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Demulsification of Synthetic Petroleum Wastewater

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ABSTRACT

Emulsion wastewater was synthesized by combining crude oil and deionized water, and it was electrochemically treated with various variable parameters such as initial O/W ratio, current density, and volumetric flowrate. A unique continuous mode system was set up to treat oily wastewater using rectangular electrochemical reactor, in which two vertical sheets of sacrificial aluminum anode, and carbon felt as cathode. This electrodes configuration was used to achieve hybrid electrocoagulation and electroflotation (EC/EF) at the same time. The electrical current in electrocoagulation dissolves the sacrificial anode, introducing Al^{3+} with a positive charge into the bulk of oily wastewater. While electroflotation allows the formation of extremely finely dispersed gas bubbles, demulsification could be accomplished through the addition of chemicals. The demulsification process of wastewater was indicated by the removal of chemical oxygen demand (COD) with several parameters such as initial crude oil concentration (100, 200, 300 ppm), current density (10, 20, 30) mA cm^{-2}, emulsion flow rate (2, 4, 6) l/h with operation time up to 120 minutes. The results showed that the demulsification process gave high COD removal rate at the first 30 minutes of analysis, with current density (20 or 30) mA cm^{-2}, and the best results coincided at the highest anode weight loss. At the same time, by comparing the treated wastewater's initial and end turbidities, the treatment process' effectiveness was assessed. Experimental results indicated that an increase in oil separation efficiency with increasing cathode surface area, increasing curing time, current density, and a decrease the electrolyte concentration. It was discovered that 30–40 minutes and 30 mA cm^{-2} were the best for oil separation.

Keywords: Demulsification, Oil/water emulsion, Electrocoagulation, Electroflotation

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1. Introduction

Free oil, emulsified oil, and suspended solids are the main wastewater contaminants connected to crude oil storage, desalting, and fractionation. During storage, water and suspended particles in crude oil are separated. The sludge at the bottom of the oil layer is made up of the water layer. When the water layer is removed, emulsified oil at the oil-water interface commonly ends up in the sewers. Both the chemical oxygen demand (COD) and the biological oxygen demand of this waste are high (BOD). One of three sources typically provides the wastewater from the fractionation of crude oil. Water taken from above accumulators serves as the primary source, followed by recirculation or hydrocarbon transfer to other fractionators. The second source of trash is the discharge from oil sample lines. Although it ought to be able to be separated, emulsions might form in the sewage. A third waste source is the extremely stable oil emulsions that develop in the

barometer condensers used to lower the pressures in the vacuum distillation units [1].
Water quality has become a major issue for Third-World countries due to pollution from point and non-point sources, making water and energy critical issues for the twenty-one century. [2]. Oil is the scattered phase in a two-phase dispersive system with water as the continuous phase for oily wastes [3]. Stable oil-in-water (O/W) solutions are emulsions that disperse oil droplets in water. [4]. Surfactants increase emulsion stability and make it more difficult to remove oil droplets. Surfactant creates a coating to stop oil droplets from coalescing. The concentration of the surfactant affects the stability of the emulsion. [5].
By dissolving sacrificial anodes under the influence of an applied voltage, active coagulant precursors are produced as a result of the electrochemical technology known as electrocoagulation, which is used to remediate contaminated water. The process of electrocoagulation, which removes contaminants from wastewaters by means of a number of processes working in concert, is complex. [6].
The Al^{3+} ions produced hydrolyze right away to create the appropriate hydroxides and/or polyhydroxides with an insufficient pH. According to reports, compared to those produced by traditional Al coagulants, the A^{2+} hydroxides and polyhydroxides from the electrochemical dissolution have a greater affinity to collect the contaminants in the wastewater. This results in more coagulation. Additionally, the gas bubbles that develop as a result of water electrolysis can cause coagulated materials and contaminants to float. Consequently, electroflotation could also be crucial in an electrocoagulation cell. [**7**].
Al dissolution and electron transfer are prevented by the development of an inhibitory layer on the surface of the Al electrode, restricting Al3+ to the solution. As a result, the EC system is often built to function in a high voltage environment, typically greater than 10 V, in order to dissolve the inhibitory layer. Because of this, applying a high voltage for prolonged operation results in considerable energy consumption and a high likelihood of electrode destruction [8]. Pollutant removal from wastewater has utilized a variety of processes, such as coagulation-flocculation, Fenton process, Chemical sedimentation [9], and adsorption. However ,these techniques are severely constrained because using large chemical concentrations to clean wastewater may result in secondary contamination [10]. EC is a cost-effective and environmentally benign technology for treating wastewater compared to other approaches [11]. Through the electrolytic oxidation of iron or aluminum sacrificial anodes, coagulants are produced in-situ in EC [12]. The EC produces coagulants that help remove contaminants by adsorption or precipitation [13]. A number of different types of wastewater, including those containing oil [14], fluoride and arsenic [15], dyes and suspended particles [16], surfactant, chromium ions [17], and phosphate, have been effectively treated using electrocoagulation/electroflotation (EC/EF)[18].

