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Study of Electro-Fenton Oxidation for the Removal of oil content in refinery wastewater

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Abstract. In this study, refinery wastewater treatment scheme, the electro- Fenton oxidation process is obtainable. Through Fenton oxidation treatment, numerous working limits remained examined, for instance hydrogen peroxide, electrolysis time and pH. The effects of the working variables including the pH (2-9), hydrogen peroxide concentration (20-60 mg/L) and the reaction time (10-30 minutes) and remained thoughtful through means of answer surface methodology and Minitab-17. The current, agitation speed and sodium chloride of the aqueous solution consumed remained engaged as 1 Amps, 200 rpm and 0.2 g congruently. Beneath the finest standards of the employed variables extra than 98% oil removal in refinery wastewater.

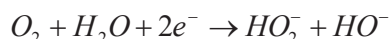
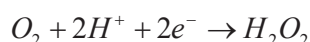
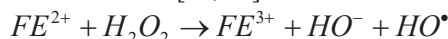
Keywords: Refinery wastewater, Organic content, Electro-Fenton, Hydroxyl radicals.

1. Introduction

Crude oil is malformed hooked on petroleum and additional valuable side-products finished refining developments. Crude oils refining produces large volumes of wastewater generated which contains of storm water, process water, cooling water and sewage [1], the oily wastewater produced remains 0.4–1.6 times the processed crude oil volume. This water contains contaminants remain toxic in nature even at micro quantities [2]. The wastewater composition is extremely variable and complex. The major hydrocarbon groups contemporary in refinery wastewater comprise alkanes, alkenes, alkynes, aromatics and complex hydrocarbon compounds covering oxygen, nitrogen, and sulphur [3, 4]. In specific, the organic content in oily wastewater can be in the variety of 20–200 ppm [5]. This water necessity remain separated as of the crude oil and disposed of in a way that fixes not violate ecological standards [6, 7]. the classical treatment developments consume remained organization to be fewer energetic aimed at removing around contaminants from wastewater because of their non-biodegradable, poisonous and intractable countryside [8]. Due to their toxicity and their potential carcinogenic effect, these effluents can cause irreparable damage to human health and the environment [1]. The purpose of meet environmental rules along with reuse and recovering of oily waste water, numerous researchers have attentive on treating oily waste water [2]. These wastes are a main source of water environmental contamination. Usually, the wastes are complete of frequent organic and inorganic components arising from the feedstock nature, which is calm mostly of hydrocarbons lengthways by an extensive variety of additional mechanisms [3], [4]. These obliging reuses conventional discount the elimination of drinkable water, a tremendously valued creation in frequent world areas [9]. Many conventional approaches have continued second hand to eliminate the organic content in refinery wastewater: biological treatment [10], membrane separation [11, 12], coagulation /flocculation and adsorption [5]. These approaches remain non-destructive through way of the fair transmission the non-recyclable substantial from unique phase toward alternative hooked on mud which leases aimed at a new type of pollution that (needless to approximately) wants another treatment [13]. Beyond the numerous physical-chemical approaches that



consume remained thoughtful ended years in the achievement of refinery wastewater, chemical processes have grown a predominant sole for the removal of organic content in oily wastewaters. Advanced Oxidation Processes (AOPs) have remained about defined by way of close ambient temperature behaviour procedures founded on tremendously reactive radicals [14]. In new-fangled year's keep have endured focused on chemical oxidation growths remains nameless by way of electro-oxidation [15, 16]. The Electro- oxidation scheme, an environs friendship and capability method, stood second hand to brand the oxidized oil content in refinery wastewater finished adding the substance and oxidizing agent in the reactions [17, 18].



Several researchers deliberate the elimination of organic pollutant by using electro Fenton oxidation : photovoltaic Electro-Fenton Oxidation [6], electro –Fenton processes [7], heterogeneous electro-Fenton [9, 10], bio-electro-Fenton [11], solar photo electro-Fenton process [12], Electro-catalytic [13]. This research engrossed on organic removal in refinery wastewater through electro-chemical oxidation and discoveries the finest worth of H_2O_2 concentration, learning the possessions of pH and electrolysis time in Electro- chemical processes.

