Treatment of Petroleum Contaminated Soil using Supercritical Fluid Extraction (SFE) Technology

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ABSTRACT

In Canada, about 60% of contaminated sites involve petroleum hydrocarbon (PHC) contamination and most of these sites have been abandoned due to contamination. Among current technologies used for soil remediation, supercritical fluid extraction (SFE) is a relatively recent and potentially viable method. The main aim of this research was to investigate the application of SFE for removal of PHCs from contaminated soils.

In the first phase, the effects of SFE operational parameters including fluid pressure, fluid temperature, time duration and mode of extraction on the removal efficiency of PHCs from a spiked sandy soil (with diesel fuel with a ratio of 5 wt%) were investigated. SFE experiments were performed at different pressures (15, 33 and 50 MPa) and temperatures (30, 75 and 120 °C). The combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles (60 min in total) led to the highest PHC removal percentage. According to response surface methodology (RSM), the optimum pressure and temperature were found to be 50 MPa and 69.3 °C, respectively. According to experimental results, the optimum combination of pressure and temperature determined to be 33 MPa and 75 °C; which resulted in the extraction percentages of 99.2%, 91.7% and 86.1% for PHC F2, F3 and F4 fractions, respectively.

In the second phase, the influence of several parameters including soil water content, soil pH and addition of modifier on PHCs removals from a field-contaminated sandy soil using SFE were experimentally investigated. SFE experiments were performed at 33 MPa pressure and temperatures of 45 and 75 °C. Three water content levels of 8%, 14% and 20% at two levels of pH 6.5 and 7.5 were investigated. The extraction of total petroleum hydrocarbon fractions (TPHF), the sum of F2, F3, and F4 fractions, decreased due to the increase in the water content from 8% to 20% at both pH 6.5 and 7.5. The difference of extractions of all PHC fractions at pH values of 6.5 and 7.5 were not statistically significant (at $p < 0.05$ confidence level) at all three water content levels and pH did not have a significant influence on the PHC removal efficiency. Addition of acetone as a modifier (33.7% TPHF removal) was more effective than hexanes (24.3% TPHF removal) to decrease the concentrations of PHCs for the field contaminated soil.

In the third phase, the influence of soil texture and grain size on the extraction of PHC fractions was investigated. SFE experiments were performed at 33 MPa pressure and 75 °C temperature. Three types of soils (soil A, B and C) were spiked with diesel fuel with a ratio of 5 wt%. Soil A, B and C had different particle sizes and were categorized as sand, silt loam and clay, respectively. Soil A (sand) which had the largest particle size resulted in the highest TPHF removal percentage while soil C (clay) with the smallest particle size led to the lowest TPHF removal percentage. A higher clay content in soil C resulted in a lower extraction of PHCs.

In the fourth phase, the effects of pressure and temperature on the extraction of PHC fractions from a clay soil spiked with diesel fuel with a ratio of 5 wt% were investigated. SFE experiments were performed at three pressures (15, 33 and 50 MPa) and temperatures (30, 75 and 120 °C). According to the statistical analysis including factorial design and RSM, the optimized combination of pressure and temperature was selected at 42.8 MPa and 120 °C; which resulted in the removal percentages of 74.9% and 65.6% for PHC F2 and F3 fractions, respectively. The optimum combination of pressure and temperature based on the experimental results was selected at 33 MPa and 120 °C that led to 70.3%, 58.4% and 32.6% removal of PHC F2, F3 and F4 fractions, respectively.

Keywords: petroleum hydrocarbon; supercritical fluid extraction; contaminated soil; soil remediation; sand; clay; soil pH; water content; modifier addition; soil grain size; response surface methodology; optimization; statistical analysis

Dedication

To my beloved wife, **Mojdeh**

and my dear parents, **Hossein** and **Mina**

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It is an honor for me to thank those people who made this thesis possible and words fail to appreciate them in a way that it should be.

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Contents

List of Abbreviations

Abbreviation	**Definition**
ACS	American Chemical Society
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BTEX	Benzene, toluene, ethylbenzene and xylenes
CCME	Canadian Council of Ministers of the Environment
CO_2	Carbon dioxide
DDT	Dichloro-diphenyl-trichloroethane
FID	Flame ionization detector
GC	Gas chromatography
HPLC	High-performance liquid chromatography
ICDD	International centre for diffraction database
K-D	Kuderna-Danish
MOE	Ontario Ministry of Environment
Pc	Critical pressure
PAH	Polyaromatic (polycyclic aromatic) hydrocarbon
PCB	Polychlorinated biphenyl
PFC	Perfluorinated compounds
PHC	Petroleum hydrocarbon
POP	Persistent organic pollutant
PXRD	Powder x-ray diffraction
RSM	Response surface methodology
SC-CO_2	Supercritical carbon dioxide

Abbreviation	**Definition**
SCE	Supercritical extraction
SCF	Supercritical fluid
SCW	Supercritical water
SFE	Supercritical fluid extraction
SFT	Supercritical Fluid Technologies Inc.
Tc	Critical temperature
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
TPHF	Total petroleum hydrocarbon fractions
US EPA	United States Environmental Protection Agency
VOC	Volatile organic compound

Chapter 1: Introduction

1.1 General background

Approximately 300,000 contaminated sites in the United States [1] and about 30,000 brownfields (i.e. commercial or industrial contaminated sites which were abandoned) in Canada have been reported in the early 2000s [2]. In Germany, the number of contaminated sites was reported to be close to 300,000 [3]. In Netherlands alone, there were as many as 100,000 contaminated sites [4]. These contaminated sites have been polluted with various materials including petroleum products (petroleum hydrocarbons (PHCs) or total petroleum hydrocarbons (TPHs)); organic compounds such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and pesticides; heavy metals (Pb, Cd, Cr, Co, etc.); and radioactive elements (U, Pu, Am, Th and others) [2]. Most of these substances are persistent organic pollutants including PAH, PCB, chlorobenzenes and pesticides having high chemical and/or biological stability accompanied with strong lipophilicity that can cause problems to human health and the environment [5]. These substances can be threatening in different ways, for example being absorbed by plants and animals and entering the human food chain, discharged into groundwater and surface water, or released into the air and subsequent exposure. In Canada, approximately 60% of contaminated sites involve PHC contamination accounting for multibillions of dollars in environmental liabilities and remediation costs [6,7]. If they are remediated, their development would have positive effects on the economy (due to land’s value) and society. Therefore, remediation techniques have been considered to remediate these contaminated sites [2].

Following are the main options to manage the contaminated sites: 1) abandon the land use and do nothing for the contamination, 2) contain and enclose the pollution to prevent the further transport and spread of contaminants, 3) excavate the contaminated soil and transport to a landfill, and 4) remediate the contaminated soil with either in-situ or ex-situ remediation techniques [8]. Technologies used to treat contaminated environmental matrices are generally classified as physical, chemical, and biological processes. Physical and chemical technologies (or separation-based technologies) involve the extraction of pollutants from matrices. Physical processes include soil vapor extraction, soil washing/flushing, stabilization, and thermal desorption. The most frequently used chemical treatment technologies include solvent extraction and chemical oxidation/reduction. Land-treatment/land-farming, bioreactors, bioremediation, biodegradation and phytoremediation are the examples of biological treatment processes [9–11].

