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Statistical Analysis for COD Reduction From Refinery Wastewater By Electro- Photo-Fenton Process Using Titanium and Stainless Steel Electrodes

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Abstract

Environmental problems at the present time are among the most important challenges facing humans, countries, and regions because of their multiple harms to our planet and everything in it. Among the environmental problems discharging of wastewater in oil, refineries are the largest problem because it contains many harmful pollutants, especially organic pollutants. The case study was to a reduction of the organic pollutants from the wastewater associated with the Qayyarah refinery in Iraq. Samples of the organic pollutants were represented by chemical oxygen demand (COD). The technique of merging the electrocoagulation process with Photo-Fenton was applied using a titanium electrode (cathode) and a stainless steel electrode (anode). By applying Takeuchi's method through the Mini Tap program and using statistical methods, we got the results and the final values: The highest COD removal efficiency was 95.238. STANDARD deviation 2.651, (Shapiro-Wilk Statistics efficiency = 0.977, p-Value = 0.813. The optimal conditions for this experiment were as follows: current density= 400 mA cm-2, Sodium sulfate concentration = 3 gm L-1, pH= 6, hydrogen peroxide concentration =400 mg L-1, ferrous sulfate =50 mg L-1, time =40 minute

Key words: COD; Refinery Wastewater; Titanium; Stainless Steel;Fenton.

1. Introduction

Petroleum refining and refining operations aim to produce more than 2500 materials, including liquefied petroleum gas, kerosene, gasoline, diesel fuel, jet fuel, lubricating oils, and raw materials for various petroleum, and petrochemical industries [1-2]. Oil refineries use a wide range of physical, mechanical, chemical and biological processing processes [3]. Wastewater from petroleum treatments contains many organic and inorganic components that need to remove pollutants and unwanted substances before they are discharged outside the oil facility [4]. Wastewater in refineries is variable and is a complex mixture containing a high percentage of organic matter and a certain content of hydrocarbons, represented by chemical oxygen demand (COD), heavy metals and other suspended solids, depending on the design of the plant, operating conditions and the type of crude being processed treat it [5]. The amount of wastewater generated and its characteristics depend on the configuration of the process [6]. As a general guide, approximately (3.5-5) cubic meters of waste water is usually generated per ton of crude oil ,especially when recirculating cooling water [1], While the researcher [7] mentioned that the amount of water used during refining operations generally ranges from (0.4 - 1.6) of the volume of used oil. The refineries generate polluted wastewater, which has chemical oxygen demand (COD) and biochemical oxygen demand (BOD) levels of about (300-600) milligrams per liter and (150-250) milligrams per liter, respectively. Also generate solid waste and sludge ranging from 3 up to 5 kg /ton of crude processed [8],). Because there is a high concentration of polycyclic aromatic substances in petroleum refinery wastewater, it is considered a very hazardous waste [2]. Wastewater treatment from refineries and petrochemical industries generally uses primary and secondary treatments to separate organic materials with all their well-known names, in

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addition to separating suspended solids[9]. Processing techniques can generally be categorized into two main methods, physical methods like; skimmer tank, API, and filtration, and reactive methods like; chemical flocculation/coagulation methods, advanced oxidation methods ,or biological treatment [10]. Coagulation is effective for removing high concentration organic pollutants and heavy metals in water and wastewater [11]. Electrocoagulation (EC) is an electrochemical method for treating contaminated water, it has been successfully implemented in various dissolved or colloidal wastewater pollutants [12]. Electrocoagulation is an electrochemical technique consisting of in situ coagulation production by electrolyzing through stainless steel and aluminum ions from the electrodes. Metal ion generation occurs at the anode, when hydrogen gas is released from the cathode. Hydrogen gas aids in the flotation of erupting particles to the surface. During this process, the electrodes can be arranged in a unipolar nor bipolar position. EC also provides contaminant removal by synchronous cathode reactions, either by precipitation on the cathode or flotation depending on the hydrogen composition gas at the cathode [13]. The possibilities of the EC method can be summarized as follows; it is easy to operate, highly efficient, economical, operation conditions are almost natural, and does not require the addition of chemicals[14]. In the electrical conduction process, coagulant species are produced on-site using the electrolysis of sacrificial anode, generally made of aluminium or iron by electric current applied between metal electrodes [13]. At the anode electrode, the metal is oxidized into cation as shown in the equations. [15].

