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Original Article

Removal of COD and TOC From Petroleum Synthetic Wastewater Containing Cyclic Aromatic Hydrocarbons Using the Photo-Fenton Process by the Box-Behnken Method

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Abstract

Background: In the last few decades, concern over environmental safety has increased significantly. One of the main causes of environmental degradation is the discharge of untreated pollutants into water bodies. This study examined the efficiency of the photo-Fenton oxidation process to remove chemical oxygen demand (COD) and total organic carbon (TOC) from petroleum wastewater.
Methods: Experiments were designed using the Box-Behnken method- a model of the response surface method (RSM) by MINITAB software. First, a wooden chamber equipped with UV lamps installed in the center was applied. The effect of effective parameters on the photo-Fenton process, including naphthalene concentration (10-70 µg/L), pH (2-7), H_2O_2 (50-800 mg/L), Fe (5-80 mg/L), contact time (10-120 minutes) and UV rays was investigated.
Results: The highest removal efficiency of the COD (case 89.27) was at achieved at pH = 2, UV = 24, naphthalene concentration 10 µg/L, Fe concentration 36.06 mg/L, hydrogen peroxide content 800 mg/L, and contact time 120 min. Besides, the highest removal efficiency of the process in removing TOC was 71.04% obtained at 2 pH = 24, UV = 24, and a reaction time of 120 min.
Conclusion: Based on the results of this research, the photo-Fenton process has a significant efficiency in removing COD and TOC from petroleum effluents containing cyclic aromatic hydrocarbons and can be utilized as an efficient method for the treatment of petroleum wastewaters.
Keywords: Naphthalene, Advanced oxidation process, COD, TOC, Photo-Fenton, Petroleum effluent

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Introduction

Over the past few decades, there has been a dramatic increase in concern about environmental safety. This is largely due to human societies accelerating urbanization, industrialization, and the development of agricultural activities, which have led to the spread of environmental pollution. Water pollution is a significant issue that has various consequences on the environment and human health.[1] A significant portion of these wastes comprises petroleum or oily materials from the petroleum and petrochemical industries. These materials are primarily composed of aromatic and aliphatic organic components that are resistant to biological decomposition and have the potential to be toxic to humans.[2,3] Oil refinery wastewater contains a variety of complex substances, such as oil, gas, wax, grease, metals, minerals, and hydrocarbons.[4,5] This type of wastewater can have adverse effects on various environmental elements, including clean water, human health, underground water sources, air quality, marine life, and agricultural production.[6,7] Due to the inefficiency of treatment methods, oil refinery wastewater can be hazardous to the environment and other vital systems. It has the potential to become mutagenic and toxic to humans.[8] Petroleum hydrocarbons are a mixture of chemicals that can enter the ground through transportation and traffic accidents (such as fuel spills), improper oil storage, and the discharge or leakage of organic solvents from industrial sites.[9] These organic compounds are among the most common types of pollutants found in petroleum wastewater and are classified as priority pollutants by the United States Environmental Protection Agency (EPA). As social and political concerns about the environment continue to grow and new regulations are established for the industry, it has become necessary to treat this wastewater to meet specific discharge limits set by regulatory bodies.[10,11]

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that contain two or more condensed benzene rings Due to the carcinogenic, mutagenic, and teratogenic properties of some of them, PAHs have received increased attention in recent years.[12] PAHs are produced through both natural and human activities, such as pyrolysis, car exhaust, and coal refining.[13]

Oil leaks can have severe impacts on human health, causing problems such as burns, eye irritation, and respiratory issues. Continuous inhalation of these chemicals can lead to lung damage and increase the risk of exposure to other harmful gases. Therefore, it is necessary to perform proper treatment of petroleum wastewater using appropriate processes.[14] There are several methods available for treating petrochemical and refinery wastewater, including biological methods, membrane separation, electrocoagulation, ozonation, advanced purification methods, advanced oxidation processes (AOPs), and physicochemical methods such as adsorption, ion exchange, coagulation, and combined technologies.[15]

AOPs are among the most effective and efficient technologies for degrading and removing dangerous, resistant, and non-biodegradable organic pollutants from industrial wastewaters.[16,17] These processes are defined by the generation of hydroxyl radicals. The main purpose of them is to produce highly reactive free radicals that are very sensitive and use non-selective materials to reduce the contaminated organic composites present in an environment such as wastewater, soil, marine environments, etc.[18] A major advantage of the AOPs over traditional water purification methods is its ability to remove pollutants and prevent the production of toxic compounds. For example, filtration, surface absorption, and flotation are not effective in completely separating organic pollutants (as non-destructive physical separation methods). These methods only destroy pollutants and transfer them to other stages, resulting in the production of a huge quantity of waste.[19] AOPs produce highly reactive hydroxyl radicals (OH•) that can completely mineralize organic pollutants, degrade resistant organic materials, and require less energy compared to other direct oxidation processes.[20,21] Hydroxyl radicals are efficient in destroying organic chemicals because they are reactive electrophiles.[22] Studies have reported that the photo-Fenton process uses less Fe and produces less sludge. Furthermore, the use of ultraviolet rays in this system can kill microorganisms present in polluted water. The efficiency of Fenton reactions can be significantly affected by various operating parameters, such as the concentration of organic pollutants in wastewater, pH, catalyst concentration, and H_2O_2 dosage.[23,24] It should be pointed out that numerous studies have investigated the removal percentage of total organic carbon (TOC) and chemical oxygen demand (COD) from petroleum wastewater containing cyclic aromatic hydrocarbons.[25] Some previous studies have optimized process parameters using different experimental design methods such as randomized complete block design and response surface method (RSM).[26,27] One of the innovations in this study is the detailed investigation of the removal of COD and TOC from wastewater containing a specific pollutant (naphthalene) at specific concentrations, using the box-Behnken experimental design method.

