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Application of the central composite design to optimization of petroleum hydrocarbons removal from oilfield water using advanced oxidation process

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Abstract: In the last few years, RSM method has been used widely to analyze, optimize and evaluate the interaction of independent factors for chemical, biochemical, and environmental processes. This study examined and evaluated the applicability of this method to manage Oilfield Produced Water to prevent marine environment due to the presence of hard degradable compounds by ozonation process. In this study simulated oil-water sample and a homogenizer reactor was used. The main reactor used in this study was impeinger equipped with sintered glass filter through which the treated oil-water was entered to reactor in the form of discontinuous flow. After ozonation and at the end of the reaction time (60 min), the concentration of oil hydrocarbons was determined by a gas chromatography device equipped with a flame ionization detector. The performance of the central composite design (CCD) approach was evaluated by the F-Value, P-Value, R^2, lack of fit test and Adequate Precision parameters to determine the influence of effective factors, including ozonation time, pH, ozone dose, and TPH concentration on the TPH removal efficiency. The mean TPH efficiency obtained from the design of the 30-step experiment resulting from surface-response method was 49.903%, with a standard deviation of 12.47. This study showed the high power of model adopted from the central composite design to predict the hydrocarbons removal from oilfield water using advanced oxidation process, and it was proved that this model can be used alone to determine the design space nature.

