International Journal of Environmental Science and Development, Vol. 10, No. 10, October 2019

Optimization of Supercritical Fluid Extraction of Hydrocarbons from a Contaminated Soil: An Experimental Approach

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***Abstract*—Soil and sediment contamination with hydrocarbons is an environmental concern, which demands for more efficient remediation techniques. Pure and modified supercritical carbon dioxide (SC CO_2) was used for the extraction of petroleum hydrocarbons from soil contaminated with crude oil. Effect of CO_2 flow rate (1 and 4 ml/min), temperature (80 and 160 °C), pressure (250 and 350 bar), and addition of 5% (v/v) organic solvent (heptane or toluene) on the extraction efficiency and on the composition of extracted hydrocarbons were investigated. The maximum extraction efficiency (92.26%) was obtained at 80 °C and 350 bar corresponding to a modified CO_2 with 5% (v/v) heptane's and CO_2 flow rate of 1 ml/min. Extraction efficiency of CO_2 increased with pressure and decreased with temperature. Chemical modification of CO_2 by adding heptane increased the extraction efficiency. Analysis of the soil after the extraction process shows that pure SC CO_2 was able to remove up to 92.86% of TPH in the contaminated soil. In addition, a significant reduction in PAH level was observed. Supercritical fluid extraction proved to be an efficient method for the remediation of hydrocarbon-contaminated soil.**

***Index Terms*—Carbon dioxide, extraction, heptane, soil, toluene, supercritical (SC).**

I. INTRODUCTION

Soil contamination with crude oil and petroleum products is often observed at industrial sites, causing environmental pollution, which can be hazardous to the health of plants, animals, and humans [1]-[6]. The hydrocarbon molecules may contain hazardous complex chemical mixtures such as total petroleum hydrocarbons (TPH), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Removal of such compounds from contaminated sites is an important and challenging problem.

The most important and widely used remediation methods are incineration, thermal desorption, biological remediation, chemical treatment and solvent extraction [7], [8]. Conventional techniques such as landfill disposal, thermal desorption, incineration and liquid solvent extraction are expensive and involve risks associated with air and residual pollution. Biological remediation is a rather slow process, with possible logistic and practical disadvantages. Mohammadi-Sichani *et al*. indicated that biological treatment were effective in the degradation of petroleum hydrocarbons contaminated soil after three months [9].

Despite great efforts and expenditure of resources to develop both technically and economically effective cleanup processes for contaminated soils, no widely accepted method has been found and further research is still needed. New methods are therefore being investigated in order to improve the remediation efficiency and lower the costs or the remediation time. Since three decades ago, supercritical fluids (SCFs) have been used as extraction media to remove various types of substances from solid matrices. The unique properties of SCFs that make them technically attractive are their enhanced ability to dissolve organic compounds, an ability, which can be easily tuned by changing temperature and/or pressure, thus changing the fluid properties from gas-like to liquid-like. This sensitivity to temperature and pressure leads to simple solute-solvent separation schemes. Supercritical fluids can have better mass transfer through a porous matrix due to their higher diffusivity than a normal liquid phase, resulting in a faster extraction [10]. Moreover, densities of SCFs are higher than those of normal gases, leading to higher solvent power than gases. Such properties allow the SCFs to dissolve and carry away materials like a liquid but also enter very small pores like a gas. Other attractive features of SCFs include low viscosity and high diffusivity that are essential to reduce mass transfer resistance during the desorption processes. Because of these special characteristics, supercritical fluids are used in extractions, separation, chemical reactions, impregnation, polymer processing, food processing, environmental remediation and pharmaceutical production [11]. The most popular fluid is supercritical carbon dioxide (SC CO_2) because it is non-toxic, non-flammable, chemically stable, readily available, inexpensive, environmentally acceptable, and can easily be separated from the products. Although SCF technology has been successfully realized for environmental remediation in the laboratory, its commercialization still lacks the significant technological improvement required in order to reach economic feasibility.

Like other new technologies, SFE technology, utilizing CO_2 as a fluid has its specific problems. One of these problems is the limited ability of SC CO_2 to dissolve and separate polar or high molecular weight organic compounds even at very high densities. To increase the efficiency of the SFE process for such compounds, the selectivity and solubilizing power of SC CO_2 can be enhanced by the addition of polar organic compounds, known as modifiers.

Significant research has been carried out in order to study various aspects of contaminant removal by SC CO_2.

Manuscript received January 2, 2019; revised July 22, 2019.

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doi: 10.18178/ijesd.2019.10.10.1191

Comprehensive presentations of various aspects on the use of this technology for extraction purpose are available in several critical reviews ([1], [12], [13]) and hundreds of other scientific articles. Pressure, temperature, composition of the crude oil and physicochemical properties of the solid matrix affect the extraction capacity of SC CO_2. Supercritical CO_2 has been successfully used for extracting a variety of organic compounds such as polycyclic aromatic hydrocarbons (PAHs) ([14]-[20]), polychlorinated biphenyls (PCBs) ([1], [18], [21]-[24]), pesticides ([25]-[27]), and hydrocarbons ([18], [28]-[33]). The extraction of these compounds was performed from various porous media, such as soils and sediments ([3]-[5], [7], [14], [15], [19], [22], [24])) or rocks ([32], [34]-[37]). These investigators have studied a combination of different parameters such as characteristics of the supercritical fluid (with and without modifier), solid matrix, operating conditions (i.e. temperature, pressure, density, and flow rate), water content and solute physical and chemical properties, in order to find the optimum conditions leading to the highest extraction yield.