The aim of this study was twofold: (1) to identify the optimal values for variables such as pH, Fe^{2+}, H_2O_2 dosage, reaction time, and UV intensity, and (2) to determine the removal efficiency of total COD and TOC from petroleum wastewater containing PAHs. To achieve these objectives, the Box-Behnken experimental design method, which is a model in the design of experiments field, was implemented to design, analyze, optimize, and validate the experiments

Materials and Methods

This research was an experimental study that was carried out on a laboratory scale in a wooden chamber with a UV lamp in the water and wastewater chemistry laboratory of the Faculty of Environment, Islamic Azad University, Ahvaz branch.

Materials

The materials used in this study include sodium hydroxide (NaOH) and hydrochloric acid (HCl) to adjust the pH of synthetic wastewater, sulfuric acid (H_2SO_4) to prepare catalyst and digester solutions to measure COD, mercury sulfate (Ag_2SO_4) and potassium dichromate ($K_2Cr_2O_7$) to prepare digester solution to measure the amount of COD, silver sulfate ($HgSO_4$) to prepare the catalyst solution to measure the amount of COD, $Fe_2(SO_4)_3$ as a source of supply of Fe ions in photo-Fenton processes, hydrogen peroxide (H_2O_2) as an oxidizer in the photo-Fenton process, all of which were produced by Merck, Germany. Also, distilled water was used to make synthetic effluents, and dilutants, making solutions and washing, and filter paper were used to separate sediments from solutions.

Photoreactor

The wooden chamber was employed as the reaction space for the synthetic wastewater samples, with three UVC lamps installed in the upper section, each with an intensity of 8W (Figure 1).

The Method of Designing Experiments

To evaluate the effect of independent variables (pH, time, naphthalene concentration, UV, $Fe_2(SO_4)_3$ concentration, and hydrogen peroxide concentration) on the response performance (COD and TOC removal efficiency) and also to optimize the variables, the RSM based on the Box Behnken design was used. And by using Minitab 19 software, a 6-variable design in three levels with three central points, 54 experiments were designed and performed to investigate the effective parameters of the COD and TOC removal process.

To investigate the effective parameters of the photo-

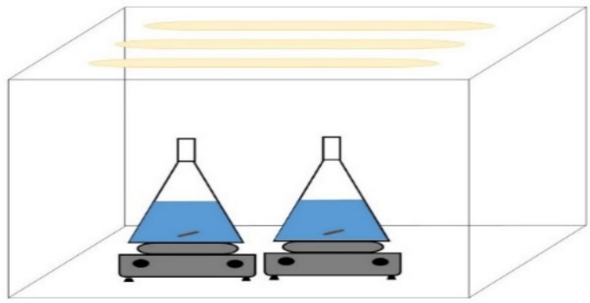

Figure 1. A Schematic View of the Chamber Built for Conducting Experiments.

Fenton process for naphthalene concentrations of 10, 40, and 70 μg/L, for pH values of 2, 4.5, and 7, for H_2O_2 volumes of 50, 425, and 800 mg/L, for the Fe concentration of 5, 42.5 and 80 mg/L, for UV rays, intensities of 8, 16 and 24 watts and reaction time of 10, 65 and 120 minutes were selected.

Test Method

After designing the experiments, all experiments were performed continuously in 1-L Erlenmeyer flasks with a fixed speed of 300 rpm and ambient temperature. In this way, the wastewater containing naphthalene was prepared synthetically.

While the desired solution was being mixed, $Fe_2(SO_4)_3$ was added to it according to the values determined in the design of the Box–Behnken experiment by the Minitab program. Then the pH was adjusted to normal using hydrochloric acid and sodium hydroxide solutions. After mixing, the determined amount of hydrogen peroxide was slowly and gradually added to the sample.

The initial COD and TOC of the effluents were measured using a spectrophotometer and a gas chromatography device, respectively, before experimenting. Finally, the Erlenmeyer flasks were placed inside the built-in chamber on the magnetic stirrer. The intensity of ultraviolet light was also adjusted by the lamps located on the top of the chamber, and according to the specific contact time, the samples were subjected to magnetic stirring at 300 rpm. After the test was completed, the samples were filtered with filter paper and the COD and TOC levels of the solutions were read. The removal efficiency of COD and TOC variables was calculated using the following equation:

$$R = \frac{C_0 - C_r}{C_0} \times 100 \quad (1)$$

To confirm the accuracy of the results, each experiment was performed in three repetitions and the average of the obtained results was used. Then the optimal parameters were determined according to the percentage of COD and TOC removal.

Sample Analysis and Mineralization and Used Devices

To calibrate the spectrophotometer device, the control sample was first used, so that the control sample was poured into the cell and other samples with a specific concentration were placed in the device, and the light absorption of each sample was read at a wavelength of 610 nm by the spectrophotometer. Finally, the calibration graph was drawn, the horizontal axis of which is the amount of absorption and the vertical axis of which is the concentration of COD read by the spectrophotometer.