Introduction

The process of oil and gas production generates a large amount of wastewater, known as wastewater of oil or oil-water fields, which in fact includes water along with oil and water added during exploitation (Fakhru'l-Razi et al. 2009, Niri et al. 2015, Mojadam et al. 2018). Oil-water contains soluble and insoluble hydrocarbons (such as benzene, toluene, ethylbenzene, xylene, naphthalene, phenanthrene, dibenzothiophene, polycyclic aromatic hydrocarbons (PAHs) and phenols), heavy metals, radioactive materials, various salts (salts concentration ppm 1000–300000), chemicals added to oil extraction (surfactants, anti-foaming agents, anti-fouling, anti-corrosion agents, and biocides), suspended particles, etc., which may cause health and environmental problems by air pollution, soil and water sources (Ekins et al. 2007, Szyczewski et al. 2016, Moradi et al. 2016). Petroleum hydrocarbons (PHCs) are prominent among organic contaminants which are frequently disposed into the marine environment in lower concentrations in the form of urban runoffs, automobile wastes, storm water, industrial effluents, or domestic wastes and occasionally in higher concentrations as a major oil spill (Ahmed et al. 2015, Sajjadi et al. 2016, Mohammadi et al. 2017, Sohrabi et al. 2017). The main components of these petroleum hydrocarbons are degraded crude oils, combusted fossil fuels, and normal alkanes (Ali et al. 2015). Petroleum hydrocarbons consist mainly of three groups of compounds, namely, alkanes, alkenes, and aromatics. Alkanes can be considered as key components of many refined petroleum products (e.g., gasoline, diesel fuel, kerosene, jet fuel, and heating oil) and can be subdivided into several types which include linear alkanes (n-alkanes), branched alkanes, isoprenoids, cycloalkanes (e.g., steranes and triterpanes), and unresolved complex mixtures (Adeniji et al. 2017). The amount of oil-water varies during oilfield exploitation. At the beginning of the exploitation, 5–15% of the extracted liquid is oil-water, but this amount reaches more than 90% after a while. On average, about 80 million barrels of oil and 250 million barrels of oil-water are produced per day in the world. As a result, the ratio of oil-water to oil is about 3 to 1. However, this value varies between 2 and 15 from one country to another (Ma and Wang 2006, de Lima et al. 2009, Khatib and Verbeek 2003, Judd et al. 2009). Iran is one of world's largest oil and gas producers, generating more than three million barrels of oil per day, and therefore, produces about 21 million barrels (3.4 mcum) of oil-water, and oil-water contains a large amount of organic and mineral compounds, which can lead to contamination of surface water, groundwater, and soil (Fakhru'l-Razi et al. 2009). It is essential that special attention must be dedicated to the management practices of the oil-water (production, reduction in origin, storage, reformed, recycling, treatment, and disposal). The U.S. Environmental Protection Agency has determined the maximum daily allowable oil and grease concentration into oil-water for discharge into the sea to be 42 mg/l and a monthly mean of 29 mg/l (Ma and Wang 2006, de Lima et al. 2009). Despite applying management options (production management, reduction in origin and recycling), significant amount of oil-water will still remain which has no qualitative requirements for discharge into the sea. Thus, it may also be necessary to consider an effective and economic process with high reliability for the treatment of such wastewaters (Fakhru'l-Razi et al. 2009, Mohammadi, Takdastan, et al. 2017). Treatment is one of the most effective options for the management of oil-water, which can transform the oil-water into a safe and even valuable product. The use of chemical and physical processes that require less space can be a good option for oil extraction facilities located on sea and offshore (Fakhru'l-Razi et al. 2009, Rezaei et al. 2018). However, physical methods can not eliminate the pollutants in the oil-water, and merely transfer them from one phase to another (Utvik 1999, Moussavi et al. 2011, Ahamadabadi et al. 2016). Mineralization of oil compounds using chemical methods also requires both high investment and operating costs. On the other hand, despite the high benefits of biological methods and due to the lack of nitrides and the low BOD/COD (Biological Oxygen Demand/ Chemical Oxygen Demand) ratio in oil-water, its biodegradability is low and it is not possible to directly use biological methods for its treatment (Ji et al. 2009, Sohrabi et al. 2017). Furthermore, due to the presence of ring-shaped aliphatic compounds, the heavy-weight aromatics and asphaltenes in the petroleum products the direct biological treatment are not possible. Some studies have also shown that one of the most obvious advantages of using chemical processes is the decomposition of these compounds into simple degradable compounds for biological processes. Because these processes require lower operating costs with a long period of refining, they are prioritized. Therefore, the BOD/COD ratio is expected to increase as an index parameter via chemical processes and the intermediate products would generate for microorganisms available and then an efficient and affordable biological process is used to produce a complete decomposition of hydrocarbons. The chemical treatment with advanced oxidation processes (AOPs) decomposes most of resistant organic compounds completely to water, carbon dioxide and mineral compounds, and transforms the rest of the resistant compounds partially into degradable materials (Afsharnia et al. 2018). For this reason, it can be used as a pre-treatment process suitable for biological processes (Cha et al. 2010, Lu and Wei 2011, Rocha et al. 2012, Charinpanitkul et al. 2010, Zhang et al. 2010, Oller et al. 2011). Nowadays, much attention has been drawn on AOP_s (Advanced Oxidation Processes) for decomposing of toxic and pollutant resistant and non-degradable pollutants compounds (Dapeng and Jiuhui 2009, Thomas et. al 2016, Ríos et al. 2017, Biglari et al. 2017). In a broad sense, AOPs are methods that under typical temperature and pressure conditions can produce as much hydroxyl radicals which are effective in water and wastewater treatment. In these processes, a combination of oxidizing agents, such as ozone and hydrogen peroxide, beams and catalysts is usually used (Leili et al. 2012). Ozone can be regarded as one of the most important oxidizing agents in these processes, which can oxidize aromatic compounds. Recently, much attention has been drawn on ozone due to its high oxidation and high disinfection capacity in the treatment industry. The ozone is used effectively to remove smell, taste, color, and organic compounds. Ozone is one of the most powerful oxidizing agents and the oxidizing power of organic and inorganic compounds with ozone is related to its oxidation potential (Moussavi and Alizadeh 2010). In many studies, researchers used different models and education methods for pollution removal or health treatment (Dehghan et al. 2017, Rahimi et al. 2016, Mohebi et al. 2012, Biglari et al. 2018, Mohammadi et al. 2017, Biglari et al. 2017, Ebrahimzadeh et al. 2017). In this study, RSM (Response-Surface Method) was used to optimize the response and to model the factors affecting the reactor function. RSM is a set of useful statistical and mathematical methods for modeling and analysis of problems in which the considered response is affected by various variables and whose goal is to examine changes in a variable at different levels of other variables as well as optimization of the response (Jamali et al. 2016). This method has considerable applications in designing the process of optimizing and improving existing designs. This method is more practical compared to other methods, since it is originated from a practical approach that involves interaction between variables, and finally, it shows the general effect of factors on the process. In most of the surface-response method problems, the form of the relationship between dependent and independent variables is unknown for researcher. Thus, the first step in the surface-response method is to determine a fundamental relationship with proper approximation between dependent and independent variables. Usually, one or several polynomials with a low degree are used in some areas of independent variables to model the relationship between independent and dependent variables. If the response is modeled well with a linear function of dependent variables, the approximation function will be a first-order one. If there is a curve in the system, a higher-order polynomial should be used to approximate the response. It is analyzed to determine the position of the optimal point. A set of independent variables are determined in such a way that the partial derivatives of the model response to be zero in terms of dependent variables. Second--order models are used in the surface-response method due to having numerous advantages so that they can act almost well for real response-surface. In addition, estimating factors in a second-order model is easy by using the least squares method. The ultimate goal of the surface-response method is to consider the optimal operating conditions for the system or to determine the area that is responsive for considered operational characteristics (Mazloomi 2013, Wu et al. 2012, Chen et al. 2011). The central composite design (CCD), Box Behnken and Dahlert methods are the most important surface-response methods for designing the test. Surface-response method used in this study is the central composite design, which is the most common design method for testing. The central composite design is one of the most important experimental designs used in process optimization studies, which is widely used to create second-order surface-response models. In the central composite design, the total number of experiments can be calculated based on both the number of independent variables and the number of repetitions of the central points (Chen et al. 2011). With reference to the above mentioned studies, the present study is aimed to evaluate the efficiency of the central composite design (CCD) method to optimize the removal of total oil hydrocarbons from Oilfield Produced Water through Advanced Oxidation Processes (AOPs)

