes (Imai et al. 1998). Recently, advanced oxidation processes (AOPs) have been received attention as one of the most effective methods to treat stabilized leachate and improved its biodegradability (Abu Amr et al. 2014; Wu et al. 2004). Persulfate ($S_2O_8^{2-}$) recorded as one of the most efficient oxidants for different types of wastewater (Liang et al. 2006). Persulfate can be activated chemically, thermally and/or photochemically to generate sulfate radical ($SO_4^{\cdot -}$) which has powerful oxidation potential (Deng et al. 2013; Gu et al. 2011; Leng et al. 2014; Lin et al. 2011). Several applications of persulfate activation for leachate treatment have been reported such as H_2O_2 , O_3 , Al_2SO_4 , $FeSO_4$, heat, UV radiation and high pH (Abu Amr et al. 2018, 2013a; Gao et al. 2012; Hilles et al. 2016, 2015; Kattle & Dulova 2017; Shiyong et al. 2009). Persulfate ($S_2O_8^{2-}$) is the newest oxidant used in *in situ* chemical oxidation (ISCO) for groundwater and soil cleanup (Huling & Pivetz 2006). $S_2O_8^{2-}$ itself is a strong oxidant with a standard oxidation potential (E°) of 2.01 V (1).



Powerful sulfate radicals: $SO_4^{\cdot -}$,

Subsequently, ($SO_4^{\cdot -} E^\circ = 2.06$ V) may initiate production of other intermediate highly Reactive Oxygen Species (ROS) such as hydroxyl radicals (OH \cdot) (2) (Huie et al. 1991).



These ROS can initiate a series of radical propagation and termination chain reactions where organics are partially and even fully decomposed (Berlin 1986). Several applications on persulfate activation for leachate treatment have been reported such as heat, UV, ozone, Iron and pH variation. However, the effect of high level of heavy metals and trace elements in leachate on the performance of persulfate oxidation still not well reported. The objectives of this study were: To investigate the performance of persulfate oxidation in treating of high concentrated landfill leachate; To determine the effect of persulfate on the COD fractions of leachate; To evaluate the performance of persulfate oxidation as pre-treatment of concentrated leachate to improve its biodegradability for post-biological treatment. In this study, high concentrated landfill leachate with low biodegradability was treated by using persulfate oxidation. The effect of heavy metals and trace elements dissolved in leachate on persulfate activation was discussed. The biodegradability of leachate effluent was improved, and the effect of persulfate oxidation on biodegradable, soluble and particulate COD fractions was determined.

MATERIALS AND METHODS

LEACHATE SAMPLING AND CHARACTERISTICS

Samples of leachate were collected from Deir El-balah sanitary landfill site, Gaza Strip, Palestine. The landfill has an area of 7 ha, receiving approximately 450 tons of municipal solid waste daily (SWMC 2012). In this study, 6 samples of leachate were collected from the collection pond of the same landfill site during the period between March 2014 and August 2015. leachate samples were collected manually from stabilized leachate pond using 2 L plastic containers. The samples were immediately transported to the laboratory, characterized, and cooled to 4°C to minimize the biological and chemical reactions. Tables 1 and 2 summarized the general characterization and heavy metals for the studied leachate. All chemicals used for the analytical determinations were of analytical grade.

EXPERIMENTAL PROCEDURE

All experiments were performed at room temperature (25°C) using 50 mL of leachate sample volume in polyethylene bottles with a volume capacity of 250 mL. Orbital Shaker (Luckham R100/TW Rotatest Shaker 340 mm x 245 mm) was used for sample shaking at 350 rpm. $S_2O_8^{2-}$ as sodium persulfate ($Na_2S_2O_8$) $M=238.09$ g/mol) was used for advanced oxidation of leachate samples. The oxidation conditions include $S_2O_8^{2-}$ dosage (g), pH and reaction time (min) were performed. A total of 21 different dosages of $S_2O_8^{2-}$ Gradually (COD/ $S_2O_8^{2-}$ (g/g); 1/1, 1/1.2, 1/1.4, 1/1.6, ..., 1/5), were performed to determine the maximum removal efficiency at optimal COD/ $S_2O_8^{2-}$ (g/g) ratio. The effects of pH variation on the oxidation process were investigated, optimum pH value was determined by

