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USE BASIL SEED IN THE REMOVAL OF PETROLEUM HYDROCARBONS FROM INDUSTRIAL WASTEWATER FOR OIL REFINERY COMPANY

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Abstract: In this work, a basil seed was used in the removal of total petroleum hydrocarbons from industrial wastewater in the refinery oil company in Basra governor by coagulation and flocculation utilizing the design of experiments technique with the method of (analyzing screening designs). The experiments' independent variables (pH, dose of the substance used for removal, and time of the experiment). Furthermore, the relationship between the independent variables of the tests and their influence on the elimination process. As previously discussed, the results revealed that the optimum model in this study is the square model, and the maximum removal was 98 percent at PH (3), dose (3 and 1) ml, and time (60 and 30) minutes, and a comparison was made between the experimental design DOE and the multiple linear regression MLR to determine the effectiveness of the system used, which proved its great effectiveness. Where there was a significant convergence between the real and predicted effects of DOE removal, MLR was too far from the real results of DOE removal.

Keywords: Flocculation and coagulation, wastewater treatment, Basil seed , TPHs

1. Introduction

Industrial operations are a major source of air, water, and soil pollution, and one of the most harmful of these pollutants is petroleum hydrocarbons, which has resulted in changes in the physical, chemical, and biological features of water due to the dumping of various industrial wastes since the industrial revolution, particularly in the last two centuries. Petroleum hydrocarbons released by industrial activities harm aquatic life and degrade ecosystems by accumulating inside food chains and causing living species to create harmful secretions. As a result, human activities endanger critical water supplies, and industrial and urban development are converging on these resources [1-2]. "Hydrocarbons" are organic compounds with solely carbon and hydrogen in their molecular structure [3]. It is one among the most essential components of crude oil, having produced through geological time and under a variety of conditions [4]. Many factors drive the formation of crude oil in the earth's deep layers, the most important of which is the intense temperature and tremendous pressure on fossil creatures [5]. Petroleum hydrocarbons account for roughly 50–98% of crude oil's total composition [6]. The remaining percentage of crude oil composition is made up of non-hydrocarbon molecules

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such as nitrogen, sulfur, and oxygen compounds (NSO), asphalt compounds, and trace elements (Co, Fe, U, Pb, V, Ni) [7-8]. This crude oil mixture is known as total petroleum hydrocarbons (TPH) [9]. Furthermore, the major components contained in crude oil can be categorized into four classes based on their solubility in organic solvents [6-8]. In this investigation, petroleum hydrocarbons will be coagulated utilizing natural coagulants. Coagulation is a procedure that, in conjunction with flocculation, is widely utilized in many industries as an essential component of the total treatment of industrial and municipal wastewater [10]. Flocculation is a physical process that is based on the accumulation of small slow-settling blocks and their agglomeration, which is generated from the coagulation process to form large-sized and high-density blocks, which are then removed by separation processes such as filtration or sedimentation by gravity, or in other ways [11-12]. Many different materials can be utilized to treat various types of water and wastewater, including inorganic coagulants, organic flocculants, composite materials, and hybrids. The most generally used coagulants are inorganic coagulants, followed by organic flocculants, composites, and hybrids [13]. Included in this research will be the use of natural coagulants that are both environmentally friendly and non-toxic is Basil Seeds (*Ocimum basilicum*). Investigate the impact of the factors and their reactions. The term "design of experiments" refers to a statistically methodical and organized approach of conducting experiments that is distinguished by covering a broad range of statistical experiments and obtaining exceptionally clear results with a small number of experiments. As the parameters vary at the same time through a series of experimental processes to establish the link between these elements that affect the response of the process outputs in order to prevent wasting time and money and to produce the optimal conditions for conducting experiments [14]. This study attempts to reduce or eliminate petroleum hydrocarbons from industrial wastewater in the Basra Governorate, which is represented as liquid waste from industries and manufacturers.

2. Materials and methods

2.1-Materials;

All solvents and materials employed in this study were analytical pure grades, including Benzene (United Kingdom), Hexane (Germany), Chloroform CHCl3 (India), Glass wool (India / Mumbai), Silica gel 100-200 mesh (India / Mumbai), Aluminum oxide Al2O3 (India / Mumbai), Sodium sulfate anhydrous Na2So4 (India / Mumbai), HCl 35 percent (India / SDFCL), KOH.