2. Materials and methods

2.1 Oily wastewater

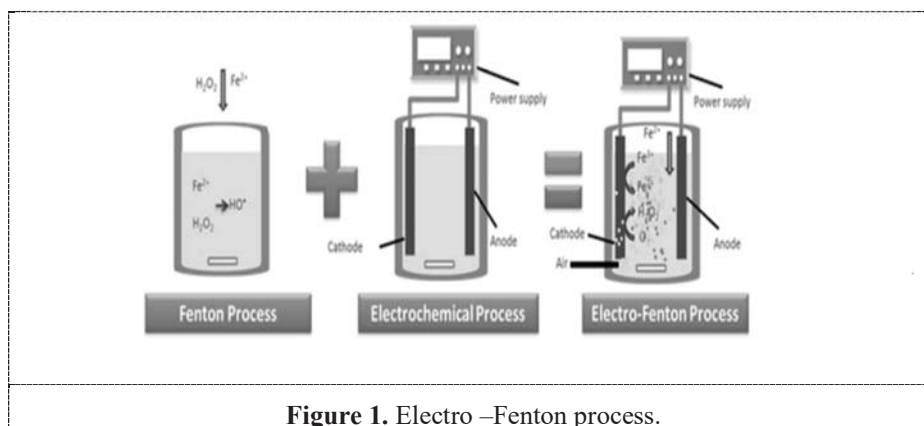
Refinery wastewater contaminated with organic droplets taster remained kind-hearted provided through the native refinery of Iraqi, Al-Muthanna government. The refinery wastewater rummage-sale in these investigations remain being elated after refinery unprotected toward the atmosphere and beforehand reserved in location similar to their innate home-based that includes oxygen undecided the behaviour process is useful. The properties of refinery wastewater are expected in Table 1.

Table 1. The properties of refinery wastewater

Parameter	value
Organic content	135 ppm
Turbidity	58.4 NTU
pH	6.75
Dissolved oxygen content	0.059 ppm
density	999 kg/ m ⁰
conductivity	111451 μ s/cm

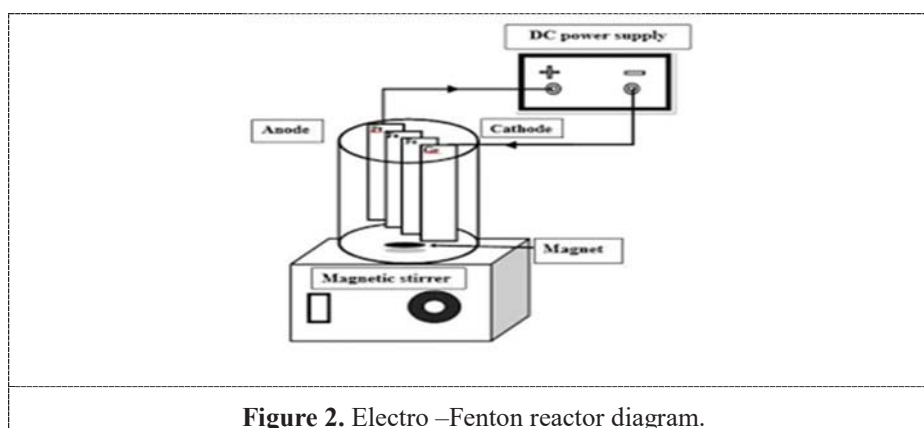
2.2 The description of electro-process

The electrodes used in the teaching was iron and Stainless steel and through method of cathode and anode congruently. The iron electrode dimensions stood 11 cm x 8 cm x 0.15 cm. The dimensions of Stainless-steel electrode were 14 cm x 9 cm x 0.34 cm. intended aimed at Electro-chemical oxidation procedure, the vigorous zone of the electrodes was earmarked by way of 25 cm² and the space of inner electrode was supported as 6 cm. This electro –Fenton configuration is exposed in Figure1.



