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Removal of COD, TDS and Ammonia (NH_3-N) in Produced Water with Electrochemical Using Aluminum (Al) and Iron (Fe) Electrode

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***Abstract*—The activities of the oil and gas industry have the potential to cause pollution for the environment. This pollution can arise due to the production of petroleum processing, storage, and industries that use petroleum. Produced water is the largest liquid waste generated by these activities. The number will increase as long as a field where exploration continues to produce. In this study, an electrochemical method using Al-Fe electrodes with the addition of 1 g/L NaCl as an agent to provide chlorine as an oxidation mediator to accelerate NH_3-N removal in produced water. Chemical reactions that occur during the electrochemical process as driving force, the reduction process is specific with conductive and active electrochemical substances then can manipulated with potential (voltage) and current time. A combination of an electrode is using aluminum and iron electrode plates with each thickness 0.1mm. The voltage variations during the process were 3, 6, 9, and 12V. This process is continuous, and samples are taken every 45, 90, 135, 180, and 225 minutes. The results showed percentage of COD removal is 53.14% from 430.25 mg/L to 201.6 mg/L, ammonia (NH_3-N) removal is 91.64% from 17.71 mg/ L to 1,48 mg/L and TDS removal is 78.14% from 12670 mg/L to 2769 mg/L. 9V for 225 minutes during the electrochemical process is an optimum condition that can reduce contaminants in produced water, so the quality standards of Minister of Environment Regulation No.19 2010 are fulfilled. The electrochemical method was chosen to produce water treatment because the equipment required is simple and easy to operate and does not cause new waste.**

***Keywords*— Produced water; electrochemical; filtration; aeration; ammonia.**

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I. INTRODUCTION

Produced water is the largest liquid waste generated exploration and production of oil and gas because produced water is generated continuously as long as the oil field continues to produce [1]. The processing of exploitation produce water that has been carried out includes biodegradation of hydrocarbon components using microorganisms [2], adsorption of dissolved organic components with activated carbon [3], cyclones [4], and coagulation-flocculation techniques [5]. Other methods that have also been used for ammonia removal include biological use (microbial utilization), water stripping, breakpoint chlorination, and ion exchange [6]. However, this method has limitations, one of which cannot reduce ammonia to a high level, many costs, and using microorganisms for processing also takes a long time.

Based on the analysis, the characteristics structure of the water oil and gas industry production in Sumatera Selatan has a COD concentration of 430.25 mg/L, TDS concentration of 12,670 mg/L, and ammonia concentration of 17.71 mg/L. The concentration exceeds the quality standards according to standard quality stipulated in Minister of Environment Regulation No.19, 2010. It has the potential to be classified as B3 waste also harm the environment and human health. Therefore, the objectives of this research are as follows:

- To find out the produced water quality of the oil and gas industry in South Sumatera
- To find out the period effect (45, 90, 135, 180, and 225 minutes), and voltage (3, 6, 9 and 12volt) to reduce the level of COD, ammonia (NH -N), and TDS in produced water using electrochemical method (1 g/L NaCl added as a mediator in oxidation process) with electrodes Al-Fe.
- To evaluate characteristics of permeate process result according to standard quality stipulated in Minister of Environment Regulation No.19, 2010.

The research that has been conducted by Said *et al.* [7] about produced water treatment with a combination of electrocoagulation (Fe electrode) and adsorption using adsorber mixture from silica (bottom ash) and activated carbon from coconut shell getting removal percentage of COD 97.39%, ammonia (NH_3-N) 69.18% and TDS 91.19%. Anugrah [8] researched produced water with combination electrocoagulation using aluminum and iron electrodes in filtration treatment using activated carbon from coconut shell obtain removal percentage of COD 98.39%, ammonia (NH_3-N) 75, 16%, and TDS 93.54%. Surahman [9] revealed that voltage, electrode surface area, and time obtained removal percentage of COD 88, 07% and TDS 31.29% using electrodes in a surface area 38.4 mm^2 while the percentage results obtained for surface area 78 mm^2 can reduce COD 92.95% and TDS 36.25%. Al-Fe electrodes can reduce COD 80-84% of domestic wastewater[10]. Yao [11] used an electrochemical method to treat dyed wastewater and added 1 g/L NaCl, which could reduce ammonia by 88.3%.

The reactions that occur during electrochemical process:

Anode (oxidation): $Al \rightarrow \quad Al^{3+} + 3e^-$

reaction around electrodes: $Al^{3+} + 2(OH^-) \rightarrow Al\ (OH)_3$

Cathode (reduction) : $Fe^{2+} + 2e^- \rightarrow \ Fe$

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

Reaction equations that occur in this process are:

$$2NH_{3(g)} + 6OH^-_{(aq)} \rightarrow N_{2(g)} + 6H_2O_{(l)} + 6e^-$$

$$6H_2O_{(l)} + 6e^- \rightarrow 3H_{2(g)} + 6OH^-_{(aq)}$$

Aluminum (Al) and iron (Fe) are selected as electrodes because of their low cost, availability in quantities, and high efficiency. The first reaction is an ammonia oxidation reaction that occurs at the anode, while the second reaction is a water reduction reaction and occurs at the cathode. The solubility of ammonia is exceptionally large in water, although solubility decreases sharply with increasing temperature. Ammonia reacts reversibly with water to produce ammonium ions (NH_4^+) and hydroxide ions (OH^-). The process of electrolyzing ammonia to produce hydrogen for waste treating with ammonia content has been developed recently [12].

