Treatment of Oily Wastewaters from Tanjung Perak Port by Electrocoagulation Using Aluminum Electrodes

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Abstract. Electrocoagulation is electrochemical water and wastewater treatment technology that is the easiest technology using an electrochemical cell supplied by DC power to the electrodes. The application of the electrocoagulation process was purposed to treat oily bilge water. The results indicated that the oil removal efficiency was achieved approximately 99.62% at an initial oil concentration of 60 g/l in batch processes. The current density of 62.5 mA/cm² applied the process produced oil removal efficiency of 99.95%. In a continuous mode with the initial water only present in the reactor, the oil removal efficiency was achieved approximately 100% with a hydraulic residence time (HRT-1) of 6 h for 60 min of operations. However, the initial oil/water emulsion at a concentration of 63.89 g/l present in the reactor, the oil removal efficiency was approximately 73.33% with HRT-1 of 6 h for 90 h of operations.

1. Introduction

Oily wastewaters are mostly disposed of by many sources, such as cooking oil industries, petroleum refineries, petrochemical, food, bilge water, and other general industrial sources. The wastewaters in the form of bilge water are generated by Ships and commercial vessels. Oil containing bilge water is derived from oily fluids, lubricants, cleaning fluids that accumulate in the lowest part of a vessel. The content of metals in bilge and ballast water is not able to be removed through treatment. These metals are able to cause human health problems for example lead poisoning when they are ingested. This oily wastewater generation is one of the problems when disposed of to the environment. Some attempts have been made to develop an improve oily wastewater treatment processes. This development of the treatments includes coagulation [1], adsorption [2], biological processes [3,4], coupling coagulation-flocculation [5], photocatalytic [6], microwave-assisted catalytic wet air oxidation [7], and electrochemical technology [8-13]. Recently, treatment of wastewater in the oil industry is mostly conducted by several methods for example electrocoagulation, ozonization, Fenton oxidation and UV working effectively. All of the methods, electrocoagulation, and electrooxidation work more effectively [14, 15]. Soeprijanto et al. [15] studied on the treatment of oily wastewater emulsion with aluminum electrodes in a batch mode. Most of the electrocoagulation were also applied to the treatment of synthesis of oil/water emulsion [5, 6,16], petroleum refinery wastewaters and strain Industry oily Wastewater [9, 19, 20], biodiesel wastewater production [21], palm oil mill effluent [22,23], pollutant from restaurant wastewaters [24,25], and pollutant from agro-industry wastewaters [26]. Also, the Electrocoagulation technologies have been widely used for the treatment of urban wastewaters [9] and the removal efficiency of heavy metal from metal plating wastewaters [28]. Electrocoagulation is a process involving chemistry and physics process using sacrificial electrodes for the generation of coagulants. The most commonly materials used as anode electrocoagulation are aluminum and iron. An electrical current was supplied between the electrodes anode-cathode with the generation of hydroxyl ions and hydrogen gas simultaneously happening at the cathode. The hydrogen production will also help the float flocculation of particles separate them from...
the water. Electrochemical reaction of the aluminum or iron metals as the anode materials can be seen as follows [29]:

For the aluminum anode:

\[
\text{Al}(s) \rightarrow \text{Al}^{3+}(\text{aq}) + 3e
\]  

(1)

With the iron electrodes:

\[
\text{Fe}(s) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2e
\]  

(2)

Oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) by anodic oxidation can be considered as follows:

\[
\text{Fe}^{2+}(\text{aq}) = \text{Fe}^{3+}(\text{aq}) + e \\
2 \text{Fe}^{2+}(\text{aq}) + 5 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow 2 \text{Fe(OH)}_3(s) + 4 \text{H}^+ 
\]  

(3)

(4)

And reaction occurring at the cathode can be represented by:

\[
2 \text{H}_2\text{O} + 2e \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-
\]  

(5)

The purpose of the study was to apply electrocoagulation process using aluminum electrodes for the treatment of oily bilge water from a Port PT. Pelindo Marine Service Tanjung Perak, Surabaya, Indonesia.

