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Studying Removal of PHCs from Deposits of Petroleum Storage Tanks by Ozonation Method: Determining Optimal Conditions by Central Composite Design Method

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ABSTRACT

Introduction: The increasing trend of petroleum production in Iran and lack of proper and systematic management of waste products in the deposition of petroleum storage tanks have made the existing hydrocarbons as a major hazards to the environment. In this study, the ozonation process was used to remove the petroleum deposits.

Materials and Methods: In this experimental study, effects of pH, ozone dose, and petroleum hydrocarbons (PHCs) concentration were evaluated. In order to measure the PHCs, using the n-pentanes, the hydrocarbons were first extracted from the environment followed by detection using the GC-FID. The response surface methodology (RSM) was used to evaluate the effect of independent variables on response function.

Results: In this study, the efficiency was calculated 45.47% in the optimal conditions of removing PHCs with respect to the optimal energy consumption for the process. Analysis of variance and regression showed that the fitted model had good agreement with the laboratory results.

Conclusion: The results demonstrated that the advanced oxidation process (AOP) of ozone at high pH levels could be a useful method for the degradation and reduction of heavy hydrocarbons in petroleum waste. However, regarding the energy consumption, it is suggested to use less costly reactions as pretreatment or final treatment steps.

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Introduction

Petroleum is an oil and mineral composition that is mainly composed of two elements of hydrogen and carbon, containing less amounts of nitrogen, oxygen, and sulfur, and is naturally found underground. Petroleum can be prepared for treatment or exporting after a preliminary treatment step. As a result of the processes of extraction, transfer, and treatment of petroleum, a large amount of oil pollutions, such as oil sludge or industrial waste, is naturally returned to the

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environment as waste [1]. Therefore, the development of oil activities in oil-rich countries has led to numerous environmental problems, one such as soil and groundwater contamination [2-4]. One of the most important compounds is the deposit found on the floor of petroleum storage tanks, which is a sticky and relatively solid compound. These types of deposits are formed by the storage and maintenance of petroleum in refinery tanks. Evacuation of the deposits to the earth causes major hazards to the environment and human health, leading to the entry of volatile hydrocarbons into the air and leakage of contaminants into groundwater and soil [5-8].

The petroleum hydrocarbons (PHCs) waste is the most important pollutant in these deposits [9, 10]. These compounds can be found in petrochemical products, such as gasoline and oils, and can be discharged into soil. The PHCs are widely used to determine the measurable amount of oil-based hydrocarbons in the environment, such as many hazardous compounds with a range of C_{10} to C_{40} [9]. Any content of PHCs in the sample indicates contamination in a site caused by the secretion of petroleum compounds. According to studies, the toxicity order of petroleum compounds is as follows: decane, octane, heptane, hexane, pentane, cyclooctene, naphthalene, para-xylene, cyclohexane, benzene, and cyclohexane. Toxicity and hazardous amount of PHCs in sediments discharged into the environment depends on the type of fractions and components. The more rings with compounds forming the major part of the hydrocarbons, the higher the accumulation and degradability of the sediments, and the need for additional treatment to reduce the environmental impact [5-8]. Although toxicity content is different across the petroleum compounds, the toxic effects of pollutants cannot be accurately predicted, since information is only available on PHCs. In general, alkanes have less toxicity than other petroleum compounds. Some effects are due to aromatic compounds [9, 10].

The surface and deep expansion of these contaminations could be prevented using a proper treatment method and appropriate management. Many of the oil deposits entering environmental resources from oil and petrochemical industries and their downstream industries are resistant to biodegradation, having a toxicity potential to humans and the environment [11]. Therefore, chemical methods are among the treatment methods for petroleum compounds used for the treatment and management of these types of waste [12-14]. Today, for the degradation of toxic compounds and the resistant and non-decomposable pollutants, advanced oxidation processes (AOP_S) have attracted great attention [12, 14-16]. In these processes, hydroxyl radicals are the main factor for the decomposition of compounds [14-16]. The hydroxyl radical with an oxidizing potential of 2.80 V is the strongest oxidant after fluorine (oxidizing potential of 2.87 V) that can non-selectively react with organic matters to decompose and mineralize them. Diversity of AOPs methods is due to the point that there are many ways to produce and create hydroxyl radicals, one of which is the process of ozonation [16]. Ozone is one of the most important oxidizers in these processes, which is capable of oxidizing aromatic compounds. Recently, ozone has attracted great attention in the treatment industry due to its high oxidation power [16-19]. Pazos et al. studied the effect of the AOP by electro photon method in the removal of PHCs from contaminated marine sediments. This process managed to remove total petroleum hydrocarbons (TPH) with the efficiency of 90% after 30 days [20].

