

Advanced Oxidation Process of Mature Landfill Leachate Containing Ferrous ion

Arseto Yekti Bagastyo*, Anita Dwi Angrainy, Isna Nufussilma Tamas, Welly Herumurti

Department of Environmental Engineering, Faculty of Civil, Environmental, and Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia

*Corresponding author: bagastyo@enviro.its.ac.id

Received: December 3, 2017; Accepted: December 29, 2017

Abstract

Advanced Oxidation Process by means of Fenton-like process was performed to treat mature landfill leachate containing 0.0069 M of Ferrous iron. Hydrogen peroxide was added to promote the oxidation of leachate at specific $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio, and conducted at pH 3 and pH 4 in completely stirred batch operated for 240 min. The highest removal of organic measured as COD was 97%, achieved at $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio of 1:5 and pH 3. Although the presence of chloride ions interfere the oxidation process, the removal of COD was obviously affected at the molar ratio of 1:15 and 1:20 at both pH, whereas the other molar ratios were unclear due to possible generation of intermediate species. While pH 3 was preferable for the Fenton-like process, neutralisation/precipitation at pH 7 and/or pH 8 was required as polishing treatment of the effluents. This may limit the application of Fenton-like process for alkaline leachate treatment.

Keywords; COD; Fe^{2+} ; Fenton; H_2O_2 ; leachate; pH

1. Introduction

Leachate generated from decomposition of solid waste and rainwater percolation in landfill site has become major problems worldwide. Leachates contain high

concentration of organic and inorganic pollutants which are varied in time and site-specific. The characteristics of leachate depends on solid waste type and composition, age of landfill, soil properties, rainfall pattern,

precipitation, landfilling techniques, etc. (Lopez et al., 2004; Renou et al., 2008). Typically, leachate in young landfills (<1 - 2 years mature) have high biodegradability characteristics of organic compounds with ratio of BOD₅/COD (> 0.60), while in mature landfills (>5 - 10 years) the ratio of BOD₅/COD is <0.3 (Deng and Englehardt, 2007).

Treatment of leachate can be conducted via biological methods (aerobic and/or anaerobic), and physico-chemical methods (i.e., coagulation-flocculation, chemical precipitation, oxidation, activated carbon adsorption, ammonium stripping, membrane-based filtration, ion exchange, and electrochemical treatment) (Badawy et al., 2013; Kurniawan et al., 2006). Biological treatments were commonly used in many landfill sites as it cost effective, reliable, and easy to operate. However, biological treatments are only showing good performance for leachate with high BOD₅/COD ratio. As for mature leachate, the treatments are ineffective due to the presence of recalcitrant organics from biochemical changes of the waste.

Advanced Oxidation Processes (AOPs) is one of many oxidation technologies that have been studied extensively for over 20 years (Cortez et al., 2011). In AOPs, strongly oxidative species (OH•) are generated in sufficient quantity to promote the destruction of organic and inorganic matter in water and wastewater, and transform them into non-toxic products (Deng and Zhao, 2015). The mechanism of AOPs can be carried

out using numerous methods, i.e., ozone based oxidation process (e.g., O₃, O₃/H₂O₂, O₃/UV), Fenton oxidation (e.g., Fe²⁺/H₂O₂, photo-Fenton, electro-Fenton), and electrochemical oxidation. Among those methods, Fenton has been indicated as the most cost-effective process for leachate treatment (Li et al., 2010). Previous study showed removal of COD as high as 89% by applying Fe²⁺/H₂O₂ molar ratio of 1:3 (Zhang et al., 2006).

Fenton process consists of four stages, i.e., pH adjustment, oxidation reaction, neutralisation and coagulation, and precipitation (Li et al., 2010). In the Fenton process, hydrogen peroxide (H₂O₂) will rapidly react with ferrous iron. This reaction instantaneously generates hydroxyl radical which responsible for the oxidation of organic matter. The pH of solution has greater effects on controlling the efficacy of Fenton process, i.e., the activity of oxidant and substrate, iron speciation, and the stability of hydrogen peroxide (Hermosilla et al., 2009). Several authors have found an effective treatment at acidic pH (between 3.0 to 4.0) due to the formation of Fe(OH)₂ (Deng and Englehardt, 2006; Singh et al., 2013). The efficacy of acidic pH on the oxidation process has been clearly defined as standard potential of hydrogen peroxide is higher at lower pH rather than in higher pH, i.e., 1.80 V (pH 0) and 0.87 V (pH 14), respectively (Neyens and Baeyens, 2003).