$$Al_{(S)} \rightarrow Al_{(aq)}^{3+} + 3e^- \quad (1)$$
$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2e^- \quad (2)$$
$$Fe_{(aq)}^{2+} + O_2 + 2H_2O \rightarrow Fe_{(aq)}^{3+} + 4OH^- \quad (3)$$

At the cathode, hydrogen gas and hydroxyl anions are formed by the reduction of water as shown in equation.(4).

$$2H_2O + 2e^- \rightarrow H_{2\,(g)} + 2OH^- \quad (4)$$

Fenton is an effective treatment process. Hydroxyl radicals (OH^-) can be produced from the reaction between aqueous iron ions and hydrogen peroxide (H_2O_2), and they can remove toxic organic pollutants from wastewater [16]. The oxidation of many organic substances with H_2O_2 was improved by adding a catalyst (Fe^{2+}) or other transition metal ions to activate the H_2O_2 molecule leading to form hydroxyl radicals. This is the real oxidizer, which shows a very high oxidation capacity of about (2.80 V) [17]. The equations (5 to 9) explain Fenton's reaction [18]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+ \quad (5)$$
$$H_2O_2 + Fe^{+3} \leftrightarrow H^+ + FeOOH^{+2} \quad (6)$$
$$FeOOH^{+2} \rightarrow HO_2^{\cdot} + Fe^{+2} \quad (7)$$
$$HO_2^{\cdot} + Fe^{+2} \rightarrow HO_2^- + Fe^{+3} \quad (8)$$
$$HO_2^{\cdot} + Fe^{+3} \rightarrow O_2 + Fe^{+2} + H^+ \quad (9)$$

Several experimental have been carried outperformed in the decomposition of organic matter using Fenton oxidation [19]. The main disadvantage of these processes lies in the cost of the reactants, H_2O_2, and Fe^{2+} ions. To avoid this, Fe^{3+} was used instead of Fe^{2+} because it is less expensive [20]. The method of electrocoagulation along with Photo-Fenton has been used by several previous researchers, Table (1) contains some of these studies. This research aims to treat the organic pollution represented by (COD) from wastewater generated in the Qayyarah refinery, one of the divisions of the North Refineries Company in Iraq, by using titanium as the cathode and stainless steel electrodes as the positive electrode and electrically connecting them according to (MONO-POLAR) a parallel method, This process is then synchronized with the Fenton reaction by adding hydrogen peroxide and ferrous directly to the reaction cell. Then find the behavior of the removal efficiency of the process and create the optimal conditions to achieve the best possible result in reducing COD of the treated samples.

2. Materials and Method

2.1 Wastewater Resource

The wastewater that we intend to treat is taken from the first unit in the Qayyarah refinery, and Table (2) shows the physical and chemical properties of this wastewater.

2.2 The Procedure

The experiments were carried out using a cylindrical reactor (Pyrex glass) with a volume of 2 liters and a diameter of 13 cm. This reactor was placed on a magnetic stirrer type (Alfa HS-860 Model) was controlled at (700 rpm) during the operation. The coagulation process was carried out using two electrodes titanium as the cathode and stainless steel as the anode. The electrodes were arranged from the outside to the inside in the form of (titanium, stainless steel, titanium, and stainless steel). The distance between one electrode and another is 1.2 cm; the electrodes were fixed at 4 cm from the bottom of the reactor to avoid the attraction between the magnetic mixer and the electrodes. The electrodes were connected parallel then connected to an electrical source (power supply) as shown in figure 1.