In this study, in order to optimize the response and to examine the factors affecting the chemical treatment process, the response surface methodology (RSM) was used. The RSM method has been widely used for analysis, optimization, and evaluation of the interaction of independent factors in numerous chemical, biochemical, and environmental processes [21-23]. The methods, such as central composite design (CCD), Box-Behnken, and Dahlert are the most important RSM for test design. RSM used in this study was the CCD, which is the most prevalent test design method [23]. According to the studies, these materials are traditionally isolated in the Iranian refineries after

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several years and disposed to the soil, followed by severe environmental pollution. Given that Iran is an oil-rich country and with regard to the importance of oil deposits, this study was designed to investigate the advanced chemical oxidation process by ozonation method in the degradation of PHCs.

Materials and Methods

Chemical materials

This study was experimentally conducted on a laboratory scale at School of Public Health, Iran University of Medical Sciences, Tehran, Iran. The chemical materials included n-pentane solvent, sulfuric acid, NaCl, HCL, potassium iodide, starch, and sodium thiosulfate made by Merck, Germany.

Sample collection and preparation

The study samples were prepared from Ray Oil Refinery in Iran and transferred to the laboratory. After removing the coarse particles, for the preparation and uniformity of the samples, a homogenizer tank connected to a water pump was used. The rapid movement of the blades, as well as the high-pressure injection into the tank, led to the uniformity of the samples[7].

Reactor characteristics

The reactor used in this study (Figure 1) was an impinger equipped with a 250 ml sintered glass filter, where the uniform mixture in the homogenizer tank of the treated oil deposits entered the reactor as a discontinuous flow and, after the ozonation and reaction time, the concentration of PHCs was determined. Along with the main reactor, two 500 ml impingers containing potassium iodide were used for the removal of output ozone before discharging into the environment. The operation of the reactor was carried out at the ambient temperature.

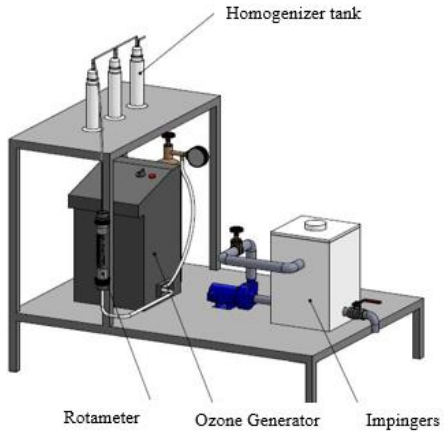

Figure 1: The total schematic of ozone reactor

Experiments

PHCs analyses

In order to measure the PHCs, the extraction of hydrocarbons was done from the environment using n-pentane followed by detection using GC-FID. In this method, a mixture of unleaded gasoline and commercial diesel fuel in 1-to-1 ratio was used as calibration standards. Before the analysis, all the samples should be extracted by normal pentane. In order to extract the samples collected in vials for volatile substances, the sample vial was first removed from the freezer and allowed to reach the ambient temperature. Then, 0.1-1g of the sample was weighed and transferred to the vial, and 5 ml of pentane was added to the sample and stirred manually or using vortex for at least 1 min. The particles were allowed to deposit for at least 4 h, preferably for all day long. While using this method to measure the hydrocarbons in oil deposits or products, such as petroleum, the sample should be properly diluted with appropriate proportions using n-pentane and analyzed directly [7].

Physical and chemical characterization

In this study, to more accurately assess the

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deposits of petroleum storage tanks, according to the standard method, the standard method of ASTM D4006 was used to measure the amount of water present in the sludge sample and the contents of common heavy metals and water content in the deposits were tested. The amount of heavy metals was determined using a polarography (Metrohm) device and atomic absorption of 240 Varian model furnace [7, 24, 25].