It should also be taken into account that the presence of other ions

in the leachate, such as bicarbonate and chloride ions (measured as alkalinity and total dissolved solid) has clearly affected the AOP performance. For example, Kiwi et al. (2000) mentioned that lower kinetics of Fenton oxidation were determined when those ions present in the solution. This is due to scavenging role of those ions to the generated hydroxyl radicals. Hence, the overall performance of Fenton process was decreased. Similarly, study by Liao et al. (2001) also noted that decreased performances were detected when chloride and bicarbonate ions exist in the solution during the UV/H₂O₂ oxidation process.

Therefore, in this study, Fenton-like process was performed by adding hydrogen peroxide into leachate already containing ferrous iron. The performances of AOPs were evaluated based on several parameters, i.e., Fe²⁺/H₂O₂ molar ratio and the addition of NaCl to examine the impact of higher salinity level contained in the leachate. Neutralisation and precipitation were carried out following the AOP experiment in order to decrease Fe²⁺ and H₂O₂ residues to minimise its impact in the effluent characteristic.

2. Materials and Methods

2.1 Leachate characteristics

Raw leachate was taken from equalisation tank of leachate

wastewater treatment plant in municipal landfill site (>5 years operation) in Gresik Regency, Indonesia. Hence, it can be ensured that the leachate characteristics is kept stabilised (i.e., not considerably fluctuated). The samples were then stored in 20 L plastic containers and immediately preserved in 4°C refrigerator until further analyses. As can be seen in Table 1, the characteristics of leachate wastewater are listed.

2.2 Oxidation treatment

On each experiment, a 2-litre of undiluted sample was placed in a beaker glass covered in aluminium foil. The pH of the solution was measured immediately and adjusted to different initial pH (i.e., pH 3 and pH 4) through the addition of H₂SO₄ (95-97% w/w, Merck). Since Fe²⁺ was readily available in the leachate (i.e., 387 mg/L ~ 0.0069 M), this catalyst was not added in order to utilise the existing Fe²⁺ ions during the AOP. In this case, the concentration of already available Fe²⁺ ions in the leachate was kept constant. Therefore, Fenton reaction was initiated with only the addition of hydrogen peroxide (30% w/w, Merck) to achieve Fe²⁺/H₂O₂ molar ratio of 1:1; 1:5; 1:10; 1:15 and 1:20. Samples were then stirred continuously at 200 rpm for 240 minutes of oxidation time. At 0, 20, 40, 60, 90, 120, 180, and 240 min of oxidation process,

Table 1 Leachate wastewater characteristics

Parameter	Concentration (mg/L)
COD	2,333
BOD ₅	475
Cl ⁻	1,260
Fe ²⁺	387
pH ^a	8.14

^a Dimensionless

samples (55 mL for each sampling time) were redrawn from the beaker for analysis. Following this, oxidation process was ended by the addition of NaOH (Merck, Germany) to increase the pH to circumneutral pH range (i.e., pH 7 and pH 8). In order to obtain complete mixing and stimulate coagulation/precipitation process, samples were stirred all over again at 200 rpm for 5 min and let it to settle down for 120 min to precipitate coagulated organic material and other chemical compounds. Finally, analysis of supernatant was conducted to evaluate the amount of Fe²⁺ and H₂O₂ residues that may remained in the solution.

2.3 Analytical methods

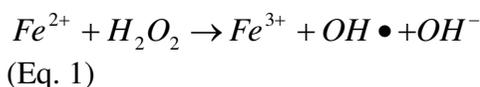
The amount of pH, BOD, COD, chloride, and iron were determined according to standard methods (APHA, 2005). Chloride and iron were analysed using argentometric and phenanthroline methods, respectively. H₂O₂ concentration were measured using Vanadate method

proposed by Nogueira et al. (2005). Vanadate method is simple, fast and reliable for hydrogen peroxide analysis. Moreover, the results are in good agreement with iodometric titration.

