



Optimization of operating parameters to remove and recover crude oil from contaminated soil using subcritical water extraction process

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ABSTRACT

Box-Behnken Design (BBD) under response surface methodology (RSM) was implemented to optimization the operating parameters and assess the removal and recovery efficiencies of crude oil from contaminated soil using subcritical water extraction. The effects of temperature, extraction time and water flow rate were explored, and the results indicate that temperature has a great impact on crude oil removal and recovery. The correlation coefficients for oil removal ($R^2 = 0.74$) and recovery ($R^2 = 0.98$) suggest that the proposed quadratic model is useful. When setting the target removal and recovery (>99%), BBD-RSM determined the optimum condition to be a temperature of 250°C, extraction time of 120 min, and water flow rate of 1 mL/min. An experiment was carried out to confirm the results, with removal and recovery efficiencies of 99.69% and 87.33%, respectively. This result indicates that BBD is a suitable method to optimize the process variables for crude oil removal and recovery from contaminated soil.

Keywords: Box-Behnken Design, Crude oil, Recovery, Removal, Subcritical water

1. Introduction

Crude oil is a complex mixture of aliphatic, alicyclic and aromatic hydrocarbons. In oil mining areas and transportation routes, large quantities of crude oil are released into the environment, making crude oil one of the main sources of environmental pollution. Soil contaminated with crude oil has thus become a major concern due to the risks to health and the environment. So far researchers have conducted numerous remediation experiments for soil contaminated with crude oil, including bio-remediation [1, 2], phytoremediation [3, 4], chemical oxidation [5], thermal remediation [6]. Also, solvent extraction [7], supercritical fluid extraction [8], and ultrasonic extraction [9] studied for crude oil remediation, but these processes extensively used for extraction of PAHs or aliphatic hydrocarbons from soils. Lim et al. [10] stated the advantages, limitations, average cost, and sustainability of all these remediation methods, and concluded that any single method was not adequate to remediate soil contaminated with crude oil. In this regard it is required to develop a new remediation approach which would be effective

to remediate crude oil contaminated soil.

Subcritical water extraction (SCWE) is an environmental-friendly extraction method that can be used to remediate soil contaminated with different organic compounds. In the SCWE process, subcritical water ($100^\circ\text{C} \leq T \leq 374^\circ\text{C}$, pressure < 22.1 MPa) is used as a solvent instead of any organic solvent [11]. When the temperature increases from 25 to 350°C, the dielectric constant of water decreases from 78 to 2 at 100 bar, and thus the water acts as a solvent. For example, the dielectric constant for ethanol is 24 under ambient conditions, which is close to the subcritical water at 250°C and 100 bar. The efficacy of subcritical water in remediating various contaminated soils has been proved, including for those with PCBs [12], PAHs [11, 13], explosives [14], lubricating oil [15], and diesel [16]. In addition, Sushkova et al. [17] explained the possibility of benzo[a]pyrene extraction from soil and plants using subcritical water extraction method, and benzo[a]pyrene accumulation, migration, and transformation in soil-plant [18]. Therefore, Subcritical water extraction could be used as a well-developed instrumental analysis method as well for monitoring studies of oil pollution [19].



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Although numerous studies have been carried out with subcritical water extraction, no data is available on the remediation of soil contaminated with crude oil. This study assessed the subcritical water extraction process in terms of its removal and recovery efficiencies to remediate soil contaminated with crude oil.

Most of the previous study focused only on the oil removal rather than the oil recovery of contaminated soil [10,15,16]. In this study, the oil recovery via subcritical water extraction has been explored. Furthermore, other authors optimize the operating conditions applied conventional methods where the effect of the variables was observed by changing a single variable and keeping the others constant except Islam et al. [16]. In this study, Box-Behnken Design (BBD) under response surface methodology (RSM) was applied to remove and recover the crude oil, and the feasibility and efficiency of RSM have already explored by researchers to optimize the process variables in the different field of science. For example, Gratuito et al. [20] synthesized activated carbon using coconut shell where process parameters optimized applying response surface methodology. Thus, it would be a better opportunity to remove and recover the oil from soil and observe the extracted oil composition using subcritical water.

This study applied BBD under RSM to optimize the process variables (namely temperature, time and flow rate) and assess the removal and recovery efficiencies of crude oil from contaminated soil through the use of subcritical water extraction.

