Application of boron-doped diamond, Ti/IrO₂, and Ti/Pt anodes for the electrochemical oxidation of landfill leachate biologically pretreated by moving bed biofilm reactor

Arso Yekti Bagastyo, Arum Sofiana Hidayati, Welly Herumurti and Ervin Nurhayati

ABSTRACT

Conventional biological treatments used in most Indonesian landfill sites are mostly ineffective in treating stabilized landfill leachates to meet the standard regulation. Thus, a combination of biological and electrochemical process is offered to successfully treat leachates containing a high concentration of organic and nitrogenous compounds. In this study, a moving bed biofilm reactor (MBBR) was applied prior to electrochemical oxidation by using boron-doped diamond (BDD), Ti/IrO₂, and Ti/Pt anodes with applied current of 350, 400 and 450 mA. The objectives were to investigate the effect of anode type and the applied current on the removal of organics as well as total nitrogen from the MBBR-treated leachate with electrochemical oxidation. The optimum removal of chemical oxygen demand (COD) observed on the Ti/Pt anode was 78% by applying 400 mA, with an estimated energy of 56.7 Wh g L⁻¹. In the case of Ti/IrO₂ and BDD anodes, the optimum removal of COD was 76 and 85% with an energy consumption of 58.9 and 36.9 Wh g L⁻¹, respectively, both achieved at 350 mA. Although all anodes showed less-satisfactory performances for total nitrogen reduction, around 46–95% removal of nitrogenous compounds was achieved by MBBR, with their partial conversion to nitrates.

Key words | active anodes, biologically treated leachate, electrochemical oxidation, non-active anode, recirculating electrochemical cell

HIGHLIGHTS

- Real stabilized leachate has been treated by combined MBBR-electrochemical oxidation process.
- Sequential removal of nitrogenous and organics compound in the leachate was obtained.
- At optimum current applied, 85, 78, and 76% COD removal achieved by BDD, Ti/Pt, and Ti/IrO₂ anode.
- BDD has the lowest energy consumption of 36.9–55.6 kWh g⁻¹ COD removed at 350–450 mA.

INTRODUCTION

Since 2016, the Indonesian government has implemented a more stringent landfill leachate standard for safe disposal to the environment. According to this regulation, the...
concentration of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total nitrogen in the leachate effluents may not exceed 150, 300, and 60 mg L\(^{-1}\), respectively.

Biological treatment is widely used in Indonesia due to its low cost and ease of field application. Unfortunately, biological processes implemented for leachate treatment are only capable of removing the biodegradable part of organic content in the leachate, whereas the non-biodegradable fractions in the system remain largely untreated. The problem is that the older the landfill the more non-biodegradable the leachate fractions (Alvarez-Vazquez et al. 2004). A previous study reported leachate effluent concentration as high as 3,399.13 mg BOD L\(^{-1}\), 9,525.6 mg COD L\(^{-1}\), and 334.43 mg total N L\(^{-1}\) at a landfill site that has been operated for 33 years (Noerfitriyani et al. 2018). This means leachate treatment in most landfill sites in Indonesia, which relies on biological treatment methods (i.e. stabilization ponds), fails to meet the requirement, particularly for stabilized landfill leachates. Nevertheless, biological treatments are proven to be effective for the removal of nitrogen, which is also contained in high concentration in the leachate (Xiong et al. 2018). Therefore, a combination of biological and non-biological processes is deemed necessary for successful leachate treatment.

Various methods have been used to biologically treat leachate, such as the membrane bioreactor (MBR) (Feki et al. 2009) moving bed biofilm reactor (MBBR) (Chaturvedi & Kaushal 2018; Xiong et al. 2018), and activated sludge (Kurniawan et al. 2010; Chaturvedi & Kaushal 2018). Xiong et al. (2018) reported that leachate treatment with MBBR was able to remove ammonia and nitrate by as much as 54–80 and 98%, respectively. The MBBR process, using floating carriers, such as polyvinyl alcohol gel media, within an aeration tank, can increase the number of microorganisms available to treat the wastewater compared to those of conventional secondary treatments for the treatment of leachate from a non-regraded solid waste disposal facility (Borkar et al. 2013; Chaturvedi & Kaushal 2018). This is due to the simultaneous bio-process mechanisms where both suspended and attached microorganisms occur within the reactor. The media provides an increase in surface area for the biological microorganisms to attach to and grow in the aeration tanks. The media is continuously agitated by bubbles and from the aeration system, which adds oxygen (Hajipour et al. 2011). The aerobic and anoxic conditions in an MBBR enable the nitrification-denitrification process to reduce the nitrogen concentration in the leachate.

