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

(Kesan Pengoksidaan Persulfat terhadap Keterbiodegredan Pekatan Larut Lesapan Anaerob Stabil)

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

ABSTRACT

Anaerobic stabilized landfill leachate was treated by persulfate (S\(_2\)O\(_8\)\(^{2−}\)) 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\(_2\)O\(_8\)\(^{2−}\) 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\(_a\)) 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

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 2004). 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 it is biodegradability (Abu Amr et al. 2014; Wu et al. 2004). Persulfate ($S_{2}O_{8}^{2-}$) 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 ($SO_{4}^{2-}$) 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 $H_{2}O_{2}$, $O_{3}$, $AlSO_{4}$, $FeSO_{4}$, heat, UV radiation and high pH (Abu Amr et al. 2018, 2013a; Gao et al. 2012; Hilles et al. 2016, 2015; Kattle & Dulova 2017; Shiying et al. 2009). Persulfate ($S_{2}O_{8}^{2-}$) is the newest oxidant used in in situ chemical oxidation (ISCO) for groundwater and soil cleanup (Huling & Pivetz 2006). $S_{2}O_{8}^{2-}$ itself is a strong oxidant with a standard oxidation potential ($E^\circ$) of 2.01 V (1).

$$S_{2}O_{8}^{2-} + 2e^{-} \rightarrow 2SO_{4}^{2-}$$

(1)

Powerful sulfate radicals: $SO_{4}^{2-}$.

Subsequently, ($SO_{4}^{2-}$ $E^\circ$ = 2.06 V) may initiate production of other intermediate highly Reactive Oxygen Species (ROS) such as hydroxyl radicals (OH) (2) (Huie et al. 1991).

$$SO_{4}^{2-} + H_{2}O \rightarrow OH^- + HSO_{4}^-$$

(2)

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. $S_{2}O_{8}^{2-}$ as sodium persulfate (Na$_2$S$_2$O$_8$) M=238.09 g/mol was used for advanced oxidation of leachate samples. The oxidation conditions include $S_{2}O_{8}^{2-}$- dosage (g), pH and reaction time (min) were performed. A total of 21 different dosages of $S_{2}O_{8}^{2-}$-Gradually (COD/$S_{2}O_{8}^{2-}$- (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/$S_{2}O_{8}^{2-}$ (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)      | 38.8±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   |
| Nitrate (mg/L)  | 4392.4±91        | 4262  | 4496  |
| Sulfate (mg/L)  | 6280.6±87        | 6153  | 6380  |
| pH              | 8.4±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 (CODᵢ). The value of COD was monitored after each day of aeration time (17 days) and the lowest value was measured as a final (CODᵡ). The fraction of biodegradable COD was calculated using the following (3):

\[
\text{COD}_{(\text{bi})} = (\text{COD}ᵢ) - (\text{COD}ᵡ) \quad (3)
\]

where CODᵢ represents biodegradability, CODᵡ represents the initial total COD in the sample, and CODᵢ denotes the constant amount of COD after optimal aeration.

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

\[
\text{COD}_{(\text{ubi})} = (\text{COD}ᵢ) - (\text{COD}ᵢ) \quad (4)
\]

where CODᵢ represents non-biodegradable COD; CODᵢ represents the initial total COD in the sample; and CODᵢ denotes the biodegradable COD.

Soluble CODᵢ 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 CODᵢ, and the difference between CODᵢ and CODᵢ 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):

\[
\text{COD}ᵢ(\%) = \left(\frac{\text{COD}ᵢ}{\text{COD}ᵢ}\right) × 100 \quad (5)
\]
PCOD (%) = [(COD – COD$_{(o)}$)/COD]×100  \hspace{1cm} (6)

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

**ANALYTICAL METHOD**

COD, BOD$_5$, and pH$_i$ 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). NH$_3$–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 NH$_3$–N were obtained using (7):

Removal (%) = $$\frac{(X_i - X_f)}{X_i} \times 100 \hspace{1cm} (7)$$

where and refer to the initial and final COD and NH$_3$–N concentrations, respectively.