2. Material and methods

The Experimental objectives of the study work including the two main steps which are:

2.1. Electrodes: -

Anode Electrode, this electrode is the sacrificial anode electrode used as the anode electrode in the cases where the cathode is carbon felt. The aluminum dimensions were, thickness of 1 mm, width 5 cm and length 10 cm, with a high purity that reached 99. 178 %.as it was tested by VAC 34mm analysis by Brucker AXS-D-76187 Karisruhe, Germany, Fig.1. A.
Cathode Electrode, thickness of 5 mm, width of5 cm, length of10 cm, porosity; 0.94, weight per unit volume; 0.5 kg/m^2.Density; 0.12 kg/ $m^{3,}$ carbon content; > or = 99% and ash content; < 0.01, supplied by Shanghai Carbon Material Company (Taiwan), Fig .1, B

Figure 1. A. Sacrificial anode, **B**. cathodes.

2.2. Experimental Reactor Design:

As shown in Fig. 2, the experiments were carried out in a laboratory making electrochemical cell (reactor) of pure transparent Perspex(cuboid) plate thickness 6 mm. With internal dimensions (5 * 11.3 * 17.7 cm), the continuous flow EC/EF reactor is made of Perspex (Poly (methyl methacrylate)) with a fixed volume that provides an emulsion flow of 1000 ml (counter current flow). The reactor contains three holes, two at the top (one with a diameter of one cm to enter the emulsion through a perforated tube with holes 5 mm in diameter, and the other as a groove for the exit of sludge in front of it), and the last hole at the 1.5 cm from the bottom of the cell, for the removal of treated water through a tube like the upper tube, its holes are for the bottom to not blocked by sedimentary solid sludge contaminants. The electrodes used in the continuous conduction process were aluminum - carbon felt. The electrodes dimensions are1.5mm thick and 5, 5 cm wide and 10,10 cm thick for aluminum and carbon felt, respectively, connected to other parts of the treatment system water emulsion, treated by the hybrid EC/EF process.

Figure 2. Shape of the EC/EF experiment reactor

3. Theory of hybrid EC/EF treatment

This section describes an oil/water emulsion that has been prepared by mixing crude oil brought from a Najaf refinery and deionized water purchased from the local market, for the purpose of treatment and study by hybrid EC/EF method. In addition, study the effect of different operating parameters (10, 20, 30 mA/cm^2 current density, 100,200, and 300 ppm initial crude oil concentration and 2,4 and 6 L/hr O/W emulsion flowrate) on COD removal efficncy, electric power consumption (SEEC), current efficiency (CE) from oil refining wastewater in case of fixed 1 cm distance between electrodes. The materials and devices used in this study are mentioned below. The tests that will be approved during the research are also mentioned.

4. Analysis of O/W Emulsion Samples

1. The analysis of deionized water was carried out in the laboratories of the Al-Hilla water department and the Al-Muimira sewerage, as for the analysis of crude oil, it was carried out in the Quality control laboratory within the Al-Najaf Al-Ashraf Refinery.
2. A synthetic laboratory stable emulsion that was used in the EC/EF reactor. It was made by mixing the specified amounts of crude oil (100, 200, and 300 ppm) with deionized water at room temperature

using a high-speed mixer (IKA® RW 16.USA) at 1500 rpm for 60 to 80 minutes. A sufficient amount of sodium chloride solution (1500 ppm), produced separately, was added to increase electrical conductivity.