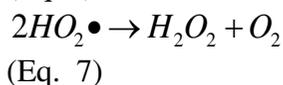
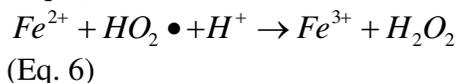
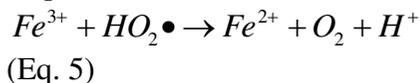
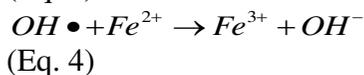
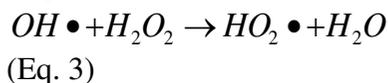
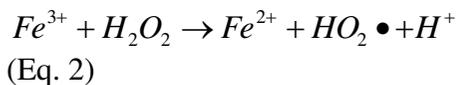
3. Results and Discussion

3.1 Effect of Fe²⁺/H₂O₂ molar ratios and pH of the solution

Hydrogen peroxide is one of strong oxidants which is useful for the treatment of organic and inorganic pollutants. However, due to its low rate reaction, H₂O₂ alone cannot be effectively used to degrade recalcitrant organics in the stabilised leachate (Hermosilla et al., 2009). Therefore, the availability of Fe²⁺ ions in the leachate may benefit the AOP performance to initiate Fenton process. In Fenton process, the presence of Fe²⁺ will rapidly activate H₂O₂ to form hydroxyl radicals (oxidation potential 2.8V), through following reaction (Deng and Englehardt, 2006; Li et al., 2010):



Moreover, the combination of Fe^{2+} and H_2O_2 also stimulate a series of catalytic mechanism (Deng and Englehardt, 2006), as follows:



Each chain reaction has greater impact on the efficacy of Fenton system. Thus, the ratio of Fe^{2+}/H_2O_2 must be determined thoroughly to ensure enough amount of $OH\bullet$ is available for the oxidation process. In order to achieve better understanding the effect of Fe^{2+}/H_2O_2 dosage on the Fenton-like process, different Fe^{2+}/H_2O_2 molar ratios (i.e., 1:1; 1:5; 1:10; 1:15 and 1:20) were evaluated. In this case, the concentration of H_2O_2 added into the leachate was adjusted to the targeted Fe^{2+}/H_2O_2 molar ratio with the unchanged concentration of Fe^{2+} .

As seen on Figure 1, the optimum efficiency of COD removal (97%)

occurred at Fe^{2+}/H_2O_2 molar ratio of 1:5 and pH 3. At this point, mass of COD remained in the solution was ~ 140 mg. When molar ratio of Fe^{2+}/H_2O_2 is equal (i.e., 1:1), the COD removal were decreased to 85%. This indicates that there was insufficient availability of hydrogen peroxide in the system that can be activated to generate $OH\bullet$ radicals (please refer to reaction Eq. 1). This result is in line with study by Cortez et al. (2011), suggesting that at molar ratio of $Fe^{2+}/H_2O_2 < 1:3$, the lower removal efficiency of COD was more likely caused by lower production of $OH\bullet$. However, while the COD removal at molar ratio of Fe^{2+}/H_2O_2 at 1:10 and 1:15 were comparable at equal level, the increase of H_2O_2 addition in the Fenton system up to Fe^{2+}/H_2O_2 molar ratio of 1:20 resulted in a drop of COD removal reaching 77% (i.e., ~ 1073.2 mg of COD was remained in the effluent). Since the catalyst Fe^{2+} in this study was not adjusted to higher level, leading to the excess of H_2O_2 . Therefore, the decrease of COD removal at 1:20 (pH 3) can be explained by the scavenging role of excess hydrogen peroxide generation to $OH\bullet$ radicals to form hydroperoxyl radicals ($HO_2\bullet$) (reaction Eq. 3). These $HO_2\bullet$ radicals was less reactive compared to $OH\bullet$ radicals, and this is attributed to the decreasing of oxidation process on recalcitrant compounds (Cortez et al., 2011; Zhang et al., 2005).

Furthermore, Kang and Hwang (2000) describes the correlation

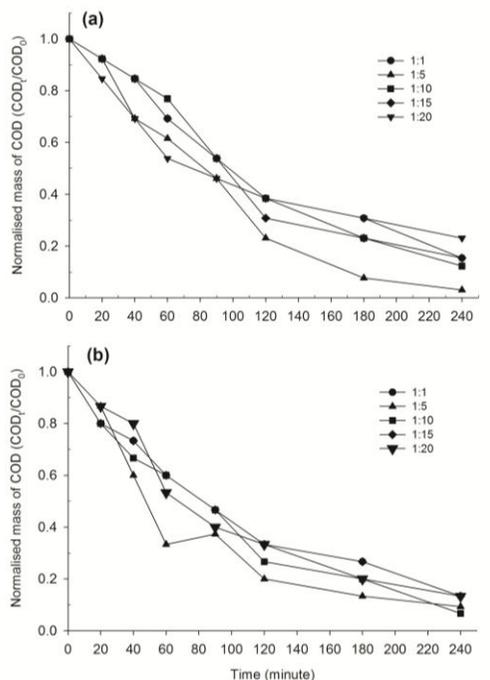


Figure 1. COD removal based on $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio at a) pH 3; and b) pH 4

