Ferrate Potassium used as oxidant and coagulant for organic removal in produced water

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Abstract

In current study, an assessment has been done for the efficacy of using coagulation and oxidation technique for removing organic pollutants from industrial water of petroleum refinery, that will give an advantage to reuse treated water, and reduce environment pollutions. The study shows at low Fe (VI) concentrations potassium ferrate (VI) (K_2FeO_4) has outstanding antiseptic possessions and can deactivate a wide range of microorganisms. In addition, using Fe (VI) presenting Fe (III) as a byproduct, which is a harmless and an ecologically friendly substance ion, because its treatment does not produce any chlorination. For the data, the experimental designed via response surface methodology by the Box-Behnken design remained rummage-sale to analyze the three effects operating limits: ferrate concentration, oxidation time, pH, and their properties on the approach of the aforementioned pollutants removal. The study revealed that the constancy of potassium ferrate solution peaked at a pH of 6-7 and that a high concentration of ferrate solution was more stable than a low concentration.

Keywords: *Produced water, oil /water emulsion, refinery wastewater, water treatment, BBD.*

1. Introduction

In the time of water resource shortness, huge amounts of water are regularly injected into oil and gas industrial institutions to facilitate the recovery of oil [1]. This water lingers at the surface with contaminants, salt, and extra solutes, and remains usually recognized by way of "produced water" (PW) [2], and unique from one oilfield to another due to variations in the crude oil produced [3]. The PW is composed of two theoretical building blocks that can be created below, above, or privileged the hydrocarbon area or later additional fluids [4], and rummage-sale in the crude oil removal [5]. Organic and inorganic contaminants in generated water continue to cause serious ecological concern [6]. Treatment was active before eradication aimed at the assessment that oilfield wilds seek ecological contaminations [7]. The chemical composition of the contaminated water is highly complicated and varied. Alkynes, alkenes, aromatics, alkanes, polynuclear aromatics, and other complex hydrocarbon molecules containing nitrogen, oxygen, and sulfur are among the families of hydrocarbons that are presented throughout the PW process [8]. These materials are hazardous for nature. It is crucial to handle this before removal. By treating wastewater, it may be possible to enhance wastewater separation, recover lost pollutants, recycle used water, protect downstream amenities, and maintain environmental permits [9]. There are numerous problems with conservative separation tactics [10]. Chemical oxidation is a widespread and effective method used in water treatment operations to eliminate dangerous microorganisms and eliminate artificial organic materials. Currently, chemical oxidants such as chlorine, ozone, hydrogen peroxide, etc. are employed [11]. The redox possible of ferrate (VI) ions remains higher than that of molecular ozone in acidic circumstances (2.2 V) [12]. significantly, potassium ferrate (VI) has shown a number of benefits, including increased discrimination, and harmless ferric ions of by-product by way of ecologically benign water [13]. Ferrate (VI) has also been rationally and successfully used in various applications, such as super-iron batteries [14]. Because the byproducts of K_2FeO_4's redox reactions are rust-like iron oxides that are environmentally safe, the substance has received interest for use in "green chemistry" K_2FeO_4 has been referred to as a "green oxidant." On the other hand, some related oxidants, such chromate, are thought to be environmentally dangerous [15]. But the fundamental issue with

using K_2FeO_4 is that it is frequently overly reactive, as evidenced through the fact that it decomposes when it comes into contact with water [16].

The K_2FeO_4 decomposition in the aqueous solution shadows through equation (1) [17]:

$$4K_2FeO_4 + 10H_2O = 4Fe(OH)_3 + 8KOH + 3O_2 \tag{1}$$

The rate equation can be basic as equation (2):

$$\frac{-[K_2FeO_4]}{dt} = K[K_2FeO_4]^n \tag{2}$$

Where $d[K_2FeO_4]/dt$ is the oxidation rate, (t) is the oxidation time, (k) is the reaction kinetic constant and (n) is the order of this reaction. Aimed at the K_2FeO_4 composition, usually, it follows the one-order reaction. The equation is assumed by equation (3):

$$\frac{-[K_2FeO_4]}{dt} = Kt \tag{3}$$

And second-order reaction with a number of organic compounds [C] can be expressed as following in equation (4) [18]:

$$\frac{-[K_2FeO_4]}{dt} = K[K_2FeO_4]C \tag{4}$$

This research focused on eliminating organic matter from PW by means of ferrate potassium action and determining the optimal levels of oxidation duration, ferrate potassium concentration, and pH.

