Environmental Health Engineering and Management Journal 2023, 10(2), 141–147
http://ehemj.com
doi 10.34172/EHEM.2023.16

Environmental Health Engineering and Management Journal

Original Article

Open Access Publish Free

The use of a pumice stone in removal of petroleum hydrocarbons from industrial wastewater through coagulation and flocculation

Haider Kamel Alzaidy[1*], Firas Mustafa Al Khatib[1], Ammar Salman Dawood[2]

[1]Department of Environment, College of Science, University of Basrah, Basrah, Iraq
[2]Department of Civil Engineering, College of Engineering, University of Basrah, Basrah, Iraq

Abstract

Background: Petroleum hydrocarbons that are released from industrial processes cause damage to aquatic life and degrade ecosystems by accumulating in the food chain, allowing living organisms to produce toxic secretions.

Methods: In this study, a pumice stone was used to remove total petroleum hydrocarbons (TPHs) from industrial wastewater in the south refinery company in Iraq/Basrah by coagulation and flocculation processes using the design of experiments (DOE) approach using the method of analyzing screening designs and measurement of the samples using GC instrument.

Results: The maximum removal was 99% at pH 3, coagulation dose of 0.5 g, and time of 60 min, and a comparison was made between the DOE and the multiple linear regression (MLR) to determine the effectiveness of the system used, which proved its incredible effectiveness.

Conclusion: According to the results, a great convergence between the actual and prediction results of removal was found, while MLR was very far from the actual and predicted removal results. The high efficiency of pumice stone was found in removing petroleum hydrocarbons from the industrial wastewater of the South Refineries Company. Pumice stone is widely available in the market and cheap economically.

Keywords: Pumice, Wastewater, Hydrocarbons, Flocculation and coagulation, Petroleum

Citation: Kamel Alzaidy H, Al Khatib FM, Dawood AS. The use of a pumice stone in removal of petroleum hydrocarbons from industrial wastewater through coagulation and flocculation. Environmental Health Engineering and Management Journal 2023; 10(2): 141–147. doi: 10.34172/EHEM.2023.16.

Article History:
Received: 3 May 2022
Accepted: 17 October 2022
ePublished: 12 May 2023

***Correspondence to:**
Haider Kamel Alzaidy,
Email: hk632737@gmail.com

Introduction

Industrial activities are a significant source of air, water, and soil pollution. One of the most dangerous pollutants is petroleum hydrocarbons, which has resulted in changes in water's physical, chemical, and biological characteristics because of the disposal of various industrial wastes since the industrial revolution, especially in the last two centuries. Petroleum hydrocarbons that release from industrial processes cause damages to aquatic life and degrade ecosystems by accumulating in the food chain, allowing living organisms to produce toxic secretions. As a result, human activities threaten key water supplies, and industrial and urban expansion are adjacent to these resources (1,2). Organic molecules containing only carbon and hydrogen in their molecular structure are called "hydrocarbons" (3). It is one of the most essential components of crude oil, and it is formed through geological time and under various conditions (4). Crude oil is formed in the deep layers of the earth under the influence of many factors, the most important of which is the extreme temperature and high pressure on fossil organisms (5). Petroleum hydrocarbons constitute about 50-98% of the total composition of crude oil (6). The non-hydrocarbon compounds constitute the remaining percentage of the crude oil composition, such as nitrogen, sulfur, and oxygen compounds (NSO), asphalt compounds, and minimal amounts of trace elements (Co, Fe, U, Pb, V, Ni), and wastewater of South Refinery Company contain on the same composition and properties of crude oil (7,8). This mixture of crude oil is called total petroleum hydrocarbons (TPHs) (9) and, to throw more light on the key components found in crude oil, they can be classified into four classes based on their solubility in organic solvents (6-8). This study will treat petroleum hydrocarbons using natural coagulants' by coagulation. Coagulation is combined with the flocculation process widely used in many industries as a vital part of the comprehensive treatment of industrial and municipal wastewater (10). Flocculation is a physical process. It is based on the collection of small blocks that are slow to settle and their agglomeration, which is formed from the coagulation process to form large-sized and high-density blocks, which are later removed by separation processes such as filtration or sedimentation by gravity or other ways (11,12).

