

Extraction and Recovery of Polycyclic Aromatic Hydrocarbons in Petroleum Contaminated Soils Using Supercritical Water by Response Surface Methodology

Motamedimehr, Sh.* and Gitipour, S.

School of Environment, College of Engineering, University of Tehran, Tehran,
Iran

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ABSTRACT: Finding an environment-friendly and affordable method to remove contaminated soils from Polycyclic Aromatic Hydrocarbons (PAHs) has now become an attractive field for researchers, with super-critical fluid extraction being an innovative process in the field of contaminated soil treatment. Extraction with super-critical fluid is a simple and rapid extraction process that uses super-critical fluids as solvents. The present study has investigated the extraction of contaminated soil with Polycyclic Aromatic Hydrocarbons (PAHs) by means of batch supercritical water reactor, employing variables like pressure (100–300 bar), temperature (60–140 °C), residence time (0.5–3 hours), and base, acidic, and neutral pH values. In order optimize the process parameters, Response Surface Methodology (RSM) has been used. Results show that removal efficiency of PAHs is between 82%-100%, where the highest PAHs removal efficiency (100%) has been observed in Test No. 22, with a pressure of 300 bars, temperature of 500°C, acidic pH equal to 5, and duration of 3 hours. In addition, the lowest removal efficiency of these compounds (82%) has been obtained in Test No. 26, with a pressure of 300 bars, temperature of 350°C, base pH of 9, and duration of half an hour. According to the results from this study, it has become clear that residence time is the most important and most effective parameter for removing PAHs from contaminated soil. Afterwards, temperature and pH are most influential with pressure showing the least effect. Using supercritical water method in appropriate conditions can eliminate more than 99% of aromatic contamination.

Keywords: Soil treatment, PAHs, Supercritical Fluid, Batch reactor, RSM.

INTRODUCTION

Finding an environment-friendly and affordable method for removing contaminated soils from PAHs is one of the attractive areas for researchers (Gan S. et al., 2009). In comparison to Soxhlet extraction, extraction with subcritical water is better recovered, especially for compounds with low molecular weight (Diphare and Muzenda, 2014, LEI, PAN et al., Lübeck,

Malmquist et al., 2019, Qu, Gong et al., 2019). Juhani Kronholm et al. used the oxidation, subcritical water, and supercritical water extraction techniques to extract polycyclic aromatic hydrocarbons and Toluene from contaminated sea sand, using Hydrogen Peroxide oxidants. Results from this study showed that extraction efficiency increased with temperature and time, with the best results belonging to temperature of 300°C and 40 min of extraction time. Benzaldehyd and Benzoic acid were the most abundant

* Corresponding Author, Email: motamedimehr@ut.ac.ir

mediators of the reaction in the oxidation process and Phenol, p-Cresol, and Benzyl alcohol turned out to be mediators as well (Kronholm, Kalpala et al., 2002, Kronholm, Kuosmanen et al., 2003). Mohammad Nazrul Islam et al. investigated the PAHs in contaminated soils, using subcritical water extraction. Water temperature ranged from 100°C to 300°C, the extraction time was between 15 and 60 minutes, and the flow rate varied from 0.5 to 2.0 ml/min to determine their effect on removal efficiency of PAHs as a target. More than 95% of the extraction of Phenanthrene, Fluoranthene, and Pyrene from contaminated soil was observed at 300°C for 30 minutes and 250°C for 60 minutes at a constant pressure of 100 bar (Yang Y. et al., 2006). They also analyzed four models of kinetics for sub-critical water extraction of PAHs at high temperatures. The sub-critical water extraction data, obtained at temperatures of 200°C and 250°C, corresponds to the four hypothetical models. Extraction parameters can be used for conceptual design in development and enhancement of industrial SCWE devices to the industrial ones (Islam, Jo et al., 2012, Islam, Jo et al., 2014a, Islam, Jo et al., 2014b, Islam, Jung et al., 2017, Qu, Gong et al., 2019).