**STATISTICAL ANALYSIS**

The results of COD and NH$_3$–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 NH$_3$–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 NH$_3$–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 S$_2$O$_8^{2-}$ DOSAGES**

The performance of different S$_2$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 NH$_3$–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 NH$_3$–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 NH$_3$–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 (SO$_4^{2-}$) that has high oxidation potential (E°= 2.6 V) (Killian et al. 2007). Rastogi et al. (2009) summarizes the effects of iron ions on persulfate activation as given in (8) and (9),

$$\text{Fe}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} + \text{Fe}^{2+} \hspace{1cm} (8)$$

$$\text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{3-} \hspace{1cm} (9)$$

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 NH$_3$–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 |
| NH$_3$–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: Sum of squares, Mean: mean of squares, Pr(>F): P-value
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$_2$O$_2$, 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; Shiying 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 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$_2$O$_8^{2−}$

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$_3$-H 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 ($E^{°} = 2.80$ and $E^{°} = 2.70$, 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).

$$S_2O_8^{2−} + OH^{-} → HSO_4^{-} + SO_4^{2−} + \frac{1}{2} O_2$$ (10)

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$_2$O$_8^{2−}$

In this section, the effect of reaction time variation on the S$_2$O$_8^{2−}$ oxidation was evaluated (Figure 3). The reaction time varied between 30 and 240 min and the level of COD and NH$_3$-N was monitored 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$_2$O$_8^{2−}$ dosage were kept constant at 7 and 1/4.2 COD/S$_2$O$_8^{2−}$, 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
and 55%, respectively, but did not change considerably after 60 min. Thus, it can be concluded that the optimum reaction time for $S_2O_8^{2-}$ 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 BOD$_5$/COD ratio has improved from 0.09 to 0.1. Persulfate oxidation process

---

**TABLE 7. The results of ANOVA for the effect of reaction time on COD and NH$_3$-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 NH$_3$-N removal efficiency**

**FIGURE 4. Effect of persulfate on biodegradability of leachate**
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 unbiodegradable 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.

**ACKNOWLEDGEMENTS**

The authors wish to acknowledge the staff in Public Health Laboratory at the Palestinian Ministry of Health, especially Eng. Samy Lobbad and Eng. Mohammad Al Khateeb for their great efforts, solid waste management council and the Municipality of Deir El-balalah, especially Eng. Wesam Abu Jalamb for facilitating and supporting the sampling processes and all landfill-related issues.

**REFERENCES**

Abu Amr, S.S., Alkarkhi, A.F.M., Alslaibi, T.M. & Abujazar, M.S.S. 2018. Performance of combined persulfate/aluminum sulfate for landfill leachate treatment. *Data in Brief* 19: 951-958.

Abu Amr, S.S., Aziz, H.A., Adlan, M.N. & Alkaseeh, J.M. 2014. Effect of ozone and ozone/persulfate processes on biodegradable and soluble characteristics of semi-aerobic stabilized leachate. *Journal of Environmental Progress And Sustainable Energy* 33: 184-191.

Abu Amr, S.S., Aziz, H.A., Adlan, M.N. & Bashir, M.J.K. 2013a. Pretreatment of stabilized leachate using ozone/persulfate oxidation process. *Chemical Engineering Journal* 221: 492-499.

Abu Amr, S.S., Aziz, H.A. & Adlan, M.N. 2013b. Optimization of stabilized leachate treatment using ozone/persulfate in the advanced oxidation process. *Waste Management* 33: 1434-1441.

Agamuthu, P. 2001. Heavy metal contamination of soil-derived interstitial water in the coastal regions of Selangor Malaysia. *Malays. J. Sci. B* 20: 127-134.

Alkassasbeh, J.Y., Heng, L. & Salmijah, S. 2009. Toxicity testing and the effect of landfill leachate in Malaysia on behavior of common carp (*Cyprinus carpio L.*), 1758; Pisces, Cyprinidae). *American Journal of Environmental Sciences* 5: 209-217.