For each experiment, the required amount of H_2O_2 and Fe^{+3} was added to the Electrocoagulation reactor for Fenton's reaction. Sodium sulfate, which represents the electrolytic factor, was added to increase the electrical conductivity of water. Different concentrations of HCl and NaOH solutions were also prepared to control the acidity of the process.

2.3 Methods of analysis

A sufficient amount of wastewater was taken, which was subsequently treated. The pH, conductivity, and temperature were measured in the laboratories of the Chemical Engineering Department / The University of Baghdad. The efficiency of the removal of organic matter was determined by the measurement of COD analysis (5220 D Method). (APHA, 2012) was used to determine chemical oxygen demand (COD), and the measurements were repeated two to three times for accuracy. Total dissolved solids for wastewater were measured using a TDS meter before and after each experiment.

2.4 Design of experiment

The experiment was designed using Minitab software and by choosing the Takeuchi method, the study included six variables, one dependent variable represented by COD removal efficiency, and five independent variables represented by current density, Sodium sulfate concentration (electrolytic factor), acidity function (pH), hydrogen peroxide concentration and ferrous sulfate concentration. Which are shown in Table (3):

Table (4) shows the summary of the experiment design, their values were determined based on previous studies.

3. Result and Discussion

After completing the experiments and making the COD analysis, the statistical side of the obtained results will be interpreted and discussed in this part. The statistical analysis was studied depending on the resulted data obtained according to the Takeuchi method.

3.1 Statistical description of the studied variables

Table (5) represents the statistical description of the statistical indicators represented by the arithmetic mean, standard deviation, and the highest and lowest value for each variable.

Where is the arithmetic mean of the Efficiency was 90.976, with a standard deviation of 2.651, the lowest value of the variable being 83.809, and the highest value is 95.238.

The best conditions were as follows: the current density was 400 mA/ cm^2, the Sodium sulfate concentration was 3 g/L, the acidity function (pH) at 6, the peroxide concentration at 400 mg/L, and the concentration of iron at 50 mg /L.

To test whether the probability distribution of the studied variables is identical to the normal distribution, the (Shapiro-Wilk) statistical test was used, where the hypothesis of this test states as follows:

- The null hypothesis: the data are normally distributed
- Alternative Hypothesis: The data are not normally distributed

The test results were shown in Table (6). From the results of Table (6) for the Shapiro-Wilk test, it is noted that the P-value of the Efficiency variable was greater than 0.05, which means we accept the null hypothesis, which states that this variable is normally distributed. As for all other variables, the P-value was less than 0.05, which means that we will reject the null hypothesis and accept the alternative hypothesis, which states that these variables do not follow a normal distribution.

3.2 Detecting linear overlap between the explanatory variables (Multicollinearity)

The problem of linear interference is one of the serious problems facing studies when finding influence relationships between the explanatory variables and the dependent variable, as this problem makes the process of separating the effect of each interpreted variable on the dependent variable, which leads to obtaining inaccurate estimations and thus arriving at incorrect and confusing decisions. To detect the existence of such a problem, the values of the Variance Inflation Factor and the Tolerance factor are found, as shown in Table (7). Through Table (7), it is noted that all values of (VIF) are less than 10, which indicates that there are no linear relationships between the interpreted variables. The values of the Tolerance coefficient were greater than 0.1, which also indicates that there is no problem with the multiplicity of a linear relationship between the explanatory variables.

3.3 The results of the assessment and the test of morale

After overall tests have been conducted to explore the studied variables, at this stage, a test is conducted for the hypothesis that finds the significance of the predictive model of the effect of the explanatory variables on the dependent variable, as follows:

- The null hypothesis (H0): There is no significant effect of the explanatory variables on the efficiency variable.
- The alternative hypothesis (H1): There is a significant, statistically significant effect of the explanatory variables on the efficiency variable.

