Electro-oxidation of landfill leachate using boron-doped diamond: role of current density, pH and ions

F. Agustina, A. Y. Bagastyo and E. Nurhayati

ABSTRACT

Electro-oxidation using a boron-doped diamond (BDD) anode can be used as an alternative to leachate treatment. Aside from the hydroxyl radical, BDDs are capable of generating chloride and sulfate radical species that play significant roles in the oxidation of pollutants. This research investigated the role of Cl⁻/SO₄²⁻ ions at molar ratios of 237:1, 4:1 and 18:1, and the influence of applied current density (i.e. 50, 75 and 100 mA cm⁻²) on the removal of organic and ammonium contaminants. The results show that current density had considerable effects on chemical oxygen demand (COD) and colour removal, while ion composition of Cl⁻/SO₄²⁻ at pH 3, 5 and 8.5 (original pH) gave different effects on COD and ammonium removal. The pH had a significant effect on the COD removal at the ratio of 237:1, but showed no dramatic effect at the ratio of 18:1, giving ~40% of COD removal at all pHs tested. This indicates that electro-oxidation at the ratio of 18:1 could be effectively conducted at a wide range of pH. Furthermore, the optimum ammonium removal was obtained at pH 8.5 with the ratio of 237:1. This process was found to be ineffective in increasing the biodegradability index of the leachate; instead, it exhibited mineralization of organic content.

Key words | boron-doped diamond anode, electrochemical oxidation, leachate

INTRODUCTION

Leachate generated from municipal solid waste landfill is a wastewater containing organic and inorganic contaminants, including some refractory and toxic compounds. Due to its complex composition, landfill leachate is one of the major environmental problems concerning water pollution (Fernandes et al. 2018) in the context of solid waste management. Landfill leachates have been identified as potential sources of ground and surface water contamination, if they are not properly collected, treated and safely disposed (Tatsi et al. 2005).

The composition of landfill leachates varies depending on landfill characteristics, such as waste type and its composition, water content and its degree of compaction, landfilling technique (waterproof covers, liner requirements such as clay and geotextiles), climate and seasonal weather variation, and age of landfill leachate (Renou et al. 2008). As the landfill age increases, most of the biodegradable organic matter contributed to the leachate matrix; that is, determined as biochemical oxygen demand (BOD) concentration, is decomposed in the stabilization process. As a result, the remaining organic matter contained in the leachate will be dominantly non-biodegradable. Therefore, the organic matter determined as chemical oxygen demand (COD) will be the dominant non-biodegradable fractions, and will largely remain unchanged (Fernandes et al. 2015), whereas BOD will be decreased. This leads to a lower ratio of BOD/COD in the leachate generated from a ‘mature’ landfill site. This type of leachate has recently become of concern to governments, particularly in developing countries, as an advanced treatment process is required to support the existing biological processes.

Electrochemical oxidation is one of the effective physico-chemical methods applied to remove organic pollutant and inorganic nutrients, such as ammonia, particularly contained in landfill leachate wastewater. The efficiency of electro-oxidation depends on various parameters such as current density, type of anode, pH, as well as the type and concentration of electrolyte (i.e. ionic compound) used during the process (Anglada et al. 2011). In terms of applied current density, Zhou et al. (2016) reported that COD removal increases with increasing current density. Increasing current density during electro-oxidation yielded
enhancement of pollutant removal, which may be attributed to a higher amount of the formed hydroxyl radicals at the anode surface or by the accelerated generation of chlorine/hypochlorite compounds (Mandal et al. 2017).

Based on the different heterogeneous species formed from water discharge, anodes were classified as ‘active’ and ‘non-active’ (Comninellis 1994). Active anodes interact strongly with OH’, forming chemisorbed ‘active oxygen’ species that lead to electrochemical conversion of organic pollutants. On the other hand, non-active anodes, such as boron-doped diamond (BDD), interact weakly with OH’ to form physisorbed OH’; that is, one of the strongest oxidants. This leads to mineralization of organic compounds. Therefore, non-active anodes, such as BDD, are attractive to be implemented for the treatment of wastewater containing recalcitrant organic contaminants like leachate wastewater.