2. Materials and methods

2.1. Materials

In this study, ferrate potassium (K_2FeO_4) from Merck (Indian), sodium chloride (NaCl), carbon tetrachloride (CCl_4), sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4) from Merck (India) were utilized. 1N base or acid remained second-hand to change the pH of the solution.

2.2. Produced water

The laboratory of the Al-hidib oil field in the Al-Kut governorate remained ambitious through the essential aimed at produced water tasters that were sourced from the Midland Oil Company. Table 1 lists this water's characteristics. To break up the organic emulsion at the conclusion of each experiment, 40 ml of PW is added along with 0.2 gram of salt chloride in the separating funnel, then 4 ml of carbon tetrachloride was added, followed by 2 minutes of vigorous shaking. After the solution divided into two different layers after 20 minutes, the lower (organic) layer was determined using a UV-1800 spectrophotometer (Shimadzu Inc., Japan). WTW pH-720 meter was used to detect conductivity and pH readings.

Table 1: Specification of produced water

Limits	Values	Limits	Values
Organic content	250.11 (ppm)	Conductivity	112543 µs/cm
Turbidity	110.4 NTU	TDS	72027.52 (ppm)
TSS	20.2 (ppm)	Viscosity	1.055 m Pa/S
Specific gravity	0.9962	Iron	0.38 (ppm)

2.3. Ferrate potassium procedure

K_2FeO_4 experiments were completed in a 250 mL glass beaker of PW. For the oxidation and coagulation tests, magnetic stirrer was rummage-sold as an oxidation reactor, and the gator had been standardized previous to aim for velocity incline in relative toward the rate of mixing. 150 mL of generated water with undetectable turbidity were placed in a glass beaker and filled to capacity. To reduce the quick squalor of potassium ferrate in aqueous solution, fresh potassium ferrate solution made from deionized distilled water and pH buffer solution was made right before each examination. Finished quick mixing of ferrate potassium and PW with predetermined pH levels, the oxidation examinations were approved out. K2FeO4 was added in various amounts toward the glass beaker. The beaker was agitated at several mixing times and 200 rpm speeds. After the agitation reached a stationary state, the mixture was permitted to settle planned for 25 minutes.

2.4. Ferrate potassium procedure

In this research, unproven circumstances aiming at PW mineralization through the potassium ferrate method remained improved by means of the Box-Behnken-Design (BBD) method underneath RSM. By use of experimental design software,

data analysis, and graph plotting, Minitab-17 was a rummage sale. The high and low values of the independent variables, such as time (X1), pH (X2), and ferrate potassium (X3), in the oil content were recorded in table 2.

Table 2: Employed limits

Parameters	levels
X_1: time (min)	2-12
X_2: pH	3-9
X_3: Potassium Ferrate (ppm)	25-100