Alvarez-Vazquez, H., Jefferson, B. & Simon, J. 2004. Membrane bioreactors vs conventional biological treatment of landfill leachate: A brief review. *Journal of Chemical Technology & Biotechnology* 79(10): 1043-1049.

Aucott, M. 2006. *The Fate of Heavy Metals in Landfills: A Review.* New York: Academy of Sciences.

Berlin, A.A. 1986. Kinetics of radical-chain decomposition of persulfate in aqueous solutions of organic compounds. *Kinetics and Catalysis* 27: 34-39.

Bila, D.M., Montalvao, A.F., Silva, A.C. & Dezotti, M. 2005. Ozonation of landfill leachate: Evaluation of toxicity removal and biodegradability improvement. *Journal of Hazardous Materials B* 117: 235-242.

Block, P.A., Brown, R.A. & Robinson, D. 2004. Novel activation technologies for sodium persulfate in situ chemical oxidation. *4th Int. Conf. on the Remediation of Chlorinated and Recalcitrant Compounds*. Booker, T.J. & Ham, R.K. 1982. Stabilization of solid waste in landfills. *J. Environ. Eng.* 108: 1089-1100.

Bozkurt, S., Moreno, L. & Neretnieks, I. 2000. Long-term processes in waste deposits. *The Science of the Total Environment* 250: 101-121.

---

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

| COD Fraction          | Raw leachate (mg/L) | Effluent after persulfate oxidation (mg/L) |
|-----------------------|---------------------|------------------------------------------|
| Biodegradable COD     | 7381                | 6374                                     |
| Un-Biodegradable COD  | 13067               | 4781                                     |
| Soluble COD<sub>s</sub> | 14343              | 8765                                     |
| Particulate PCOD      | 6105                | 2390                                     |

**TABLE 6. Biodegradable and soluble COD fractions of stabilized leachate**

| Fraction     | Raw leachate (%) | Effluent after persulfate oxidation (%) |
|--------------|------------------|----------------------------------------|
| Soluble COD  | 70%              | 78%                                    |
| Biodegradable COD | 36%            | 57%                                    |
Bueno, P.M. & Bertazzoli, R. 2005. Electrodegradation of landfill leachate in a flow electrochemical reactor. *Chemosphere* 58: 41-46.

Cameron, R.D. & Koch, F.A. 1980. Toxicity of landfill leachates. *JWPCF* 52: 760-769.

Deng, J., Shao, Y., Gao, N., Deng, Y., Zhou, S. & Hu, X. 2013. Thermally activated persulfate (TAP) oxidation of antiepileptic drug carbamazepine in water. *Chemical Engineering Journal* 228: 765-771.

Deng, Y. & Casey, M.E. 2011. Sodium sulphate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate. *Water Research* 45: 6189–619.

Furman, O., Teel, A., Ahmad, M., Merker, M. & Watts, R. 2011. Effect of basicity on persulfate reactivity. *J. Environ. Eng.* 137(4): 241-247.

Gasim, M.B., Surif, S., Mokhtar, M., Hj Toriman, M.E., Abd. Rahim, S. & Bee, C.H. 2010. Analisis banjir Disember 2006: Tumpuan di kawasan Bandar Segamat, Johor. *Sains Malaysia* 39(3): 353-361.

Gao, Y., Gao, N., Deng, Y., Yang, Y. & Ma, Y. 2012. Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. *Chem. Eng. J.* 195-196: 248-253.

Geenens, D., Bixio, A. & Thoeye, C. 2001. Combined ozone-activated sludge treatment of and fill leachate. *Water Science and Technology* 2: 359-365.

Gu, X.G., Lu, S.G. & Li, L. 2011. Oxidation of 1,1,1-trichloroethane stimulated by thermally activated persulfate. *Industrial and Engineering Chemistry Research* 50(19): 11029-11036.

Hilles, A.H., Abu Amr, S.S., Hussein, R.A., Arafa, A.I. & El-Sebaie, O.D. 2015. Effect of persulfate and persulfate/H2O2 on biodegradability of an anerobic stabilized landfill leachate. *Waste Management* 44: 172-177.

