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Treatment of Produce Water with a Combination of Electrocoagulation with Iron (Fe) Electrodes and Adsorption Using Silica and Activated Carbon

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Abstract— **Production, the oil and gas industry, has a problem with an enormous volume of liquid waste, and 80% of the liquid waste produced is water, which is called produced water. This water differs from water because it contains dangerous chemicals and other elements in oil and gas. In this study, an adsorption process followed the electrocoagulation process using Iron electrodes with voltage variations of 3, 6, 9, and 12V using silica sand from bottom ash and active carbon from a coconut shell. It proposed the combination of these processes as an alternative method for treating produced water. It carries this combination method out in a continuous reactor series where sampling is done at the 30, 60, 90, 120, and 150 minutes. The results of the study show that the highest decrease in oil and grease (98.14%) from the initial content of 377 Mg/L becomes 7 Mg/L, COD (97.39%) from the initial content of 430.25 Mg/L to 11.24 Mg/L, TDS (91, 19%) from the initial content of 12670 Mg/L to 989 Mg/L, Ammonia (69.18%) from the initial content of 17.71 Mg/L to 5.46 Mg/L, Alkalinity (92.84%) of the initial content 317.86 Mg/L to 7 Mg/L, Total Hardness (93.74%) from the initial content of 201.84 Mg/L to 12.63. The best conditions are to get at 12V voltage for 150 minutes to reduce produced water to meet quality standards based on Minister of Environment Regulation no. 19 of 2010.**

Keywords— **Electrocoagulation; adsorption; produced water.**

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I. INTRODUCTION

Petroleum business activities have an essential role in national economic growth. Petroleum is Indonesia's major export commodity, used as a source of fuel and raw materials for the petrochemical industry. The largest Oil and Gas Industry Field in Indonesia with 201 production wells and 73 injection wells resulting in production from the upstream oil and gas industry in southern Sumatera will affect the overall Oil and Gas Industry production target achievement. Some oil and gas wells in Indonesia are old wells that require more water injection into wells to extract oil. The average water production in each well reaches 80% of total fluid production. After going through the stages of separation of oil and water, the water resulting from the separation, called produced water, is injected back into the well [1]. However, if the well is slipping, then the produced water cannot be injected into the well so it must be discharged into the environment.

Injecting produced water into wells raises several problems such as plugging emergence or scale formation in stubbing and injection well strings. The emergence of deposits in stubbing and injection well strings is caused by high alkalinity and total hardness in produced water. In produced water that causes high alkalinity are carbonate ions (CO_3^{2-}) and bicarbonate ions (HCO^{3-}), and those that cause high Total Hardness are Magnesium (Mg^{2+}) ions and calcium ions (Ca^{2+}) [3].

The produced water treatment system in the upstream oil and gas industry in South Sumatra is not optimal because the produced water is not treated before injecting, but only by treatment by washing the process of the tank to the water tank through the skimmer tank and nutshell filter. In the nutshell filter filtration process only occurs with the help of zeolite as an adsorbent, but because produced water contains high metal ions such as Ca-Hardness content of 80 mg / l, Mg-Hardness 94.58 mg / l, CO_3^{2-} and HCO_3^{2-} 2185.92 mg / l and Silica 20.40 mg / l, causing the nutshell filter to saturate and cause the scale to occur in the injection well piping system circuit [1-2]. From an economic point of view the impact of produced water quality results in very high operating costs and injection wells maintenance costs. Therefore, other treatments are needed before the produced water is flowed to the skimmer and nutshell filter (Upstream oil and gas industry in southern Sumatera).

In a study conducted by Susilowati [4] in the electrocoagulation process using the Fe-Al multi-plate for wastewater treatment from the batik industry, a COD reduction was 68.8%. With this satisfactory result, we can say is that this method has a better effect than the usual coagulation method. Gandhimati [5] conducted a study using three electrodes used, namely Fe, Zn, and Al. Each type of electrode has a different effect. The best results in this study were obtained in Al metals with a decrease in TSS of 95.3%, while for Fe a decrease of 94.39% and Zn of 91.96%. Using this type of electrode is influenced by metal reactivity and coagulant formation to bind existing impurities.

Electrocoagulation is an electrochemical water treatment method wherein the anode occurs the release of active coagulant in metal ions (usually aluminum or iron) into the solution. In contrast, at the cathode, an electrolysis reaction occurs in the release's form of hydrogen gas [6], [7]. Adsorption is a process of absorption by certain solids of certain substances that occur on the surface of solids because of atoms or molecules' attraction without seeping in. Activated carbon is an adsorbent able to absorb heavy metals 3.22 times greater than silica gel and many activated carbons on the market. The price is very affordable, so it is easy to apply [8].

Iron (Fe) was chosen as electrode material in the electrocoagulation process because of its low cost, abundant availability, and high efficiency. In the electrocoagulation process, the anode will dissolve and produce active coagulants (in this case, Iron ions) [9], [27], following reaction equation 1:

Anode (oxidation):

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Cathode (Reduction):

Acid : $2H^+ + 2e^- \longrightarrow 2\,[H] \longrightarrow H_2$

Acid with oxygen: $O_2 + 4H^+ + 4e^- \rightarrow 2O^- + 4\,[H] \rightarrow 2H_2O$

II. Materials and Methods

The tools and materials used in treated water production are electrocoagulation reactors with Fe electrodes, and the voltage source comes from the power supply. In addition, the tools used are adsorption tubes containing silica and activated carbon. The silica used is made from bottom ash, which is neutralized using 1 M HCL and 6 M NaOH, which are then activated using 8 M. HNO 3 activated carbon used the most from coconut shell activated using HCL and KOH. Furthermore, the equipment used is an oven that functions to remove the water content contained in silica and activated carbon besides the furnace needed to function to heat the coconut shell. The treatment process takes two tanks for the initial waste collection and produced water treatment collection. The waste treatment results are taken using a 300 ml plastic bottle and stored in the refrigerator. To calculate time variations, a digital stopwatch is used.

