Use Straw in the Removal of Petroleum Hydrocarbons from Industrial Wastewater for South Refinery Company in Basra Province

Haider Kamel Alzaidy, Firas Mustafa Al-Khatib, and Ammar Salman Dawood

ABSTRACT

(In this study, a straw was employed at the coagulation and flocculation of total petroleum hydrocarbons from industrial wastewater in the refinery oil company in Basra province, using the design of experiments approach using the method of (analyzing screening designs). Independent factors in the experiments (pH, dose of the substance used for removal, and time of the experiment). Furthermore, the link between the test's independent variables and their impact on the elimination process. As previously stated, the results revealed that the square model is the optimum model in this study, and the maximum removal was 100% at PH (3), dose (2) g, and time (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. MLR was too distant from the real consequences of DOE removal when there was a strong convergence between the real and expected impacts of DOE removal.

Keywords: Flocculation and Coagulation, Straw, TPHs, Wastewater Treatment.

I. INTRODUCTION

Industrial operations are a major source of air, water, and soil pollution, and one of the most dangerous of these pollutants is petroleum hydrocarbons, which has resulted in changes in the physical, chemical, and biological properties of water since the industrial revolution, particularly in the last two centuries, due to the dumping of various industrial wastes. Petroleum hydrocarbons emitted by industrial processes disrupt aquatic life and degrade ecosystems by accumulating inside food chains and causing living animals to produce toxic secretions. As a result, human activities jeopardize essential water supplies, and industrial and urban expansion are putting a strain on them [1],[2]. “Hydrocarbons” are organic molecules whose molecular structure consists only of carbon and hydrogen [3]. It is one among the most important components of crude oil, having been created throughout geological time and under various circumstances [4]. The severe warmth and great pressure on fossil animals are the most essential elements driving the creation of crude oil in the earth's deep strata [5]. Petroleum hydrocarbons make up around 50-98% of the entire makeup of crude oil [6]. Non-hydrocarbon molecules such as nitrogen, sulfur, and oxygen compounds (NSO), asphalt compounds, and trace elements (Co, Fe, U, Pb, V, Ni) make up the remaining fraction of crude oil composition [7]-[8]. Total petroleum hydrocarbons (TPHs) are the name given to this crude oil combination [9]. Furthermore, the principal constituents of crude oil may be divided into four groups based on their solubility in organic solvents [6]-[8]. Petroleum hydrocarbons will be coagulated using natural coagulants in this study. Coagulation is a method that, together with flocculation, is widely used in many businesses as an integral component of total industrial and municipal wastewater treatment [10]. Flocculation is a physical process based on the accumulation of small slow-settling blocks and their agglomeration, which is generated by the coagulation process to form large-sized and high-density blocks, which are then removed by separation processes such as filtration or gravity sedimentation, or in other ways [11],[12]. Many diverse materials, including inorganic coagulants, organic flocculants, composite materials, and hybrids, can be used to treat various types of water and wastewater. Inorganic coagulants are the most often used coagulants, followed by organic flocculants, composites, and hybrids [13]. A straw will be used in this study as a natural coagulant that is both ecologically friendly and non-toxic. Examine the effects of the components and their replies. The phrase “design of experiments” refers to a statistically systematic and planned strategy to performing tests that distinguish itself by covering a wide variety of statistical experiments and producing extraordinarily clear findings with a limited number of trials. As the parameters fluctuate concurrently via a series of experimental processes to establish the relationship between these factors that
impact the response of the process outputs to avoid wasting time and money and to provide the ideal circumstances for conducting experiments [14].

The purpose of this research is to minimize or remove petroleum hydrocarbons from industrial wastewater in the Basra Province, which is defined as liquid waste from industries and manufacturers.

II. MATERIALS AND METHODS

A. Material

Benze (United Kingdom), Hexane (Germany), Chloroform CHC13 (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 were all analytical pure grades used in this study.