Data for CO_2 extraction at extremely high pressures and temperatures are scarce in the literature, especially for soil contaminated with crude oil. Al-Marzouqi *et al* in 2007 showed that SC CO_2 at 300 bar and 120 °C is able to extract about 70% of hydrocarbons from a typical UAE soil contaminated with crude oil [33]. Meskar *et al*. in 2018 employed diesel oil to study the effect of pressure and temperature on the CO_2 extraction process [38]. They have concluded that petroleum hydrocarbon removal rates is increasing with pressure at constant temperature, however, increasing temperature did not result in higher PHC removal rates at constant pressure. The objective of the present study was to investigate the ability of pure and modified CO_2 under supercritical conditions to remediate soil contaminated with crude oil and achieve higher extraction efficiencies. The effects of CO_2 flow rate, temperature, pressure, and modifier (heptane or toluene) on the extraction capacity of the SCF and on the composition of extracted hydrocarbons were investigated. The extent of residual oil in the matrix after SFE was also determined.

II. EXPERIMENTAL

A. Material

Carbon dioxide (purity of 99.995%) was supplied by Abu Dhabi Oxygen Company. Crude oil (average molecular weight = 281.5 g/mole and density = 0.8634 g/ml) was obtained from Bu Hasa oil field (Abu Dhabi, UAE) and was filtered to remove all sand particles. Hydrocarbon composition of the crude oil used in this study indicates the presence of mainly light and moderate hydrocarbons, i.e. 80% hydrocarbons less than C20. The chemical modifiers (n-heptane and toluene) and the organic solvents (dichloromethane and methanol) were of analytical grade with purity ≥99% and were supplied by Sigma Aldrich. Soil samples (bulk density = 1.6 g/ml and average particle size = 150 μm) were collected from Sahel oil field, which is near Bu Hasa oil field in the UAE. The size distribution of the soil sample was: 11% less than 106 μm, 29.56% between 106 and 150 μm, 44.07% between 150 and 212 μm, 12.52% between 212 and 300 μm, 2.81% between 300 and 600 μm, 0.03% between 600 and 850 μm, and 0.01% between 850 to 1180 μm. The porosity and permeability of the soil were 35% and 20.15 Darcy, respectively.

B. Experimental Design

Extraction of hydrocarbons with SCFs from contaminated soil was carried out by following the full factorial experimental design with four factors. The factors investigated were (in parentheses are the variable coded values): pressure with values of 250 (−1) and 350 (1) bar, temperature 80 (−1) and 160 (1) °C, flow rate of 1 (−1) and 4 (1) ml/min and fluid type pure SC CO_2 (1), modified SC CO_2 with 5% (v/v) toluene (2) and modified SC CO_2 with 5% (v/v) n-heptane (3). This design was used to find the best conditions for the extraction of oil from contaminated soil and to study the effects of all factors (temperature, pressure, flow rate of SCF, and type of modifier) on the extraction efficiency. The total number of factor-level combinations was 24. Each experiment was repeated twice, resulting in a total number of 48 experiments. Experiments were run in random order to eliminate various types of biases due to uncontrolled nuisance factors. The statistical analysis was performed using the statistical package SPSS (SPSS inc., Version 15.0). Table I shows the order of the experiments and the factor-level combinations. All the statistical analyses of the effects of variables on the extraction efficiency were performed using a multi-way analysis of variance (ANOVA) with two replications per cell. Also, whenever applicable, Tukey's HSD Test was used to identify the factor-level combinations that yield the extraction efficiency. A level of 5% was used as the cut-off value for statistical significance.

C. Experimental Apparatus

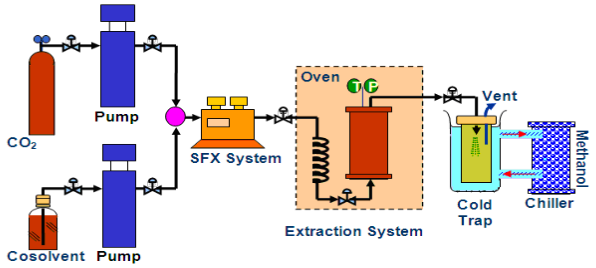


Fig 1. Experiment setup for supercritical fluid extraction.

Fig. 1 shows schematic diagram of the supercritical fluid extraction system used in this study. The experimental setup consisted of a 260-ml capacity syringe pump and a controller system (ISCO 260D), a 100-ml stainless steel extraction chamber (DBR-JEFRI 100-10-BE), and a cold trap as described earlier [33]. The extraction chamber was kept in an air-circulating oven (Memmert ULE 400) with a temperature control ranging from 30-250 ℃. Pressure within the extraction chamber was measured and controlled by the ISCO system. The temperature of the extraction chamber was measured by a J-type thermocouple (Omega model JMTSS-062-U-12) connected to a thermometer (Barnant, model 692-0230) and controlled by the oven. A micro-metering valve (HIP 15-12AF1-V) was used as the expansion valve at the exit of the extraction chamber to achieve a good control of the flow rate. Circulating methanol at -15 ^{o}C was used as a cold trap to separate CO_2 from other components of the mixture.

