The treatment of stabilized landfill leachate using iron-activated persulfate and peroxymonosulfate oxidation

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Graphical abstract

INTRODUCTION

Landfilling is the most common method of solid waste management throughout the world (Hoornweg and Bhada-Tata, 2012). One of the main environmental issues of landfilling is the generation of landfill leachates. Landfill leachates contain high organic content and a wide range of chemicals, including hazardous substances such as heavy metals (Bashir et al., 2015). The untreated leachates can emerge into the environment and cause serious soil and water pollutions (Deng and Englehardt, 2006). Therefore, it is critical to apply an efficient water treatment method to treat hazardous leachates to protect the environment.

In the landfill treatment plant, leachates are commonly treated biologically as the primary treatment process. Unfortunately, the biological treatment has been found to be ineffective in degrading high molecular weight compounds in leachates (Trebuout et al., 2001). As a result, coagulation-flocculation is often added to the leachate treatment to enhance organic content removal. However, this method is not always satisfactory in reducing organic content to the level that satisfied the environmental quality standards (Kurniawan et al., 2006). As a result, recent researches have been focused on the development of advanced oxidation processes (AOPs) to enhance the efficiency of leachate treatment. These methods including Fenton, ozone-based AOP, UV/H₂O₂, and photocatalysis (Liu et al., 2016; Jung et al., 2017; Hassan et al., 2016).

Recently, SR-AOP has drawn an increasing attention in the degradation of various organic pollutants (Asaithambi et al., 2017). During SR-AOP, sulfate radical (SR) (E° = 2.5-3.1 V) is one of the main reactive species that degrade organic compounds in water. SR can be produced using persulfate (PS) and peroxymonosulfate (PMS) through numerous activation methods such as heat, the addition of transition metals, and ultraviolet light. (Zhou et al., 2015). Meanwhile, the SR has been reported to have a longer radical lifetime (30-40 µs) and thus increases the probability to react with the non-biodegradable pollutant and the removal of organic content (Zhou et al., 2015).

SR-AOP was found to be efficient in degrading organic pollution such as pharmaceuticals in water, but most of these studies intensively focused on the treatment of individual compound (Anipsitakis et al., 2006; Olmez-Hanci et al., 2013; Ghanbari et al., 2016). The application of SR-AOP in real wastewater treatment is rarely reported. Recently, Fagier et al., (2016) reported that the high efficiency of SR-AOP in the removal of organic matter in distillery wastewater. This study showed that the efficiency of organic content removal in the distillery wastewater could be reduced at neutral pH. Therefore, SR-AOP has been classified as one of the potential water treatment methods to be
considered for industrial scale water treatment (Ghanbari and Moradi, 2017). This study aimed to evaluate the efficiency of SR-AOP in the degradation of COD in pre-treated stabilized landfill leachate (SLL). The effects of the main parameters, such as dosage, pH, type of oxidant to ferrous ion ratio, and reaction time were examined. Also, zebrafish (Danio rerio) was used to evaluate the ecotoxicity of the SR-AOP treated landfill leachate.

EXPERIMENTAL

Chemicals and reagents

Sodium hydroxide was purchased from Fluka (Germany). FeSO4.7H2O (99.5 %), while potassium peroxymonosulfate (PMS) (99 %), and potassium persulfate (PS) (99 %) were obtained from Acros Organics (USA). H2SO4 (95-97 %), FeCl3, and sand were purchased from Merck (Germany).

Landfill leachate pre-treated by coagulation-flocculation

SLL sample was collected from a sanitary landfill in Selangor, Malaysia. The SLL was first treated with coagulation-flocculation treatment with 1.4 g/L of FeCl3 as coagulant at pH 6. The coagulation-flocculation pre-treatment was started with the agitation of the mixture for 2 min at 200 rpm, followed by slow mixing for 30 min at 50 rpm. Then, the agitation was stopped, and the floc was left to settle for 1 h. After that, the treated SLL was then filtered through a sand filter before treated with SR-AOP.