B. Wastewater Sources

The wastewater samples for this investigation were collected from South Refineries Company’s final basin, which is located at 30°27’38N, 47°39’47E. This water contains oil concentrations caused by industrial processes that occur on crude oil when it is turned into fuel and other oil derivatives, and these samples were tested for oil contamination. The calculated value of the South Refinery Company’s industrial raw wastewater sample, comprising total hydrocarbon petroleum, is 14,480 mg/l.

C. Extraction of Petroleum Hydrocarbons

For extracting hydrocarbons from wastewater, according to the UNEP (1989) method, 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 through the separation column, as detailed in the method UNEP.

D. Coagulation and Flocculation Processes

The tests were carried out at room temperature using the Jar Test apparatus, 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 established by the DOE software, and the samples were allowed to settle without shaking for 35 minutes after being mixed at a rate of Equation (1) was used to calculate the elimination efficiency of petroleum hydrocarbons:

\[
\text{Removal Efficiency} = \frac{C_i - C_f}{C_i} \times 100
\]  

where C\(_i\) and C\(_f\) are the starting and ultimate pollutant concentrations, respectively.

E. Design of Experiment (DOE)

The Minitab (v. 20) program was used to statistically design experiments and study the influence of the experimental factors (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. The technique of analyzing screening designs was used for the independent variables of the experiments (pH, dosage, and experiment period) to create an equation and test the effectiveness of this equation to predict Elimination.

In this study, the standard form of CSD (create screening design) is ASD, which consists of factorial points (k represents factors= 3). The independent variables (factors) were PH wastewater (represented by X\(_1\)), dose (represented by X\(_3\)), and time (means by X \(_2\)) As shown in Table I, these components have three levels: low level (1), central level (0), and high level (+1). Preliminary tests are typically performed to ascertain the precise values of the coded quantities of these components. Table I also includes these codes.

To show the relationship between the components (X\(_1\), X\(_2\), and X\(_3\)) and the studied response, the second-order polynomial equation shown in (2) is employed (Y).

\[
Y = f(x) = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j>i}^{n} \beta_{ij} x_i x_j
\]  

where Y indicates the response model (hydrocarbons petroleum removal); 0 denotes the constant coefficient; I indicate the linear term coefficient; ii indicates the square term coefficient; ij indicates the quadratic term coefficient; represent the number of independent variables; and Xi and Xj indicate the coded values of the independent variables.

F. Multiple Linear Regression (MLR)

In this study, multiple linear regression (MLR) equations are used since they reveal linear relationships involving more than two variables. The MLR equation denotes a linear connection between a response variable (Y) and many predictor variables (x\(_1\), x\(_2\), x\(_3\)). Equation (3) depicts the generic MLR equation:

\[
Y \text{ Removal} = 0.804 - 0.00907 X_1 + 0.00082 X_2 + 0.0297 X_3
\]  

III. RESULT AND DISCUSSION

A. Statistical Analysis

Table I shows the 13 tests used to analyze the coefficients for independent variables in the coagulation and flocculation process (2). (pH, time, and dosage) Many models, such as linear, square, and 2-way interaction, may be used to establish the correlation of experimental data and construct a regression equation for each reaction.
Although these models may be connected to experimental data, careful model selection is required since the chosen model connects with experimental data based on its appropriateness. Thus, the square model was proposed to explain the correlation between experimental data and all responses based on the experimental data, since it is the best model to depict the correlation between experimental data and all answers, with the lowest F value and P-value. As a consequence, this model was implemented. In terms of coded components, (4) reflects the final square model for removal response.

\[
Y_{\text{Removal}} = 1.607 - 0.1959X_1 - 0.03006X_2 + 0.3941X_3 + 0.01538X_1 \cdot X_1 + 0.000321X_2 \cdot X_2 - 0.0963X_3 \cdot X_3 + 0.000114X_1 \cdot X_2 - 0.00143X_1 \cdot X_3 + 0.000652X_2 \cdot X_3
\]