Ozone analysis

To determine the ozonation capacity of the ozone generator (Pasargad Ozone Company) as well as the ozone content entering the treatment system, the ozone gas generated by ozone generators was measured using the 2350E (potassium iodide) technique of the standard method book [26].

Experiments design

Sample size

Initially, in order to begin the experiments, the initial PHCs concentration was measured in the real samples for 3 times. Then, the experimented concentration range was determined. Furthermore, according to the equation, the RSM based on the interactions of factors was obtained at 3 levels with 3 factors of ozone concentration (mg/min), pH, and PHCs concentration (mg/g), and 6 iterations at the central point of 20 experiments. The surface response was determined to evaluate optimal conditions and removal model based on the efficiency of removal of PHCs. In order to examine the effects of time, the design basis was in such a way that the optimal conditions for the removal of PHCs were first determined by RSM and, then, the kinetics of reactions was examined at optimal conditions.

Sampling design and data analysis

The RSM was used to evaluate the effect of independent variables on response function (removal efficiency of TPH) as well as predicting the best response rate. The RSM used in this study was the CCD, which is one of the most important experimental designs used in the optimization process. In this method, all the factors were studied at 5 levels (+ α, + 1, 0, -1, and - α) (Table 1). The independent variables in this study included ozone concentration (mg/min), pH, and TPH concentration (mg/g). The dependent variable in this study was the removal efficiency of PHCs. The first step in using the RSM is to find an appropriate approximate correlation between the response and independent variables. The data of the CCD method were used to determine the polynomial regression equations as follows:

Equation 1:

$$Y = \beta_{\circ} + \sum_{i=1}^{k} \beta_1 X_1 + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1}^{K} \sum_{j=1}^{K} \beta_{jj} X_i X_j + \epsilon$$

Where Y is the response value, β is the constant number, β_i is the linear regression coefficient, β_{ii} is the second-order regression coefficient, β_{ij} is the interaction regression coefficient, and ϵ is the error rate[23].

Table 1: The real and encoded values of independent variables used in the experiment design

Variable	Variable code	Range of variations of real values of variables at encoded level				
		-α	**-1**	**0**	**+1**	**+α**
PH	A	9	9.61	10.50	11.39	12
PHCs concentration(mg/g)	B	50	80.40	125	169.6	200
Ozone dose(mg/min)	D	5	6.01	7.50	8.99	10

Ethical issue

This study was conducted and approved by observing the ethical principles of the research ethics committee of Iran University of Medical Sciences (IR.IUMS.REC. 29464).

Results

Sample characteristics

In this study, for more precise examination, the physical and chemical properties of the deposits were analyzed (Table 2). Characteristics of the waste samples under the chemical process are given in Table 2.

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Table 2: The characteristics of physical and chemical parameters of the real samples

Parameter	Unit	Mean (SD)
pH	-	5.7(± 0.8)
PHCs	mg/g	178(± 15)
Water	mg/g	435(± 11)
Fe	mg/kg	5862(± 35)
Ni	mg/kg	21.66(± 1.6)
V	mg/kg	19.57(± 1.5)
Zn	mg/kg	19.133(± 1.7)

Performance of AOP

The approach used in this study to design and perform experiments was the RSM based on the CCD. Initially, to determine the range of test, the real concentration of PHCs was calculated in the deposits. Then, in accordance with the RSM based on the CCD, the design matrix for the RSM tests to determine the effect of three independent variables on the removal of TPH is expressed in Table 3. Based on the experimental model design presented in Table 3, after adjusting the desired pH and specific concentrations, ozonation was carried out for a defined period (25 min) and, at the end, the removal efficiency of PHCs in each step was determined by the GC-FID device.

