THE USE OF MULTI-REACTOR CASCADE PLASMA ELECTROLYSIS FOR LINEAR ALKYLBENZENE SULFONATE DEGRADATION

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Abstract

Plasma electrolysis is a method that can produce large amounts of hydroxyl radicals to degrade organic waste. The purpose of this study is to improve the effectiveness of Linear alkylbenzene sulfonate (LAS) degradation by using multi-reactor cascade plasma electrolysis. The reactor which operated in circulation system, using 3 reactors series flow and 6 L of LAS with initial concentration of 100 ppm. The results show that the LAS degradation can be improved multi-reactor cascade plasma electrolysis. The greatest LAS degradation is achieved up to 81.91% with energy consumption of 2227.34 kJ/mmol that is obtained during 120 minutes by using 600 Volt, 0.03 M of KOH, and 0.5 cm of the anode depth.

Keywords: LAS degradation; plasma electrolysis; hydroxyl radical

Introduction

Linear alkylbenzene sulfonate (LAS) is an anionic surfactant alkyl chain containing about 10-14 carbon atoms which is bound to the aromatic rings sulfonated [1]. LAS is one type of organic compounds which commonly found in detergent content at this time. Its use is fairly widespread among industries and households alike. Wastewater that contained LAS will flow into the river, so that the river will become polluted. This condition can cause some problems (e.g. shallowing waters, inhibiting oxygen transfer, inhibiting microbial growth) that endanger human life and ecosystem of the river [2]. LAS is biodegradable (can be degraded by microorganisms), however, properties of biodegradable LAS began decreased at concentrations above 50 ppm [3].

In these decades, a growing interest has been attracted to using plasma electrolysis for removal of organic pollutants from water because it has high removal efficiency and environmental compatibility [4]. Plasma electrolysis is a one method that can be produce large amounts of hydroxyl radical (•OH) and used to degrade organic waste. Some researchers indicated that many organic pollutants can be destroyed by plasma electrolysis and the final products are either non-toxic or less toxic compounds, such as, carbon dioxide, water, inorganic salts, etc [5]. This is because plasma electrolysis method can production of reactive species such as hydroxyl radicals, hydrogen radicals (•H), oxygen radicals (•O) and molecules (H₂O₂, O₃, etc.) [6].

Plasma electrolysis process begins with the gas formation on Faraday electrolysis occur both at the anode and cathode. Oxygen gas is formed at the anode while hydrogen gas is formed at the cathode. Faraday electrolysis develops into plasma electrolysis on the power supply voltage is high enough. In addition, the plasma is obtained using asymmetric electrodes, glow discharge occurs at the electrodes with a smaller area. Plasma phenomenon is characterized by a drastic decrease in current as indicated by the appearance plasma on the anode [7].
In anode plasma electrolysis process produced reactive species such as \(\text{H}_2\text{O}_2\), \(\text{OH}^\bullet\), \(\text{H}^\bullet\), and \(\text{e}^-\). Hickling theory states are two zones formation in the plasma electrolysis. In the primary reaction zone, water was ionized or activated, and the bombarded with each other to break the bonds by electron transfer. This phenomenon produces compounds \(\text{OH}^\bullet\) and \(\text{H}^\bullet\). Both of them are possible to interact to form \(\text{H}_2\text{O}_2\) and \(\text{H}_2\). Then, a mixture of \(\text{•OH, •H, H}_2\text{O}_2\) and \(\text{H}_2\) diffused out of the primary zone (that was called plasma later) and interacted each other with substrates or compounds dissolved in solution or liquid phase in the second reaction zone [8].

This research is also focused on the several parameters that can affect the process LAS degradation with plasma electrolysis, which include anode depth and amount of reactors. These two parameters can affect the production of hydroxyl radical [9], where hydroxyl radical is an oxidizing agent that can degrade LAS.

**Experimental**

The LAS waste (100%) used in the plasma electrolysis process was a synthetic LAS procured from Merck (Indonesia). Potassium hydroxide (KOH) was procured from Merck and used as an electrolyte solution. All aqueous solutions were prepared with distilled water from Bratachem, Indonesia. The plasma electrolysis process was operated in circulation mode and the experimental set-up is shown in Fig. 1. The reactor was made of a transparent acrylic tube with cylindrical solid cathode of stainless steel SS-314 which placed at the top reactor and anode made of tungsten is placed at the top reactor. A single anode and cathode used in each reactor. The reactor which operated in circulation system, using 6 L of LAS with initial concentration of 100 ppm.