TABLE 1. General characteristics of landfill leachate from DELS

Parameter	Values (Average)	Min	Max
COD (mg/L)	19765±287	19344	20125
BOD (mg/L)	1861.6±81	1778	1980
BOD/COD ratio	0.097±0.0092	0.088	0.11
EC (mS/cm)	38.84±1.7	37.2	41.6
TDS (mg/L)	25220±225	24964	25543
Nitrate (mg/L)	3672±105	3550	3820
Ammonia (mg/L)	3406.4±65	3324	3490
Chloride (mg/L)	6947.8±45	6880	6997
Sulfate (mg/L)	851.2±14	832	868
Alkalinity (mg/L)	24346.4±161	24110	24530
Hardness (mg/L)	7254.4±92	7120	7360
Calcium (mg/L)	1613.2±51	1556	1680
Magnesium (mg/L)	779.2±14	760	796
Potassium (mg/L)	4392.4±91	4262	4496
Sodium (mg/L)	6280.6±87	6153	6380
pH	8.404±0.1	8.3	8.52

TABLE 2. Average heavy metals concentrations within leachate of the current study

Heavy Metal	Symbol	Concentration(mg/L)
Copper	(Cu)	0.44
Lead	(Pb)	0.143
Nickel	(Ni)	4.63
Manganese	(Mn)	0.08
Cadmium	(Cd)	0.259
Zinc	(Zn)	5.84
Iron	(Fe ²⁺)	48.7

applying different pH values between 3 and 11. The pH was adjusted using 5 M of NaOH and H₂SO₄ reagent (Abu Amr et al. 2013a). The effect of reaction time was studied between 30 and 240 min. all oxidation processes were performed using continues shaking process at 350 rpm. The performance of persulfate oxidation was evaluated according to COD and ammonia removal efficiencies.

DETERMINATION OF COD FRACTIONS

The fractions of biodegradable and non-biodegradable COD were determined through the aeration of 1000 mL leachate sample (before and after persulfate oxidation process); an air pump (Model - AP-3500, Power: 5 W, Pressure: 0.012 Mpa, Output: 2 × 2L/min, Voltage: AC 220V, Frequency: 50 Hz) was used. COD was measured as an initial (COD_i). The value of COD was monitored after each day of aeration time (17 days) and the lowest value was measured as a final (COD_f). The fraction of biodegradable COD was calculated using the following (3):

$$\text{COD}_{(bi)} = (\text{COD}_i) - (\text{COD}_f) \quad (3)$$

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.

Non-biodegradable COD_(ubi) fraction is calculated as the difference between the total COD and COD_(bi), as is shown in the following (4):

$$\text{COD}_{(ubi)} = (\text{COD}_i) - (\text{COD}_{bi}) \quad (4)$$

where COD_(ubi) represents non-biodegradable COD; COD_i represents the initial total COD in the sample; and COD_{bi} denotes the biodegradable COD.

Soluble COD_(s) was determined using the ZnSO₄ coagulant 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. 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 filters of 7 to 10 μm. COD was then measured as soluble COD_(s), and the difference between COD_(s) and COD_i was determined as particulate COD (PCOD). Fractions of soluble and particulate COD are calculated by the following (5) and (6) (Abu Amr et al. 2014):

$$\text{COD}_{(s)} (\%) = [\text{COD}_{(s)} / \text{COD}] * 100 \quad (5)$$

$$\text{PCOD (\%)} = [(\text{COD} - \text{COD}_{(s)})/\text{COD}] * 100 \quad (6)$$

where COD is the total COD (mg/L); PCOD is particulate COD (mg/L), and $\text{COD}_{(s)}$ is the total soluble COD (mg/L).

