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Research Article

Electrocoagulation Method Using Al/Graphite Electrode for Removal Surfactant LAS (Linear Alkylbenzene Sulfonate)

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Abstract

An increasing number of laundries have caused water contamination by surfactants. One commonly used surfactant is LAS (Linear Alkylbenzene Sulfonate), a material difficult to decompose, polluting the environment. Electrocoagulation was carried out using Al/Graphite electrode, applied to LAS surfactant artistic waste. This study aims to determine the functional ability of the Al/Graphite electrode in reducing surfactant through electrocoagulation. Various variations were carried out, on the voltage parameters (3,6,9,12) Volt; NaCl concentration (0;0.4;0.8;1.2;1.6;2) g/L; pH (3,5,7,9,11) and time (10,20,30,40,50) minutes. To analyze the changes in the sample before and after electrocoagulation, characterization was carried out using a UV-VIS spectrophotometer and FTIR. A kinetic study was conducted to determine the reaction order of electrocoagulation surfactant. Based on a study, removal at condition voltage 9 Volt, initial pH of the solution 9, electrocoagulation time 50 minute, and the addition of NaCl electrolyte 2 g/L, obtained surfactant concentration was 0,785 mg/L with removal efficiency 97,45%. UV-VIS spectra show a decreased absorption at a wavelength of 653 nm. FTIR spectra showed the presence of absorption on the same functional groups, which indicated that most of the surfactant pollutants could be separated from the wastewater through the electrocoagulation process. The second-order reaction was obtained in the surfactant electrocoagulation process.

Keywords: Electrocoagulation; Al/graphite Electrode; linear alkylbenzene sulfonate; surfactant

1. Introduction

Banana (*Musa* Laundry services in Indonesia are increasing every year. In practice, many laundry services use detergent as a washing agent, which will produce various kinds of waste. According to (Afrianto 2018), laundry activities impact increasing the level of pollution of the aquatic environment. Disposal of the domestic liquid waste directly into water bodies can reduce water quality, thus affecting aquatic ecosystems and human health. The main constituent in detergents is surfactants; one of the anionic surfactants commonly used in laundry detergents is LAS (Linear Alkylbenzene Sulfonate). The commercial product of LAS as sodium salt comprises a mixture of homologs containing between 10 and 14 linear carbon atoms with a phenyl group attached to the linear alkyl chain and the sulfonate anion (Figure I) (Ramcharan and Bissessur, 2016).

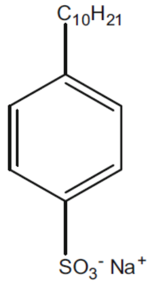

Figure 1. Linier alkylbenzene sulfonate structure

LAS surfactant is a material that is difficult to decompose, so it can pollute the environment if left continuously. These compounds' entrance, distribution, and dispersion into water resources lead to different hurt to biological and non-biological parts of aquatic ecosystems. From the point of view of non-biological aspects, detergents reduce the surface tension of the water. Foaming on the water surface reduces oxygen transfer and causes adverse visual effects. In biological systems, cause disrupts bio-membranes, alters the state and quality of the protein, disrupt biological function, and exert direct and earnest inhibitory effects on the growth, reproduction, and physiological functions of aquatic organisms by influencing membrane permeability and enzyme activity, and tissue structure. They also increase the dissolution of pollutants in water, leading to more damages to the aquatic organisms living environments (Hassanzadeh and Jafari, 2020).

There are various technologies used to remove surfactant pollutants from wastewater, such as adsorption (Amirmoshiri et al., 2020), coagulation and flocculation (Lolo et al., 2020), and the use of UV/H2O2 processes (Sakai et al., 2020). Electrochemical methods are becoming more competitive among the other proposed techniques due to their high efficiency and low cost. Other than that, since these methods do not contain harmful chemicals, they have little or no harmful effects on the environment. In recent decades, electrocoagulation/flotation (ECF) has provided a separation technique, which applies sacrificed anodes to form active coagulants and equip with precipitation and flotation to remove pollutants from water/wastewater. Briefly, ECF benefits from its simplicity, cost-effectiveness, ease to implement, production of a low amount of sludge, and minimum chemicals added (Emamjomeh et al., 2020).