To perform the COD test and prepare the control solution and the sample with an unknown concentration, after preparing the solutions, the tubes were placed in the reactor at a temperature of 148 °C for 2 hours. Then the spectrophotometer was zeroed by the control solution, then the absorbance of the sample was read by placing the vial containing the sample inside the device, and by having the absorption number and matching it with the calibration curve, the concentration was obtained. To determine the amount of COD, a DR 5000 spectrophotometer made by Hach Company (Colorado, USA).

In this research, TOC of the solutions was measured by the TOC analyzer model Multi N/C 3100 made in Germany according to the instructions of the device.

To avoid systematic error, the experiments were performed randomly. Each of the response variables for COD and TOC removal percentages was presented in the form of a polynomial regression model as a function of independent variables. Also, ANOVA analysis of variance was considered to confirm the mathematical model. The adequacy of the second-order polynomial model was evaluated with the coefficient of determination R^2 and the balanced value of R^2 to measure the validity of the model. Three-dimensional surface distribution (3D) was drawn to show the main and interactive effects between independent variables on pH, UV intensity, time, $Fe_2(SO_4)_3$ concentration, hydrogen peroxide concentration, and PAH concentration.

Results and Discussion

Residue Distribution Analysis, COD, and TOC Removal Percentage

The observed residuals against the predicted values have been shown as normal distributions in Figure 2. The residuals under analysis should ideally follow a normal distribution, and moderate deviations from normality are unlikely to significantly affect the results of the analysis. To assess the normality of the residuals, a normal probability plot can be used, and a roughly linear pattern on the plot suggests normality. However, it is important to note that other diagnostic tools should also be used to confirm normality, since non-normal distributions can also produce a linear pattern. Additionally, it is worth noting that normality is just one of several assumptions required for valid inference in linear regression, and violations of this assumption may impact the accuracy of the regression results.

Examining the Coefficient of Determination of COD and TOC Percentage Removal Model

The value of the R^2 determination coefficient for COD and TOC removal percentage response in a synthetic solution

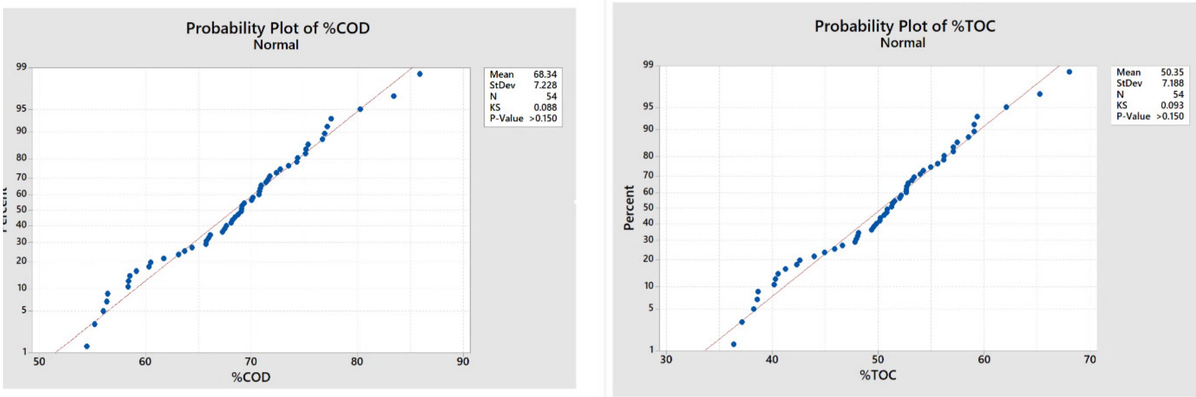

Figure 2. The Plot of Residuals for Percentage Removal of COD and TOC in Naphthalene-Containing Solution.

containing naphthalene was obtained as 98.33 and 98.29%, respectively, demonstrating the good agreement of the model with the experimental data. R^2_{adj} is equal to 96.6 and 96.51 percent, respectively.

Presenting a Suitable Model for COD and TOC Removal in a Synthetic Solution Containing Naphthalene

According to the regression results predicted by Minitab software for the removal of naphthalene in the photo-Fenton process, for COD the effect of variables A (initial concentration of naphthalene), B (Fe concentration), C (hydrogen peroxide concentration), D(UV), E (time), F (pH), the interaction effect, E*F, B*C, A*F, C*F, C*E, F*F was significant at the confidence level of 0.95. And for TOC, the effect of variables A (initial concentration of naphthalene), C (hydrogen peroxide concentration), D(UV), E (time), F (pH), the interaction of B*B, A*F, C*F, C*C, C*E, F*F, B*E, and B*C were significant at 0.95% CI.

The response surface statistical method of the Box-Behnken model was used to obtain a quadratic coded polynomial equation that describes the experimental relationship between the test variables and the percentage of COD and TOC removal efficiency in a synthetic solution containing naphthalene during the photo-Fenton process. Equations (2) and (3) were obtained based on this equation. These equations provide valuable insights into the factors that influence the efficiency of COD and TOC removal and can be used to optimize the experimental conditions for maximum removal efficiency. It should be noted that these equations are specific to the experimental conditions used in this study and may not be applicable to other scenarios without proper validation and analysis.