Methodology

Reactor characteristics

This experimental study was done at a laboratory scale, in which simulated oil-water sample was prepared to first test. The reactor used in this study was an impinger equipped with glass sinter filter with volume of 250 ml. In addition to the main reactor, two 500 ml impingers containing potassium iodide were used to remove ozone before discharging into the environment (Figure 1).

Calculating the sample size

According to equation of surface-response method based on the interactions of factors in 4 levels with 4 factors of ozone concentrations (mg/min), pH, ozonation time (min) and TPH (Total Oil Hydrocarbons) (g/l) concentration and 6 replicates at the central point, 30 experiments were obtained. At first, 10 liters of water was filled with a good proportion of oil and a fixed TPH in the homogenizer Reactor, with a specific amount of NaCl for preparing the Oilfield Produced Water, and then homogenized for 60 min. At this point, to collect the sample in impinger, 250–100 cc sample was taken from the Homogenizer Reactor and after adjusting its acidity, prepared for ozonation. The response-surface was determined to evaluate optimal conditions and the removal model based on the oil hydrocarbons removal efficiency.

Optimization of ozonation process in the oil hydrocarbons removal from oil-water by using RSM

The surface-response method can be considered as a set of useful statistical and mathematical techniques for modeling and analyzing problems in which the desired response is a function of several variables. The purpose of using this method was to optimize the response. The first step was to find the normal approximation between the response and the set of independent variables. A function was to be approximated by a polynomial of independent variables as follows:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_1 X_1 + \sum_{i=1}^{K} \beta_{ii} X_i^2 + \sum_{i=1}^{K} \sum_{j=1}^{K} \beta_{jj} X_i X_j + \epsilon \quad (1)$$