In electrochemistry, selecting the suitable electrode material is very important because it plays a role in determining the reaction. The electrode used in this study was aluminium as the anode with a resistivity value of 2.82 x 10-8 Ωm and conductivity of 3.55 x 107 S/m (Serway and John, 2010). In many cases, aluminium has better electrolysis efficiency than other electrodes (Pulkka et al., 2014). Graphite as a cathode is an inert electrode made of cheap material with good electrical conductivity (Chung, 2002). In the electrocoagulation process with aluminium anodes, Al^{3+} cations will be formed with the dominant coagulant species $Al(OH)_3$, which has kept a value of 2.0×10^{-31} (Suhartana et al., 2020)

The reactions that occur during the electrocoagulation process using aluminium anode (Zini et al., 2020):

$$Al \rightarrow Al^{3+} + 3e^- \ (anode) \quad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \ (cathode) \quad (2)$$

$$Al^{3+}{}_{(aq)} + OH^-{}_{(aq)} \rightarrow Al(OH)_3 \quad (3)$$

There will be an oxidation reaction of aluminium at the anode to produce Al3+ cations, while at the cathode, water is reduced to produce hydrogen gas and hydroxide anions (OH^-). The aluminium ion Al^{3+} resulting from a spontaneous hydrolysis reaction produces various species such as $Al(OH)_3$; $Al(OH)^{2+}$; $Al(OH)_4^-$.

Several parameters such as pH of the solution, time, and electrolyte concentration of NaCl are essential to study because these parameters influence the removal efficiency of LAS surfactant. By conducting research studies on these parameters, we can find out the optimal conditions of electrocoagulation to remove LAS surfactant. To know the removal efficiency, some characterization was carried out using UV-VIS spectrophotometry to determine whether there was a shift in the sample's wavelength before and after electrolysis and analysis with FTIR spectroscopic instruments to determine the absorption of its functional groups. Kinetic studies were carried out to determine the constant and order of the electrocoagulation reaction of LAS (Linear Alkylbenzene Sulfonate) surfactant using Al/Graphite electrodes.

2. Methodology

2.1 Equipment and Materials

The equipment used is magnetic stirrer (Faithful), analytical balance (Ohaus), power supply (CAL 60 IPA STD), graphite electrode, Aluminium electrode, UV-Vis Spectrophotometer (Genesys 10S), FTIR (Spectrum 100 Perkin Elmer), beaker glass 500 mL (Pyrex Iwaki), and other glassware. Material used are commercial LAS (Linier Alkyklbenzene Sulfonate) surfactants, NaCl (Merck), Aquades, NaOH 1M, HCl 1M, Indikator fenolftalein (Merck), H_2SO_4 1N dan 6N (Merck), *Methylen Blue* (Merck), kloroform (Merck).

2.2. Instrument Design

The electrolysis reactor consists of an aluminium anode (7 cm x 4 cm x 0,1 cm) and graphite cathode (7 cm x 4 cm x 0,7 cm) with a distance of electrode 2 cm. The set-up was then mounted on a 500 mL glass container and connected to a DC source.

