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# Research Article
# Degradation of Linear Alkylbenzene Sulfonate Using Multi-anode Contact Glow Discharge Electrolysis

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## Abstract

**Background and Objective:** Single anode contact glow discharge electrolysis (s-CGDE) is one of plasma electrolysis technology which is commonly used for waste water degradation. The aim of this research is to increase the effectiveness of waste water degradation by using multi anode CGDE (m-CGDE). **Methodology:** Synthetic Linear Alkylbenzene Sulfonate (LAS) waste was used with the initial concentration of 100 ppm in 0.02 M KOH electrolyte solution, the operating temperature was maintained in 30-60°C, using 1.6 mm diameter of tungsten anode and 5 mm diameter of SS-304 cathode. **Results:** The tests conducted were measurement of LAS concentration using Methylene Blue Active Substance (MBAS) method and measurement of $H_2O_2$ concentration as an indicator of OH radicals production using iodometric titration. **Conclusion:** Variable processes that produced the largest percentage of LAS waste degradation up to 99.97% were 700 V, 500 rpm stirring speed and 3 anodes (m-CGDE) with total energy 1264.2 kJ $mmol^{-1}$ of LAS.

Key words: CGDE, plasma electrolysis, LAS degradation

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Linear alkylbenzene sulfonate is one of the surfactants contained in detergents[1], which is ranging from 15-25%. The LAS could not be degraded by microorganism if its concentration exceeded 100 ppm. It has a benzene ring, which contains high resonance energy, thermodynamically stable and relatively resistant against microbial attack[2]. Microorganism needs a large amount of energy in the reaction to reduce barrier resonance energy that could open the benzene ring. The LAS molecular structure can be seen in Fig. 1.

Based on regulation on Minister of Environment No. Kep-51/MenLH/10/1995 BAPEDAL 1999, the maximum level of detergent in industrial waste is 3 mg $L^{-1}$ (3 ppm) and LAS concentration in aquatic media is 0.5 ppm. In other words the percentage of degradation should be achieved is 99.5%.

Different Advanced Oxidation Processes (AOPs) methods have been employed to treat LAS. The AOPs are using hydroxyl radicals (•OH) as powerful oxidizing agent (Fig. 2) which are obtained at a sufficient concentration to effectively decontaminate wastewaters[5].

Photocatalysis method using UV and $H_2O_2$ could decompose[6] LAS up to 90%. Plasma electrolysis method using s-CGDE reactor in KOH electrolyte solution is capable of degrading[7] LAS up to 99.14%. In active sludge method, LAS could be degraded until 99% after 20 days in adaption phase[8]. The AOP methods could produce OH radicals which capable of oxidizing almost all organic pollutants. These radicals can diffuse in the surrounding liquid and are able to oxidize any organic molecules although the reaction is non-selective way[9-12]. Unfortunately OH radicals formed can react in large amount with other OH radicals forming $H_2O_2$ rather than react with organic pollutant. Therefore, further researches have been conducted to increase LAS degradation by increasing the interaction between OH radicals and substrates using m-CGDE. The effect on the number of anodes on dyes waste degradation[12] shows that although the critical voltage (the voltage required for the onset of plasma) by m-CGDE is as high as the s-CGDE, the degradation rate of m-CGDE is faster than that of s-CGDE so the degradation further increases along with the number of anodes.

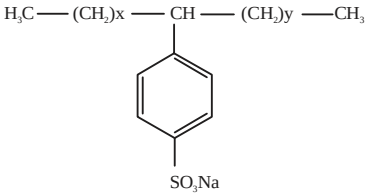


Fig. 1: LAS molecular structure[3]