Many different materials can be used to treat water and wastewater. Among the materials used as coagulants are inorganic coagulants, organic flocculants, composite materials, and hybrids. Inorganic coagulants are the most commonly used coagulants, followed by organic flocculants, composites, and hybrids (13). In this research, pumice stone (black natural rock) as a natural coagulant that is both environmentally friendly and non-toxic was used. The pumice stone contains many natural materials that contribute in removal of hydrocarbons from wastewater. Table 1 shows the main chemical composition of pumice stone (14).

Design of experiments (DOE) is used for a statistically systematic and organized method of experiments that is characterized by covering a wide range of statistical experiments and obtaining evident results with a minimum number of experiments. The factors vary at once through a set of experimental processes to determine the relationship between these factors that affect the response of the process outputs to avoid wasting time and cost and to achieve the best conditions for conducting experiments (15). This research aimed to minimize or remove petroleum hydrocarbons from industrial wastewater, represented as liquid waste from factories and manufacturers in Basra Province.

Materials and Methods

Materials

All solvents and materials that were used in this research were of analytical pure grades, including Benzene (United Kingdom), Hexane (Germany), Chloroform $CHCl_3$ (India), Glass wool (India/Mumbai), Silica gel 100-200 mesh (India/Mumbai), Aluminum oxide Al_2O_3 (India/Mumbai), Sodium sulfate anhydrous Na_2So_4 (India/Mumbai), HCl 35% (India/SDFCL), and KOH (Switzerland/Fluka).

Table 1. Chemical analysis of pumice stone

Chemical compositions	Percent
Silicon dioxide	76.2%
Aluminum oxide	13.5%
Ferric oxide	1.1%
Ferrous oxide	0.1%
Sodium oxide	1.6%
Potassium oxide	1.8%
Calcium oxide	0.8%
Titanium oxide	0.2%
Magnesium oxide	0.05%
Water	< 1.0%

Wastewater sources

The wastewater samples of this study were collected from South Refineries Company’s final basin in Basra (Iraq), which is located at 30°27’38″N, 47°39’47″E as shown in Figure 1. This wastewater contains concentrations of oil that are formed as a result of the industrial processes that take place on crude oil when converted into fuel and other oil derivatives, and these samples were tested for oil contamination. Industrial wastewater to the south refinery company contains total hydrocarbons petroleum of 14 480 mg/L before any treatment.

Coagulation and flocculation processes

The tests were carried out at room temperature using Jar Test apparatus, which consists of six jars filled with 700 mL of sample wastewater, the pH of which was changed by adding HCL (1 N) and KOH (1 N), and then, a specific dose of the pumice stone used to remove petroleum hydrocarbons was added to each jar according to the experiments that were established by the DOE software. Afterwards, the samples were allowed to settle without shaking for 35 minutes after being mixed at a speed of 200 rpm for a time duration specified by the DOE software. The removal efficiency of the hydrocarbon petroleum was calculated according to the following formula (12):

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

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

Design of experiment

In order to statistically design experiments and study the influence of the factors used in the experiments (pH, a dose of materials utilized as coagulant and flocculent in the removal of petroleum hydrocarbons, as well as experiment time) specified within the design and with the minimum number of experiments as possible, the Minitab (v. 20) program was utilized. The method of analyzing screening designs was used 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 removal, based on the values of R-squred (R^2) and residual.

In this analysis, the typical form of create screening design (CSD), ASD, consists of factorial points (k-means factors = 3). The independent variables (factors) were wastewater PH (X1), dosage (X2), and time (X3). As shown in Table 2, these factors have three levels, namely, low level (1), central level (0), and high level (+1). Preliminary experiments are often used to identify the exact values of the coded levels for these factors. Table 1 also involves these codes.