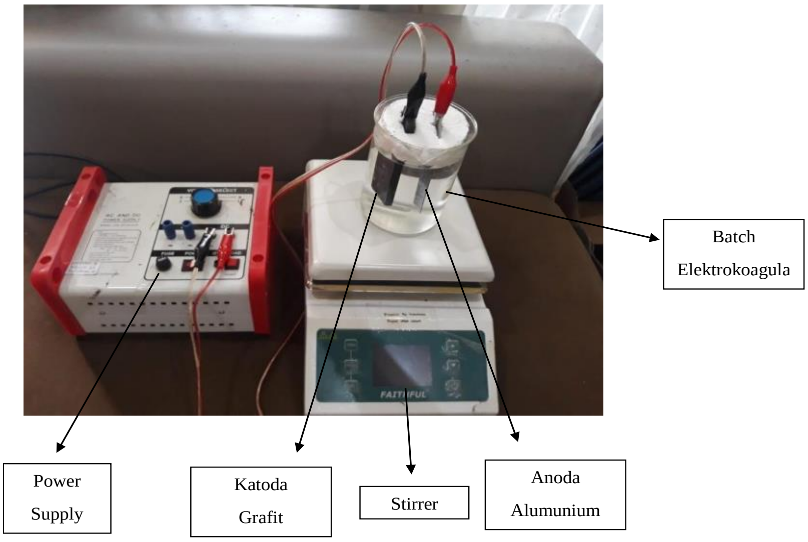

Figure 2. Electrocoagulation device set-up

2.3. Procedure

Surfactant sample preparation was weighed 2 grams of commercial surfactant sample then dissolved in 1000 mL distilled water. The mixture was stirred for 30 minutes at 250 rpm to dissolve the surfactant.

2.3.1 Electrocoagulation Process

An artificial surfactant sample of 500 mL was placed in an electrocoagulation cell. HCl and NaOH were added to the solution to regulate the acidic and alkaline atmosphere of the solution. In this study, voltage, electrolyte NaCl concentration, pH and time were varied. Al and carbon electrodes were immersed in the reactor at a distance of 2 cm. The solution was electrocoagulated at various voltages (3,6,9,12) Volts; electrolyte concentration (0;0.4;0.8;1.2;1.6;2) gram/L; pH (3,5,7,9,11) and electrocoagulation time (10,20,30,40,50) minutes. After obtaining the main parameters with the best conditions, the experiment was again conducted to determine the efficiency of reducing surfactants in water contamination. Samples were characterized using UV-VIS spectrophotometer and FTIR spectroscopy.

2.3.2 Surfactant Analysis

The surfactant content was determined using the MBAS method, which refers to (SNI 06-6989.51-2005). Anionic surfactants react with methylene blue to form blue-colored ion pairs soluble in organic solvents. The intensity of the blue color formed was measured with a spectrophotometer at a wavelength of 652 nm. The measured absorption is equivalent to the anionic surfactant level. Surfactant level testing was carried out on samples before and after electrocoagulation to determine the surfactant removal efficiency using the formula (eq. 4):

$$(Y) = \left(\frac{C_0 - C}{C_0}\right) x\ 100\% \tag{4}$$

Co (mg/L) the initial concentration and C (mg/L) the final concentration after the electrocoagulation process.

3. Result and Discussion

3.1 Effect of Voltage on the Percentage of Electrocoagulation

Voltage is commonly considered a significant factor for eliminating contaminants in the electrocoagulation process. The voltage could determine the amount of sacrifice electrodes dissolution and affect the generation of metal hydroxide flocs and the removal efficiency of contaminants (Bao et al., 2020). In this study, the voltage variation was carried out by electrolyzing the sample at a voltage of (3;6;9;12) Volt with an electrocoagulation time of 30 minutes and 2 gram/L NaCl. The effect of applied voltage on surfactant removal efficiency in this study is presented in (Table 1).

Table 1. Results of surfactant electrocoagulation analysis at various voltage

Voltage (Volt)	C_0 (mg/L)	C (mg/L)	(Y)%
3	30.783	0.935	96.96%
6	30.783	0.670	97.82%
9	30.783	0.341	98.89%
12	30.783	1.291	95.81%