Over the last couple of decades new technologies have been developed to decrease or eliminate the organic solvent requirements for conventional solvent extraction technologies. One relatively newer method compared to conventional soil treatment methods which could be practiced by industry is supercritical extraction (SCE) [5]. SCE is considered a solvent extraction method in the class of physical/chemical technologies [9,10]. Favorable and flexible characteristics of supercritical fluids (SCFs) such as high density, low viscosity and high diffusion property make supercritical fluid extraction (SFE) a potentially viable option as a solvent extraction treatment [5].

1.2 Statement of problem

SFE is a relatively newer technology compared to most conventional remediation technologies (like bioremediation) for petroleum contaminated soil and as such has not been as thoroughly studied as other soil treatment methods. Although some previous information for treatment of petroleum contaminated soil using SFE exists in the literature, there are research gaps as explained subsequently. Also, some of the available information is not complete and/or missing and/or contradictory. Therefore, more research is needed to fully understand the SFE process and the effect of different parameters in order to optimize the process.

In Canada, limited studies have been conducted for treatment of contaminated soil using SFE. Also, limited information is available on PHC fractions individually when it comes to application of SFE. PHCs are categorized into fractions according to the requirements of Canada-Wide Standard for PHC in soil by Canadian Council of Ministers of the Environment (CCME). Moreover, PHC covers a wide range of hydrocarbons (rather than one single compound) and consequently, the conclusions made based on PHC fractions would be useful for variety of hydrocarbons.

Regarding SFE operational parameters, a sufficient knowledge for the effect of temperature on the extraction of PHCs has not been acquired. The influence of soil water content on the extraction of each PHC fraction (i.e. F2, F3 and F4) has not been studied. The effect of pH on removal of contaminants from soil has been studied to less extent, and no information is available for the pH impact on each PHC fraction separately. In addition, no previous information is available for the combined effect of pH and water content on the recovery of PHC fractions from contaminated soils. Besides, more investigations should be conducted to assess the role of modifiers and their addition for removal of PHCs in the SCE process. There is also limited information in the literature on the impact of water content, pH and modifier addition on the extraction of PHCs from field-contaminated soils. Soil grain size has significant effect on SFE of petroleum contaminated soils and lack of information existed for the effect of soil grain size on removal of PHC fractions. Lastly, optimization of pressure and temperature for extraction of PHC fractions using response surface methodology (RSM) was not investigated before.

Considering the above, there is a need to study in more detail the remediation of PHCs contaminated soil using SFE by conducting a systematic assessment supported by statistical analysis.

1.3 Research Objectives

The main objective of this research is the systematic assessment of the application of SFE for treatment of PHCs contaminated soils at laboratory scale using statistical analysis. The specific objectives of the current research are summarized as follows:

- Investigation of the effect of SFE operational parameters including pressure, temperature, time duration as well as extraction modes of operation on the extraction of PHC fractions (i.e. F2, F3 and F4) from a spiked sand.
- Investigation of the effect of properties of a field-contaminated sand including water content and soil pH on the SFE treatment efficiency.
- Assessment of addition of various modifiers (co-solvents) on the extraction of PHCs from a field-contaminated sand using SFE.
- Evaluating the effect of soil particle sizes on the SFE treatment efficiency for PHC removal from three spiked soils (having different particle sizes and various contents of sand, silt and clay).
- Evaluation of the influence of pressure and temperature on the PHCs removal from a spiked clay.

- Optimization of the impact of pressure and temperature by statistical analysis including factorial experimental design and RSM for the PHC removal from two types of soils including sand and clay.

The results derived from these investigations will contribute to a better understanding of the remediation of petroleum contaminated soils using SFE and thus towards its effective application.

It should be mentioned that the results of this study were concluded based on the specific conditions and parameters under which experiments were conducted. In other words, for other conditions rather than those investigated in this study, the obtained conclusions might be different. Some of important conditions that may affect the conclusions are pressure and temperature levels, time duration and extraction mode, soil type and source of contamination. In this study, a soil spiked with diesel fuel with a ratio of 5 wt% was used. Water content in the range of 8-20% and pH in the range of 6.5-7.5 were investigated in this study. Also, modifiers were added to soil samples by 5% volume. Some characteristics of soil (e.g. organic matter content) that may affect the contaminants removal, were not considered here since they were not in the scope of this study. At last, as mentioned above, all experiments were conducted at laboratory scale.

1.4 Thesis organization and outline

This thesis is organized into eight chapters in order to facilitate the presentation of the key findings. **Chapter one** provides a brief overview and general information on contaminated sites such as their negative impacts on the environment and society and different technologies available for treatment of these contaminated sites. This chapter also presents a general description of the identified problems as well as the objectives of this research. **Chapter two** is structured to provide a literature review about the theoretical and technical aspects of SCE as a promising method which is used for treatment of contaminated soils. Apart from the fundamental background information on SFE, current knowledge and relevant previous efforts on the application of SFE in different studies are offered. The role of different parameters including temperature and pressure, soil properties, water content, flow rate of SCF and using modifiers on the overall performance of SCE is also presented.

Chapters three to six were written in a research paper format, which cover four technical papers; each paper thereby contains the associated sections including abstract, introduction, materials and methods, results and discussion, conclusion, and reference. The paper-based format would result in the repetition of some information since each paper is written independently and has to be self-sufficient. **Chapter three (technical paper I)** is intended to study the effects of SFE operational parameters including SCF pressure and temperature, time duration and mode of extraction (static and dynamic) on the removal efficiency of PHCs from a sandy soil, which was spiked with diesel fuel with a ratio of 5 wt%. In addition, factorial design and response surface methodology are applied to optimize the effect of pressure and temperature. **Chapter four (technical paper II)** deals with the influence of several parameters including soil water content, soil pH and modifier (co-solvent) on the PHCs removal from a field-contaminated sandy soil. Consequently, three water contents (8%, 14% and 20%) at two levels of pH (6.5 and 7.5) and two modifiers (acetone and hexanes) are considered. In **Chapter five (technical paper III),** the influence of soil grain size on the extraction of PHC fractions (i.e. F2 to F4) using SFE are experimentally assessed. Therefore, three types of soils (sandy, silt loam and clay) were spiked with diesel fuel with a ratio of 5 wt%. **Chapter six (technical paper IV)** investigates the effect of SCF pressure and temperature on the extraction of PHC fractions (i.e. F2 to F4) individually from a clay soil, which was spiked with diesel fuel with a ratio of 5 wt%. Moreover, factorial design and response surface methodology are applied to optimize the effect of pressure and temperature for obtaining the highest removal percentage.

Chapter seven integrates all the discussions in all phases of this study. A general discussion of results along with comparing the phases of this study is presented in this chapter. Finally, **Chapter eight** summarizes the main conclusions drawn from different phases that were performed in this research and also provides possible recommendations that could be useful for future studies. Figure 1.1 shows the organization of this thesis.