2.2- Wastewater sources

This study's wastewater samples were obtained at South Refineries Company's final basin, which is located at 30o27'38N, 47o39'47E. This water contains oil concentrations created as a result of the industrial processes that occur on crude oil when it is converted into fuel and other oil derivatives, and these samples were analyzed for oil contamination. The determined value of the industrial raw wastewater sample from the South Refinery Company including total hydrocarbons petroleum is **14,480 mg/l**.

2.3-Extraction of Petroleum Hydrocarbons

According to the UNEP (1989) method, for extracting hydrocarbons from wastewater, a certain volume of water was taken and mixed with a certain amount of chloroform, then separated the organic layer and left to dry from chloroform, and then dissolved the remainder with hexane and passed it on the separation column, as detailed in the method UNEP.

2.4- Coagulation and Flocculation Processes

The tests were performed at room temperature using the Jar Test equipment, which consists of six jars filled with 700 ml of sample wastewater, the pH of which was adjusted by adding HCL (1 N) KOH (1 N), and then a specific dose of the material used to remove petroleum hydrocarbons was added to each jar according to the experiments that were established by the DOE software, and the samples were allowed to settle without shaking for 35 minutes after being mixed at a rate of one minute. The elimination efficiency of petroleum hydrocarbons was determined using the following formula:

$$\text{Removal Efficiency} = \frac{Ci - Cf}{Ci} * 100 \dots\dots\dots\dots..(1)$$

Where Ci and Cf are the initial and the final concentration of pollutants respectively.

2.5- Design of Experiment (DOE)

The Minitab (v. 20) program was used to statistically design experiments and study the influence of the factors used in the experiments (pH, a dose of materials used as a coagulant and flocculent in the removal of petroleum hydrocarbons, as well as experiment time) specified within the design and with the fewest number of experiments as possible. Based on the values of R-sq and Residual, the approach of (analyzing screening designs) was applied for the independent variables of the experiments (pH, dose, and time of the experiment) to obtain an equation and evaluate the efficiency of this equation to predict elimination.

The typical form of CSD (create screening design) in this research is ASD, which comprises of factorial points (k represents factors= 3). PH wastewater (meaning by X1), dosage (indicates by X 3), and time were the independent variables (factors) (means by X 2) These components have three levels, as illustrated in Table 1: low level (1), central level (0), and high level (+1). Preliminary tests are frequently conducted to determine the precise values of these components' coded amounts. These codes are also included in Table 1.

Table 1. Levels of experimental factors for independent variables.

Factor	*Name*	*Unit*	*Minimum*	*Coded of Low*	*Mean*	*Coded of Mean*	*Maximum*	*Coded of Maximum*
X1	PH	-	3	-1	6	0	9	+1

X2	Time	Min.	30	-1	45	0	60	+1
X3	Dose	ml	1	-1	3	0	5	+1

The second-order polynomial equation is used to demonstrate the link between the factors (X1, X2, and X3) and the analyzed response (Y).

$$Y = f(x) = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X^2{}_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \; \dots\dots\dots\dots (2)$$

where Y is the response model (hydrocarbons petroleum removal); β0 is the constant coefficient; βi is the linear term coefficient; βii is the square term coefficient; βij is the quadratic term coefficient; k is the number of independent variables; Xi and Xj are the coded values of the independent variables.

2.6- Multiple Linear Regression (MLR)

The multiple linear regression (MLR) equations are utilized in this investigation because they show linear correlations involving more than two variables. The MLR equation expresses a linear relationship between a response variable (Y) and a number of predictor variables (x1, x2, x3). The general MLR equation is illustrated in Equation (3):

$$\boldsymbol{Y\ Removal\ TPHs} = 0.804 - 0.00371\ X1 + 0.00253\ X2 + 0.000022\ X3 \text{ --------- } \mathbf{(3)}$$

3-Results and discussion.

3.1- Statistical Analysis

There are 13 tests to evaluate the coefficients for independent variables in the coagulation and flocculation process, as indicated in Table (2). (Dosage, pH, and time). To establish the correlation of experimental data and to generate a regression equation for each reaction, many models such as linear, square, and 2-way interaction can be utilized. These models may be related with experimental data, however careful model selection is essential because the chosen model correlates with experimental data based on its adequacy. Thus, based on the experimental data, the square model was proposed to describe the correlation between experimental data and all replies, because it is the best model to reflect the correlation between experimental data and all responses, with the lowest F value and P-value. As a result, this model was used. Equations depict the final square model for removal response in terms of coded components (Eq. 4)