Where y is the response value, β_0 is constant number, β_i is the linear regression coefficient, β_{ii} is second-order regression coefficient, β_{ij} is the interactional regression coefficient, and the ϵ is error level. The least squares method was used to estimate the factors in approximate polynomials. The CCD is the most famous design used to process this model. The extracted model can also be expressed based on both the real and encoded variables. In the encoded model, comparison between the effects of variables can be easier. The percentage of effect of each variable on the response can be determined by following equation (2):

$$p_4 = (b_4^2 / \sum \frac{n}{4} b_4^2) \times 100 \quad (2)$$

where Pi is the percentage of the effect of each variable on the response and bi coefficient of the effect of the considered variable on the response.

The experiments were designed and performed according to the RSM method and the results were analyzed using Design-Expert 7.0 software.

The range of changes in the examined factors at 5 levels (α-, 1-, 0, 1+, α+) was coded. Accordingly, the code A is associated with the reaction pH variable at 5 levels (12, 10.50, 9, 7.5, 3), the B code is related to the reaction time (min) at the levels (60, 32.5, 25, 17.5, 5), the code C is related to the concentration of TPH (g/l) at 5 levels (1.50, 1.25, 1, 0.75, 0.5), and finally, the code D is related to the dose of ozone (mg/min) at the levels (10, 7.75, 5.5, 3.25, 1).

Design method and statistical analysis of data

After analyzing the results of the experiments designed by the software, all the experimental results obtained from the tests were entered into the software. After statistical modeling and regression analysis, ANOVA was used to determine both the effect and importance of each process input parameter.

In this analysis, three parameters of F-Value, P-value and R^{2*} were used for confirmation and accuracy of data processing. F-value was the ratio of the variance of the parameter to the error variance (variance of the residuals) or the ratio of mean square parameter to mean square error. It was considered at 95% level, its calculation was based on the ratio between the mean squares of the model to mean squares of error. The next parameter was P-Value, according to pure statistics, there was a probability to reject the null hypothesis based on the observed data. As this probability of a small number, our trust in the reality of the observed difference would be higher. In other words, it can be said that if in the same conditions we repeat a test 100 times the Pp-value will be changed due to repeated of the chance. The last parameter for confirmation and accuracy of data processing was R^2. The coefficient R^{2*} represents the ratio of all changes of the response predicted by model and the ratio of the SSR (Sum of Squares by the Regression) to the SST (Sum of the Squares Total). The closeness of R^{2*} to 1 was desirable and a reasonable agreement with the adjusted R^{2*} would be necessary. The largeness of R^{2*} confirmed the satisfactory match of test data with the second-order model. The Lack of fit test coefficient described the changes in the data based on the fitted model. If the model were not well--fitted, this test would be significant (Wu et al. 2012).

Analysis

To measure the TPH after extraction by n-hexane solvent, the concentration of hydrocarbons was determined by a gas chromatography device equipped with a flame ionization detector. To measure the ozone gas generated by ozone generator, E2350 (potassium iodide) method was used (Federation and Association 2005).

Results

The results of the evaluation of the ozone process efficiency in the TPH removal from oil-water were analyzed by Design Expert software to develop the best models that could describe the observed responses. The validity of the developed models was measured by ANOVA. The approach used in this study to design and perform experiments was CCD type of surface--response method. Based on this method, the design matrix related to surface-response method experiments was performed to determine the effect of four independent variables including TPH (g/l), pH, Time (min) and (mg/min) O_3 on TPH removal and the summary of the results obtained from TPH removal efficiency in 30 observations at each step specified by GC-FID were shown in Table. The mean efficiency of TPH removal was 49.903 with a standard deviation of 12.479.

ANOVA analysis results for each of the studied responses were presented in Table 2.