between the removable COD concentration and the required dose of H_2O_2 , suggesting that per 1000 mg/L of COD, 470.6 mg/L of H_2O_2 was needed. In this current study, the initial COD concentration of leachate was 2,333 mg/L, and thus the theoretical H_2O_2 dose needed to remove COD was 4,958 mg/L. Since in this study the catalyst of Fe^{2+} was not added (i.e., only utilising the existing Fe^{2+}), the theoretical H_2O_2 dose added was likely equal to the Fenton-like process occurred at $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio of 1:20. However, the results obtained both at pH 3 and pH 4 did not lead to the complete removal or even improved removal of COD compared to the other molar ratio tested. Therefore, it can be summarised that the presence

of Fe^{2+} may lower the concentration of H_2O_2 needed for complete COD removal (theoretically) due to the possible occurrence of Fenton-like oxidation. In this case, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio of 1:5 is preferable as observed in this current study, showing the highest removal of COD. Nevertheless, other oxidation reaction mechanisms could also affect the overall oxidation process, such as the presence of chloride ions, ionic metals, alkalinity, etc., which need to be further studied.

Overall, Fenton-like oxidation process at initial pH 4 in this study, resulted in quite similar removal of COD at $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio of 1:1 to 1:20, i.e., in the range of 80-90% at the final effluent. In one case, increasing the initial pH to pH 4 lead

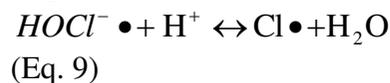
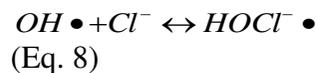
to a decrease of COD removal. For example, at the same ratio Fe^{2+}/H_2O_2 of 1:5, at higher pH (pH 4), the percentage of COD removal was decreased to 91% from 97% (at pH 3) at the final effluent.

However, in other cases, higher initial pH (at pH 4) seems to increase the COD removal, particularly at Fe^{2+}/H_2O_2 molar ratio of 1:20, i.e. 87% from 77% (at pH 3). Duesterberg et al. (2008) reported that although $HO_2\bullet$ produced by $OH\bullet$ may reduce or oxidise the iron species through reaction Eq. 5 and Eq. 6, the rate constant of each reaction were pH dependent. At pH 4, the oxidation rate of Fe^{2+} (reaction Eq. 6) was 2.40×10^6 /M.sec (Kwan and Voelker, 2002), whereas the reduction rate of Fe^{3+} by $HO_2\bullet$ (reaction Eq. 5) at pH 4 and 3 were 7.70×10^6 /M.sec and 1.76×10^6 /M.sec, respectively (Kwan and Voelker, 2002). This indicates that at pH 4, the rate of reaction stated in Eq.5 was faster than reaction as stated in Eq.6. Therefore, the generation of Fe^{2+} by redox reaction were increased considerably. In addition, this leads to the increase of oxidising capacity in the system.

3.2 Effect of chloride ions on the solution

Chloride ions is commonly present in mature leachate, which can be in the range of 100-400 mg/L (Deng and Englehardt, 2007). In this study, the effect of chloride ions on the performance of Fenton process was investigated on each Fe^{2+}/H_2O_2 molar ratios at pH 3 and pH 4. Since

there was no pre-treatment conducted to remove the initial concentration of chloride ion, evaluation was made by adding 1 g/L NaCl (Merck) into the leachate sample. The effect of chloride ions on Fenton process has been studied by several authors (Kiwi et al., 2000; Liao et al., 2001; Yang et al., 2014). Most studies reported that at low pH level, chloride ions could act as scavengers for the generated $OH\bullet$, hence decreasing the oxidation process according to these reactions:



Based on the statement above, it can be suggested that at higher concentration of chloride ions possibly lead to the decrease of COD removal by the addition of NaCl.