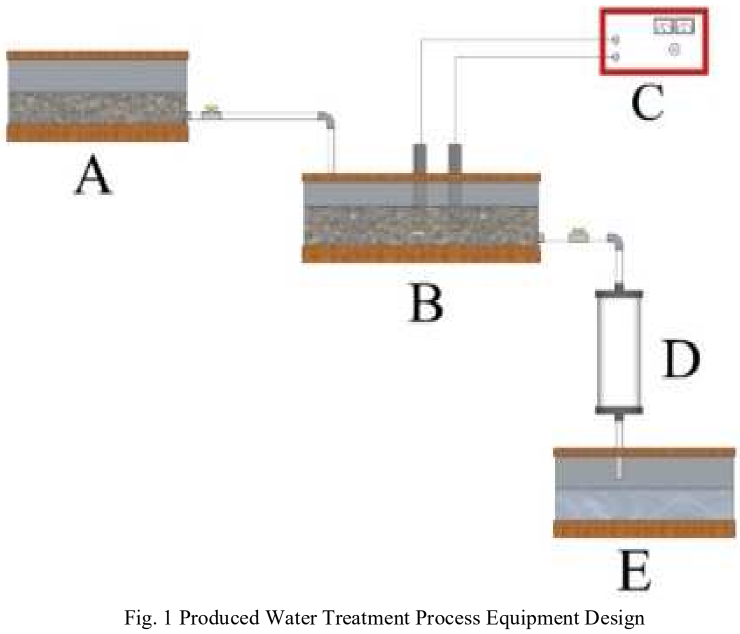

Fig. 1 Produced Water Treatment Process Equipment Design

Note: A. Produced water storage tank; B. Electrocoagulation reactor; C. Power supply; D. Adsorption tube; E. Produced water treatment tank

A. Procedure for Making Silica from Bottom Ash

Bottom ash, which has been available in the oven at 110ºC. Furthermore, bottom ash is mashed using mortal. Then the bottom ash was washed using aquadest 1: 5 for 2 hours at 90ºC. After that drying is done using an oven for 4 hours at a temperature of 110ºC. Then weigh the resulting weight. The next step is the bottom ash immersion using 1 M HCl solution. The metal extraction process is carried out for 2 hours at 90ºC with a constant stirring of 200 rpm. Extracted bottom ash is washed with distilled water to near neutral pH. The bottom ash that has been washed with aquadest is dried in an oven at 110ºC for 4 hours, then weighed the resulting weight. The next stage is extracting silica using a base solution. The base solution used was 6 M NaOH with a bottom ash ratio of 1: 4 NaOH at 60-80ºC with a stirring speed of 500 rpm for 4 hours. The next process is bottom ash filtering using Whatman 41 filter paper to separate the filtrate from the bottom ash residue.

This filtrate will be used for the next process by purifying silica using an acid solution. Bottom ash residue was dried in an oven for 4 hours at a temperature of 110°C and then weighed to see the amount of bottom ash remaining from the extraction process. The next process is silica purification used an acid solution (HNO_3 8 M) carried out for 2 hours at a speed of 400 rpm. The acid solution used is dropped into the glass baker slowly until a white precipitate is formed. Acid testing is done gradually to see the changes that occur in the filtrate used. Silica, which has been formed in the purification process, is deposited for 24 hours, then filtered and washed using aquadest before being oven for 6 hours at 110°C.

B. Procedure for Making Activated Carbon from Coconut Shells

The initial step in the manufacture of activated carbon is the preparation process in which the coconut shell material is dried and reduced in size by about 2-4cm. The prepared material is put into the furnace for 2 hours at a temperature of 600^0C. Charcoal material that is formed is then crushed and filtered to 10 mesh size. The filtered carbon is soaked using a KOH solution with a mass ratio of carbon, and KOH is 3: 1. Soaked carbon is stirred with a stirrer at 100 rpm for one hour at 120^0C. After finishing, the carbon immersion is filtered and dried in the oven for 24 hours. The dried carbon is washed with 5 M HCl and then washed again with hot distilled water until the solution changes to neutral pH. After that, do the drying for 24 hours in the oven. Chemically activated carbon is then reactivated with physics by putting carbon into an activation reactor at 750^0C. After that, the carbon is washed again using distilled water and dried in the oven for 24 hours.

C. Procedures for Producing Manufactured Water

The first step produced by water will have flowed into the electrocoagulation reactor. The output was analyzed every 30 minutes to 150 minutes with the content analyzed in the form of parameters Alkalinity, Ammonia, COD, Oils and Fats, TDS and Total Hardness. Then, flowed to the adsorption reactor, the Silica adsorbed media made from bottom ash and activated carbon made from coconut shells. The output was then analyzed for Alkalinity, Ammonia, COD, Oil and grease, TDS, and Total Hardness. Repeat these steps with the voltage 3V, 6V, 9V and 12V.

III. Result and Discussion

It shows the results of the initial sample analysis on the Produced Water in Table 1. Ammonia NH_3-N, COD, Oil and Grease and Total Dissolved Solid (TDS) have not met the Wastewater Exploration and Oil Production standards from the Land Facilities (Land onshore) which is regulated by Minister of Environment Regulation No. 19 of 2010.

TABLE I
RESULTS OF ANALYSIS OF INITIAL SAMPLES OF PRODUCED WATER

No.	Characteristic	Unit	Test Result	Threshold Limit Value
1.	Ph	-	7,56	6-9
2.	COD	Mg/L	430,25	300
4.	TDS	Mg/L	12670	4000
5.	NH_3-N	Mg/L	17,71	10
6.	Oil and grease	Mg/L	377	25
7.	Alkalinities	Mg/L	317,56	-
8.	Total Hardness	Mg/L	201,84	-

In this research, produced water treatment is carried out with 3 processes, namely Electrocoagulation, Adsorption with Silica media, and activated carbon and Electrocoagulation Combination with adsorption.

