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Removal of chemical oxygen demand (COD) and total suspended solid (TSS) using electrocoagulation process for treatment of oleochemical wastewater

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Abstract. Wastewater from oleochemical industry contains high concentration glycierin, chemical oxygen demand (COD) and total suspended solids (TSS) that can cause environmental pollution if discharged without proper treatment method. Currently, oleochemical industry used reverse osmosis membrane and submerged bed biofilm reactor to treat their wastewater. In this work, other method namely electrocoagulation treatment that capable to achieve a high removal of color, COD, biological oxygen demand (BOD) is employed. The objective of the study is to determine the optimum operating condition such as initial pH (6-9), applied current (4.0-8.0A), type of electrode (aluminium & stainless steel & and retention time (10 – 40 min) on degradation of COD and TSS in wastewater from an oleochemical industry using this process. The experimental results showed that the pollutant removal efficiencies of COD and TSS can be achieved at 62.64% and 66.12% respectively, of the initial concentration of parameters using aluminium electrode at the optimum conditions of pH 7.5, applied current 6 A and reaction time of 30 min. All the findings of the study revealed that treatment of oleochemical wastewater by electrocoagulation process at optimum conditions can be used as a treatment.

1. Introduction

Oleochemical are product from fat and oils (animals or vegetable sources). Nowadays, oleochemical industries have problem to dispose and treat their waste where categorized as wastewater and glycerin pitch, a viscous liquid, coloring brown to dark brown. It has organic compounds in the average of 1 to 2 million mg chemical oxygen demand (COD) per liter. Glycerin wastewater has a high organic compound content and has become serious problem to manage. It is also difficult to biological degrade [1]. Refinery glycerin wastewater from oleochemical industries contains several organic substrates such as 20.2% glycerol, 6.6% fatty acids (as soap) and 64.3% NaCl. [2]. Untreated wastewater from oleochemical industries has a high concentration of COD, fatty acid, sodium chloride, glycerin, the organic and inorganic residue which are harmful to the environment and can significantly cause serious health risks to human and other living organisms. Thus, it is important to manage the wastes, especially for industrial effluents to undergo treatment processes before being discharged or reused.

Nowadays, electrocoagulation (EC) has been used in many industries to treat wastewater before they are discharged, and has been successful in the treatment of different wastewaters such as urban wastewater, textile industries, laundry wastewater, restaurant wastewater, electroplating wastewater, chemical and polishing wastewater, olive mill wastewater, laundry wastewater, dairy and tannery wastewater, pulp and paper mill industry wastewater [3]. EC process have many advantages, which are

simple and easy operation, no chemical additions and a shortened reaction detention time [4]. Electrocoagulation treatment is capable to remove color, COD, BOD, TSS and others [5]. COD is of major importance in the environmental perspective; it is an indicator of the degree of pollution of the discharged wastewater. COD is widely used by regulatory agencies worldwide to gauge the overall efficiency of treatment plants [6]. All organic matters such as COD and TSS can be removed in the electrocoagulation process where formed by product on the surface of the anode and flocculated contaminants with removed ion from electrodes [7].

Electrocoagulation treatment no harmful effect on the environment because during the process, no harmful reagent is used and the treatment can run as long as current is connecting to the electrode. Recently, electrochemical technologies have been attractive to industries for the treatment of liquids, gases, and solids, but electrocoagulation is most effective in the treatment of wastewater. Besides, electrocoagulation is effective in eradicating the smallest particles using an electric field to set them in motion and subsequently coagulate them. Recently, the oleochemical industry has been faced with the issue of wastes treatment. The wastes of the oleochemical industry are categorized as wastewater and glycerin. The wastewater has an organic compound content of about 1 to 2 million mg COD per liter on average. Therefore, the purpose of this study to treat oleochemical wastewater at optimum operating condition such as initial pH, applied current, type of electrode and retention time.

2. Material and method

2.1. Sampling of wastewater
The oleochemical wastewater taken from the glycerin refinery wastewater treatment plant in Gebeng Industrial Area, Pahang. The wastewater sample was the excess solution from the batch process on production of liquid detergent dynamo.