The system of produce water treatment in the upstream oil and gas industry in South Sumatera is ineffective because the water to be injected is treated just by pass process from wash tank to water tank with skimmer tank and nutshell filter then produced water only treated with zeolite as an adsorbent. The injection piping system can build a scale. In terms of economics, it would make operating, and maintenance costs are expensive. One of the effective and simple methods of produced water treatment is electrochemical [13]. Electrochemical in alkaline conditions will produce nitrogen, and hydrogen also can produce hydrogen as fuel cells.

II. Materials and Methods

The equipment in produced water treatment using an electrochemical reactor with Al and Fe electrodes and voltage source comes from the power supply, aeration unit, NaCl tank, and filtration unit which materials contain silica, charcoal, zeolite, gravel, and rock (coral). In addition, two tanks are needed for raw waste storage, and the final sample result produced water treatment, then results are sampled using a 300 mL plastic bottle. To calculate the variation period of time, a digital stopwatch is used. The produced water samples are from the Upstream Oil and Gas Industry in South Sumatera and NaCl (1gr/L) as a chemical used in the electrochemical process.

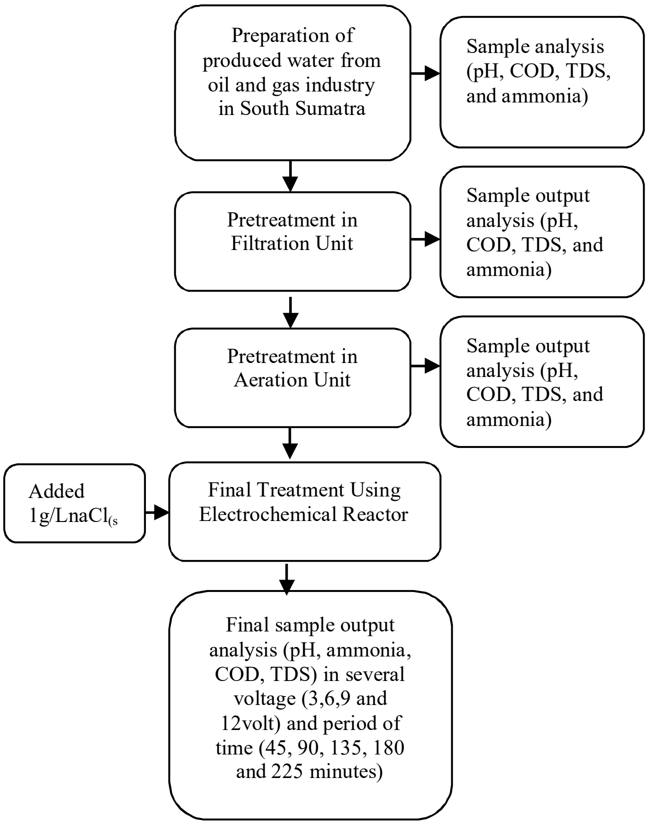

Fig. 1 Research Flow Diagram

Preliminary treatment is an analysis of produced water as raw material. Raw sample flowed to filtration unit (pre-treatment), containing materials such as silica, charcoal, zeolite, gravel, and coral for a predetermined time of variation (45, 90, 135, 180, and 225 mutes). Output from the filtration unit is conducted for samples analyzed (pH, ammonia, COD, and TDS) and then flowed in the aeration unit to contact the air supply from the aerator. Aeration unit samples will be treated for a predetermined variation period (45, 90, 135, 180, and 225 minutes). Output from aeration unit also conducted for samples analyzed (pH, ammonia, COD, and TDS) and then flowed to the electrochemical reactor which supplied with electricity from travo to combination of aluminum (Al) and iron (Fe) electrode plates which dimension l = 15cm, w = 5cm and t = 1cm and added by 1 NaCl (s) g/L for variations electrolysis time of 45, 90, 135, 180 and 225 minutes with flow rate 9.13 mL/min. Output from the electrochemical reactor is stored in a shelter tank for final analysis (pH, ammonia, COD, and TDS).

The method of collecting data in this research is observation, followed by sampling and laboratory tests. Analysis of pH determination used SNI 6989.11-2019 method. Analysis of COD content determination using SNI 6989.2-2019 method. Analysis of ammonia levels determination (NH_3-N) used SNI 06-6989.30-2005 method. Analysis of TDS content determination used SNI 6989.27-2019 method. In this research, produced water was treated using three continuous steps; filtration, aeration, and electrochemical with aluminum (Al) and Iron (Fe) electrodes.