Y Removal TPHs = 1.300 + 0.1185 X1 - 0.03582 X2 + 0.0938 X3 - 0.01202 X1*X1 + 0.000427 X2*X2 - 0.01050 X3*X3 + 0.000147 X1*X2 + 0.00062 X1*X3 - 0.000952 X2*X3----- (4)

Table 2: Experimental design and responses

RUN	PH	TIME M/H	DOSE ML	TPH MG/L	REMOVAL %
1	6	60	5	550.06	**96%**
2	3	60	5	1500.25	**90%**
3	9	30	5	2247.891	**84%**
4	3	30	3	360.64	**98%**
5	9	60	3	1500.213	**90%**
6	9	45	5	4145.933	**71%**
7	6	45	3	852.6289	**94%**
8	3	60	1	276.588	**98%**
9	3	30	5	860.887	**94%**
10	6	30	1	413.353	**97%**
11	9	60	1	1495.982	**90%**
12	9	30	1	2892.846	**80%**
13	3	45	1	1800.08	**88%**

3.2-Analysis of variance (ANOVA)

The "goodness of fit" of the square model findings for each response was determined using ANOVA. Because of their low F-value, some values in equation (4) were statistically insignificant. As a result, the response equation must discard these values. The P-value is more significant for models with a response equation (4) and a likelihood of the alpha value of e 0.05 confidence level.

These equations contain some statistically non-significant terms with a high P-value (Eq 4). Non-significant terms in response equations must therefore be deleted. The 0.003 probability (p-value) of the square model for total petroleum hydrocarbon removals is shown in Table 3. The TPHs elimination model's (p-value) indicates that the model is statistically significant.

Table 3 displays the results of an analysis of variance (ANOVA) on the terms in each response (linear, quadratic, and 2-way) model.

Response	Source	df	*F* value	*p* value	Remark

TPHs removal	X_1 X_2 $X3$	1 1 1	136.30 5.14 14.33	0.001 0.108 0.032	significant Not significant significant
	$X1X1$	1	101.13	0.003	significant
	$X2X2$	1	80.00	0.002	significant
	$X3X3$	1	15.26	0.030	significant
	$X1X2$	1	1.06	0.380	Not significant
	$X1X3$	1	0.33	0.605	Not significant
	$X2X3$	1	19.82	0.021	Not significant

Notes: X1: means PH; X2: means Time (m); X3: means Dose (ml), df: degree of freedom

The coefficient of determination (R square) was used to assess the model's quality, which shows the proportion of total variance in the response predicted by the model. When (R square) is near one, the model predicts the reaction better [14]. The coefficient of determination for TPHs removals was 0.9919. As a result, the observed and anticipated response values are strongly dependent and associated [15]. The adjusted R2 for TPHs removals was 0.9677, which is extremely similar to the R2 value in response equations. As a result, the experimental data prediction is rated adequate [16]. Table 4 shows that the total variation for TPHs removals was 96 percent based on the adjusted R square for the pollutants removal models. This can be explained by the independent variables, with only about 4% of total variation remaining unexplained by these models.

The Pareto chart can be used to identify the degree and significance of the impacts, as well as the impact of each element on the ultimate reaction to TPH elimination. Bars that cross the reference line on the Pareto chart are statistically significant. In (Fig. 1), the bars representing the factors (X1, X1X1, X2X2, X2X3, X3X3, and X3) cross the reference line (3.18). At the 0.05 level, these factors are statistically significant.