Ali Dadkhah reported the results of small-scale PAHs in batches with or without oxidation, containing moisture in contaminated soils, using subcritical water. There were some experiments in a 300-mL discontinuous volume reactor, each of them had the reactor filled with 45-50 grams of soil and 200-220 ml of twice-distilled water. For non-oxidation extraction, the reactor got pressurized with nitrogen, while oxidation experiments employed the oxidizing agent, such as air, oxygen, or hydrogen peroxide (Rivas F.J., 2006). Extraction experiments were performed at 230°C, 250°C, and 270°C for soil samples, while extraction and oxidation experiments took place at 250°C. Results showed that removal of PAHs in the contaminated soil depended on the molecular

weight of PAHs and the removal efficiency in the various experiments was 79-99%. This case was for extraction and oxidation combination in the range of 99.1% to more than 99.99%. While 28-100% of extraction PAHs could be found in the water phase, this reduction for simultaneous extraction and oxidation reached a maximum of 10%. Afterwards, in the next study, in order to find out the same temperature and oxidation reaction rate, semi-continuous experiments with a residence time of 1 and 2 hours took place, using contaminated soil at 250°C and hydrogen peroxide as oxidizing agent. In all combinations of extraction and oxidation experiments, the remaining PAHs in the soil after the test were almost indistinguishable. In the extraction of the combination and oxidation, no PAHs in the liquid phase were detected after the first 30 minutes of the experiments (Dadkhah and Akgerman, 2002, Dadkhah and Akgerman, 2006)

Previous studies used PAHs and other oil compounds with varying welds in the soil with initial concentrations, residual time and pH, and temperatures from below up to above the superconductor point, giving very promising deletion results (Diphare and Muzenda, 2014, El-Sheshtawy, Khalil et al., 2014, Gao, Wang et al., 2015, Kanarbik, Blinova et al., 2014, Ma, Shen et al., 2014). However, this method has not been commercialized in industrial scale yet, not encountering general success industrially. It needs the remaining time and the temperature to be reduced, and the process efficiency to be augmented (Kritzer P. et al. 2001, Griffith JW. et al. 2002). The focus in this research is on minimizing the remaining time and the temperature to reach the highest level of purification of the soil under experiment. It should be noted that various additives such as hydrogen peroxide will be used to achieve the above-mentioned purposes.

MATERIAL AND METHOD

Something that has to be determined prior

to the test design, considered as the input of each test design method, is the number of test variables along with their range of variations. The test variables of this study were four variables of pressure, temperature, remaining time, and the initial pH of the environment. The range of changes to these parameters is also based on past research works (Zeliang Ch. et al., 2017, Guanghua Y. et al., 2018, Sonil N. et al. 2016, Cui B. et al. 2009, Brunner G. 2009). The selected range for temperature changes, the remaining time, and the pressure was from 350°C to 500°C, 0.5 to 3 hours, and 100 to 300 bar, respectively, with the pH being base, acidic, and neutral. Polycyclic Aromatic Hydrocarbons (PAHs) from polluted soil samples were extracted by supercritical water hydrothermal method, using the batch type reactor. For the batch type, a pressure-resistant SUS316 vessel was used, the volume of which was 150 cm³. This reactor was heated, using an electrical heater.(Figure 1)

The experiment was designed with the help of Design Expert v.11 software. As you can see, the 30 tests for this study were based on the four parameters considered. With the exception of the central point (200 bar, 425 ° C, neutral pH, and 1.75 hours), for which five repetitions were taken into consideration, the number of replicates for all points varied. Table 1 shows the experimental design, presented by the Design Expert software, as well as the results of experiments, performed on its basis, including removal percentage of Polycyclic Aromatic Compounds.

The preliminary examination of the results showed that the removal efficiency of PAHs ranged between 82% and 100%. The highest removal efficiency (100%) was obtained in Test No. 22 (pressure 300 bar, temperature of 500 ° C, acidic pH of 5, and duration of 3 hours) and the lowest (82%) in Test No. 26 (pressure 300 bar, temperature of 350 ° C, base pH of 9, and duration of half an hour). (Figure 2).