ANALYTICAL METHOD

COD, BOD_5 , and pH, were immediately tested after each run of the experiments according to the Standard Methods for the examination of water and wastewater (APHA 2005). Leachate was stirred uniformly before being analyzed. COD concentration was determined by the open reflux method No. (5220). $\text{NH}_3\text{-N}$ concentration was determined by the using Phenol Method No. (4500), UV-VIS spectrophotometer at 640 nm. A portable digital pH/Mv meter was used to measure pH value. The results of each test are calculated as the average of the three measurements, and the difference between the measurements of each value was less than 3%. The removal efficiencies of COD and $\text{NH}_3\text{-N}$ were obtained using (7):

$$\text{Removal (\%)} = [(X_i - X_f)/X_i] \times 100 \quad (7)$$

where X_i and X_f refer to the initial and final COD and $\text{NH}_3\text{-N}$ concentrations, respectively.

STATISTICAL ANALYSIS

The results of COD and $\text{NH}_3\text{-N}$ removal were analyzed statistically by analysis of variance (ANOVA) to test whether the setting of selected factors, namely persulfate dosage, pH and reaction time affect the percentage of COD and $\text{NH}_3\text{-N}$ removals (Talebi et al. 2014). Furthermore, Tukey's test for multiple comparisons was used to identify the source of difference in the COD and $\text{NH}_3\text{-N}$ removal by comparing all possible combination of different settings (levels) of selected factors. R statistical software was used for analyzing the data.

RESULTS AND DISCUSSION

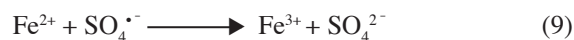
EFFECT OF $\text{S}_2\text{O}_8^{2-}$ DOSAGES

The performance of different $\text{S}_2\text{O}_8^{2-}$ dosage in the oxidation of leachate was studied in term of COD and ammonia

removal efficiency. The data for two responses COD and $\text{NH}_3\text{-N}$ removals were analyzed by analysis of variance (ANOVA) to test the effect of different persulfate dosages on the two responses. The results of ANOVA (Table 3) showed that a significant effect of the persulfate dosage on both COD ($p < 2e-16$) and $\text{NH}_3\text{-N}$ removals ($p < 2e-16$) as shown in Table 3.

The results of Tukey's test for multiple comparisons showed that some of persulfate dosages did not show a significant effect on COD removal (insignificant differences between selected ratios) such as persulfate dosages 1/1.2 and 1/1, 1/1.8 and 1/1, 1/2 and 1/2.8, 1/2.2 and 1/2.8, 1/2.4 and 1/2.8, 1/2.6 and 1/3, 1/4.8 and 1/3.4, 1/5 and 1/3.8, 1/4.4 and 1/4. Furthermore, the percentage of $\text{NH}_3\text{-N}$ removal was not affected (insignificant effect) by some dosages of persulfate, for instance, 1/2.6 - 1/2.4, 1/2.4 - 1/2.2, 1/2.4 - 1/2, 1/2.2 - 1/2, 1/5 - 1/4.8, 1/4.8 - 1/4.2, 1/5 - 1/4.2, 1/3.6 - 1/3.4 as presented in Tables 4 and 5. As shown in Figure 1, the removal of COD and ammonia was increased by increasing of persulfate dosage. The maximum removal of COD and ammonia was reported at persulfate dosage of 4.2 g.

This may be due to the persulfate activation by iron ions and initiate sulfate radical ($\text{SO}_4^{\cdot-}$) that has high oxidation potential ($E^\circ = 2.6 \text{ V}$) (Killian et al. 2007). Rastogi et al. (2009) summarizes the effects of iron ions on persulfate activation as given in (8) and (9),



It was found that the lower iron concentration in soil could be used as a persulfate activator to slow down the consumption of persulfate and to increase the overall degradation of the organic contaminants, and the reason for the increase in oxidation was due to the slower rate of persulfate consumption (Bozkurt et al 2000; Killian et al. 2007). Furthermore, Tan et al. (2012) achieved a high level of iron reduction in the aqueous solution used iron ions for persulfate activation. Li et al. (2014) employed Zero valent (Zn^0) for the activation of persulfate for degradation of methyl orange. Deng and Casey (2011) achieved

TABLE 3. The results of ANOVA for the effect of persulfate dosages on COD and $\text{NH}_3\text{-N}$ removals