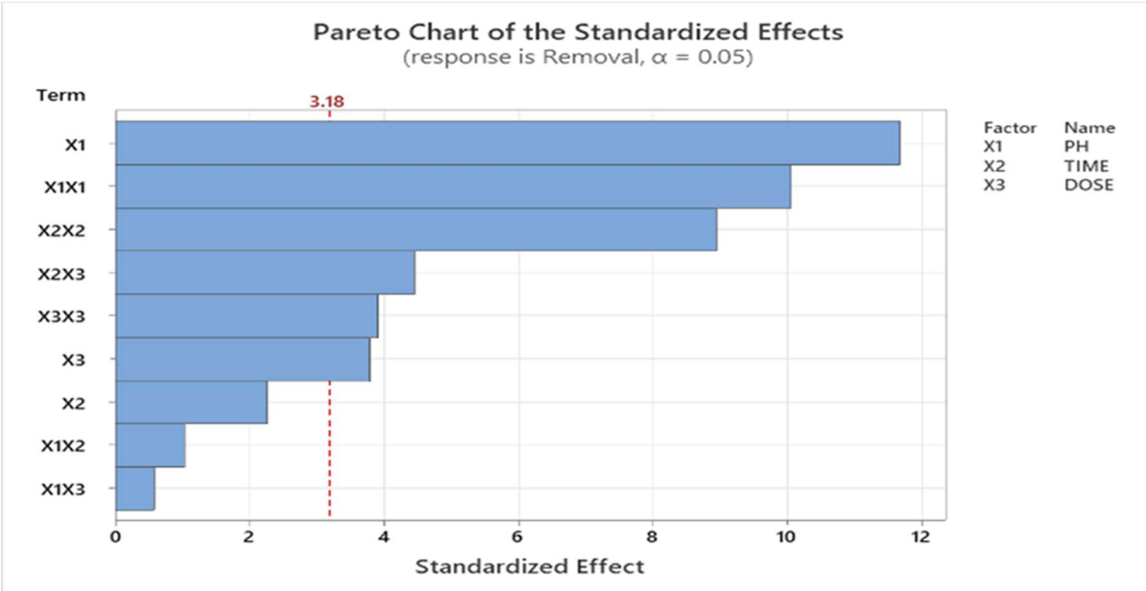


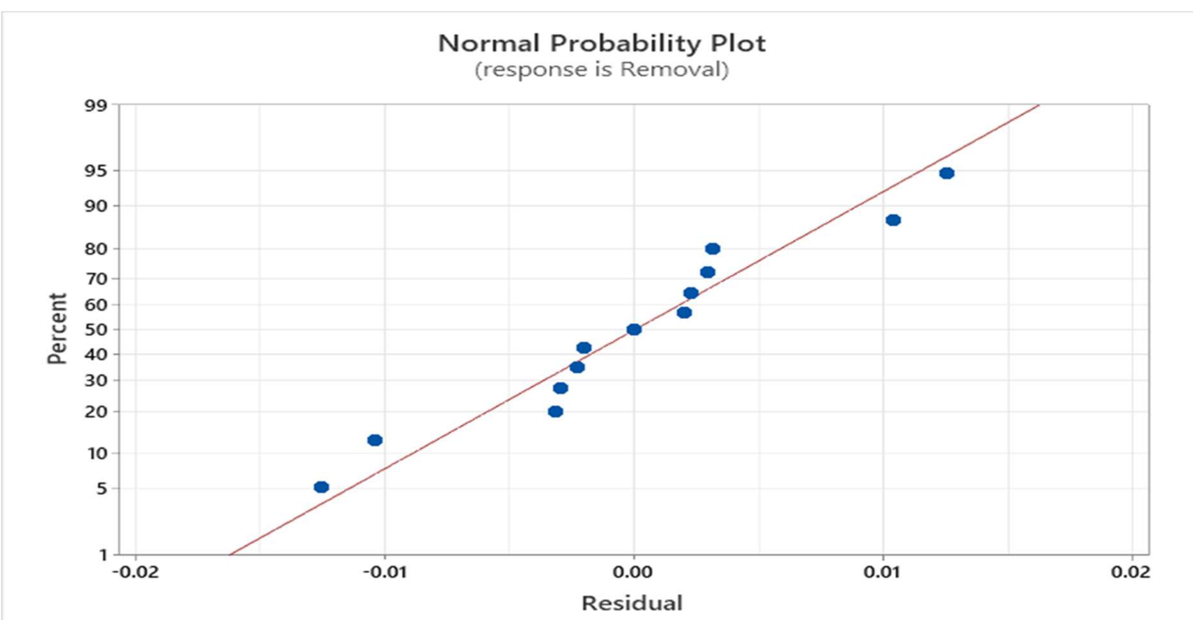
Figure.1) the Pareto chart shows the importance of the effects in the removal TPHs by a Basil seed

To determine if the distribution of samples is normal or abnormal, we utilize a normal probability plot (fig.2), which presents the distribution of samples closest to the picture reference line, which is a normal distribution.

(Figure.2) display the normal probability plot to determine sample distribution and residual in removal TPHs by a basil seed.

3.3- MLR

The coefficient of determination for TPHs removals was 0.4192. This suggests that there is relatively minimal reliance and correlation between the observed and predicted response levels. [15]. MLR had a probability (p-value) of 0.506 for total petroleum hydrocarbon removals. The TPHs elimination model's (p-value) suggests that it is not statistically significant.