Through the data in Table (8), it is noted that the p-values of the t-test of the four explanatory variables (Na_2SO_4, pH, H_2O_2, Fe^{+3}) were all greater than 0.05, meaning that the null hypothesis was accepted, which states that the four explanatory variables are not significant and have no significant effect on the dependent variable Efficiency. As for the p-value that goes back to the t-test due to the current density variable, it was less than 0.05, which means that the null hypothesis was rejected and the alternative hypothesis accepted, which states that the current density variable has a significant effect on the Efficiency variable.

3.4 Effect of variables on removal efficiency

The response surface can be clarified for the effect of the interpreted variables on the Efficiency variable to plot the response surface, the predicted values of the efficiency variable were drawn with the current density, Na_2SO_4, pH, H_2O_2 variables, as shown in the figures (3,4,5 and 6) below:

When observing these relationships between the variables through the above graphics, the effect of the electrolyte solution, pH, and peroxide concentration with current density is noted on the removal efficiency. While the effect of ferrous concentration appeared to be less than the other variables. Ferrous acts as a catalyst for the dissolution of peroxide to free radicals [24]. While both the electrolyte solution and the pH significantly correlate with the current density in the removal of organic pollutants, because they are among the factors affecting the electrocoagulation process. [13].

Figure (7) shows the effect of time on the efficiency of removal under optimal conditions, the process of removing organic matter from wastewater takes about 40 minutes.

Table (1): previous study

Researcher	Type of process	Electrode material	Type of wastewater
[15]	Electrocoagulation and Fenton/Photo-Fenton processes	Anode: Fe Cathode: Al	Removal of phenolic compounds from oil refinery wastewater
[21]	Electrocoagulation Process Coupled with Advance Oxidation Techniques	Anode: Fe Cathode: Al	Dairy Industry Wastewater
[22]	Electrocoagulation (EC) followed by electro-Fenton	Anode: Fe Cathode: Fe	Treatment of olive oil mill wastewater
[23]	Electrocoagulation	Anode: Ti Cathode: Ti	Carwash wastewater

Table(2): The physical and chemical properties of wastewater in Qayyarah refinery

No.	Tests	Wastewater
1	pH	7.2
2	Temperature, ºC	26-32
3	COD, ppm	750-900
4	T.D.S, ppm	230
5	Oil, ppm	8.6
6	Conductivity, ms	380
7	Turbidity, Ftu	97
8	NaCl %	0.7

Table(3): The Variables for the Parallel Stainless Steel – Titanium Model

description	Variable	No
Dependent parameter	EFFICIENCY (y)	1
Independent parameters	Current density (X1)	2
	(X2) Na_2SO_4	3
	pH (X3)	4
	H_2O_2 (X4)	5
	Fe^{+3} (X5)	6

Table (4): Design of Experiments by Takeuchi's method in Minitab program

NO.	Current density (mA/cm^2)	Na_2SO_4 (gm/L)	pH	H_2O_2 (mg/L)	Fe^{+3}(mg/L)
1	100	1	2	100	50
2	100	2	4	250	75
3	100	3	6	400	100
4	100	4	8	550	125
5	100	5	10	700	150
6	250	1	4	400	125
7	250	2	6	550	150
8	250	3	8	700	50
9	250	4	10	100	75
10	250	5	2	250	100
11	400	1	6	700	75
12	400	2	8	100	100
13	400	3	10	250	125
14	400	4	2	400	150

15	400	5	4	550	50
16	550	1	8	250	150
17	550	2	10	400	50
18	550	3	2	550	75
19	550	4	4	700	100
20	550	5	6	100	125
21	700	1	10	550	100
22	700	2	2	700	125
23	700	3	4	100	150
24	700	4	6	250	50
25	700	5	8	400	75