Table 3: The experiment design and results

Testing stage	Factor 1 A: pH	Factor 2 B: PHCs (mg/g)	Factor 3 C: O_3(mg/min)	Efficiency %
1	9.61	80.40	6.01	20.7176
2	10.50	125	7.50	44.516
3	9.61	169.60	8.99	36.5191
4	10.50	125	7.50	49.7557
5	9.61	17.50	6.01	1.2595
6	11.39	25	6.01	59.313
7	10.50	50	7.50	57.2672
8	10.50	125	7.50	48.855
9	10.50	200	7.50	32.1832
10	10.50	125	10	65.9695
11	11.39	32.50	8.99	63.3435
12	11.39	80.40	6.01	60.3359
13	10.50	125	7.50	37.7557
14	11.39	80.40	8.99	71.068
15	10.50	125	7.50	53.0299
16	10.50	125	5	26.5954
17	9.61	80.40	8.99	34.4275
18	9	125	7.50	31.5878
19	12	125	7.50	59.6947
20	10.50	125	7.50	40.4275

Effect of pH, ozone concentration, and PHCs concentration

Figure 2 (a, b) reveals that by increasing pH over time, the removal efficiency of PHCs increased at ozone doses of 7.5 mg/min (a) and 8 mg/min (b). In this study, the effect of ozone concentration of 5-10 mg/min was investigated. As shown in Figure 2 (c, d), by increasing ozone doses in the ozonation process from 6.01 to 8.99 mg/min, the removal efficiency increased in at pH 10 and 11. For better understating of individual effects and interaction of variables, three- (3D) and two-dimensional (2D) plots were used (Figure 2). The effect of the main variables on the studied responses is presented in Figure 3. This figure shows the variations of responses in the conditions in which, except for the

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desired factor, the other factors were constant at their zero level. In Figure 4, the GC analysis chart is shown before and after the treatment process in optimal energy consumption conditions. It was observed that the AOP with ozone, in addition to the removal of PHCs, led to the degradation of higher-molecular-weight compounds to lower-molecular-weight compounds.