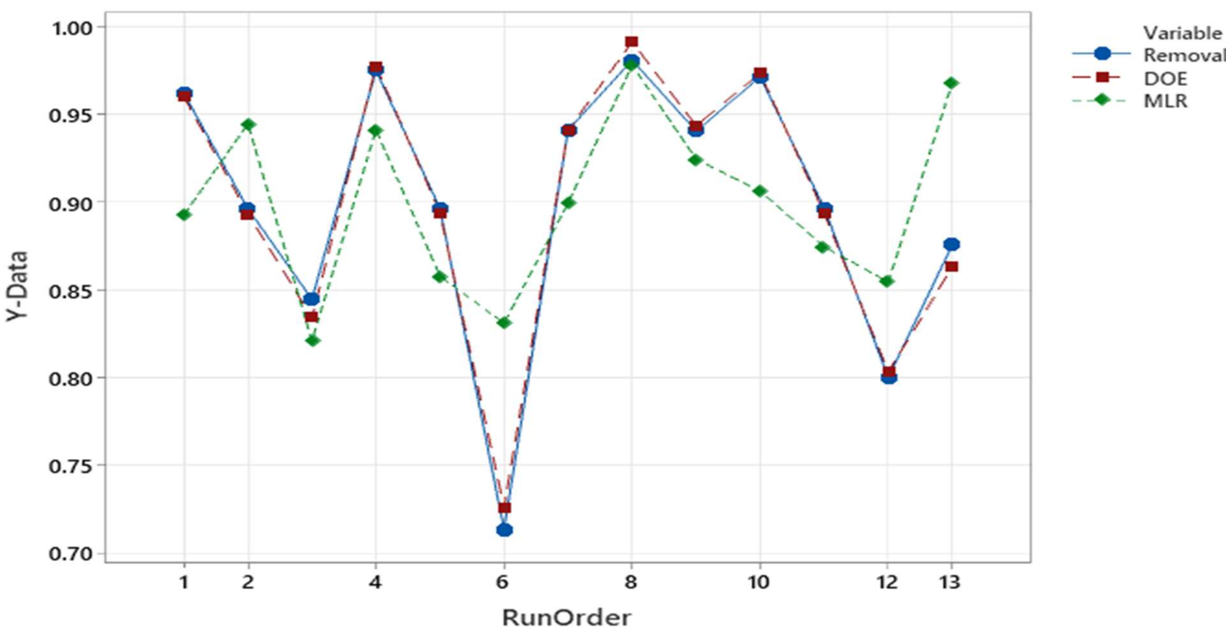
3.4- Comparison between DOE and MLR

The scatterplot (Figure 3) shows the difference between DOE and MLR. It was discovered that the DOE model's results are statistically more significant in the calculation removal than the MLR model's results. Where there was a significant convergence between the real and predicted results of DOE removal, MLR was quite far from the real removal results.

(Figure.3) display comparison between DOE, MLR, and the extent to which they predicted the real removal

3.5- Analysis of the coagulation Process

For each model, the responses of experimental variables are displayed in 3D surface plots, and these graphs can be utilized to determine the major interactions between the variables. The greatest elimination of total petroleum hydrocarbons employing basil seeds was 98 percent at pH 3 and doses of (3 and 1) ml at times of (30 and 60) minutes, according to Table No. (2). The lowest clearance rate was 71 percent at pH 9 and a dosage of 5 ml over 45 minutes. Figure No. (4) depicts the relationship



between the PH and dose factors in total hydrocarbon removal, as the removal percentage increases at PH (3.5 to 7) and a dose between (1 to 5) ml to achieve a maximum removal rate of greater than 95 percent. At PH 9 and a dose of 5 ml, however, the elimination is reduced by less than 75%.

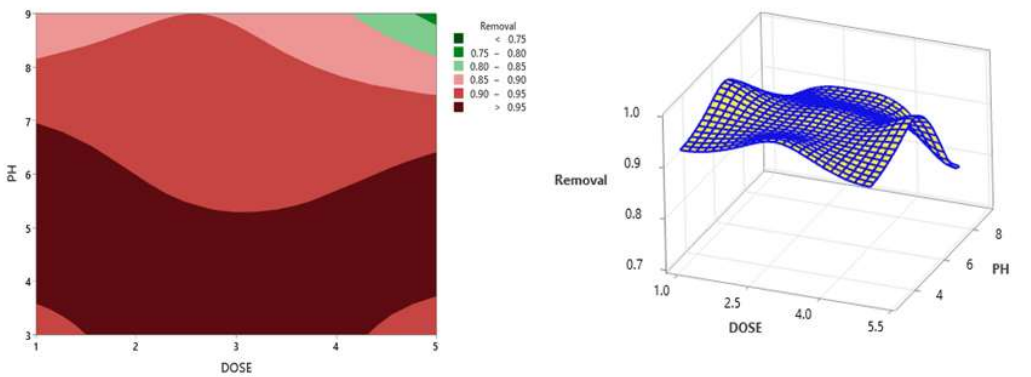


Figure No. (4) Contour plot and 3D surface plot for the relationship between the PH and dose variables in hydrocarbon removal