TABLE II
RESULTS OF ANALYSIS OF PRODUCED WATER AFTER THE ELECTROCOAGULATION PROCESS WITH FE-FE ELECTRODES

Volt	Time (Min)	Oil & Grease (Mg/L)	Ammonia (Mg/L)	COD (Mg/L)	TDS (Mg/L)	Alkalinities (Mg/l)	Hardness (Mg/l)
3 V	0	377	17.71	430.25	12670	317.56	201.84
	30	345.7	17.12	391.59	12098	275.65	182.73
	60	302.67	16.35	350.09	11475	232.19	162.48
	90	289.3	15.92	299.68	10253	191.09	140.79
	120	235.3	14.88	264.23	9231	146.7	121.68
	150	198.73	14.63	235.87	7234	108.63	103.24
6 V	0	377	17.71	430.25	12670	317.56	201.84
	30	327.69	16.97	383.53	11091	271.55	179.61
	60	273.48	16.05	342.19	9765	227.71	156.49
	90	202.36	15.36	297.56	7938	183.29	135.25
	120	142.78	14.21	252.81	5432	140.82	111.39
	150	93.53	11.76	210.25	4875	92.61	91.6
9 V	0	377	17.71	430.25	12670	317.56	201.84
	30	306.3	16.18	386.78	10693	267.17	176.48
	60	235.6	14.6	240.9	8875	219.83	152.7
	90	164.9	12.85	298.12	6739	171.11	131.19
	120	94.28	11.17	250.5	3485	123.98	106.16
	150	25.07	10.07	209.72	2785	88.48	87.51
12 V	0	377	17.71	430.25	12670	317.56	201.84
	30	305.26	15.23	352.23	10511	266.71	174.54
	60	231.68	13.74	271.91	8535	212.85	147.8
	90	161.17	11.06	208.12	6052	167.29	121.61
	120	88.67	12.84	231.7	7834	112.8	92.04
	150	20.31	15.82	257.04	9875	68.72	70.97

TABLE III

RESULTS OF ANALYSIS OF PRODUCED WATER AFTER AN ADSORPTION PROCESS WITH SILICA AND CARBON MEDIA

Time Min)	Unit					
	Oil & Grease (Mg/L)	Ammonia (Mg/L)	COD (Mg/L)	TDS (Mg/L)	Alkalinities (Mg/l)	Total Hardness (Mg/l)
0	377	17.71	430.25	12670	317.56	201.84
30	301.7	16.15	420.67	11477	279.63	184.61
60	237.1	14.01	408.32	10175	242.34	159.97
90	165.9	12.99	397.35	9091	199.67	138.23
120	97	11.47	391.02	7684	164.25	115.17
150	26.9	9.89	383.65	6704	128.9	98.72

TABLE IV

RESULTS OF ANALYSIS OF PRODUCED WATER AFTER THE PROCESS OF COMBINATION OF ELECTROCOAGULATION AND ADSORPTION WITH SILICA AND ACTIVATED CARBON MEDIA

Volt	Time (Min)	Oil & Grease (Mg/L)	Ammonia (Mg/L)	COD (Mg/L)	TDS (Mg/L)	Alkalinity (Mg/L)	Hardness (Mg/L)
3 V	0	377	17.71	430.25	12670	317.56	201.84
	30	316	16.92	367.38	11311	283.4	189.76
	60	251	16.12	304.5	9950	210.37	154.77
	90	153.3	15.32	241.62	8601	192.63	137.8
	120	92.1	14.51	178.76	7244	111.24	123.6
	150	72.8	13.72	115.87	5874	98.73	101.62
6 V	0	377	17.71	430.25	12670	317.56	201.84
	30	299.7	16.38	349.56	10597	272.63	172.33
	60	227	15.05	258.82	8516	209.84	151.8
	90	127.8	13.49	188.23	6447	175.8	128.6
	120	77.5	11.92	107.5	4378	104.65	112.46
	150	24.6	10.08	26.82	2670	82.64	78.98
9 V	0	377	17.71	430.25	12670	317.56	201.84
	30	285	15.6	347.76	10249	256.8	170.89
	60	215.3	14.57	266.29	7831	201.77	143.5
	90	104.9	13.06	181.48	5431	150.45	118.68
	120	21.8	9.81	100.33	2984	84.3	74.74
	150	11.3	6.73	17.84	1182	43.72	44.96
12 V	0	377	17.71	430.25	12670	317.56	201.84
	30	256	14.8	346.46	9851	225.65	155.83
	60	178.7	12.3	260.7	6535	190.86	108.76
	90	67.5	9.89	178.85	3923	101.81	97.5
	120	11.8	8.13	65.86	2034	75.63	68.42
	150	7	5.46	11.24	989	22.75	12.63

A. The Effect of Electrocoagulation Process, Adsorption and Combination of Electrocoagulation with Adsorption on Chemical Oxygen Demand (COD)

One important parameter in produced water must be considered COD (Chemical Oxygen Demand) contained in the produced water with a large enough value. COD is the amount of oxygen needed to break down all organic matter contained in water [3]. High COD content will cause odor because the content of organic substances in it causes oxygen to unable break it down. The amount of COD contained in produced water before processing is 450.25 Mg/L. Figure 2 shows the electrocoagulation process at a voltage of 12 V and 120 to 150 minutes, an increase in COD value from 231.7 mg / l to 257.04 mg / l. This is due to the presence of COD, which is soluble in waste. It is also caused by using voltage that is too high and too long to cause the electrodes to break down into produced water because the content of organic substances causes oxygen to not break it down, so the COD value goes up. While a significant decrease in COD value occurs in fig. 4, the process of a combination of electrocoagulation and adsorption at sampling times of 0 to 90 minutes. At 3 V voltage and 90 minutes' time it has been able to reduce the COD value to meet the produced water quality standards. The decrease in COD concentration shows the reduction of organic compounds in liquid waste, because basically COD measurement aims to see the amount of oxygen needed to oxidize organic compounds in water [10], [11].