In addition, BDD is one of the non-active anodes having the capability of generating reactive oxygen species (ROS), such as heterogeneous OH’ and H2O2, and O3, from the electrochemical process. Besides ROS, BDD anodes are also capable of generating inorganic radical species such as chloride (Cl’, Cl2) and sulfate (SO42-) in the presence of their corresponding ion (Davis et al. 2014; Farhat et al. 2017). During the electrochemical process, the sulfate ion can be oxidized to form SO42-. This species may demonstrate 10–15 fold higher removal rates of several persistent organic contaminants compared to OH’ based anodic oxidation (Farhat et al. 2015). The addition of the chloride ion gradually decreases the rate constant of organic compound removal measured as total organic carbon (TOC) in Na2SO4 anolyte, as reported by Farhat et al. (2017). This inhibiting effect of chloride is a consequence of more pronounced scavenging of SO42- by Cl- (Equation (1)). In the presence of chloride, the electro-generated OH’ can be expected to be scavenged by the Cl- and converted to chloride radical species.

\[
\text{SO}_4^{2-} + \text{Cl}^- \rightarrow \text{Cl}^+ + \text{SO}_4^{2-}
\]  

(1)

It is interesting to note that the presence of ionic compounds, for example chloride and sulfate ions, have significant roles in the removal of organic pollutants, which can be affected by their concentration and pH of the wastewater. Therefore, this study aims to investigate the role of sulfate and chloride ions that are available in different ratios on the oxidation of landfill leachate wastewater. The treatment efficiency was evaluated based on the removal of COD and ammonia. Furthermore, BOD and TOC concentrations were also determined to evaluate the oxidation mechanism of organic pollutants in the leachate.

**METHODS**

**Samples and reactor materials**

The leachate used in this study was sampled from the influent of the leachate treatment facility of a municipal solid waste landfill located in Gresik, Indonesia. The characteristics of the leachate are summarized in Table 1. The experiments were conducted in a single cell acrylic reactor (internal dimensions: 4 × 2 × 10 cm, with an actual volume of 80 mL). The reactor was run in a batch recirculation mode. Boron-doped diamond was used as anode and silver was used as cathode with each surface area 8 cm² and an electrode gap of 20 mm.

**Experimental set-up for electrochemical oxidation**

This study was comprised of two experimental steps; that is, (i) an experiment to investigate the role of current density and (ii) the main experiment to investigate the role of the supporting ion and pH. The first step of the experiment was conducted by evaluating three different constant current densities; that is, 50, 75, and 100 mA cm⁻² without pH adjustment (pH 8.5) and electrolyte addition. In this experiment, 1 L landfill leachate was pumped into the reactor and recirculated for 6 hours at a flow rate of 2 mL s⁻¹ (Figure 1). Samples taken after 0.2, 4 and 6 h of electro-oxidation were filtered using a PTFE 0.45 μm syringe filter (CNW Technologies) for further analyses. The concentration of COD, true colour intensity, pH and conductivity were measured.

The main experiment of landfill leachate electro-oxidation was conducted at a constant current density of 75 mA cm⁻². In this experiment, 1 L landfill leachate was

<table>
<thead>
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<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td>–</td>
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</tr>
<tr>
<td>Conductivity</td>
<td>mS cm⁻¹</td>
<td>10.74</td>
</tr>
<tr>
<td>COD_total</td>
<td>mg O₂ L⁻¹</td>
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</tr>
<tr>
<td>Cl⁻</td>
<td>mg L⁻¹</td>
<td>1,400</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>mg L⁻¹</td>
<td>535</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>mg L⁻¹</td>
<td>40.58</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg O₂ L⁻¹</td>
<td>350</td>
</tr>
<tr>
<td>BOD₅/COD</td>
<td>–</td>
<td>0.17</td>
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</table>
continuously recirculated for 7 hours at a flow rate of 2 mL s⁻¹. Similarly, samples taken after 0, 1, 2, 3, 5 and 7 h of electro-oxidation were filtered by using a PTFE 0.45 μm syringe filter (CNW Technologies). The experiments were conducted at pH 3, pH 5 and the original pH (pH 8.5). Nitric acid was added to adjust the leachate pH to 3 and 5. In order to assess the role of generated active species such as radical chloride and radical sulfate, the supporting ions (i.e. NaCl and Na₂SO₄) were added to the leachate. The supporting ions added were 0.05 M NaCl, 0.05 M Na₂SO₄, and 0.025 NaCl + 0.025 M Na₂SO₄. This addition was intended to reach molar ratios of Cl⁻ : SO₄²⁻ in the leachate 237:1, 4:1 and 18:1, respectively. The concentration of COD, BOD₅, ammonium, sulfate, chloride, TOC, and total chlorine were measured.

**Analytical methods**

COD was measured using closed reflux and colourimetric method (Merck and Spectroquant NOVA). True colour intensity was measured by means of absorbance at 420 nm wavelength using the Genesys20 spectrophotometer. Ammonium was measured using the Genesys20 spectrophotometer (Nessler method). BOD₅ was measured using the Winkler method. Total chlorine was measured using DPD (N,N-diethyl-p-phenylenediamine) method (Hach). pH and conductivity were monitored by using a pH meter and electrical conductivity meter (Lutron).