2.2. Chemical
The chemicals and reagents used in this study were 50% of sodium hydroxide (NaOH) manufactured by Merck, 98% of sulfuric acid (H_2SO_4) manufactured by Thermofisher scientific.

2.3. Method of characterizations
The wastewater samples were characterized to identify the amount of the parameters in the sample before and after treatments. They were characterized for COD, BOD, TSS, and pH.

2.3.1 Chemical Oxygen Demand (COD). The wastewater sample was filtered using Whatman filter paper with diameter of 125mm to remove large components by simple filtration method Then, the COD of the wastewater sample was measured by a standard method using a Hach spectrophotometer (DR2400) and Hach COD reactor [8]. The COD was measured before and after the treatment

2.3.2 Total Suspended Solid (TSS). The TSS in the wastewater sample was measured by a vacuum filtration method, whereby the sample was filtered through a glass fiber filter (GF/CTM) diameter 47 mm. The filter disk was dried in the oven at 103°C to 105°C for 1 h, cooled in a desiccator, and weighted.

2.4. Electrocoagulation Treatment
The equipment for the EC process was shown in figure 1. The wastewater samples were poured into the container that contains the electrodes. Some parameters (initial pH of wastewater sample, applied voltage; reaction time and type of electrodes) were varied throughout the analysis. First, in order to study the effect of initial pH of the sample, the pH was varied from pH 4 to pH 9; the pH was adjusted with 5 % of sodium hydroxide and 5 % sulphuric acid. The applied current was varied between 4.0 to 8.0 A and the reaction time was varied between 10 min to 40 min [9]. The electrodes used for the experiment are stainless steel and aluminium, each situated approximately 1.5 cm apart and dipped in the wastewater [8].
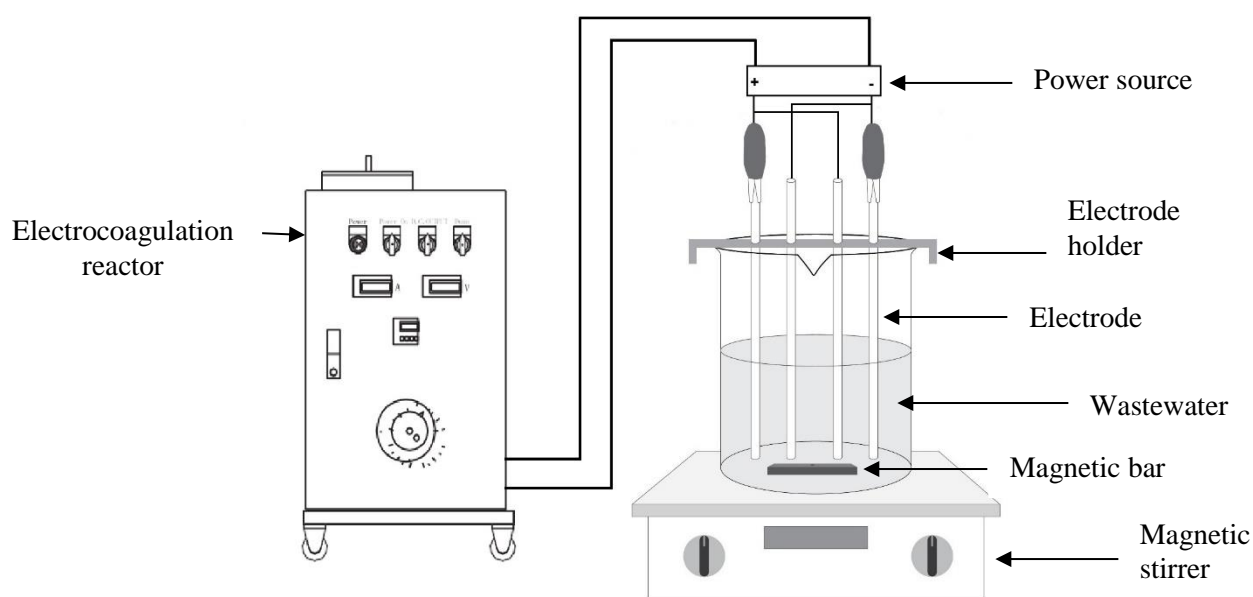
Figure 1. Set up for electrocoagulation process

Reaction occurred during electrocoagulation process as stated in equation (1-2) whereas at cathode occurred reduction reaction and oxidation reaction at anode [10].