Sulfate radical based advanced oxidation process

The SR-AOP reactions (PMS/Fe(II) and PS/Fe(II)) were carried out in batch mode at room temperature. At first, 25 mL of pre-treated SLL was added into a glass vial. Then, oxidants (PS or PMS) and catalyst (FeSO4.7H2O) were added. By using an orbital shaker, the mixtures were shaken at 150 rpm. In this study, the effect of four SR-AOP operating conditions on COD reduction was investigated. These parameters were oxidants to Fe(II) ratio (PMS:Fe(II) and PS:Fe(II)), pH, oxidant dosage, and reaction time. PMS:Fe(II) and PS:Fe(II) were determined by varying the concentration of Fe(II) at 12 mM of PS and PMS. Then, by using the optimized ratio, the effect of pH was conducted by adjusting the pH of pre-treated SLL using H2SO4 or NaOH. The effect of oxidant dosage was then investigated by varying the concentration of PS and PMS from 5 to 20 mM at pre-determined PMS:Fe(II) and PS:Fe(II) and pH. SR-AOP reactions for the above operating parameter were performed at 1 h reaction time. For reaction time optimization, the experiment was carried out from 0.5 until 5 h. All data from this study were analyzed using descriptive statistics method.

Characterization of leachates

All the physicochemical parameters of SLL were determined according to the APHA (2012) standard method. The turbidity and color were determined by Spectroquant Colorimeter Move-100 (Merck). COD measurement was conducted using the closed tube digestion method (Westwood 2007). Total Organic Carbon (TOC) was analyzed using the TOC analyzer (TOC-L, Shimadzu, Japan). The concentration of anions was determined using an Ion Chromatograph (Dionex ICS-1100).

Toxicity investigation

Acute toxicity of the treated leachate was evaluated by using zebrafish. This species has been classified as a model vertebrate for chemical and aquatic toxicity testing (Moșneag et al., 2014). The various pathway that controls the development of zebrafish is highly correlated with human physiology (Hollert and Keiter, 2015). Acute toxicity testing was conducted based on OECD Guideline (OECD, 2013). Ten similar size of fishes were transferred into a 5 L container for each concentration. The experiment was performed in triplicate and conducted for 48 h and 96 h without feeding. The mortality of the fish was recorded for LC50 determination. 96 h LC50 were converted to toxic unit values (TU) according to the following equation and then considered as an indication of the comparison.

\[
\text{Toxicity Unit (TU)} = \frac{100\%}{LC_{50}}
\]

RESULTS AND DISCUSSION

Landfill leachate characteristic

Coagulation-flocculation experiment was performed using FeCl3 as coagulant as described by Amor et al., (2015). The main chemical characteristics of the raw and pre-treated SLL are shown in Table 1. The results indicated that nearly 100 and 94% of turbidity and color were successfully reduced through coagulation-flocculation. The organic content (TOC and COD) was also significantly reduced after coagulation-flocculation. However, it was found that COD concentration was not complying with the allowable discharge standard in many countries. Kurniawan et al., (2006) reported that the maximum discharge standard of landfill leachate in the USA, Germany, France, Hong Kong, and South Korea, were 200 mg/L of COD. In this study, the COD concentration after coagulation-flocculation was 276 mg/L. The pre-treated SLL was then treated with SR-AOP.

Table 1 Chemical characteristic of SLL and pre-treated SLL.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SLL</th>
<th>Pre-treated SLL</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.59 ± 0.08</td>
<td>4.53 ± 0.05</td>
</tr>
<tr>
<td>COD (× 10² mg/L)</td>
<td>11.2 ± 0.2</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>TOC (× 10² mg/L)</td>
<td>3.56 ± 0.06</td>
<td>1.07 ± 0.04</td>
</tr>
<tr>
<td>Turbidity (× 10² FAU)</td>
<td>3.0 ± 0.1</td>
<td>Not detected</td>
</tr>
<tr>
<td>Colour (× 10³ Pt-Co)</td>
<td>50.98 ± 0.02</td>
<td>3.1 ± 0.1</td>
</tr>
</tbody>
</table>