Hilles, A.H., Abu Amr, S.S., Hussein, R.A., Arafa, A.I. & El-Sebaie, O.D. 2016. Performance of combined sodium persulfate/H2O2 based advanced oxidation process in stabilized landfill leachate treatment. *Journal of Environmental Management* 166: 493-498.

Huang, K.C., Couttenye, R.A. & Hoag, G.E. 2002. Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE). *Chemosphere* 49: 413-420.

Huie, R.E., Clifton, C.L. & Neta, P. 1991. Electron transfer reaction rates and equilibria of the carbonate and sulfate radicalanions. *Radiation Physics and Chemistry* 38: 477-481.

Huling, S.G. & Privetz, B.E. 2006. In-situ Chemical Oxidation (EPA/600-R-06/072). US EPA.

Imai, A., Onuma, K., Inamori, Y. & Sudo, R. 1998. Effects of preozonation in refractory leachate treatment by the biological activated carbon fluidized bed process. *Environ. Technol.* 19: 213-221.

Jeeva, M. & Umar, H. 2012. Study of leachate migration at Sungai Sedu, Telok Datuk waste disposal site by geophysical and geochemical methods. *Sains Malaysia* 41(7): 829-840.

Jumaah, M.A., Othman, M.R. & Yusop, M.R. 2016. Characterization of leachate from Jeram sanitary landfill-Malaysia. *International Journal of ChemTech Research* 9: 571-574.

Kang, K.H., Shin, S.H. & Park, H. 2002. Characterization of humic substances present in landfill leachates with different landfill ages and its implications *Water Res.* 36(16): 4023-4032.

Kattel, E. & Dulove, N. 2017. Ferrous ion-activated persulphate process for landfill leachate treatment: Removal of organic load, phenolic micropollutants and nitrogen. *Environmental Technology* 38(10): 1223-1231.

Kesson, M.A. & Nilsson, P. 1997. Seasonal changes of leachate production and quality from test cells. *J. Environ. Eng.* 123: 892-900.

Killian, P.F., Bruell, C.J., Liang, C. & Marley, M.C. 2007. Iron (II) activated persulfate oxidation of MGP contaminated soil. *Soil & Sediment Contamination* 16(6): 523-537.

Kjeldsen, P. & Christophersen, M. 2001. Composition of leachate from old landfills in Denmark, *Waste Manage. Res.* 19: 249-256.

Kjeldsen, P., Grundtvig, A.A., Winther, P. & Andersen, J.S. 1998. Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source: Landfill history and leachate composition. *Waste Manage. Res.* 16(1): 3-13.

Kurniawan, T.A. 2011. *Treatment of Landfill Leachate*. LAMBERT Academic Publishing.

Kurniawan, T.A., Lo, W.H. & Chan, G.Y.S. 2006. Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Hazard. Mater. B.* 129: 80-100.

Leng, Y., Guo, W. & Shi, X. 2014. Degradation of Rhodamine B by persulfate activated with Fe3O4: effect of polyhydroquinone serving as an electron shuttle. *Chemical Engineering Journal* 240: 338-343.

Li, H., Guo, J., Yang, L. & Lan, Y. 2014. Degradation of methyl orange by sodium persulfate activated with zero-valent zinc. *Separation and Purification Technology* 132: 168-173.

Liang, C., Wang, Z.S. & Mohanty, N. 2006. Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20°C. *Science of the Total Environment* 2-3: 271-277.

Lin, Y.T., Liang, C. & Chen, J.H. 2011. Feasibility study of ultraviolet activated persulfate oxidation of phenol. *Chemosphere* 82(8): 1168-1172.

Lopes de Morais, J. & Zamora, P.P. 2005. Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. *Hazard. Mater. B.* 123: 181-186.

Mejri, R., Matejka, G., Lafrance, P. & Mazet, M. 1995. Fractionnement et caracterisation de la matiereorganique deslixiviats de dechrgesd’orduresmenageres. *Revue des Sciences de L’eau* 8(2): 217-236.