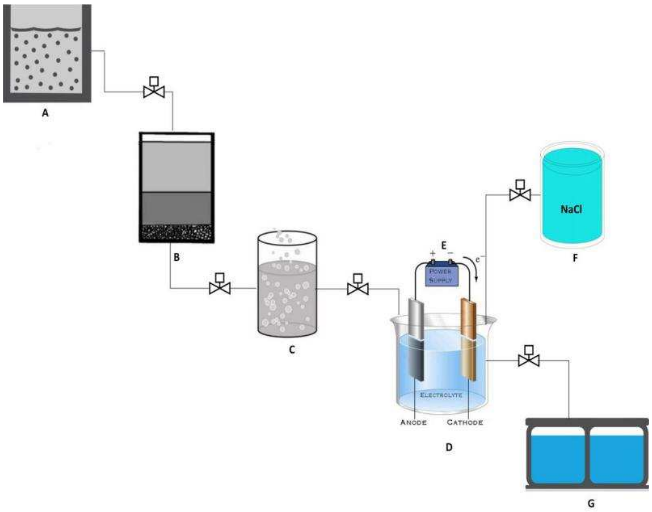

Fig. 2 Produce Water Treatment Equipment Design

Note A. Raw material (produce water) tank; B. Filtration unit; C. Aeration unit; D. Electrochemical reactor; E. Powers supply; F. Solution tank of NaCl; G. Final shelter tank.

III. Results and Discussion

The results of the initial sample analysis on produced water from the Upstream Oil and Gas Industry in South Sumatra are shown in Table 1. It can be seen that parameters of NH_3-N, COD, TDS have not qualified according to standard quality stipulated in Minister of Environment Regulation No.19, 2010.

TABLE I
ANALYSIS RESULT OF RAW SAMPLES OF PRODUCED WATER

No	Parameter	Unit	Test Result	Threshold Limit Value
1	pH	-	7.56	6-9
2	COD	mg/L	430.25	300
3	NH_3-N	mg/L	17.71	10
4	TDS	mg/L	12670	4000

TABLE II
ANALYSIS RESULT OF PRODUCE WATER IN FILTRATION UNIT

Time (min)	pH	COD (mg/L)	NH_3-N (mg/L)	TDS (mg/L)
0	7.56	430.25	17.71	12670
45	7.02	424.70	17.22	12254
90	6.87	413.90	16.76	11764
135	6.63	402.70	16.10	11311
180	6.48	391.10	15.72	11085
225	6.27	387.30	15.64	10972

TABLE III
ANALYSIS RESULT OF PRODUCE WATER IN AERATION UNIT

Time (min)	pH	COD (mg/L)	NH_3-N (mg/L)	TDS (mg/L)
0	7.56	430.25	17.71	12670
45	6.98	422.70	17.04	12048
90	6.82	458.30	16.82	11762
135	6.51	398.76	16.51	11554
180	6.34	382.88	16.44	11231
225	6.12	361.63	16.37	11062

TABLE IV
ANALYSIS RESULT OF PRODUCE WATER IN ELECTROCHEMICAL REACTOR

Volt	Time (min)	pH	COD (mg/L)	NH_3-N (mg/L)	TDS (mg/L)
3	0	7.56	430.25	17,71	12670
	45	6.84	351.90	5.57	11776
	90	9.85	351.50	3.86	13698
	135	9.83	351.50	2.98	11804
	180	9.49	278.40	2.86	9939
	225	9.79	257.20	2.75	8007
6	0	7.56	430.25	17.71	12670
	45	6.75	342.90	4.96	11776
	90	9.32	340.76	3.34	12641
	135	8.64	312.16	2.88	10767
	180	8.17	254.34	2.05	8944
	225	7.49	228.66	1.71	7120
9	0	7.56	430.25	17.71	12670
	45	6.72	325.60	4.21	11735
	90	8.38	309.10	3.93	10569
	135	8.38	276.80	2.76	8022
	180	7.72	232.50	1.91	4008
	225	7.13	201.60	1.48	3621
12	0	7.56	430.25	17.71	12670
	45	6.70	301.70	3.86	10972
	90	8.06	299.30	3.12	8726
	135	7.87	269.60	2.41	5326
	180	7.24	307.40	2.72	2769
	225	6.79	354.70	3.64	3901

A. Impact of Filtration Process on Chemical Oxygen Demand (COD), NH_3-N and Total Dissolved Solids (TDS)

1) Chemical Oxygen Demand (COD): COD (Chemical Oxygen Demand) is the amount of oxygen needed to elaborate all organic material contained in water [14]. Produced water processed in this research has a sufficiently large COD content of 430.25 mg/L. If contaminated with the environment, the high COD content can cause B3 (toxic and hazardous materials) and the health of the surrounding (humans). The high COD content also certainly reduces the ability of water sources to protect the ecosystem.

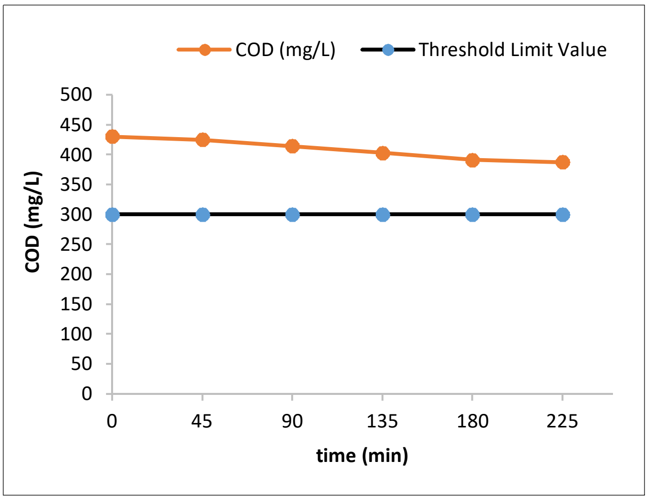

Fig. 3 Impact of Filtration Process on COD reduction

The large COD content of produced water is certainly not proper with the quality standard of Wastewater Exploration Oil and Gas Production Activities which is 300 mg/L, so produced water needs a treatment to fulfill the quality standard. In order to obtain these quality standards, several steps were taken, like filtration. The function of the filtration process is to separate solids and colloids from the liquid. The screening process also can be a primary treatment process. The media filter used is silica, gravel, charcoal, and zeolite. Although it was not too significant in reducing COD from 430.25 mg/L to 387.3 mg/L, pre-treatment would facilitate further work.