Based on (Table 1) indicates that increasing applied voltage can increase surfactant removal from the sample with optimum voltage (9 volts). According to Faraday's law, the voltage increase might contribute to more cations dissolved from the sacrifice anode. The electrolytic reaction at the cathode increased the hydroxyl group (OH-) concentration, enhancing the driving force of charged particles in the solution and accelerating the formation of more metal hydroxide flocs to facilitate the adsorption (Bao et al., 2020). If the voltage is raised above the optimum (9 volts), it will decrease surfactant removal. According to (Moussa et al., 2017), in some cases, the actual anode dissolution does not match the one calculated using Faraday's law, which indicates that other electrochemical reactions might occur at the anode. Several authors suggested that the evolution of oxygen at the anode might occur at alkaline pH and sufficiently high anodic potential (eq. 5), which might explain the mismatch of theoretical and actual anodic dissolution.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{5}$$

3.2 Effect of Electrolyte Concentration on the Percentage of Electrocoagulation

Supporting electrolytes are needed to increase the conductivity of the solution, reduce the resistance of the resolution, suppress the migration current, and increase the mobility of ions in the solution (Wahyuni et al., 2021). In this study, variations in electrolyte concentration were carried out by electrolyzing the sample with NaCl electrolyte (0; 0.4; 0.8; 1.2; 1.6; 2) gram/L with applied voltage 9 volts and electrocoagulation time 30 minutes. The effect of electrolyte concentration on surfactant removal efficiency in this study is presented in (Table 2).

Table 2. Results of surfactant electrocoagulation analysis at various concentrations of NaCl

Electrolyte (gram/L)	C_0 (mg/L)	C (mg/L)	(Y)%
0	30.783	2.936	90.46%
0.4	30.783	1.699	94.48%
0.8	30.783	2.491	91.91%
1.2	30.783	1.866	93.94%
1.6	30.783	1.422	95.38%
2	**30.783**	**1.364**	**95.57%**

Based on Table 2 indicates that increasing electrolyte concentration can increase surfactant removal from the sample with optimum removal efficiency is 95.57% at a concentration of NaCl 2 gram/L. NaCl is one of the most effective electrolytes to remove the corrosion protective layer from the aluminium electrode surface. Ion Cl^- is strongly adsorbed on the electrode surface so that it helps the hydration process of the passive film layer on the anode and tends to break down the passive film formed on the surface of the aluminium anode and rate of the formation of stable aluminium hydroxides ($Al(OH)_3$) into the solution would be increased, it occurred due to the ion exchange reactions of hydroxides and supporting electrolyte ions (Cl^-), as shown below in Reactions (eq. 6)–(eq. 10):

$$Al_2O_3 + 6Cl^- + 6H^+ \rightarrow 2AlCl_3 + 3H_2O \tag{6}$$

$$Al(OH)_3 + Cl^- \rightarrow Al(OH)_2Cl + OH^- \tag{7}$$

$$Al(OH)_2Cl + Cl^- \rightarrow Al(OH)Cl_2 + OH^- \tag{8}$$

$$Al(OH)Cl_2 + Cl^- \rightarrow AlCl_3 + OH^- \tag{9}$$

$$AlCl_3 + Cl^- \rightarrow AlCl_4^- \tag{10}$$

The above reactions contributed to the breakdown of the corrosion protective layer from the aluminium anode electrode surface. After the breakdown of this corrosion protective layer from the aluminium anode electrode surface, the rate of the formation of stable aluminium hydroxides ($Al(OH)_3$) into the solution would be increased, which will lead to an increase in the removal rate due to co-precipitation or adsorption with $Al(OH)_3$ (Maitlo et al., 2018).

3.3 Effect of Initial pH on the Percentage of Electrocoagulation

The initial pH variation of the solution was carried out to determine the effect of the pH that could be applied in the process, with the addition of HCl for acidic conditions and the addition of NaOH for alkaline conditions. Variations in pH concentration were carried out by electrolyzing the sample at pH (3,5,7,9,11) with applied voltage 9 Volts, electrocoagulation time 30 minutes, and the addition of 2 gram/L NaCl. The effect of the initial pH of the solution on the surfactant removal efficiency in this study is presented in Table 3.