As can be seen on Figure 2 below, the effect of chloride ions as $OH\bullet$ scavengers is clearly seen at Fe^{2+}/H_2O_2 molar ratio of 1:15 and 1:20, both at pH 3 and pH 4, i.e., in the range of 75% to 85%. However, the effect of chloride ions by adding 1 g/L NaCl seems to be insignificant on the COD removal at Fe^{2+}/H_2O_2 molar ratio of 1:10, both at pH 3 and pH 4, i.e., in the range of 86% to 93%. Nevertheless, excess of H_2O_2 addition did not benefit the Fenton process regardless the presence of chloride ions. This condition will only lead to lower generation of $OH\bullet$. The reaction of chloride and other ion scavengers (e.g., sulphate and carbonate) with

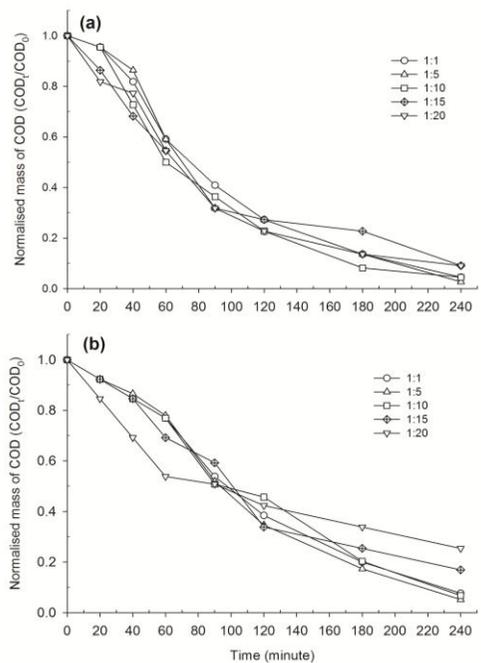


Figure 2. COD removal based on Fe²⁺/H₂O₂ molar ratio and with the addition of NaCl at a) pH 3; and b) pH 4

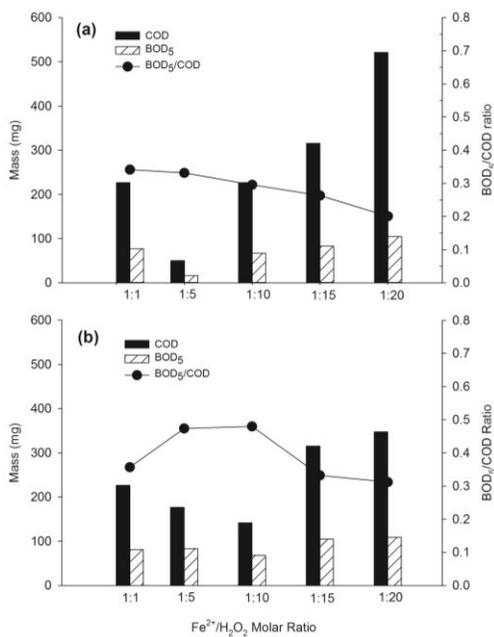


Figure 3. Remaining mass of COD and BOD₅ and its ratio without the addition of NaCl at a) pH 3; and b) pH 4

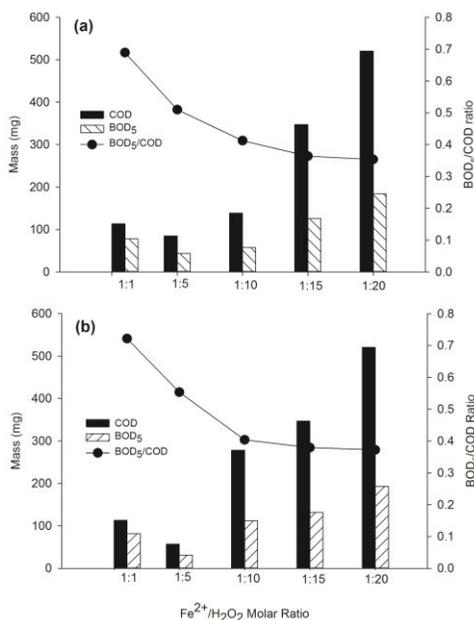


Figure 4. Remaining mass of COD and BOD₅ and its ratio with the addition of NaCl at a) pH 3; b) pH 4

OH• will significantly interfere the oxidation process when these ions present at higher concentrations, i.e., not only decreasing the oxidation process, but also the possible generation of intermediate species. Interestingly, at Fe²⁺/H₂O₂ molar ratio of 1:1 and 1:5, the COD removal was likely increased when NaCl was added at both pH 3 and pH 4. Although the increase was insignificant (i.e., ~5%), this result may suggest that reactive oxidation species other than OH• was generated. This reactive species then reacts with the organic compounds in the leachate to possibly form intermediate species which can not be measured by using the COD analytical method (Bagastyo et al., 2013).