(4)

B. Analysis of Variance (ANOVA)

ANOVA was used to measure the “goodness of fit” of the square model findings for each answer. Some values in equation (4) were statistically insignificant due to their low F-value. As a result, these values must be discarded by the response equation. For models with (4) and a likelihood of the alpha value of e 0.05 confidence level, the P-value is higher. These equations contain a number of statistically insignificant terms with a high P-value as shown in (4). Non-significant terms in response equations must be eliminated. Table III shows the 0.002 probability (p-value) of the square model for total petroleum hydrocarbon removals. The (p-value) of the TPHs elimination model indicates that the model is statistically significant.

To test the model’s quality, the coefficient of determination (R square) was utilized, which represents the proportion of total variance in the response predicted by the model. The model predicts the reaction better when (R square) is close to one [14]. TPHs removals had a coefficient of determination of 0.9921. As a result, the observed and predicted response values are highly dependent and related [15]. TPHs removals had an adjusted R2 of 0.9683, which is quite close to the R2 value in response equations. As a consequence, the prediction of experimental data is graded adequately [16]. Based on the corrected R square for the pollutant removal models, Table II reveals that the overall variance for TPHs removals was 96 percent. The independent variables can explain this, with only around 4% of the total variance remaining unexplained by these models.

The Pareto chart may be used to determine the magnitude and relevance of the effects, as well as the impact of each element on the overall reaction to TPH removal. On the Pareto chart, bars that cross the reference line are statistically significant. The bars indicating the variables (X1X1, X2X2, X3X3, X3 and X1) in Fig. 1, cross the reference line (3.18). These factors are statistically significant at the 0.05 level.

To assess if the sample distribution is normal or abnormal, we use a normal probability plot as shown in Fig. 2, which displays the sample distribution that is closest to the image reference line, indicating a normal distribution.

![Fig.1. Pareto chart shows the importance of the effects in the removal TPHs by a Straw.](image)

TABLE II: EXPERIMENTAL DESIGN AND RESPONSES

<table>
<thead>
<tr>
<th>No.</th>
<th>pH</th>
<th>Time (m/h)</th>
<th>Dose (g/l)</th>
<th>TPHs (mg/l)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>60</td>
<td>3</td>
<td>3200.72</td>
<td>78%</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>30</td>
<td>3</td>
<td>1380.94</td>
<td>90%</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>60</td>
<td>1</td>
<td>2069.42</td>
<td>86%</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>30</td>
<td>1</td>
<td>4300.25</td>
<td>70%</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>45</td>
<td>1</td>
<td>3200.66</td>
<td>78%</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>60</td>
<td>1</td>
<td>2520.81</td>
<td>83%</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>45</td>
<td>3</td>
<td>2690.07</td>
<td>81%</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>30</td>
<td>1</td>
<td>2920.06</td>
<td>80%</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>60</td>
<td>2</td>
<td>923.11</td>
<td>94%</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>30</td>
<td>3</td>
<td>2427.27</td>
<td>83%</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>30</td>
<td>2</td>
<td>2.27</td>
<td>100%</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>60</td>
<td>3</td>
<td>690.27</td>
<td>95%</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>45</td>
<td>2</td>
<td>3590.95</td>
<td>75%</td>
</tr>
</tbody>
</table>