At cathode:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{1}$$

At anode:

$$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^- \tag{2}$$

3. Result and discussion

### 3.1. Characteristics of oleochemical industry
The quality of the sampled wastewaters were tested in terms of the pH, COD, BOD, and TSS as showed in table 1. The wastewater contained high levels of COD and TSS, which were 87,000 mg/L and 983 mg/L, respectively.

**Table 1.** The characteristics of sampled wastewater.

Parameters	Value	Unit
pH	11.35	-
Chemical oxygen demand (COD)	87,000	mg/L
Biological oxygen demand (BOD)	362	mg/L
Total suspended solid (TSS)	983	mg/L

3.2. Effect of initial pH

The initial pH has the highest impact on the electrocoagulation dosage rate and bubble generation rate, which affects the waste removal efficiencies from the sample. The pH of the wastewater was adjusted using 5% of H_2SO_4 or NaOH to pH 6, pH 7, pH 7.5, pH 8 and pH 9 to determine the initial pH effect on the highest removal efficiencies of COD and TSS. For this study, the EC process was kept constant at 6 A and 30 min in each batch experiment reactor while using both aluminium and stainless steel electrodes. Generally, as shown in figure 2 and figure 3, the removal efficiency of the pollutant increased as the initial pH increased to the alkali level. At pH 7.5, the highest removal efficiencies achieved were 62.64 % for COD and 66.12 % for TSS using aluminium electrode. Meanwhile, the highest removal efficiencies of 56.90 % for COD and 63.71 % for TSS were achieved using aluminium electrode. For the removal mechanisms of TSS, it is mainly contributed by an increasing removal efficiency of the coagulate particles in the pH range of 4-7 [11]. After EC process, final pH increased due to the reaction occurred at cathode whereas it has produced hydrogen bubbles with OH- ions [12].
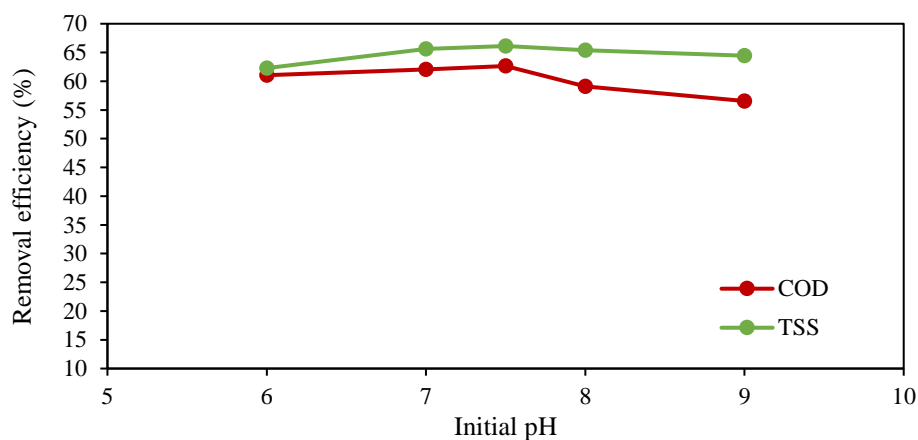
Figure 2. Removal efficiency for COD and TSS affect by initial pH. Applied current: 6A; reaction time: 30min; monopolar series using aluminium electrodes.
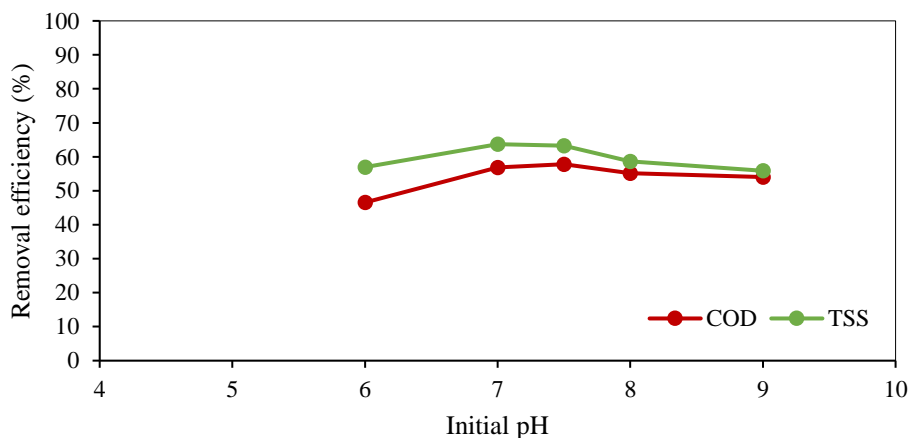
Figure 3. Removal efficiency for COD and TSS affect by initial pH. Applied current: 6A; reaction time: 30min; monopolar series using stainless steel electrodes.