Furthermore, as illustrated in Figure 3 and Figure 4 below, the mass

ratio of BOD₅/COD remained in the solution at both pH 3 and 4 were decreased with the increasing H₂O₂ concentration added into the oxidation process regardless the higher concentration of chloride ions. For example, without the addition of NaCl and at the same pH 3, the ratio of BOD₅/COD were 0.34 and 0.20, at molar ratio Fe²⁺/H₂O₂ of 1:1 and 1:20, respectively. Although the ratio of BOD₅/COD in the solution with the addition of NaCl was slightly higher than without the addition of NaCl, the decreasing ratio of BOD₅/COD at pH 3 was also observed, i.e., 0.69 to 0.35 at molar ratio of Fe²⁺/H₂O₂ = 1:1 and Fe²⁺/H₂O₂ = 1:20, respectively. Lower ratio of BOD₅/COD indicates that a lot of refractory compounds were still remained in the leachate. The amount of H₂O₂ added in the solution was too

excessive, resulting side reaction between $\text{OH}\cdot$ and H_2O_2 . This side reaction leads to the decrease of oxidation process.

Overall, the lowest mass of organic compounds (as COD and BOD) remained in the leachate effluent was less than 100 mg, achieved both at $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1:5$, in pH 3 without NaCl, and pH 4 with NaCl, respectively. Thus, it can be concluded that the initial pH of leachate affects the reaction process and generation of intermediate species in the Fenton-like oxidation system. In addition, the initial pH of leachate seems to give more effect on the oxidation process than the addition of NaCl. This is to say that Fenton-like oxidation is pH-dependent process, since in acidic condition (i.e., pH 3 and pH 4), more soluble irons were available to accelerate the consumption of H_2O_2 to produce $\text{OH}\cdot$ or was only consumed by other competitive ions (Zhang et al., 2005).

3.3 Neutralisation/Precipitation

After conducting Fenton-like oxidation for 240 min, neutralisation/precipitation was performed to achieve: (i) acceptable pH level of effluents as regulated before release to water bodies; (ii) deficiency of residual ferrous iron and hydrogen peroxide to minimise further possible reaction in the environment; (iii) determination of the optimum $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio (i.e., correct dose of hydrogen peroxide for the available ferrous iron) suggested for the Fenton-like process of leachate

containing Fe^{2+} . These experiments were conducted at controlled pH of 7 and pH 8 for the effluents of Fenton-like oxidation conducted without the addition of NaCl.

In general, the results show that residual ferrous iron and hydrogen peroxide was in the range of $9.2 \times 10^{-6} - 1.8 \times 10^{-5}$ M and $8.9 \times 10^{-6} - 1.6 \times 10^{-5}$ M at all $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio, respectively, i.e., after 120 minutes of neutralisation/precipitation (Table 2). This indicates that both ferrous iron and hydrogen peroxide were not completely decomposed during Fenton-like process. As mentioned earlier in section 3.1, the concentration of H_2O_2 added into the leachate containing Fe^{2+} to achieve $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio of 1:20 was close to the amount of theoretical H_2O_2 needed for complete COD removal of the leachate. Since the residual of Fe^{2+} and H_2O_2 after neutralisation/precipitation at 1:20 molar ratio for both initial pH 3 and pH 4 were similar to the other molar ratio tested, the amount of theoretical H_2O_2 needed was still manageable at the polishing treatment. Nevertheless, the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio of 1:20 confirmed an excessive addition of H_2O_2 to generate hydroxyl radicals utilised in the Fenton-like oxidation as explained above.