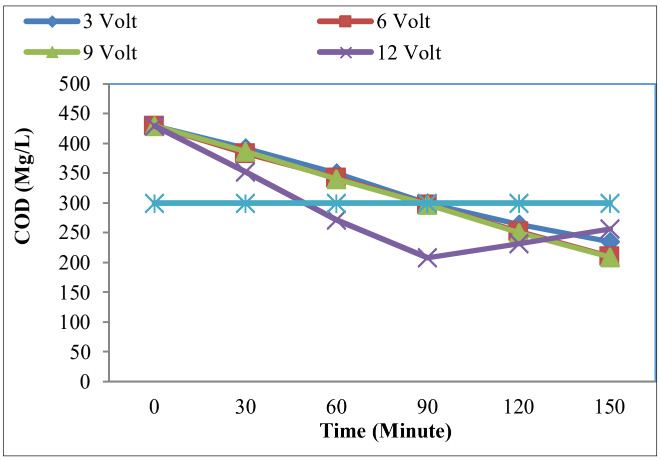

Fig. 2 The Effect of Electrocoagulation Process on COD reduction

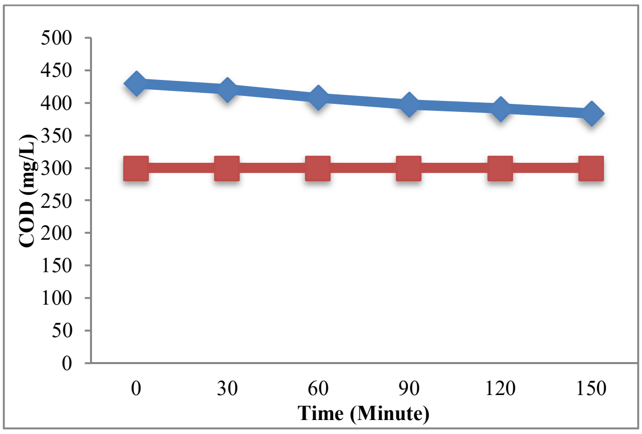

Fig. 3 Effect of the adsorption process on COD reduction

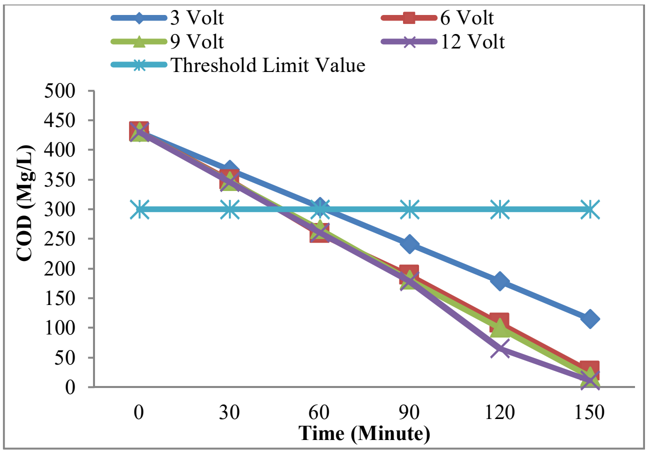

Fig. 4 Effect of Combination Process between Electrocoagulation and Adsorption on COD reduction

The decrease in COD concentration in electrocoagulation is because of the oxidation and reduction processes in the electrocoagulation reactor. Following are the reactions that occur in the electrocoagulation process [12]:

- On the surface of the positive electrode (anode):
  $Fe \rightarrow Fe^{2+} + 2e^{-}$
- About electrodes :
  $Fe(OH)^{2+} + H_2O \rightarrow Fe(OH)_3 + H^{+}$
- On the surface of the negative electrode (cathode):
  $Fe^{2+} + 2e^{-} \rightarrow Fe$
  $2H_2O + 2e^{-} \rightarrow H^{2+} + 2OH$

On the surface of the positive electrode, Fe releases its electrons into Fe^{2+} which bind OH to form Fe $(OH)_2$ into coagulant. From the chemical equation above, the formation of oxygen and hydrogen gas affects the reduction of COD. Hydrogen gas helps contaminants float or lift. This reduces dissolved organic or dissolved material, including flock Fe $(OH)_2$, which binds organic waste and captures some organic waste that is not collected on the cathode plate. H_2 production resulting from redox reactions causes organic material to be reduced. Some molecules contained in waste are captured by Fe $(OH)_2$ ions then removal by H_2 as organic compounds to form bubbles that can reduce COD [13], [14]. Organic compounds in liquid waste are reduced, so the need for oxygen to oxidize also becomes reduced. In addition, by combining electrocoagulation with filtration, the decrease in COD value is higher because the filtration with silica media and activated carbon can adsorb organic content in produced water.

B. Effect of Electrocoagulation, Adsorption and Combination of Electrocoagulation with Filtration Against Total Dissolved Solid (TDS)

One parameter utilized for measuring water quality is Total Dissolved Solid (TDS). Produced water is one of the waters that has a very high Total Dissolved Solid (TDS). The results of the initial analysis of produced water showed a TDS content of 12670 mg / L, to meet quality standards Waste water Exploration and Oil and Gas Production Activities from the old onshore facilities.