Table 3. Results of surfactant electrocoagulation analysis at various initial pH

pH	C_0 (mg/L)	C (mg/L)	(Y)%
3	30.783	2.675	91.31%
5	30.783	2.022	93.43%
7	30.783	1.443	95.31%
9	**30.783**	**1.399**	**95.46%**
11	30.783	1.553	94.95%

Based on Table 3 indicates that the surfactant removal efficiency tends to be better at the initial pH of the neutral to a slightly alkaline solution, with the best efficiency of 95.46% at the initial pH solution 9. The dominant species in the solution will also be different at different pH values. At pH < 3.5; the dominant species is Al^{3+}, for pH values between 4 - 9.5 $Al(OH)_3$ species dominates which are effective for coagulation and when pH >10, the species $Al(OH)_4{}^-$ Formed and is a weak coagulant (Moussa et al., 2017).

3.4 Effect of Contact Time on the Percentage of Electrocoagulation

The treatment time of the solution is an essential characteristic of the electrocoagulation process since it is directly related to the amount of the coagulant generated (Dimoglo et al., 2019). Time variation was carried out by electrolyzing the sample at a time (10,20,30,40,50) minutes with applied voltage 9 Volts, pH 9, and the addition of 2 gram/L NaCl. The effect of contact time on surfactant removal efficiency in this study is presented in (Table 4).

Table 4. Results of surfactant electrocoagulation analysis at various contact time

Time (minutes)	C_0 (mg/L)	C (mg/L)	(Y)%
10	30.783	1.902	93.82%
20	30.783	1.653	94.63%
30	30.783	1.364	95.57%
40	30.783	1.119	96.36%
50	**30.783**	**0.785**	**97.45%**

Based on table 4 indicates that increasing electrocoagulation time can increase surfactant removal from the sample**.** The anode serves as the coagulant in an EC cell, where it dissociates to give metal cations when DC is passed through the cell. The dissociation of anode follows Faraday's law. The number of metal cations released from the anode depends on the electrolysis time and current density (Moussa et al., 2017). The efficiency of pollutant removal will increase with increasing time because the formation of aluminium hydroxide as coagulant from the anode increases simultaneously with the increasing time.

3.5 Kinetic Study

Kinetic studies were carried out to determine the constants and the order of the electrocoagulation reaction of LAS surfactants with Al/Graphite electrodes. The kinetic study was carried out integrally using time variation data using the graphical method. The first and second-order reaction kinetics models are proposed in this study with the following equation (eq. 11) – (eq. 14) (Prayitno and Ridantami, 2017):