To demonstrate the relationship between the factors

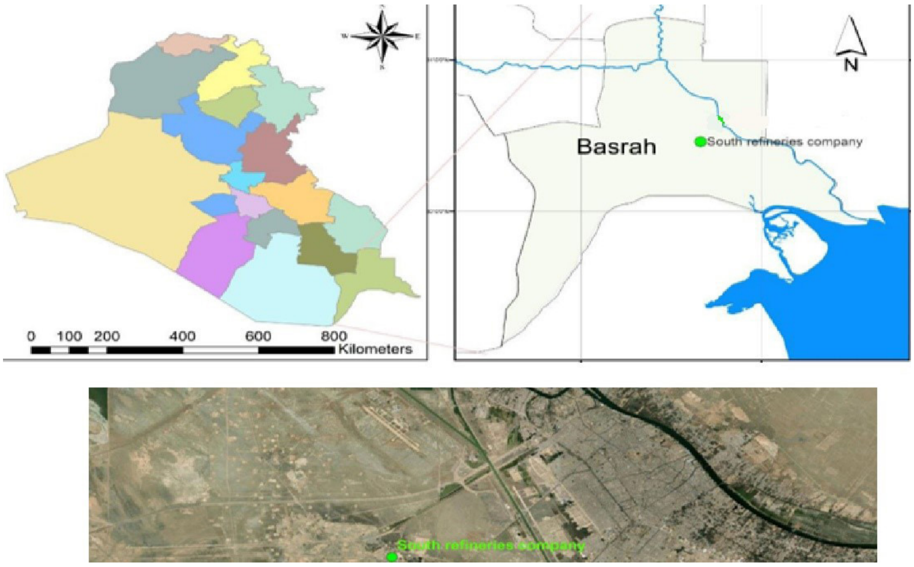

Figure 1. Sampling locations of South Refinery Company

Table 2. 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	g/L	0.5	-1	1	0	1.5	+1

(X1, X2, and X3) and the studied response, the second-order polynomial equation (Y) is used (12) :

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

Where Y is the response model (hydrocarbons petroleum removal), $\beta 0$ 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.

Multiple linear regression (MLR)

In this study, the MLR equation is used because it displays linear correlations involving more than two variables. The MLR equation describes a linear relationship between a response variable (Y) and several predictor variables (X1, X2, X3). Equation (3) demonstrates the general MLR equation from this study:

$$Y \ Removal \ TPHs = 0.804 - 0.00371 \ X1 + 0.00253 \ X2 + 0.000022 \ X3 \quad (3)$$

Results

As shown in Table 3, there are 13 tests to investigate the coefficients for independent variables in the coagulation process (dosage, pH, and time). Different models, such as linear, square, and 2-way interaction, can be used to determine correlation of experimental data and create a regression equation for each reaction. These models may be associated with experimental data, but careful selection of the optimal model is required because the selected model correlates with experimental data based on its adequacy. Thus, based on the experimental data, the 2-way model was proposed to represent the correlation between experimental data and all responses. It is the best model to represent the correlation between all responses

Table 3. Experimental design and responses

Run	X_1 pH	X_2 Dosage (g)	X_3 Time (m)	THPs %
1	9	1.5	30	0.932661
2	3	0.5	60	0.991424
3	9	1	60	0.985399
4	3	1.5	60	0.831451
5	3	1.5	30	0.933065
6	6	1.5	30	0.833874
7	6	1.5	60	0.940741
8	3	1	30	0.938176
9	3	0.5	45	0.967871
10	9	0.5	30	0.708231
11	6	1	45	0.931288
12	9	1.5	45	0.948520
13	9	0.5	60	0.976001

and experimental data, with the lowest F-value and *P* value. As a result, this model was applied. The final 2-way model for removal response in terms of coded factors is shown in Eq. (4).

$$Y\ Removal\ TPHs = 0.971 - 0.0563\ X1 + 0.00059\ X2 + 0.000118\ X3 - 0.00229\ X1{*}X1 + 0.000020\ X2{*}X2 - 0.000000\ X3{*}X3 + 0.001034\ X1{*}X2 + 0.000034\ X1{*}X3 - 0.000006\ X2{*}X3 \quad (4)$$

ANOVA was used to determine each response's "goodness of fit" of the 2-way model results. Some values in Eq. (4) were statistically insignificant due to their low F-value. As a result, these values must be disregarded from the response equation. The *P* value is more significant regarding the response Eq. (4) for models and has the probability of the alpha value of 0.05 confidence level.