3. The emulsion O/W was tested for its properties as shown in Table (1) using a method or instrument for each test and then acidified and kept at a temperature of less than 4°C in the refrigerator to be prepared for analysis operations after adding the digestion solutions and catalyst.

Variable, (unit)	value
pH	7.8
Temperature (°C)	36
Total Hardness (TH)	200
Alkalinity (as $CaCO_3$mg/L)	238
Conductivity Ec (μs/cm)	3400
Turbidity (NTU)	130
Sulfates as SO^{4-} (mg/L)	14.4
Chlorides as CL^- (mg/L)	101.2
Nitrates as NO_3^- (mg/L)	0.007
Total Solids (TS mg/L)	2050
Total Dissolved Solid (TDS mg/L)	1730
Total Suspended Solid (TSS mg/L)	320
Chemical Oxygen Demand (COD mg/L) for 100 ppm crude oil	1108
Chemical Oxygen Demand (COD mg/L) for 200 ppm crude oil	1124
Chemical Oxygen Demand (COD mg/L) for 300 ppm crude oil	1141

Table 1. Synthetic petroleum oily wastewater emulsion properties.

5. Results and Discussion

The efficiency of the EC/EF process was primarily assessed by monitoring DOC. The efficiency of DOC removal was expressed as:

$$COD\ Removal\ (\%) = \frac{COD\ (t=0) - COD\ t}{COD\ (t=O)}\ x100 \quad (1)$$

5.1. Effect of an initial crude oil concentration

Fig. 4, 5 and 6 shows the COD Removal efficiency with the effect of increase an initial O/W emulsion concentration (100,200, and 300 ppm) for 30 mA/cm^2 current density with O/W flow rate to the treatment reactor 2, 4 and 6 L/hr. The COD removal efficiency decreased with increase the initial O/W emulsion concentration were 96.93,80.24 and 76.51%, for 2 L/hr O/W emulsion flow rate, the COD removal efficiency were 89.07, 87.81 and 74.19% for 4 L/hr O/W emulsion flow rate, the COD removal efficiency were 84.11,80.54 and 66.37 for 6 L/hr O/W emulsion flow rate, respectively. From the above results it appears very clearly that the efficiency of demulsification is directly proportional to the residence time of the emulsion in reactor (low O/Wemulsion flow rate), also, the COD removal efficiency is directly proportional to the increase in current density applied, while it is inversely proportional to the increase in the concentration of the initial O/W emulsion concentration. The decomposition of oil droplets resulting from anode dissolution is particularly effective at low oil concentrations. Less efficient breakdown of oil droplets can occur with higher emulsion O/W concentration. Hence, EC process is less effective at emulsion O/W concentrations o4ver 100 ppm, this finding was largely agreed with another researcher [19].

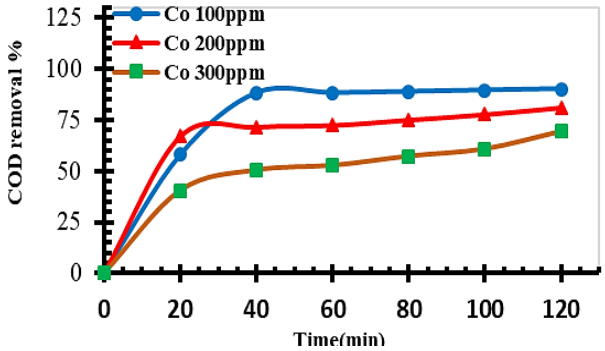

Figure 4. COD removal efficiency vs time with different concentrations of O/W. Al-C-felt electrode, current density **30** mA/cm^2, volumetric flowrate **2**L/hr.