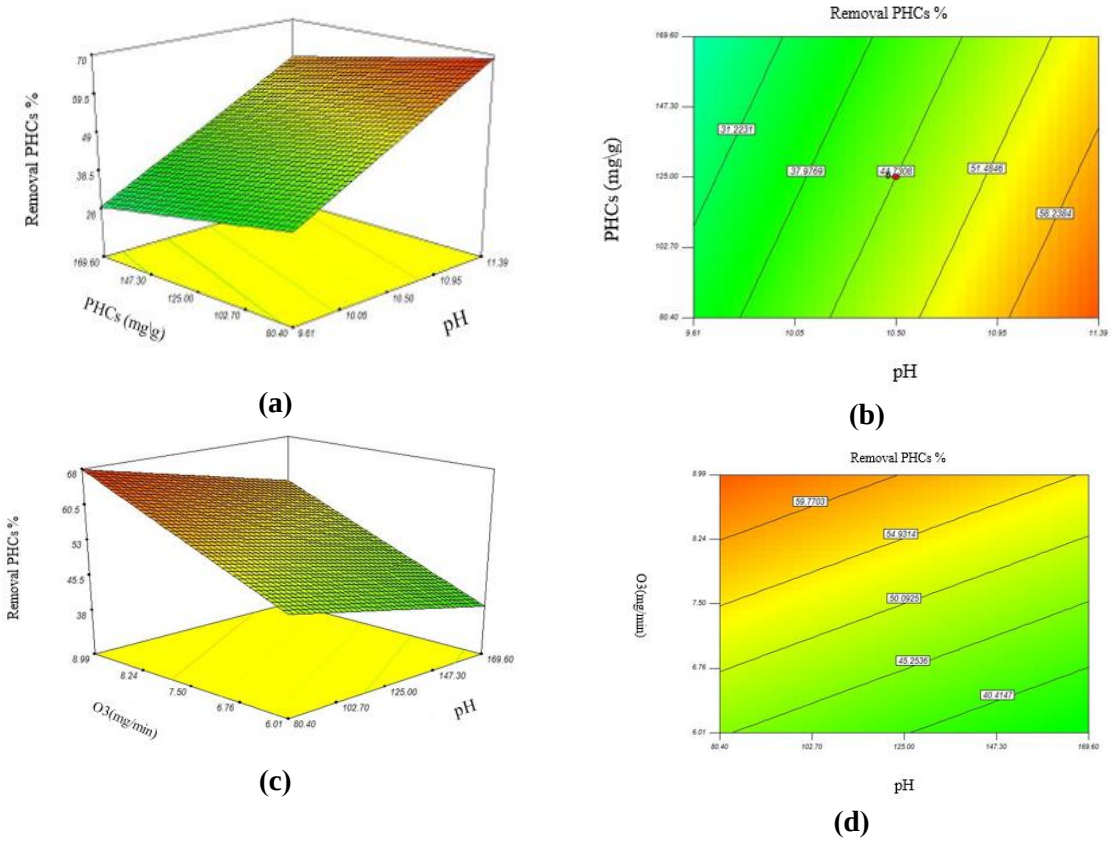

Figure 2: The interaction of variables, including (a) three-dimensional view of changes in PHCs and pH; (b) two-dimensional view of changes in PHCs and PH; (c) three-dimensional view of changes in PHCs and ozone dose in the removal of PHCs by ozonation process; and (d) two-dimensional view of changes in PHCs and ozone dose

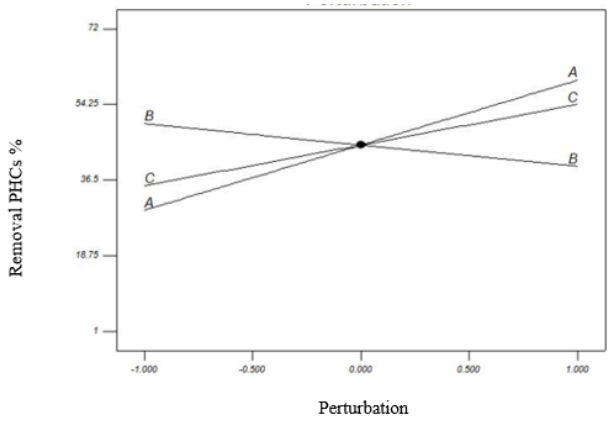

Figure 3: The effect of independent factors on the removal efficiency of PHCs from deposits with ozonation process (pH of 10.5, ozone dose of 7.50 mg/min, PHCs concentration of 125 mg/g, and reaction time of 25 min)

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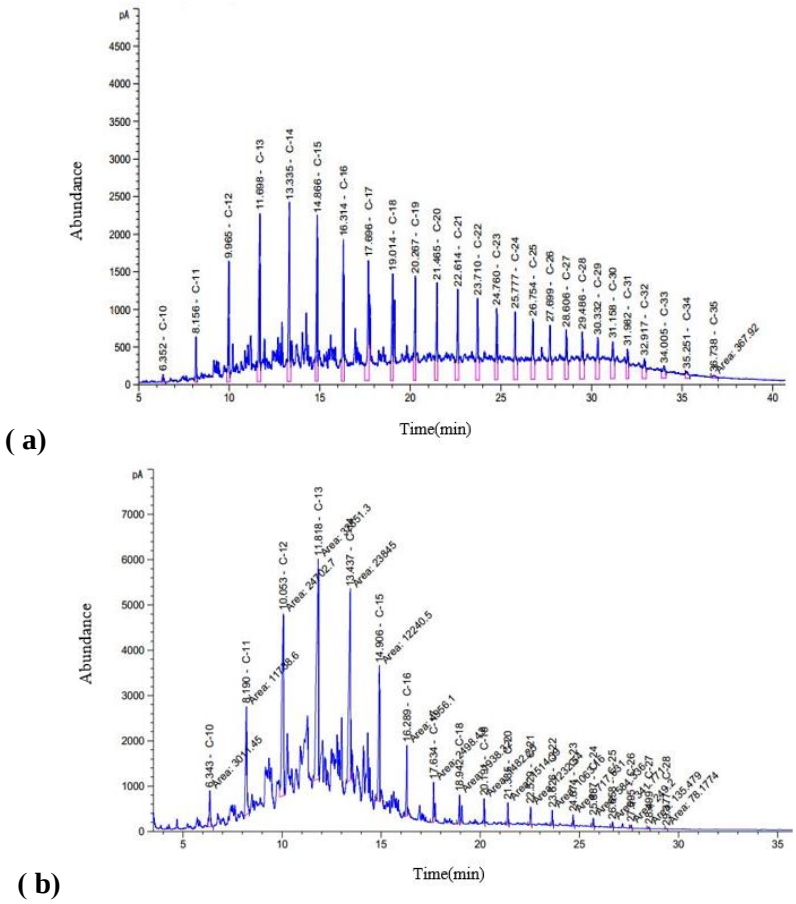