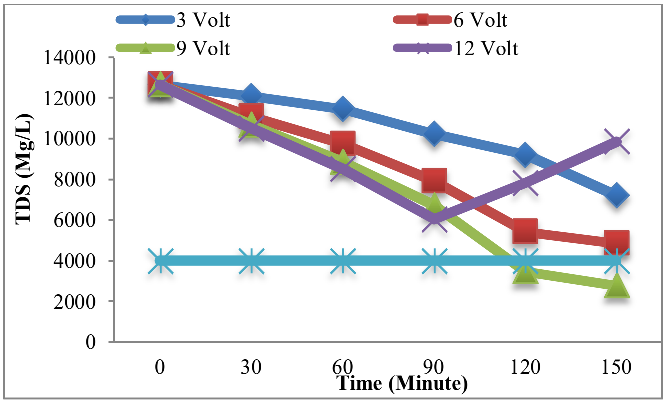

Fig. 5 The Effect of Electrocoagulation Process on TDS reduction

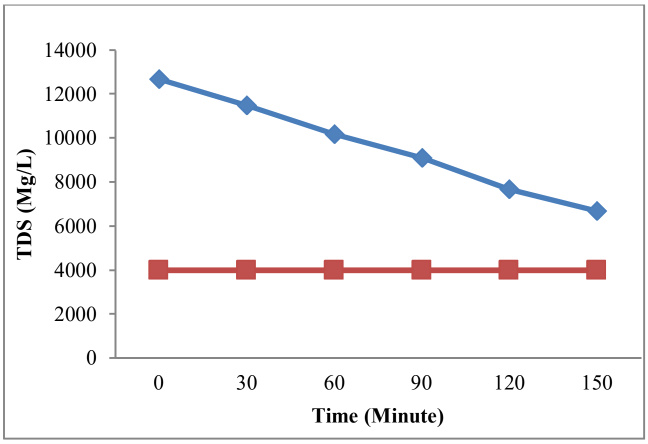

Fig. 6 Effect of the adsorption process on TDS reduction

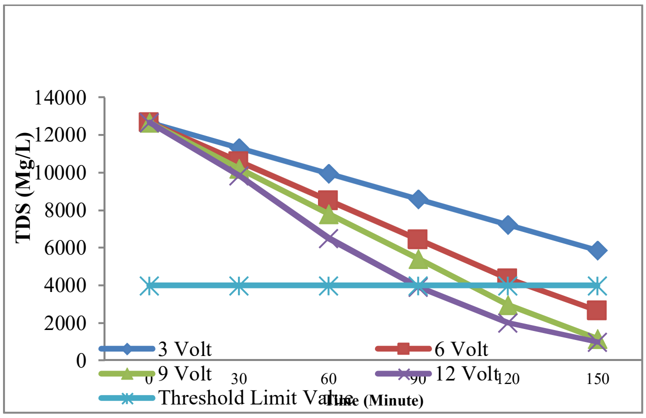

Fig. 7 Effect of Combination Process between Electrocoagulation and Adsorption on TDS reduction

In fig. 5, the electrocoagulation process at a voltage of 12 V at 90 minutes to 150 minutes an increase in the TDS value from 6052 mg / l to 9875 mg / l is because of decreased electrolysis performance because with a long time the electrodes dissolve in the water produced, causing an increase in TDS, other than that. This is related to the length of time of electrocoagulation and the voltage given during the electrocoagulation process. The longer the electrocoagulation time and the greater the applied voltage, the more flocks can be produced which can bind the contaminants to the waste. The resulting flocks can partially settle and some are flattened onto the surface. We assume it that the amount of TDS value is because when sampling flock that has formed has been taken along at the time of measurement. While a significant decrease in TDS levels occurs in fig. 7, the combination process of Electrocoagulation and Adsorption caused by clumping of particles carried out by the coagulation process with electrodes as a coagulant forming unwanted flocks by perfecting the process of adsorption of pores on activated carbon smaller than water particulates produced, so it can separate the dissolved solid contained in the produced water in the oil and gas industry. The influence of the time and the addition of a high voltage or voltage successfully reduces the TDS content, which is very significant.

C. The Effect of Electrocoagulation Process, Absorbs and Combination of Electrocoagulation and Absorption on Total Ammonia (NH_3-N)

Ammonia is one of the water pollutants and toxic substances and harmful organic matter. The higher the total ammonia content (NH_3-N) in water, it will cause poisoning in the biota. Therefore, this parameter is listed in the liquid waste quality standard, specifically in Wastewater Exploration and Oil and Gas Production Activities from the old onshore facilities. The NH_3-N content in the produced water before processing is 17.71 mg / L, which shows that the NH_3-N content does not meet the quality standard Wastewater Exploration and Oil and Gas Production Activities from the old onshore facilities based on the Minister of Environment Regulation no.19 of 2010.