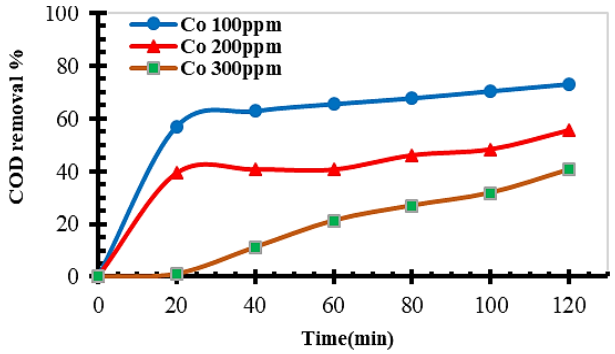

Figure 5. COD removal efficiency vs Time with different concentrations of O/W. Al-C-felt electrode, current density **30** mA/cm^2, volumetric flowrate **4**L/hr.

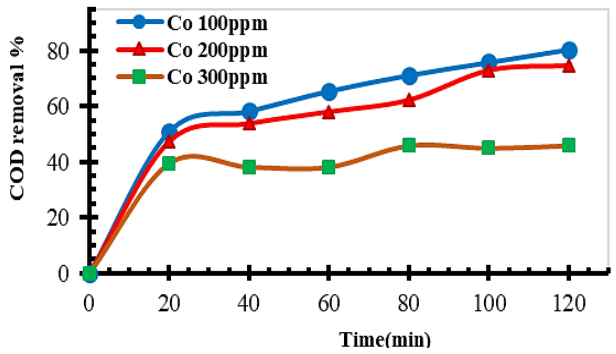

Figure 6. COD removal efficiency vs time with different concentrations of O/W. Al-C-felt electrode, current density **30** mA/cm^2, volumetric flowrate **6**L/hr.

5.2. Effect of Current Density

For an initial crude-oil concentration of 100 ppm (Co equal to 1108 mg/L initial O/W initial emulsion concentration) with increase current density (10,20 and 30 mA/cm2) and O/W emulsion flow rate. Fig. 7, 8 and 9 shows the COD removal efficiency were 66.6,82 and 99.8% for 2L/hr O/W emulsion flow rate, for 4L/hr O/W emulsion flow rate, the COD removal efficiency were 36.9,43.6 and 98% and for 6 L/hr O/W emulsion flow rate the COD removal efficiency were: 45.9 ,52.7and 83.73%, respectively. At the total treatment time (120 min), the EC/EF results of the O/W treatment showed that the current density had a significant effect on COD removal efficiency, The improved COD removal efficiency increases with increasing current density of 10-20-30mA/cm2. Using O/W emulsion with an initial concentration of 100ppm, and a volumetric flow rate of 2 L/hr, Figure (4-1) shows the COD removal efficiency with time at various current densities. It was obvious that increasing current density led to a higher final COD removal efficiency of contaminants. This may be explained by the fact that when current density rises, the rate of anodic dissolution of aluminum rises due to the formation, and release of Al3+ on the anode's surface. Resulting in a greater amount of coagulant, and flocs formation. As a result, the removal of organics has become more efficient. Significantly in fact, these observations are largely in agreement with previous investigations by [20].

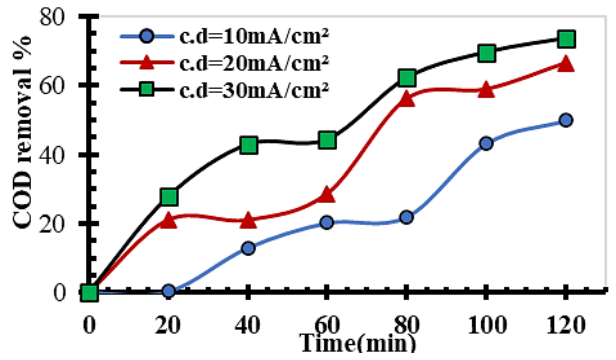

Figure 7. The effect of changing current density on the effectiveness of removing COD during EC/EF of O/W treatment, Al- C. felt electrode; initial O/W conc.**100**ppm; volumetric flow rate **2** L/hr.