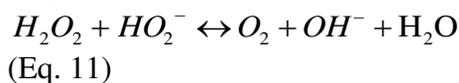
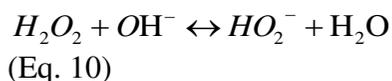
However, although complete decomposition was not observed, the residues were at negligible concentration (Zhang et al., 2005). The residues were at very low concentrations for further reaction. Therefore, neutralisation/precipitation of the effluent performed at pH 7

Table 2 Residual Ferrous Iron and H₂O₂

Residual Fe ²⁺ (in Molar unit)					Residual H ₂ O ₂ (in Molar unit)				
Fe ²⁺ /H ₂ O ₂ M Ratio	Initial pH 3		Initial pH 4		Fe ²⁺ /H ₂ O ₂ M Ratio	Initial pH 3		Initial pH 4	
	pH 7	pH 8	pH 7	pH 8		pH 7	pH 8	pH 7	pH 8
1:1	1.2x10 ⁻⁵	1.4x10 ⁻⁵	1.8x10 ⁻⁵	1.7x10 ⁻⁵	1:1	9.8x10 ⁻⁶	8.9x10 ⁻⁶	1.1x10 ⁻⁵	1.1x10 ⁻⁵
1:5	1.3x10 ⁻⁵	1.4x10 ⁻⁵	1.8x10 ⁻⁵	1.7x10 ⁻⁵	1:5	1.5x10 ⁻⁵	1.5x10 ⁻⁵	1.2x10 ⁻⁵	1.2x10 ⁻⁵
1:10	9.7x10 ⁻⁶	1.0x10 ⁻⁵	1.7x10 ⁻⁵	1.6x10 ⁻⁵	1:10	1.6x10 ⁻⁵	1.6x10 ⁻⁵	1.4x10 ⁻⁵	1.4x10 ⁻⁵
1:15	1.1x10 ⁻⁵	1.1x10 ⁻⁵	1.6x10 ⁻⁵	1.5x10 ⁻⁵	1:15	1.3x10 ⁻⁵	1.4x10 ⁻⁵	1.5x10 ⁻⁵	1.5x10 ⁻⁵
1:20	9.2x10 ⁻⁶	9.2x10 ⁻⁶	1.4x10 ⁻⁵	1.5x10 ⁻⁵	1:20	1.5x10 ⁻⁵	1.4x10 ⁻⁵	1.6x10 ⁻⁵	1.4x10 ⁻⁵

and/or pH 8 can be reasonably accepted for polishing step of Fenton-like oxidation process. Moreover, iron contaminant was effectively removed from the leachate by means of precipitation. Iron were removed and separated as iron oxide precipitates.

Table 2 also shows that there was no considerable difference on the final concentration of Fe²⁺ and H₂O₂ residues between pH 7 and pH 8. Therefore, performing neutralisation/precipitation at pH 7 was preferable due to less volume of NaOH added into the effluents. Furthermore, as pH of the effluents were increased to pH 7 and pH 8, more decomposition of H₂O₂ was occurred without improving oxidation although the decomposition of iron concentration was so slow, producing iron oxide precipitates (Zhang et al., 2005). In this case, the decomposition of H₂O₂ to produce oxygen follows the reactions below:



4. Conclusions

The specific amount of H₂O₂ to obtain the targeted Fe²⁺/H₂O₂ molar ratio (i.e., 1:1; 1:5; 1:10; 1:15 and 1:20) were introduced in the solution as the only oxidant. The experiments were conducted at room temperature in acidic condition, i.e., pH 3 and 4. Although complete removal of organic matters were not achieved, this study clearly verified the effectiveness of AOPs for leachate treatment, particularly when Ferrous ions present in the leachate to initiate Fenton-like oxidation. In all experiments, the average removal of COD was more than 80% (i.e., more than 3,700 g/L of COD was removed in a 2-L of leachate treated per batch). The highest COD removal (97%) was achieved at Fe²⁺/H₂O₂ ratio of 1:5 at pH 3, whereas the lowest removal (77%) was achieved at Fe²⁺/H₂O₂ ratio of 1:20 at pH 3. The presence of chloride ions (and other competitive ions) seems to affect the oxidising process at certain condition. However, the effect of NaCl added was likely insignificant for COD removal, with possible intermediate species

generated during the process. Furthermore, the decrease of BOD₅/COD ratio was observed with the increasing Fe²⁺/H₂O₂ molar ratio. Overall, initial pH of the solution plays an important role in the Fenton-like oxidation mechanism, by means of initiation of hydroxyl radicals and other competitive species, and thus limiting its application for alkaline leachate condition. In addition, neutralisation/precipitation was required as polishing treatment of the effluents before releasing to the water environment.

