Effect of Flow Rate on Electrochemical Oxidation of Landfill Leachate Using DSA and BDD Anode

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Abstract. The leachate produced in municipal mixed waste landfill contains mostly organic pollutants in various forms. Biological treatment that popularly applied for the treatment only capable of removing biodegradable portion of the organics whilst the recalcitrant parts will leave the system untreated. Therefore, a pretreatment prior to biological process to increase biodegradability of leachate is essential. The physicochemical method such as electrochemical oxidation is an appropriate pretreatment alternative because it has high efficiency in degrading such pollutants. The purpose of this study was to examine the effect of flow rate (1.5 and 5 mL s⁻¹) and anodes (boron-doped diamond (BDD) and dimensionally stable anode (DSA)) on the efficiency of electrochemical oxidation process to degrade leachate. The parameters analyzed were COD, BOD, ratio of BOD₅/COD (biodegradability index, BI), TDS and pH. The results showed that the increase in BI when BDD and DSA used were 0.386 and 0.179, respectively. The best COD removal was achieved by BDD and DSA at current density of 30 mA cm⁻² with the flow rate of 5 mL s⁻¹. BDD could remove 83 % COD (1.56 g) while DSA 68 % (1.08 g) with specific energy consumption of 0.00268 kWh g⁻¹ and 0.00186 kWh g⁻¹, respectively.

Keywords: Boron-doped diamond, current density, dimensionally stable anodes, electrochemical oxidation, leachate

1. Introduction

There are various approach and technology applied in the solid waste management practices worldwide such as recycling, landfilling, composting and incineration. Among them, sanitary landfill is by far the most abundantly implemented in both developed and developing countries due to its simplicity and economic advantages [1]. The treatment of the leachate produced as the consequence of operating a landfill, especially in developing countries, favourably employ biological process due to its ease of implementation and relatively low cost [2]. Unfortunately, as in the case of Indonesia, the mixed municipal waste that goes into the landfill lead to the formation of many recalcitrant organics in the leachate, especially when the landfill is aged. This type of organics is non-biodegradable, thus render biological process ineffective [3]. Physical-chemical process is one alternative that can be implemented to treat recalcitrant compounds in matured leachate [4]. Electrochemical oxidation is one of the physical chemical processes that is widely applied in wastewater treatment to degrade various recalcitrant organics such as phenolic compounds, surfactants, dyes and other pollutants contain in industrial wastewater as well as leachate.
The effectiveness of the electrochemical oxidation process is affected by several factors including the type of anode, pH of the solution, current density applied, electrolytes, and other operational conditions. For the application in leachate treatment, previous study reported using BDD anode and stainless-steel cathode under current density of 30 mA cm\(^{-2}\) and solution pH of 3 could remove COD up to 56\% [5]. Another study at the same pH using BDD anode and silver cathode with the addition of 0.05 M NaCl and current density of 50 mA cm\(^{-2}\) achieved highest COD removal of 60\% [6]. Using DSA (Ti/IrO\(_2\)) showed COD removal of 68 \% under current density of 50 mA cm\(^{-2}\) [7]. The objective of this study was to determine the effect of flow rate and anode types on the removal efficiency of organic pollutants (COD) in electrochemical oxidation process of leachate as well as the capability of the process to alter the biodegradability of the treated wastewater.

2. Materials and Methods

2.1. Materials
The raw leachate used in this study was taken from the influent of leachate treatment in a matured landfill in Gresik, Indonesia. Prior to being used in the electrooxidation process, the leachate was filtered with filter paper to remove large suspended solids. The characteristics of the leachate is presented in Table 1. The experiments were conducted at initial pH of 3, adjusted by adding nitric acid (Merck). A 0.05 M NaCl (Merck) was added into the leachate as the supporting electrolyte [6]. All chemicals used are of analytical grade.

2.2 Experimental
The study was conducted in laboratory scale using 80 mL undivided electrochemical cell made of acrylic (4 cm x 10 cm x 2 cm). The anodes used are BDD (8 cm\(^2\)) and DSA (6 cm\(^2\)) and the cathode used is stainless steel with the same sizes. The reactor treated 1 L of leachate and was operated in batch recirculation mode for 4 hours applying current density of 30 mA cm\(^{-2}\). Samples were taken at \(t_0\) (initial), \(t_1\) (15 minutes), \(t_2\) (30 minutes), \(t_3\) (60 minutes), \(t_4\) (120 minutes) and \(t_5\) (240 minutes). The flowrates applied were 1.5 and 5 mL s\(^{-1}\). The reactor set up is shown in Figure 1.