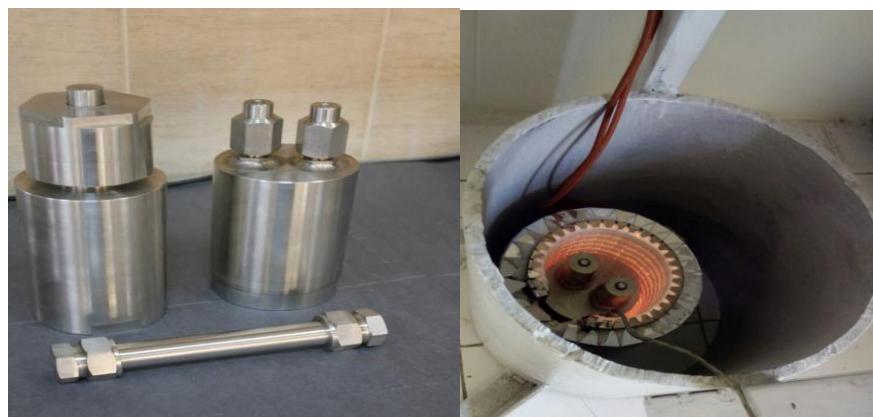


Fig. 1. High-pressure batch type reactor with electrical furnace



Fig. 2. extracted contamination after supercritical water oxidation process

Table 1. Experimental design and results

| Pressure (bar) | Temperature(°C) | pH | RT(hours) | PAHs Removal (%) |
|-----------------------|------------------------|-----------|------------------|-------------------------|
| 1 | 300 | 500 | 9 | 3 |
| 2 | 300 | 500 | 9 | 0.5 |
| 3 | 100 | 350 | 5 | 0.5 |
| 4 | 300 | 350 | 9 | 3 |
| 5 | 300 | 500 | 5 | 0.5 |
| 6 | 200 | 425 | 7 | 0.5 |
| 7 | 200 | 425 | 9 | 1.75 |
| 8 | 200 | 500 | 7 | 1.75 |
| 9 | 200 | 425 | 7 | 1.75 |
| 10 | 300 | 350 | 5 | 3 |
| 11 | 100 | 425 | 7 | 1.75 |
| 12 | 300 | 425 | 7 | 1.75 |
| 13 | 200 | 425 | 7 | 3 |
| 14 | 100 | 350 | 9 | 0.5 |
| 15 | 200 | 350 | 7 | 1.75 |
| 16 | 100 | 500 | 9 | 0.5 |
| 17 | 100 | 350 | 9 | 3 |
| 18 | 200 | 425 | 7 | 1.75 |
| 19 | 100 | 500 | 9 | 3 |
| 20 | 200 | 425 | 7 | 1.75 |
| 21 | 200 | 425 | 7 | 1.75 |
| 22 | 300 | 500 | 5 | 3 |
| 23 | 200 | 350 | 5 | 1.75 |
| 24 | 200 | 425 | 7 | 1.75 |
| 25 | 100 | 500 | 5 | 3 |
| 26 | 300 | 350 | 9 | 0.5 |
| 27 | 200 | 425 | 7 | 1.75 |
| 28 | 100 | 350 | 5 | 3 |
| 29 | 300 | 350 | 5 | 0.5 |
| 30 | 100 | 500 | 5 | 0.5 |

RESULT AND DISCUSSION

The process of result analysis for the tests includes analysis of variance or ANOVA, calculation of regression to assess the accuracy of the fitting data model, determination of the effects of each of the parameters, and their interference effects on the response variable or the same target quantity that can be very useful for its optimization. Subsequently, the numerical model, presented by the software, is employed to predict the results and the surface response graphs, and results are analyzed statistically with the help of the Design Express software. Then, in order to evaluate the models' performance in result prediction, the values they predict are calculated with the experimental values obtained from the comparison tests as well as the percentage error rate for each experiment.

Finally, the results of the analyses are compared with those of similar research works and the final conclusion of the analyses and comparisons will be presented.

The first step in data analysis is the analysis of variance. The software provides data analysis results in the form of variance analysis, based on calculation of data variance as well as the least squares of the remainders. The data variance and benchmarking R^2 are analyzed to evaluate the validity of the data analysis model for the experiments' results as shown in Table (2). With the help of the analysis of variance, the degree of fitness of the model, its accuracy for variable response data, and the percentage of the removal of multi-aromatic hydrocarbon compounds are evaluated here.