2. Materials and Experimental Set-up

2.1. Materials

Bilgewater was collected from a Tanjung Perak Port in Surabaya, Indonesia. Sodium hydroxide and Hydrochloric acid were used to adjust the pH. Salts were used for the electrolyte. All of the chemicals were purchased at shops Chemistry in Surabaya, Indonesia. Aluminum plates were purchased at a flea market in Surabaya, Indonesia.

2.2 Experimental Set-up

The batch and continuous electrochemical reactor were constructed in a Laboratory scale (Figure 1).

Figure 1. Apparatus of electrocoagulation process:(1) Bilge water tank storage; (2) Peristaltic pump; (3) Electrocoagulation reactor; (4) Aluminum Electrodes; (5) Voltmeter and power DC; (6) Ampere meter; (7) Influent of fluid; (8) effluent of fluid.

A volume of the glass reactor was 15 l, and the effective volume was 10 l. Aluminum electrodes with dimensions of 20 cm × 8 cm × 0.2 cm were used and vertically mounted with a distance of 4 cm and immersed at a depth of 8 cm to the solutions. The electrodes were then connected to DC power supply with an electric current approximately 10 A used as a source of direct current. The total area of effective work electrodes was 160 cm\(^2\). The process was kept constant at around 15-90 min. Sampling was
conducted for analyzing oil content every 15 min. The oil concentration was measured gravimetrically. The efficiency of oil removal during the process was measured using Equation (6) [30,31]:

$$\text{Eff} = \frac{C_0 - C}{C_0} \times 100\%$$  \hspace{1cm} (6)

Where $C_0$ and $C$ is the concentration of oily wastewater before and after electrocoagulation process in mg/l, respectively.

3. Results and Discussions

3.1 Batch Process

3.1.1 The Effect of pH on Electrocoagulation Process

In a batch process of electrocoagulation was carried out using Aluminum electrodes for 60 min. Table 1 shows the correlation between pH and time. The results indicated that the pH changed during the process. The pH increased from 6.41 to 7.43 with a time of 15 to 30 min. However, after 30 min the pH decreased slowly up to 60 min and achieved 7.08. It indicated that during the process $\text{Al}^{3+}$ ions were released in solutions came from a sacrificial anode and water electrolysis process that generated gas and hydroxide ions as well as the release of electrons with time according to ionic reactions. The increase in hydroxide ions in a solution might cause an increase in the pH that caused alkaline conditions. The decreasing in pH after 30 min was because of the reaction between hydroxide and $\text{Al}^{3+}$ ions that were released from the anodes which generated precipitation of $\text{Al(OH)}_3$.

| Time (min) | pH  |
|-----------|-----|
| 15        | 6.43|
| 30        | 7.43|
| 45        | 7.31|
| 60        | 7.08|

3.1.2 Effect of Initial Concentration

A variety of initial concentration of oily wastewater from 60-145 g/l was conducted in a batch process. Figure (2) shows the correlation between the efficiency of oil removal and time at different oil content. The results show that the initial oil removal was rapid approximately for 15 min, then afterward, the removal was relatively constant. It was obtained that the removal was achieved by 99.62%, 99.50%, 98.12% and 96.25% for 15-60 min, respectively, at the initial concentration of 60 g/l, 75 g/l, 90 g/l, and 145 g/l, respectively. However, these results contradict the results of some authors. Sekman et al. [32] showed the electrocoagulation time for removal of these pollutant determined for 20 min, the removal efficiency of 81% at the initial oil & grease concentration of 600 mg/l. Ulucan et al. [33] studied that oil & grease removal obtained was 81.7% in approximately 13 min at the initial oil & grease content of 338 mg/l. Also, Chavalparit and Ongwandee [21] studied that removal of oil & grease was 98.42% for 25 min operation at an initial concentration of 6,020 mg/l.
Figure 2. The influence of the initial oil concentrations on removal efficiency in a batch mode.