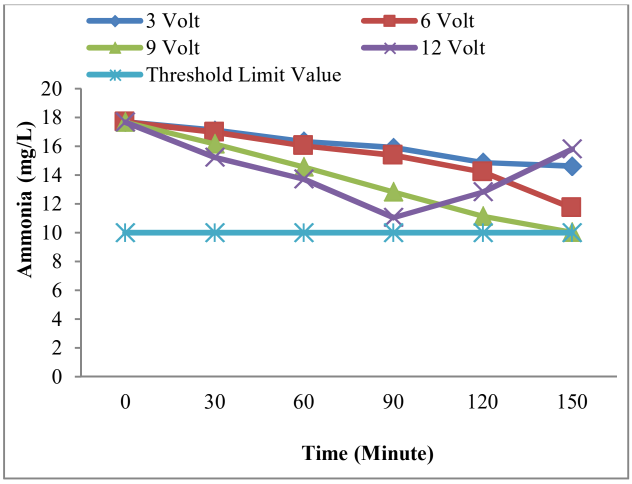

Fig. 8 The Effect of Electrocoagulation Process on Ammonia reduction

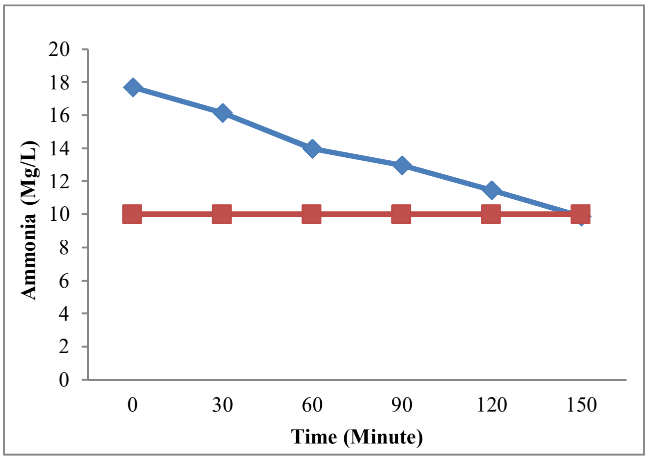

Fig. 9 Effect of the adsorption process on Ammonia reduction

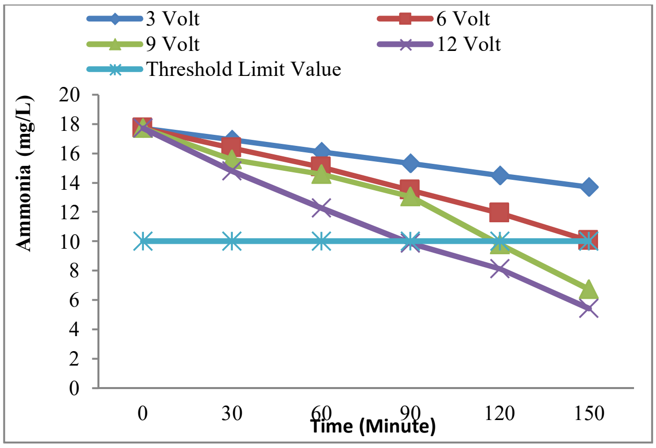

Fig. 10 Effect of Combination Process between Electrocoagulation and Adsorption on Ammonia reduction

In fig. 8, the electrocoagulation process with a voltage of 3, 6 and 9 Volta stable decline is the best results with a decrease in ammonia levels up to 10.07 mg / L. This decrease occurs because each time more and more NH_3 is oxidized to N_2 so that the remaining NH_3 concentration in produced water will be less. The following is decomposition reaction of ammonia in the electrocoagulation process [15]:

Anode :

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

Cathode :

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

$$2NH_{3(l)} \longrightarrow N_{2(g)} + 3H_{2(g)}$$

At the anode the ammonia oxidation reaction occurs, whereas at the cathode the water reduction reaction forms hydrogen to form hydrogen gas helps the contaminants float or lift, this reduces organic material in the produced water.

But at a voltage of 12 Volt Ammonia levels increased at 90 minutes to 150 minutes, ammonia levels increased from 11.06 mg / L to 15.82 mg / L, this is due to the higher voltage electrodes which decompose into water to form flocks to be inhibits the NH_3 oxidation process. In Figure 10, produced water treatment using electrocoagulation combination and adsorption methods can reduce ammonia levels with a very significant decrease. This shows that the remaining ammonia concentration will decrease with increasing time. The longer the sampling time, the more NH_3 is oxidized to N_2 so that the remaining concentration of NH_3 in the produced water will be less. In addition, the NH_3-N content produced meets the quality standards for Wastewater Exploration and Oil and Gas Production Activities from the old onshore facility.

D. The Effect of Electrocoagulation Process, Adsorption and Combination between Electrocoagulation and Adsorption on Oil & Grease

One pollutant that affects water quality is Oil & Grease content. Oil & Grease is of compounds collection that covers material that is dissolved in water, producing water. This parameter is included in the standard parameters for waste water quality because oil and fat in water are considered dangerous for aquatic and human life. The oil and fat content comprises lipid compounds, ester compounds, alcohols, and other volatile compounds. These compounds are compounds that are not soluble in water and have a lighter density than water so that these compounds float above the water surface. Although oil and water cannot theoretically be fused because of their different polarity properties, but both can form an emulsion that can block the entry of sunlight into the water and prevent the dissolution of oxygen in the water. The produced water shows an Oil & Grease content of 377 mg / L and does not meet the Wastewater Exploration and Production Standards for Oil and Gas quality from the old onshore facility based on the Minister of Environment Regulation No. 19 of 2010 with a maximum level of 25 mg / L.