**RESULTS AND DISCUSSION**

**Effect of current density on the removal of COD and the decrease of colour intensity**

To determine the efficiency of electro-oxidation in degrading organic compounds, the removal of COD and the decrease of colour intensity were observed. Figure 2 shows the normalized COD mass [COD/COD₀] and colour absorbance decrease during electro-oxidation of leachate at the unadjusted pH in three different constant current densities. At higher applied current density; that is, 100 mA cm⁻², removal of COD was increased up to 49% at the end of the experiment, although there was a slight increase in COD observed after 2 h electro-oxidation. Similarly, up to 36% decrease of colour intensity was observed.

Zhou et al. (2016) reported that electro-oxidation of landfill leachate at a current density of 50 and 100 mA cm⁻² under pH 5.2 removed 0.66 g and 0.68 g COD, respectively, after 6 hours' operation. A similar result was obtained in this study, where 0.43, 0.53 and 0.72 g COD were removed when current densities of 50, 75 and 100 mA cm⁻² were applied, respectively, after 6 h of electro-oxidation. Both results were comparable since the electro-oxidation of leachate was conducted at the same current density, although the pH difference might cause the difference in COD degradation performance.
Higher current density applied to the system indeed increases specific energy consumption. After 6 h electro-oxidation at 50, 75 and 100 mA cm$^{-2}$ the specific energy consumptions were 22.1, 42.2 and 62.4 Wh L$^{-1}$, respectively, which is equal to an energy consumption of 51.5, 80.1, and 86.4 Wh g$^{-1}$ COD removed, respectively.

It can be noted that increasing the current density from 75 mA cm$^{-2}$ to 100 mA cm$^{-2}$ did not considerably affect the energy consumption to remove COD mass. A similar result was reported by Anglada et al. (2014). To eliminate 30% of COD, energy consumption of 102 kWh kg$^{-1}$ COD and 134 kWh kg$^{-1}$ COD were needed at 8.4 A and 18 A, respectively. This also indicates that at higher current density of 100 mA cm$^{-2}$, energy was more consumed not only for oxidation of organic compounds, but also for oxidation of other ions in the leachate (i.e. dominantly chloride ions), leading to the indirect oxidation of organics, measured as COD.

**Effect of Cl$^-\text{ and SO}_4^{2-}$ on the removal of COD and ammonium without pH adjustment**

In order to assess the role of formed active species such as chloride and sulfate radicals on electro-oxidation, the initial leachate was adjusted to simulate three different molar ratios of Cl$^-$ and SO$_4^{2-}$ ions without pH adjustment as shown in Table 2. Evaluation of the electro-oxidation treatment was based on the removal of COD and ammonium. Figure 3 shows the normalized mass of COD [COD/COD$_0$] and ammonium [NH$_4^+$/NH$_4^+\text{}_0$] measured up to 7 h of electro-oxidation process at a constant current density of 75 mA cm$^{-2}$.

Overall, at the final electro-oxidation of 4.56 Ah L$^{-1}$, COD removal at a molar ratio of 237:1 was the lowest (i.e. 0.48 g COD) amongst the other two molar ratios. Electro-oxidation of leachate at molar ratios of 4:1 and 18:1 showed a similar mass of COD removed; that is, 0.74 g and 0.73 g, respectively. This implies that the presence of sulfate ions may increase organic removal in the leachate due to the formation of sulfate reactive species during electrochemical process. Farhat et al. (2015, 2017) reported that the removal of organic pollutants was 10–15 fold higher when sulfate ions were present in the bulk system compared to OH$^-$-based anodic oxidation via indirect oxidation, due to the formation of sulfate reactive species such as SO$_4^{2-}$.

As mentioned earlier, electro-oxidation of organic matter can occur not only on the anode but also through indirect oxidation by oxidant/reactive species formed during the process. In this study, the concentration of chloride ions in the leachate is relatively high; that is, 1.50–3.55 g L$^{-1}$ (Table 2). Thus, the formation of chloride reactive species was expected as the dominant oxidative species in the anodic oxidation of leachate. Table 3 shows the total chlorine (the sum of free and combined chlorine compounds) formed after 7 h of electro-oxidation (4.56 Ah L$^{-1}$) for all the experiments.