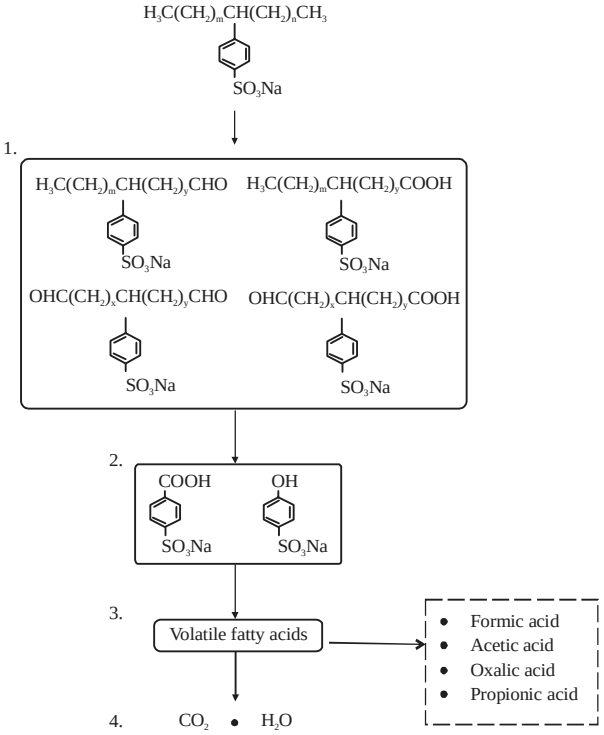


Fig. 2: Scheme of LAS Degradation[4]

Interaction between OH radicals and LAS has been performed by using m-CGDE in this study and the results are presented and discussed.

## MATERIALS AND METHODS

The main equipment used in this study was m-CGDE with the limit usage of three anodes. The reactor scheme[2] can be seen in Fig. 3. The LAS waste was used with the initial concentration of 100 ppm in 0.02 M KOH electrolyte solution, the operating temperature was maintained in 30-60°C, using 1.6 mm diameter of tungsten anode and 5 mm diameter of SS-304 cathode. The tests conducted were measurement of LAS concentration using Methylene Blue Active Substance (MBAS) method, measurement of $H_2O_2$ concentration as an indicator of OH radicals production using iodometric titration and measurement of oxalic acid concentration using permanganometry titration method.

The LAS degradation is defined as:

$$\text{Degradation}\,(\%) = \frac{M_1 - M_2}{M_1} \times 100\% \quad (1)$$

where, $M_1$ (mg $L^{-1}$) is initial concentration of LAS and $M_2$ (mg $L^{-1}$) is LAS concentration after degradation process. Hydrogen peroxida and oxalic acid concentration (M) can be defined as: Energy consume for LAS degradation per mol LAS can be written as:

$$\text{Energy consume}\left(\frac{\text{Joule}}{\text{mol}}\right) = \frac{W}{\text{Degradation of LAS}} \quad (2)$$

$$W = V.I.t \quad (3)$$

where, W is electrical energy (Joule), V is voltage (volt), I is current (ampere) and t is operation time (second).

## RESULTS AND DISCUSSION

**Characterizations of current and voltage in CGDE:** In current-voltage curve, $V_B$ and $V_D$ are very important point that show the breakdown from normal electrolysis to the onset of glow discharge[9,13,14]. Several different regions were illustrated from m-CGDE in KOH solution[15].

**$0<V<V_B$:** Ohmic region; conventional electrolysis occurred with small bubbles of gas leaving the anode. The $V_B$ was termed as breakdown voltage[2,16].

**$V_B<V<V_D$:** Transition region; vapor sheath appeared and covered the anode surface. This condition made the current started to decrease with the applied voltage. The gas bubbles in vapor sheath undergo the process of formation and collapse, so the oscillation of current occurs[9]. The $V_D$ is term as critical voltage or midpoint voltage[2,17].