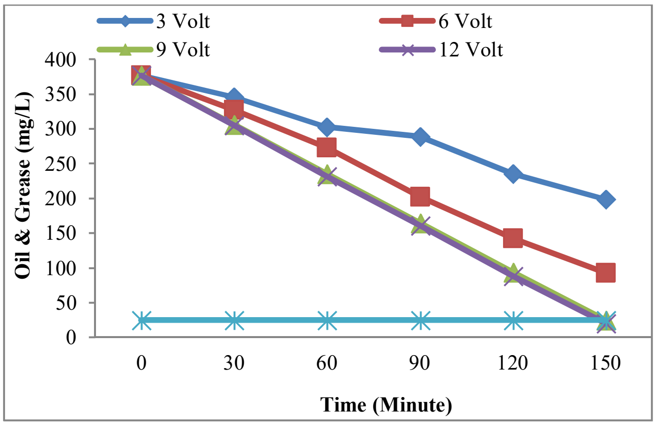

Fig. 11 The Effect of Electrocoagulation Process on oil & grease reduction

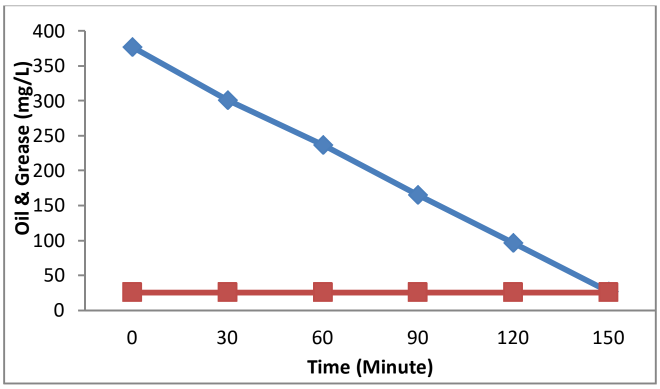

Fig. 12 Effect of the adsorption process on oil & grease reduction

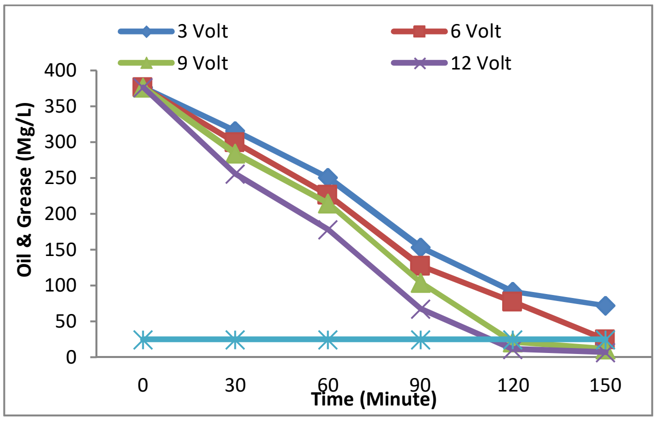

Fig. 13 Effect of Combination Process between Electrocoagulation and Adsorption on oil & grease reduction

In the fig. 13, Produced water treatment by electrocoagulation and methods Adsorption combinations can reduce oil and fat content stably over time. This is due to the two electrocoagulation processes that are combined with Adsorption able to work optimally. Overall, with this combination method can reduce oil and fat content according to quality standards Waste water Exploration and Oil and Gas Production Activities from the old onshore facilities, namely the voltage parameters 6 V, 9 V and 12 V.

E. The Effect of Electrocoagulation Process, Adsorption and Electrocoagulation Combination with Adsorption on Alkalinity

One content that has an impact on water pollution is the alkalinity content. Alkalinity is a measurement of water's capacity to neutralize weak acids, although weak acids or weak bases can also be the cause. The constituents of aquatic alkalinity are bicarbonate (HCO^{3-}), carbonate (CO^{3-}) and hydroxide (OH^-) anions. Salts from other weak acids such as Borate (H_2BO^{3-}), Silicate ($HSiO_3^-$), phosphate (HPO_4^{2-} and $H_2PO_4^-$), sulfide (HS^-), and ammonia (NH_3) also contribute to the alkalinity in slight amounts.

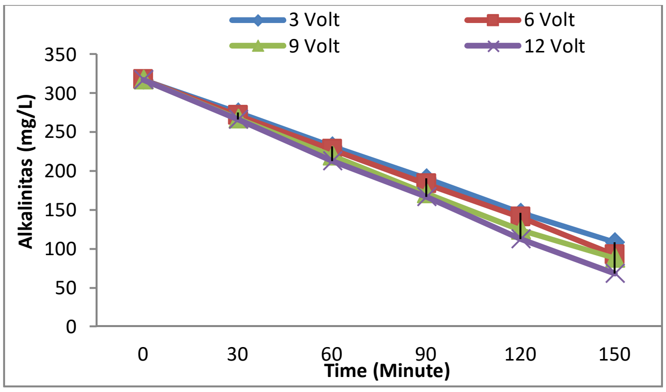

Fig. 14 The Effect of Electrocoagulation Process on Alkalinity reduction

Produced water requires these alkalinity ions in certain concentrations, if the alkalinity level is high (compared to Ca^{2+} and Mg^{2+} levels, i.e. low hardness levels) the water becomes aggressive and causes crust in the injection well piping system, conversely low alkalinity and unbalance with high hardness can cause $CaCO_3$ scale on the pipe wall of the installation which can reduce the cross section of the wet pipe. In the water produced, the initial alkalinity was 317.56 mg /L.

Although in quality standards Waste water Exploration and Oil and Gas Production Activities from the onshore facilities have not been determined for alkalinity but in produced water it is important to note the alkalinity because it can cause damage to the injection well piping system which can cause high maintenance costs.

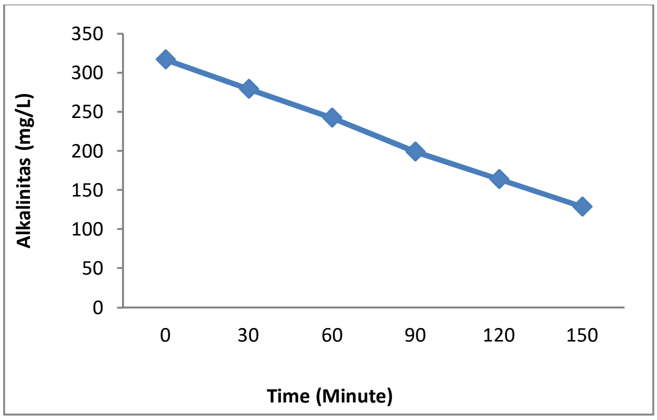

Fig. 15 Effect of the adsorption process on Alkalinity reduction

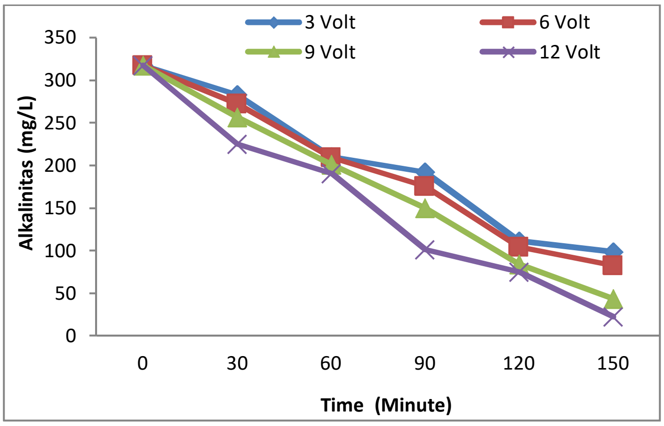

Fig. 16 Effect of Combination Process between Electrocoagulation and Adsorption on Alkalinity reduction