SR-AOP optimization

In this study, two different types of oxidants, namely PS (S2O8²⁻) and PMS (HSO5⁻) were used to generate SR. In water, these oxidants showed high solubility and stability at different pHs (Zhou et al., 2015; Fagier et al., 2016). Therefore, this method can be an added advantage to leachate treatment since the leachate may turn acidic after coagulation-flocculation. In this study, Fe(II) was used as a catalyst to activate the SR because of its low toxic and environmentally friendly (Rastogi et al., 2009). The SR formation from Fe(II) activated PS and PMS are illustrated by the following equations:

\[
S_{2}O_{8}^{2-} + Fe^{2+} \rightarrow SO_{4}^{2-} + SO_{2}^{2-} + Fe^{3+} \quad k = 2.0 \times 10^{8} \text{M}^{-1}\text{S}^{-1}
\]

\[
HSO_{5}^{-} + Fe^{2+} \rightarrow SO_{4}^{2-} + OH^{-} + Fe^{3+} \quad k = 3.0 \times 10^{3} \text{M}^{-1}\text{S}^{-1}
\]

The effect of the operating condition of SR-AOP on the COD reduction was examined by varying the PS:Fe(II) and PMS:Fe(II) ratios, pH, oxidant’s dosage, and reaction time (Fig. 1). The effect of oxidant:Fe(II) ratio was investigated by varying the Fe(II) concentration from 1 to 24 mM. The oxidants (PS and PMS) concentration was fixed at 12 mM. The result from these experiments was presented as the percentage reduction of COD versus PS:Fe(II) and PMS:Fe(II) (Fig. 1a). The control experiment was first setup without the addition of Fe(II) to investigate the possibility of PS and PMS in reducing the concentration of COD of pre-treated SLL. It was found that less than 3% of COD was reduced without the addition of Fe(II). The increasing Fe(II) concentration was found to enhance the percentage of COD reduction for the treatment of both systems. As shown in Fig. 1a, percentage of COD reduction was found to increase with increasing PS:Fe(II) and PMS:Fe(II) from 1:0.5 to 1:2. This result was due to the generation of the higher amount of SR and consequently, increased the COD reduction efficiency (Rastogi et al., 2009). However, when the PS:Fe(II) and PMS:Fe(II) were increased to 1:3, no significant increment of COD reduction was observed. This result was attributed to the utilization of SR by the excess amount of Fe(II), as shown in Equation 4 (Matzek and Carter, 2016). In this situation, the rate of scavenging reaction of SR by Fe(II) (Eq. 4) is greater than the SR production rate (Eq. 2 and 3). Therefore, the SR formation was...
The pH effect on the COD reduction efficiency was investigated from pH 3 to 7. The percentage of COD reduction was found to vary from 19.7 to 21.7 % for PMS and PS treatment systems, respectively (Fig. 1b). This result indicated that pH did not significantly influence the COD reduction. The data were found to be in agreement with some of the previous studies which indicated that the optimum organic pollutants removal efficiency occurred at acidic conditions due to acid-catalysis formation of SR (Zhang et al., 2015). This phenomenon is probably due to the complexion of dissolved organic pollutant with Fe(II) in landfill leachate. Organic-Fe(II) complexation can prevent the Fe(II) from being precipitated, thus enhanced the COD removal (Wu et al., 2014). Therefore, it could be an added advantage for this method to be coupled with coagulation-flocculation, which often lowering down the pH of the pre-treated landfill leachate. The optimum pH condition for SR-AOP was in the range of 4–5. Therefore, no additional pH adjustment is needed.