$$\%COD = 64.79 - 0.0642\ concentration + 0.1912\ Fe + 0.02166\ H_2O_2 + 0.300\ UV + 0.0196\ Time - 2.628\ pH - 0.000404\ concentration * concentration - 0.002385\ Fe * Fe - 0.000009\ H_2O_2*H_2O_2 + 0.00292\ UV*UV + 0.000067\ Time * Time + 0.1817 pH*pH - 0.000067 concentration*Fe - 0.000000\ concentration*H_2O_2 - 0.00099\ concentration*UV + 0.000209\ concentration*Time - 0.02600\ concentration*pH - 0.000077\ Fe*H_2O_2 - 0.00049\ Fe*UV + 0.000330\ Fe*Time + 0.00812\ Fe*pH + 0.000274\ H_2O_2*UV - 0.000067\ H_2O_2*Time - 0.001068\ H_2O_2*pH + 0.00138\ UV*Time + 0.0063\ UV*pH + 0.00754\ Time*pH \quad \text{Eq. (2)}$$

$$\%TOC = 47.56 - 0.0575\ concentration + 0.1932\ Fe + 0.02142\ H_2O_2 + 0.232\ UV + 0.0127\ Time - 2.678\ pH - 0.000404\ concentration*concentration - 0.002402\ Fe*Fe - 0.000009\ H_2O_2*H_2O_2 + 0.00389\ UV*UV + 0.000083\ Time*Time + 0.1857\ pH*pH - 0.000078\ concentration*Fe - 0.000007\ concentration*H_2O_2 - 0.00079\ concentration*UV + 0.000186\ concentration*Time - 0.02700\ concentration*pH - 0.000075\ Fe*H_2O_2 - 0.00045\ Fe*UV + 0.000361\ Fe*Time + 0.00732\ Fe*pH + 0.000270\ H_2O_2*UV - 0.000065\ H_2O_2*Time - 0.001061\ H_2O_2*pH + 0.00146\ UV*Time + 0.0106\ UV*pH + 0.00790\ Time*pH \quad \text{Eq. (3)}$$

Effect of Variables With Response Surface Plots

Figures 3-10 — three-dimensional graphs — show the effect of parameters of initial naphthalene concentration , hydrogen peroxide, Fe, UV, time, and pH on COD and TOC removal rate in a synthetic solution containing naphthalene.

The Effect of Initial Concentration of Naphthalene on COD and TOC Removal Efficiency

The initial concentration of the pollutant is a very important factor and variable in the photo-Fenton process.[28] The interaction effect of the initial concentration of dissolved naphthalene concerning Fe, hydrogen peroxide, time, UV, and pH on COD removal efficiency has been presented in Figures 3 and 6 and TOC removal efficiency in Figures 7 and 10. In all the figures, increasing the initial concentration of naphthalene decreased the removal efficiency of COD and TOC in the photo-Fenton process. At low initial pollutant concentrations, radiation losses are reduced and lamp light penetrates water more effectively and accelerates photo-Fenton oxidation reactions.[29] By increasing the initial concentration of naphthalene, a large amount of UV radiation is trapped by naphthalene molecules and leads to no collision with hydrogen peroxide molecules, as a result, the production of hydroxyl radicals in photodecomposition decreases.[30] In AOPs, the ratio of the produced hydroxyl radical to the amount of pollutant is very important, and with the increase of the amount of

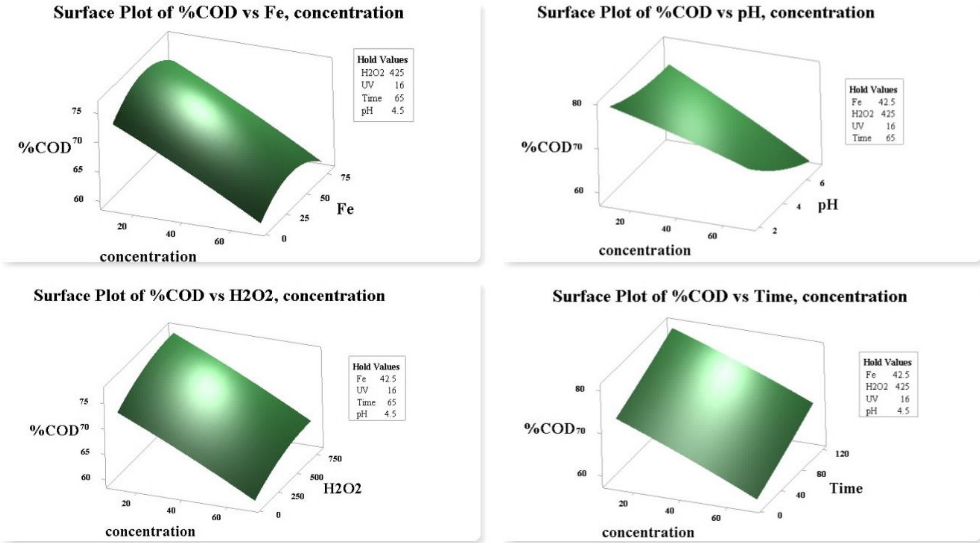

Figure 3. Three-Dimensional Response Surface Diagram Between the Variables of (Fe, C), (pH, C), (H_2O_2, C), (Time, C) on COD Removal Efficiency in a Synthetic Solution Containing Naphthalene.