It can be confirmed that the formation of total chlorine increases with the increasing of chloride concentration at all pH, except at pH 5. In acidic conditions, the formed chlorine species can possibly be stripped out, decreasing its presence in the bulk system (Deborde & von Gunten 2008).
Thus, the total chlorine measured at pH 3 was relatively lower than at other pH conditions. It is expected that by increasing the chloride concentration, the indirect oxidation can be improved (Cabeza et al. 2007). However, it is also expected that higher chloride concentration may lead to competition between oxidation of the intended organic pollutant and oxidation of chloride at the anode surface.

Furthermore, besides contributing to the COD removal, chlorine species also play an important role in the removal of ammonium. In this study, the removal of ammonium at molar ratio of 237:1, 4:1, and 18:1 after 4.56 Ah L\(^{-1}\) of electro-oxidation was 0.245 g, 0.122 g and 0.215 g, respectively. It can be noted that higher removal of ammonium was obtained at higher chloride concentration; that is, approximately 50–60% removal at a molar ratio of 237:1 and 18:1. Ammonium is mainly removed through the reaction with chlorine/hypochlorite generated during electro-oxidation (Chu et al. 2008; Mandal et al. 2017). In addition, ammonium is oxidized to form chloramines and other species; that is, NH\(_2\)Cl, NHCl\(_2\), NOH, N\(_2\) and NO\(_3^-\) (Mandal et al. 2017). Cabeza et al. (2007) suggest that the kinetic of ammonium removal was improved with increasing chloride concentration in the electro-oxidation process. As reported in the study, when the chloride concentration was increased from 1,420 mg L\(^{-1}\) to 8,570 mg L\(^{-1}\), an increase of ammonium removal was achieved from around 35% to a nearly complete removal.

**Effect of pH on the removal of COD and ammonium at pH 3 and pH 5**

The removal of COD at a molar ratio of 237:1 was enhanced in acidic conditions. The electro-oxidation process at a ratio of 237:1 and pH 5 obtained higher COD removal than in the case of the original pH 8.5, whereas at pH 3 COD removal was improved to twofold higher than electro-oxidation at pH 5 (Figures 3 and 4(a)). The COD mass removals at ratio 237:1 under original pH, pH 5 and pH 3 were 0.48 g, 0.58 g and 1.19 g, respectively. Bagastyo et al. (2012) also observed that COD removal rates at pH 5 were higher than those at pH 7 and 9.

**Table 3**  Total chlorine formed after 7 h of electro-oxidation

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Cl(_2) (mg L(^{-1}))</th>
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<tbody>
<tr>
<td>Molar ratio 237:1 at original pH (pH 8.5)</td>
<td>202</td>
</tr>
<tr>
<td>Molar ratio 4:1 at original (pH 8.5)</td>
<td>54</td>
</tr>
<tr>
<td>Molar ratio 18:1 at original (pH 8.5)</td>
<td>179</td>
</tr>
<tr>
<td>Molar ratio 237:1 at pH 5</td>
<td>133</td>
</tr>
<tr>
<td>Molar ratio 4:1 at pH 5</td>
<td>27</td>
</tr>
<tr>
<td>Molar ratio 18:1 at pH 5</td>
<td>87</td>
</tr>
<tr>
<td>Molar ratio 237:1 at pH 3</td>
<td>56</td>
</tr>
<tr>
<td>Molar ratio 4:1 at pH 3</td>
<td>55</td>
</tr>
<tr>
<td>Molar ratio 18:1 at pH 3</td>
<td>112</td>
</tr>
</tbody>
</table>

Figure 3  (a) [COD/COD\(_0\)] and (b) [NH\(_4^+\)/NH\(_4^+\)\(_0\)] during 7 h of electro-oxidation without pH adjustment.
also previously reported that COD removal at acidic pH was faster than at circumneutral. With an initial COD of 136 ± 8 mg L⁻¹, a complete COD removal was obtained after 5.2 and 6.6 Ah L⁻¹ at acidic and circumneutral pH, respectively. However, in the present study, pH has no considerable effect at a ratio of 18:1. The COD removals at original pH, pH 3 and pH 5 were 0.73 g, 0.72 g, and 0.73 g, respectively. Therefore, the electro-oxidation process of leachate that has a ratio of 18:1 could possibly be conducted in a wide range of pH values.

In contrast, ammonium removal seems to be affected by pH value (Figure 4). In the experiment at ratios of 4:1 and 18:1, removal of ammonium at pH 3 was higher than at pH 5. Ammonium removal at pH 3 and 5 at a ratio of 4:1 was 0.195 g and 0.09 g and similarly at a ratio of 18:1 was 0.2 g and 0.088 g, respectively. However, in the electro-oxidation process at a ratio of 237:1, the ammonium removal at pH 3 was lower than at pH 5. This result indicates that there is competition for COD and ammonium removal during the electro-oxidation process, signified by the high removal of COD obtained at pH 3 with a ratio of 237:1.