Some statistically non-significant terms with a high *P*value can be found in these equations (4). As a result, non-significant terms in response equations must be removed. For example, Table 4 displays the 0.002 probability (*P* value) of the 2-way model for removal of TPH. The *P*value in the TPHs removal model indicates that the model is statistically significant.

Discussion

To evaluate the model's quality, the coefficient of determination (R^2) was used, which reflects the proportion of total variance in the response predicted by the model. The model predicts the response better when (R^2) is close to one (14). For TPHs removal, the coefficient of determination was 0.9940. This indicates that the observed and predicted response values are highly dependent and correlated (16). TPHs removal had an adjusted R^2 of 0.9759, which is very close to the R^2 value in response equations. As a result, the prediction of experimental data is deemed satisfactory (16). The adjusted R^2 for the pollutants removal models, as shown in Table 4, indicated that the total variation for TPHs removals was 97%. This may be explained by the independent variables, with only roughly 3% of total variation remaining unexplainable by these models.

Table 4. 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	11 1	8.01 93.14 7.71	0.066 0.002 0.069	Not significant Significant Not significant
	X1X1	1	4.68	0.119	Not significant
	X2X2	1	0.23	0.664	Not significant
	X3X3	1	0.08	0.791	Not significant
	X1X2	1	66.88	0.004	Significant
	X1X3	1	78.10	0.003	Significant
	X2X3	1	64.77	0.004	Significant

Notes: X1: PH; X2: Dosage (g); X3: Time (m), df: Degree of freedom.

The Pareto chart can be used to determine the magnitude and importance of the effects, as well as to comprehend the impact of each factor on the final response to TPHs removal. On the Pareto chart, bars that cross the reference line are statistically significant. In Figure 2, the bars that represent factors (X2, X1X3, X1X2, and X2X3) cross the reference line that is at 3.18. These factors are statistically significant at the level of 0.05. Equation (4) is the final form of TPHs removal which was concluded from equation (2)

To find out the distribution of samples within the normal or abnormal distribution, normal probability plot (Figure 3) was used, indicating more samples distribution close to the photo reference line that is a normal distribution.

Multiple linear regression

For TPHs removal, the coefficient of determination was 0.2186, indicating that the observed and predicted response values have very little dependence and correlation (17). The probability (*P* value) of MLR for removal of TPHs was 0.506. The *P* value in the TPHs removal model indicates that the model is not statistically significant.

Comparison between DOE and MLR

Scatterplot (Figure 4) displays the difference between DOE and MLR. It was noticed that the results from the DOE model are statistically more significant in the calculation removal than the results of the MLR model. Furthermore, there was a great convergence between the actual and prediction results of removal of DOE, while MLR was very far from the real removal results.

Analysis of flocculation process

The responses of experimental variables are shown in 3D surface plots for each model. These graphs can be used to determine the significant interactions between the variables.

According to Table 3, the maximum removal of TPHs using pumice stone was 99% at pH 3 with a dose of 0.5 g and at a 60-minute time. At the same time, the lowest removal rate was 70% at a pH 9 and a dose of 0.5 g at a 30-minute time. The contour plot and 3D surface plot drawings in Figure 5 represent the relationship between pH and dose variables in total hydrocarbon removal, as the removal increases within pH 6-9 and dose of 0.7, 1.4 g to obtain maximum removal of more than 95%. However, at pH 5.5-9 and dose of 0.5 g, the removal decreases to 80%-85%.