3. Results and discussion

3.1. FTIR analysis

The uncommon potassium ferrate's FTIR spectra in the range of 500-4000 are displayed in Figure 1. Damage-causing functional groups (hydroxyl, carboxyl, and amine) were discovered to be present on the surface of potassium ferrate using FTIR spectral analysis. The broad band at 3123.32 in pure bark powder is attributed to polymeric complexes' hydroxyl ($^-$OH) broadening or amine ($^-$NH2) stretching. The bands that appeared in the range 2922.30-2906.22 could be credited for the ($^-$CH2) symmetrically extending vibrations. It was thorough enough to convey the presence of functional groups on the potassium ferrate [19].
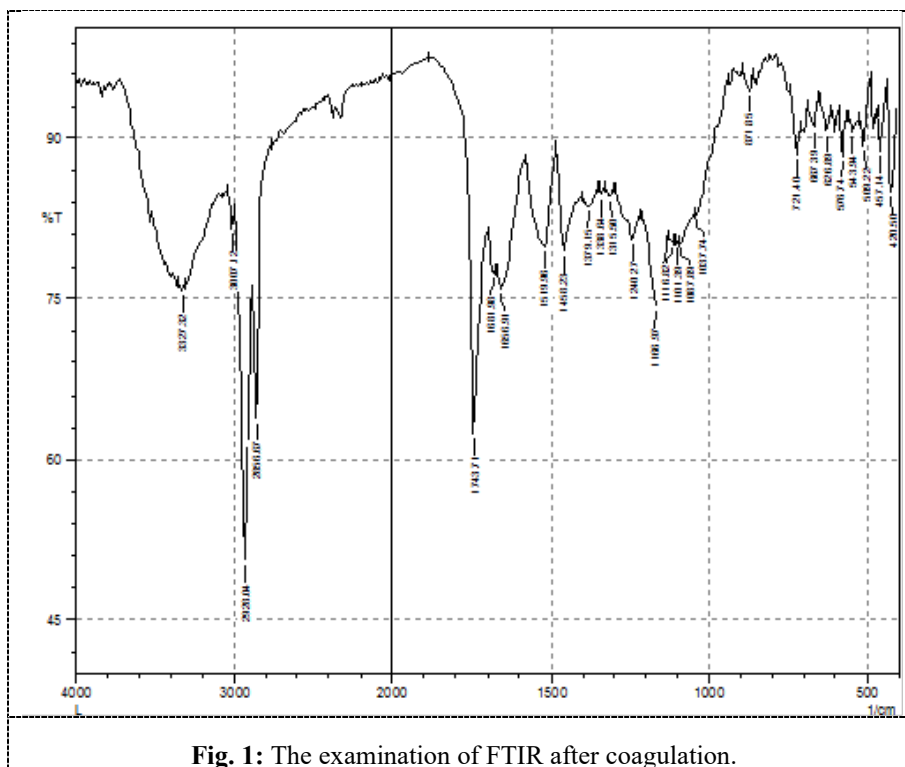

Fig. 1: The examination of FTIR after coagulation.

3.2. Statistical examination

Table 3 explain the values of the operational variables and the responses of the final concentration of oil content, and the removal competence for each run.
Based on experimental results, the mathematical equation (5) shown below is developed in terms of actual subjects linking the oil content response to the operational variables revealing the connections amid these variables:

$$\text{Organic Removal} = -34.19 + 7.757\ X_1 + 16.497\ X_2 + 0.2663\ X_3 - 0.4964\ X_1^2 - 1.2905\ X_2^2 + 0.0323\ X_1 X_2 + 0.02649\ X_2 X_3 \qquad (5)$$

ANOVA with a focus on the response surface model is demonstrated in Table 4. Degree of freedom, sum of squares for all parameters, adjusted sum of squares, adjusted mean of squares, Fisher-value, and P-test result were evaluated in this table. Solitary (6.38%) of the whole alternatives is not armour-plated through study, rendering to the constant of multiple correlation of the model, which is 99.88% consistent with the statistical meaning of the regression. In this model, R^2 and the adjusted manifold correlation coefficient (adj. R^2 = 98.37%) matched well.
Figure 2 displays the ideal conditions for the experimental work for the coagulation and oxidation systems as a consequence by means of Minitab software. More than 82% of the elimination was organic.