2.3 Electro -Fenton procedure

In electro-Fenton oxidation technique, the experimental remained approved obtainable in a Fenton reactor comprising of 800 cm³ glass reactor 200 cm³ of refinery wastewater. The electrodes remained linked to a RXN-305D (DC power source), and additional 0.2 gm of NaCL. The voltage of DC was conserved by way of 29.6 v. The power source operates predictable at 5 min toward sweep the ions of iron in the oxidation reactor and previously complement quantities of H₂O₂ with the current and agitation speed and was secure at 1 Amps and 250 rpm congruently aimed at completely trials by way of bare in Fig.2. Instances remained quiet at steady time intermissions, centrifuged at 3000 rpm aimed at 10 minutes and the supernatant was tranquil aimed at oil approximation. Extra educations remained approved out finished variable the hydrogen peroxide amount, pH and electrolysis time. Preceding to usage in Electro-oxidation process, actual electrodes remained systematically cleaned by water to remove additional debris. The electrodes stood previously saturated in 1M hydrochloric acid aimed at 1 h shadowed by 1M sodium hydroxide aimed at extra hour. The electrodes remained put in distilled water as soon as not in practice. Then all usage, the electrodes remained eroded in 1M hydrochloric acid and 1M sodium hydroxide to eliminate slightly imaginable contamination.



2.4 Oil efficiency and UV spectrophotometer

The oil removal in refinery wastewater treatment remained envisioned through means of the subsequent (Eq. (1)):

$$\eta = \frac{C_o - C_t}{C_o} \times 100 \quad \dots (1)$$

Wherever η , efficiency of oil; C_o , measured concentration beforehand the action (ppm); C_t concentration worth afterward action (mg/L).

The difference in the oil content in refinery wastewater thru the electro-chemical oxidation method remained measured through UV-1800 Shimadzu (UV spectrophotometer, Japan) at 312 nm and the consequences remained rehabilitated hooked on the acquiescent concentrations (C).

2.5 Organic content determination in refinery wastewater

The organic content of refinery wastewater was strongminded by a UV-spectra meter (UV-1800 Shimadzu, Japan) spectrophotometer associated to a PC at maximum absorption wavelength (312 nm) NaCl (0.25 gm) has been added to (50 ml) of the refinery waste-water in the separating funnel in order to break the oil emulsion. Carbon tetra chloride (5 ml) has been added with the vigorous shaking for 2 min. After that for 20 min, when the solution separated into two distinct layers, the lower (organic) layer has taken for the absorbance measurement and from the calibration curve the oil concentration was obtained.

2.6 The design of experimental

In this education, the new conditions optimization heading for refinery wastewater treatment by electro-oxidation procedure remained presented through the central composite design (CCD) technique underneath RSM. The software Design Expert Minitab-17 remained used envisioned aimed at the untested design, quadratic classical, data examination, extraction and chart intrigue. The autonomous variables of electrolysis time (X1), hydrogen peroxide (X2) and pH (X3). They stood coded finished squat and high levels in the central composite design by way of bare in Table 2.

Table 3 demonstrations the usual and coded working variables by the Design Minitab software aimed at untried arrangements.

Table 2. Working limits

Limits	Varieties
X ₁ : electrolysis time (min)	10-30
X ₂ : H ₂ O ₂ concentration (ppm)	20-60
X ₃ :pH	2-9

Table 3. Usual and coded working variables

Usual Variable (Xi)	Oblique Variables				
	-2	-1	0	1	2
X ₁ : Electrolysis time (min.)	10	15	40	25	30
X ₂ : H ₂ O ₂ concentration (ppm)	20	25	35	45	60
X ₃ : pH	0.5	0.88	1.25	1.63	2

3. Results and discussion

3.1 Replicas of Regression

In this daily, relations amid the replies and the self-governing variables remained got finished the following second-order classical finished a least-squares technique [19]:

$$Y = B_0 + \sum_{i=1}^q B_i X_i + \sum_{i=1}^q B_{ii} X_i^2 + \sum_i \sum_j B_{ij} X_i X_j + \varepsilon \quad (2)$$

Anywhere Y remains the thoughtful replies; X_1, X_2 , to X_q are the employed variables; B_0 remains regression coefficient, B_i remains the linear regression coefficient, B_{ii} remains the squared regression coefficient then B_{ij} remains the cross-product regression coefficient; ε remains a random error. Table 4 demonstrates the working variables worth, percentage elimination of the deliberate responses, i.e. oil elimination.