What is more important in the analysis of variance is the choice of a suitable

model for fitting the data and evaluating the proportionality of the proposed model, based on the data. For this purpose, Design Express has defined the p-value parameter, expressed for the two cases of Model Fit and Lack of Fit. The confidence level for data analysis is considered by default with software 99% or 0.99, so the value of P for the model's fit should be less than 0.01, for the proportion of the model to be acceptable and significant. Therefore, the value of P for the disproportion should be

greater than 0.01, and in fact, the disproportion should be meaningless in order for the model to be fit. The results, presented by the software, are shown in the section "analysis of variance" (Table 3). As can be seen from Table (2), the linear model has a suitable fit among the various models (linear, quadratic, and third grade) for fitting the data obtained from the experiments. The value of P for the linear model is below 0.01 and for the Lack of Fit, above 0.01.

Table 2. Summary Table for the Analysis of Variance

| Source | Sequential p-value | Lack of Fit p-value | Adjusted R^2 | Predicted R^2 | |
|-----------|-----------------------|------------------------|-------------------|--------------------|-----------|
| Linear | < 0.0001 | 0.0193 | 0.8075 | 0.7354 | Suggested |
| 2FI | 0.3638 | 0.0190 | 0.8149 | 0.4599 | |
| Quadratic | 0.6111 | 0.0142 | 0.8019 | 0.3291 | |
| Cubic | 0.0957 | 0.0258 | 0.8992 | -2.8990 | Aliased |

Table 3. The Complete Table of the Analysis of Variance

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|--------------|-------------------|----|----------------|---------|----------|-------------|
| Model | 400.94 | 4 | 100.24 | 31.40 | < 0.0001 | significant |
| A-Pressure | 2.00 | 1 | 2.00 | 0.6266 | 0.4361 | |
| B-Temperaure | 40.50 | 1 | 40.50 | 12.69 | 0.0015 | |
| C-pH | 37.56 | 1 | 37.56 | 11.77 | 0.0021 | |
| D-RT | 320.89 | 1 | 320.89 | 100.53 | < 0.0001 | |
| Residual | 79.80 | 25 | 3.19 | | | |
| Lack of Fit | 77.09 | 20 | 3.85 | 7.12 | 0.0193 | significant |
| Pure Error | 2.71 | 5 | 0.5417 | | | |
| Cor Total | 480.74 | 29 | | | | |

In order to evaluate the adequacy of the model in fitting the data, one of the most important assumptions is to examine the model accuracy, measured by means of the analysis of variance and the criteria, calculated by the software. The values in the output of the program are displayed after the Anova table and in the Model Summary field, respectively, from left to right, which includes three values of

regression, adjusted, and prediction. In the evaluation of the correctness of the model, adjusted- R^2 shows more accurate results than regression- R^2 because it uses the average squares (MS) rather than sum of squares (SS), and its advantage is that the degrees of data freedom, actually reflecting the number of factors, are involved in the calculation.

The adjusted value is closer to 1 or

100%, indicating the accuracy of the model. For data on percentage removal of PAHs, according to Table (2), the adjusted value is 80.75%. This means that the resulting model covers more than 80% of the data, indicating the optimal model's reliability.

With regard to the values of p-value in Table (4) for linear effects, and based on the same criteria, as described above, concerning the values of p-value, we can find that among the linear effects, the three factors of temperature, pH, and remaining time are of great importance. As for the choice of a linear model, none of the effects of squares and interactions have been effective, yet to find out about the conditions and level of linear effects' impact, the coefficient table, provided by the software should be used. Table (4) shows the impact coefficients for the percentage of PAHs removal. One point concluded from the negative sign of the impact coefficients is that their effect is decreasing, i.e., as they increase, the response quantity is reduced, and in case of a positive sign, it is vice versa. The greater the modulus of the numerical value of the impact coefficients, the greater the effect.

According to Table (4), it can be said that the impact of pressure is lower than other parameters, having a somewhat reduced effect. The temperature parameter

has an incremental effect, that is, by increasing the temperature, the efficiency of PAHs removal is increased. The effect of temperature is greater than the effect of pressure and pH; the latter, having a reducing effect on the removal efficiency of PAHs. This means that by increasing the pH, the amount of aromatic elimination declines. Finally, the remaining time has the greatest effect on increasing the removal efficiency of PAHs from contaminated soil.