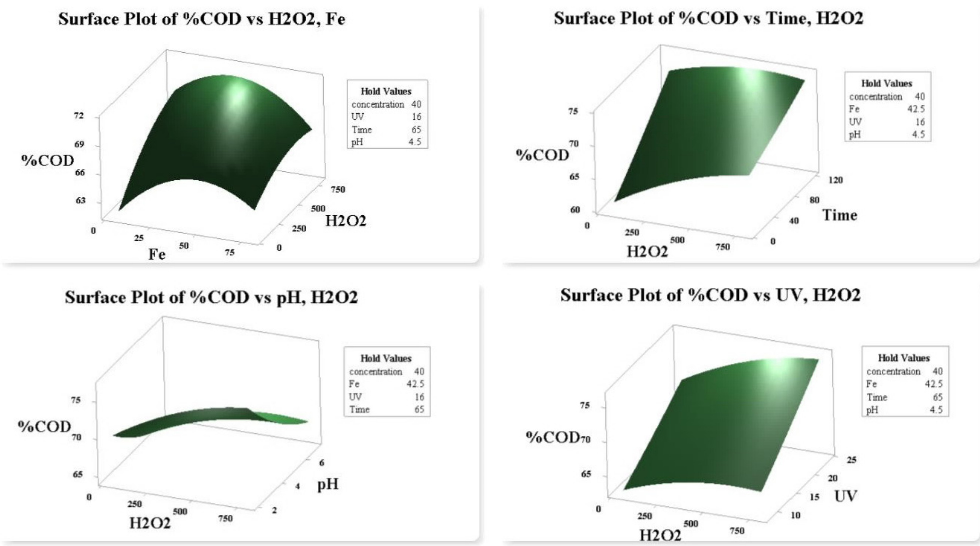

Figure 4. Three-Dimensional Response Surface Diagram Between the Variables of (H_2O_2, Fe), (Time, H_2O_2), (pH, H_2O_2), (UV, H_2O_2) on COD Removal Efficiency in a Synthetic Solution Containing Naphthalene.

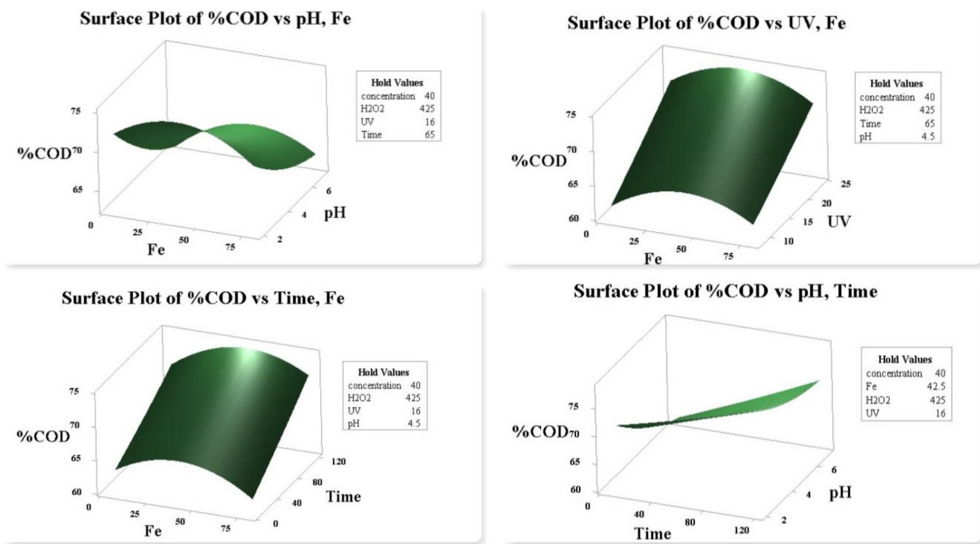

Figure 5. Three-Dimensional Response Surface Diagram Between the Variables of (pH, Fe), (UV, Fe), (Time, Fe), (pH, Time) on COD Removal Efficiency in a Synthetic Solution Containing Naphthalene.

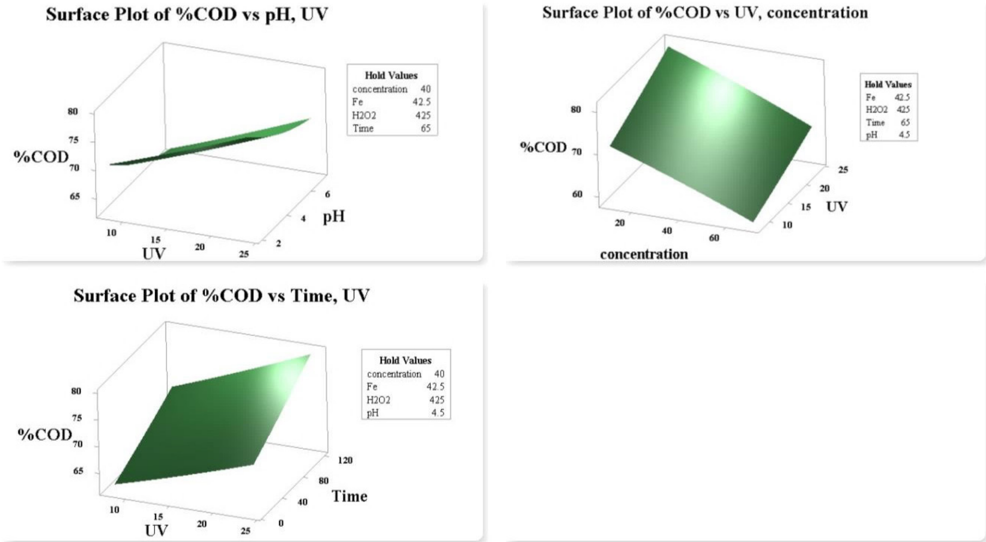

Figure 6. Three-Dimensional Response Surface Diagram Between the Variables of (pH, UV), (UV, C), (Time, UV) on COD Removal Efficiency in a Synthetic Solution Containing Naphthalene.