TABLE I: EXPERIMENTAL ORDER AND FACTOR-LEVEL COMBINATIONS

Experiment order	Temperature	Pressure	Flow Rate	Fluid Type
10	–1	1	1	1
34	–1	1	1	1
43	1	1	–1	1
40	1	–1	1	1
46	1	1	1	1
28	–1	–1	1	1
25	–1	–1	–1	1
4	–1	–1	1	1
16	1	–1	1	1
22	1	1	1	1
13	1	–1	–1	1
1	–1	–1	–1	1
19	1	1	–1	1
31	–1	1	–1	1
7	–1	1	–1	1
37	1	–1	–1	1
18	1	–1	1	3
6	–1	–1	1	3
21	1	1	–1	3
33	–1	1	–1	3
30	–1	–1	1	3
45	1	1	–1	3
42	1	–1	1	3
27	–1	–1	–1	3
39	1	–1	–1	3
24	1	1	1	3
3	–1	–1	–1	3
12	–1	1	1	3
15	1	–1	–1	3
9	–1	1	–1	3
36	–1	1	1	3
48	1	1	1	3
26	–1	–1	–1	2
41	1	–1	1	2
35	–1	1	1	2
29	–1	–1	1	2
38	1	–1	–1	2
11	–1	1	1	2
5	–1	–1	1	2
20	1	1	–1	2
8	–1	1	–1	2
2	–1	–1	–1	2
47	1	1	1	2
14	1	–1	–1	2
23	1	1	1	2
17	1	–1	1	2
44	1	1	–1	2
32	–1	1	–1	2

Factors code: Temperature (80 ℃ = –1, 160 ℃ = +1), Pressure (250 bar= –1, 350 bar = +1), CO_2 flow rate (1 ml/min= – 1, 4 ml/min= +1), Fluid type (Pure SC CO_2 = 1, SC CO_2 + 5 % (v/v) toluene = 2, SC CO_2 + 5 % (v/v) heptane = 3).

D. Experimental Procedure

Soil samples were spiked with 10 w/w% crude oil and placed in the extraction chamber. The extraction chamber was kept in the oven at the desired temperature until thermal equilibrium was reached (30-60 min). The chamber was then pressurized with CO_2 to the desired pressure and kept for another 30 minutes to reach equilibrium. In the case of modified CO_2, the second syringe pump was used to deliver the co-solvent (heptane or toluene), which was mixed with the CO_2 stream at desired ratio. Pure and modified carbon dioxide at supercritical condition was then added to the ISCO SCF Extraction system (SFX system) and equilibrated for about 15 minutes. The temperature of the SFX system was maintained at the same temperature as the oven which had the extraction chamber that contained the sample. The SCF was allowed to flow through the coil of tubing and enter the extraction chamber from the bottom. The fluid was equilibrated with the spiked soil sample for at least 30 minutes. The supercritical solution was then allowed to flow into a vial and the extract was separated from the supercritical fluid by depressurizing the system in the cold trap. For the runs with pure CO_2, mass of the extract collected in the vial was measured at different volumes of CO_2 (15, 25, 35, 50, 100, 150, 200, 300 and 400 ml) passed through the sample. For the runs with modified CO_2, mass of the extract collected in the vial was only measured at 400 ml of the SCF passed through the sample. At the end of the experiment (after 400 ml of the fluid was passed through the sample), the extraction process was stopped and the pressure in the extraction chamber was slowly dropped to atmospheric pressure.

After extraction, the residual oil remaining in the soil sample was removed from the soil matrix by soxhlet extraction using dichloromethane. The original crude oil, the extract (collected from the SFE process), and the residual oil (collected from the soil samples) were analyzed by a gas chromatograph (Chrompack, CP9001) as previously explained [33]. Hydrocarbon profiles of the extracts and the residues were compared to that of the original crude. The residual hydrocarbons in the soil, after SFE process, were also analyzed for concentration of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbons (PAHs). In addition, surface topography of the soil samples after SFE process was obtained by Scanning Electron Microscopy (JEOL 5600).

E. Determination of Total Petroleum Hydrocarbon (TPH) in the Treated Soil

About 5 g of the homogenized soil was placed in a 50 ml beaker. The sample was acidified to pH 2 with approximately 0.1 ml of concentrated hydrochloric acid. Then 5 g $MgSO_4$ was added to the acidified sample and stirred to create a smooth paste. The paste was spread on the sides of the beaker and left for about 15-30 minutes at room temperature until the material was solidified. The solids were transferred to a mortar and grinded to a fine powder. The powder was then added to a paper extraction thimble. The thimble was placed in a soxhlet apparatus and extracted using n-haxane. After removing the solvent the amount of TPH was calculated from the weight of residue and the sample.