S.O.V*	Df	Sum Sq	Mean Sq	F value	Pr(>F)
COD removal					
Dosage	20	2.29075	0.014537	555.1	< 2e-16
Residuals	21	0.00055	0.000026		
$\text{NH}_3\text{-N}$ removal					
Dosage	20	1.1858	0.05929	3557	< 2e-16
Residuals	21	0.0004	0.00002		

* S.O.V : Source of Variation, Df: Degrees of freedom Sum, Sq: Sum of squares, Mean Sq: mean sum of squares, Pr(>F): P-value

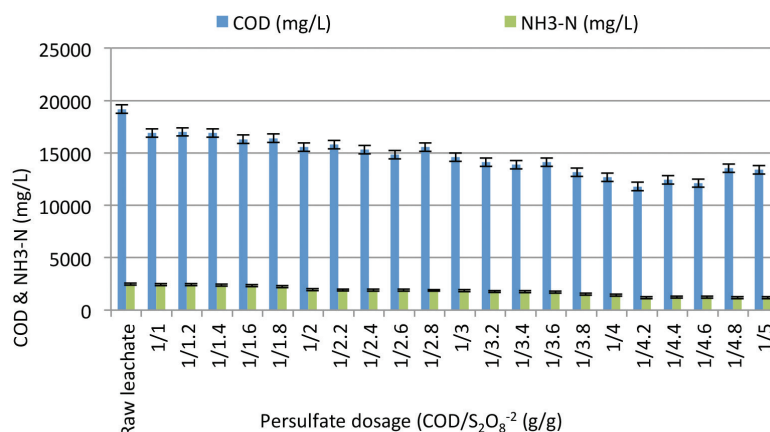


FIGURE 1. Effects of varying dosages of $S_2O_8^{2-}$ on COD and NH_3-N removal efficiency

TABLE 4. The non-significant difference (similar) of persulfate dosages for COD removal

Ratio 1	Ratio 2	P-value
1/1	1/1.2	0.789
1/1	1/1.4	0.942
1/1	1/1.8	0.831
1/1.2	1/1.4	0.878
1/1.2	1/1.8	0.842
1/1.4	1/1.8	0.875
1/1.6	1/1.8	0.931
1/2	1/2.2	0.995
1/2	1/2.4	0.987
1/2	1/2.8	0.878
1/2.2	1/2.4	0.846
1/2.2	1/2.8	0.943
1/2.4	1/2.8	0.964
1/2.6	1/3	0.850
1/3	1/3.2	0.945
1/3	1/3.6	0.976
1/3.2	1/3.6	0.751
1/3.2	1/4.8	0.813
1/3.4	1/3.6	0.835
1/3.4	1/4.8	0.985
1/3.4	1/5	0.877
1/3.6	1.48	0.841
1/3.8	1/4.8	0.934
1/3.8	1/5	0.795
1/4	1/4.4	0.918

55% removal for COD at 50°C used persulfate dosage ($S_2O_8^{2-}:12COD_0 = 0.1:2$). In literature, several applications for activation of persulfate have been reported such heat, UV, ozone, Iron ions, H_2O_2 and pH (Abu amr et al. 2013a; Furman et al. 2011; Gao et al. 2012; Hilles et al. 2016; Hung et al. 2002; Lin et al. 2011; Rastogi et al. 2009; Shiyong et al. 2009). However, persulfate can be efficiently activated by the natural clay minerals and inorganic components found in leachate (Agamuthu 2001; Block et al. 2004). Furthermore, the activation of persulfate can occur with the executing of the high level of heavy metals and trace

TABLE 5. The non-significant difference (similar) of persulfate dosages for NH_3-N removal