The relationship between PH and time in the removal of petroleum hydrocarbons is outlined by the 3D plot and a contour plot (Figure 6), indicating that an increase

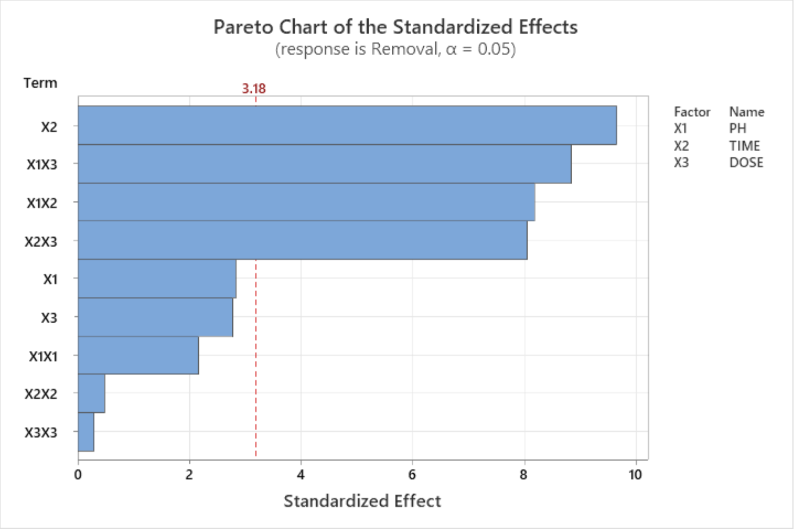

Figure 2. The Pareto chart indicating the importance of the effects in the removal of TPHs by a pumice stone

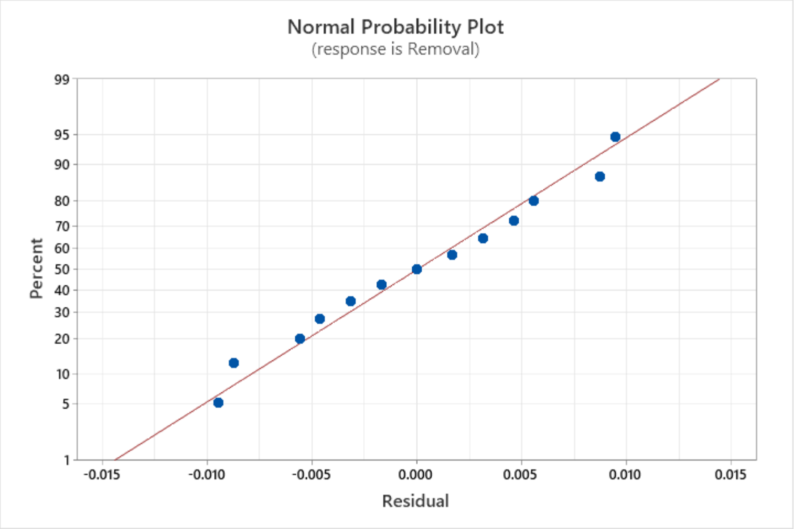

Figure 3. Normal probability plot of samples distribution and residual in the removal of TPHs by a pumice stone