Table (5): Statistical description of the studied variables

Case Summaries						
	Efficiency	**Current density**	**Na_2SO_4**	**pH**	**H_2O_2**	**Fe^{+3}**
N	25	25	25	25	25	25
Missing Value	0	0	0	0	0	0
Mean	90.97	400	3	6	400	50
Std. Deviation	2.651	216.5	1.443	2.88	216	21.6
Minimum	83.81	100	1	2	100	20
Maximum	95.24	700	5	10	700	80

Table (6): Test of Normality

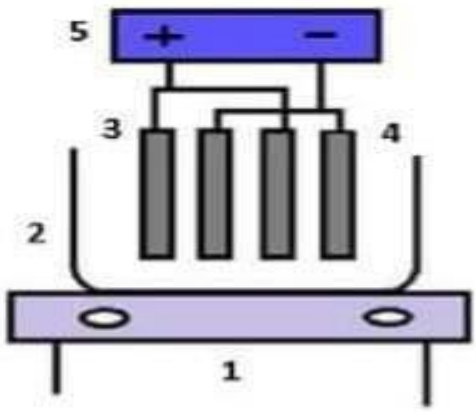
	Shapiro-Wilk		
	Statistics	df	p-Value
EFFICIENCY (y)	0.977	24	0.813
Current density (X1)	0.890	24	0.013
(X2) Na_2SO_4	0.890	24	0.013
pH (X3)	0.885	24	0.011
H_2O_2 (X4)	0.890	24	0.013
Fe^{+3} (X5)	0.899	24	0.020

Table (7): Tests to detect the presence of the problem of Collinearity Statistics

Collinearity Statistics		
	Tolerance	VIF
Current density (X1)	0.997	1.003
(X2) Na_2SO_4	0.997	1.003
pH (X3)	1.000	1.000
H_2O_2 (X4)	0.997	1.003
Fe^{+3} (X5)	0.994	1.006

Table (8): Values of the estimated parameters, standard error, t-test values and significance of each variable

Variable	**Coefficients**	**S.E.**	**$t_{cal.}$**	**p-value**
constant	**88.472**	**0.902**	**98.06**	**0.000**
Current density (X1)	**0.006**	**0.001**	**3.853**	**0.0012**
Na_2SO_4 (X2)	**0.115**	**0.264**	**0.436**	**0.667**
pH (X3)	**0.026**	**0.137**	**0.196**	**0.846**
H_2O_2 (X4)	**0.0023**	**0.002**	**1.161**	**0.260**
Fe^{+3} (X5)	**-0.024**	**0.022**	**-1.06**	**0.303**



Figure(1): Electrocoagulation reactor: Monopolar electrodes with parallel connection (MP); (1) Stirrer and temperature controller; (2) EC cell; (3) anode(stainless steel); (4) cathode(Titanium); (5) power supply.

Figure (2): A photograph of the system used in the experiments

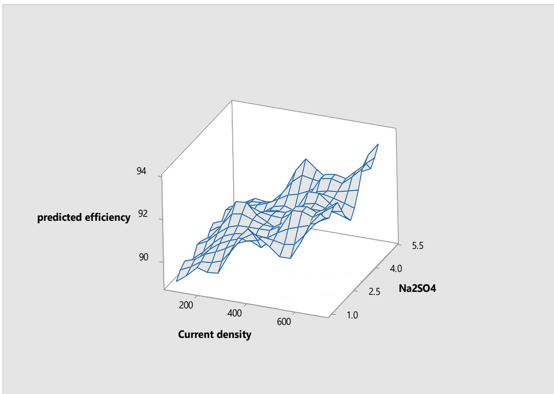


Figure (3): The response surface to the effect of the explanatory variables on the variable Efficiency (current density and Na2So4)