The effect of oxidant dosage concentration on COD reduction was investigated using PMS:Fe(II) and PS:Fe(II) of 1:2 and 1 h reaction time. The concentration of oxidants (PMS and PS) was varied from 5 mM to 20 mM (Fig. 1c). COD reduction efficiency was found to increase with increasing oxidant dosage from 5 to 15 mM. In PMS:Fe(II) and PS:Fe(II) system, the percentage COD reduction was increased from 18.7 % to 24 % and from 15.7 % to 22.8 %, respectively. The increased percentage of COD reduction was due to higher production of SR, which favored the oxidation process (Olmez-Hanci et al., 2013). However, the COD removal efficiency of both treatment systems was found to decrease after the oxidant dosage of 20 mM. This result was attributed to the scavenging reaction of SR by the excess amount of Fe(II) and PS, as indicated in Eq. 5 and 6. The rate of SR production was much lower than the rate of scavenging reaction. In addition, peroxysulfate (SO52−) (E° = 1.1V) and persulfate radical that (SO4•−) (E° = 2.1V) generated from the reaction are weaker oxidants in comparison with SR (E° = 2.5-3.1 V), thus higher PS and PMS dosage could lower the COD reduction efficiency (Jaafarzadeh et al., 2016). Furthermore, SR may self-react and inhibit the COD reduction efficiency (Eq. 7) (Olmez-Hanci et al., 2013).

\[ SO_4^{2−} + SO_2^{−} \rightarrow SO_3^{2−} + SO_3^{2−} \quad k = 6.1 \times 10^{4} \text{M}^{-1}\text{s}^{-1} \quad (5) \]

\[ HSO_3^{−} + SO_2^{−} \rightarrow SO_3^{−} + HSO_4^{−} \quad k = 1 \times 10^{3} \text{M}^{-1}\text{s}^{-1} \quad (6) \]

\[ SO_4^{2−} + SO_3^{−} \rightarrow SO_4^{2−} \quad k = 4 \times 10^{6} \text{M}^{-1}\text{s}^{-1} \quad (7) \]

The effect of reaction times on the percentage of COD concentration was measured after 0.5, 1, 2, 3, and 5 h (Fig. 1d). After the first 3 h reaction, both PS:Fe(II) and PMS:Fe(II) systems showed significant COD reduction. The percentage of COD reduction for PS:Fe(II) and PMS:Fe(II) after 3 h of reaction time were 33.6 and 34.6 %. The efficiency of COD reduction was found to increase slowly to 34.7 and 35.2 % after 5 h for PS:Fe(II) and PMS:Fe(II), respectively. Hence, 3 h of reaction time was sufficient to achieve the highest efficiency in COD reduction of pre-treated SLL. At all reaction times, PMS:Fe(II) showed slightly higher COD removal as compared to PS:Fe(II). This condition might be due to the high reactivity of PMS as compared to PS in generating SR. As shown in the Eq. 6 and 7, PMS is 1000 times more reactive than PS.

**Treatment of SLL using optimized SR-AOP**

The efficiency of the combination of coagulation-flocculation with PMS:Fe(II) and PS:Fe(II) was re-evaluated using the previous optimized condition. The overall efficiency of the evaluated treatment methods is presented in Table 2. It has been observed that 83.9 and 84.8 % of COD were reduced from SLL by the combination of coagulation-flocculation treatment coupled with PS:Fe(II) and PMS:Fe(II), respectively. The final effluent was found to comply with the discharge standard, which is below 200 mg/L of COD.