In some cases, a biological process is used as a first step to remove the bulk of COD in the leachate (Kurniawan et al. 2010). Subsequently, further chemical processes, such as advanced oxidation processes (AOPs), are applied to deal with the remaining organic contaminants to produce effluent that meets the quality standards (Ding et al. 2018). Among the AOPs that have been studied, electrochemical oxidation stands out for its robustness, versatility, amenability to automation and for having little to no requirement for chemical addition (Anglada et al. 2011). However, a combination of biological process and electrochemical oxidation has recently been applied in wastewater treatment due to its higher efficiency at a relatively low cost compared to standalone electrochemical oxidation. By converting non-biodegradable pollutants into more biodegradable fractions as the pre-treatment or destroying the persistent contaminants as the post-treatment, the current efficiency in electrochemical oxidation can be improved, and yet the energy cost can be lowered (Zhao et al. 2010).

The types of anode materials and applied current density are some common factors affecting how the electrochemical oxidation process proceeds (Deng & Engelhardt 2007). Researchers suggest that in the electrochemical oxidation process, pollutants are either removed by (i) a direct process, where organics are oxidized by transferring electrons to the anode directly, or (ii) by an indirect one where some electro-active species are electrochemically generated, which then act as mediators to carry out the degradation process. Electrode material can in fact influence the generation of mediators such as reactive oxygen species (‘OH), reactive chlorine species (Cl\(_2\) and HClO), and reactive sulfate species (SO\(_4^{2-}\)) (Martínez-Huitle & Brillas 2008). The nature of active anodes (e.g. carbon, graphite, IrO\(_2\), RuO\(_2\), and Pt), which have low overpotential for oxygen evolution and strong interaction with the chemically adsorbed ‘OH, has resulted in partial oxidation of organic compounds. Conversely, non-active anodes such as SnO\(_2\), Sb/TiO\(_2\), PbO\(_2\), and BDD are capable of fully degrading organic pollutants, due to their higher overpotential for oxygen evolution and generation of highly reactive physically adsorbed ‘OH on their surface from water oxidation (Martínez-Huitle & Ferro 2006a; Panizza & Cerisola 2009; Panizza & Martinez-Huitle 2013; Garcia-Segura et al. 2018).

High oxygen potential is required for electrodes to produce oxidants so that the applied current is not exhausted for an oxygen evolution reaction that can reduce the efficiency of the electrochemical process. Some electrodes such as PbO\(_2\) and SnO\(_2\) anodes as well as BDD have shown wide potential windows and high overpotential that they can delay oxygen evolution to a higher potential (Patel et al. 2015). Among those anodes, BDD has a
significant impact on oxidant generation, has higher current efficiency, and is more resistant to electrochemical corrosion. The mechanism of electrochemical oxidation on a BDD anode can be described as follows (do Vale-Júnior et al. 2019; dos Santos et al. 2020; Fortunato et al. 2020):

\[ BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^- \] (1)

\[ BDD(\cdot OH) + R \rightarrow BDD + mH_2O + nCO_2 + xH^+ + ye^- \] (2)

Recently, electro-oxidation mediated by active chlorine has particularly attracted attention due to the abundant occurrence of chloride in wastewater. A type of anode with lower oxygen potential and at the same time having high efficiency in treating chloride containing wastewater is dimensionally stable anode (DSA) materials such as IrO₂, RuO₂, Pt, and Ti-IrO₂/RuO₂. In this respect, indirect oxidation of ammonia through active chlorine has also been observed. However, in the presence of chloride, the use of BDD electrodes must consider proper current applied to the electrochemical system so that the formation of toxic by-products such as chlorates, perchlorates, or halogenated organic compounds can be avoided.