3.1.3. Effect of Current Density

Figure (3) shows the correlation between oil removal efficiency and current density. The removal of oil was affected by the current density. The results showed that an increase in current density might cause an increase in oil removal. The applied current density of 62.5 mA/cm$^2$ in the process achieved a maximum oil removal efficiency 99.95% and the use of a current density of 36.39 mA/cm$^2$ minimum removal was found to be 68.33%. This was due to the fact that an increase in current densities would cause an increase in the amount of the Aluminum anodes dissolved in the solutions, therefore an increase in the formation of metal hydroxide flocs. Thus, the formation of complexed aluminum hydroxide could lead oil removal. Therefore, the efficiency of oil removal increased with increasing current density. However, this result contradicts the results of some authors. Ulucan et al. [34] found to be oil & grease removal efficiency of 81.7% under a current density of 9.87 mA/cm$^2$. Chavalparit and Ongwandee [21] found that oil & grease removal efficiency was approximately 98.42% at a current density of 20.8 mA/cm$^2$.

Figure 3: Effect of current density on oil removal.
3.2 Continuous Mode

3.2.1. Effect of Oil Removal on the water present in a Basin

These experiments were conducted in order to obtain time steady state of oil removal in a continuous mode. At starting-up of the experiment, an electrocoagulation reactor was filled with only water, then oily bilge water was introduced continuously at oil concentration of 63.89 g/l with a variety of hydraulic residence time (HRT-1 = 6 h; HRT-2 = 5 h; HRT-3 = 4.5 h; HRT-4 = 4 h), respectively. The HRT might cause the effect of oil removal during the process. The results of the experiments are shown in Figure (4) indicating that the oil removal was obtained 100% with HRT-1 at steady state conditions of approximately 5 min and followed by 94%, 93.33%, and 87.5%, respectively, with the HRT-2, HRT-3, HRT-4 and time of approximately 60 min, respectively.

![Figure 4](image)

Figure 4. The influence of HRT on oil removal efficiency at the initial water present in a basin.

3.2.2. Effect of Oil Removal on the Oil Present in a Basin

The effect of oil removal efficiency is shown in Figure (5). At Starting-up of the experiments, oil/water emulsion synthetic was filled in the reactor at a concentration of approximately 63.89 g/l. A variety of HRT was introduced to the reactor, and they showed influences on oil removal. The results indicated that an increase in the HRT might cause a decrease in oil removal. At steady state, all of the experiments was achieved for 90 min. The maximum efficiency of oil removal was obtained by 73.33% with HRT-1 and followed by the efficiency of oil removal of 60%, 50% and 48% with HRT of HRT-2, HRT-3, and HRT-4, respectively.

![Figure 5](image)

Figure 5. The influence of HRT on oil removal efficiency at the initial oil present in a basin.
Conclusions
The experiments could be concluded that electrocoagulation process had a potential for the treatment of oily bilge water. The treatment of oily wastewater using electrocoagulation process achieved a high removal efficiency in a short time. The maximum efficiency of oil removal was around 99.62% and the minimum was 96.25% at an initial oil concentration of 60 g/l and 145 g/l in batch processes, respectively. The maximum oil removal of 99.95% and a minimum of 68.33% with the current density of 62.5 and 36.39 mA/cm², respectively. In a continuous process with the initial water only present in the basin, the maximum oil removal efficiency was achieved approximately 100% with a hydraulic residence time (HRT-1) of 6 h for 60 min of operations. In a continuous process with the initial oil/water emulsion at a concentration of 63.89 g/l present in the basin, the maximum oil removal was achieved approximately 73.33% with HRT-1 of 6 h for 90 h of operations.