While the link between the PH and time factors in hydrocarbon removal is outlined by the 3D plot and a contour plot drawing (Fig. 5), as the removal increases within the range of PH (3 to 7) and time (30 to 60) minutes to achieve removal greater than 95 percent. However, the clearance percentage drops by less than 75% at pH (8.6 to 9) and time (35 to 50) minutes.

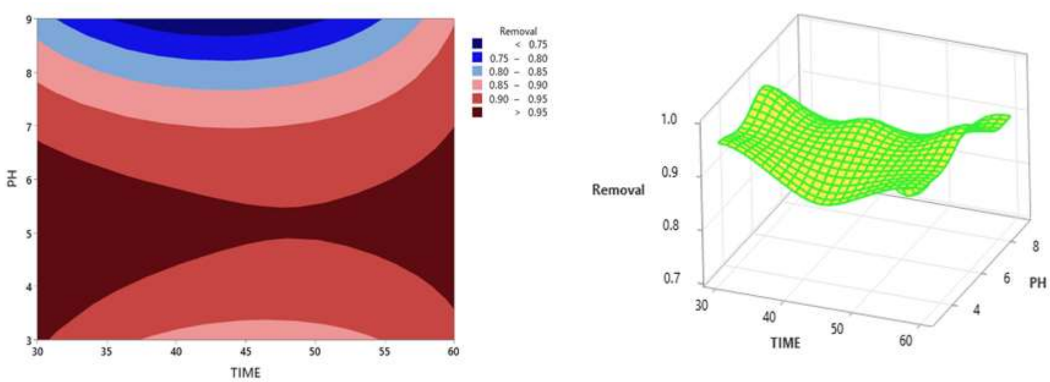


Figure No. (5) Contour plot and 3D surface plot for the relationship between the PH and time variables in hydrocarbon removal

In terms of the link between the dose and time factors in the effectiveness of petroleum hydrocarbon removal, the removal percentage increases at doses (2 – 4) ml and periods (30 – 45) minutes to achieve high removal of more than 95%. However, at a dose of (4.7-5) ml and a time of (40-50) minutes, the clearance percentage is less than 75%. As illustrated in Figure No (6).

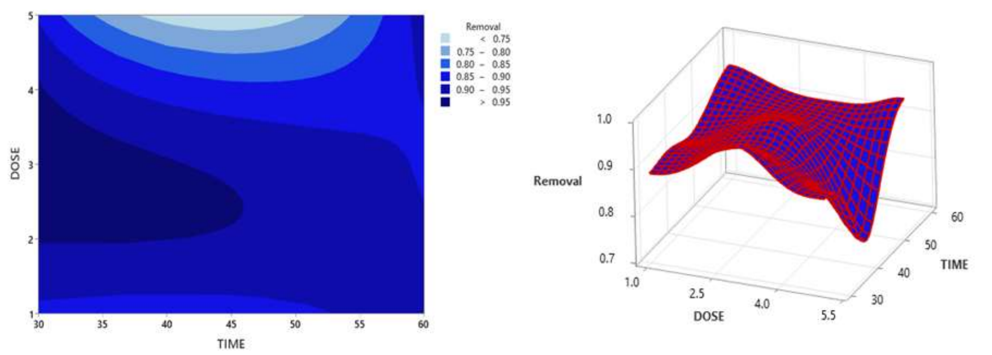


Figure No. (6) Contour plot and 3D surface plot for the relationship between the dose and time variables in hydrocarbon removal

Conclusion

This study employed a basil seed to remove total petroleum hydrocarbons from industrial effluent to the Basra governor's refinery oil firm. The method of (analyzing screening designs) was utilized for the studies' independent variables (pH, dose of the substance used for removal, and time of the experiment). The results were validated using ANOVA, and the effect of pH, time, and dose on optimal operating conditions was investigated using (MLR) modeling and comparison with DOE to obtain the best modeling. As a result, we found that the best basil seed dosage was (3 and 1) ml, the optimum PH was (3), and the optimum time was (60 and 30) minutes to accomplish 98 percent elimination.

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