In the fig. 16, Produced water treatment using electrocoagulation methods combination Adsorption able to reduce the content of alkalinity, which is very significant. Alkalinity content also affects hardness content / hardness in produced water, this is due to the following reactions [13], [27]:

Reaction at anode:

$$H_2O_{(l)} \longrightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^-$$

Cathode reaction:

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

$$HCO_3^-{}_{(aq)} + OH^- \longrightarrow CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

$$CO_3^{2-}{}_{(aq)} + Ca^{2+}{}_{(aq)} \longrightarrow CaCO_{3(s)}$$

F. The Effect of Electrocoagulation Process, Adsorption, and Combination of Electrocoagulation with Adsorption on Total Hardness

Total hardness is a dangerous content in wastewater. The presence of calcium (Ca) and magnesium (Mg) ions in the water will cause hardness to the water. Water will have a level of hardness that is too high is very detrimental because several things, including can cause rust/corrosion on tools made of iron and can cause sediment or crust in processing containers [16]. Therefore, the content hardness is very dangerous in the produced water because it can form deposits and crust, which can damage the injection wells' system and cause expensive maintenance costs.

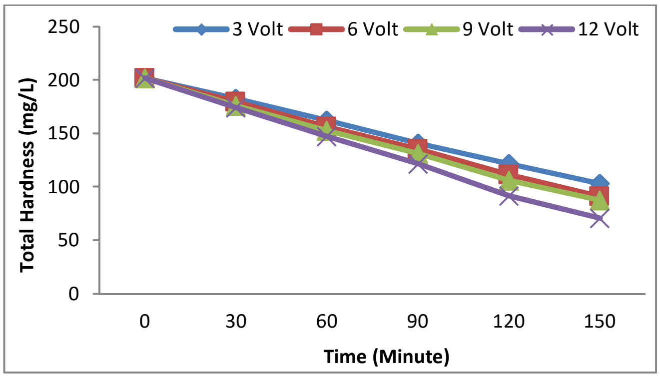

Fig. 17 The Effect of Electrocoagulation Process on Total hardness reduction

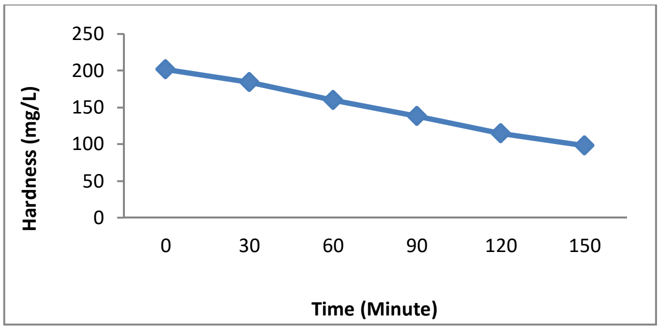

Fig. 18 Effect of the adsorption process on Total hardness reduction

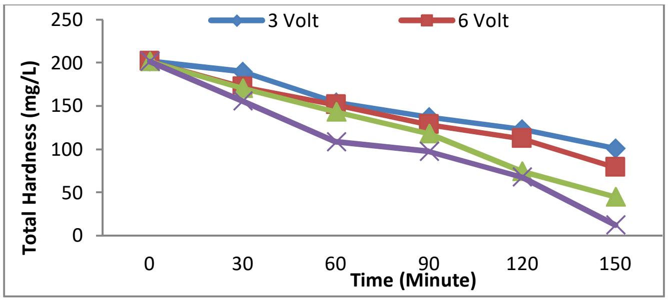

Fig. 19 Effect of Combination Process between Electrocoagulation and Adsorption on Total hardness reduction

Judging from the results of the three methods carried out it can be seen from fig.19, Produced water treatment using electrocoagulation methods combination Adsorption can provide a very high decrease in hardness compared to those using only the electrocoagulation method or the filtration method alone. The decrease in hardens value also influences the decrease in alkalinity, this is caused by the following reaction in electrocoagulation [13], [27]:

Reaction at anode:

$H_2O_{(l)} \longrightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^-$

Cathode reaction:

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

$HCO_3^-{}_{(aq)} + OH^- \longrightarrow CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$

$CO_3^{2-}{}_{(aq)} + Ca^{2+}{}_{(aq)} \longrightarrow CaCO_{3(s)}$

IV. CONCLUSIONS

Produced water treatment processes using a combination of electrocoagulation and adsorption methods can reduce the content COD, TDS, Ammonia (NH_3-N), Oil and Grease, Alkalinity and Total Hardness in produced water. Voltage and time variations in the electrocoagulation method have an influence on the reduction of contaminants in produced water, with a reduction percentage of COD 51.63%, TDS 78.02%, Ammonia 43.12%, Oil and Grease 94.61%, Alkalinity 78.36%, and Total Hardness of 64.84% of the initial waste. The time variation in the adsorption process has an influence on the reduction of contaminants in produced water, with a reduction percentage of COD 10.83%, TDS 47.09%, Ammonia 44.16%, Oil and Grease 92.86%, Alkalinity 59.41%, and Total Hardness 51.09% of initial waste. Stress and time variation in the process of combination between electrocoagulation and adsorption has an influence on the decrease in the content COD, TDS, Ammonia (NH_3-N), Oil and Grease, Alkalinity and Total Hardness on produced water with the percentage of optimum decrease in COD 97.39%, TDS 91.19%, Ammonia 69.18%, Oil and Grease 98.14%, Alkalinity 92.84% and total hardness of 93.74% of the initial waste with parameters optimum voltage at 12 V and a time of 150 minutes. Overall produced water treatment by comparing Electrocoagulation, adsorption and Combination Electrocoagulation-adsorption methods have been able to reduce contaminants contained in produced water but which meet quality standards Wastewater Exploration and Oil and Gas Production Activities from the old onshore facilities based on environment minister regulation no. 19 of 2010 using only a combination of electrocoagulation and adsorption methods.

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