2) Ammonia (NH3-N): Produced water treatment using filtration with silica, gravel, charcoal, and zeolite has decreased from ammonia content of 17.71 mg/L to 15.64 mg/L stables over time. This shows that reduction occurred using filter media, although not too significant, but this media can facilitate the primary processing of produced water. Using the filtration process as primary treatment is also useful to control the migration of dangerous contaminants such as NH3-N so ammonia content in produced water will decrease until it fulfills Wastewater Quality Standard for Oil and Gas Exploration and Production Activities based on Minister of Environment Regulation No.19, 2010. High levels of ammonia can indicate contamination of organic material from the source. Ammonia is present in relatively small amounts if high dissolved oxygen is in the sample [15].

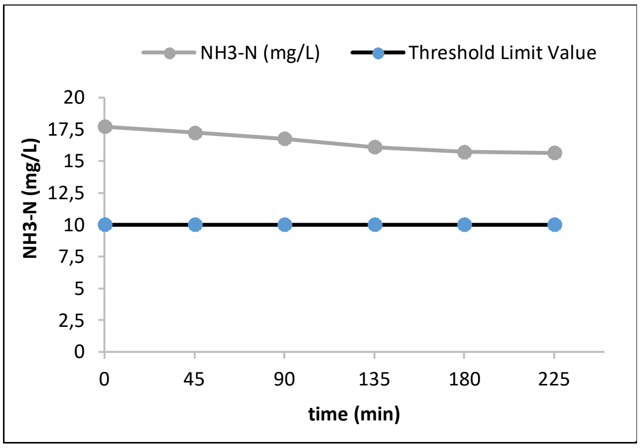

Fig. 4 Impact of Filtration Process on Ammonia reduction

3) Total Dissolved Solid (TDS): Produced water treated using filtration (silica, gravel, charcoal and zeolite) can decrease TDS value on stable every time. Sources of total dissolved solids include all dissolved cations and anions [16]. Total dissolved solids usually consist of organic substances, inorganic salts, and dissolved gases. If total dissolved solids increase, it will affect the hardness in the solution. Samples in 225 minutes, using filtration process was able to reduce TDS from 12670 mg /L to 10972 mg /L. The filters are used form of silica, gravel, charcoal, and zeolite, which aim to remove dissolved solids contamination in produced water. Decrease in TDS levels by using filter caused the pores in media filer such as charcoal and zeolite, which are smaller than produced water particulate, to separate dissolved solids in produced water. However, the results of using filtration to produce water treatment have not reached the standard quality, so the further process is needed to reach a TDS value that matches the standard quality.

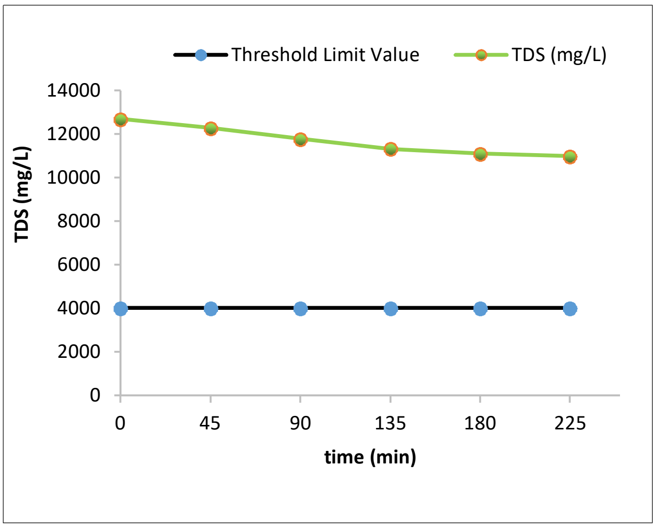

Fig. 5 Impact of Filtration Process on TDS reduction

B. Impact of Aeration Process on Chemical Oxygen Demand (COD), NH3-N and Total Dissolved Solids (TDS)

1) Chemical Oxygen Demand (COD): Increasing amounts of microorganisms can cause a high-level value of dissolved oxygen "Dissolved Oxygen" (DO), most of the oxygen is used for respiration of these microorganisms. By decreasing DO, it will affect the life of ecosystems and other aquatic biotas. The average COD levels obtained from the results of this research were 404.85 mg/L. This shows if the results are not still fulfilling tolerance set by standard quality Minister of Environment Regulation No.19, 2010. The main objective of the aeration process is O_2 in the air can react with cations in treated water. Cation's reaction and oxygen produce oxidation of metal, which is difficult to dissolve in water to precipitate easily. The benefits from this process are eliminating tastes in wastewater, odors, and unnecessary gases (CO_2, methane, hydrogen sulfide).