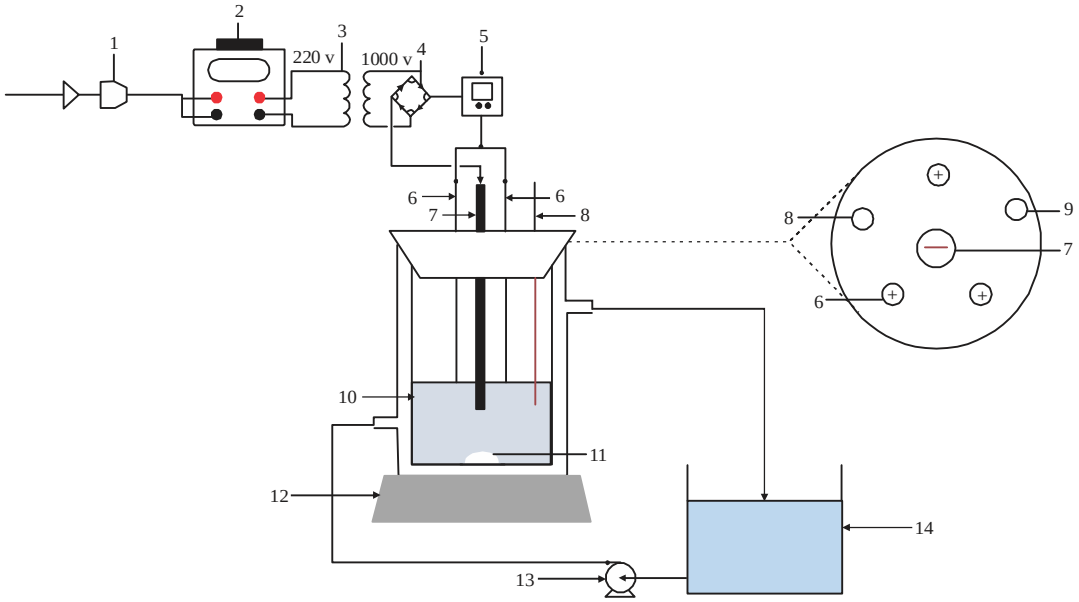


Fig. 3: Schematic diagram of CGDE triple-anode reactor for LAS waste treatment[2], 1: MCB, 2: Slide regulator, 3: Trafo, 4: Diode bridge, 5: Multi-meter, 6: Anode, 7: Cathode, 8: Thermometer, 9: Sample hole, 10: LAS waste, 11: Magnetic stirrer, 12: Stirrer, 13: Pump and 14: Cooling water

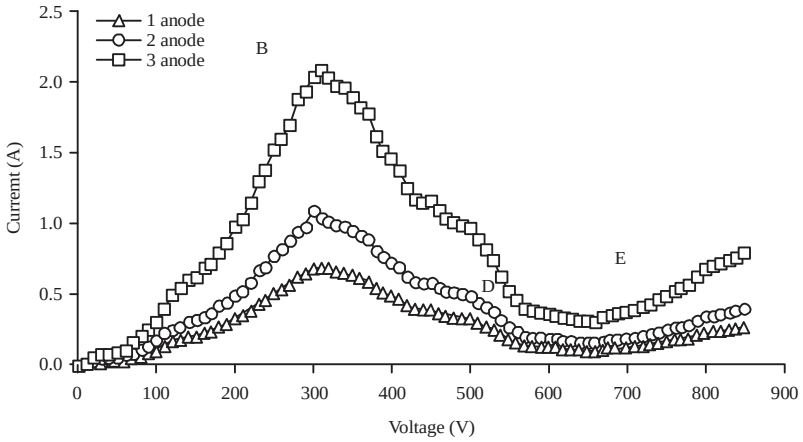


Fig. 4: Characteristic of m-CGDE current-voltage with different anode, electrolyte: 0.02 M KOH, anode material: Tungsten

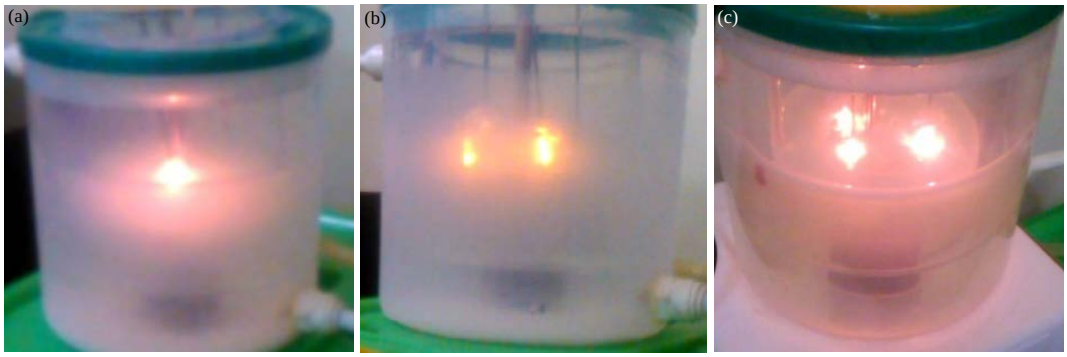


Fig. 5(a-c): Visualization of plasma formation with different number of anodes, (a) 1 anode, (b) 2 anodes and (c) 3 anodes, electrolyte: 0.02 M KOH, voltage: 700 V, anode material: Tungsten

**$V>V_D$:** Glow discharge region; the current started to increase steadily with the rising voltage. In section D-E glow discharge became yellow due to the presence of kalium ion in anolyte[14].