Table 4. Consequences of the deliberate variables

Run	X_1 : Electrolysis time (min)	X_2 : H_2O_2 concentration (ppm)	X_3 : pH	Oil removal (%)
1	15	20	7	93.24
2	25	20	7	94.62
3	15	45	7	94.85
4	25	45	7	96.46
5	15	30	3	96.92
6	25	30	3	98.07
7	15	45	3	94.85
8	25	30	3	96.46
9	10	30	5	95.31
10	30	20	5	96
11	20	60	5	95.77
12	20	35	5	93.93
13	20	35	9	91.4
14	20	35	2	98.07
15	20	35	5	96.46
16	20	35	5	96.23
17	20	35	5	96.46
18	20	35	5	96.23
19	20	35	5	96.46
20	20	35	5	96.46

It was found from Table (4) that the regression F-value is 59.96 and the probability P value is 0, indicating the significance of the model. The correlation coefficient for this model, $R^2=0.92$, the average of the residues is 4.86 the responses, and the independent variables were observed.

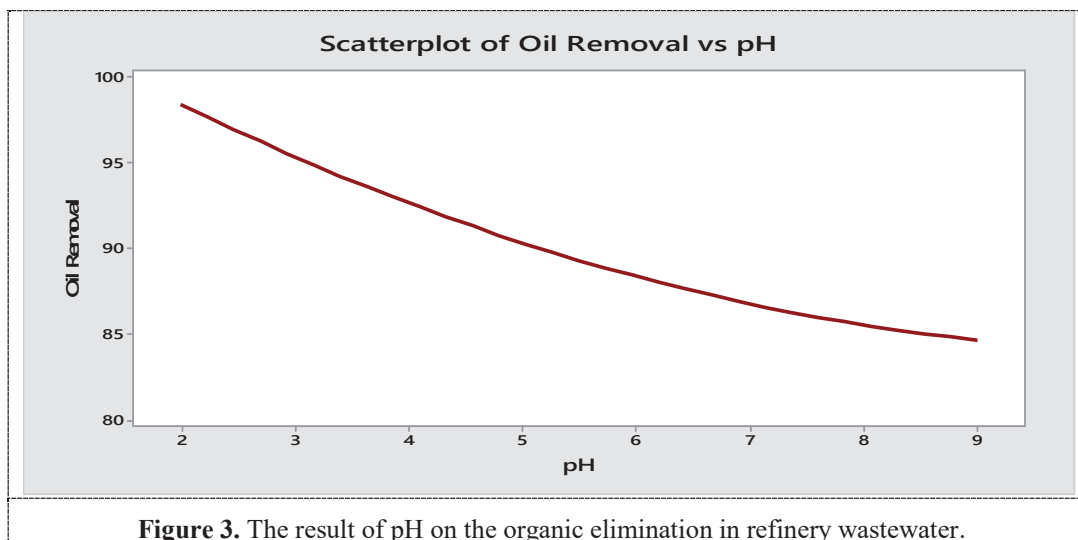
Table 5: ANOVA test results for the Electro oxidation process.

Effect	Sum of Squares	DF	Mean Squares	F-value	P-value
Regression	18130.17	12.0000	1510.848	59.95827	0
Residual	453.57	18.0000	25.198		
Total	18583.74	30.0000			