When using aluminium as electrode, the electrolysis undergoes form aluminium ions, which is follow by spontaneous hydrolysis, and it is influenced from the initial pH of oleochemical wastewater. Besides, pH values between 4 to 9.5, aluminium formed in and react as coagulation to trap the colloidal [13]. At the anode, the reaction made it slightly acidic while at cathode being slightly alkaline due to formation

of hydrogen and p OH- [12]. Compare to stainless steel electrode, using aluminium as an electrode made the pH to neutralize where it stabilizes the amount of production and consumption of OH- [14].
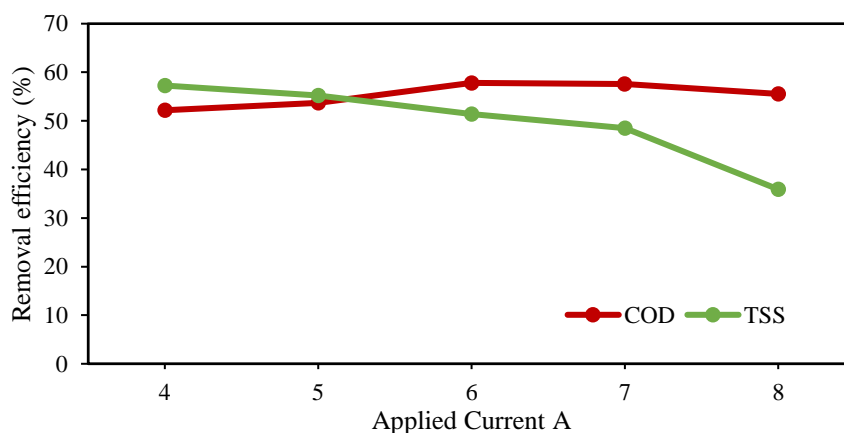
3.3. Effect of applied current

The applied current was studied by varying the voltage level from 4.0 to 8.0 A and the corresponding applied voltage range from 10 -20 V. Each experiment was conducted at the same pH value of 7.5 and a constant reaction time of 30 min. Figure 4 and 5 show the removal efficiencies of COD and TSS as a function of the applied current. An increasing removal efficiency can be observed when the applied current was increased from 4.0 to 8.0 A. Applied current gave major impact to the production rate of coagulant, bubble production and growth of floc [15, 16] whereas when increase current intensity will increase the removal of organic matters [17]. However, removal of COD and TSS decreased after 6A or did not show any improvement in the percentage of COD and TSS removal although increasing in applied current will increase COD and TSS removal but due to the surface of the electrode corrode. The reaction occurred at both electrodes made the surface of electrode reduced and increase the total of floc in a sample.