Figure 4: Graph of changes in the petroleum hydrocarbon compounds before (a) and after (b) the ozonation process in optimal conditions

Statistical analysis of the process

In order to determine the effect and importance of each of the process input parameters, ANOVA was used. In this analysis, three parameters of F-value, P-Value, and R^2 were used for the approval and precision of data processing. R^2 is the parameter for the approval and precision of data processing. Coefficient R^2 represents the total ratio of response variations predicted by the model and also the sum of squares regression (SSR) to total sum of squares (SST). Proximity of R^2 to 1 is desirable and an optimal agreement with the adjusted R^2 is essential. Given the statistical parameters listed in Table 4, the total regression coefficient was 0.8196 considering all the R^2 independent parameters of the model for the removal efficiency. The adjusted regression coefficient that only considered effective parameters (Adj-R^2) was 0.7858 for the removal efficiency model and the regression coefficient predicted by the model (Pred R^2) for the removal efficiency response was 0.6890. Therefore, in this study, there was a satisfactory agreement between experimental and predicted regression coefficients by the model.

Reaction kinetics

In order to determine the kinetics of the PHCs degradation reaction in the ozonation process, the curves of the linear equations of zero, first, and second degree reactions were plotted and drawn according to the linear curve linear regression equation. The kinetic diagram of the ozonation reaction in PHCs removal is also shown in Figure 5.

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Table 4: The analysis of variance for the removal model of PHCs

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	
Model	4758.50	3	1586.17	24.23	> 0.0001	Significant
Residual	187.32	6	31.22			
Lack of fit	874.89	11	79.54	2.31	0.1836	Not significant
Pure Error	172.34	5	34.47			
Cor Total	5805.72	19				