F. Determination of Polycyclic Aromatic Hydrocarbon (PAHs) in the Treated Soil

A total of 16 common PAHs were analyzed by extracting them from soil with hexane:acetone (50:50) using soxhlet extraction method. After carefully evaporating the solvent under nitrogen, a 20 μl aliquot of the extract was injected into an HPLC (Waters 2695 Alliance Separation Module), Waters 474 Scanning Fluorescence Detector coupled with Waters 486 UV Detector and Waters Millennium 32 Chromatographic Manager workstation. The HPLC column used in this study was a chromosphere-3PAH column (100*4.6 mm ID, 3 μm). The 16 PAH compounds were detected by ultraviolet (UV) and fluorescence detectors simultaneously.

III. Results and Discussions

The CO_2 extraction efficiency (the ratio of extracted hydrocarbons to the initial amount of crude oil in place) is used throughout this study to evaluate the capacity of CO_2 to extract hydrocarbons from the soil. The average extraction efficiencies obtained at each of the investigated operating conditions are tabulated in Table II and shown in Fig. 2. Values of density, viscosity and kinematic viscosity of pure CO_2 at the pressures and temperatures used in this study were also calculated using NIST Chemistry WebBook in order to investigate their influence on the SFE process. Although both density and viscosity of CO_2 always increase with pressure and decrease with temperature, the combined property (kinematic viscosity) does not show a constant effect with pressure and temperature. The temperature and pressure combinations employed in this study were: 250 and 350 bar at 80 and 160 ℃. Bu Hasa crude oil, which was used in this study, contains significant amount of light hydrocarbons [33]. Therefore, n-heptane and toluene were chosen as chemical modifiers for the SC CO_2 to investigate the effect of a polar and a non-polar modifier with the same carbon number. n-heptane, a non-polar aliphatic hydrocarbon, and toluene, an aromatic hydrocarbon with a polarity index of 2.4, have high solvency for hydrocarbons.

The lowest value of extraction efficiency (68.38% ± 1.99) was obtained for modified SC CO_2 (with an addition of 5 % toluene) at 250 bar, 160 ℃ and CO_2 flow rate of 4 ml/min, while the maximum efficiency (92.26 % ± 5.40) was found for SC CO_2 (with an addition of 5 % n-heptane) at 350 bar, 80 ℃ and CO_2 flow rate of 1 ml/min. The highest efficiency obtained by SC CO_2 alone (without modifier) was 78.51 % ±0.46, which was obtained at 350 bar, 160 ℃ and CO_2 flow rate of 1 ml/min. The complexity of crude oil mixture containing many compounds with significantly different physico-chemical properties that vary with temperature and pressure are believed to cause such a large variation in the extraction capacity of SC CO_2.

TABLE II: Properties and Average Extraction Efficiencies of Supercritical Fluids for Soil Samples Contaminated with Crude Oil

Temperature (℃)	Pressure (bar)	CO_2 flow rate (ml/min)	Modifier 5% (v/v)	CO2 density (g/ml)	CO2 viscosity (μPa·s)	CO2 kinematic viscosity × 108 (m2/s)	Average extraction efficiency (%) ± SEM*
80	250	1	–	0.68622	56.03	8.17	72.32 ± 0.49
80	250	4	–	0.68622	56.03	8.17	75.07 ± 0.92
80	350	1	–	0.78897	70.376	8.92	77.76 ± 0.78
80	350	4	–	0.78897	70.376	8.92	77.40 ± 0.55
160	250	1	–	0.39294	33.905	8.63	68.44 ± 0.43
160	250	4	–	0.39294	33.905	8.63	69.03 ± 1.47
160	350	1	–	0.52948	43.726	8.26	78.51 ± 0.46
160	350	4	–	0.52948	43.726	8.26	77.91 ± 0.37
80	250	1	n-Heptane	–	–	–	80.40 ± 2.96
80	250	4	n-Heptane	–	–	–	79.51 ± 2.99
80	350	1	n-Heptane	–	–	–	92.26 ± 5.40
80	350	4	n-Heptane	–	–	–	87.68 ± 1.20
160	250	1	n-Heptane	–	–	–	73.03 ± 2.18
160	250	4	n-Heptane	–	–	–	78.23 ± 4.66
160	350	1	n-Heptane	–	–	–	85.07 ± 0.55
160	350	4	n-Heptane	–	–	–	82.91 ± 5.02
80	250	1	Toluene	–	–	–	76.05 ± 2.58
80	250	4	Toluene	–	–	–	71.65 ± 1.43
80	350	1	Toluene	–	–	–	77.63 ± 3.30
80	350	4	Toluene	–	–	–	81.01 ± 0.56
160	250	1	Toluene	–	–	–	72.35 ± 3.02
160	250	4	Toluene	–	–	–	68.38 ± 1.99
160	350	1	Toluene	–	–	–	70.38 ± 0.15
160	350	4	Toluene	–	–	–	70.13 ± 2.38

*SEM: Standard Error of the Mean

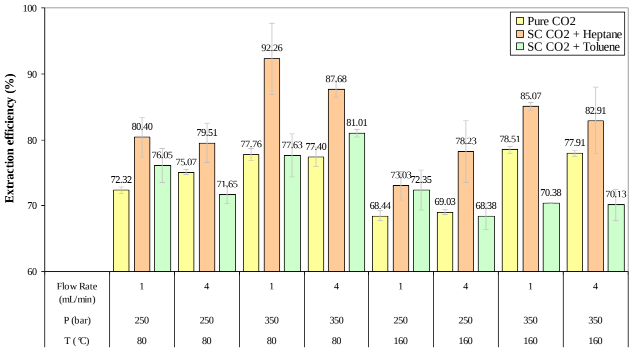


Fig. 2. Average extraction efficiency for all runs.