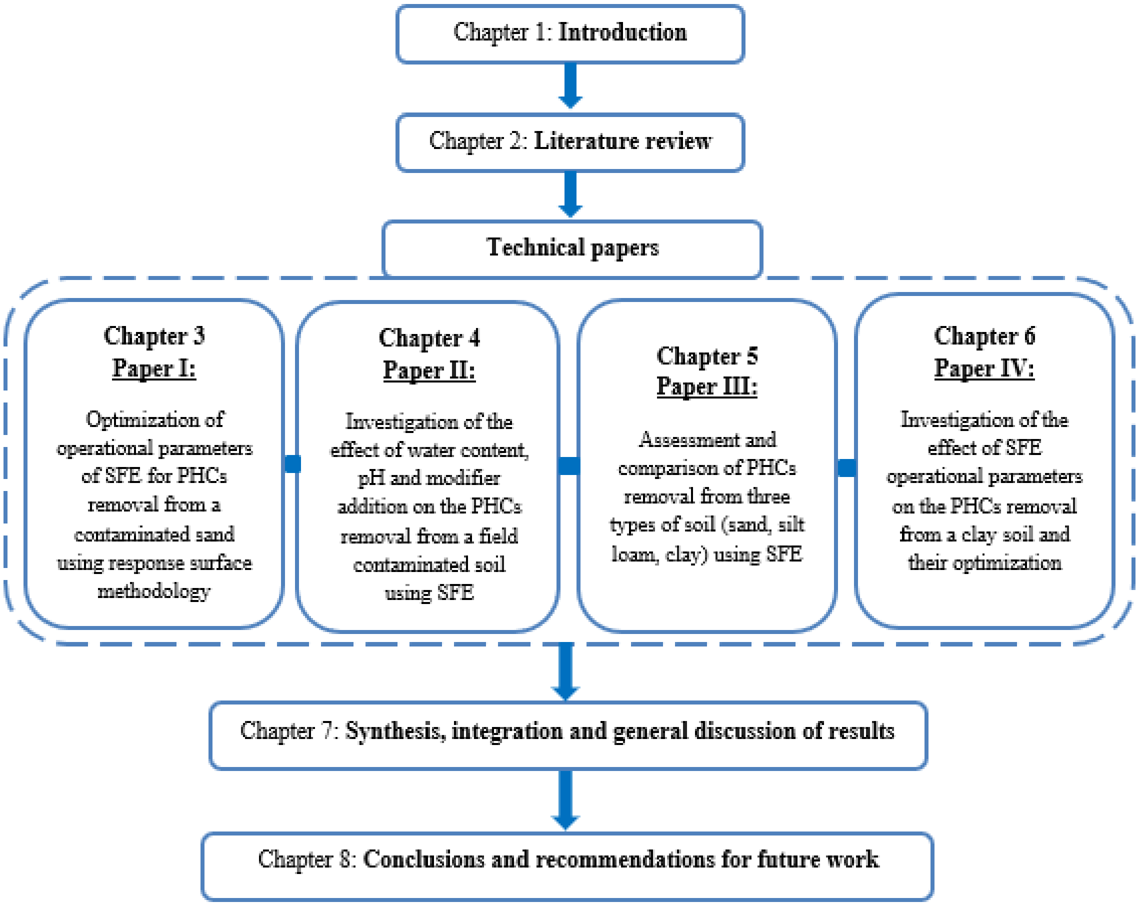

Figure 1.1. Organization of the thesis

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Chapter 2: Literature Review

2.1 Remediation technologies and advantages of supercritical fluid extraction

Despite the fact that there are various techniques to treat contaminated soil, their applications may be limited due to different parameters such as cost, time, efficiency, etc. [1]. As an instance, excavation is expensive and the need to replace the contaminated soil with clean soil may further increase the associated cost [2]. In addition, some treatment technologies may only be suitable for a special kind of pollutant and they do not work well for other types of contamination that might be available at a contaminated site. Similarly, some treatment technologies may be effective for some soil types (e.g. sand), but they may not be applicable for other types of soil [3].

When it comes to treatment of biodegradable contaminants such as petroleum compounds, bioremediation is a relatively low-cost treatment technology and may result in production of by-products and residues, but the main drawback is that it is a very time-consuming process where the treatment can last even for several years in some cases [2]. Compared to bioremediation, supercritical fluid extraction (SFE) is a fast technology [3].

In SFE, the target contaminant (i.e. petroleum compounds in this research) is extracted from the soil matrix by supercritical fluid (SCF) and then, the contaminant is separated from SCF easily by adjusting pressure and temperature. However, other conventional solvent extraction methods may need further extraction of solvents. In addition, solvent requirement for SFE is low compared to conventional solvent extraction and consequently SFE produces less waste. There are no hazardous residues remaining in soil treated by SFE. Furthermore, solvent extraction methods that use organic solvents may result in a low removal percentage of contaminants [3,4]. In general, the applicability of common solvent extraction is more restricted than SFE [5]. Thermal treatment/high temperature oxidation can be costly and may also cause air pollution [1]. Compared to thermal techniques, SFE does not have detrimental effect on the soil fabrics [6,7] and SFE needs lower amount of energy than thermal treatment [6]. Other advantages of SFE (in the case of supercritical carbon dioxide (SC-CO_2)) include mild critical points of CO_2, non-flammable and non-toxic characteristics of CO_2 and quick reaction rates of SC-CO_2 system [8].

One specific property of SFE is that it can be coupled with analytical devices to transfer the extracts directly without sample handling such as on-line delivery of the extracted substances to analytical equipment like gas chromatography (GC) and high-performance liquid chromatography (HPLC) [9]. Supercritical fluid can be recovered using a recompression unit and recycled for use in another extraction, which is another advantage of SFE [3]. When considering all these aspects among available techniques, SFE appears as a potentially viable technology that could be applied for treatment of contaminated soils [3,10,11].

The main drawback of SFE is that it requires that contaminated soil should be excavated at the site which may result in higher costs than in-situ technologies. Moreover, in the SFE process, the source of pollution is only extracted from the soil matrix, and SFE does not destroy pollutants [3]. SFE process also presents some trade-off aspects such as: a) the investment cost of SFE compared to that of other classical remediation technologies, and b) the safety of SFE system as it works with high pressure that may cause related hazards [12].

2.2 Supercritical state

When a fluid is at a special state which is above its critical temperature (T_c) and critical pressure (P_c), it is in supercritical state and the fluid is called supercritical fluid or SCF [3,4,10]. Figure 2.1 illustrates the phase (pressure-temperature) diagram for gases and their supercritical region [4].

Carbon dioxide is the most commonly used gas for supercritical extraction. Its critical pressure and temperature are 7.4 MPa and 31 °C, respectively [13].