Ratio 1	Ratio 2	P-value
1/1	1/1.2	0.962
1/1	1/1.4	0.853
1/1	1/1.6	0.933
1/1	1/1.8	0.875
1/1.2	1/1.4	0.965
1/1.2	1/1.6	0.862
1/1.2	1/1.8	0.904
1/1.4	1/1.6	0.932
1/1.4	1/1.8	0.965
1/1.6	1/1.8	0.873
1/2	1/2.2	0.869
1/2	1/2.4	0.963
1/2	1/2.6	0.941
1/2	1/2.8	0.795
1/2.2	1/2.4	0.944
1/2.2	1/2.6	0.986
1/2.2	1/2.8	0.888
1/2.2	1/3	0.845
1/2.4	1/2.6	0.947
1/2.4	1/2.8	0.870
1/2.4	1/3	0.789
1/2.6	1/2.8	0.944
1/2.6	1/3	0.732
1/2.6	1/3.2	0.971
1/2.8	1/3	0.938
1/2.8	1/3.2	0.987
1/3	1/3.2	0.912
1/3	1/3.4	0.934
1/3.2	1/3.4	0.894
1/3.2	1/3.6	0.941
1/3.4	1/3.6	0.902
1/4.2	1/4.4	0.890
1/4.2	1/4.6	0.865
1/4.2	1/4.8	0.955

elements in leachate can take place in nature. Ahmed et al. (2010) reported the effect of Iron and manganese oxide in soil on persulfate activation.

EFFECTS OF PH VARIATION ON LEACHATE TREATMENT PROCESSES USING $S_2O_8^{2-}$

pH showed a significant effect on both COD and NH_3-N removals since the p-values are very small ($P < 0.003$) and ($p < 2e-16$) for COD and NH_3-N removals respectively as presented in Table 6. This indicates that some or all pH values will give different removal percentage for COD and NH_3-N . The data were further investigated by Tukey's test; the test showed that pH 5-10, 6-10, 7-10, 5-11, 6-11, 7-11, 7-3, and 9-7 give different COD removal while other values have a similar effect. The behavior of pH was different with NH_3-N removal since all values showed significant differences except for two pH values 4 and 3 did not show a significant difference on the NH_3-N removal as both values considered acidic and have the similar effect for NH_3-N removal. This could be due to the production of sulfate and hydroxyl radicals under the effect of high pH (Tizaoui et al. 2007). Both radicals (and OH) have high oxidation potential ($E^\circ = 2.80$ and $E^\circ = 2.70$, respectively) (House 1962). At high pH value, hydroxyl radical can act to activate persulfate and initiate sulfate radical as shown in (10) (Furman et al. 2011; Ocampo 2009).



Nevertheless, the maximum removal efficiency in the current work was obtained at pH7, while significant removal efficiency was obtained at low pH 3 - 4 (Figure

2). Deng and Ezyske (2011) used persulfate for leachate oxidation and achieved higher removal for COD and NH_3-N at low pH4.

EFFECTS OF REACTION TIME VARIATION ON LEACHATE TREATMENT PROCESSES USING $S_2O_8^{2-}$

In this section, the effect of reaction time variation on the $S_2O_8^{2-}$ oxidation was evaluated (Figure 3). The reaction time varied between 30 and 240 min and the level of COD and NH_3-N was monitor after each run. The results for COD and NH_3-N removals were statistically analyzed using ANOVA. As shown in Table 7, the results for both COD ($p < 0.0255$) and NH_3-N ($p < 19e-06$) removals were significant. Tukey's test further analyzed the results, the results of Tukey's test showed that some periods (min) such as 30-120, 30-150, 30-210, 30-240, 60-30, and 90-30 gave different COD removal while other periods did not show a significant difference between them, while the periods that gave different percentage of NH_3-N removal are 30-120, 60-120, 30-150, 60-150, 30-180, 60-180, 30-240, 60-30, and 90-30, while other periods did not show a difference in NH_3-N removal. The reaction time was varied between 30 min and 240 min, and the initial pH and $S_2O_8^{2-}$ dosage were kept constant at 7 and 1/4.2 COD/ $S_2O_8^{2-}$, respectively. The removal of COD and ammonia were improved as the reaction time increased. The maximum removal efficiencies for COD and NH_3-N reached 45%,

TABLE 6. The results of ANOVA for the effect of pH on COD and NH_3-N removals

S.O.V	Df	Sum Sq	Mean Sq	F value	Pr(>F)
COD removal					
pH	8	0.0616	0.0077	9.625	<0.00133
Residuals	9	0.0072	0.0008		
NH_3-N removal					
pH	8	0.1356	0.01696	2.577e+30	<2e-16
Residuals	9	0.00001	0.0000011		