Figure 4 shows the current-voltage characteristics in the m-CGDE reactor. The $V_B$ and $V_D$ generated are almost the same but the current required to achieve $V_B$ and $V_D$ values are different. The more number of anodes (where the plasma is formed) then the larger the current read as well. This can happen because the more number of anodes, strong current is required to ignite the plasma and also gets larger with the same voltage value. The energy requirements needed to generate the plasma becomes larger.

Based on the curve of current-voltage characteristic in Fig. 4, the area below the curve is the power required for Joule heating, as shown in Table 1, the Energy (E) and Power (P) required in B and D point.

Table 1 shows the increase in energy along with the increasing number of anodes. This could happen because more energy is required to make sheath gas on three anodes rather than just on one anode. Strong currents that flow increasing further with the addition of the anodes, so that, although $V_B$ and $V_D$ voltages are almost the same, significant current differences result in significant energy differences as well. Figure 5 shows the visualization of plasma formation by using different number of anodes.

Table 1: Joule heating energy requirements for the formation of plasma

| No. of anode | $E_B$ (kJ) | $P_B$ (kJ sec$^{-1}$) | $E_D$ (kJ) | $P_D$ (kJ sec$^{-1}$) |
|---|---|---|---|---|
| 1 | 117.86 | 0.06 | 424.37 | 0.10 |
| 2 | 161.33 | 0.09 | 640.36 | 0.16 |
| 3 | 353.57 | 0.19 | 1273.12 | 0.32 |

**Effect of anode numbers:** The effect on the number of anodes in LAS waste degradation and OH radicals production can be observed by doing variations on the number of anodes. The anode was made of tungsten material with a diameter of 1.6 mm. All of three anodes were dipped into waste solution as deep as 5 mm in any trial process. The fixed variable

conditions were KOH electrolyte solution of 0.02 M, LAS initial concentration of 100 ppm, optimum voltage of 700 V and optimum stirring speed of 500 rpm which have been obtained in the previous variable tests. Observation time was carried out within 30 min for the sampling test of LAS degradation and for the production of OH radicals with the temperature maintained at 30-60°C.

The increased number of anodes results in more OH radicals production, characterized by the increased level[2,17] of $H_2O_2$ as shown in Fig. 6. The plasma formed spreads many facets, so that this plasma deployment will increase the interaction between OH radicals and LAS. In other words, the more number of anodes the more the chance for OH radicals to attack LAS. Figure 7 shows the percentage increase of LAS waste degradation along with the increasing number of anodes. The fact that level of $H_2O_2$ is increased by 30% with three anodes (2.6 mmol) when compared with one anode (2 mmol) in Fig. 6. Meanwhile, the degradation of LAS with three anodes is increased by only 3% (Fig. 7). This can be explained that OH radicals recombined into $H_2O_2$ rather than reacted with LAS.

The plasma phenomenon formed for one, two and three anodes has relatively the same size (Fig. 5). This may happen because the applied voltage of 700 V was equal, but the current read on the multi-meter for each anode was different. Table 2 shows the comparisons of current and energy values versus the number of anodes within 30 min and a voltage of 700 V. The current value obtained increases disproportionately, different from the previous test result[13]. The exact possible reason is due to the distance between the anodes which are relatively close (only 3 cm), resulting in the sheath gas from Joule heating formed in the anodes interplays (Fig. 8). It can also affect the OH radicals formed. Table 3 shows the energy requirements needed to form $H_2O_2$, the