Table 3: Studied variables results

Run	X$_1$: time (min)	X$_2$: pH	X$_3$ Ferrate Potassium concentration (ppm)	Oil removal (%)
1	2	3	62.5	35.41
2	12	3	62.5	44.21
3	2	9	62.5	52.4
4	12	9	62.5	63.14
5	2	6	25	41.6
6	12	6	25	52.8
7	2	6	100	64.8
8	12	6	100	76.8
9	7	3	25	43.1
10	7	9	25	53.9
11	7	3	100	59.73
12	7	9	100	82.45
13	7	6	62.5	72.38
14	7	6	62.5	73.4
15	7	6	62.5	72.66

Table 4: Study of alteration for oil elimination

Source	DOF	Seq. SS	Adj. MS	Fisher Value	P–test Value
1-Model	9	2925.43	325.05	469.73	0.0001
Linear	3	1897.84	632.61	914.19	0.0001
X1	1	228.34	228.34	329.97	0.0001
X2	1	602.74	602.74	871.02	0.0001
X3	1	1066.76	1066.76	1541.57	0.0001
Square	3	990.98	990.98	477.35	0.0001
X$_1$^{2}	1	568.57	568.57	821.64	0.0001
X$_2$^{2}	1	498.05	498.05	719.73	0.0001
X$_3$^{2}	1	7.28	7.28	10.52	0.023
2-Way Interaction	3	36.62	36.62	17.64	0.004
X$_1$*X$_2$	1	0.94	0.94	1.36	0.296
X$_1$*X$_3$	1	0.16	0.16	0.23	0.651
X$_2$*X$_3$	1	35.52	35.52	51.33	0.001
Error	5	3.46	0.69		
Lack-of-Fit	3	2.90	0.97	3.49	0.231
Pure Error	2	0.56	0.28		
Total	14	2928.89			
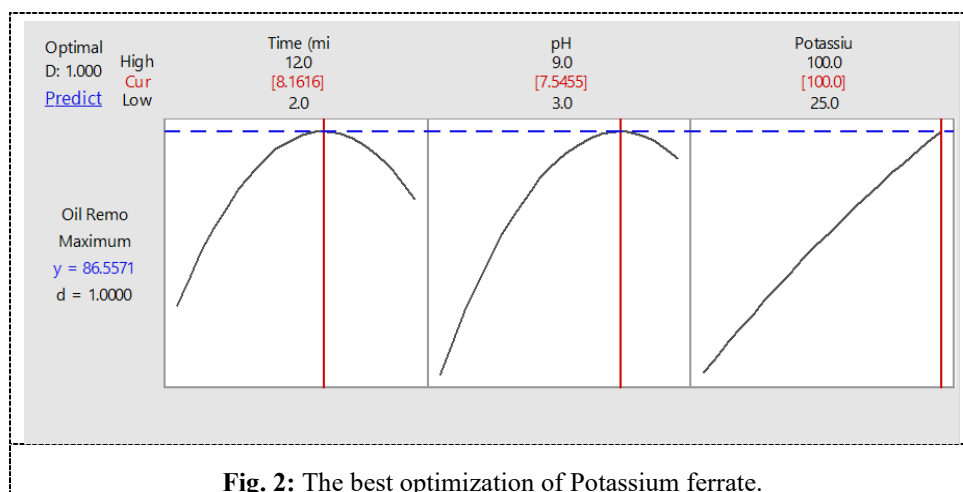
Fig. 2: The best optimization of Potassium ferrate.

3.2.1. The effect of oxidation time

Prior to teaching the coagulation and oxidation, it is crucial to evaluate the impact of reaction time on the oxidation. Trials are conducted with adsorption times ranging from 2 to 12 minutes at concentrations ranging from 25 to 100 ppm, and the results are shown in Figure 3. It is clear that all oxidation processes are profitable quickly, and oxidation symmetry can be obtained in less than ten minutes. Additional lengthening of the oxidation process does not obviously improve its

capabilities [20]. The fact that all active areas on the oxidant surface are initially vacant and the wastewater concentration is high, may be the cause of the uniqueness. Due to the outdated, insufficient access to superficially active locations, only a very slight increase in the organic acceptance is actually felt. As a result, 10 minutes was chosen as the ideal oxidation duration for organic content aimed at all evenness tests.