* S.O.V : Source of Variation, Df: Degrees of freedom Sum, Sq: Sum of squares, Mean Sq: mean sum of squares, Pr(>F): P-value

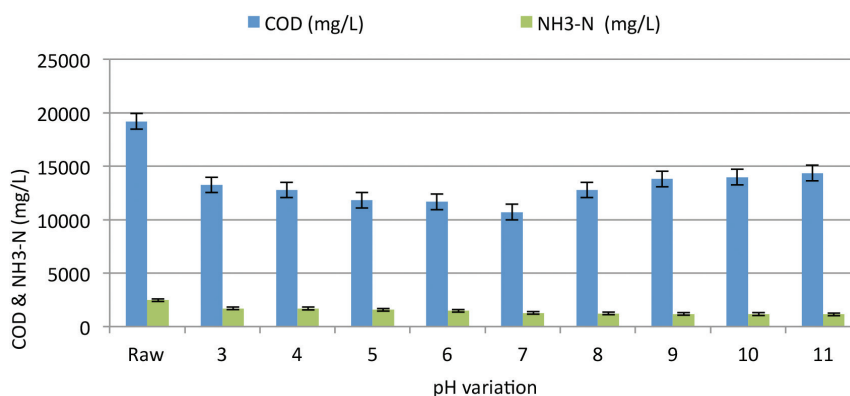
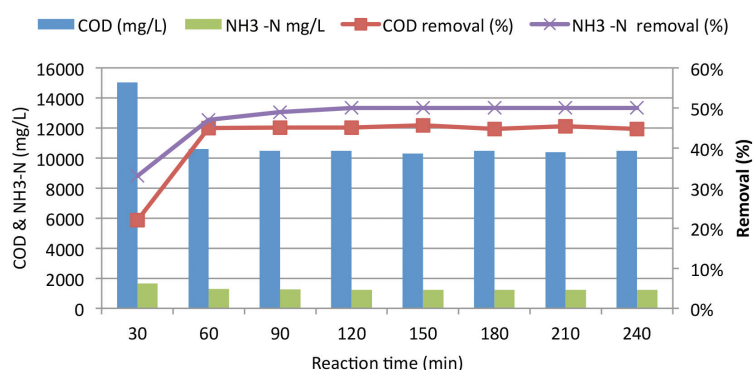


FIGURE 2. Effect of pH variation on COD and NH_3-N removal efficiency

TABLE 7. The results of ANOVA for the effect of reaction time on COD and NH₃-N removals

S.O.V	Df	Sum Sq	Mean Sq	F value	Pr(>F)
COD removal					
Time	7	0.0988	0.014114	4.499	<0.0255
Residuals	8	0.0251	0.003138		
NH ₃ -N removal					
Time	7	0.0455	0.0065	57.78	3.19e-06
Residuals	8	0.0009	0.000112		

* S.O.V : Source of Variation, Df: Degrees of freedom Sum, Sq: Sum of squares, Mean Sq: mean sum of squares, Pr(>F): P-value

FIGURE 3. Effects of reaction time variation on COD and NH₃-N removal efficiency

and 55%, respectively, but did not change considerably after 60 min. Thus, it can be concluded that the optimum reaction time for S₂O₈²⁻ oxidation process for anaerobic stabilized leachate treatment is 60 min.

RELATION BETWEEN LEACHATE BIODEGRADABILITY AND OXIDATION USING PERSULFATE

The effect of persulfate on the leachate biodegradability was also studied. The effect of persulfate on leachate biodegradable COD fraction was investigated. In this

part, biodegradability was measured by removing COD through lab-scale aeration process. Figure 4 shows the degradable COD in the batch aeration method before and after applying the persulfate oxidation process of the leachate. The initial kinetic removal of COD in the first thirteen days of aeration increased gradually. The increasing removal of COD stabilized in raw leachate on the tenth day of aeration, whereas removal of COD continued to increase after persulfate and stabilized at the thirteenth day of aeration. The BOD₅/COD ratio has improved from 0.09 to 0.1. Persulfate oxidation process