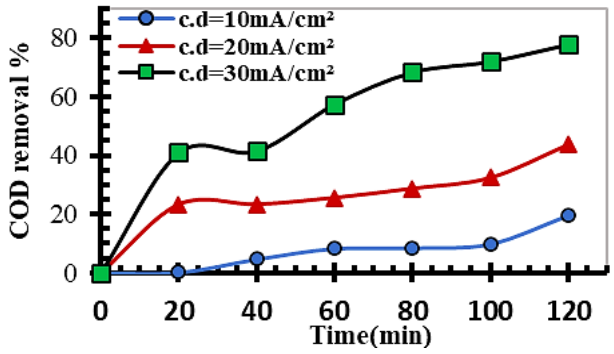

Figure 8. The effect of changing current density on the effectiveness of removing COD during EC/EF of O/W treatment, Al- C. felt electrode; initial O/W conc.**100**ppm; volumetric flow rate **4**L/hr.

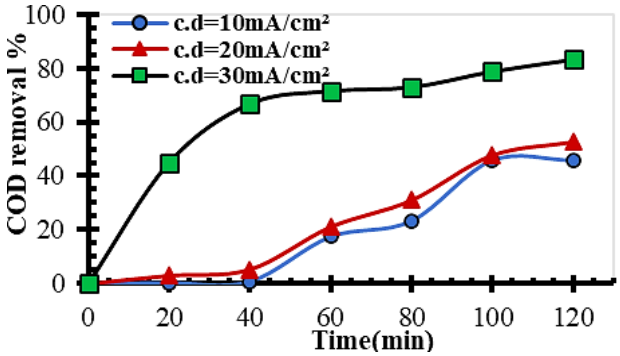

Figure 9. The effect of changing current density on the effectiveness of removing COD during EC/EF of O/W treatment, Al- C. felt electrode; initial O/W conc.**100**ppm; volumetric flow rate 6L/hr.

5.3. Effect of emulsion volumetric flowrate

The effect of increasing flow rate on decay COD removal efficiency ratio is shown starting in the Fig. 10, 11 and 12, initial O/W emulsion concentration 100 ppm, and current density of 10,20,30 mA/cm^2, respectively. for a current density of 30 mA/cm^2, the COD removal efficiency was decreased from optimum results 99.8% at 2L/hr O/W emulsion flow rate to 98% at 4L/hr O/W emulsion flow rate and 83.73% for 6L/hr O/W emulsion flow rate, respectively). The best COD removal efficiency (99.8%) results were obtained with a flow rate of 2 L/hr and current density of 30mA/cm^2. Fig. 10 show the optimum condition which give the most efficient removal of COD under 100ppm O/W concentration,30mA/cm^2 current density were (99.8%, 98% to 83.73%) respectively. Exactly as expected, the COD removal efficiency of emulsions O/w was found to decrease when the flow rate was increased from 2,4-6L/hr in the continuous operating mode. As slower flow rate increases uptime. A higher run time means that the untreated wastewater solution stays in the EC/EF reactor for a longer time, which in turn provides a longer reaction time. This is consistent with what was achieved by researchers [21].

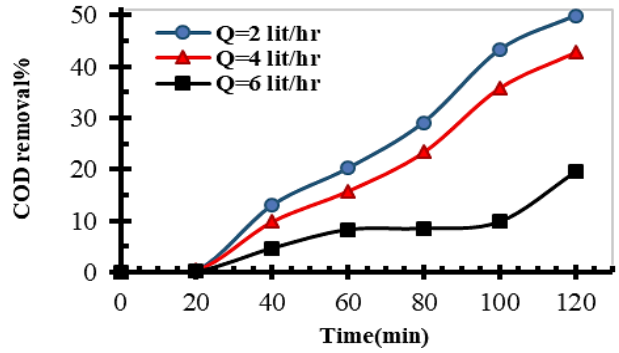

Figure 10. COD removal efficiency vs time with different O/W emulsion flowrates **100** ppm O/W. Al-Carbon.felt electrodes, current density **10** mA/cm^2.