2. Materials and Methods

2.1. Soil Contamination Procedure

A fraction of 250 g air-dried, homogenized, and sieved (< 2 mm) non-polluted soil was contaminated by mixing with crude oil. The physiochemical properties of the soil sample are shown in Table 1. To spike the soil, 10 g of used crude oil were liquefied in 250 mL of dichloromethane in a beaker, and 250 g of fresh soil were then added. The mixture of soil-solution slurry was aged for 24 h under rotation. After aging, the dichloromethane was separated via evaporation, and the soil was then air-dried until reaching a constant weight. The soil was accumulated in a glass bottle at room temperature, and the bottle was closed tightly and kept for more than a month prior to use. In the terms of total petroleum hydrocarbon (TPH), the initial concentration of the crude oil in the spiked soil was 8,401 mg/kg.

Table 1. Physiochemical Properties of Used Soil

Properties	Value
pH	7.92
EC ($\mu\text{m/cm}$)	95.8
Total organic matter (%)	12.92
Total moisture content (%)	5.91
Sand	26.34
Silt	59.98
Clay	13.68
Contamination status	Spiked
TPH concentration in soil (mg/kg)	8,401.25

2.2. Subcritical Water Extraction Process

Distilled water was used as an extraction solvent, and helium gas was purged for 30 min in water to remove the dissolved oxygen. A lab-scale subcritical water reactor was used, and the experiments were carried out in the dynamic mode. The detailed extraction process is described in the literature. In short, 10 g of contaminated soil were inserted into an extraction cell (1 cm i.d. \times 10.8 cm length), and both the inlet and the outlet of the cell were capped with a 0.2 μm stainless steel microfilter that was installed into the heating chamber. Outside the heating chamber, a cooling unit and a pressure control valve were linked with the outlet of the eduction reactor using a stainless-steel tube. The inlet of the eduction cell unit was linked using stainless steel tube from the high-pressure pump (Series II, Chrom Tech, Inc.). Two thermocouples (West 6100+ temperature controller) were connected to the apparatus to monitor the water temperature at the pre-heater unit and extraction cell. After setting the desired condition, the water was pumped vertically, and the heating system was turned on. After attaining the desired temperature, timing began to take into account the desired extraction period, and the water pump and heating were switched off upon reaching the desired extraction. The pressure was then released to ambient condition, and the reactor was left to cool to room temperature. The soil sample was then collected from the extraction cell to analyze the remaining concentration of crude oil (via TPH), and the effluent water sample was collected to recover the extracted oil.

2.3. Experimental Design and Optimization Analysis

This study used BBD under RSM to optimize the removal and recovery efficiencies of crude oil. RSM is a combined mathematical and statistical technique, and the feasibility of using this technique has been proven in various areas of science. Three major operating parameters were controlled for the SCWE process of crude oil from contaminated soil. Table 2 illustrates the coded and actual operating conditions of the factors, namely the temperature (x_1), time (x_2), and water flow rate (x_3). Three factors-three levels BBD design was applied using BBD with three center runs, and a total of 15 experimental runs were given using software, as shown in Table 3. Design Expert 10 software and ANOVA were performed to analyze the experimental results and statistical analysis. The second order polynomial model was used to fit the response variables of crude oil extraction and recovery, and it is presented as follows:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 \quad (1)$$

where Y is the estimate response; β_0 is a constant; β_1 , β_2 , and β_3 are the linear coefficients; β_{12} , β_{13} , and β_{23} are the interaction coefficients between the three factors; β_{11} , β_{22} and β_{33} are the quadratic coefficients.

Table 2. Variables and Its Experimental Range

Variables	Factor	Coded and actual value		
		-1	0	1
Temperature ($^{\circ}\text{C}$)	X1	200	250	300
Time (min)	X2	60	90	120
Flow rate (mL/min)	X3	1	1.5	2

Table 3. Experimental Design, Removal and Recovery Efficiencies of the BBD

Run	Experimental design			Experimental plan			Observed removal (%)	Observed recovery (%)
				X ₁	X ₂	X ₃		
1	0	0	0	250	90	1.5	92.86	69.51
2	1	0	1	300	90	2	99.7	75.8
3	-1	-1	0	200	60	1.5	86.2	62.5
4	1	1	0	300	120	1.5	99.79	88.6
5	0	0	0	250	90	1.5	92.86	69.51
6	0	1	-1	250	120	1	98.28	82.12
7	-1	0	-1	200	90	1	94.98	48.08
8	0	1	1	250	120	2	98.15	86.64
9	0	-1	-1	250	60	1	96.48	94.46
10	-1	0	1	200	90	2	91.76	46
11	1	0	-1	300	90	1	99.59	71.76
12	0	-1	1	250	60	2	92.12	90.53
13	0	0	0	250	90	1.5	92.86	69.51
14	-1	1	0	200	120	1.5	88.26	35.29
15	1	-1	0	300	60	1.5	99.8	79.15

2.4. TPH Analysis

The standard Korean test method was employed in the TPH analysis, following the methodology detailed by Park et al. [21]. A GC-FID was used to analyze the TPH concentration. The crude oil removal and recovery efficiencies were quantified using the following equations.