$$-\frac{dC}{dt} = K_1 . C \tag{11}$$

$$C_t = C_0 . e^{-K_1 t} \tag{12}$$

$$-\frac{dC}{dt} = K_2 . C^2 \tag{13}$$

$$\frac{1}{C_t} = \frac{1}{C_0} + K_2 . t \tag{14}$$

The results obtained are presented in the form of a graph

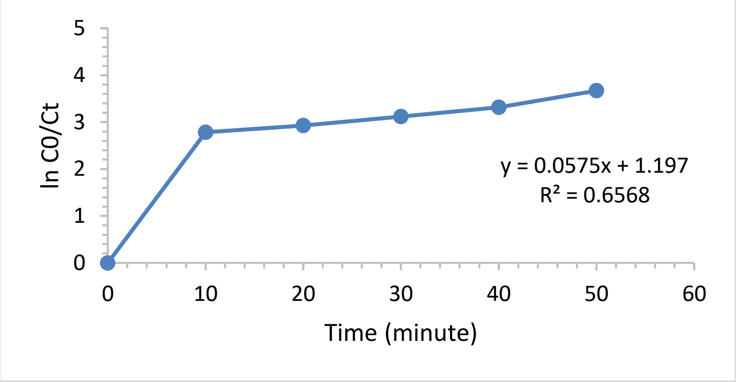

Figure 3. First-order graph

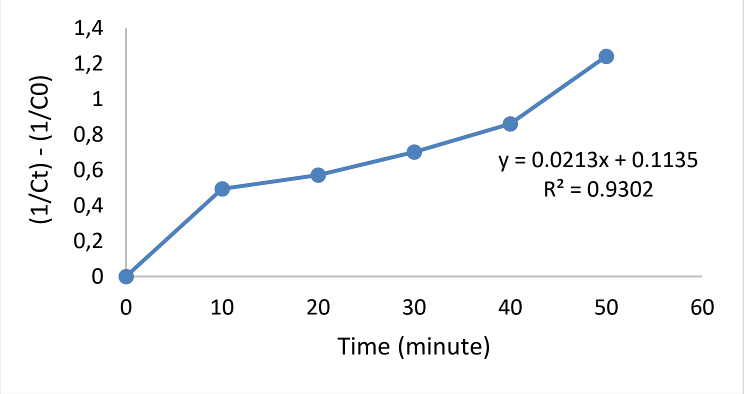

Figure 4. Second-order graph

Based on the graph above, the regression coefficient value of the second-order is greater than the first order, so the reaction kinetics is more suitable if predicted with the second order.

3.6 Optimum Conditions for Electrocoagulation

The electrocoagulation process was carried out at the initial pH of solution 9; the electrolyte concentration was 2 grams/L, with an electrocoagulation time of 50 minutes, and the applied voltage was 9 Volts. Optimum conditions were chosen by considering the results of decreasing surfactant levels for each parameter variation carried out. The analysis carried out on the sample after the electrocoagulation process under the best conditions included measuring the surfactant levels in the sample and analysis using UV-VIS and FTIR spectrophotometers. The results showed that the surfactant removal efficiency at the best conditions with Al/graphite electrodes was 97.45%. It was better than the previous studies, where the removal efficiency of LAS was 96.70% (Amirmoshiri et al., 2020).

Analysis using a spectrophotometer indicates a change in the solution after the electrocoagulation process. Surfactant wavelength scanning was carried out using the MBAS (Metylen Blue-Anionic Surfactant) method at a wavelength of 500 – 750 nm. The results obtained are described in the sample spectra before and after the electrocoagulation process (Figure 5).

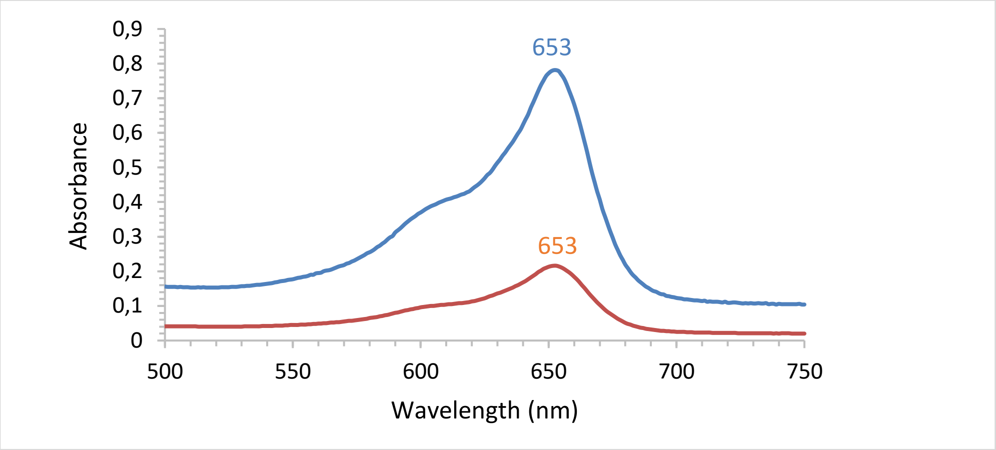

Figure 5. UV - VIS Spectra before and after electrocoagulation

Based on (Figure 5), there is a decrease in the absorption intensity from 0.781 to 0.216 with the same wavelength value at 653 nm. These results indicate a decrease in the concentration of pollutants in the solution after electrocoagulation.