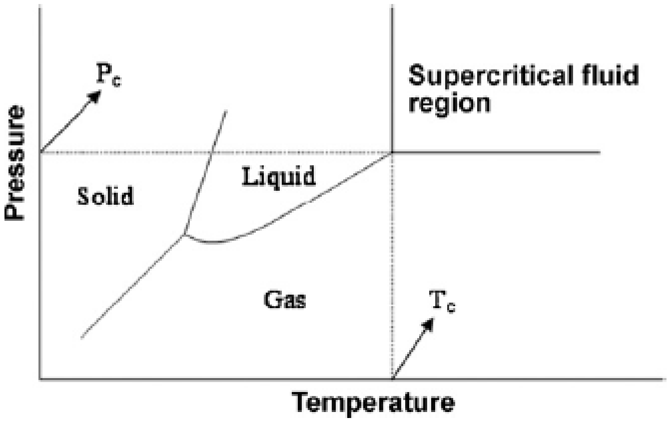


Figure 2.1. Phase diagram for gases [4]

When a compound is in supercritical state, it shows properties similar to both gases and liquids and in fact SCF intermediates between the properties of gases and liquids [14]. However, it stands as a single fluid phase [4].

Table 2.1 provides different properties of gases, supercritical fluids and organic liquids [4]. As shown in this table, the density of supercritical fluids is greater than that of normal gases and approximately close to liquids (high density like liquids). Considering viscosity, SCFs have lower values than liquids, similar to gases (low viscosity as gases). Diffusivity of SCFs is higher than liquids and less than gases, which leads SCFs showing promising transport characteristics (high diffusivity like gases). Considering these specific properties, SCFs are considered as favorable solvents for extraction. In addition, having zero surface tension allows SCFs to move into various matrices readily [4,9–11,14,15]. Mass transfer is quick within the supercritical state. In addition, changes in pressure and temperature may change the viscosity and diffusivity. In other words, the solvating power of the fluid can be tuned by applying different pressures and temperatures [9,10].

Table 2.1. Comparison of physical properties of gases, SCF, and organic liquids [4]

Phase	Density (g/cm^3)	Viscosity (P) $\times 10^4$	Diffusivity (cm^2/s) $\times 10^4$
Gases	~0.001	0.4-3.4	100-10000
Organic liquids	0.6-1.1	32-251	0.05-0.2
Supercritical fluid	0.2-0.9	2.1-10.8	0.11-3.45

Various densities of SCF can be achieved via slight alteration of temperature and pressure that define the solubility strength of solvent. Thus, through small changes in temperature and pressure, SFE would be able to selectively extract different substances [10,16,17]. If substances are sufficiently distinctive (e.g. having different polarities), they can be fractionated with SCF and extraction would be performed selectively. However, for organic compounds which have similar polarities, they may not be removed from complex matrices favourably. When extraction is not able to remove the substances selectively, selective sorbents may be added to the extraction vessel to retain those substances which are not desired to be removed [18].

2.3 A typical SFE process

A typical SFE process to treat contaminated soils comprises an extraction vessel (or a reactor) where the contaminated soil is contained and exposed to SCF. Usually, the extraction vessel is surrounded by a heating unit. The SCF is available in a tank (cylinder) and it is pressurized via a pump. In order to maintain a high pressure in the extraction vessel, a restrictor may be required. SCF, which is often CO_2, is carried into the extraction vessel and dissolves/extracts contaminations from the solid phase. The SCF containing contaminants is then released from the extraction vessel via a depressurization valve. When the fluid is depressurized, the extracted contaminants are separated from the fluid due to the reduction in their solubility. The contaminants are collected in a collection system and fluid (i.e. CO_2) can be recovered, if desired. The soil is then discharged, once the vessel is depressurized. The soil can be reused or returned to the site if the concentrations of contaminations in the soil are below the limits set by the authorized agencies and regulators [4,19]. In general, SCE can be conducted in the three modes including static-mode, dynamic-mode and combination-mode [4].

Three successive stages are involved in the SFE process. The first step is removing the compound from the matrix and dissolving it into the SCF. This step usually controls the total removal percentage for heterogeneous environmental matrices [20]. The second step is an elution of the analyte from the extraction vessel which depends on the fluid flow rate, sample size and conventional chromatographic partitioning between fluid and matrix [21]. The third step is collection of the analyte which is affected by instrument properties like restrictor system and type of trapping systems. In order to reach high yield of extraction, each of these steps must be optimized [18].

SCE can be performed as a single-stage treatment process or combined with pre- and/or post-treatment steps as follows [11]:

- *Pre-treatment*: Removal of large particle sizes such as rock, roots and debris; adjustment of moisture content to an optimum value; and if needed adjustment of other soil characteristics (e.g. pH and chemical composition) can be performed in this step to enhance the efficiency.

- *Post-treatment*: SCE does not destroy pollutants. After the pollutants are separated by SCE, they may have high concentrations and can be treated in another treatment step or can be disposed appropriately.

2.4 Applications of SFE

2.4.1 History and early applications

SCFs (as solvents) were used at food industry as early applications to extract various solid and liquid matrices including coal, coffee (for extraction of caffeine), tobacco (for reducing the nicotine content with minimum loss of aroma), fruit aromas (for extraction the constituents of the aroma of apple, pear, orange juice and orange hulls), and water (for alcohols extraction) [10]. The first commercial-scale application of SFE was started in the late 1970s and early 1980s; with decaffeinated coffee and tea in Germany [17]. The development of commercial applications of SFE, for example in the food industry, then appeared quickly in other regions like Europe and North America [3]. Because of rigorous environmental regulations for the use and elimination of organic solvents in industry, SFE is becoming as a potentially viable and promising technology [17,22].

2.4.2 Environmental applications

Some examples of environmental applications of SCE processes in the mid of 1980s are as follows: extraction of oil from metal fines (mill scale) and bleaching clay in the pilot scale by subcritical and supercritical CO_2 were done by Kingsley (1985) [23]. According to Kingsley’s work, flow rate of fluid affects the extraction of materials. In addition, Kingsley concluded that a static mode before conducting extraction would enhance the recovery of bleaching clay [23]. Brady et al. (1987) [24] used SC-CO_2 for extraction of PCBs and DDT (dichloro-diphenyl-trichloroethane) from contaminated topsoil and subsoils. Modifiers were also applied to determine their effect on SCF strength for extraction. The results indicated that addition of methanol as modifier (5% by weight) improved DDT extraction by 100%. While, the addition of toluene as modifier (5% by weight) resulted in only 75% recovery of DDT [24]. Removal of chlorinated aromatics such as trichlorophenol from soil as a model compound for PCBs and dioxins by supercritical ethylene was investigated by Eckert et al [25]. Using ethylene as SCF led to extraction of all trichlorophenol from soil [25]. With further progress of this process, many substances including volatile organic compounds (VOCs) and persistent organic pollutants (POPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and various pesticides from environmental matrices have been extracted using SCFs such as supercritical carbon dioxide (SC-CO_2) and supercritical water (SCW) in the SCE [11].

A large-scale environmental application of SFE systems for treatment of wastewater and solid wastes was reported by Clean Harbors and Ensco Inc. [17]. Removal of PCBs from contaminated harbor sediments in pilot-scale SFE unit was conducted by CF Systems Corporation (CF Systems) as a part of the US EPA's Superfund Innovative Technology Evaluation (SITE) Program. PCBs from contaminated harbor sediments were removed by 90% using a mixture of liquefied propane and butane as the extraction solvent. CF Systems is a technology-based company in the hazardous-waste-treatment and resource-recovery business [26]. Also, removal of organic contaminants from refinery contaminated materials was performed in a commercial plant by CF Systems [26,27].