![Figure 1](image_url) **Figure 1** Schematic Diagram of Multi-Reactor Cascade: 1. LAS container, 2. Pump, 3. Cooling Coil, 4. Thermometer, 5. Cathode (Stainless steel), 6. Anode (Wolfram), 7. Diode bridge, 8. Power analyser, 9. Transformer, 10. Slide regulator, 11. Source voltage.
The anode used was a tungsten (wolfram) with 1.6 mm in diameter. The cathode was made of stainless steel that was 5 mm in diameter and placed along the 30 mm immersed in a solution of the system. The cathode separated from anode with distance 40 mm. During the experiment, the temperature was maintained at 50 ± 1 °C by circulating LAS continuously through a cooling coil. The high voltage applied in plasma electrolysis was set 600 Volts. The solution for treatment was prepared by dissolving a known amount of LAS in a KOH with the concentration solution at 0.03 M. In addition, the variety of the anode depths were 0.5 cm, 1 cm, and 1.5 cm from the surface of solution.

The discharge voltage and current in the plasma electrolysis process were measured using HELES UX-838TR multimeter. A small portion of LAS after the degradation was measured by Methylene Blue Active Substance (MBAS) method developed according to ASTM D 2330-02. This test method is to determine the LAS concentration and degraded products. The amount of Hydrogen peroxide (H₂O₂) as an indicator of the presence of hydroxyl radical was tested using the iodometric titration method. Iodometric titration was used as analytical method in order to represent the oxidizing agent formed through the release of gaseous iodine (I₂). Chemical Oxygen Demand (COD) was measured by the potassium dichromate standard method. Oxalic acid analysis was conducted to determine intermediate results LAS degradation. Oxalic acid analysis measured by titration permanganometry method.

Results and Discussion

Effect of Anode Depth on The LAS Degradation

Table 1 shows, the amount of LAS after degradation in the condition of the immersed anode 1.5 cm had the greatest value in comparison to the conditions of 0.5 cm and 1 cm. This is because the surface area of the anode that immersed deeper in the electrolyte solution is larger so that the sheath gas formation around the anode will be larger and more H₂O gas molecules ionized to form hydroxyl radical where is the location of the plasma formed [6]. The gas sheath around the anode is sufficiently stable at higher surface area so that more water vapor are produced when plasma is formed. The large gas sheath allows the amount of excited electrons increase, so that the current increases. This condition triggers the increasing of energy consumption. At anode depth of 0.5 cm, the energy used for gas formation with smaller volume due to position of anode that was near from solution surface, so the plasma formed and stabilized more quickly due to the lower influence of hydrostatic pressure.

| Anoda depth (cm) | Time (minute) | LAS Degradation (%) | Energy Consumption for LAS degradation (kJ/mmol LAS) |
|------------------|---------------|---------------------|---------------------------------------------------|
| 0.5              | 5             | 37.05               | 87.58                                             |
|                  | 60            | 50.58               | 662.85                                            |
|                  | 120           | 56.21               | 1260.10                                           |
| 1                | 5             | 52.30               | 268.20                                            |
|                  | 60            | 54.42               | 1058.40                                           |
|                  | 120           | 57.70               | 2030.40                                           |
| 1.5              | 5             | 65.56               | 473.40                                            |
|                  | 60            | 71.91               | 1404.00                                           |
|                  | 120           | 74.17               | 1944.00                                           |
The stability of plasma can resist electron effectively. Based on these phenomena, the depth of 0.5 cm produce lower energy consumption rate per mmol degraded LAS than depth of 1 cm and 1.5 cm. However, the increasing of energy consumption is not proportional with the increasing of the LAS degradation. Figure 2 shows the increasing anode depth causes the plasma size and brightness increase.

**Figure 2** Visualization of Plasma at 600 V With 0.03 M KOH Electrolyte Concentration due to The Effect Anode Depth (a) 0.5 cm, (b) 1 cm, and (c) 1.5 cm.

LAS oxidation reaction with OH radicals is a complex reaction mechanism and produce the intermediates. The mechanism of LAS oxidation reaction mechanism consists of five stages [10]. Petterson proposed a simplified reaction mechanism, shown in Figure 3.