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_r}{C_0} \times 100 \quad (2)$$

where C_0 is the primary concentration of TPH in soil (mg/kg) and C_r is the remaining concentration in the treated soil (mg/kg).

$$\text{Recovery efficiency (\%)} = \frac{\text{mass of TPH in the effluent (mg)}}{\text{mass of TPH extracted from the soil sample (mg)}} \times 100 \quad (3)$$

3. Result and Discussion

3.1. Crude Oil Removal Using the RSM Approach

Table 3 illustrates the experimental runs from BBD and the removal and recovery percentages of crude oil. The maximum removal and recovery efficiencies of crude oil were 99.8% and 94.46%, respectively. Table 4 presents the results of the ANOVA for the quadratic model of the oil removal, and these results imply that the model was significant at $p < 0.05$. The regression model shows a good correlation between the temperature and response ($p = 0.0017$). However, the extraction time ($p = 0.1753$) and water flow rate ($p = 0.28$) are not well correlated with the response. The coefficient of determination (R^2 value) and adjusted R^2 value were 0.91 and 0.74, respectively. As a result of the ANOVA analysis, a second-order polynomial equation was determined as follows:

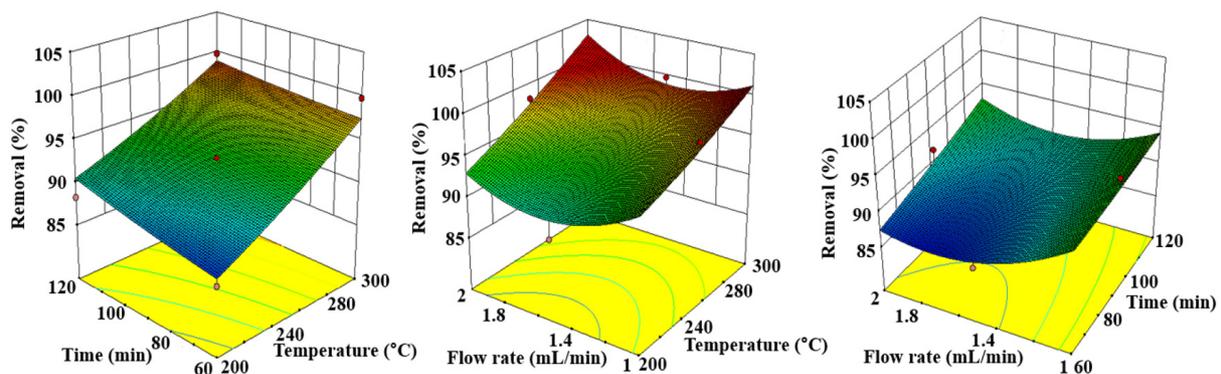


Fig. 1. 3D plot of the process variables of crude oil removal; (a) temperature and time, (b) flow rate and temperature, (c) flow rate and time.

Table 4. ANOVA Results for Regression Model in the Removal of Crude Oil Using SCWE

Source	Sum of square	DF	Mean square	F value	P value (Prob>F)
Model	242.52	9	26.95	5.61	0.0361
x_1	117.47	1	117.47	36.92	0.0017
x_2	11.98	1	11.98	2.49	0.1753
x_3	7.05	1	7.05	1.47	0.28
$x_1 x_2$	1.07	1	1.07	0.22	0.6568
$x_1 x_3$	2.77	1	2.77	0.58	0.4819
$x_2 x_3$	4.28	1	4.28	0.89	0.3885
x_1^2	0.68	1	0.68	0.14	0.7218
x_2^2	0.15	1	0.15	0.031	0.8661
x_3^2	37.75	1	37.75	7.85	0.0379
Residual	24.04	5	4.81	-	-
Lack of fit	24.04	3	8.01	26,707.86	< 0.0001
Pure error	0.0006	2	0.0003	-	-

$$Y(\%) = 97.88 + 4.71x_1 + 1.22x_2 - 0.94x_3 - 0.52x_1x_2 + 0.83x_1x_3 + 1.04x_2x_3 + 0.43x_1^2 + 0.2x_2^2 + 3.2x_3^2 \quad (4)$$