In the case of landfill leachate, electrochemical degradation using BDD have shown its capability in removing both the organic and the ammonium loading after some pre-treatments (Cabeza et al. 2007). This present study investigated the oxidation capability of both non-active BDD, and active (Ti/IrO₂ and Ti/Pt) anodes to treat the real landfill leachate effluents after MBBR treatments. The leachate used in this study was taken from a stabilized landfill facility in Gresik, Indonesia. The area of the site is 6 hectares, and it has been receiving disposal of 217 tons of solid waste materials each day since 2002. Thus, the leachate produced can be classified as stabilized leachate (Alvarez-Vazquez et al. 2004). The facility has a leachate treatment facility applying an anaerobic baffled reactor (ABR) that essentially did not work well. Leachate samples for this study were taken at the inlet of this ABR during the rainy season. The characteristics of raw leachate are presented in Table 1.

### Experimental Methods and Materials

#### Landfill leachate sampling

The leachate used in this study was collected from the municipal landfill facility in Gresik, Indonesia. The area of the site is 6 hectares, and it has been receiving disposal of 217 tons of solid waste materials each day since 2002. Thus, the leachate produced can be classified as stabilized leachate (Alvarez-Vazquez et al. 2004). The facility has a leachate treatment facility applying an anaerobic baffled reactor (ABR) that essentially did not work well. Leachate samples for this study were taken at the inlet of this ABR during the rainy season. The characteristics of raw leachate are presented in Table 1.

### MBBR experiment

Prior to the electrochemical oxidation process, the raw leachate was treated in an MBBR reactor that had been acclimatized for 21 days. This MBBR was applied through 36 hours of aerobic and 9 hours of anoxic process for each cycle. MBBR preparation was carried out through the stages of seeding and acclimatization to achieve a stable condition of the microorganisms to degrade organic matter in leachate. The microorganism seeds were obtained from the return activated sludge in the clarifier unit of a sewage treatment facility in Surabaya, Indonesia.

The MBBR reactor was made from a cylindrical plastic container equipped with a submersible pump and aerator. The seeding process was started by mixing 30% leachate and 70% sucrose as the organic source in 18 L of sludge, and then aerated for seven days. The composition of leachate and sucrose was changed every seven days by increasing the amount of the mixed leachate. The bio-carrier media used in this reactor was Kaldness 1, made of HDPE with a surface area of about 500 m² m⁻³.

#### Table 1 | Characteristics of raw and MBBR-treated leachate

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Raw leachate</th>
<th>MBBR-treated leachate</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>8.5</td>
<td>8.3</td>
<td>–</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS m⁻¹</td>
<td>484.38</td>
<td>291.41</td>
<td>40</td>
</tr>
<tr>
<td>TSS</td>
<td>mg L⁻¹</td>
<td>40</td>
<td>68</td>
<td>–</td>
</tr>
<tr>
<td>TDS</td>
<td>mg L⁻¹</td>
<td>3,100</td>
<td>1,865</td>
<td>40</td>
</tr>
<tr>
<td>COD</td>
<td>mg O₂ L⁻¹</td>
<td>1,440</td>
<td>816</td>
<td>43</td>
</tr>
<tr>
<td>BOD₅</td>
<td>mg O₂ L⁻¹</td>
<td>323</td>
<td>212</td>
<td>34</td>
</tr>
<tr>
<td>BOD₅/COD</td>
<td>–</td>
<td>0.224</td>
<td>0.26</td>
<td>–</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>mg L⁻¹</td>
<td>54.71</td>
<td>13.6</td>
<td>75</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>mg L⁻¹</td>
<td>23.4</td>
<td>1.09</td>
<td>95</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>mg L⁻¹</td>
<td>78.3</td>
<td>42.31</td>
<td>46</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>mg L⁻¹</td>
<td>1,899</td>
<td>999.7</td>
<td>47</td>
</tr>
</tbody>
</table>
Electrochemical oxidation experiment

The electrochemical oxidation experiments were conducted at a laboratory scale using an undivided electrochemical reactor made of acrylic with an effective volume of 80 mL (4 × 2 × 10 cm) treating 2 L leachate samples. The anodes used were BDD, Ti/IrO2 and Ti/Pt, while the cathode was stainless steel with a surface area of 6 cm² each. The reactor was operated in batch recirculation mode, using a peristaltic pump with a flow rate of 5 mL s⁻¹, for 10 hours. The required electrical power was provided through a direct current power supply (LWK 305D, Cody, China) with current-voltage monitoring. The process was operated in a galvanostatic mode (a constant current was maintained by applying different currents, i.e. 350, 400 and 450 mA). The reactor setup is shown in Figure 1.