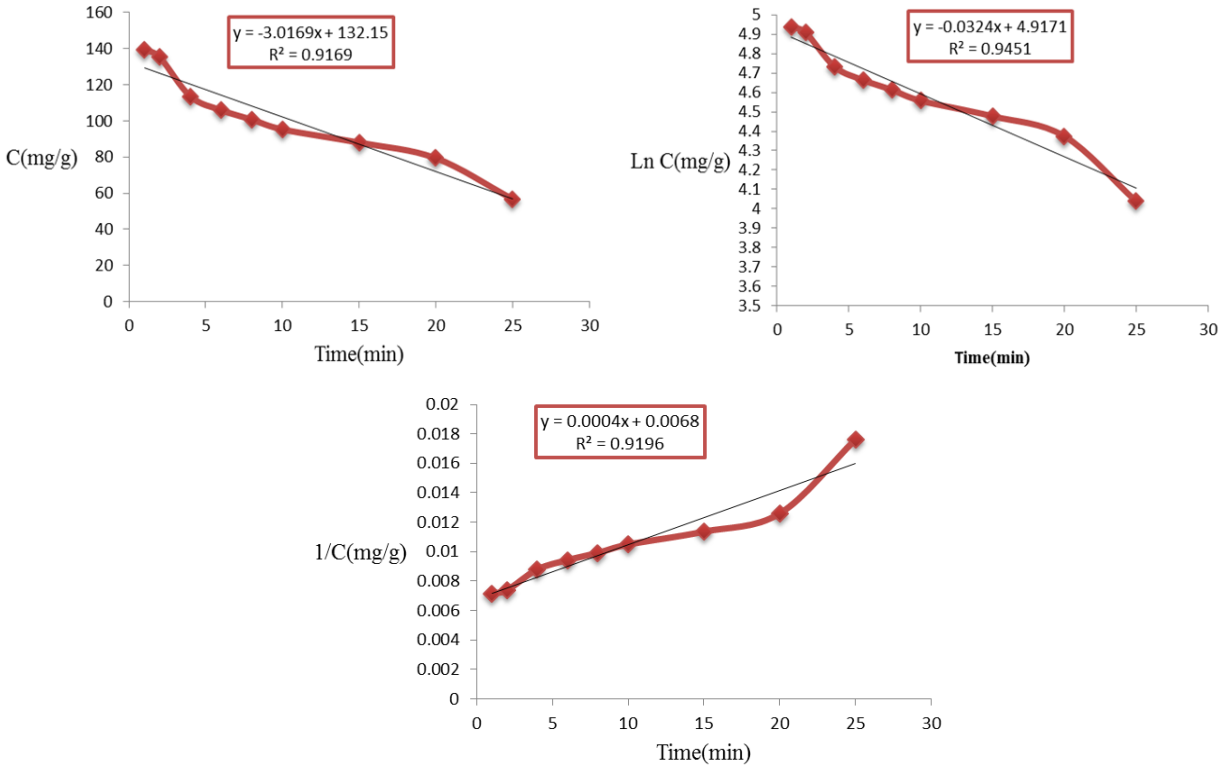

Figure 5: Determination of kinetics of PHCs degradation by ozonation process

Discussions

This study aimed to investigate the removal of PHC from the deposits of crude oil storage tanks through the ozonation process, since these sediments are classified as hazardous wastes for humans and the environment[2-4].The water content in these samples was 43.5% and the rest was composed of oil compounds and solids. Given this type of waste was periodically isolated from the floor of the relevant reservoirs; the sample used in this study was directly taken from oil storage tanks. However, the stored samples isolated from the reservoirs and kept in barrels outside might have been semi-solid with lower water content. Therefore, despite their nature, they might have been semi-solid, since this temporary storage outside leads to very low moisture content. Different studies have reported the water content of 5-83% in this type of wastes [27, 28]. Regarding the concentration of various elements, especially metals, in these types of waste, Table 2 shows that the available iron content (mg/kg) (5862) was very high and concentration of other elements had a decreasing trend from Nickel, vanadium, and zinc, which was less than 50 mg/kg. Al-Futaisi et al. studied oil reservoir sludge in Jordan. They reported the concentrations of zinc and nickel in the range of 74-759 and 0.4-18.8 mg/kg, respectively [29]. Comparison of these results showed that the samples used in this study contained higher nickel concentration and lower zinc concentration compared to those examined by

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Al-Futaisi[29]. One of the most important parameters in the formation of active radical hydroxyl in the AOPs was pH [17]. Therefore, in this study, before any other parameter, the effect of pH 9 to 12 on ozonation efficiency in the values of other parameters was investigated. The alkaline pH range was considered for this study, since studies on the removal of petroleum compounds with AOPs have confirmed the effect of high pH levels [19]. Studies have demonstrated that ozone directly and indirectly reacts with organic material (mainly radical hydroxyl). In direct reaction, ozone is selectively reacted with oil organic annular compounds, while in the indirect reaction method, ozone is converted into secondary oxidants through chain reactions (mainly radical hydroxyl), having much higher oxidizing potential than the ozone molecule [17, 18]. By increasing pH in the ozonation process, the contribution of indirect ozone reaction in the degradation and decomposition of organic compounds increased. Hence, stronger oxidizers, such as radical hydroxyl raised the removal efficiency of oil compounds. Therefore, due to the production of radical hydroxyl and conversion of ionic mode at pH 12, the removal efficiency of PHCs from oil waste was higher than other pH levels. Farzadkia et al. studied the efficiency of the ozonation process in the removal of PHCs from oilfield water and concluded that by increasing pH, the removal efficiency of TPH increased [30]. Many studies have examined the effect of pH on AOPs in the removal of oil waste and obtained similar results [31-33]. In this study, the effect of ozone concentration of 5-10 mg/min was investigated. The removal efficiency increased at pH 10 and 11. Mazlumi et al. studied the removal of hydrocarbons using catalytic ozonation process from groundwater resources. They concluded that by increasing the injected ozone dose, the oxidation efficiency of the compounds increased [34]. Aghapour et al. also reported that the removal efficiency of catechol increased from 28% to 70% by increasing ozone dose from 2.1 to 3.1 mg/min [35]. In this study, the effect of PHCs concentration on the PHCs decomposition in the ozonation process in the waste was also examined. Comparison of the results of this study showed that increasing the concentration reduced efficiency. At low concentrations, the need for reaction time would be very low; as a result, the reactor volume and relevant costs also reduced. Different studies have reported similar results regarding the reduced efficiency of the ozonation process with an increase in the concentration of the pollutants [35-37]. The CCD used in this study was the most common experimental design method. In recent years, the RSM has been widely used in numerous chemical, biochemical, and environmental processes for analysis [21-23]. According to the statistical data, the F-value of the removal model of PHCs was 24.23, which implied the significance of the model. The prob > F (P-Value) values of less than 0.05 indicated that the model was statistically significant with the confidence interval of 95%. The results also showed that the p-value of each of the variables alone was less than 0.0001. High p-value of lack of fit parameter as well as small F-value of lack of fit parameter implied the insignificant lack of fit parameter of the model associated with the pure error and, in other words, the matching of the model prediction with real values. Lack of fit of the test coefficient described the changes in the data around the fitted model. If the model were not fitted properly, this test would be significant. The adequate precision indicator is the predicted response-to-error ratio or the signal-to-noise ratio; if the indicator is equal to or greater than 4, the precision of the model would be acceptable. In this study, the AP value in all the cases was higher than 4, indicating high power of the model in predicting the results. This model can be used alone to determine the nature of the design space (adequate precision: 16.4). The response surface statistical method was used to obtain Equation 2 that indicated the experimental relationship of test variables and encoded efficiency percentage.