Results of the multi-way ANOVA based on the original values of extraction efficiency show that temperature, pressure and fluid type have significant effect on the extraction efficiency, but the flow rate of the CO_2 does not have a significant effect, i.e. Sig. >0.05 (Table III). Moreover, pressure and fluid type interact. This means that the effect of pressure depends on which fluid is used and vice versa, which is not the case with temperature. However, by checking the validity of the ANOVA model using residual analysis, the normality assumption was found to be satisfied, i.e. the p-value was higher than 5%. But, the homogeneity of variance assumption was found to be satisfied with respect to the factors flow rate, temperature and pressure, but it was not satisfied with respect to fluid type. This violation of the assumptions of ANOVA should not have adverse effects on the validity of the method because when the model is balanced (i.e., there are equal numbers of replications per cell) ANOVA is robust to such a violation [36].

TABLE III: STATISTICAL ANALYSIS BASED ON A MULTI-WAY ANOVA

Source	**Type III Sum of Squares**	**df***	**Mean Square**	**F****	**Sig.**
Corrected Model	1760.595$^{(a)}$	23	76.548	6.394	0.000
Intercept	283,086.096	1	283,086.096	23,646.971	0.000
Temperature	246.404	1	246.404	20.583	0.000
Pressure	458.761	1	458.761	38.322	0.000
Fluid Type	759.580	2	379.790	31.725	0.000
Flow Rate	2.316	1	2.316	0.193	0.664
Temperature*Pressure	0.906	1	0.906	0.076	0.786
Temperature*Fluid Type	36.043	2	18.021	1.505	0.242
Pressure*Fluid Type	86.269	2	43.134	3.603	0.043
Temperature*Pressure*Fluid Type	64.238	2	32.119	2.683	0.089
Temperature*Flow Rate	0.718	1	0.718	0.060	0.809
Pressure*Flow Rate	1.245	1	1.245	0.104	0.750
Temperature*Pressure*Flow Rate	2.800	1	2.800	0.234	0.633
Fluid Type*Flow Rate	7.423	2	3.712	0.310	0.736
Temperature*Fluid Type*Flow Rate	21.330	2	10.665	0.891	0.423
Pressure*Fluid Type*Flow Rate	66.958	2	33.479	2.797	0.081
Temperature*Pressure*Fluid Type*Flow Rate	5.604	2	2.802	0.234	0.793
Error	287.312	24	11.971		
Total	285,134.003	48			
Corrected Total	2,047.907	47			

(a) R Squared = 0.860 (Adjusted R Squared = 0.725)

* df: degrees of freedom.

** F: Test Statistics.

A. Effect of Temperature

Fig. 3 illustrates the effect of temperature on the extraction efficiency. Values on the figure (including bars showing the standard error of the mean) represent the mean value of extraction efficiency for 24 experiments at each temperature. Results indicate that temperature has an inverse effect on the extraction efficiency. This might be due to the increase in the kinematic viscosity and interfacial tension due to the decrease in CO_2 density with an increase in temperature.

B. Effect of Flow Rate

Effect of flow rate (1 and 4 ml/min) on the extraction efficiency is shown on Fig. 4. Values on the figure represent the mean value of the extraction efficiency for 24 experiments at each flow rate. Decreasing the flow rate usually ensures more contact time and results in higher extraction efficiencies for a given amount of CO_2 used. However, saturation is achieved at certain flow rates, below which the flow rate does not affect the extraction efficiency of the solvent. Results indicate that flow rate does not affect the extraction efficiency for the conditions used in this study. Therefore, the extraction process should be operated at 4 ml/min in order to reduce the extraction time.

C. Effect of Pressure and Fluid Type

Due to the interaction between pressure and fluid type, effect of these parameters cannot be shown separately, therefore, Fig. 5 shows the effect of both pressure and the fluid type on the extraction efficiency. Each point on Fig. 5 represents the mean value of extraction efficiency for 8 experiments for each fluid type at a given pressure. As shown in the figure, the extraction efficiency of pure and modified SC CO_2 increases as the pressure is increased. This might be due to the decrease in the kinematic viscosity due to the increase in CO_2 density with an increase in pressure. Moreover, the extraction efficiency of the modified SC CO_2 by 5% (v/v) heptane is higher than that of both pure SC CO_2 and modified SC CO_2 with 5% (v/v) toluene. The higher extraction efficiency when utilizing heptane can probably be attributed to the richness of Bu Hasa crude oil in aliphatic non-polar hydrocarbon compounds such as n-alkanes (C_6-C_{22}) as reported in 2007 by Al-Marzouqi *et al*. [33]. However, due to the interaction between pressure and fluid type, the extraction efficiency of modified SC CO_2 with 5% (v/v) toluene is found to be higher than that for pure SC CO_2 at the low pressure (250 bar) but lower at the high pressure (350 bar).