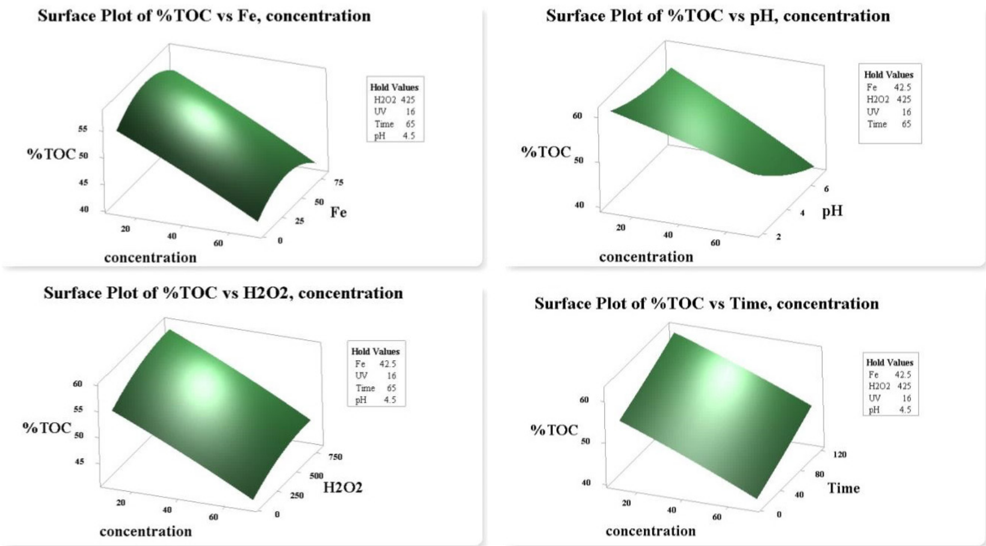

Figure 7. Three-Dimensional Response Surface Diagram Between the Variables of (Fe, C), (pH, C), (H_2O_2, C), (Time, C) on TOC Removal Efficiency in a Synthetic Solution Containing Naphthalene.

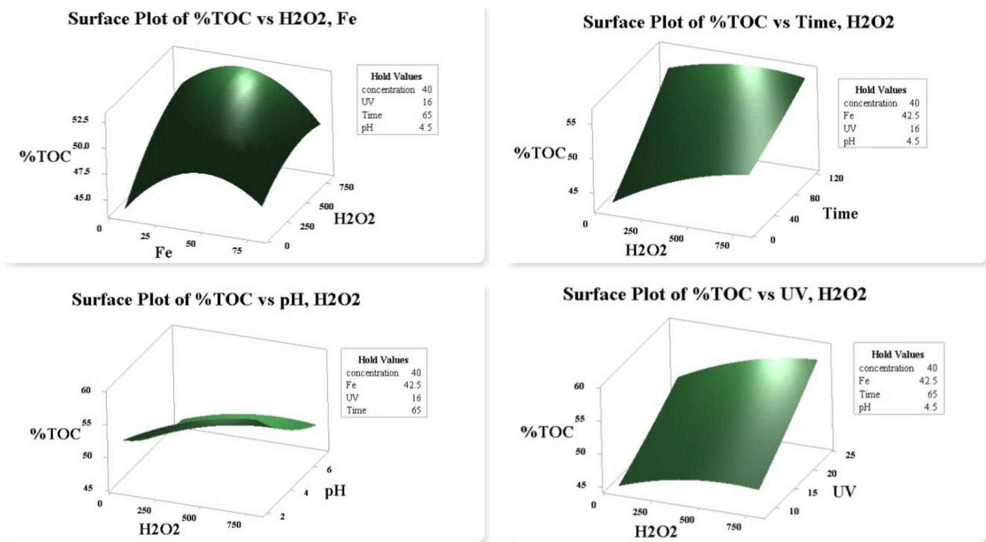

Figure 8. Three-Dimensional Response Surface Diagram Between the Variables of (H_2O_2, Fe), (Time, H_2O_2), (pH, H_2O_2), (UV, H_2O_2) on TOC Removal Efficiency in a Synthetic Solution Containing Naphthalene.

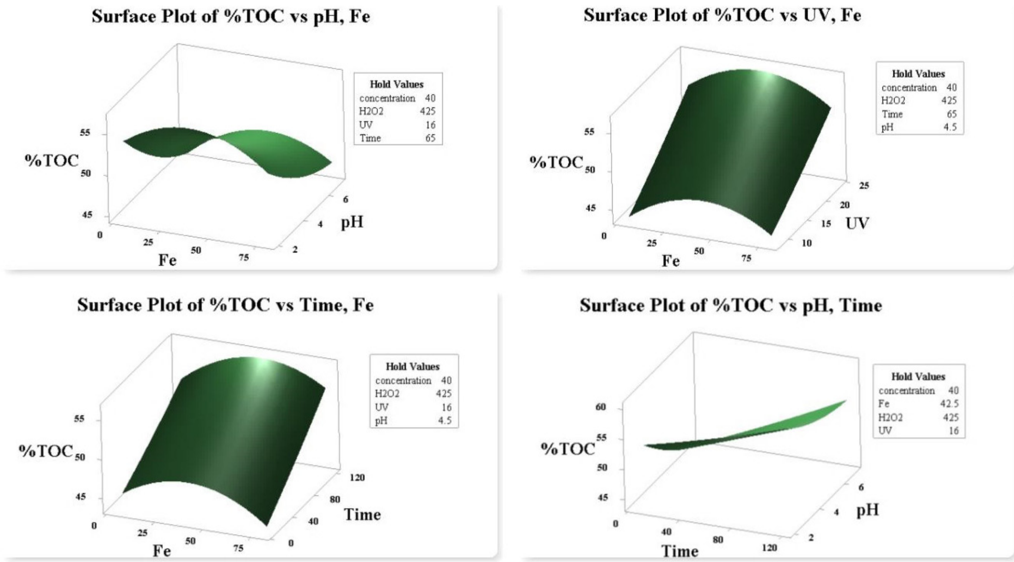

Figure 9. Three-Dimensional Response Surface Diagram Between the Variables of (pH, Fe), (UV, Fe), (Time, Fe), (pH, Time) on TOC Removal Efficiency in a Synthetic Solution Containing Naphthalene.