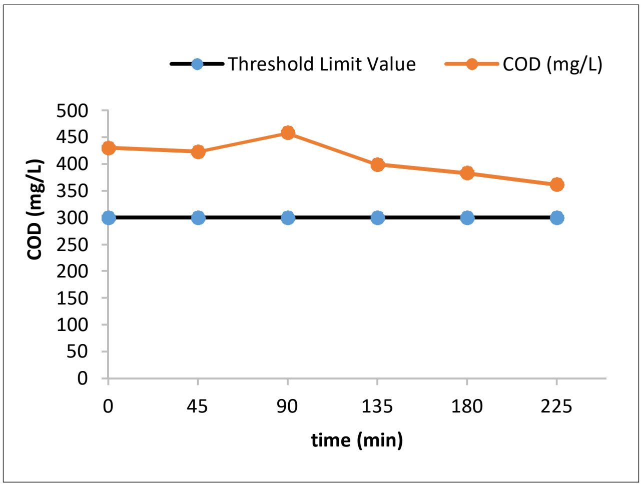

Fig. 6 Impact of Aeration Process on COD reduction

The correlation between aeration time and COD value can be seen in Figure 6. The effect of the index is 0.16 or 16%, meaning that aeration time can decrease the COD value. Figure 5. also shows that the time needed to elaborate organic materials contained in produced water has not worked optimally until 225 minutes. The experimental results show a fluctuating curve between aeration time with DO value seems to fluctuate. This can be seen in the sampling results during 90-minute COD value increases to 458.3 mg/L, its mean that DO value does not correlate with aeration. According to the theory, the longer the aeration process, the more COD parameters should be deposited, so the water concentration should decrease. It causes the longer of aeration time, the more oxygen put into a sample, so COD deposit is high.

2) Ammonia (NH3-N): Ammonia can cause toxic conditions for aquatic life. This concentration depends on pH and temperature, which affects water. Ammonia levels will increase with increasing pH and temperature. Ammonia nitrogen that presents in water as ammonium (NH_4^+) based on the equilibrium reaction as follows:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

The main function of aeration is to increase dissolved oxygen levels in water and release the content of gases dissolved in water and help in water stirring. Aeration can be used to remove dissolved gas content, oxidation of iron and manganese in water, reduce ammonia in water through the nitrification process. Oxygen (O_2) generated from the aeration process can also be useful in oxidizing NH_3 compounds. NH_3 compounds, which are toxic compounds for aquatic life, can be oxidized directly to become NO_3. The compound formed (NO_3^-) can bind to metals in solution to form new compounds, and H^+ that is formed can bind to OH^- which results from the reaction between CO_2 and O_2, so it does not cause a decrease in pH of treated water. The oxidation reaction of NH_3 compounds [17] is as follows:

$$NH_3 \rightleftarrows NH_4^+$$

$$NH_4^+ + 2O_2 \longrightarrow 2H^+ + NO_3^- + H_2O$$

The reaction above also explains that increasing oxygen dissolved due to the aeration process causes odor pollutants such as NH3 converted into other materials (NO3-), which are relatively safer for the environment. These processes cause NH_3 can be reduced, and the effluent becomes safer.

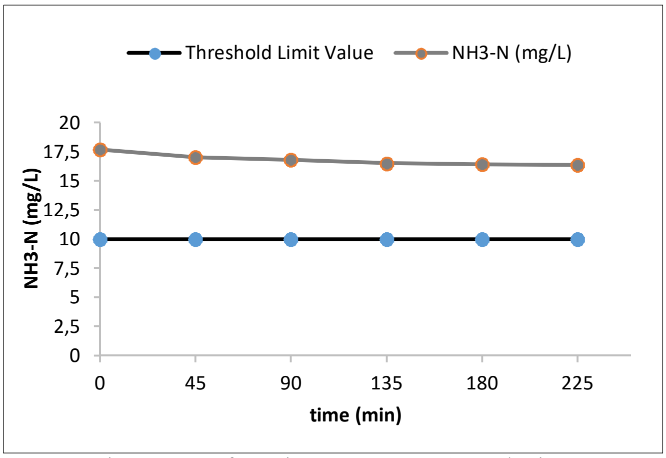

Fig. 7 Impact of Aeration Process on NH3-N reduction

Produced water treatment with aeration process in this research, ammonia levels have decreased steadily over time. Ammonia content from produce water was reduced from 17.71 mg/L to 16.37 mg/L. This shows that the aeration process can decrease ammonia content even though it has not reached the standard of quality. The results show that the vulnerable aeration time 45-225 minutes can decrease ammonia levels. Based on the analysis of results, the optimum aeration time is 225 minutes; aeration time affects decreased ammonia and organic matter levels.

3) Total Dissolved Solids (TDS): One problem in produced water is the higher concentration of dissolved solids in water (TDS). TDS can be a combination of solutes (organic and inorganic substances) that are contained in the solution. To be released into water, TDS must fulfill the applicable quality standards according to standard quality stipulated in Minister of Environment Regulation No.19, 2010 4000 mg/L. Aeration is an effort to increase the oxygen concentration contained in the wastewater oxidation process can run well. Figure 8 shows a decrease in TDS value from 12670 mg/L to 11062 mg/L for 225 minutes, even though the results obtained have not fulfilled standards quality by using this aeration process. The results of this research are in line with the statement [18] that the bigger aeration velocity is given to a certain limit, the more effective to reduce pollutants in wastewater.