Comparing the two electrodes materials, COD removal was rapidly increased when using stainless steel electrode compare to aluminium electrode because stainless steel have a higher molecular weight compare to aluminium electrode. Because of that, stainless steel electrode more precipitate than aluminium electrode and leads to the formation of heavier coagulant [18]. However, COD removal decreased from 7.0 A by stainless steel compare to aluminium electrode and also more efficiency for TSS removal.
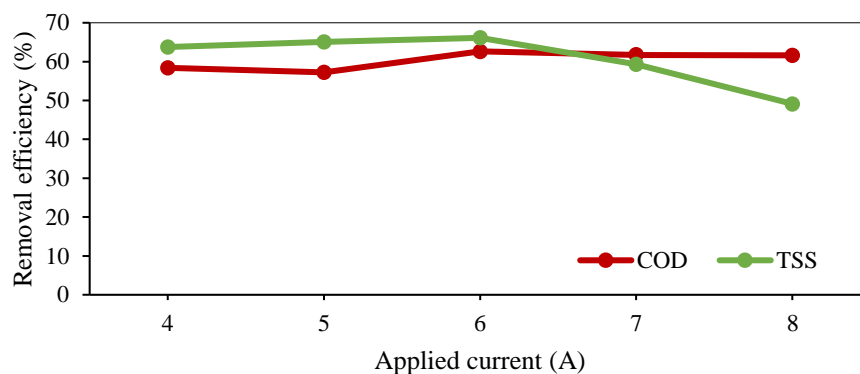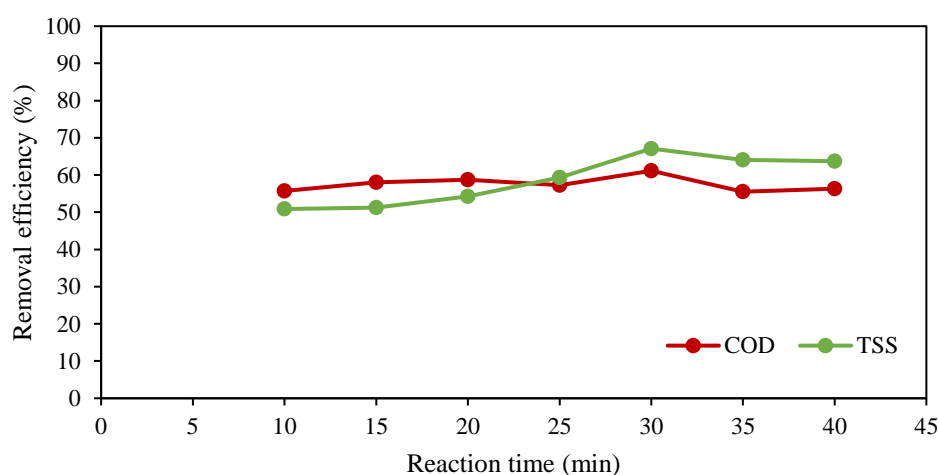

Figure 4. Removal efficiency for COD and TSS affect by applied current. Initial pH: 7.5; reaction time: 30min; monopolar series using aluminium electrodes.
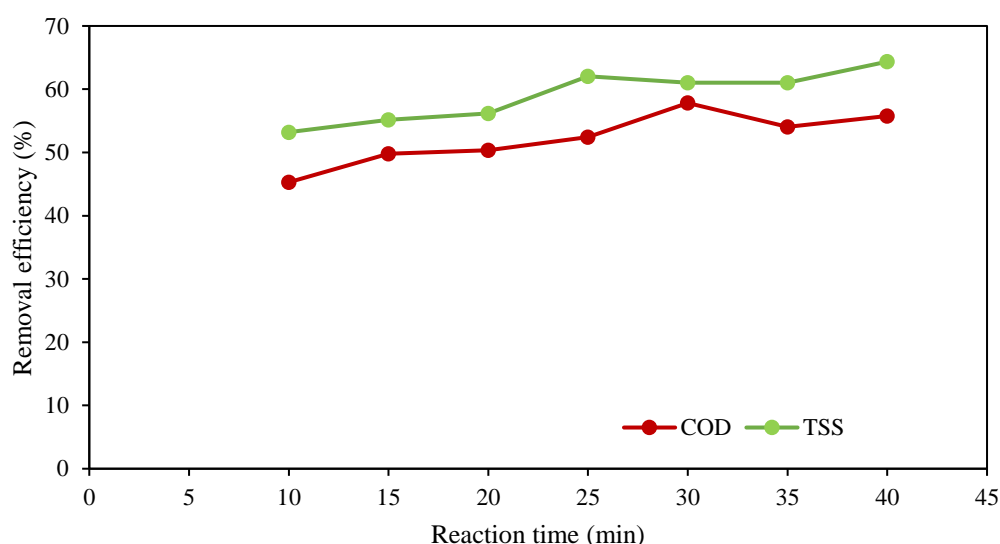