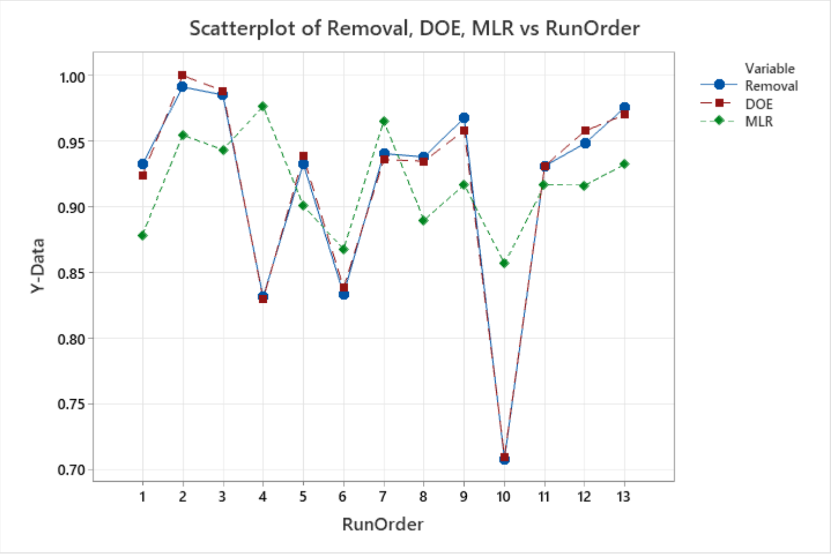

Figure 4. Display comparison between DOE, MLR, and the extent to which they predicted the real removal

in the removal percentage at pH 3 to 3.5 and 6.5 to 9, and a time between 35 to 60 minutesled to a maximum removal more than of 95%. But at pH 5.5 to 9 and time 30 to 33 minutes, a removal percentage less than 85% was obtained.

In regard to the relationship between the dose and time variables in the effectiveness of petroleum hydrocarbon removal, the removal percentage increases at doses 0.5-1.2 g and times 44-60 min to obtain removal of more than 95%. But at a dose of 0.6-0.7 g and a time of 33-35 min, the removal percentage will be less than 80%, as shown in Figure 7.

Conclusion

This study used a pumice stone to remove TPHs from industrial wastewater in the South Refinery Company. The method of analyzing screening designs was used for the independent variables of the experiments (pH, dose of the substance used for removal, and time of the experiment). ANOVA was used to validate the results and investigate the effect of pH, time, and dose on optimal operating conditions and utilized (MLR) modeling and comparison with DOE to obtain the best modeling. According to the results, the optimum dosage of the pumice stone was 0.5 g, the optimum PH was 3, and the optimum time was 60 min to achieve removal of 99%.

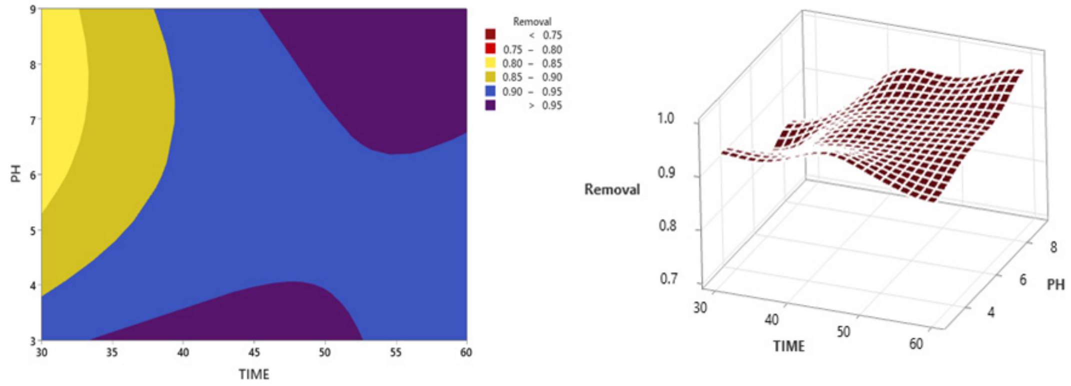

Figure 5. Contour plot and 3D surface plot for the relationship between the PH and dose variables in hydrocarbon removal