Discussion

Natural gas and oil play an important role in today›s modern societies. However, the oil and gas production process generates a large amount of sewage, known as sewage of oil fields or oil-water. On the other hand, despite the high benefits of biological methods, its biodegradability is low and it would not be possible to directly use biological methods for its treatment due to the lack of nitrides and the low BOD/COD ratio in oil-water. Thus, it was necessary to use a combined process (Fakhru'l-Razi et al. 2009, Ekins, Vanner and Firebrace 2007). In this study, ozonation process and analysis using experiment design software RSM method were used to apply the management option of oil-waters. In this study, Design Expert software version 7 was used, which is Windows-based software, and experiments were designed appropriately to identify the factors affecting the study process (Majlesi and Hashempour 2016, Uzun and Şahan 2017). This software used a variety of methods to design an experiment. In this study, the surface-response method was used to determine optimal conditions. Based on the statistical data for the models given in Table 2, the F-value of the model was obtained 14.79, which indicated the significance of the model. High value of P-value showed lack of fit parameter 0.4992 and also low value of F-value indicated non-significant lack of fit of model with regard to pure error and in other words, values predicted by the model were matched with real values. Another test that was used to validate the models

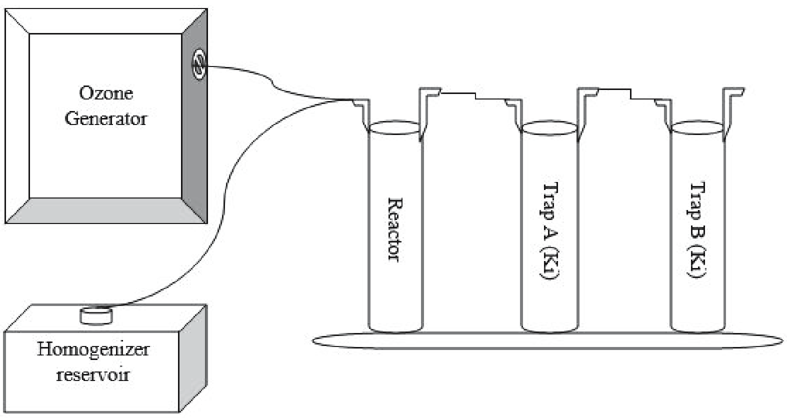

Fig. 1. Total schematic of ozone reactor

Table 1. Design of experiments

Testing stage	Factor 1	Factor 2	Factor 3	Factor 4	R (%)
	A: pH	B:Time (min)	C:TPH (g/l)	D:O_3 (mg/min)	
23	9	25	1	1	26.5
18	10.50	32.50	0.75	7.75	73.3

Table 2. ANOVA analysis results

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	4356.12	14	311.15	14.79	< 0.0001
A-pH	1224.80	1	1224.80	58.23	< 0.0001
B-time	459.64	1	459.64	21.85	0.0003
C-TPH	6.11	1	6.11	0.29	0.5978
D-O3	2419.04	1	2419.04	115.01	< 0.0001
AB	18.86	1	18.86	0.90	0.3587
AC	29.03	1	29.03	1.38	0.2584
AD	7.97	1	7.97	0.38	0.5475
BC	23.11	1	23.11	1.10	0.3111
BD	4.53	1	4.53	0.22	0.6494
CD	17.41	1	17.41	0.83	0.3773
A^2	80.86	1	80.86	3.84	0.0688
B^2	9.32	1	9.32	0.44	0.5157
C^2	22.31	1	22.31	1.06	0.3193
D^2	41.63	1	41.63	1.98	0.1799
Residual	315.50	15	21.03		
Lack of Fit	215.33	10	21.53	1.07	0.4992
Pure Error	100.17	5	20.03		
Cor Total	4671.63	29			

was linear regression test. In this test, regression coefficient, experiment regression coefficient, and prediction regression coefficient were calculated and reported. Regression and variance analysis was used to examine the consistency of the proposed models and to evaluate the statistical significance of the model factors. In this study, the total regression coefficient was calculated 93.25 by taking into account all independent parameters of R^2 model for the removal efficiency. The adjusted regression coefficient considering only the effective parameters for the removal efficiency model was 0.8694 and the regression coefficient was estimated 0.7036 R^2 model to response the removal efficiency. Therefore, there was a satisfactory match between the regression coefficient of the experiment and the regression coefficient predicted by the model in this study. Adequate Precision index was also the ratio of predicted response to its error, or the ratio of signal to noise, and if this index was equivalent to or greater than 4, the precision of the model could be adequate (Wu et al. 2012). In this study, the AP value in all cases was higher than 4, which indicated the high power of the model in predicting the results, and this model would be used alone to determine the design space nature (Adequate Precision: 14.029).