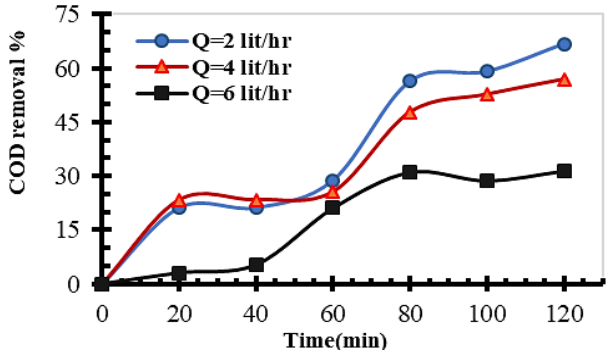

Figure 11. COD removal efficiency vs time with different O/W emulsion flowrates **100** ppm O/W. Al-Carbon.felt electrodes, current density **20** mA/cm^2.

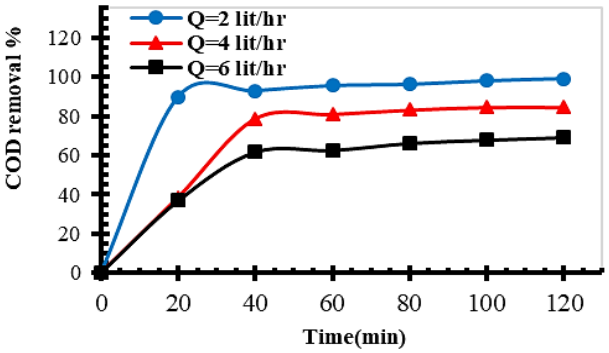

Figure 12. COD removal efficiency vs time with different O/W emulsion flowrates **100** ppm O/W. Al-Carbon.felt electrodes, current density **30** mA/cm^2.

6. Conclusions

This study looked at the treatment of oily wastewater utilizing a well-designed single electrochemical reactor and hybrid electrocoagulation/electroflotation (hybrid EC/EF). The demulsification process of the created emulsion by extensive mixing of crude oil with water for various O/W emulsion concentrations was studied and investigated. The COD elimination efficiency was determined.

The O/W starting concentration (100, 200, and 300 ppm) and current density (10, 20, and 30 mA/cm2) throughout the 120 minutes of continuous treatment reactor were the most crucial operational conditions employed in the demassification process in the EC/EF process. The effectiveness of the EC/EF process's COD elimination was investigated using Al-C felt electrodes. For O/W emulsion flowrates of 2, 4, and 6 L/hr, the Al-C felt offered COD removal efficiencies of 44.43, 32.16, and 21.64 percent, respectively.

Results indicated that the hybrid EC/EF process was found to be an efficient demulsification process for the removal of COD. The hybrid EC-EF method is favored over other types of procedures because it combines the operational and process units into a single electrochemical reactor, requires no chemicals, is easy to use, has a quick reaction time, and is extremely effective for treating oily wastewater. The results after the active treatment period (20–30 minutes) demonstrated that felt electrodes could be used in a continuous hybrid EC/EF process with COD removal efficiencies of 58,51 and 1.05 percent for 2,4 and 6 L/hr O/W emulsion flowrates, respectively, for an initial O/W emulsion of 300 ppm and 30 mA/cm2 with Al–C.felt.

7. References

[1] L. Yu, M. Han, F. He," A review of treating oily wastewater," *Arabian journal of chemistry*," Vol 10, Supplement 2, May, pp. S1913-S1922, 2017

[2] S. Chaturvedi, "Electrocoagulation: a novel waste water treatment method," *International journal of modern engineering research* ;Vol 3(1), Jan ,pp.93-100, 2013.

[3] H. Eskandarloo , M. Selig, "Abbaspourrad A. In situ H_2O_2 generation for de-emulsification of fine stable bilge water emulsions," *Chemical Engineering Journal*. Vol. 335:pp.434-442, 2018.

[4] C. Sun, T. Leiknes, J. Weitzenböck, B. Thorstensen, "The effect of bilge water on a Biofilm—MBR process in an integrated shipboard wastewater treatment system," *Desalination* ;Vol.236, Jan, issues (1-3): pp.56-64, 2009.

[5] S. Maiti , I. Mishra, S. Bhattacharya,J. Joshi," Removal of oil from oil-in-water emulsion using a packed bed of commercial resin,*" Colloids and Surfaces A: Physicochemical and Engineering Aspects*.Vol. 389,Sep. Issues 1–3 (1-3):291-8, 2011.