Experiments were performed with the MBBR treated leachate. To eliminate suspended particles (measured as total suspended solid, TSS), the sample was filtered using filter paper. Afterwards, sulfuric acid was added to adjust the pH from 8.3 to 6. Our previous study has confirmed that the COD removal was preferred in a lower pH rather than in the actual leachate pH, and correspondingly pH increase was observed in the treated effluents (Agustina et al. 2019). Therefore, although more acidic pH was favorable, the initial pH in this study was adjusted to pH 6 to optimize the COD removal with smaller amount of acid addition. Also, it was meant to target the final pH at the regulated effluent standard (pH 6–9). Samples were taken after 0, 1, 2, 3, 5, 7, and 10 h of electrochemical oxidation and the concentration of COD, BOD₅, total chlorine, ammonium, nitrate, nitrite, and total dissolved solid (TDS, which corresponds to conductivity value) as well as pH were measured.

Analytical method

A 25-mL sample was collected from the feed tank in each time sampling. Prior analysis, all samples were filtered using 0.45 μm Sartorius Stedim cellulose acetate filter. The analyses of all parameter were conducted according to the Standard Method for Examination of Water and Wastewater (APHA 2005). COD was analyzed by the closed reflux and colorimetric methods (Merck and Spectroquant NOVA), while BOD₅ was measured by titrimetric method with Winkler analysis. The pH, TDS/conductivity and DO values were measured using a hand-held YK-2005WA pH/ORP/DO/TDS/Conductivity meter unit (Lutron, Taiwan). Total chlorine was measured by DPD (N,N-diethyl-p-phenylenediamine) reagents (Hach), while chloride was measured by the Argentometric Mohr titration method. Nitrogen, in the form of ammonium, nitrite, and nitrate were measured using the Genesys 20 Spectrophotometer, according to Nessler and Lorenz method. The data reported in this study was the average value of duplicate analytical measurements.

RESULTS AND DISCUSSION

Biological treatment of leachate using MBBR

The MBBR pre-treatment successfully removed some constituents, as can be seen in Table 1. As expected, this biological treatment performed very well in removing nitrogenous compounds but lack the capability to remove organic contaminants. This is due to the relatively low biodegradability index of the leachate (BOD₅/COD of 0.224), indicating a high content of recalcitrant organic contaminants.

Each cycle of this MBBR was operated through 36 hours of aerobic and 9 hours of anoxic process. Chen et al. (2008) reported that the decrease in ammonium concentration will be optimum when the aerobic process in the MBBR is more than 1.25 days (>30 hours) due to the assimilation of microorganisms and nitrification. The biochemical reaction of the nitrification process is shown in Equations (3)–(5) (Im et al. 2001).

\[
\begin{align*}
\text{Nitrosomonas} & \\
2\text{NH}_4^+ + 3\text{O}_2 & \rightarrow 2\text{NO}_2^- + 4H^+ + 2\text{H}_2\text{O} \quad (4) \\
2\text{NO}_2^- + \text{O}_2 & \rightarrow 2\text{NO}_3^- (5)
\end{align*}
\]
Anoxic conditions promote the denitrification process (Equation (6)) to convert nitrate to N₂ gas by denitrifying bacteria and thereby completing the nitrogen cycle (Wu et al. 2014).

$$\begin{align*}
\text{NO}_3^- + S + \text{CO}_2 + \text{H}_2 + \text{NH}_4^+ & \rightarrow \text{N}_2 + 2\text{SO}_4^{2-} + \text{H}^+ + C_5\text{H}_7\text{NO}_2
\end{align*}$$

(6)

The COD/ammonia (C/N) ratio, which represents the relative amount of carbon and nitrogen source in the system, can influence the nitrification and denitrification processes as well as simultaneous removal of COD by microorganisms (Yadu et al. 2018). The experimental condition of this study was 26.32 of C/N, and it resulted in the removal of COD, ammonium, nitrite, and nitrate of up to 43, 75, 95, and 46%, respectively. Concentration of nitrate (NO₃⁻) concentration occurred. Nitrate is the end product of ammonium oxidation; thus, a reduction process is required to convert it to nitrogen gas (i.e. denitrification). This process is mediated by Pseudomonas and Clostridium in an anaerobic condition. On the other hand, the presence of oxygen in the aerobic and anoxic stage of the applied MBBR process means the conversion of nitrate to N₂, N₂O, or NO₂ could possibly be absent. The effluent characteristics and removal efficiency of MBBR are also presented in Table 1.