In study conducted by Jamali et al entitled "Optimization of nitrate removal from aqueous solutions by electrocoagulation through surface-response method", results showed that the response-surface method by using the CCD was appropriate to optimize the variables effective in the nitrate removal process via electrocoagulation method. The nitrate removal efficiency in optimal conditions of reaction time 68 min, electrical potential difference 17 volts and pH equal 10 was 88% and the degree of desirability of the model was 98% (Jamali 2016).

By using the statistical method of the response-surface, the following equation showing the experimental relationship between test variables and the percentage of efficiency was obtained:

$$\begin{gathered}\text{Efficiency (\%)} = + 44.29 + 7.14\,A + 4.38\,B - 0.50\,C + \\ + 10.04\,D + 109\,AB + 135\,AC + 0.71\,AD \\ - 1.20\,B\,C + 0.53\,BD + 1.04\,CD + 1.72\,A^2 - 0.58\,B2 + \\ + 0.90\,C^2 + 1.23\,D^2\end{gathered} \tag{3}$$

In above equation A is equal to pH, B is equal to the time in minutes, C is the TPH concentration factor in g/l and C is the ozone dosage ratio in mg/min.

The model to predict the influence of the ozonation process on the efficiency of TPH removal was based on both the parameters encoded in equation 1 and the real parameters shown in Equation 3. Providing the predicted model based on encoded values it was allowed to compare the effects of independent variables on the response variable. The magnitude of the coefficient of each variable, regardless of its positive or negative value, indicated the importance of that variable in independent variations on the response variable. Therefore, Equation 3 shows that three variables of pH, time, and dose of ozone had a positive effect and TPH concentration had a negative effect on the rate of removal efficiency. Aghapour et al. (2015) in own research used to design the experiments, and it is reported that the design of the experiments was appropriate to identify the factors affecting this process and also analysis of variance and regression indicated that the fitted model had a high match with experimental results (Aghapour et al. 2015).

Figure 3 shows the fit of values obtained in experiment versus values predicted by the model for the ozone process efficiency in the TPH removal. In this Diagram, the real values were the responses measured from the results of the experiments, and the proposed values obtained by estimating the functions were evaluated for the model. In Figure 1, the adjacency of points to a 45-degree line showed that they were appropriate to predict the response. In order to develop a better understanding of individuals of the interaction effects between variables, three-dimensional (3D) and two-dimensional (2D) plots were used (Figure 2). In Figure 2-a, a 2D plot is shown for determining the amount of TPH removal with pH variations and TPH concentration at a time of 32.50 minutes and an ozone dose of 7.57. In the ozonation process, the most important parameter was pH in range of 6 up to 12. . The ozonation process had the highest removal efficiency in the initial pH of 10.50. By increasing pH in the ozonation process,