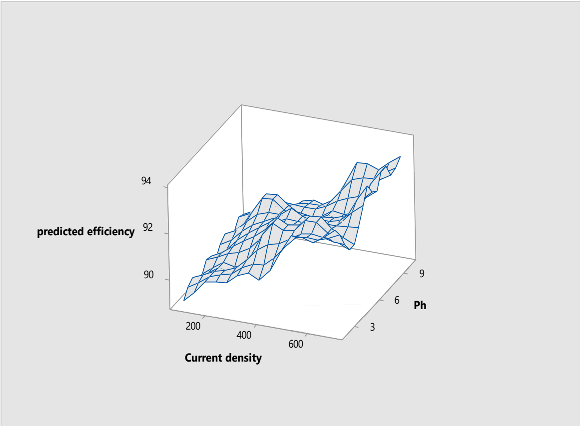


Figure (4): Response surface to the effect of the explanatory variables on the variable Efficiency

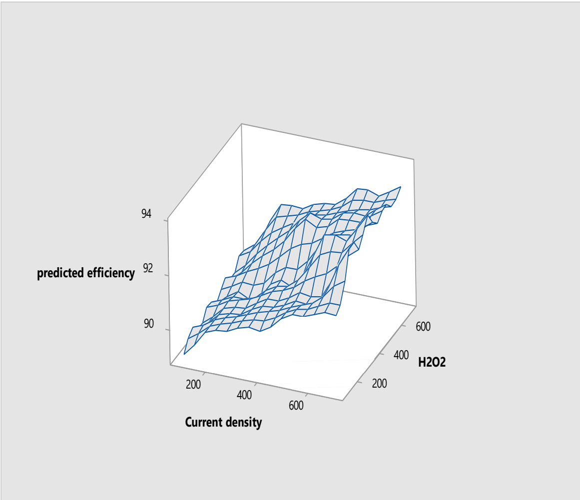


Figure (5): Response surface to the effect of the explanatory variables on the variable Efficiency

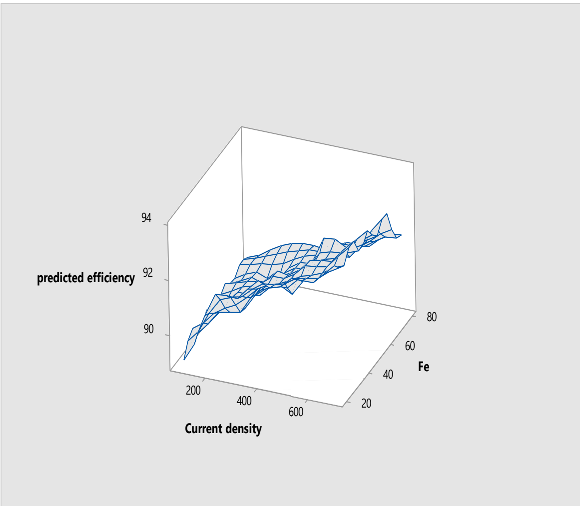
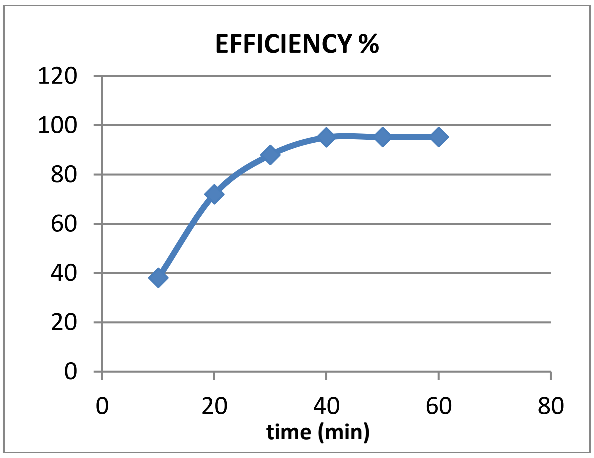


Figure (6): Response surface to the effect of the explanatory variables on the variable Efficiency



Figure(7): Relationship between removal efficiency and time

4. Conclusions

The results obtained prove the high effectiveness of the method combining electrocoagulation with the Fenton method to reduce COD. Through the results, we can summarize the conclusions as shown below.