Surface diagrams are two-dimensional graphic templates to display the simultaneous effects of their parameters along with their binary interactions on the response variable. Therefore, there will be level charts equal to the number of binary interactions of the parameters. In each surface graph of a dual interaction, there are two other parameters in a constant value. These constant values are the same values of the center point in the experiment design. Also, with the help of surface diagrams, an optimal approximation value can be estimated for each of the factors, examined in the design of the experiment to achieve the highest amount of target quantity (here, the percentage removal of PAHs). The following figure illustrates the surface graph for two parameters of pressure and temperature, as well as constant parameters of pH and remaining time (Figure 3, 4).

Table 4. Table of impact coefficient

| Factor | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|--------------|----------------------|----|----------------|------------|-------------|--------|
| Intercept | 91.68 | 1 | 0.3262 | 91.01 | 92.36 | |
| A-Pressure | -0.3333 | 1 | 0.4211 | -1.20 | 0.5339 | 1.0000 |
| B-Temperaure | 1.50 | 1 | 0.4211 | 0.6327 | 2.37 | 1.0000 |
| C-pH | -1.44 | 1 | 0.4211 | -2.31 | -0.5772 | 1.0000 |
| D-RT | 4.22 | 1 | 0.4211 | 3.35 | 5.09 | 1.0000 |

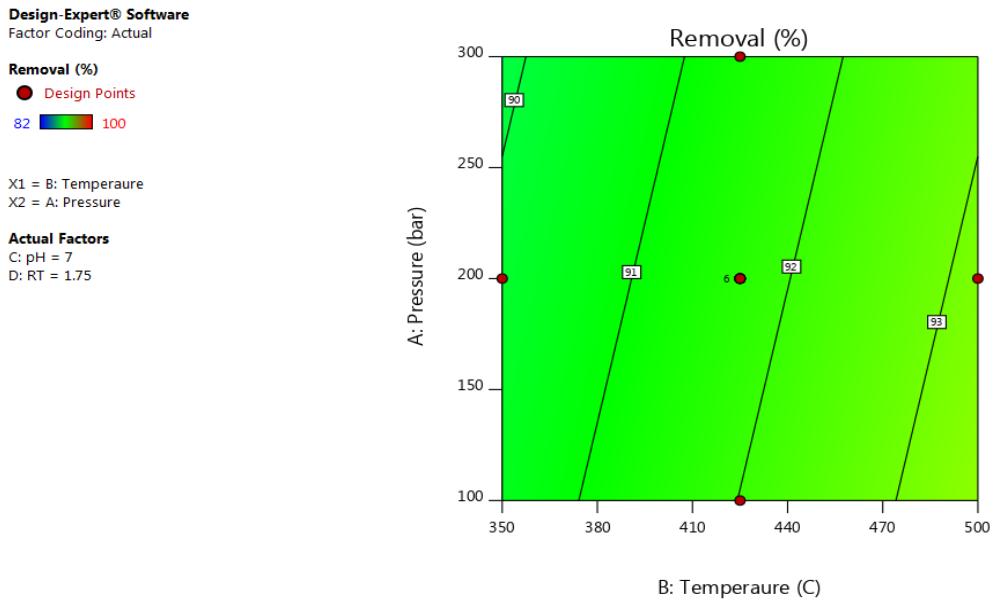


Fig. 3. Surface diagram of the removal percentage of PAHs in terms of temperature and pressure