**Table 2** Summary of the performance of selected treatment process (Reaction condition: oxidant: Fe(II) ratio = 1:2, pH = 5.2, dosage = 12 mM, reaction time = 3 h).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw Leachate</th>
<th>Coagulation-Flocculation (CF)</th>
<th>Total Removal after CF +</th>
<th>PMS-Fe(II)</th>
<th>Total Removal after CF +</th>
<th>PS-Fe(II)</th>
<th>Colour (× 10^2 Pt/Co)</th>
<th>Turbidity (× 10^2 FAU)</th>
<th>TOC (× 10^2 mg/L)</th>
<th>COD (× 10^2 mg/L) (% removal)</th>
<th>Removable Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMS-Ferrihydrite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw Leachate</td>
<td>11.2 ± 0.2</td>
<td>2.6 ± 0.1 (76.8)</td>
<td>2.6 ± 0.1</td>
<td>1.7 ± 0.2</td>
<td>11.2 ± 0.2</td>
<td>1.7 ± 0.2</td>
<td>1.7 ± 0.2</td>
<td>3.1 ± 0.1</td>
<td>50.98 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>3.47 ± 0.06</td>
<td>0.95 ± 0.04 (72.6)</td>
<td>0.95 ± 0.04</td>
<td>0.65 ± 0.02</td>
<td>3.47 ± 0.06</td>
<td>0.65 ± 0.02</td>
<td>0.65 ± 0.02</td>
<td>Not Detected</td>
<td>(100)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>3.0 ± 0.1</td>
<td>0.70 ± 0.03 (26.3)</td>
<td>0.70 ± 0.03</td>
<td>0.65 ± 0.02</td>
<td>3.0 ± 0.1</td>
<td>0.65 ± 0.02</td>
<td>0.65 ± 0.02</td>
<td>Not Detected</td>
<td>(100)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Ecotoxicity analysis**

The changes in the ecotoxicity of SLL after coagulation-flocculation and SR-AOP treatments were investigated using zebrafish. The ecotoxicity of this study was assessed through the determination of LC50 for 48 h and 96 h (Table 3). LC50 is the concentrations of the standard, which is below 200 mg/L of COD. The ecotoxicity of this study was assessed through the determination of LC50 for 48 h and 96 h (Table 3). LC50 is the concentrations of the standard, which is below 200 mg/L of COD. The ecotoxicity of this study was assessed through the determination of LC50 for 48 h and 96 h (Table 3). LC50 is the concentrations of the standard, which is below 200 mg/L of COD.
zebrafish. In general, the treatment of pre-treated SLL using PS/Fe(II) shows higher potential application since it yields effluent with lower toxicity as compared to PMS/Fe(II).

**Table 3** LC50 (% v/v) of SLL and treated SLL on zebrafish after 48 and 96 h exposure.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>48 h LC50</th>
<th>96 h LC50</th>
<th>Toxicity Unit (TU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Leachate</td>
<td>11.0 ± 0.2</td>
<td>9.9 ± 0.2</td>
<td>10.14 ± 0.02</td>
</tr>
<tr>
<td>Coagulation-Flocculation</td>
<td>58.7 ± 0.7</td>
<td>57.4 ± 0.7</td>
<td>1.74 ± 0.02</td>
</tr>
<tr>
<td>PS-Fe(II)</td>
<td>55.0 ± 0.5</td>
<td>54.3 ± 0.2</td>
<td>1.84 ± 0.02</td>
</tr>
<tr>
<td>PMS-Fe(II)</td>
<td>33.4 ± 0.3</td>
<td>32.0 ± 0.2</td>
<td>3.13 ± 0.03</td>
</tr>
</tbody>
</table>

**CONCLUSION**

This study investigated the efficiency of SR-AOP in the treatment of pre-treated SLL. Almost 76.8 % of COD from SLL was removed after coagulation-flocculation pre-treatment. However, the treated SLL still required additional treatment since the COD concentration was exceeded the maximum discharge standard. It was found that the operating parameter in SR-AOPs treatment such as the ratio of PS and PMS to Fe(II), PS and PMS dosage, and reaction time had influence on the efficiency of COD removal. However, the pH did not show significant influence on the efficiency of COD reduction in SR-AOPs. By using the optimized condition, 30.8% and 34.6% of COD were effectively reduced using PS-Fe(II) and PMS-Fe(II), respectively. The COD concentration of SLL after SR-AOP treatment was lower than the standard discharge limit for most of the countries. This finding indicated that SR-AOPs treatment could be an alternative method to other conventional leachate treatment. In term of toxicity of effluent, the toxicity was increased slightly due to the presence of sulfate ion after SR-AOPs. The method for removal of sulfate ions such as ion exchange or chemical precipitation needs to be considered before practically applied the SR-AOPs in the real leachate treatment system.

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