Table 1 shows that biologically treated leachate still contains high organic and inorganic compounds. The efficiency of biological organic degradation is limited when leachate contains a considerable amount of non-biodegradable organics, so that it must be supported by physical chemical processes (Cosset et al. 1998). In this case, electrochemical oxidation treatment was applied to degrade and break down the non-biodegradable pollutants and ammonium through the formation of OH and free chlorine (Bagastyo et al. 2014; Ding et al. 2018). This is discussed in the following sections.

**Electrochemical oxidation of MBBR-pretreated leachate**

**The effect of anode type and applied current on removal efficiency**

The subsequent electrochemical oxidation process aimed to further remove the remaining organics and nitrogenous content released from MBBR. Figure 2 shows the COD and BOD degradation capability of different anodes under different applied currents.

At a Ti/Pt anode, increasing the current from 350 to 400 mA increased the removal of COD. It is in agreement with previous research, which reported that the application of higher current resulted in higher removal of COD (Turro et al. 2012). However, increasing it further to 450 mA did not give the same effect. After a 10-hour process, the Ti/Pt anode was capable of removing 59, 78, and 78% of COD when 350, 400, and 450 mA current were applied, respectively; while BOD removals were 47, 56, and 57% respectively. The specific electrical charge required to remove 78% COD was 2.37 Ah L⁻¹ and 2.65 Ah L⁻¹ when 400 and 450 mA current were applied, respectively. This indicates that at higher currents, energy is not only consumed for organic oxidation but also for the oxidation of ions (especially Cl⁻) in the leachate, which eventually drives the process of indirect oxidation of pollutants as well as bulk oxygen generation (Agustina et al. 2019). This means that within the current range applied in this study, when using Ti/Pt anode, the optimum condition was 400 mA, which resulted in the COD removal of 78% (i.e. with the residual COD concentration of 225 mg L⁻¹, this equivalent to the removal of 1.344 of COD removed).

Conversely, after 10 h electrochemical oxidation, there was also no significant effect on the COD removal by increasing applied current from 350 to 450 mA at Ti/IrO₂ and BDD anodes, although an increase in demand for electric charge was observed (from 2.06 to 2.65 Ah L⁻¹). However, in terms of total COD mass removed, the effect of increasing applied current from 350 to 450 mA was observed (Table 2). After 10 h process, 1.266, 1.344, and 1.378 g of COD were removed under 350, 400, and 450 mA applied current, respectively, for Ti/IrO₂. Whereas...
at BDD, increase in COD mass removed as the applied current increased was not significant. This is probably due to the consumption of energy for chlorine formation (Figure 3(c)). Nevertheless, at both anodes, the optimum current was the lowest current applied in this study; that is, 350 mA, which is equal to a current density of 58.3 mA cm$^{-2}$.

A similar study, which investigated the process under a current density of 13–78 mA cm$^{-2}$, found that when current density exceeded 65 mA cm$^{-2}$ no further effect on COD removal could be observed (Quan et al. 2015). This indicates that 65 mA cm$^{-2}$ could be the limiting current density within the experimental conditions applied, and that the process at current density higher than that was controlled by the diffusion of chloride ions towards the anode surface.

Overall, in terms of COD removal at optimum applied current, BDD was found to be the best with 85%, followed by Ti/IrO$_2$ and Ti/Pt, with 76 and 78%, respectively (Table 2). This is due to the nature of BDD as a non-active anode (Comninellis 2017) that has electrocatalytic power to generate reactive oxygen species, such as $\cdot$OH, on its surface. According to Fernandes et al. (2015), weak adsorption of $\cdot$OH at the BDD anode results in more efficient organic oxidation. Whilst active anodes, such as Ti/IrO$_2$ and Ti/Pt, have strong adsorption properties against $\cdot$OH, so the oxygen evolution potential tends to be lower than that of non-active anodes (Mandal et al. 2017) and have much higher electrocatalytic power for generating chlorine active species than reactive oxygen species (Martínez-Huitle et al. 2009). This is attributed to the much higher oxidation potential of BDD (2.2–2.6 V) compared to Ti/Pt (1.7–1.9 V) and Ti/IrO$_2$ (1.5–1.8 V) (Patel et al. 2015). Therefore, BDD acts as a non-active anode whilst Ti/Pt and Ti/IrO$_2$ as an active anode.