Acknowledgement

This study was financially supported by Institut Teknologi Sepuluh Nopember (ITS) under Laboratory Research Grant Scheme 2017 No. 855/PKS/ITS/2017.

References

APHA. Standard Methods for The Examination of Water and Wastewater. 21st ed. American Public Health Association, Washington, D.C. 2005.

Badawy M. I., El-Gohary F., Gad-Allah T. A., Ali M. E. M. Treatment of landfill leachate by Fenton process: parametric and kinetic studies. *Desalination and Water Treatment* 2013; 51(37-39): 7323-7330.

Bagastyo A. Y., Batstone D. J., Rabaey K., Radjenovic J. Electrochemical oxidation of electro dialysed reverse osmosis concentrate on Ti/Pt-IrO₂, Ti/SnO₂-Sb and boron-doped diamond electrodes. *Water Research* 2013; 47: 242-250.

Cortez S., Teixeira P., Oliveira R., Mota M. Evaluation of fenton and ozone-based advanced oxidation processes as

mature landfill leachate pre-treatments. *Journal of Environmental Management* 2011; 92(3): 749-755.

Deng Y., Englehardt J. D. Treatment of landfill leachate by the Fenton process. *Water Research* 2006; 40: 3683-3694.

Deng Y., Englehardt J. D. Electrochemical oxidation for landfill leachate treatment. *Waste Management* 2007; 27: 380-388.

Deng Y., Zhao R. Advanced oxidation processes (AOPs) in wastewater treatment. *Current Pollution Reports* 2015; 1: 167-176.

Duesterberg C. K., Mylon S. E., Waite T. D. pH Effects on iron-catalysed oxidation using Fenton's reagents. *Environmental Science and Technology* 2008; 42: 8522-8527.

Hermosilla D., Cortijo M., Huang C. P. Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes. *Science of the Total Environment* 2009; 407: 3473-3481.

Kang Y. W., Hwang K.-Y. Effects of reaction conditions on the oxidation efficiency in the fenton process. *Water Research* 2000; 34(10): 2786-2790.

Kiwi J., Lopez A., Nadtochenko V. Mechanism and kinetics of the OH-radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl⁻). *Environmental Science and Technology* 2000; 34: 2162-2168.

Kurniawan T. A., Lo W. H., Chan G. Y. S. Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. *Journal of Hazardous Materials* 2006; B129: 80-100.

Kwan W. P., Voelker B. M. Decomposition of hydrogen peroxide and organic compounds in the presence of dissolved iron and ferrihydrite. *Environmental Science and Technology* 2002; 36: 1467-1476.

Li W., Zhou Q., Hua T. Removal of organic matter from landfill leachate by advanced oxidation processes: A

- review. *International Journal of Chemical Engineering* 2010; 2010: 1-10.
- Liao C. H., Kang S. F., Wu F. A. Hydroxyl radical scavenging role of chloride and bicarbonate ions in the H_2O_2 /UV process. *Chemosphere* 2001; 44: 1193-1200.
- Lopez A., Pagano M., Volpe A., Pinto A. C. D. Fenton's pretreatment of mature landfill leachate. *Chemosphere* 2004; 54: 1005-1010.
- Neyens E., Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials* 2003; B98: 33-50.
- Nogueira R. F. P., Oliveira M. C., Paterlini W. C. Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate. *Talanta* 2005; 66: 86-91.
- Renou S., Givaudan J. G., Poulain S., Dirassouyan F., Moulin P. Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials* 2008; 150: 468-493.
- Singh S. K., Tang W. Z., Tachiev G. Fenton treatment of landfill leachate under different COD loading factors. *Waste Management* 2013; 33: 2116-2122.
- Yang Y., Pignatello J. J., Ma J., Mitch W. A. Comparison of halide impacts on the efficiency of contaminant degradation by sulfate and hydroxyl radical-based Advanced Oxidation Processes (AOPs). *Environmental Science and Technology* 2014; 48: 2344-2351.
- Zhang H., Choi H. J., Huang C.-P. Optimization of Fenton process for the treatment of landfill leachate. *Journal of Hazardous Materials* 2005; B125: 166-174.
- Zhang H., Choi H. J., Huang C.-P. Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor. *Journal of Hazardous Materials* 2006; B136: 618-623.