Fig. 3: The effect of time on oxidation treatment.
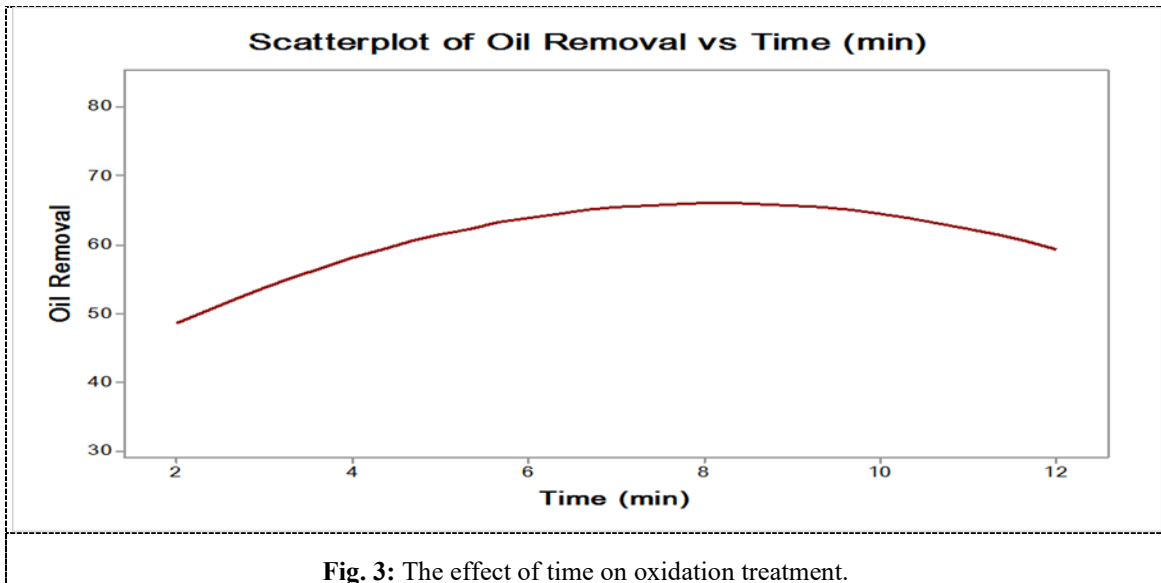
3.2.2. The effect of pH

Figure 4 depicts the effects of potassium ferrate removal of organic content in generated water at various pH levels. It was discovered that the rate of organic elimination initially increased with a rise in pH values, peaking at pH 6 -7, and then slightly reduced with an increase in pH values. The rate of organic content removal peaked when the pH was near to 9, then began to fall as the pH increased. These occurrences were mostly caused by potassium ferrate's different redox potentials. The elimination rate of organic content was clearly effective at pH 6-7 because potassium ferrate's redox potential looked to be at its highest under acidic conditions [21]. But as the pH increased, the main form of potassium ferrate's reduction result was Fe^{3+}, with weaker flocculation. When the pH of the solution reached 9.0, potassium ferrate's redox potential fell but its stability in solution was improved, leading to dramatic flocculation effects on the elimination of organic content. In general, the clearance rate of organic content fell significantly as the flocculation reaction gradually decreased with the increase in solution alkalinity [22].