Figure 5. Removal efficiency for COD and TSS affect by applied current. Initial pH: 7.5; reaction time: 30min; monopolar series using stainless steel electrodes.

3.4. Effect of retention time

The reaction time was varied from 10 to 40 min to observe the pollutant removal efficiencies and the results are shown in figure 6 and 7. Each batch of the experiment was conducted at the same pH value of 7.5 and an applied current of 6 A. The pollutants removal efficiency was observed to increase with respect to the reaction time; however, a reaction time of more than 30 min did not enhance the pollutants removal efficiency as also being stated in some studies where the optimal reaction time for the treatment of oily wastewater was reported to be approximately 30 min [13, 19]. Meanwhile, the change in the final pH of the wastewater sample was due to the formation of hydroxide ions at the cathode electrode. Formation of floc become larger as the reaction time increased and this is mainly why the removal efficiency of the pollutant was increasing.

Figure 6. Removal efficiency for COD and TSS affect by reaction time. Initial pH: 7.5; applied current: 6.0A; monopolar series using aluminium electrodes.

Figure 7. Removal efficiency for COD and TSS affect by reaction time. Initial pH: 7.5; applied current: 6.0A; monopolar series using stainless steel electrodes.

According to Faraday's law, the removal efficiency for COD and TSS increase due to the amount of coagulants produced when the retention time of EC process increased [15]. COD removal increased proportionally from 10 to 30 min and then constant due to molecules interaction and coagulant become

weak [20]. After 30 min, COD and TSS removal decreased due to electrode passivation. Furthermore, low efficiency removal of COD because the formation of hydroxide flocs in solution decreased [21].

3.5. Optimum conditions
From the analysis of the operating conditions of the EC process, the optimum conditions were identified and were run as one-factor-at-a-time. The performances of the electrodes changed under similar operational conditions of the EC process. The highest removal efficiency was achieved using aluminium electrodes at 62.64% for COD, and 66.12 % for TSS. The final pH of the treated wastewater was 8.69. Steel is iron that contain a small amount of carbon. Stainless steel electrodes were found to transfer higher numbers of iron ions into the sample during the EC process [22] and produced a higher volume of sludge. Due to the relative parity of the costs of both electrodes, as well as availability, it will be a good choice to use aluminium electrodes for higher treatment efficiencies during EC processes.

From the results of the experiments at the optimum EC operation condition, the pollutant removal efficiencies using stainless steel electrode were higher compared to using stainless steel electrode. After EC process, aluminium electrode formed where its react to trap the colloids and become precipitates [13] while stainless steel electrode formed as a weak coagulant and no adsorption capacity of pollutants [23]. Thus, aluminium electrode is considered more efficient in the treatment of wastewaters using EC processes.