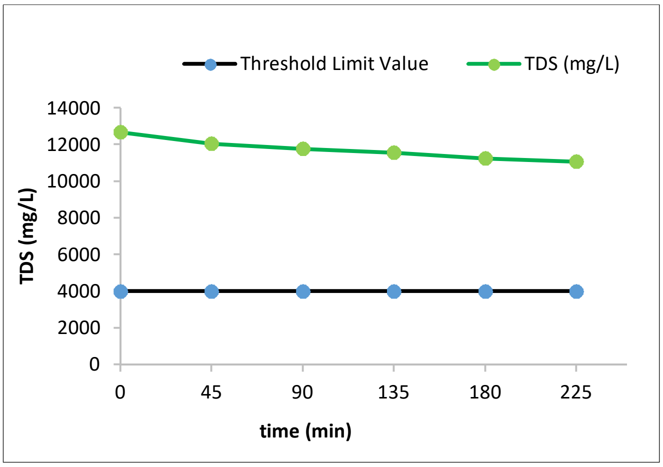

Fig. 8 Impact of Aeration Process on TDS reduction

C. Impact of Electrochemical Process with Electrodes Al-Fe on Chemical Oxygen Demand (COD), NH3-N and Total Dissolved Solid (TDS)

1) Chemical Oxygen Demand (COD): Electrolysis is process of treating raw water or liquid waste by applying an electric current to aluminum or iron metal as electrodes. The anodized electrode will be ionized by an electric current, metal ions will function as coagulant. This is exactly same as coagulation process with the addition of chemicals, various contaminants such as heavy metal ions, organic and inorganic colloid particles can bind, charge then coagulates and settles. The electrolysis process by utilizing an electric current applied to pair electrode that proven effective in removing or reducing various contaminants / impurities in water, such as COD parameter. Current strength affects the metal ionization process which used as anode electrode to determinant of electrochemical system reaction in reducing COD.

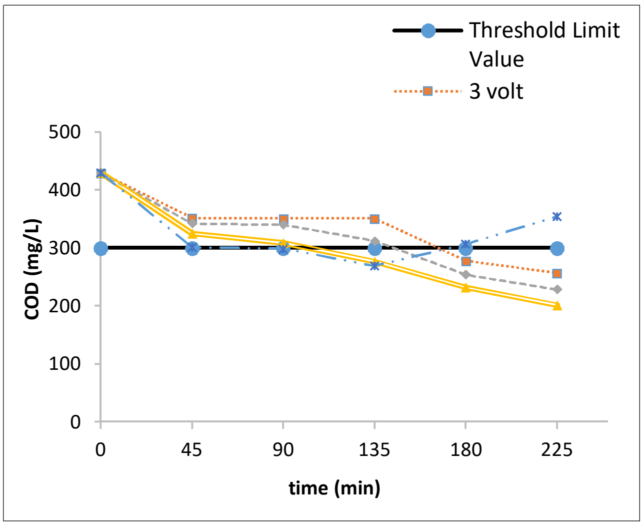

Fig. 9 Impact of Electrochemical Process on COD reduction

Figure 9. shows the COD level with the best decrease and fulfills the standard of quality is when 9 volts have applied for 225 minutes, from a COD level of 430.25 mg/L to 201.6 mg/L. The decrease in COD concentration indicates the decrease of organic compounds in liquid waste because the purpose of measuring COD value is to know the amount of oxygen needed to oxidize organic compounds in water [19].

The decrease in COD levels that occurred from this research results was due to oxidation and reduction processes in the reactor. During the electrolysis process, there will be a release of Al_3^+ from electrode plate (anode) to form $Al(OH)_3$ flocks which can bind contaminants and particles in produced water [20]. Suppose two electrodes placed in electrolyte solution and current electric is applied. In that case, an electrochemical process will occur, the symptoms of electrolyte decomposition, which will make positive ions (cations) move to cathode and receive electrons while negative ions (anions) will move to anode and release electrons which oxidized [21].

The reactions that occur during electrochemical process:

Anode (oxidation) : $Al \rightarrow Al^{3+} + 3e^-$

reaction around electrodes: $Al^{3+} + 2(OH^-) \rightarrow Al\ (OH)_3$

Cathode (reduction) : $Fe^{2+} + 2e^- \rightarrow Fe$

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

From the reaction above, Al will release its electrons on the positive electrode surface to form $Al_3^{+,}$ which will bind OH to form Al $(OH)_3$ into coagulant and gas, foam, and floc. Furthermore, the floc formed will bind organic or inorganic substances to produce water, so the floc will tend to settle. The OH^- ion will undergo oxidation to form oxygen (O_2). H+ ions will be reduced to hydrogen as bubbles at the cathode and reduced in solvent (water).

The reaction equation also shows that the formation of oxygen and hydrogen will affect reducing COD in produced water. Hydrogen will help the impurities in produced water to float and be lifted. This causes a reduction of dissolved organic. Using electrochemical methods that show a significant reduction percentage of 53.14%. However, at 12 volts, COD from 180 to 225 min increased. COD at 135 min increased from 269.6 mg/L to 307.4 mg/L and 354.7 mg/L; due to the high voltage and duration of contact, the more electrodes would decompose and a build-up floc-formed which inhibits the oxidation process.