- The highest COD removal efficiency was 95.238. Standard deviation= 2.651.
- Through the (Shapiro-Wilk) test, it is noted that the (P-value) of the Efficiency variable was above 0.05, which means we accept the null hypothesis, which states that this variable has a normal distribution.
- Shapiro-Wilk Statistics efficiency = 0.977, p-Value = 0.813.
- There is no linear relationship between the explanatory variables and the values of the tolerance coefficient.
- There is no problem of multiple linear relationships between the explanatory variables.
- Through the statistical analysis, it was found that the current density is the most influential factor on the efficiency of removal.
- The optimal conditions for this experiment were as follows: current density = 400 mA cm^{-2}, Sodium sulfate concentration = 3 gm L^{-1}, pH=6, hydrogen peroxide concentration = 400 mg L^{-1}, ferrous sulfate = 50 mg L^{-1}, time = 40 minute.
- The process of electrocoagulation is very fast compared to the process of Fenton, which is slow in the processing of organic materials, and since the time of removal was rather fast, the effect of electrocoagulation appeared higher than what is the effect of Fenton, which led to the electrocoagulation process is the main process in removing organic pollutants, while the Fenton process was a secondary process with less effect than the electrocoagulation process.

- The value of the acid function here is for the total process (electrocoagulation + photo-Fenton) simultaneously, were the results showed that the best acidity function is 6, because the effect of the electrocoagulation process, which tends to work in neutral conditions for many researchers, was greater than the effect of the Fenton process.

5. Conflicts of interest

"There are no conflicts to declare".

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7. References

[1] M. Abdulkarim and A. Embaby (2006), Refinery wastewater treatment: a true technological challenge, *Conference: The Seventh Annual UAE University Research Conference. UAE UniversityAt: Al Ain, United Arab Emirates, DOI: 10.13140/RG.2.1.4642.8562*.

[2] D.A. Iljuboury, P. Palaniandy, H.B. Abdul Aziz, Treatment of petroleum wastewater by conventional and new technologies A review , *GlobalNEST J., **19**, 3 (2017).*

[3] *C. E. Burklin, et al., Revision Of Emission Factors For Petroleum Refining, EPA-450/3-77-030, U. S. Environmental Protection Agency, Research Triangle Park, NC, October 1977.*

[4] Y. Mikhak, M.M.A. Torabi, A. Fouladitajar, Sustainable Water and Wastewater Processing, Chapter 3, Refinery and petrochemical wastewater treatment (2019).

[5] S. J. Kulkarni, Wastewater Treatment for Lead Removal: A Review, *IJSRSET J, 1, 3 (2015).*

[6] Corrêa, Albertina X. R., Tiepo, Erasmo N., Somensi, Cleder A., Sperb, Rafael M., Radetski, Claudemir M.(2010), Use of Ozone-Photocatalytic Oxidation (O3 /UV/ TiO2) and Biological Remediation for Treatment of Produced Water from Petroleum Refineries, *Journal of Environmental Engineering 136 (1),40-45. DOI: 10.1061/(ASCE)EE.1943-7870.0000111*.

[7] A. Alva-Argáez, Antonis C. Kokossis, R. Smith. The design of water-using systems in petroleum refining using a water-pinch decomposition,*Chemical Engineering Journal,Volume 128, Issue 1,2007,Pages 33-46,ISSN 1385-8947,https://doi.org/10.1016/j.cej.2006.10.001.*

[8] Pollution Prevention and Abatement Handbook, *WORLD BANK GROUP, Effective July 1998*

[9] B. Wang, W. Yi, G. Yingxin, Z. Guomao, Y. Min, W. Song, H. Jianying, *Environ, Sci. Technol. J., **49** (2015).*

[10] S. Zueva, V. Corradini1, E. Ruduk2, and F. Veglio, Treatment of petroleum refinery wastewater by physicochemical methods, *E3S Web of Conferences 161, 01042 (2020).* h ttps://doi.org/10.1051/ conf/20 2016101042 *ICEPP-2020* e3s

[11] K. Lal,and A. Garg, Effectiveness of synthesized aluminum and iron based inorganic polymer coagulants for pulping wastewater treatment, *Journal of Environmental Chemical Engineering, 7(5), 2019*, 103204,ISSN 2213-3437, https://doi.org/10.1016/j.jece.2019.103204.