In addition, the three anodes tested in this study showed good performance in producing reactive chlorine species

### Table 2 | Energy consumption after 10-hour electrochemical oxidation process

<table>
<thead>
<tr>
<th>Anode</th>
<th>CURRENT (mA)</th>
<th>Q (Ah L$^{-1}$)</th>
<th>COD removal</th>
<th>GCE (Wh g$^{-1}$)</th>
<th>SEC (g)</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/Pt</td>
<td>350</td>
<td>2.06</td>
<td>1.227</td>
<td>59</td>
<td>1.17</td>
<td>42.1</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>2.37</td>
<td>1.344</td>
<td>78</td>
<td>1.13</td>
<td>56.7</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>2.65</td>
<td>1.347</td>
<td>78</td>
<td>1.00</td>
<td>68.6</td>
</tr>
<tr>
<td>Ti/IrO$_2$</td>
<td>350</td>
<td>2.06</td>
<td>1.266</td>
<td>76</td>
<td>1.21</td>
<td>58.9</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>2.37</td>
<td>1.285</td>
<td>77</td>
<td>1.08</td>
<td>68.9</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>2.65</td>
<td>1.378</td>
<td>80</td>
<td>1.03</td>
<td>70.2</td>
</tr>
<tr>
<td>BDD</td>
<td>350</td>
<td>2.06</td>
<td>1.463</td>
<td>85</td>
<td>1.40</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>2.37</td>
<td>1.446</td>
<td>87</td>
<td>1.21</td>
<td>45.8</td>
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<td></td>
<td>450</td>
<td>2.65</td>
<td>1.446</td>
<td>87</td>
<td>1.08</td>
<td>55.6</td>
</tr>
</tbody>
</table>

![Figure 3](image_url) | Concentration of COD, BOD and Cl$_2$ in the treated leachate after electrochemical oxidation treatment using (a) Ti/Pt (b) Ti/IrO$_2$ and (c) BDD anodes.
from chloride oxidation, detected as total chlorine (Figure 3). In wastewater containing chloride, the indirect electrochemical oxidation process through the formation of \( \text{Cl}_2/\text{OCl}^- \) has a more significant effect on the removal of pollutants than other mechanisms (Chiang et al. 1995) because it can occur in the bulk solution.

Figure 4 shows the concentration of nitrogenous compounds in the treated leachate. It is clear that the electrochemical process applied in this study did not effectively remove the nitrogenous compounds. The total nitrogen removed after 10-hour processes were less than 20% for the three electrodes used. Among all nitrogenous compounds that constituted total nitrogen, the \( \text{NH}_4^+ \) fraction underwent the most degradation compared to the organic-N, \( \text{NO}_3^- \) and \( \text{NO}_2^- \).

A previous study showed that ammonium was adsorbed predominantly at the Ti/IrO2 and Ti/Pt anodes with a current density of lower than 80 mA cm\(^{-2}\) (Kim et al. 2006). At higher applied current, hydroxyl ions will be more strongly adsorbed at the anode surface compared to ammonia, which leads to oxygen evolution rather than ammonia conversion to nitrogen. (Pérez et al. 2012) explained that ammonium degradation occurs mainly due to the indirect oxidation by \( \text{Cl}_2 \) or HClO according to the reactions in Equations (7)–(11).

\[
\text{NH}_4^+ + 4\text{HClO} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} + \text{H}^+ \quad (7)
\]

\[
\text{NH}_2\text{Cl} + \text{HClO} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad (8)
\]

\[
\text{NOH} + \text{NHCl}_2 \rightarrow \text{N}_2 + \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad (9)
\]

\[
2\text{NH}_4^+ + 3\text{HClO} \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^- \quad (10)
\]

\[
\text{NH}_4^+ + 4\text{HClO} + \text{NO}_3^- + \text{H}_2\text{O} + 6\text{H}^+ + 4\text{Cl}^- \quad (11)
\]

Kapalka et al. (2010) explained that chlorine was formed due to the electrooxidation process of chloride ions and was subsequently hydrolyzed into hypochloric acid. Then, it would react with ammonium to form chloramine, which would break down into nitrogen gas. These mechanisms have also been reported by Garcia-Segura et al. (2018a), where active chlorine species is higher than molar ratio of \( \text{NH}_3/\text{NH}_4^+ \), it has resulted in overall oxidation of chloramine species into nitrogen gas and nitrate ions. This reaction is more dominant than further oxidation to chlorate and perchlorate at low pH.