2) Ammonia (NH3-N): Nitrogen ammonia is the main toxic in human living. A higher concentration of ammonia will increase algae growth and eutrophication. Based on its toxicity, ammonia also can interfere with biological processing [18]. The addition of NaCl in the electrochemical process provides chlorine as a mediator in oxidation. The formation of chlorine occurs at anode (equation a) at pH < 3.3, the dominant active chlorine species is Cl_2 and at higher pH forms HClO at pH < 7.5 (equation b) and ClO at pH > 7.5 (equation c).

In principle, the electrochemical process under strong acid conditions is the best choice where chlorine is the strongest oxidizing agent, followed by HClO [22]. However, the system often results in desorption that hinders the function of chlorine as an oxidizing agent. Therefore, a higher pH value could theoretically increase electrochemical oxidation of pollutants in which HClO and ClO are not affected by gas desorption and can function as oxidizing agents [25]. The following reaction for chlorine evolution in the oxidation process:

(a) $Cl \rightarrow \frac{1}{2} Cl_2 + e$

(b) $Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$

(c) $HOCl \rightarrow ClO^- + H^+$

The efficiency of NH_3-N removal will depend on the characteristics of produced water. Increased levels of Cl^- can increase the removal of pollutants. The higher the electrolyte concentration is given, the more effective of conductivity. Thus, electrochemical oxidation will be more economical if treated water has a high salinity [23]. The mechanism of ammonia removal involves a reaction mediated by chlorine and forming nitrogen so total N removal can occur. NH_3-N level in raw produced water is 17.71 mg/L and exceeds standard quality of Wastewater Exploration Oil and Gas Production Activities (onshore) according to Minister Environment Regulation No.19 2010, which is 10 mg/L.

The following reaction of ammonia with hypochlorite and hypochlorous acid formed during the electrochemical process:

$$NH_3^+ + ClO^- \rightarrow NH_2Cl + OH^-$$

$$NH_3^+ + HOCl \rightarrow NH_2Cl + H_2O$$

The main product of ammonium oxidation is nitrogen [24]. Nitrogen remains the dominant production by added NaCl. Based on the results, measurement of pH in produce water until 225 min have ranged from 6.7 - 8.06, which shows that the dominant chlorine compounds are HOCl and ClO^-.

Based on Figure 10, the electrochemical method using Al - Fe electrodes at variation voltage 3, 6, 9, and 12 volts can reduce ammonia levels (NH_3-N). 9 volts with electrolysis time of 225 min was the best decrease from ammonia level of 17.71 mg/L to 1.48 mg/L. The percentage of removal is 91.64%. Figure 9 shows that 12 volts in 225 min of sampling, ammonia level in produced water have increased from 2.72 mg/L to 3.64 mg/L; it can happen because the high voltage applied during the electrochemical process will speed up the process of floc forming that can inhibit NH_3 oxidation process.

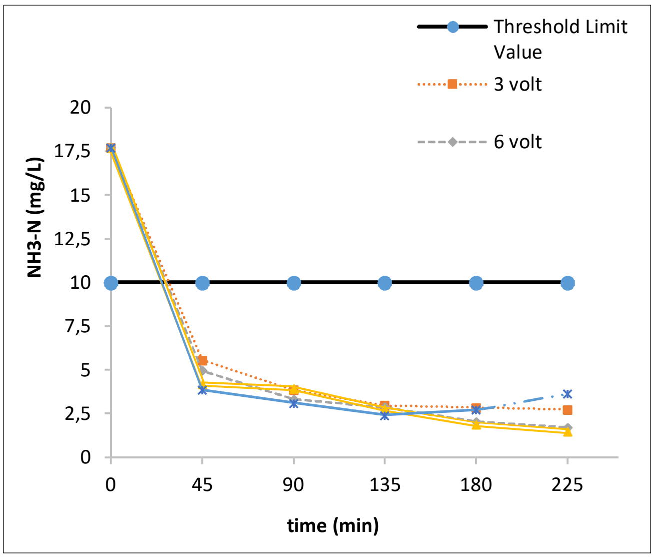

Fig. 10 Impact of Electrochemical Process on NH_3-N reduction

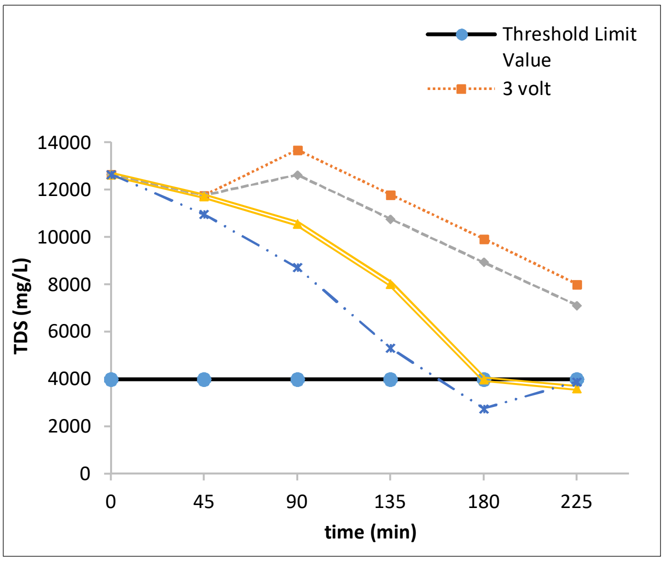

Fig. 11 Impact of Electrochemical Process on TDS reduction

3) Total Dissolved Solid (TDS): TDS (Total Dissolved Solid) measures solutes including organic and inorganic substances in solution. Produced water is one of the waters that have an extremely high TDS content. Initial sample analysis shows that TDS content in produced water to be treated is 12670 mg/L and does not fulfill to standard quality.