Mohd, R.T., Wan, Z.Y., Abd Rahim, S. & Jasni, Y. 2011. Groundwater quality at two landfill sites in Selangor, Malaysia. *Bulletin of the Geological Society of Malaysia* 57: 13-18.

Monje, I.R. & de Velasquez, M.T.O. 2004. Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachate by coagulation-ozonation coupling processes. *Water Res.* 38(9): 2359-2367.

Nanny, M.A. & Ratasuk, N. 2002. Characterization and comparison of hydrophobic neutral and hydrophobic acid dissolved organic carbon isolated from three municipal landfill leachates. *Water Res.* 36: 1572-1584.

O’man, C. & Hynning, P. 1993. Identification of organic compounds in municipal landfill leachates. *Environ. Pollut.* 80: 265-271.

O’Melia, C.R., Becker, W.C. & Au, K.K. 1999. Removal of substances by coagulation. *Water Sci. Technol.* 40(9): 47-54.

Ocampo, A.M. 2009. Persulfate activation by organic compounds. PhD thesis. Washington: Washington State University (Unpublished).

Paxeus, N. 2000. Organic compounds in municipal landfill leachates. *Water Sci. Technol.* 42(7-8): 323-333.
Poznyak, T., Luis Bautista, L.G., Isaac, R., C’ordova, I. & Elvira Rios, L. 2008. Decomposition of toxic pollutants in landfill leachate by ozone after coagulation treatment. *Journal of Hazardous Materials* 152: 1108-1114.

Qasim, S.R. & Chiang, W. 1994. *Sanitary Landfill Leachate: Generation, Control and Treatment.* Lancaster: Technomic Publishing.

Rastogi, A., Al-Abed, S.R. & Dionysiou, D.D. 2009. Sulfate radical-based ferrous peroxydisulfate oxidative system for PCBs degradation in aqueous and sediment systems. *Applied Catalysis B: Environmental* 85: 171-179.

Renou, S., Givaudan, J.G., Poulain, S., Dirassouyan, F. & Moulin, P. 2008. Review: Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials* 150: 468-493.

Rivas, F.J., Beltrán, F., Carvalho, F., Acedo, B. & Gimeno, O. 2004. Stabilized leachates: Sequential coagulation–floculation + chemical oxidation process. *Hazard. Mater. B.* 116: 95-102.

Sabahi, E.A., Rahim, S.A., Zuhairi, W.W., Nozaey, F.A. & Alshaebi, F. 2009. Leachate composition and groundwater pollution at municipal solid waste landfill of Ibb city, Yemen. *Sains Malaysiana* 38(3): 295-304.

Shabiiyam, M.A. & Dikshit, A.K. 2012. Treatment of municipal landfill leachate by oxidants. *American Journal of Environmental Engineering* 2: 1-5.

Shiying, Y., Ping, W., Xin, Y., Guang, W., Wenyi, Z. & Liang, S. 2009. A novel advanced oxidation process to degrade organic pollutants in wastewater: Microwave-activated persulfate oxidation. *Journal of Environmental Sciences* 21: 1175-1180.

Solid Waste Management Council (SWMC). 2012. Annual report of Khan Younis and Deir Al-balah governorates.

Talebi, A., Norli, N., Teng, T.T. & Alkarkhi, A.F.M. 2015. Nickel ion coupled counter complexation and decomplexation through a modified supported liquid membrane system. *RSC Advances* 5: 38424-38434.

Talebi, A., Norli, N., Teng, T.T. & Alkarkhi, A.F.M. 2014. Optimization of COD, apparent colour and turbidity reductions of landfill leachate by Fenton reagent. *Desalination and Water Treatment* 52: 1524-1530.

US EPA (Environmental Protection Agency). 2005. *Urban Watershed Management Research Terminology.* http://www.epa.gov/ednnrmrl/terminology.html.

Wu, J.J., Wu, C.C., Ma, H.W. & Chang, C.C. 2004. Treatment of landfill leachate by ozone-based advanced oxidation processes. *Chemosphere* 54(7): 997-1003.

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

Received: 3 April 2019
Accepted: 15 August 2019