| Parameter | unit | Concentration |
|-----------|------|---------------|
| pH        |      | 8.58          |
| TDS       | g L\(^{-1}\) | 7.93         |
| COD       | mg O\(_2\) L\(^{-1}\) | 2011         |
| Cl\(^-\)  | mg L\(^{-1}\) | 5198         |
| NO\(_3\)\(^-\) | mg L\(^{-1}\) | 14.77        |
| NO\(_2\)\(^-\) | mg L\(^{-1}\) | 7.601        |
| NH\(_4\)\(^+\) | mg L\(^{-1}\) | 173.776      |
| SO\(_4\)\(_2\)\(^-\) | mg L\(^{-1}\) | 1033.33      |
| BOD\(_5\) | mg O\(_2\) L\(^{-1}\) | 133.33       |
| BOD\(_5\)/COD |       | 0.066         |

The reactor was operated in batch recirculation mode for 4 hours applying current density of 30 mA cm\(^{-2}\). Samples were taken at \(t_0\) (initial), \(t_1\) (15 minutes), \(t_2\) (30 minutes), \(t_3\) (60 minutes), \(t_4\) (120 minutes) and \(t_5\) (240 minutes). The flowrates applied were 1.5 and 5 mL s\(^{-1}\). The reactor set up is shown in Figure 1.
2.3 Analytical method
Parameters analyzed included COD (closed reflux colorimetry, Spectroquant Nova), BOD₅ (DO meter, Lutron), ratio of BOD₅/COD (biodegradability index, BI), pH (pH Meter Lutron) and TDS. Samples were filtered using PTFE 0.45 μm syringe filter before analysis. All analytical methods are based on Standard Method of the Examination of Water and Wastewater [8].

3. Results and Discussion
As can be seen in Table 1, the COD concentration of the raw leachate was quite high with very low ratio of BOD₅/COD (0.066). Having such characteristic, this leachate fell into stabilized leachate category [4]. Stabilized leachate is difficult to treat using biological treatment due to the high content of recalcitrant organic compounds, hence the very low BI. Biological treatment is effective to degrade organic pollutants when the ratio of BOD₅/COD > 0.5 [2]. Therefore, pre-treatment process is required to improve the biodegradability index of leachate before it can be treated using biological treatment.

3.1 COD Removal of Leachate
To determine the efficiency of electrooxidation in degrading organic compounds, the removal of COD was observed, as can be seen in Figure 2. COD removal on DSA anodes at flow rate of 1.5 mL s⁻¹ and 5 mL s⁻¹ was 40 % (0.76 g) and 68 % (1.45 g), respectively. While on BDD anodes the COD removal was 57 % (0.80 g) and 83 % (1.57 g), respectively. After a 4-h operational time, the highest decrease in COD was found when flowrate applied was 5 mL/s.

Within this study range of operational condition, it was found that the reactor run with higher flow rate degraded COD. High flow rates increase turbulence and diffusion flow in the reactor thereby accelerating mass transfer [9]. Additionally, an electrooxidation process with too low flowrate must be avoided, because it can increase the electrolyte residence time within the cell, consequently the temperature might increase leading to the increase of gas formation that can inhibit solution flow and affect mass transport in the reactor [10].
Figure 2. Removal of COD under different flow rate (1.5 mL s\(^{-1}\) and 5 mL s\(^{-1}\)) using (a) DSA anodes (b) BDD anodes [Leachate treated: 1 L, current density applied: 30 mA cm\(^{-2}\), initial pH: 3, supporting electrolyte: 0.05 M NaCl].

3.2 BOD Removal of Leachate

Analysis of BOD concentration was performed to indicate the amount of biodegradable fraction of the organic pollutants in leachate during the process. Figure 3 shows the BOD concentration during experiment.

Figure 3. Removal of BOD under different flow rate (1.5 mL s\(^{-1}\) and 5 mL s\(^{-1}\)) using (a) DSA anodes (b) BDD anodes [Leachate treated: 1 L, current density applied: 30 mA cm\(^{-2}\), initial pH: 3, supporting electrolyte: 0.05 M NaCl].