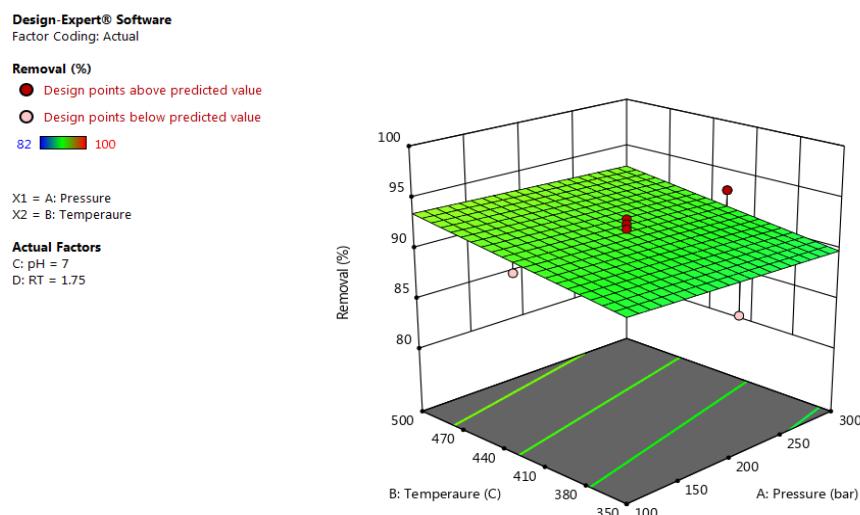


Fig. 4. 3D diagram of the removal percentage of PAHs in terms of temperature and pressure

Ultimately, what produces the software analysis is the mathematical-statistical model based on the data, presented at the end of the numerical analysis in the equation section. This model is, in fact, an expanded mathematical-statistical equation in which you can see each of the parameters of temperature, pressure, pH, and the remaining time. The β values, with different indexes, are fixed coefficients of the equation, whose values are calculated in the expanded form by the software. The model also predicts the fixed value of the

equation β and the dual interaction coefficient. The model, presented by the software, for the efficiency of PAHs' removal and assessment of the adequacy and performance of the model is presented.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_i x_j$$

According to the suggestion and the choice of linear model for fitting the data by the software, the statements about the effects of squares and interactions' effects of the

parameters are eliminated from the model. Therefore, the mathematical model presented by the software is as follows:

$$\text{Removal \%} = 89.99 - 0.003 * \text{Pressure} + 0.02 * \text{Temperaure} - 0.72 * \text{pH} + 3.37 * \text{RT}$$

The final part of the software analysis is devoted to introduction of optimal conditions in order to achieve the highest

efficiency for PAHs compounds' removal. According to the statistical analysis, the highest removal efficiency of aromatic compounds is achieved under conditions of 100 bar pressure, temperature of 500 °C, acidic pH of 5, and a remaining time of 3 hours at 99.18%. Figures 4 and 5 show the optimization results.

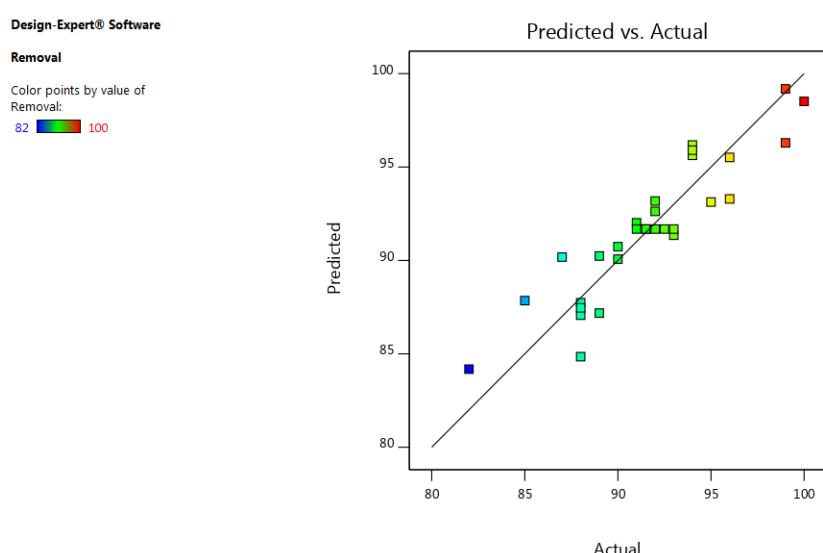


Fig. 5. Removal percentage of PAHs compounds, based on experimental results and mathematical-statistical model