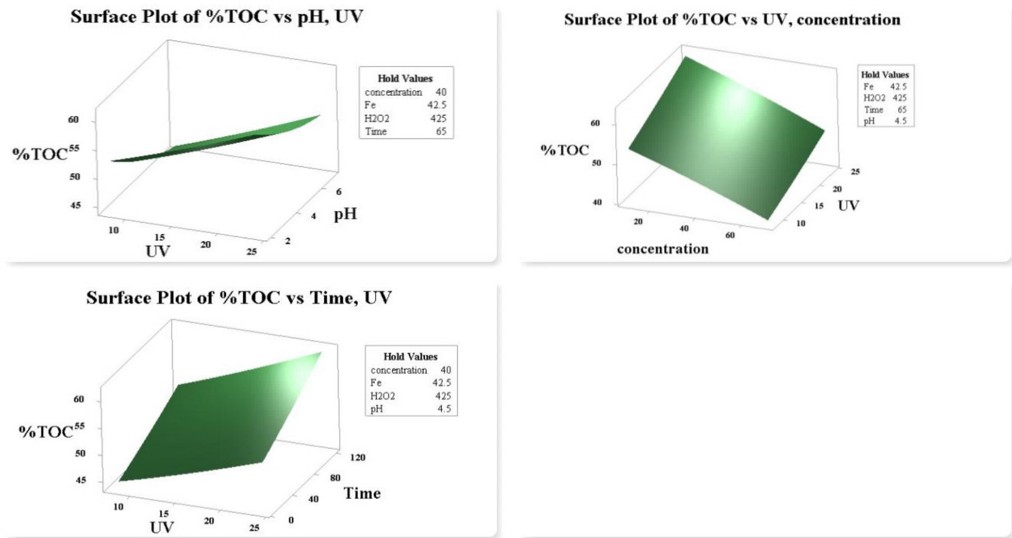

Figure 10. Three-Dimensional Response Surface Diagram Between the Variables of (pH, UV), (UV, C), (Time, UV) on TOC Removal Efficiency in a Synthetic Solution Containing Naphthalene.

pollutant, more oxidizing substances should be produced.[29] It has been proven that the rate of decomposition increased after diluting the initial concentration of the emulsion. The reduction in turbidity favors UV penetration, leading to improved oil removal rates.[31]

The Effect of Hydrogen Peroxide Concentration on COD and TOC Removal Efficiency

The effect of hydrogen peroxide concentration on COD removal efficiency is presented in Figures 3 and 4 and also on TOC removal efficiency in Figures 7 and 8. COD and TOC removal efficiency in all graphs increased with increasing hydrogen peroxide concentration, which could be due to the increased production of hydroxyl radicals due to increasing hydrogen peroxide concentration, which increases the efficiency of the photo-Fenton process. Hydrogen peroxide, as a strong oxidizer, decomposes naphthalene into side compounds. The oxidation power of hydrogen peroxide is in the range of 1.78 eV. Also, this oxidizer causes the decomposition of organic compounds due to the production of hydroxyl radicals and prevents the creation of electron holes. The electron released from hydrogen peroxide is absorbed by oxygen, and an oxygen radical is created, which produces peroxide and hydroxyl radicals in collision with other hydrogen peroxide molecules.[32] At low concentrations of hydrogen peroxide, the removal efficiency decreases due to the decrease in the production of active hydroxyl radicals.[33]

By increasing the concentration of hydroxyl radicals to a certain concentration, the oxidation process increased. When hydrogen peroxide is present in excess, it begins to react with hydroxyl radicals and acts as a free radical scavenger. However, when the concentration of H_2O_2 exceeded the optimal value, the reaction rate decreased as a result of the so-called excessive inhibitory effect of H_2O_2 in the reaction with the hydroxyl radical ($^{\bullet}OH$).[11]

The Effect of Fe Concentration on COD and TOC Removal Efficiency

The effect of Fe concentration on COD removal efficiency has been presented in Figures 3-5 as well as on TOC removal efficiency in Figures 7-9. The main and initial reaction that causes the production of hydroxyl radical is between hydrogen peroxide and Fe ion. Since the hydroxyl radical is the most active factor in Fenton, the oxidation rate of organic compounds is highly dependent on the initial concentration of Fe ions. The removal efficiency in the synthetic solution containing naphthalene increased by increasing the initial concentration of Fe up to 42.5 mg/L, which can be caused by the formation of hydroxyl radicals. Further, by increasing the initial concentration of Fe up to 80 mg/L, the removal efficiency decreases, because in this case, these Fe ions form a complex with hydroxyl radicals, which reduces the free hydroxyl radicals in the solution, and finally, the efficiency of the process decreases.[34] The addition of Fe ions increases the turbidity of the wastewater during photo treatment, which prevents the absorption of UV light necessary for the photo-Fenton process. An excess of Fe ions may react with a compound that produces an OH radical that inhibits the rate of the reaction.[31,35]