Table 2: Current and energy values on variation of the number of anodes

| No. of anodes | Current (A) | Energy (kJ) |
|---|---|---|
| 1 | 0.15 | 189.0 |
| 2 | 0.22 | 277.2 |
| 3 | 0.30 | 378.4 |

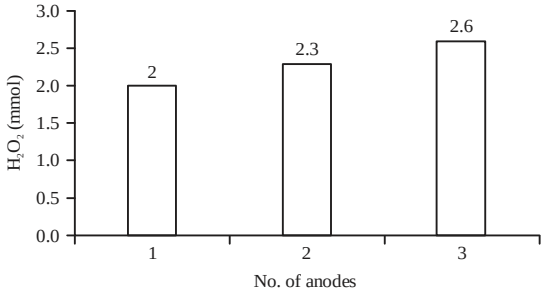


Fig. 6: $H_2O_2$ level comparison on variation of the number of anodes. Within 30 min process, electrolyte: KOH 0.02 M, anode: Tungsten, voltage: 700 V, stirrer speed: 500 rpm

Table 3: Energy requirements per mmol of $H_2O_2$ formed on variation of the number of anodes

| No. of anodes | Energy per mmol $H_2O_2$ formed (kJ $mmol^{-1}$) |
|---|---|
| 1 | 94.5 |
| 2 | 120.5 |
| 3 | 145.4 |

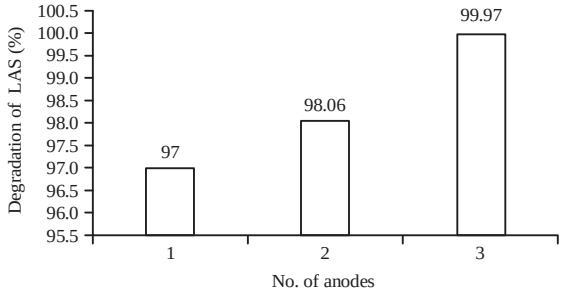


Fig. 7: Percentage degradation of LAS on variation of the number of anodes within 30 min process, electrolyte: KOH 0.02 M, [LAS] initial: 100 ppm, anode: Tungsten, voltage: 700 V, stirrer speed: 500 rpm

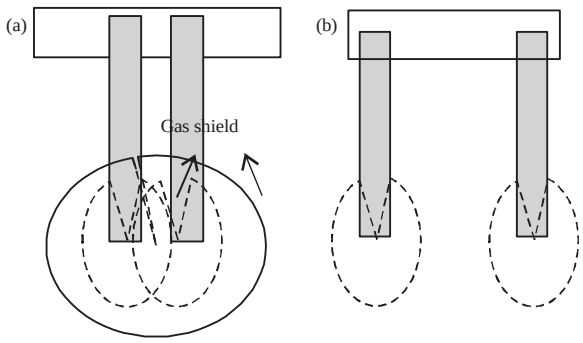


Fig. 8(a-b): Anodes distances, (a) Close anodes and (b) Distant anodes

Table 4: Energy requirements per mmol of degraded LAS on variation of the number of anodes

| No. of anodes | Energy per mmol of degraded LAS (kJ $mmol^{-1}$) |
|---|---|
| 1 | 1268.5 |
| 2 | 1283.9 |
| 3 | 1264.2 |

necessary energy requirements also further increase with the additional number of anodes due to the interaction between the plasma formed in a close distance.

When calculating energy requirements per mmol of degraded LAS is conducted, then the energy difference becomes less significant, relatively the same and the energy required per mmol of degraded LAS by three anodes is smaller than one anode (Table 4). Thus, the CGDE triple-anode reactor has been able to increase the effectiveness of s-CGDE in LAS waste degradation as well as energy consumption. This reactor can improve the effectiveness of LAS degradation up to 99.97% within 30 min.

## CONCLUSION

The application of multi-anode Contact Glow Discharge Electrolysis (m-CGDE) reactor has been proved to increase the percentage of LAS waste degradation, characterized by the more number of anodes the larger the production of OH radicals and percentage of LAS degradation.

The consumption of energy needed to process LAS waste using m-CGDE requires energy of 1264.2 kJ $mmol^{-1}$ and 30 min time to degrade LAS with higher percentage of degradation up to 99.97%.

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