TABLE III: ANALYSIS OF VARIANCE (ANOVA) ON THE TERMS IN EACH RESPONSE (LINEAR, QUADRATIC, AND 2-WAY) MODEL

<table>
<thead>
<tr>
<th>Response</th>
<th>Source</th>
<th>DF</th>
<th>F value</th>
<th>p value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPHs removal</td>
<td>X1</td>
<td>1</td>
<td>31.54</td>
<td>0.011</td>
<td>significant</td>
</tr>
<tr>
<td></td>
<td>X2</td>
<td>1</td>
<td>6.47</td>
<td>0.084</td>
<td>Not significant</td>
</tr>
<tr>
<td></td>
<td>X3</td>
<td>1</td>
<td>37.62</td>
<td>0.009</td>
<td>significant</td>
</tr>
<tr>
<td></td>
<td>X1X1</td>
<td>1</td>
<td>138.33</td>
<td>0.001</td>
<td>significant</td>
</tr>
<tr>
<td></td>
<td>X2X2</td>
<td>1</td>
<td>37.69</td>
<td>0.009</td>
<td>significant</td>
</tr>
<tr>
<td></td>
<td>X3X3</td>
<td>1</td>
<td>66.93</td>
<td>0.004</td>
<td>significant</td>
</tr>
<tr>
<td></td>
<td>X1X2</td>
<td>1</td>
<td>1.53</td>
<td>0.519</td>
<td>Not significant</td>
</tr>
<tr>
<td></td>
<td>X1X3</td>
<td>1</td>
<td>0.37</td>
<td>0.584</td>
<td>Not significant</td>
</tr>
<tr>
<td></td>
<td>X2X3</td>
<td>1</td>
<td>1.94</td>
<td>0.258</td>
<td>Not significant</td>
</tr>
</tbody>
</table>

Notes: X1: means PH; X2: means Time (m); X3: means Dose (g), df: degree of freedom.
Fig. 2. The normal probability plot to determine sample distribution and residual in removal TPHs by a Straw.

C. MLR

For TPHs removals, the coefficient of determination was 0.2000. This implies that there is little dependency and connection between observed and expected response levels. [15]. For total petroleum hydrocarbon removals, MLR had a probability (p-value) of 0.358. The (p-value) of the TPHs elimination model indicates that it is not statistically significant.

D. Comparison between DOE and MLR

Fig. 3 depicts the distinction between DOE and MLR. The DOE model's findings were shown to be statistically more significant in the calculation elimination than the MLR model's results. MLR was considerably far from the real removal outcomes where there was a strong convergence between the real and anticipated results of DOE removal.

E. Analysis of the coagulation Process

The experimental variable responses are shown in 3D surface plots for each model, and these graphs may be used to detect the significant interactions between the variables. According to Table I, the highest elimination of total petroleum hydrocarbons using basil seeds was 100 percent at pH 3 and dosages of (2) g at durations of (30) minutes (2). The lowest clearance rate was 70% at pH 6 and a dose of 1 g over 30 minutes. Fig. 4 demonstrates the link between the pH and time variables in complete hydrocarbon removal, as the removal percentage increases at pH (3 to 3.5) and a time (30 to 35) m to obtain the removal rate (90 percent - 96 percent). At pH (5.6 to 7.5) and duration (30 to 35) m, however, the elimination is decreased by less than 72%.

While the 3D plot and contour plot drawing (Fig. 5) shows the relationship between the pH and dose components in hydrocarbon removal, as the removal rises within the range of pH (3) and dosage (1.6 to 2.7) g to achieve removal more than 96 percent. However, at pH (5 to 7) and dosage (1 to 1.4) g, the clearance percentage declines by less than 72%.
In terms of the link between the dose and time factors in the effectiveness of petroleum hydrocarbon removal, the removal percentage increases at doses (1.6 – 2.6) g and periods (30 – 33) minutes to achieve high removal of more than 96%. However, at a dose of (1 to 2.5) g and a time of (30-50) minutes, the clearance percentage is less than 78%. As illustrated in Fig. 6.

IV. CONCLUSION

This study employed a straw to remove total petroleum hydrocarbons from industrial effluent to the south refinery company in Basra province. 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 straw dosage was (2) g, the optimum PH was (3), and the optimum time was (30) minutes to accomplish 100 percent elimination.

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REFERENCES


Haider Kamel Zayer Al. Zaidy is an MSC student in the Department of Environment, college of science, University of Basrah, Iraq, an employee at south refinery company, and a trainer certified by the academy. Al Zaidy has many research publications in the world I have an environmental patent.