D. Compositional analysis of extracts and residues

Gas chromatograms of the original crude, extracted oil obtained from the SFE process, and the residual oil remaining in the soil samples are shown in Fig. 6 for a representative run. As shown in the figure, a modified CO_2 with 5 % heptane at 350 bar, 80 ^{o}C and CO_2 flow rate of 1 ml/min is capable of extracting gasoline and diesel range hydrocarbons (up to C_{22}). Only a very small amount of hydrocarbons remained in the soil sample as residue, suggesting that chemically modified CO_2 (with 5% heptane) at this pressure and temperature can extract a wide range of hydrocarbons, in agreement with the results of extraction efficiency (Table II). Similar results were obtained for the pure and modified CO_2 with 5 % toluene at the same conditions (350 bar and 80 ℃). The residual oil remaining in the soil sample was not significantly different in the case of chemically modified CO_2 as compared with extraction by pure CO_2 at the same conditions. This might be due to the high density of SC CO_2 at the studied pressures (250 and 350 bar). Therefore, the enhancement in the solvating power of SC CO_2 by the addition of 5 %

heptane or toluene was not very significant at these high pressures.

E. Scanning Electron Microcopy (SEM)

Scanning electron micrographs of selected soil samples are shown on Fig. 7. The results obtained from these images are in agreement with the results obtained for extraction efficiency. The SEM image of the untreated soil contaminated with Bu Hasa crude oil (a) and treated sample with pure SC CO_2 at 250 bar and 160 ℃ (b) showed some remaining hydrocarbons. Therefore, pure SC CO_2at the low pressure and high temperature was not able to completely remediate the contaminated soil. However, pure and modified SC CO_2, at high pressure and low temperature, were able to effectively remove the crude oil from the contaminated soil, which is in agreement with the previous observations obtained by the GC analysis of the extracts and residues and with the results in Table II.

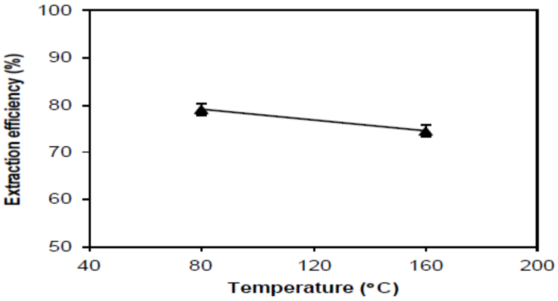


Fig. 3. Effect of temperature on the extraction efficiency.

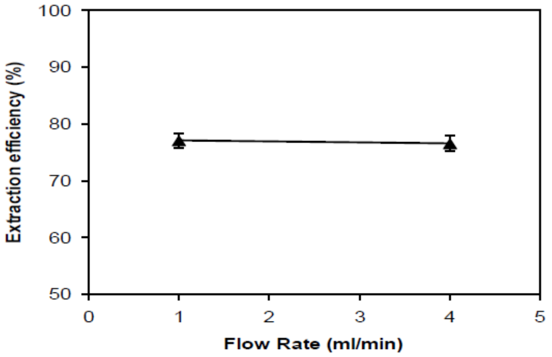


Fig. 4. Effect of CO_2 flow rate on the extraction efficiency.

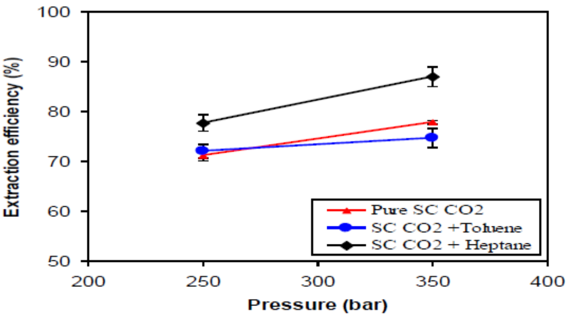
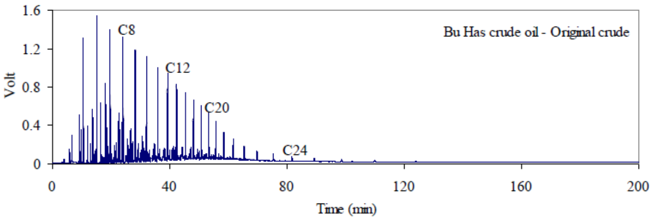


Fig. 5. Effect of pressure and fluid type on the extraction efficiency.