Fig. 1(a) illustrates the effect of temperature and time on crude oil removal. The effect of temperature on crude oil removal can be seen to be strongly significant ($p = 0.0017$), but the interactive effect of these two factors is not significant ($p = 0.6568$) (Table 4). The removal efficiency of crude oil increased as the temperature increased. For example, in the condition at 250°C for 60 min, 96.48% of crude oil was removed, but the removal efficiency increased to up to 99.8% at 300°C for 60 min. The high temperature reduces the surface tension and cohesive energy of water, therefore reducing the dielectric constant and viscosity and thus allowing for more extraction and dissolution of crude oil in water under the subcritical condition. These results are in agreement with previous studies conducted by several authors [11, 16, 22].

Fig. 1(b) shows the effect of the water flow rate and temperature on crude oil removal. The water flow rate had a slight impact on the crude oil removal compared to the effect of the temperature. At high temperatures, the effect of the flow rate was negligible. For example, 99.8% removal was observed at 1.5 mL/min, and a similar result (99.59%) was achieved at 1 mL/min, as shown in Table 3. Therefore, the extraction of crude oil can be concluded to be solely dependent on the water temperature. In runs 9 and 12 (Table 3), the removal efficiencies decreased from 96.48% to 92.12% as the water flow rate increased from 1 mL/min to 2 mL/min at 250°C. This is might be due to the lack of internal diffusion for a higher flow rate. The removal of organic compounds from soil matrix has been reported to be controlled by internal diffusion rather than external mass transfer [16].

The effect of the water flow rate and removal time are shown in Fig. 1(c), which illustrates that crude oil removal increased little as time increased. For instance, the removal rate increased from 96.48 to 98.15% when the extraction run time was extended

to 120 min from 60 min. It would be the worst decision to consider increasing the time to more than 60 min regarding the effective removal of crude oil. An increase in the flow rate decreased the removal efficiency because a different mass transfer zone formed due to channeling or lack of residence time of the water for optimal diffusion. However, at a high temperature, the flow rate within the design boundary of 1 to 2 mL/min did not play a vital role in the removal of crude oil.

3.2. Crude Oil Recovery Using the RSM Approach

Table 5 shows the ANOVA results for the second order quadratic model for the crude oil recovery, and the results indicate that the model is significant at $p < 0.0001$. For a 95% confidence interval, the P values of the ANOVA results illustrate that the extraction temperature ($p < 0.0001$) and time ($p = 0.0058$) had a larger effect on crude oil recovery than the extraction flow rate ($p = 0.7445$) for crude oil recovery (Table 5). The coefficient of determination ($R^2 = 0.99$) and the adjusted R^2 value (0.97) indicate that the model was well correlated. The results of the ANOVA analysis produced the following second order polynomial equation:

$$Y(\%) = 69.51 + 15.42x_1 - 4.26x_2 + 0.32x_3 + 9.81x_1x_2 + 1.53x_1x_3 + 2.11x_2x_3 - 15.57x_1^2 + 12.46x_2^2 + 6.47x_3^2 \quad (5)$$

Fig. 2 shows the interactive effects of the process variables in three-dimensional response surface plots for crude oil recovery. The highest recovery of 94.46% was observed at 250°C for 60 min. In contrast with oil removal, crude oil recovery was low. For example, the highest removal efficiency for crude oil of 99.8% was observed at 300°C for the 60 min extraction, and the recovery was found to be 88.6% at the same operating condition. This means that the high temperature reduced the recovery efficiency, and this might have increased the crude oil degradation. Many organic compounds have been reported