In all experiments, the electro-oxidation process at the original pH of the leachate (Figure 3) obtained higher ammonium removal than at pH 5 (Figure 4). Chu et al. (2008) also mentioned that the best ammonium removal was obtained at pH 8. Higher ammonium removal was obtained at alkali pH due to the volatilization of ammonium to form NH₃ (Deborde & von Gunten 2008).

Changes of biodegradability index (BOD₅:COD ratio) of landfill leachate

There are two oxidation mechanisms of pollutants in an electrochemical system; that is, (i) electrochemical conversion in which organics are transformed to be more biodegradable and (ii) electrochemical combustion, in which organics are completely oxidized to CO₂ and H₂O (Comninellis 1994). BOD₅ was measured to evaluate the electrochemical conversion of this process. Table 4 shows the changes of biodegradability index after 7 h electro-oxidation for all the experiments.
BOD₅ value was decreased in all experiments, as well as the BOD₅:COD ratio, except at the ratio of 237:1 at pH 3, when there was a slight increase of BOD₅:COD ratio. In the experiments at original pH and pH 5, all ratios of Cl⁻:SO₄²⁻ resulted in similar BOD₅:COD ratios. Labiad et al. (2013) reported that in anodic oxidation of reverse osmosis concentrate of landfill leachate using a BDD anode, there was a slight increase in BOD₅:COD from 0.43 to 0.51 after 24 h. In other words, the experimental condition of the present electro-oxidation study was not suitable for enhancing the biodegradability index of landfill leachate. However, the decrease of the BOD₅:COD ratio indicates that electrochemical combustion may take place.

To evaluate the electrochemical combustion process, TOC was measured to indicate the mineralization of organic pollutants (Table 5). TOC removals of 16–31% were achieved after 4.57 Ah L⁻¹. The maximum TOC removal was obtained at the ratio of 4:1 under original pH, whereas the minimum TOC removal was obtained at a ratio of 237:1, also under original pH; that is, 208.7 mg and 128 mg TOC, respectively. For all of the experiments, the COD removal was higher than TOC removal. A previous study suggested that faster COD removal than DOC removal indicates the formation of organic by-product compounds, such as chlorinated organic compounds (Bagastyo et al. 2012).

### Energy consumption

This electro-oxidation process requires electrical energy. To analyse the energy consumption under different experimental conditions, the specific energy consumption (g Wh⁻¹) was calculated using Equation (2) below:

\[
E_{sp} = \frac{\Delta X}{V I t}
\]

where \( \Delta X \) is mass removed (g), \( V \) is the cell voltage (volts), \( I \) was the applied current intensity (A) and \( t \) was the duration of electro-oxidation process (hours). This specific energy consumption was evaluated based on the mass of COD and ammonium removed (Table 6).

Based on Table 6, the optimum energy consumption based on COD removal was obtained at the ratio of 237:1 and pH 3, whereas the optimum energy consumption regarding ammonium removal was attained at the ratio of 237:1 at the original pH of the leachate. Overall, the optimum energy consumption for COD was achieved at pH 3 at all ratios; meanwhile, the optimum energy consumption of ammonium was obtained at the ratio of 237:1.

### CONCLUSIONS

In this study, the role of current density and variation of ratio Cl⁻:SO₄²⁻ at different pH were investigated. Current
density plays an important role, as proven in that the higher current density could increase the removal of COD and true colour intensity of the landfill leachate up to 49% and 36%, respectively. However, higher current density leads to an increase of specific energy consumption. In the electro-oxidation process for landfill leachate under original pH, the presence of sulfate ions may increase the removal of COD, while higher ammonium removal was achieved at higher chloride concentrations. On the other hand, the role of Cl⁻:SO₄²⁻ at different pH of leachate gives a different effect on COD and ammonium removal. In the electro-oxidation process with a ratio of 237:1, the COD removal increase at acidic conditions, whereas at the ratio of 4:1, there was a slight increase of COD removal in acidic conditions. However, at the ratio of 18:1, no substantial effect of pH on the COD removal was observed, indicating that the electro-oxidation process at this ratio could be conducted within a wider range of pH conditions. In contrast, ammonium removal seems to be more affected by pH value. The optimum ammonium removal was obtained at the ratio of 237:1 at original pH 8.5, due to the volatilization of ammonium to form ammonia. Furthermore, this electro-oxidation system was found to be effective in mineralization of organics but ineffective in increasing the index of biodegradability of landfill leachate.

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