3.1.1 The effect of pH

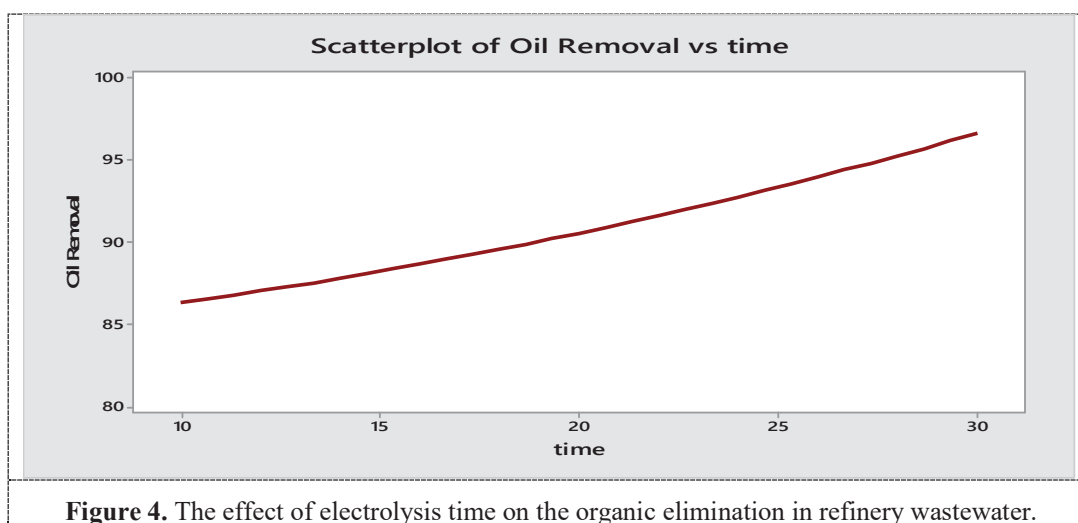
Through the intention of education, the importance of pH on the performance of the electro-oxidation procedure, investigations remained presented by pH of 2 to 9. The organic elimination increased with the decreasing pH, which affected maximum of 98.05% aimed at 3 pH with 30 minutes and 30 mg/L H_2O_2 at current of 1 Amps through method of exposed in (Fig. 3). Inferior organic removals remained touched for 9 pH, which were 91.35% with 20 minutes and 30 ppm of H_2O_2 , similar tendency stood stated aimed at squalor of oil by electro-Fenton oxidation. The natural pH of the oily wastewater remained changed through addition sulfuric acid. It is clear from the consequences in Fig.3. That the presentation of the electro-oxidation procedure remains extremely reliant scheduled the preliminary pH of the aqueous emulsion. The best presentation stood originate toward remain on the pH of the

suspension deprived of slightly alteration. These consequences suggest that the early pH theatres significant role in the start of the reaction intermediates. In additional arguments, pH is the regulatory limit in the H_2O_2 decay; at very squat pH, the H_2O_2 decomposes gradually then the reaction rate develops actual slow [20].



3.1.2 The effect of electrolysis time

In the direction of assess the electrolysis time effect, experimentations remained led through working behavior circumstances that were dependable with refinery wastewater and 1 Amps. Supreme elimination remained reached through 35 ppm hydrogen peroxide and 3 pH at minimum 30 minutes, the organic exclusion in refinery wastewater remains increase by surge the electrolysis time by way of exposed in Fig .4.This remained rendering by [21]. The increase electrolysis time the increase organic elimination competences in the refinery wastewater due to the noteworthy action of the adsorption procedure happened through the electro- Fenton reactor through method of the electrolysis time drawn-out [22] so complete organic elimination was gotten.



3.1.3 The effect of hydrogen peroxide

In the direction of determine the best H_2O_2 concentration to treat the refinery wastewater by means of electro-Fenton process; the H_2O_2 dose was wide-ranging from 20 to 60 ppm. By way of exemplified in Fig. 5, the oil elimination augmented as the H_2O_2 concentration augmented from 20 to 35 ppm and reduced afterward. Obviously, the H_2O_2 concentration remains a key influence that meaningfully effects the reaction kinetics since the OH radicals number produced in the -Fenton reaction is directly associated to the H_2O_2 concentration. Though, when the concentration of H_2O_2 exceeds the best worth, the reaction rates reduced by way of a consequence of the consequently named scavenging result of additional of H_2O_2 reacting with $\cdot OH$, thus lessening the OH obtainable toward destroy the wastewater organics [20].