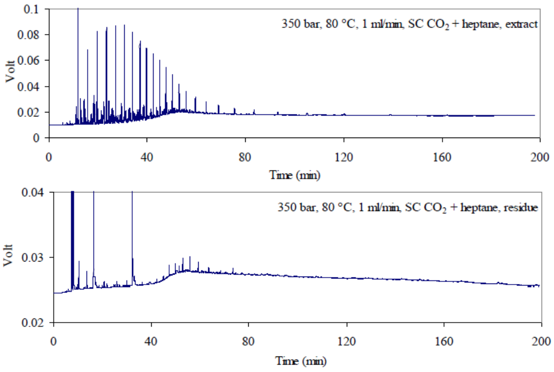
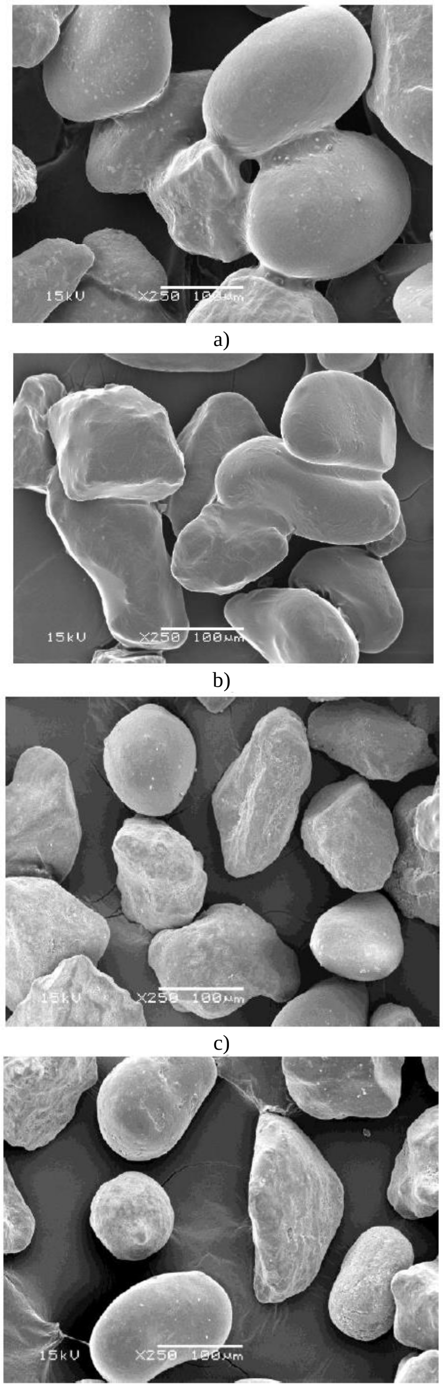


Fig. 6. Gas chromatograms of the original Bu Hasa crude oil, extract obtained from SFE, and the residue. SFE conditions: 350 bar, 80 ℃, 1 ml/min, SC CO_2 + 5% (v/v) heptane.



a)

b)

c)

d)

Fig. 7. Contaminated soil with Bu Hasa crude oil (a) and soil after extraction by: pure SC CO_2 at 250 bar, 160 ℃(b), pure SC CO_2at 350 bar, 80 ℃(c),SC CO_2 + 5% (v/v) heptane at 350 bar, 80 ℃ (d).

F. Analysis of Total Petroleum Hydrocarbon

TABLE IV: TPH ANALYSIS OF THE CLEAN SOIL, SOIL SPIKED WITH CRUDE OIL BEFORE SFE AND TREATED SOIL AFTER THE SFE PROCESS

Sample	**SFE T (°C)**	**SFE P (bar)**	**TPH (μg/mg)**	**TPH Removal (%)**	**Extraction Efficiency (%)**
Clean soil	–	–	< 0.23	–	–
Spiked soil with crude oil before SFE	–	–	56875	–	–
Treated soil after SFE	80	350	4057	92.86	78.69
	160	250	13564	76.15	69.22
	160	350	5129	90.98	77.95
	80	250	9361	83.54	71.83

The capacity of pure SC CO_2 to extract TPH from soil saturated with Bu Hasa crude oil was investigated for some selected runs (Table IV). As shown in the table, pure SC CO_2 at high pressure (350 bar) and low temperature (80 °C), is capable of extracting 92.86% of TPH from the polluted soil compared to 90.98% removal of TPH at the same pressure and higher temperature (160 °C).Removal percentage was less at the lower pressure of 250 bar (83.54% and 76.15% at 80 and 160 ^{o}C, respectively), which matches the results obtained from the extraction efficiency of SC CO_2.This study shows that pure SC CO_2 can effectively remediate the contaminated soil and thus reduce the harmful effects of the TPH compounds on the environment.

The PAHs measurement was conducted for selected runs to investigate the efficiency of SC CO_2 in extracting PAHs from soil samples contaminated with Bu Hasa crude oil. Concentration of 16 PAHs in the selected soil samples after the SFE process is tabulated in Table V. Results show that the modified SC CO_2 with 5% (v/v) heptane at low temperature (80 °C) and high pressure (350 bar) was not able to completely remove naphthalene, acenaphthene, anthracene, fluoranthene and chrycene from the contaminated soil. Also, the extraction by pure SC CO_2 at the same pressure and temperature was the worst among all other conditions to extract the fluoranthene, pyrene, benzo (b) flouranthene, benzo(g,h,i) perylene and indeno (1,2,3-cd) pyrene. However, pure SC CO_2 at 160 °C and 350 bar resulted in a better extraction of the 16 PAHs. This might be attributed to the effect of high temperature, which increases the volatility of the PAHs and thus increases their solubility in the fluid. Further studies are needed to confirm this result.