Meanwhile, there was no significant decrease in nitrate levels. This was due to the more dominant ammonium oxidation and the lower capability of stainless-steel cathodes to reduce nitrate ions. The mechanism of nitrate removal reaction on the electrode surface based on Mook et al. (2012) is expressed in Equations (12)–(17).

Reaction of nitrate ion and water molecules:

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (12)
\]

\[
2\text{NO}_3^- + 6\text{H}_2\text{O} + 10\text{e}^- \rightarrow \text{N}_2 + 12\text{OH}^- \quad (13)
\]

\[
\text{NO}_3^- + 6\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{NH}_3 + 9\text{OH}^- \quad (14)
\]
Reaction of nitrite ion and water molecules:

\[
2NO_2^- + 4H_2O + 6e^- \rightarrow N_2 + 8OH^- \tag{15}
\]

\[
NO_2^- + 5H_2O + 6e^- + NH_3 + 7OH^- \tag{16}
\]

\[
NO_2^- + 4H_2O + 4e^- \rightarrow NH_2OH + 5OH^- \tag{17}
\]

Cathode materials that have been tested on nitrate reduction are Zn, Cu, Ti, Fe, Pt, Cu/Ni, and Cu/Zn. The highest nitrate reduction ability is shown by Cu/Zn cathode, because Cu is the most effective cathode and the addition of Zn can significantly increase electrocatalytic activity in nitrate removal (Fan et al. 2021). The effectiveness of Cu/Zn in nitrate reduction could also be justified with the pseudo-first order rate constant \(k_f\). Compared to those cathode materials, Cu and Zn have similar nitrate reduction kinetics (i.e. \(k_f = 4.1-4.2 \times 10^{-5} \text{ s}^{-1}\)), which is 1.1-3.15 fold higher than Ti, Fe, Pt, and Ni (Fajardo et al. 2021). In the previous study, Li et al. (2009) found that the application of a Ti/Pt anode and Cu/Zn cathode was able to remove nitrate by 74%. Moreover, the highest nitrate removal efficiency was obtained at a pH range of 7-8, whereas at pH 5 the efficiency would be low due to the formation of hydrogen at the cathode during nitrate reduction (Kuang et al. 2017). Another obstacle to nitrate removal in this study is that the oxidation-reduction reaction occurred in one compartment, which can result in the oxidized ions being reduced again or vice versa, causing difficult ion removal in the reactor.

From the experiment result, it can be concluded that this electrochemical oxidation process is less effective in removing the TDS values measured in the leachate. This is likely to occur because the anode and cathode are in the same compartment. The existence of the anode and cathode in the same compartment can cause ions that have previously undergone oxidation to again undergo reduction back to the original ions.

Acidic pH can increase the rate of removal of COD through the reduction of carbonate ions (CO\(_3^2\)) and bicarbonate (HCO\(_3^-\)), because they are a type of ion that can interfere in oxidation by the formed ‘OH (Anglada et al. 2010). In addition, theoretically at base condition, currents will be used more for the process of oxygen formation than by the oxidation process of organic compounds. This is because, at basic pH, the energy needed for oxygen formation (O\(_2\) potential) is smaller than at acidic pH; that is, 0.42 V in an alkaline and 1.229 V in an acidic condition (Chu et al. 2008). Meanwhile, the pH increases with the prolonged operating time due to the electrolysis of water, and at the same time, the generation of hydrogen gas at the vicinity of the cathode is followed by the increase of hydroxide ions. Nevertheless, this increase in the pH is within the range of 6-9 of the effluent quality standard.