[12] Moussa DT, El-Naas MH, Nasser M, Al-Marri MJ. A comprehensive review of electrocoagulation for water treatment: Potentials and challenges. Journal of Environmental Management. 2017;186:24-41. DOI: 10.1016/j.jenvman.2016.10.032

[13] Hakizimana JN, Gourich B, Chafi M, Stiriba Y, Vial C, Drogui P, Naja J. Electrocoagulation process in water treatment: A review of electrocoagulation modeling approaches. *Desalination. 2017;*404:1-21. DOI: 10.1016/j.desal.2016.10.011

[14] B. Özyurt and Ş. Camcıoğlu(2018), Applications of Combined Electrocoagulation and Electrooxidation Treatment to Industrial Wastewaters, in: intechopen,turkey, *Wastewater and Water Quality,pp.71-89.*

[15] E. Hernández-Franciscoa, J. Peralb, L.M. Blanco-Jerez. (2017) Removal of phenolic compounds from oil refinery wastewater by electrocoagulation and Fenton/photo-Fenton processes. *Journal of Water Process Engineering*, 19 (1) ,96–100.

[16] A.H.F. Tahir, N. Obeid, and S. Abdul Jabbar,(2016), REMOVAL OF VEGETABLE OIL FROM WASTEWATER BY PHOTO-FENTON PROCESS, *Journal of Engineering and Sustainable Development,20 (03),36-46.*

[17] X. Wang, S. Chen, X. Gu, K. Wang, Pilot study on the advanced of landfill leachate using a combined coagulation, Fenton oxidation and biological aerated filter process, *Waste Management 29 (2009) 1354–1358.*

[18] Francisca C. Moreira, Rui A.R. Boaventura, Enric Brillas, Vítor J.P. Vilar, Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, *Applied Catalysis B: Environmental,202, 2017, 217-261,ISSN 0926-3373, https://doi.org/10.1016/j.apcatb.2016.08.037.*

[19] A. Bach, G. Zelmanov, R. Semiat, Wastewater mineralization using advanced oxidation process, *Desalination Water Treat. 6 (2009) 152–159.*

[20] S. Wang, A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, *Dyes Pigment 76 (2008) 714–720*.

[21] A. L. Torres-Sánchez, S. J. López-Cervera, C. de la Rosa, M. Maldonado-Vega, M.Maldonado-Santoyo, J. M. Peralta-Hernández.(2014) Electrocoagulation Process Coupled with Advance Oxidation Techniques to Treatment of Dairy Industry Wastewater, *Int. J. Electrochem. Sci., 9(1), 6103 – 6112.*

[22] Flores N, Brillas E, Centellas F, Rodr´ıguez RM, Cabot PL, Garrido JA, Sir´es I. (2017) Treatment of olive oil mill wastewater by single electrocoagulation with different electrodes and sequential electrocoagulation/electrochemical Fenton-based processes. *Journal of Hazardous Materials 2010. https://doi.org/10.1016/j.jhazmat.2017.12.059*.

[23] Z. B. G̨nder · G. Balcıoğlu · Y. Kaya1 · I. Vergili, Treatment of carwash wastewater by electrocoagulation using Ti electrode: optimization of the operating parameters, *International Journal of Environmental Science and Technology,2019,1-12.*

[24] Garrido-Ramirez, E.G., Theng, B.K.G, Mora, M.L. (2010), Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions ,A review‖. *Applied Clay Science, 47(1), 182–192, ISSN 0169-1317*.