Other examples of applications of SFE are environmental remediation, metal separation process, remediation of toxic metals in solid wastes, material research, reprocessing of spent nuclear fuel in supercritical CO_2 [8].

2.5 Supercritical fluids (SCFs) and fluid choices

SCF is a selective process with more affinity towards the pollutants than the bulk material of the matrix [11]. Considering removing a solute from matrix, there are two factors that should be considered for selection of the solvent type: solvent should not be dissolved into the matrix and solute should be dissolved into the solvent. The solubility of solute in the solvent (i.e. SCF) is highly dependent on density [10].

The first and the most commonly used SCF, which is used for about 90% of all analytical SFE applications, is carbon dioxide [18]. The characteristics of CO_2 are: non-poisonous, non-flammable or non-explosive, chemically inactive, and fairly low critical point (31 °C and 7.4 MPa). CO_2 can be obtained in high purity at a relatively low cost. CO_2 has good properties including high diffusivity with low surface tension and viscosity. The separation of CO_2 from the matrix and solute is also possible without any difficulties. In addition, there are no environmental negative impacts caused by CO_2 for analytical applications. Since CO_2 is a non-polar solvent, it acts as an efficient solvent for non-polar organic compounds such as hydrocarbons and is suitable for lipophilic compounds as well. The main disadvantage of CO_2 is that it is not able to extract polar compounds owing to its low polarity [12,13,18,28–30].

The second favorable option to use as SCF is nitrous oxide (N_2O). Due to the chemical structure of N_2O, it works well for polar compounds [31]. However, a significant drawback of this fluid is that it may lead to explosions if it is employed for samples with high organic content [28]. Sulfur hexafluoride (SF_6) is not a polar molecule and it is able to extract aliphatic hydrocarbons from a mixture containing both aliphatic and aromatic hydrocarbons [32]. Freons, especially $CHClF_2$ (Freon-22), is another choice as SCF that can result in higher extraction than CO_2 in some cases [31]. The next selection of SCF is H_2O which has mainly been used for destruction of hazardous organics. Applications of H_2O in environmental analyses have been restricted, due to high critical values (374 ^{o}C and 22.1 MPa) along with the corrosive nature of H_2O at supercritical state. H_2O is an environmentally acceptable solvent and its high polarity strength may lead to it being used more in the future [18].

Other fluids selected as SCFs in different applications include argon, propane, ethylene, ethane, benzene, etc., while their applications may be restricted due to some problems such as safety, disposal, toxic emissions, and flammability [12,13,18,28–30].

2.6 Modifiers (co-solvents)

Due to the non-polar nature of CO_2, it can be used as SCF in the extraction of non-polar organic compounds such as hydrocarbons. In order to enable CO_2 to extract polar compounds, modifiers such as methanol and water are added to enhance the polarity of the fluid. Because of the addition of modifiers, solubility of polar substances into SCF increases and the SCF becomes more powerful to remove pollutants from a soil [13,18]. Thus, SCE can be conducted with carbon dioxide alone or mixed with modifiers among which methanol is the most commonly used one (T_{cr} = 239 °C; P_{cr} = 8.1 MPa) [11]. The drawback of the use of a co-solvent is that the addition of a co-solvent may affect some of the most desirable aspects of SFE, namely the application of less solvent. Consequently, an additional step is later needed to separate contaminants and co-solvents, which adds to the costs and use of energy [4].

The modifiers are usually organic solvents. Modifiers can be added to the extraction fluid in the three following ways:

1) Direct addition of a modifier to the contaminated sample (soil). This process is cost-effective and can be performed easily [18].

2) Premixed fluids. In this process, the modifier is added to the CO_2 tank (cylinder) [18].

3) Using a separate modifier pump. This way of addition of modifier is very precise. It should be taken into consideration that the concentration of a modifier can be constant in this method and

the density of CO_2 is kept at a required level. It is possible to change concentrations of modifiers while conducting the SFE, which is not feasible for two other methods of modifier addition [18].

According to Langenfeld et al. (1994) [33] PAH and PCB extraction efficiencies from contaminated sediments did not differ significantly between the addition of low concentrations and high concentrations of a modifier. The results showed that the modifier worked as an agent in the separation of compounds from active sites rather than as a solvent. They indicated that the effect of modifier's nature on increasing the recovery was more important than the concentration of a modifier [33]. Methanol (MeOH) is one of the most favorable modifiers used for the extraction. Other modifiers that have been frequently used include acetone, toluene, hexane and methylene chloride (or dichloromethane). Using the modifiers that interfere with the analytical procedure, for example, modifiers that interfere with GC detectors should be avoided [18].

2.7 The effect of soil and contaminant properties on SCE

Extraction of pollutants from the soil matrix depends on the properties of pollutant, soil and SCF (solvent) and also on the interaction of these [21]. The most important properties of a pollutant are its solubility [34], interactions between pollutant and soil, type of polluted soil (e.g. spiked vs. aged) and the effect of modifiers [35].

Organic pollutants can be available in two forms on the solid surface: adsorbed state and the deposited state. Extraction of the part of organic contaminant which is deposited as a separate phase on the solid surface is carried out by dissolution in the SCF. Extraction of the part of organic contaminant which is adsorbed on the solid phase is governed by the adsorption/desorption equilibrium [10,15].

In the case of organic contaminants that are deposited, modifiers can enhance the process of extraction noticeably; owing to the fact that they enhance the dissolution of organic substances into the SCF. Since SCFs have low surface tension (close to zero), they are able to penetrate the pore structure of the matrix efficiently and remove the organics that were deposited in the pores of the matrix. In the case of adsorbed organics, there are double and triple interactions among solid, organic and SCF [10] and equilibrium data and dynamic parameters are needed [4].

When the solid matrix has water, the extraction will be more difficult. In this state, organic pollutants can be available in four forms: adsorbed on dry soil, dissolved in soil moisture, adsorbed on soil which is covered by a water layer (partitioning between soil and water), and as a separate organic phase. The simplest phase to remove is the separate organic phase, which can be performed by dissolution. On the other hand, it is more complicated to extract other forms since the extraction involves various types of equilibrium (soil/water/SCF partitioning) associated with extraction of different species (water and the organic contaminants) [10].

2.8 SFE of organic compounds

Since carbon dioxide has non-polar characteristic, SFE using CO_2 at supercritical state has the ability to extract most non-polar compounds including PHCs, PAHs, PCBs, furans, some phenols (depending on the pH), dioxins and non-polar pesticides from polluted soil. The extraction of these organic compounds is controlled by variations in temperature and pressure of fluid, presence of modifiers, characteristics of soil (such as soil type and moisture content) and type of target contaminant, which were discussed before [36].