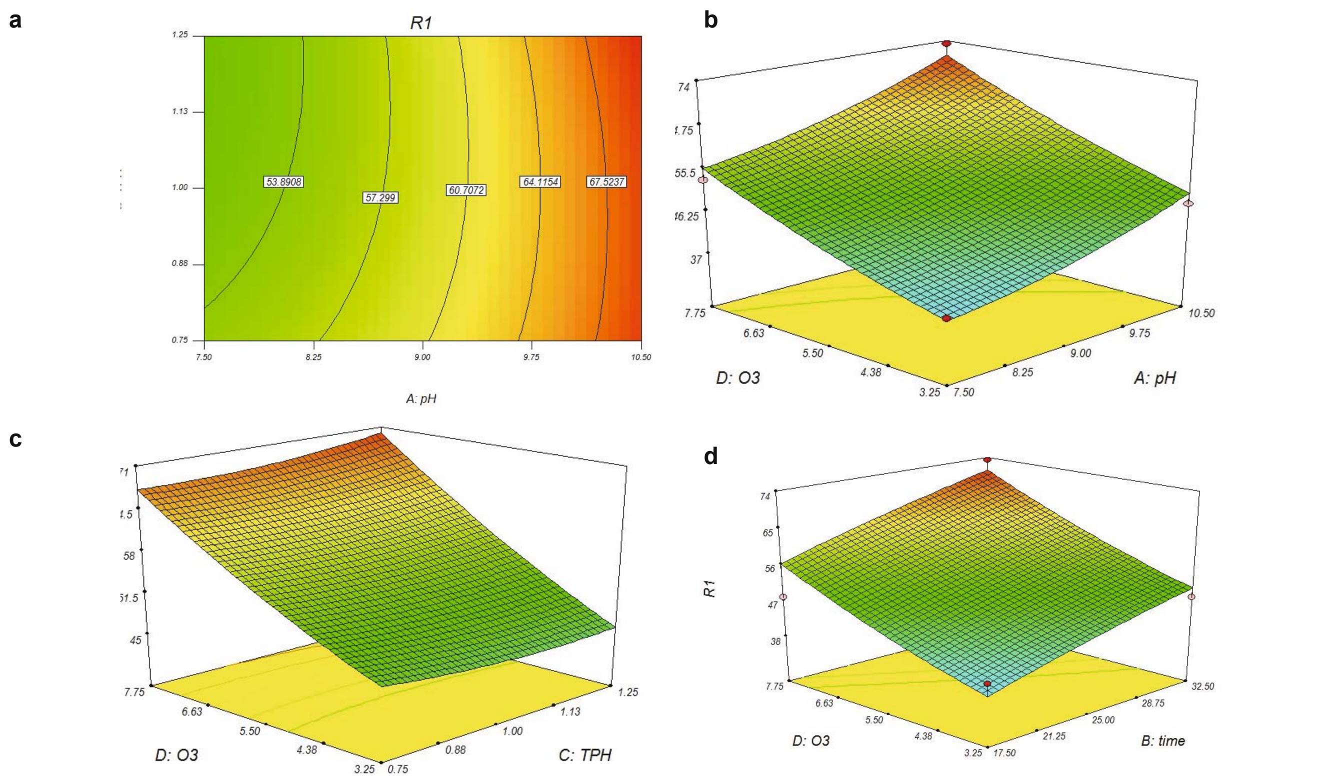

Fig. 2. Interaction between variables (a) Two-dimensional view of changes in pH and TPH concentration; (b) 3-dimensional view of changes in ozone dose and pH, (c) 3-dimensional view of time and ozone dose changes; (d) 3-dimensional view of changes in ozone dose and TPH concentration in removal of oil hydrocarbons by ozonation process