As can be observed in Figure 3 (a), using DSA when the flowrate was 5 mL s\(^{-1}\) an increase in BOD mass (g) occurred at 15- and 30-minute operation time. The increases were as much as 70% (0.09 g) and 68% (0.08 g) of the previous BOD mass (g), respectively. Whereas at the 60-, 120- and 240-minute operation time, there were decreases in BOD mass, i.e., 20% (0.04 g), 25% (0.03 g), 25% (0.03 g), respectively. When the flow rate was 1.5 mL s\(^{-1}\), during the 15- and 30- minutes operation time there were increases in BOD (g) mass consecutively, i.e., 7% (0.02 g), 85% (0.31 g), respectively. At 60-, 120- and 240-minute operation time there were decreases in BOD mass compared to previous mass. At the end of process (240 minutes) a 60% decrease in BOD mass (0.22 g) from the initial BOD.
mass (0.37 g) occurred. Based on those results, the largest removal of BOD mass (g) occurs in the reactor operated under 1.5 mL s\(^{-1}\) flowrate which could remove BOD mass (g) up to 60% of the initial BOD mass. Whereas when operated under 5 mL s\(^{-1}\) flowrate, only 25% of the initial BOD mass was removed.

Applying BDD anode (Figure 3.(b)) and 5 mL s\(^{-1}\) flowrate showed an increase in BOD mass during the 15- and 30-minute operation time by 20% (0.06 g), and 400% (0.49 g) of the initial BOD mass, respectively. Afterward, the BOD mass decreased constantly. BOD mass at t\(_5\) (240 minutes) showed a decrease of as much as 48% (0.14 g) from the initial mass (0.24 g). Based on the results above, the largest increase in BOD mass (g) occurs during reactor operations applying 5 mL s\(^{-1}\) flowrate, in which 4 times (0.49 g) BOD mass was occurred. Meanwhile, the highest BOD mass removal after the end of operation was occurred when 1.5 mL s\(^{-1}\) flow rate was applied, with 48% (0.14g) of the initial BOD (g) mass (0.24 g) was removed.

### 3.3 Ratio of BOD\(_5\)/COD

The change in the BOD\(_5\)/COD ratio is calculated at all sample points, namely t\(_0\) (initial), t\(_1\) (15 minutes), t\(_2\) (30 minutes), t\(_3\) (60 minutes), t\(_4\) (120 minutes) and t\(_5\) (240 minutes), and showed in Figure 4. This value was calculated to indicate the level of biodegradability of the treated water along the process.

![Figure 4](image)

**Figure 4.** Change of BOD\(_5\)/COD value with variations of flow rate 1.5 mL s\(^{-1}\) and 5 mL s\(^{-1}\) (a) DSA anodes (b) BDD anodes [Leachate treated: 1 L, current density applied: 30 mA cm\(^{-2}\), initial pH: 3, supporting electrolyte: 0.05 M NaCl].

The analysis showed that the BOD\(_5\)/COD ratio when applying BDD anode and 5 mL s\(^{-1}\) flowrate 5.5 times and while DSA anode 2.6 times. Additionally, during the process the pH was relatively unchanged from initial pH condition (pH 3), and TDS was slightly decrease (2-7%) of about 7-8 g L\(^{-1}\). Based on this result, flowrate of 5 mL s\(^{-1}\) was better applied compared to 1.5 mL s\(^{-1}\) because it showed a significant increase in the BOD\(_5\)/COD ratio and a high COD removal. High flow rates increase turbulence and diffusion of flow in the reactor thereby accelerating mass transfer in the reactor [9]. This study showed that the optimum removal was performed by the BDD anode at 5 mL s\(^{-1}\) flowrate in which COD was removed by 83% (1.56 g), and could increase the BOD\(_5\)/COD ratio up to 5 times (0.386). The specific energy consumption required by the optimum point is 0.00268 kWh g\(^{-1}\).
3.4 Monitoring of pH and TDS

During the electrooxidation process, the pH and TDS change were monitored. The monitoring result showed no significant changes in both TDS and pH during the experiments.

TDS monitoring through electrooxidation process using BDD and DSA showed it was within the range of ± 7-8, except when BDD anode with 1.5 mL s⁻¹ flowrate (± 9.5). From the result there is no significant change in TDS can occur due to acidic pH conditioning and addition of NaCl. Besides, the reactor is an unvided cell (one compartment) where the anode and cathode are located in the same compartment thus there is no ionic migration to other compartment as in the case of divided cell. Nevertheless, an observable pH-decrease when using BDD anode operated under 1.5 mL s⁻¹. The decrease was due to to ions formed with chlorine (free chlorine) during the electrooxidation process.

4. Conclusions

Applying 5 mL s⁻¹ flowrate resulted in a COD removal efficiency of 68% for DSA anodes and 83% for BDD anodes. An increase in the BOD₅/COD ratio was 2.6 times for the DSA anode and 5.5 times for the BDD anode compared to the initial ratio. When the flowrate was 1.5 mL s⁻¹, the COD removal efficiency of 40% for the DSA anode and 57% for the BDD anode were achieved. The BOD₅/COD ratio for DSA anodes decreased 25% from the initial ratio and a 10% increase for BDD anodes.

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