The addition of a catalyst is crucial to the photo-Fenton process, but excessive amounts of the catalyst can have a negative impact on the removal process. Excess catalyst can consume the hydroxyl radicals produced during the process, leading to reduced efficiency. Additionally, using excessive amounts of the catalyst can result in increased sludge production and a financial burden.[36] When the amount of Fe exceeds the optimal level, it can react with compounds that produce hydroxyl radicals and inhibit the reaction speed, leading to decreased efficiency in COD and TOC removal. Moreover, excessive amounts of Fe can increase turbidity in the treated wastewater.[11] Therefore, it is important to carefully control the amount of catalyst added to the wastewater and ensure that it is within the optimal range to achieve maximum efficiency in the photo-Fenton process.

The Effect of UV on COD and TOC Removal Efficiency

The effect of UV on COD removal efficiency is presented in Figures 4-6 and also on TOC removal efficiency in Figures 8-10. As can be seen, the percentage of COD and TOC removal increased with the increase of UV radiation. These observations suggest that UV photolysis produced more reactive hydroxyl intermediates, leading to further degradation of pollutants.[37] The combination of photolysis with hydrogen peroxide, which is a strong oxidant due to the production of hydroxyl radicals, makes it easier to decompose and increases the efficiency of the process.[38]

The Effect of pH on COD and TOC Removal Efficiency

The effect of pH on COD and TOC removal efficiency is presented in Figures 3-6 and 7-10, respectively. The highest percentage of COD removal was observed at a pH of 3.[39] The results indicate that COD and TOC removal efficiency decrease with increasing pH. This is because hydroxyl radicals are formed in larger quantities in an acidic environment. At low pH, the formation of $Fe(OH)^{2+}$ slows down the reaction with hydrogen peroxide, reducing the production of hydroxyl radicals and, consequently, the efficiency of the process. In alkaline pH, Fe^{2+} is converted to Fe^{3+} and precipitates as Fe(OH)3, leaving the catalytic cycle. Studies have shown that acidic conditions are the optimal range for the Fenton reaction.[40] However, some researchers suggest that reactions may occur at higher pHs. Nonetheless, at higher pHs and alkaline environments, the H_2O_2 decomposition reaction becomes slower and more limited. Therefore, it is important to carefully control the pH of the solution during the photo-Fenton process to achieve maximum efficiency in the removal of COD and TOC.

On the other hand, very acidic or very basic solutions can delay the photocatalytic process of the pollutant. This may be because oil is a non-ionic compound, and better efficiency can be achieved at the pH of the point of zero charge of the catalysts. This pH is also close enough to the natural pH (6.8) of the irradiated oil solution.[31] At a pH higher than 3, the majority of Fe(II) is precipitated as $Fe(OH)_3$, leading to the elimination of the reaction between H_2O_2 and Fe^{2+}. Furthermore, under alkaline conditions, COD removal is reduced because H_2O_2 decomposes more rapidly into H_2O and O_2.[11,36] Therefore, it is important to carefully control the pH of the solution during the photo-Fenton process to ensure optimal efficiency in the removal of COD and TOC.

The Effect of Reaction Time on COD and TOC Removal Efficiency

The effect of time on COD removal efficiency is presented in Figures 3-6 and also on TOC removal efficiency in Figures 7-10. Appropriate reaction time is one of the effective factors in performing AOPs. Over time, the amount of intermediate products resulting from the decomposition of hydrogen peroxide increases. By creating mixing in the test environment, the chance of contact between Fe ions and the intermediate products of hydrogen peroxide decomposition increases. This leads to an increase in the production of hydroxyl radicals in the environment and, consequently, an improvement in the efficiency of the process. Therefore, it is important to carefully consider the mixing conditions during the photo-Fenton process to achieve optimal efficiency in the removal of pollutants. The content of COD and TOC removal increases with increasing time. In all graphs, the reaction speed increased with increasing reaction time.[11]

In this study, the highest removal percentages for COD and TOC were 89.21 and 71.04%, respectively. In a survey conducted by Safa and Mehrasbi, the observations showed that, the TOC removal percentage was lower than the COD removal percentage.[39] And in another study conducted by Aljuboury et al, COD and TOC removal percentages were found to be 64 and 78%, respectively.[11] In 2021, research was conducted by Mohadesi and colleagues, and under optimal conditions, COD removal was reported as 77.08%.[40]

Conclusion

The highest percentage of COD and TOC removal was obtained using the photo-Fenton process in optimal conditions: pH = 2, UV = 24, optimal concentration 10 µg/L, Fe content 22.42 mg/L, hydrogen peroxide content 800 mg/L, reaction time 120 minutes. The obtained results showed that this process had a significant effect on the treatment of petroleum effluents containing cyclic aromatic hydrocarbons and can be used as an efficient method for the treatment of petroleum wastewaters. Also, the small difference between the observed and predicted values confirmed that the Box Behnken is an effective method to optimize the photo-Fenton oxidation process in the decomposition of chemically required oxygen and TOC in petroleum effluents containing PAHs. In the end, it is recommended that other aromatic hydrocarbons in the same concentration should be investigated to check the efficiency of this useful method.

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Competing Interests

The authors declared no conflict of interest.

Ethical Approval

There were no ethical considerations to be considered in this research.

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