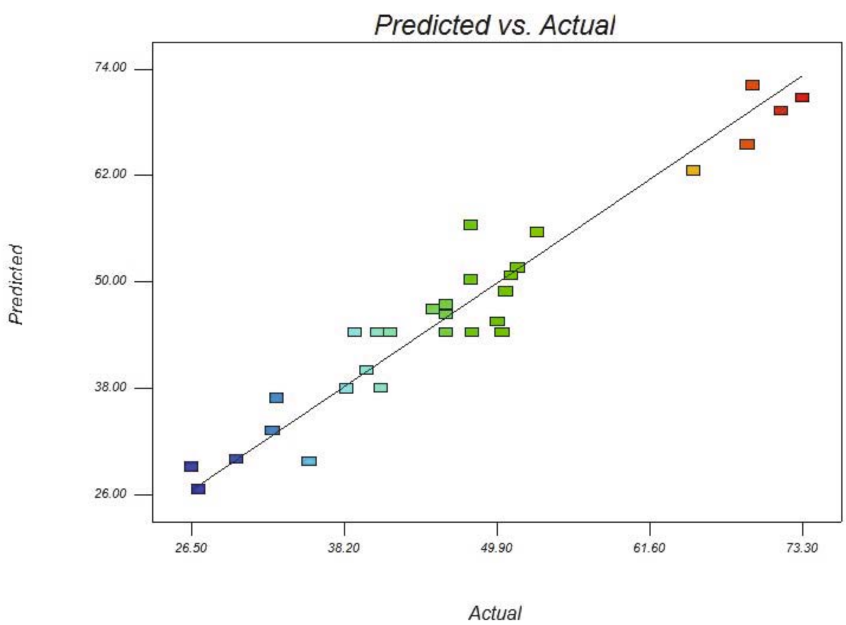

Fig. 3. Fit the real values versus the values predicted by the model for the ozone process efficiency in the TPH removal from oil-water

the contribution of the indirect ozone reaction in the degradation and decomposition of organic compounds improved. Therefore, a stronger oxidizing agent such as radical hydroxyl enhanced the efficiency of TPH removal. In addition, the reactivity and ion reaction rate of organic compounds with ozone, and especially the radical hydroxyl, were usually much higher than their non-ionic mode. Therefore, with respect to the production of radical hydroxyl and transformation of ionic mode to pH of 10.50, the TPH removal efficiency from oil-water was greater than other TPHs, and it was selected as the optimum pH for the ozonation process. In a study conducted under title "The efficiency of the electrical coagulation process in removing oil hydrocarbons from contaminated groundwater" it was found that by increasing pH, the TPH removal efficiency also improved (Moussavi, Khosravi and Farzadkia 2011). In another study conducted by Valdes et al, they confirmed the role of radical hydroxyl at high pH in the COP (Catalytic Ozonation Process) in the benzothiazole removal in an aqueous medium (Valdés and Zaror 2006).

Figure 2-a illustrated a 3-D plot to determine the value of TPH removal with changes in the ozone dose and PH at a time of 32.50 min and a TPH concentration of 0.75. As the ozone dose increased in the ozone process, the removal efficiency also improved. In addition, the effect of the concentration of oil hydrocarbons on their decomposition in the ozonation process in oil-water was also investigated in this study. Some studies indicated that the increased concentration could lead to reduce the efficiency. At low concentrations, less reaction time would be required. As a result, the volume of the reactor and the related costs would be reduced. Figure 2-c illustrates the TPH removal over time and changes in ozone doses when the pH value was 10.50 at a concentration of 0.75 TPH. In this study, the effect of reaction time ranging from 10 to 40 min on the decomposition of oil hydrocarbons was examined. The TPH decomposition in the ozonation process followed an increasing trend as reaction time improved, while this increasing trend in pH of 10 was slightly more than that of pH of 8. The results of a study to remove catechol with catalytic ozonation in combination with the biological process showed that the removal efficiency of oil compounds was directly correlated with ozone response time and ozone dose (Aghapour, Moussavi and Yaghmaeian 2015). Figure 2-d demonstrates the TPH removal with changes in ozone dose and the TPH concentration when pH was 10.50 and reaction time was 30 min.

Conclusions

The current study showed high power of model derived from the CCD to predict the results, and it was proved that this model might be used alone to determine the design space nature. In this study, the effective parameters including initial pH of the solution, reaction time, TPH concentration and ozone dose were optimized by the surface-response method. The results of the study indicated that the treatment process using ozonation method could be used as pre-treatment of cost-effective systems to decompose the complex hydrocarbon compounds and to transform them into more decomposable compounds. The mean TPH efficiency obtained from designing 30-step experiment, or from the surface-response method was 49.903%, with a standard deviation of 12.479.

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