4. Conclusions
It can be concluded that the EC treatment process has a potential of treating wastewaters that contain a high glycerine composition, which contributed to a high COD. The experimental study found that the pollutant removal efficiencies of COD and TSS were 62.64 % and 66.12 % respectively, of their initial concentration. The effect of the initial pH of the sample, the applied voltage, the reaction or contact time, the electrode arrangement, and the type of electrodes to the pollutant removal efficiencies was studied to determine the optimum operating conditions of the EC process. From the study, it showed that the optimum operating conditions of the EC process for the highest removal efficiencies of the pollutants were: initial pH value of 7.5, applied current of 6A, and 30 min reaction time using aluminium electrode in the monopolar series arrangement. From this study, only pH of the treated wastewater was achieved at levels below the stipulated EQA 2009 regulation standard values. The EC process itself is not a treatment strategy to achieve a Standard B of the EQA requirements where the COD and TSS removal efficiencies are expected to be 62.64 % and 66.12 %, respectively. The EC process is recommended for the pre or post-treatment process, which can be combined with other treatment methods such as chemical treatment or physical treatment (membrane filtration, adsorption, and ion-exchanged technology) to achieve the EQA stipulated performance levels.

References
[1]   Sarah M 2005 *J. Teknik SIMETRIKA* **4** 271-274
[2]   Aziati A S 2012 *2nd International Conference on Chemical, Biological & Environmental Sciences* **222** 701
[3]   El-Taweel Y A, Nassef E M, Elkheriany I and Sayed D 2015 *Egyptian Journal of Petroleum* **24**(2) 183–192
[4]   Nawarkar C J and Salkar V D 2019 *Fuel* **237** 222–226
[5]   Butler E, Hung Y T, Yeh R Y and Suleiman Al Ahmad M 2011 *Water* **3** 495–525
[6]   Moreno H A, Cocke D L,and Gomes J 2007 *Separation and Purification Technology* **56**(2) 204–211
[7]   Kim W, Yu, C, Son D, Chang D, Kim D and Hong K 2017 *Journal of Electrochemical Science and Technology* **8**(1) 35–42

[8]   Wang C T, Chou W L and Kuo Y M 2009 *J. Hazard. Mater.* **164** 81–86
[9]   Hidayatillah A 2014 *Proceeding of International Conference on Research, Implementation and Education of Mathematics and Science* 2014 **5** 18–20
[10]   Hong K, Chang D, Bae H, Sunwoo Y, Kim J and Kim D 2013 *Int. J. Electrochem. Sci.* **8** 8557–8571
[11]   Gürses A, Yalçin M and Doar C 2002 *Waste Manag.* **22**(5) 491–499
[12]   Moussa D T, El-Naas M H, Nasser M and Al-Marri M J 2017 *J. Environ. Manag.***186** 24–41
[13]   Xu X and Zhu X 2004 *Chemosphere* **56**(10) 889–894
[14]   Vasudevan S, Lakshmi J and Sozhan G 2011 *Desalination* **275**(1–3) 260–268
[15]   Mollah M Y, Schennach R, Parga J R and Cocke D L 2001 *J. Hazard. Mater.* **84** 29–41
[16]   Aouni A, Fersi C, Ben M, Ali S and Dhahbi M 2009 *J. Hazard. Mat.* **168** 868–874
[17]   Nasrullah M, Zularisam A W, Krishnan S, Sakinah M, Singh L and Fen Y W 2019 *Chinese J. Chem. Eng.* **27**(1) 208–217
[18]   Adamovic S, Prica M., Dalmacija B, Rapajic S, Novakovic D, Pavlovic Z and Maletic S 2016 *Arab J. Chem.* **9** 152–162
[19]   Tir M, and Moulai-mostefa N 2008 *J. Hazard. Mater.* **158**(1) 107–115
[20]   Ahmad Samir N 2013 *Civil and Environmental Research* **3**(13) 61–74
[21]   Fajardo A S, Rodrigues R F, Martins R C, Castro L M and Quinta-ferreira R M 2015 *Chem. Eng. J.* **275** 331–341
[22]   Ilhan F, Kurt U, Apaydin O and Gonullu M T 2008 *J. Hazard. Mater.* **154** 381–389
[23]   Genuchten C M Van Dalby K N, Ceccato M, Stipp S L S and Dideriksen K 2017 *J. Environ. Chem. Eng.* **5**(5) 4958–4968