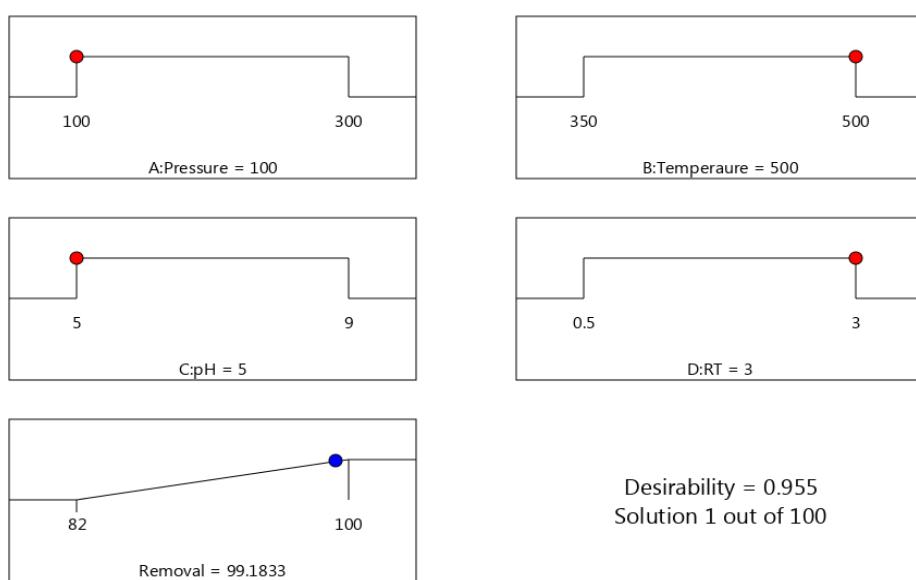
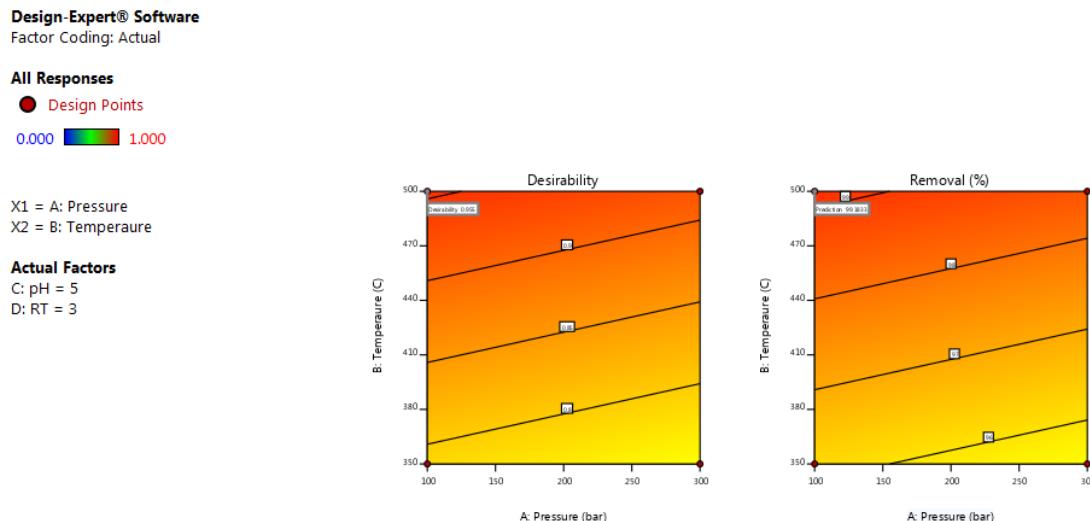


Fig. 6. Optimization of test parameters to maximize the removal percentage of PAHs

**Fig. 7. Optimization charts for the removal percentage of PAHs**

CONCLUSION

According to this study's results, it is clear that time remaining was the most important and most effective parameter in PAHs removal from contaminated soil. After that, temperature and pH had the most effect, with pressure showing the least effect. Using supercritical water method in appropriate conditions could eliminate more than 99% of aromatic contamination. The optimal remaining time of the process turned out to be 3 hours in this study, while it had been 60 minutes in previous studies. It is also confirmed that by increasing the remaining time, the removal efficiency of the PAHs compounds could be significantly increased. Studies also confirmed the high efficiency of PAHs compounds' removal at pressures of about 100 bars, similarly mentioned in previous studies. The pH parameter, neglected in previous studies, proved to be as important as temperature, and acidic environments were more potent to remove aromatic pollutants. The appropriate temperature range for optimal removal of PAH compounds was slightly higher than the reported ones in previous studies. Overall, results showed that the supercritical water method to remove PAH compounds is a beneficial and promising way that can be applied effectively and widely in future.

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