Equation 2:

Efficiency (%) = +47.67+18.09 A-9.54 B+15.78 C-17.90 AB-2.97 AC+5.74 BC-4.51 A^2-10.86 B^2-3.90 C^2

In which, A indicates PH, B is PHCs concentration factor (mg/g), and C is the ozone

dose factor (mg/min). Analysis of variance for the removal of petroleum compounds in this study is presented in Table 4. For the kinetics analysis of the reaction, the effect of reaction time on decomposition of PHCs in the ozonation process was removed in periods of 1, 2, 4, 6, 8, 10, 15, 20, and 25 min. According to Figure 3, the decomposition of PHCs with the AOP by ozone followed a first-order reaction with R^2 of 0.9451. One of the major advantages of AOPs is the production of radicals, especially hydroxyl radicals. In order to ensure the production of hydroxyl radicals, under optimal conditions of ozonation process, ozonation reaction was performed again. It was conducted using a concentration of 1 M radicals of tert-butanol, sodium bicarbonate, sodium carbonate, and sodium sulfate, indicating the presence of tert-butanol radicals. The rate of ozonation reduction was greater than the studied cases. In this study, the removal of PHCs from the deposits of petroleum storage tanks by ozonation process was studied. Also, the impact of parameters affecting the oxidation reaction of organic compounds, such as pH of waste, PHCs concentration, and ozone dose was studied on the efficiency of the chemical process. In this study, pH 11.39, ozone dose of 6.01 mg/min, and PHCs concentration of 169.59 mg/g were selected as optimal conditions based on the optimal energy consumption for the process. In such conditions, the degradation efficiency of 45.4742 % was achieved. Also, the optimal conditions with respect to the high efficiency of the process was equal to 64.505% at pH 11.39, ozone dose of 8.99 mg/min, and PHCs concentration of 169.59 mg/g.

Conclusion

The results of the study showed that the advanced ozone oxidation process at high pH can be a beneficial method for the degradation and reduction of heavy hydrocarbons in petroleum waste, but with regard to the energy consumption, it is suggested that less costly reactions be used for pre-treatment or final treatment. Treatment of petroleum compounds using chemical methods also requires high investment and operating costs. On the other hand, despite the high advantages of biological method due to the lack of nutrients and low BOD_5/COD ratio in oily sludge, its biodegradability is low and cannot be used directly for treatment. Therefore, it is necessary to use a combined process, which is the chemical process of non-biodegradable compounds into simpler and more accessible compounds to enhance the performance of the biological process. According to the results of this study and other studies and the increasing trend of oil extraction and production in the country and lack of proper and principled management of produced sludge and the presence of contaminated soil and water in different areas, it is suggested that the economic feasibility of using the combined ozonation process should be performed with environmentally friendly biological processes.

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Conflicts of interest

The authors declare no conflicts of interest.

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