Energy efficiency

In this study, the energy efficiency for electrochemical process was estimated based on instantaneous current efficiency (ICE) and specific energy consumption (SEC) (Anglada et al. 2009). The ICE value can be described as follows (Martínez-Huitle & Ferro 2006b):

\[
ICE = \frac{FV}{(\text{COD})_t - (\text{COD})_{t+\Delta t}} \tag{18}
\]

where \(F\) is the Faraday constant (96,487 C mol\(^{-1}\)); \(V\) the electrolyte volume (L); \(\text{COD}_t\) and \(\text{COD}_{t+\Delta t}\) are the chemical oxygen demands (g L\(^{-1}\)); \(I\) is the applied current (A); and \(\Delta t\) is the electrolysis time (s). The ICE during the process is presented in Figure 5. The average current efficiency during a 10-h electrochemical process is presented as general current efficiency (GCE) (Panizza & Martínez-Huitle 2013), calculated using Equation (18), with \(\text{COD}_t\) as initial at \(t = 0\) and \(\text{COD}_{t+\Delta t}\) the final concentration (Table 2).

As shown in Figure 5, the ICE of all anodes reached above 1 in the first 180 minutes at all applied currents. This could suggest that the electrochemical oxidation is dominated by the indirect oxidation mechanism. An ICE value of 1 indicates that the applied current intensity is able to perform complete oxidation of a target pollutant, such as COD (Anglada et al. 2009; Martínez-Huitle & Andrade 2011). However, after prolonged oxidation time, the available COD was limited, thus the energy provided is consumed for chlorine formation from the available chloride in the wastewater.

Meanwhile, SEC can be calculated using the following equation (Anglada et al. 2009):

\[
Q = \frac{I \cdot A \cdot t}{V} \tag{19}
\]

\[
Q = Q \cdot v \tag{20}
\]

where \(W\) is the energy consumption (Wh L\(^{-1}\)); \(I\) is the current density (A m\(^{-2}\)); \(A\) is the electrode area (m\(^2\)); \(t\) is the electrolysis time (s); \(V\) is the electrolyte volume (L); and \(v\) is the cell potential (V).
Table 2 presents the energy consumption calculated at the end of the process. It shows that, for all types of anode, the increase in current intensity caused an increase in energy consumption but did not exhibit a significant effect on the amount of COD mass removed. At Ti/Pt anode with a current of 450 mA, the energy consumption was greater than with the current of 400 mA, while the mass of COD removed was quite similar, namely 1.344 g and 1.347 g, respectively. Likewise, the lowest current intensity applied in the BDD anode showed the highest COD removal with less energy consumption.

In general, BDD requires lower energy to remove a higher amount of COD mass, followed by Ti/Pt and then Ti/IrO2. At the end of the process, the highest efficiency of energy consumption was shown by BDD at the applied current of 350 mA, which removed 85% of COD (1.463 g) with an energy consumption of 36.9 Wh g⁻¹. These values of specific energy consumption are similar to the previous studies, yielding 9.4–62.9 Wh g⁻¹ COD using BDD anodes at current density range of 50–78 mA cm⁻² (Agustina et al. 2019; Bagastyo et al. 2020). Moreover, the effluent COD was achieved in the ranges of 225–336, 208–230, 128–150 mg L⁻¹ on Ti/Pt, Ti/IrO₂, and BDD anodes, respectively. These results indicated that COD effluent has mostly met the requirement of the leachate quality effluent standard (i.e. 300 mg L⁻¹).

**CONCLUSIONS**

MBBR pre-treatment was found to have satisfactory performance in removing nitrogenous content of the stabilized leachate but lack the capability to degrade most of the organic contaminants due to the large non-biodegradable fractions. Subsequent electrochemical oxidation completed its role to remove most of the COD. The anode materials were confirmed to be affecting the overall process of electrochemical oxidation. Among the three anodes tested (i.e. BDD, Ti/IrO₂ and Ti/Pt), the highest COD removal efficiency; that is, up to 87% of COD was achieved at BDD anode, whereas at Ti/IrO₂ and Ti/Pt, the highest COD removal efficiency was 80 and 78%, respectively. Furthermore, BDD also required lower energy to remove a higher...
amount of COD mass, followed by Ti/Pt then Ti/IrO₂. This superiority of BDD owes to its nature as a non-active anode. Despite its excellence in removing organic content, electrochemical oxidation did not perform well in removing nitrogenous compounds. In this case, MBBR performance can be improved prior to the electrochemical oxidation, targeting more on the removal of nitrogenous compounds.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


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