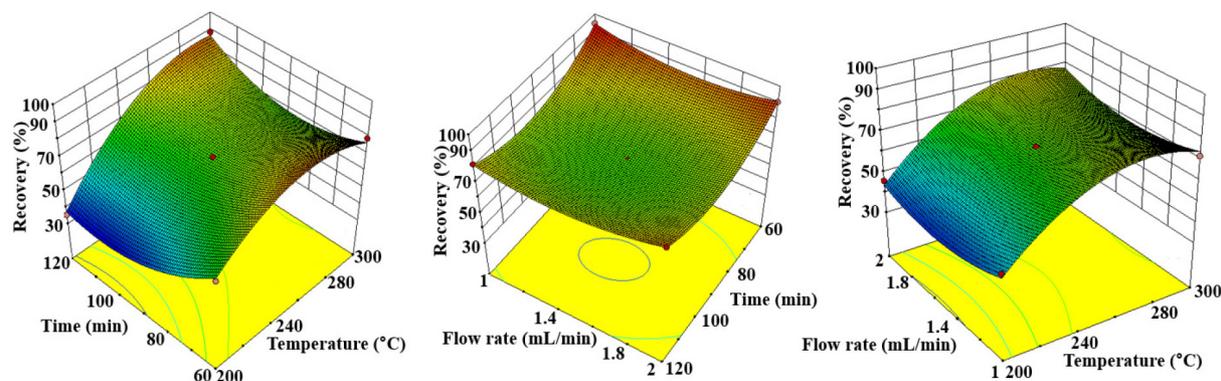


Fig. 2. 3D plot of the process variables of crude oil recovery; (a) time and temperature, (b) flow rate and temperature, (c) flow rate and time.

Table 5. ANOVA Results for Regression Model in the Recovery of Crude Oil Using SCWE

Source	Sum of square	DF	Mean square	F value	P value (Prob>F)
Model	4,167.67	9	463.07	67.6	0.0001
x_1	1,902.83	1	1,902.83	277,076	< 0.0001
x_2	144.93	1	144.93	21.16	0.0058
x_3	0.81	1	0.81	0.12	0.7445
$x_1 x_2$	337.09	1	337.09	49.21	0.0009
$x_1 x_3$	9.36	1	9.36	1.37	0.2951
$x_2 x_3$	17.85	1	17.85	2.61	0.1676
x_1^2	894.96	1	894.96	130.64	< 0.0001
x_2^2	573.12	1	573.12	83.66	0.0003
x_3^2	154.5	1	154.5	22.55	0.0051
Residual	34.25	5	6.85	-	-
Lack of fit	34.25	3	11.42	-	-
Pure error	0	2	0	-	-

Table 6. Suitable Solutions Selected from Model and Their Experimental Results

Suitable solution	Operational conditions			Predicted removal (%)	Observed removal (%)	Predicted recovery (%)	Observed recovery (%)
	Temp. (°C)	Time (min)	Flow rate (mL/min)				
A	250	120	1	97.4	98.7	81.75	83.3
B	300	120	1.5	98.92	98.7	86.75	82

to be degraded in subcritical water during hydrothermal treatment of contaminated soil due to hydrolysis or acid/base-catalyst reactions [14, 23]. In this study, several degraded products, such as phenol, 3-methyl-2-cyclopentanone, 3,4-dihydroxy-5-aminopyridazine and 1,4-dimethoxy-2,6-dimethylbenzene were identified via GC-MS analysis in the treated soil residue, and these had not been present in the contaminated soil. Although the quantity of degradation products was not determined, degradation at high temperature could be assumed to be responsible in reducing the oil recovery. However, it is difficult to explore the detailed mechanism of the crude oil degradation since crude oil is composed a wide range of hydrocarbons. The interactive

effects between flow rate and temperature ($p = 0.2951$) and between flow rate and time ($p = 0.1676$) were not significant for crude oil recovery (Table 5).

3.3. Confirmation Experiment

To obtain the best removal and recovery efficiencies of crude oil (setting the target removal efficiency to 99.9), experiments were performed by resolving the regression equation within the same range of operating parameters. A total of 63 suitable solutions were listed using software (Design-Expert 10) according to the desirability factor. Among these, two suitable solutions were selected to ensure the accuracy of the regression solutions

from the experiments. Table 6 shows suitable solutions for A and B and of the results that were obtained. An oil removal of about 98.7% and oil recovery of 83.3% were obtained for a while a similar removal (98.7%) but lower recovery (82.0%) was observed for B. In contrast to oil recovery, the observed oil removal efficiencies should be noted to be close to the predicted value (99.9%).

4. Conclusions

The BBD under RSM was used to optimize the process variables namely, temperature, extraction time and water flow rate for crude oil removal and recovery in the subcritical water extraction process. It showed that the temperature is the most crucial variable for subcritical water extraction process. As can be seen from this study results that the removal efficiency of crude oil was increased with increasing temperature within the range studied (200-300°C); however, in the case of oil recovery, it was decreased at 300°C, might be due to degradation process. The optimum conditions for maximum crude oil removal and recovery were found to be 250°C, 120 min, and 1.5 mL/min according to the quadratic model. Under these experimental conditions, crude oil removal and recovery were found to be 99.69% and 87.33%, respectively.

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