**Figure 3** The mechanism of LAS degradation [10].
The first stages of the degradation produce alkyl chain sulfonated aromatic compounds such as sulfophenyl aldehyde (SPA), sulfophenyl carboxylic acid (SPC), sulfophenyl dialdehyde (SPDA), and carboxyl sulfophenyl aldehyde (CSPA). These compounds will be oxidized further in the second stage to produce aromatic compounds that have shorter alkyl chains such as carboxylic acid and sulfophenyl derivatives. These compounds will be oxidized further in the third stage to produce volatile fatty acids. In the fourth stage degradation of volatile fatty acids into carboxylic acid, oxalic acid and formic acid. The fifth stage is the mineralization of organic compounds that produce CO$_2$ and H$_2$O.

**Effects of Multi- Reactor Cascade on The LAS Degradation**

Table 2 shows the effects of multi-reactor cascade on LAS degradation and energy consumption. The result shows that LAS degradation increased with the number of reactor. After 120 minutes process, LAS degradation were 56.21%, 71.34% and 81.91%. This occurred because the increasing number of reactors will increase the number of points to form a plasma so that the interaction between •OH with increasing LAS [9]. Table 2 too shows that the energy consumption per mmol LAS lowest in five minutes. It occurs because the amount of LAS degraded very much in 5 minutes early ie 37.05% (one reactors), 48.43% (two reactors) and 66.65% (three reactor). Increasing the number of reactors will increase the amount of energy consumed per mmol LAS based on Table 2. During the 120 minute process, the amount of energy consumption three reactors higher than two reactors and one reactors because the increasing number of plasma formation point, so that joule heating energy required to form a sheath of gas is increasing. Based on Table 2, multi-reactor cascade effectively accelerated the LAS degradation process.

**Table 2 Effects of Multi- Reactor Cascade on LAS Degradation and Its Energy Consumption in 120 Minutes Process at 600 V**

| Number of reactor | Time (minute) | LAS Degradation (%) | Energy consumption for LAS degradation (kJ:mmol LAS) |
|-------------------|---------------|---------------------|-----------------------------------------------|
| 1                 | 5             | 37.05               | 134.92                                        |
|                   | 60            | 50.58               | 757.90                                        |
|                   | 120           | 56.21               | 1279.37                                       |
| 2                 | 5             | 29.19               | 313.19                                        |
|                   | 60            | 48.43               | 1476.30                                       |
|                   | 120           | 71.34               | 1555.02                                       |
| 3                 | 5             | 66.65               | 499.31                                        |
|                   | 60            | 71.38               | 1588.79                                       |
|                   | 120           | 81.91               | 2227.34                                       |

3.3. Analysis of Chemical Oxygen Demand

COD are important indicators of waste degradation such as LAS. The COD changes during LAS degradation shown in Figure 4. COD degradation has increased achieve 33.88% during the 120 minutes process. But the percentage of COD degradation is not proportional to amount of LAS are degraded achieve 81.91% during 120 minutes process. This is caused by the intermediate products that are detected as COD and hydrogen peroxide formed in plasma electrolysis process that interfere the COD measurement shown in equation (1) [11]:

\[ 3\text{H}_2\text{O}_2 + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \rightarrow 3\text{O}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]  

(1)
Analysis of Oxalic Acid

Oxalic acid is one of the intermediate products of the most widely produced and the most stable of the LAS degradation process by •OH [12]. This occurred because the reaction rate constants of oxalic acid with •OH smallest compared to other intermediate products which is $4.7 \times 10^7$ M$^{-1}$S$^{-1}$ [13].

Figure 4 COD Degradation in 120 Minutes Process at 600 V with 0.03 M KOH with 0.5 cm Anode Depth Using Three Reactors.

Figure 5 shows that the LAS concentration decreased while the oxalic acid production increased along with increasing of operational time up to 120 minutes. It is caused by the decreasing of amount of LAS in the plasma electrolysis process and the interaction between hydroxyl radical with the organic compounds towards further degradation until produce final product, i.e. H$_2$O and CO$_2$.

Figure 5 Comparison of LAS Degradation and Oxalic Acid Production for 0.03 M KOH Electrolyte with 0.5 cm Anode Depth Using Three Reactors.
Conclusions

This research has successfully degraded LAS using plasma electrolysis. The results show that the LAS degradation can be improved multi-reactor cascade plasma electrolysis. The greatest LAS degradation is achieved up to 81.91% with energy consumption of 2227.34 kJ/mmol of the energy consumption that is obtained during 120 minutes by using 600 Volt, 0.03 M of KOH, and 0.5 cm of the anode depth and initial concentration of LAS is 100 ppm.

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