TABLE V: PAHS ANALYSES OF THE CLEAN SOIL, SPIKED SOIL WITH CRUDE OIL BEFORE SFE AND TREATED SOIL AFTER THE SFE PROCESS. REMOVAL EFFICIENCIES (%) ARE SHOWN IN PARENTHESIS. REMOVAL EFFICIENCY WAS ASSUMED 100% FOR PAH CONCENTRATION < LOD*

Sample		Clean soil	Spiked soil with crude oil before SFE	Treated soil after SFE				
Temperature (℃)		–	–	80	160	160	80	80
Pressure (bar)		–	–	350	250	350	250	350
Modifier		–	–	–	–	–	–	Heptane
PAH (µg/kg)	Naphthalene	<7.89	10648	<7.89 **(100%)**	<7.89 **(100%)**	<7.89 **(100%)**	<7.89 **(100%)**	78 **(99.26%)**
	Acenaphthylene	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7	<10.7
	Acenaphthene	<5.12	3260	7.89 **(99.75%)**	16.8 **(99.48%)**	15.4 **(99.52%)**	16 **(99.50%)**	19.5 **(99.40%)**
	Flourene	<5.53	357	<5.53 **(100%)**	<5.53 **(100%)**	<5.53 **(100%)**	<5.53 **(100%)**	<5.53 **(100%)**
	Phenanthrene	<4.85	10417	279 **(97.32%)**	66.8 **(99.35%)**	75.1 **(99.27%)**	553 **(94.69%)**	292 **(97.19%)**
	Anthracene	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99
	Fluoranthene	<4.98	947	42.3 **(95.53%)**	32.3 **(96.58%)**	<4.98 **(100%)**	8.19 **(99.13%)**	40.2 **(95.75%)**
	Pyrene	<5.00	3921	924 **(76.43%)**	274 **(93.01%)**	63.1 **(98.39%)**	393 **(89.97%)**	622 **(84.13%)**
	Benzo(a)anthracene	<4.90	1168	<4.90 **(100%)**	9.53 **(99.18%)**	11.4 **(99.02%)**	<4.90 **(100%)**	9.85 **(99.15%)**
	Chrycene	<4.92	1107	9.85 **(99.11%)**	<4.92 **(100%)**	10.3 **(99.06%)**	<4.92 **(100%)**	10.8 **(99.02%)**
	Benzo(b)flouranthene	<4.54	<4.54	<4.54	<4.54	<4.54	<4.54	<4.54
	Benzo(k)flouranthene	<4.61	<4.61	<4.61	<4.61	<4.61	<4.61	<4.61
	Benzo(a)pyrene	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99	<4.99
	Dibenzo(a,h)anthracene	<5.34	283	<5.34 **(100%)**	<5.34 **(100%)**	<5.34 **(100%)**	<5.34 **(100%)**	<5.34 **(100%)**
	Benzo(g,h,i)perylene	<5.45	750	37 **(95.06%)**	<5.45 **(100%)**	<5.45 **(100%)**	<5.45 **(100%)**	13.8 **(98.16%)**
	Indeno(1,2,3-cd)pyrene	<5.42	326	36.2 **(88.89%)**	<5.42 **(100%)**	<5.42 **(100%)**	<5.42 **(100%)**	<5.42 **(100%)**
Extraction efficiency (%)		**–**	**–**	**78.69**	**69.22**	**77.95**	**71.83**	**97.66**

* LOD: limit of detection.

IV. CONCLUSIONS

Effects of temperature, pressure, CO_2 flow rate and two modifiers (heptanes and toluene) at 5% (v/v) on the extraction capacity of SC CO_2were investigated. The results of this study indicate that SC CO_2 is an effective solvent, which leads to high extraction efficiencies when applied at high pressures. Furthermore, the results from this study show that the flow rate does not have a significant effect on the efficiency of SC CO_2. Therefore, it is recommended to use the high flow rate, i.e. 4 ml/min, in order to reduce the time required for the remediation of contaminated soil. Moreover, the temperature, i.e. 80 and 160 °C, has no significant effect on the extraction efficiency of SC CO_2 at the high pressure (350 bar). Therefore, it is recommended to apply the low temperature during the extraction process in order to save energy. Chemical modification of CO_2 by adding 5% heptane was more effective than the same level of modification by toluene. The optimum condition to extract hydrocarbons from soil contaminated with Bu Hasa crude oil was by modified SC CO_2 with 5% heptane at high pressure (350 bar), low temperature (80 °C), and flow rate of 1 ml/min. Supercritical CO_2 was able to remove 92.86% of the TPH present in contaminated soil. Additionally, pure SC CO_2 and SC CO_2 chemically modified with 5% (v/v) heptane were capable of significantly reducing the concentration levels of PAHs in the soil contaminated by Bu Hasa crude oil.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Abdulrazag Y. Zekri and Ali H. Al-Marzouqi; Designed the study and analyzed the data. Adel A. Azzam; assembled the extraction system and conducted the experimental work. Abdulrahman Y. Alraeesi; aided in interpreting the results and worked on the manuscript. All authors had approved the final version.

ACKNOWLEDGEMENT

The authors would like to thank Abu Dhabi National Oil Company (ADNOC), UAE, for providing the real samples to complete this study.

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