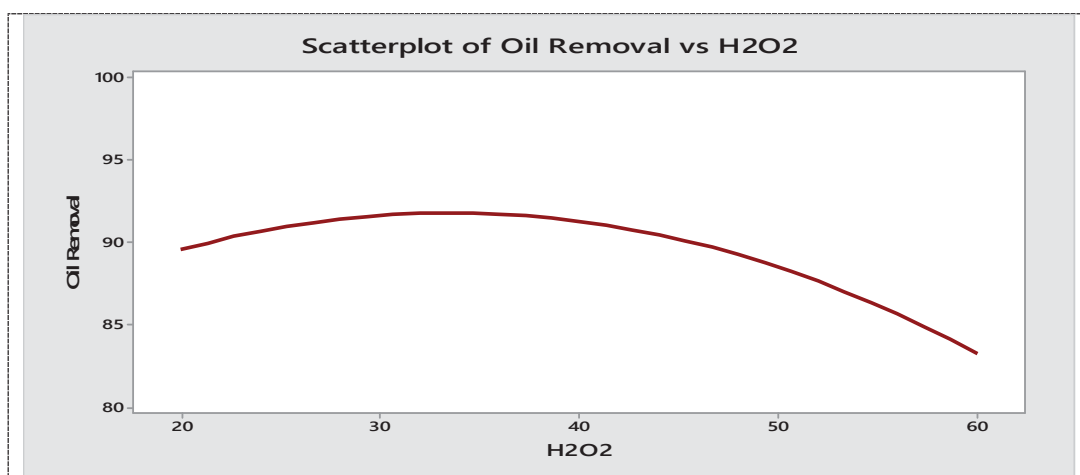


Figure 5. The result of H_2O_2 on the organic elimination in refinery wastewater.

3.1.4 The optimization of working variables

The finest worth of electrolysis time, H_2O_2 concentration and pH and remained became finished by means of an arithmetical software program. Figure 6 elucidates the penalties of the D-optimization dimension.

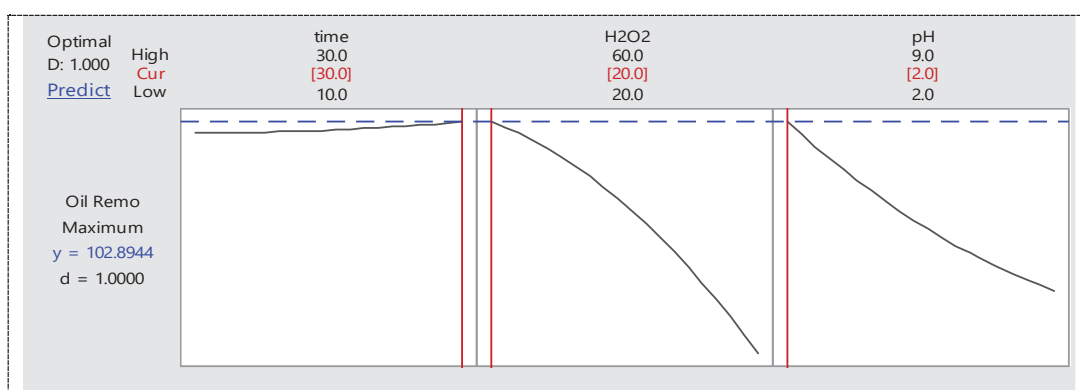


Figure 6. The best values of the working variables and the authenticated values of the deliberate replies aimed at the refinery wastewater treatment.

4. Conclusion

This paper shows the feasibility of performing electro-Fenton oxidation remediation of oil content bearing refinery wastewater by directly connecting the electro-oxidation reactor to the photovoltaic

generator. In this education, the electro-Fenton method was future to treat organic from oily wastewater. Lastly, the operating conditions were improved and obtainable to attain the finest consequences with the uppermost quantity of organic reduction. The mathematical associations originate have high regression coefficients aimed at altogether the thoughtful replies, which demonstration the satisfactory alteration of the polynomial second order model. The premium organic elimination (98%) remained got at pH of three, electrolysis time of 30 minutes and 35 mg/L of hydrogen peroxide. It seems that the Nano-porosity can remain used by way of a supplementary agent to hurry the decay of H_2O_2 and finally principal to upsurge in production of hydroxyl ions. Owing to the competence of electro-chemical process, this technique can be future as a relaxed method to refinery wastewater conduct.

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Conflict of Interest

No conflict of interest is declared by the authors.

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