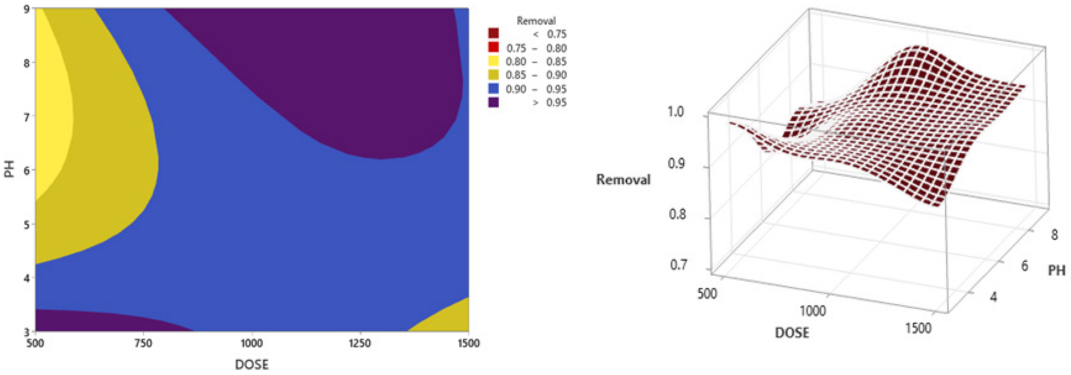

Figure 6. Contour plot and 3D surface plot for the relationship between the PH and time variables in hydrocarbon removal

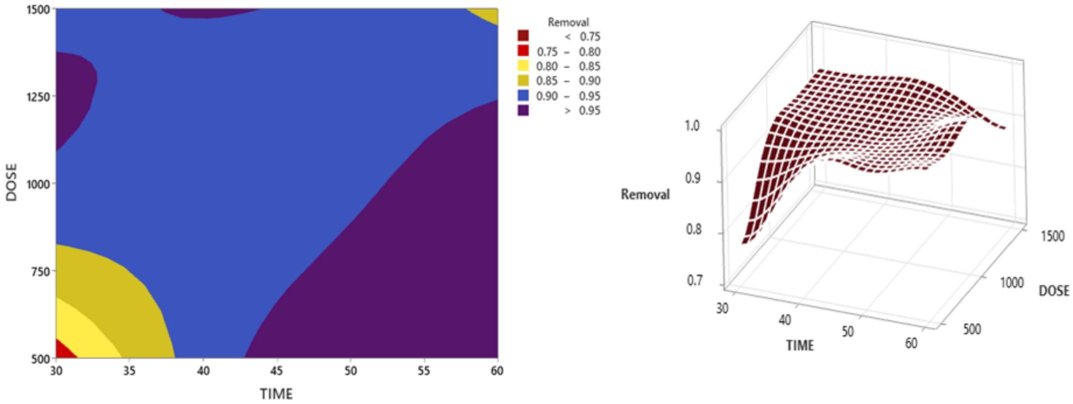

Figure 7. Contour plot and 3D surface plot for the relationship between the dose and time variables in hydrocarbon removal

Because of the efficiency of the pumice stone in the removal of hydrocarbons from wastewater, it is recommended to use it in the removal of hydrocarbons. Also, further studies are recommended to test it in the removal of other pollutants such as trace elements.

Acknowledgments

This study was extracted from a master's thesis conducted at Department of Environment, College of Science, University of Basrah, Iraq, under the supervision of Dr. Firas Mustafa Al-Khatib and Dr. Ammar Salman Dawood. The authors would like to thank them for their assistance in accomplishing the thesis and research and all others who involved in the realization of this study.

Authors' contribution

Conceptualization: Haider Kamel Alzaidy.
Data curation: Haider Kamel Alzaidy.
Formal analysis: Ammar Salman Dawood.
Funding acquisition: Firas Mustafa Al Khatib.
Investigation: Firas Mustafa Al Khatib.
Methodology: Ammar Salman Dawood.
Project administration: Firas Mustafa Al Khatib.
Resources: Ammar Salman Dawood.
Software: Ammar Salman Dawood.
Supervision: Firas Mustafa Al Khatib
Validation: Firas Mustafa Al Khatib
Visualization: Ammar Salman Dawood.
Writing–original draft: Firas Mustafa Al Khatib.
Writing–review & editing: Firas Mustafa Al Khatib.

Competing interests

The authors declare that there is no competing interests.