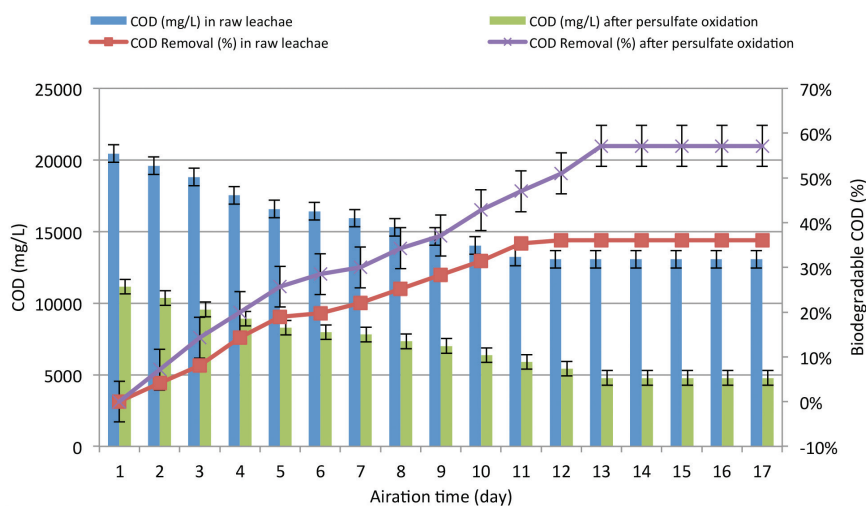


FIGURE 4. Effect of persulfate on biodegradability of leachate

TABLE 8. Effect of persulfate oxidation on COD fractions of stabilized leachate

	Raw leachate		Effluent after persulfate oxidation	
	mg/L	(%)	mg/L	(%)
Biodegradable COD	7381	36	6374	57
Un-Biodegradable COD	13067	64	4781	43
Soluble COD _(s)	14343	70%	8765	78
Particulate PCOD	6105	30%	2390	22

increases the biodegradability of high-molecular-weight organic compounds through the decomposition of large organic molecules, thereby increasing the effectiveness and turning them into compounds that are easily assimilated biologically (Bila et al. 2005). During advanced oxidation process using persulfate, the biodegradability of leachate is enhanced due to fragmentation of organic compounds from long chains to lower chains degraded to carbon dioxide (Geenens et al. 2001). Table 8 summarizes the effect of persulfate oxidation on COD fractions of stabilized leachate. As shown in Table 6, the biodegradable and soluble COD fractions were improved from 36% to 57 % and from 70% to 78% after persulfate oxidation process, respectively.

CONCLUSION

The current study determined the optimum conditions for anaerobic stabilized landfill leachate treatment using persulfate oxidation. Increasing of the persulfate dosages was followed by increasing the organic and ammonia removal efficiency, particularly, in the presence of heavy metals such as iron, which play a major role inactivate of persulfate and produce sulfate radicals. pH variation is a very important player in the oxidation processes; the study shows that the 7 pH is the most efficient situation to produce optimum removal efficiency of COD, especially in the leachate with a high concentration of refractory organic contaminants, while the alkaline situation is more preferable for efficient removal of ammonia. The reaction time is important to be enough for the complete removal of the COD and ammonia. Biodegradability was investigated in the current study. The biodegradable and soluble COD fractions were improved, while the un-biodegradable and particulate COD fractions were reduced. Therefore, biological processes were observed to be affected positively. Persulfate oxidation does not produce undesirable sludge that is inevitably formed and needs to be properly disposed of during extra treatment steps. Moreover, persulfate is a low-cost chemical. Therefore, SR AOP may be an alternative for HR-AOPs in leachate treatment.

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Ahmed H. Hilles
Environment Quality Authority
Palestinian Authority
Palestine

Salem S. Abu Amr & Abbas F.M. Alkarkhi*
Malaysian Institute of Chemical & Bioengineering Technology
Universiti Kuala Lumpur (UniKL, MICET)
78000 Melaka
Malaysia

Md Sohrab Hossain
Division of Environmental Technology
School of Industrial Technology
Universiti Sains Malaysia
11800 Penang
Malaysia

*Corresponding author; email: Abbas@unikl.edu.my

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