2.8.1 SFE of petroleum hydrocarbons (PHCs)

PHCs are complex groups of organic compounds which are created from crude oil including variety of aliphatic and aromatic hydrocarbons (including PAHs) and also a number of various additives [37]. PHCs are categorized into four fractions according to Canada-Wide Standard for PHC in Soil requirements by Canadian Council of Ministers of the Environment (CCME). The concentrations of these PHCs fractions are compared with regulatory standards to check if the soil has acceptable conditions for different land applications [38]. Based on designated ranges of equivalent carbon number (ECN), these four fractions of PHCs are defined as below [39]:

- PHC F1: nC_6 to nC_{10}

- PHC F2: $>nC_{10}$ to nC_{16}

- PHC F3: $>nC_{16}$ to nC_{34}

- PHC F4: $>nC_{34}$ to nC_{50+}

These four fractions are categorized based on parameters including analytical factors, physical and chemical properties, toxicological characteristics and biological responses in soils. Fraction 1 (F1) is composed of aromatic sub-fractions ($>C_8$ to C_{10}) and aliphatic sub-fractions (C_6 to C_8 and $>C_8$ to C_{10}), which represents volatile fraction of majority hydrocarbons. For example, BTEX (benzene, toluene, ethylbenzene and xylenes) as aromatic compounds are placed in this fraction. F2 is composed of aromatic and aliphatic sub-fractions ($>C_{10}$ to C_{12} and $>C_{12}$ to C_{16}), which represents semi-volatile fraction. F3 is composed of aromatic and aliphatic sub-fractions ($>C_{16}$ to C_{21} and $>C_{21}$ to C_{34}). While F4 are expected to be less mobile (low volatile and low soluble), great portion of crude oils and petroleum products are categorized in this fraction. In general, compounds that fall in F1 and F2 fractions are soluble and volatile. On the other hand, low mobility compounds (i.e. less volatile and less soluble) form F3 and F4 fractions [39].

Different activities associated with production, transportation and consumption of fuels may lead to pollution of soils by PHCs including leakage of fuel from aboveground tanks, railroad cars, underground storage tanks or pipelines, spills around production areas and unsuitable dumping of PHC contaminated wastes (like refinery wastes) [4,22,37].

As it was mentioned before, the extraction efficiency of PHCs from polluted soils using SFE are affected by some parameters such as the dissolution of the PHCs in the solvent, the sorption and desorption of PHCs from soil, water content of the soil, the availability of other organic components in the soil, extraction mode and the use of modifiers as well as temperature and pressure used for SFE process [36]. PHC removal from soil is generally not an easy task.

Most studies on removal of PHCs using SFE have been performed for spiked soils rather than field-contaminated soils [40,41]. For example, Low and Duffy (1995) [34] extracted diesel fuel and TPHs from soils using SFE. Spiked soils (mainly clay and other soil types) were used. Combinations of static and dynamic modes (or pseudo-dynamic mode) without using a modifier were applied in the SFE procedure. They studied the effect of pressure from 15 MPa to 35 MPa at temperatures of 40 and 80 °C. When temperature changed from 40 °C to 80 °C, pressure should be increased from 17.5 MPa to 36.5 MPa to keep the density constant (at 0.8 g/ml). Also, the increase of temperature from 40 °C to 80 °C at 15.2 MPa resulted in hydrocarbons with a higher molecular mass to be extracted more effectively than those with a lower molecular mass while density decreased [34]. In another study by Morselli et al. (1999) [42], SCF with addition of acetone as a modifier was used to remove saturated and aromatic fractions of crude oil from a spiked sandy clay loam. SFE was conducted in combination of static and dynamic modes. Other experimental conditions were pressure of 22.7 MPa, temperature of 80 °C, 5% (v/v) acetone addition and pure CO_2 density of 0.65 g/ml which resulted in 70-100% recovery of PHCs. Adding modifier at 5% increased the recovery of aromatic fractions, while 10% concentration of modifier decreased removal of both saturated and aromatic fractions [42]. Firus et al. (1997) [43] extracted diesel fuel and PHCs from two types of soil. The first soil was a field-contaminated clayey loam, which was weathered for 20 years. The second one was loamy sand spiked by diesel fuel with ratios of 5 wt% and 10 wt%. Only dynamic-mode was done in SFE without the use of a modifier. Temperatures changed from 50 to 100 °C at 20 MPa. The efficiency was 21% for the weathered contaminated soil and 95% for the spiked soil [43].

2.8.2 SFE of polycyclic aromatic hydrocarbons (PAHs)

PAHs can be seen in the form of fused aromatic rings extensively and they exist in diversified values of molecular weights and boiling points that are common in soil. Incomplete burning of fuels leads to PAHs creation, which could result in contamination of soil either through release of wastes of industries or petroleum spills. Since PAHs cannot be dissolved highly and they have low vapor pressures, they are adsorbed and deposited when they are in contact with soil [4].

Removal of PAHs from polluted soil containing great amount of humic substances via SFE is not easily feasible. In order to yield higher removal percentages, some organic solvents in small percentages are added to SCF [44]. The effects of addition of co-solvents to SCFs to remove PAHs from real soil samples were investigated by Lutermann et al. (1998) [44,45] and Hollender et al. (1997) [46]. When co-solvents with higher concentrations and reduced polarity were applied, greater recoveries of PAHs (especially high molecular weight PAHs) were obtained. They also applied SFE without addition of a co-solvent and they observed opposite effects. Extraction of PAHs from a soil with high contents of humic acids was enhanced noticeably when co-solvents were used. 10 mol.% of methanol was added to SCF and led to higher extractions of PAHs from a soil [44–46]. Interactions between contaminants and soils including van der Waals forces, electron donor–electron acceptor interactions and hydrogen bonding are broken due to application of co-solvents which have various physical and chemical characteristics [46]. Extraction of PAHs from soil samples using SFE in a two-stage process were conducted by Lojkova et al. (2005) [47]. The first stage is SFE with static mode and the second stage is SFE with solvent trapping. The efficiency of the combined process was compared to SFE and to soxhlet extraction. The SFE yielded 220-300% of naphthalene, 180-240% of acenaphtylene, and 120-150% of acenaphthene of that attained by soxhlet extraction, which confirms that the combined procedure yielded higher efficiencies [47].

2.9 SFE of inorganic compounds (metals, lanthanides and actinides)

SFE is considered as a potentially viable technique among the existing techniques to extract heavy metals from various matrices such as soils [4]. Due to non-polar nature of SC-CO_2 and consequently weak interactions between solvent-solute with charged species [48], the extraction of these materials from soils using SFE was not considered feasible before [13]. For metals removal (including lanthanides and actinides) from soils via SFE, the addition of an appropriate complexing or chelating agent either to the soil or to the SCF (SC-CO_2) is employed. Then, reactions between chelating agents and metals occur that change charged metal ions to a neutral complex or chelate which is soluble in SCF [17,49]. The factors that affect removal of these charged species from soils using SFE are properties of chelating agents, metal chelate dissolution, quantity of chelating agents, soil properties (including pH, moisture content and soil type), temperature, pressure, duration of extraction, and chemical forms of the metal compounds available in the soil [4,36]. Therefore, the choice of appropriate chelating agents plays an important role. The good properties of chelating agents include metal complexes show high stability, chelating agents and their metal complexes can be dissolved easily in SCF, chelation kinetics are quick, and feasibility of selective removal of a metal ion (or some metal ions). The chemical nature of complexes affects the solubilities of metal complexes in SCF remarkably [4]. The quantity of chelating agent should be enough that can contain the sample and complex the metal species existing in the sample [50]. However, the amount of heavy metals existing in the real samples is usually low and it might not be possible to access the environmental sample easily. Considering temperature and pressure, they have contrasting effects and it should be considered for optimization of the extraction. In fact, raising the temperature (while pressure is constant) results in increase in solute's vapor pressure; however, it leads to reduction in the density of SCF slowly [4].