Ethical issues

The authors confirm that all data obtained during the investigation are as reported in the manuscript and no data from the study has been or will be published separately elsewhere.

References

1. Goel PK. Water Pollution: Causes, Effects and Control. New Age International; 2006.
2. Elijah AA. A review of the petroleum hydrocarbons contamination of soil, water and air and the available remediation techniques, taking into consideration the sustainable development goals. Earthline Journal of Chemical Sciences. 2022;7(1):97-113. doi: 10.34198/ejcs.7122.97113.
3. Patel V, Shah K. Petroleum hydrocarbon pollution and its biodegradation. International Journal of Chemtech Applications. 2014;2(3):63-80.
4. Stogiannidis E, Laane R. Source characterization of polycyclic aromatic hydrocarbons by using their molecular indices: an overview of possibilities. In: Whitacre DM, ed. Reviews of Environmental Contamination and Toxicology. Cham: Springer; 2015. p. 49-133. doi: 10.1007/978-3-319-10638-0_2.
5. United Nations Environment Programme (UNEP). Determination of Petroleum Hydrocarbons in Sediments. UNEP; 1992.
6. Zhu E, Venosa AD, Suidan MT, Lee K. Guidelines for the Bioremediation of Marine Shorelines and Freshwater Wetlands. US Environmental Protection Agency; 2001.
7. Alzaidy HK, Alkhatib FM, Dawood AS. Use basil seed in the removal of petroleum hydrocarbons from industrial wastewater for oil refinery company. J Hunan Univ Nat Sci. 2022;49(5):741-50.
8. Al-Khatib FM. Determination the Concentrations, Origin and Distribution of Hydrocarbon Compounds in Water, Sediments and Some Biota of Hor Al-Howaiza, South of Iraq and Their Sources [dissertation]. Basra, Iraq: University of Basrah, College of Science, Biology Department; 2008.
9. Nwabueze AA, Nwabueze EO, Okonkwo CN. Levels of petroleum hydrocarbons and some heavy metals in tissues of *Tympanotonus fuscatus* periwinkles from Warri River of Niger Delta area of Nigeria. J Appl Sci Environ Manage. 2011;15(1):75-8. doi: 10.4314/jasem.v15i1.65679.
10. Divakaran R, Pillai VN. Flocculation of kaolinite suspensions in water by chitosan. Water Res. 2001;35(16):3904-8. doi: 10.1016/s0043-1354(01)00131-2.
11. Howe KJ, Hand DW, Crittenden JC, Trussell RR, Tchobanoglous G. Principles of Water Treatment. John Wiley & Sons; 2012.
12. Dawood AS, Li YL. Response surface methodology (RSM) for wastewater flocculation by a novel (AlCl3-PAM) hybrid polymer. Adv Mat Res. 2012;560-561:529-37. doi: 10.4028/www.scientific.net/AMR.560-561.529.
13. Wantala K, Khongkasem E, Khlongkarnpanich N, Sthiannopkao S, Kim KW. Optimization of As(V) adsorption on Fe-RH-MCM-41-immobilized GAC using Box-Behnken design: effects of pH, loadings, and initial concentrations. Appl Geochem. 2012;27(5):1027-34. doi: 10.1016/j.apgeochem.2011.11.014.
14. Pumice [Internet]. Available from: https://geologyscience.com/rocks/igneous-rocks/extrusive-igneous-rocks/pumice/. updated 2021 Feb 20.
15. Montgomery DC. Design and Analysis of Experiments. John Wiley & Sons; 2017.
16. Sharma P, Singh L, Dilbaghi N. Optimization of process variables for decolorization of Disperse Yellow 211 by *Bacillus subtilis* using Box-Behnken design. J Hazard Mater. 2009;164(2-3):1024-9. doi: 10.1016/j.jhazmat.2008.08.104.
17. Ghafari S, Abdul Aziz H, Isa MH, Zinatizadeh AA. Application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. J Hazard Mater. 2009;163(2-3):650-6. doi: 10.1016/j.jhazmat.2008.07.090.