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References
[1] Bensadok K, Benammar S, Lapicque F and Nezzal G 2008 J. Hazard. Mat. 152 423–30.
[2] El-Naas M H, Al-Zuhair S and Alhaija M A 2010 Chem. Eng. J. 162 997–05.
[3] Kuyukina M S, Ishina I R, Serebrennikova M K, Krivorutchko A B, Podorozhko E A, Ivanov R V and Lozinsky V I 2009 Int. Biodeterior. Biodegrad. 63 427–32.
[4] Lu W, Qu L, Henry K and Dai L 2009 J. Power Sources 189 1270-1277.
[5] Santo C E, Vilar V J P, Botelho C MS, Bhatnagar A, Kumar E and Boaventura R A R, 2012 Chem. Eng. J. 183 117–23.
[6] Shahrezaei F, Mansouri Y, Zinatizadeh A A L and Akhbari A 2012 Powder Technol. 221 203–12.
[7] Sun Y, Zhang Y and Quan X 2008 Sep. Purif. Technol. 62 565-70.
[8] Abdelwahab O, Amin N K and El-Ashtoukhy E S Z 2009 J. Hazard. Mat. 163 11–16.
[9] El-Naas M H, Al-Zuhair S, Al-Lobaney A and Makhlfou S 2009 J. Environ. Manag. 91 180–85.
[10] Yang C L 2007 Sep. Purif. Technol. 54 388–95.
[11] Yavuz Y, Koparal A S, Öğütveren Ü B 2010 Desalination 258 201–205.
[12] Wei L, Guo S, Yan G, Chen C, and Jiang X 2010 Electrochim. Acta 55 8615-20.
[13] Yan L, Ma H Z, Wang B, Wang Y F and Chen Y S 2011 Desalination 276 397–02.
[14] Asselin M, Drogui P, Brar S K, Benmoussa H, Blais J F 2008 J. Hazard. Mat. 151 446–55.
[15] Soeprjianto S, Perdani A D, Nury D F and Pudjiastuti L 2017 110015. http://dx.doi.org/10.1063/1.4982345.
[16] Canizares P, Martinez F, Jimenez C, Saez C and Rodrigo M A 2008 J. Hazard. Mat. 151 44–51.
[17] Carmona M, Khemis M, Leclerc J P and Lapicque F 2006 Chem. Eng. Sci. 61 1237–46.
[18] Fouad Y O A, Konsowa A H, Farag H A and Sedahmed G H 2009 Chem. Eng. J. 145 436-40.
[19] Martinez-Delgadillo S A, Morales-Mora M A and Barceló-Quintal I D 2010 Sust. Environ. Res. 20, 227-31.
[20] Ozyonar F 2016 I. J. Electrochem. Sci. 11 1456 – 71.
[21] Chavalparit O and Ongwanee M 2009 J. Environ. Sci. 21 1491–96.
[22] Daud Z, Latiff A A A, Azis N A A and Awang H 2013 Aust. J. Basic Appl. Sci. 7 457-63.
[23] Un U T, Koparal A S and Ogutveren U B 2009 J. Environ. Manag. 90 428–33.
[24] Chen X, Chen G and Yue P L 2000 Sep. Purif. Technol. 19 65–76.
[25] Xu X and Zhu X 2004 Treatment of refractory oily wastewater by electrocoagulation process, Chemosphere, 56 889–94.
[26] Drogui P, Asselin M, Brar S K, Benmoussa H and Blais J F 2008 Sep. Purif. Technol. 61 301–10.
[27] Cotillas S, Cañizares P, Martin De Vidales M J, Sáez C, Rodrigo M A and Llanos J 2014 Chem. Eng. Trans. 41 133-38.
[28] Rehman A, Kimb M, Reverberi A P and Fabiano B 2015 Chem.Eng. Trans. 43 2251-56.
[29] Balasubramanian N and Srinivasakannan C 2010 Nova Science Publishers, Inc. NY. The USA, 19.
[30] Daneshvar N, Oladegaragoze A and Djafarzadeh N 2006 J. Hazard. Mat. B129 116–22.
[31] Daneshvar N, Ashassi-Sorkhabi H and Tizpar A 2003 Sep. Purif. Technol. 31 153–62.
[32] Sekman E, Top S, Uslu E, Varank G and Bilgili M S 2011 J. J. Environ. Res. 5 1079-86.
[33] Ulucan K, Kabuk H A, Ilhan F, Kurt U2014 Int. J. Electrochem. Sci. 9, 2316 – 26.