Extraction of metals using SFE mixed with an appropriate chelating agent was presented by Wai et al. (1993) [51] and Liu et al. (1993) [52] SC-CO_2 including the fluorinated ligand lithium bis (trifluoroethyl) dithiocarbamate (LiFDDC) applied to remove Cu^{2+}, CO^{2+}, Cd^{2+}, Zu^{2+}, and Hg^{2+}. Interactions between negatively charged ligand ($FDDC^{-}$) and metal ions lead to create metal chelates which are neutral and can be dissolved into SC-CO_2. The chelation-SFE which is in-situ method can be applied in environmental problems; however, its accomplishment is controlled by efficiency of the ligand binding and dissolution of the ligand-metal compound [51–53]. Lin et al. (1993 and 1994) [54,55] used chelating agents including various fluorinated β-diketones added to CO_2 for extraction lanthanides and actinides [54,55].

2.10 Factors affecting the SFE process

Based on the information presented in the previous section, it is apparent that the factors that could have an effect on performance of SCE are numerous such as fluid and solid properties, thermodynamic and kinetic parameters (temperature, pressure, density, and flow rate), moisture content and characteristics of substance to be dissolved. It would be beneficial to optimize these parameters that lead to an effective and productive extraction process. However, in general it may not be possible to define a singular plan for optimization; specifically, it would be less applicable for treatment plants on large scale [11].

2.10.1 Temperature and pressure

Pressure and temperature are the most important factors when it comes to the supercritical state and the efficiency of SCE process, both in terms of theory and application, in the extraction. Through changing pressure and temperature (which affects solvent power), it could be possible to control the extraction of a substance from a matrix [10,16,17].

Both density and solvent capacity increase by increasing pressure and drop by increasing temperature. Based on the type of compounds to be removed, these parameters (pressure and temperature) are selected [29]. The density of a fluid is affected by both these factors (i.e. pressure and temperature). Reaching a high pressure at a temperature neighbouring the critical temperature results in the highest density of a fluid that can be achieved. In other words, the highest solubility is attained when SCF density is maximum at a fixed temperature. In fact, the volatility of a material and the solvation strength of SCF control the dissolution of a material into a SCF [56]. This implies that for substances that have a high vapor pressure, the dissolution can be increased noticeably by increasing temperature while pressure remains unchanged. On the other hand, raising temperature can lead to a reduction in solubility for compounds having insufficient vapor pressures because the density is reduced [57].

Hawthorne and Miller (1994) [58] extracted chlorophenols, S- and N-heterocycles, and pesticides from soil, and PAHs from soil and soot by SFE and soxhlet extraction. SC-CO_2 at 40.5 MPa pressure and 50 °C temperature resulted in much lower removal than soxhlet extraction. SFE at 40.5 MPa pressure and 200 °C temperature in 30 min showed comparable removal with soxhlet extraction in 18 hours. Additional increases in temperature up to 350 °C did not change recoveries noticeably, which may be because of some of the analytes were degraded at that temperature level. They deduced if there are strong interactions between contaminants and the matrix; temperature had more significant effects on reaching higher removal percentages than pressure. Also, they concluded increasing temperature could be applied instead of using modifiers to improve extraction [58]. Considering most SFE apparatus work with temperatures less than 150 °C, utilization of a higher temperature may not be feasible. Nevertheless, a temperature no greater than 150 °C can be efficient for extraction [18].

In general, the effect of raising temperature in achieving high recoveries has not been explained well. But it may happen because of two phenomena: First, the kinetics of desorption mechanism can likely increase by raising temperature [21,58,59], and consequently results in greater recovery for substances that are desorbed. Second, the solubility can be highly increased by increase in temperature for substances that have high vapor pressures while density drops by increase in temperature at fixed pressure. In order to specify what exactly is happening in the process, more research should be conducted [18].

Another study exhibited the dissolution capacity and extraction recoveries were mainly affected by pressure. Density of SCF at specific pressure and temperature values commonly define the solvent power or dissolution capacity [29]. Dependency of density on pressure at different temperatures is presented in Figure 2.2 [7].

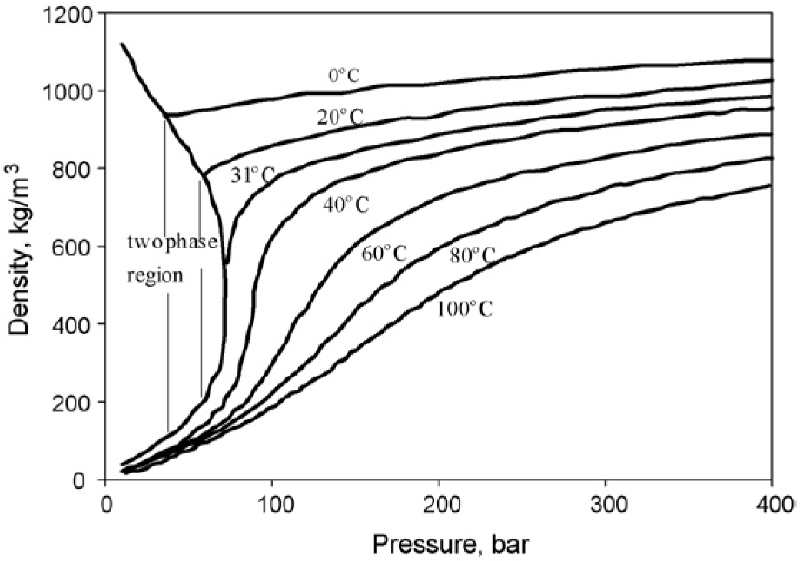


Figure 2.2. Density behavior of CO_2 calculated by equation of Bender [7]

2.10.2 Water content

Water usually exists in different amounts in environmental samples such as soil. The water available in the soil sample may freeze in the restrictor tip of the SFE apparatus because of the Joule-Thomson cooling effect of the expanding CO_2 at the restrictor outlet. Therefore, if the water content is too high, an issue that has been observed is that of restrictor plugging due to frozen water, which consequently influences the SFE operation and the removal efficiency. Adding a drying agent to the sample can be used as a good technique to prevent restrictor plugging, although this might result in selectively retaining some analytes. Burford et al. [60] showed that adding drying agents to dry samples (petroleum waste sludge) could retain phenols and anilines, while adding drying agents to wet samples did not retain any analytes. They suggested that drying agents can be added at the outlet end of the extraction vessel instead of mixing with the sample. This solution allowed volatile analytes to be efficiently extracted while preventing restrictor plugging [60].