[6] C. An, G. Huang, Y. Yao, S. Zhao," Emerging usage of electrocoagulation technology for oil removal from wastewater,: A review," *Science of the Total Environment*. Vol 579, 1 Feb 2017, pp 537-556, 2017.

[7] C. Wang, W. Chou, Y. Kuo," Removal of COD from laundry wastewater by electrocoagulation/electroflotation," *Journal of hazardous materials*. Vol 164, Issue 1, 15 May, Pages 81-86, 2009.

[8] D. Ghernaout, M. Naceur, B. Ghernaout," A review of electrocoagulation as a promising coagulation process for improved organic and inorganic matters removal by electrophoresis and electroflotation," *Desalination and Water Treatment*.Vol.28, Apr, Issue (1-3): pp287-320, 2011.

[9] H. Zhang, S. Bukosky, W. Ristenpart," Low-voltage electrical demulsification of oily wastewater," *Industrial & Engineering Chemistry Research*. Vol.57, Jun, Issue (24):pp.8341-8347, 2018.

[10] J. Do, M. Chen. "Decolourization of dye-containing solutions by electrocoagulation." *Journal of applied electrochemistry*. Aug;24(8):785-790, 1994.

[11] H.Moreno-Casillas, D. Cocke, J. Gomes, P. Morkovsky, J. Parga, E. Peterson, "Electrocoagulation mechanism for COD removal." *Separation and purification Technology*. Vol.56 , Aug, Issue(2):pp.204-211, 2007.

[12] M. Mollah, P. Morkovsky, J. Gomes, M. Kesmez, J. Parga, D. Cocke, "Fundamentals, present and future perspectives of electrocoagulation, "*Journal of hazardous materials*. Vol. 114, Oct, Issues 1–3,pp.199-210, 2004.

[13] M. Changmai, M. Pasawan, M. Purkait, "Treatment of oily wastewater from drilling site using electrocoagulation followed by microfiltration." *Separation and purification Technology*.Vol. 210, Feb, pp. 463-472, 2019.

[14] X. Chen , G. Chen, P. Yue," Separation of pollutants from restaurant wastewater by electrocoagulation," *Separation and purification technology*. Vol.19, Jun, Issues(1-2),pp.65-76, 2000.

[15] P. Kumar, S. Chaudhari, K. Khilar, S. Mahajan," Removal of arsenic from water by electrocoagulation," *Chemosphere*. Vol.55, Jun, Issues (9),pp. 1245-1252, 2004.

[16] O. Larue, E. Vorobiev, C. Vu, B. Durand," Electrocoagulation and coagulation by iron of latex particles in aqueous suspensions," *Separation and purification technology*. Vol.31, May, Issu.(2),pp.177-192, 2003.

[17] P. Gao, X. Chen, F. Shen, G. Chen, "Removal of chromium (VI) from wastewater by combined electrocoagulation–electroflotation without a filter ," *Separation and purification technology*. Vol.43, May Issue(2),pp.117-123, 2005.

[18] S. İrdemez, Y. Yildiz, V. Tosunoğlu," Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes," *Separation and purification Technology*. Vol.52, Dec, Issue.(2),pp.394-401 2006.

[19] K. Dermentzis , D. Marmanis, A. Christoforidis, K. Ouzounis," Electrochemical reclamation of wastewater resulted from petroleum tanker truck cleaning." *Environmental Engineering & Management Journal (EEMJ),*Vol.13, Sep, Issue.(9),pp. 2395-2399, 2014.

[20] A. Mazumder, Z. Chowdhury, D. Sen, C. Bhattacharjee," Electric field assisted membrane separation for oily wastewater with a novel and cost-effective electrocoagulation and electroflotation enhanced membrane module (ECEFMM)," *Chemical Engineering and Processing-Process Intensification*. Vol.151,107918, 2020.

[21] M. Kobya, E. Demirbas, A. Dedeli, M. Sensoy," Treatment of rinse water from zinc phosphate coating by batch and continuous electrocoagulation processes,*" Journal of Hazardous Materials*. Vol.173, Jan, Issues (1-3),pp.326-334, 2010.