Fig. 4: The effect of pH on oxidation treatment.
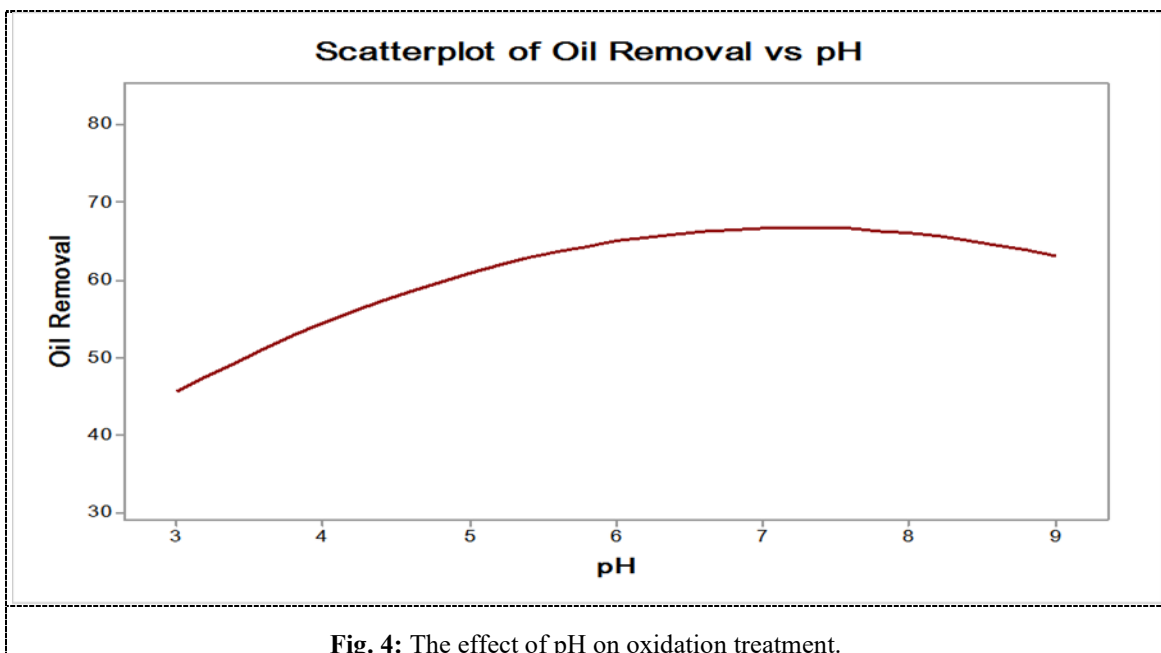
3.2.3. The effect of potassium ferrate

The experiments are displayed in the following oxidation schemes. Figure 5 demonstrations how the recovery of oil content from produced water remained affected through oxidation. As can be seen in the figure 5, the concentration of potassium ferrate increased, increasing organic elimination from 48.2% at 25 ppm to the maximum elimination of 74.3% at 100 ppm. Figure 5 shows how quickly the reaction between the organic content and the ferrate occurred, with a significant amount of organic matter degrading within the first two minutes and then more gradually over the course of the following eight to ten minutes. This was true for all Fe (VI) organic content molar ratios between 25 and 100 ppm, and it was clear that the rate of reaction rose dramatically with molar ratio [23].
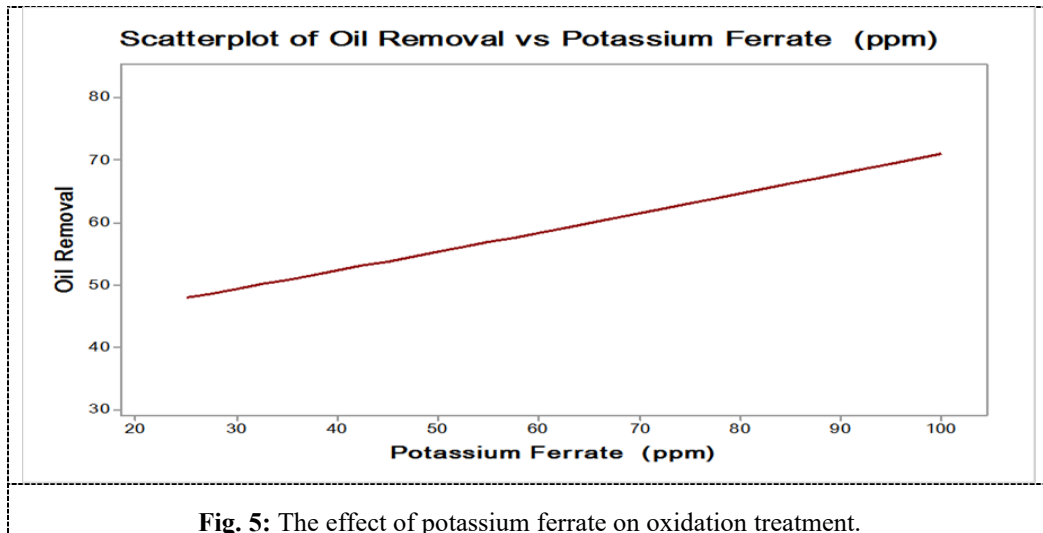