Figure 11. shows that produced water treated by electrochemical methods using Al-Fe electrodes can decrease TDS. The sampling results at 12 volts in 180 min showed the best TDS reduction from 12670 mg/L to 2769 mg/L. The percentage of removal is 78.14%. Based on Figure 10. It also can be seen that the length of contact and the higher voltage applied, the more effective to decrease TDS in produced water. It can happen because the particles contained in produced water are negatively charged. The same charge is a repulsive force between particles to be in a stable state.

During the electrochemical process, positive and negative ions produced by electrodes (Al and Fe) will destabilize the particles in water [25]. At anode electrode, it will an oxidation reaction as anions (negative ions) and form Al_3^+ and bind OH^- to form Al $(OH)_3$ while at cathode it will produce hydrogen (H_2), which functions to lift the floc formed to surface. The floc formed over time will increase in size and eventually settle to the bottom of the electrochemical reactor.

The decrease of TDS content is also due to an increasing voltage. The increasing voltage will affect the electrode. The electrode (Al) used will elaborate potential which causes Al to oxidize became Al $(OH)_3$. Significant decrease in TDS content, it turns out from data research results for 12 volts, and sampling in 225 min has increased from 2769 mg/L to 3901 mg/L. This increase can occur because the performance of the electrochemical process has decreased due to too long of contact. Another factor of concern to increase TDS content can occur because the formed floc was carried and read in measurement when sampling.

D. Percentage of COD, TDS and Ammonia (NH3-N) Removal from Previous Research

The allowance for COD, TDS and ammonia (NH3-N) values from previous research are shown in Figure 12. It can be seen that the allowance for NH_3-N, COD, and TDS parameters in order to fulfill the standard quality of Wastewater for Oil and Gas Exploration and Production Activities according to Minister of Environment Regulation No. 19 2010 can be treated using an alternative electrolysis method.

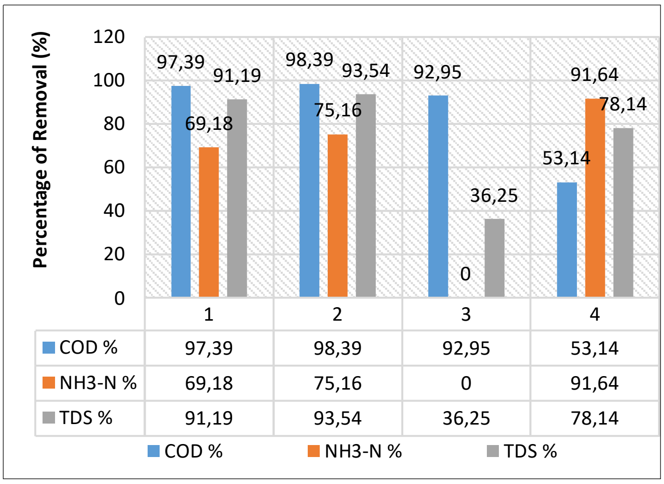

Fig. 12 Percentage of COD, TDS, and Ammonia (NH_3-N) Removal from Previous Research

Note:

1. The combination method of Electrocoagulation (Fe) and Adsorption mixed of silica from bottom ash and activated carbon (coconut shell) [7]
2. The combination method of Electrocoagulation (Al-Fe) and Filtration using activated carbon (coconut shell) [8]
3. Electrocoagulation (Al) [9]
4. Electrochemical (Al-Fe)

Based on Figure 12, the largest percentage of removal COD (98.39%) and TDS (93.54%) in produced water are using the electrocoagulation method (Al-Fe electrode) with a filter that contains activated carbon from coconut shell. Figure 12. also shows the selection of an electrochemical method

(Al-Fe) with simple pre-treatment of filtration and aeration process that can be used as an alternative treatment because it can reduce 91.64% ammonia (NH_3-N) in produced water.

IV. Conclusion

The conclusions of this paper are (1) Variation of time that given during filtration process in produced water treatment has an effect on the percentage of COD reduction up to 10%, NH_3-N up to 11% and TDS up to 13% from raw sample, (2) Variation of time that given during aeration process in produced water treatment affects the percentage of COD reduction up to 16%, NH_3-N up to 7% and TDS up to 13% from the raw sample and (3) The variation of voltage and time that given during the electrochemical process in produced water treatment has an effect on the percentage of COD reduction up to 53.14%, NH_3-N up to 91.64% and TDS up to 78.15%. The result of the optimum condition is shown at 9 volts for 225 min during the electrochemical process. Produced water treatment by three processes, filtration and aeration as pre-treatment. The final process using electrochemical with Al-Fe electrodes can reduce contaminants in produced water according to standard quality stipulated in Minister of Environment Regulation No.19, 2010.

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