Analysis using FTIR spectroscopy was also carried out to determine the absorption of the sample functional groups before and after the electrocoagulation process, as shown in (Figure 6). FTIR spectra of the sample before processing showed an absorption with a broad peak at wave number 3369.76 cm^{-1} which indicated the presence of an OH group from dissolving the sample using distilled water. A wavenumber 1643.36 cm^{-1} indicates the presence of a C=C group, at wave number 1205.24 cm^{-1} indicates the sulfonate group, and wavenumber 1032.68 cm^{-1} indicates alkylbenzene sulfonate (Ramcharan and Bissessur 2016).

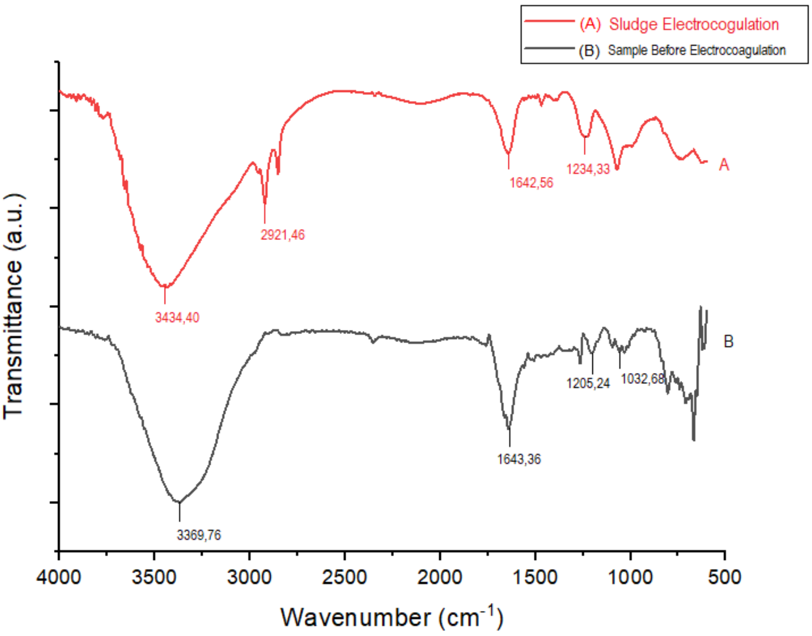

Figure 6. FTIR Spectra before and after electrocoagulation

Based on (Figure 6) FTIR spectra after electrocoagulation, it is assumed that the surfactant sample has been adsorbed to the $Al(OH)_3$ floc, this can be indicated by the presence of an absorption peak with a widening at 3434.40 cm^{-1} which indicates the presence of an OH group that may appear due to the formation of $Al\ (OH)_3$ as a coagulant. A wavenumber 2921.46 cm^{-1} indicates the presence of an aliphatic C-H group due to the presence of aliphatic chains in the sample, at wave number 1642.56 cm^{-1} indicates the presence of a C=C group, at wave number 1234.33 cm^{-1} indicates the sulfonate group. The similarity spectra between samples before the electrocoagulation process and the sludge from electrocoagulation indicate that most surfactant pollutants can be separated from the liquid waste through the electrocoagulation process.

4. Conclusion

The best efficiency percentage was obtained at 97.45% at applied voltage 9 Volts, the addition of electrolyte NaCl 2 gram/L, electrocoagulation time 50 minutes, and the initial pH of the solution 9. Supporting electrolytes and increased electrocoagulation time can increase surfactant removal from the sample. The electrocoagulation process tends to be better at a neutral condition to slightly alkaline pH. Based on the kinetic studies, the reaction kinetics of the electrocoagulation of LAS surfactant with Al/Graphite electrodes corresponded to the second-order with reaction constant value 0.0213 (mg/L)-1. min-1. UV-VIS and FTIR spectrophotometric analysis showed that most surfactant pollutants could be adsorbed on Al(OH)3 floc and separated from the liquid waste through the electrocoagulation process.

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