Fig. 5: The effect of potassium ferrate on oxidation treatment.

3.3. Interaction plot of variables

The significances in figure 6 show that, with the exception of high concentrations that tend to drop directed by a specific retro because of a lack of sufficient places on the surface of the oxidation substantial in the way of reaching a comparatively high removal ratio, the high competence response of abolition along the time of oxidation is directed at all initial organic concentration values [24].
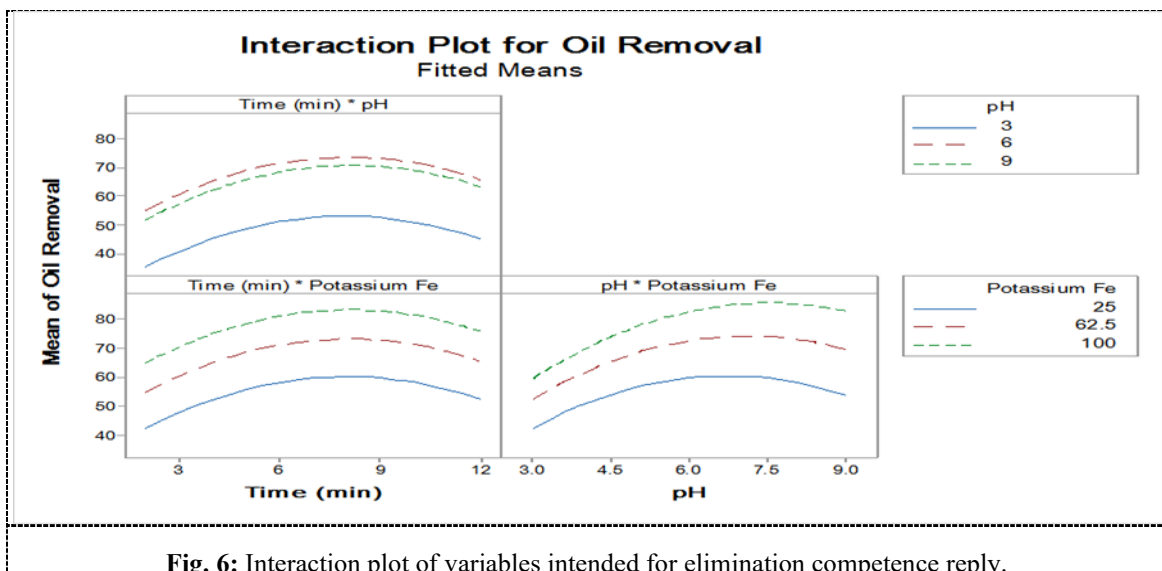

Fig. 6: Interaction plot of variables intended for elimination competence reply.

4. Conclusion

The study presented the viability of using the potassium ferrate by way of oxidant and coagulant aimed at refinery wastewater, particularly for removing oil content and other organic impurities, as a suitable oxidant. The content of potassium ferrate, oxidation time, and solution pH all had an impact on the removal effects. For the efficient use of potassium ferrate in the process of treating water. Fe (VI) is, nevertheless, largely stable in a middle pH range of 6-7. The proposed potassium ferrate oxidation method may have compensatory effects on the wastewater treatment process in

refineries. Consequently, potassium ferrate in oxidation scheme enhanced through response surface method has a cheerful future in the water and wastewater setting aimed at both organic and inorganic pollutant elimination.

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