The presence of low water content (e.g., 1 or 2%) is helpful by making clay surfaces wet [61] or covering areas of entrapment (or adsorption sites). If the water content is higher, this may affect the recovery [18]. For instance, Hawthorne et al. (1992) [31] showed the efficiency of SFE of PAHs from a waste sludge increased when water content was reduced by drying the sample [31]. Snyder et al. (1993) [62] confirmed the same effect when water content was increased and caused recovery of organophosphate and organochlorine pesticides from soil to drop [62]. Lee and Peart (1994) [63] compared extraction efficiencies of samples which were dried completely and samples with a low water content (5%), which showed that dry samples resulted in lower extraction efficiencies. Extraction of PCBs and chlorinated benzenes from dry sediments was low, however, raising water content (from 11 to 50 wt.%) did not result in a reduction in the extraction percentage [63].

2.10.3 Characteristics of the soil

Characteristics of soil that can influence the extraction are the soil type (i.e. sand, silt and clay quantities that form the soil), particle size, shape, surface area, porosity, organic matter content and soil moisture content [16,64–67]. Although some scientists expressed that the effect of soil type could not be determined properly due to complicated interactions between soil and pollutants, soil type affects the extraction efficiency for treatment of soil [36]. If there are special interactions between solutes and matrix active surfaces, it will affect the extraction process noticeably [67]. As an example, pollutants that are attached to organic substances of soil have different interactions than those pollutants attached to inorganic substances; this may lead to a different extraction recovery. In addition, some obstructions can prevent the extraction of contaminants including contaminants are located in interstitial micropores in the soil particles or between clay plates, contaminants are masked by the bulk organic material, or contaminants are covered with water [20].

In general, removal of substances by SFE process from solid matrices (specifically from porous materials like soil) can be assumed to involve the following phases: (1) penetration of SCF into pores of substances (2) dissolution of analytes into supercritical matrix (3) distribution of compound of solute and supercritical matrix to solid interface, and (4) diffusion of compound to bulk SCF. Therefore, solid matrix properties such as pore size and connectivity are critical since SCF needs to be distributed in the solid matrix during SCE. Particle size in the solid matrix (specifically porous materials like soil) influences the SCE of contaminants because of changing the diffusion path [4]. Sample size is one of the characteristics of the solid matrix that would affect the SCE as well. There are some factors that should be considered to determine the sample size required for extraction including the detection limit of the analytical method and the size of the extraction vessel [68,69]. Soil samples required for performing SFE on the laboratory scale are commonly small (around 10 grams), however, larger extraction vessels are also available [18].

SFE recovery can be affected by the clay type (swelling vs. non-swelling) if water exists [18]. Swelling in clay may cause some contaminants to become more accessible and therefore could be easily extracted by SCF [3]. Chen et al. (1997) [70] studied PCBs removal from contaminated soils and sediments by SFE. They investigated three soil types including sand, till and clay. Sand and clay had the lowest and the highest percentages of clay, respectively. In addition, total organic carbon (TOC), which is related to organic matter content, was the lowest for sand and the highest for clay. Till was composed of 81.2% sand, 12.5% silt and 6.3% clay. Till had the clay percentage and TOC quantities between those of sand and clay. According to the obtained results, sand had the quickest PCBs removal among these three soil types. They also compared PCBs removal for air-dried clay and till samples. The desorption of PCBs in clay was lower than till since clay had higher clay and higher organic matter contents. Higher organic matter and clay contents led to a decrease of PCBs extraction. Therefore, they concluded that extraction of pollutants from soils that had lower percentages of clays was easier than those soils having higher amounts of clays; i.e. SFE of clay soil is more difficult than sandy soil [70]. Also, higher organic contents in soil lead to lower recovery compared to soils contain lower organic matter [70,71].

Chen et al. (1997) [70] also compared PCBs removal from real field contaminated samples and spiked samples. Spiked samples showed greater and faster extraction than real field contaminated samples. Their results indicated that PCBs were bound stronger to real field contaminated samples than spiked samples. Therefore, the removal of pollutants from real field contaminated soils was more difficult than spiked soils [70].

2.10.4 Flow rate of SCF

A significant factor, especially in dynamic-mode of extraction, is flow rate of CO_2. Generally, if CO_2 flow rate is low, it results in slower velocity of fluid that has more possibility to diffuse into internal solid structure causing higher extraction efficiency [4]. Considering flow of SCF, it should be enough to sweep the empty spaces of the vessel that affects extraction efficiency. In order to sweep the empty spaces of the vessel adequately, at least 4-5 vessel volumes should be applied. It should be mentioned sweeping the sample volume several times does not necessarily lead to a higher recovery since the total recovery in most cases is limited by the kinetics of the extraction (not the elution) [21,56,59,72]. Actually, one easy method to find out what process controls the extraction is altering the flow rate and finding out if the recovery would change or not accordingly [20].

Principally, two processes that control the extraction efficiency are kinetics, which is related to desorption process, and thermodynamics (or chromatographic retention), which is related to dissolution of analytes [11,20]. The total percentage of extraction is controlled by the slowest factor [11,29]. Chromatographic retention (i.e. solubility process) controls the extraction, if the recovery varies by changing the flow rate correspondingly [11,18,29]. For these situations, any actions such as raising flow rate and/or altering other extraction parameters that leads to enhance the dissolution would increase the recovery as well. In fact, recovery corresponds to flow rate of extraction. In these cases, if smaller sample size is applied, faster recovery would be achieved. Also, static extraction would not work as efficiently as dynamic extraction, because less amount of fluid covers the sample [18]. Therefore, dynamic extraction would be more appropriate to be applied in this condition [11]. In contrast, for some samples (might have lower concentration of contamination), flow rate of extraction does not affect the recovery and the extraction is limited by the kinetics of desorption. In this case, percentage of extraction is approximately alike for large and small samples, provided the empty spaces are swept adequately [72,73]. In addition, efficiency of static extraction would be closely similar to the dynamic extraction with the same duration and either mode (static/dynamic) can be applied evenly [11,72,73].

2.10.5 Addition of modifiers

Based on the properties of the matrix and analytes, suitable modifiers are chosen and no specific plan exists for the selection of a modifier. Extraction of some solutes increases by the addition of low percentages of a co-solvent (less than %15). The polarity of a co-solvent plays a significant role for extraction [11].

Yang et al. (1995) [74] extracted PAHs from three samples (marine sediment, diesel soot, and air particulate matter) using SFE with pure CO_2 and CO_2 modified with MeOH, diethylamine, or toluene and their results showed sample matrix and modifier character control the effects of modifier. Using organic modifiers and raising temperature at the same time can result in high extraction efficiencies; however, their combined effect in the recovery has been studied to less extent [18]. As an example, the combined effect of temperature and modifier on the PAHs removal from various substances was investigated by Yang et al. (1995) [74] that indicated there was no relationship between temperature and sample matrix. Considering the addition of modifiers, however, it significantly depends on the matrix. According to the results observed, the effect of modifiers at high temperature leads to higher extraction efficiency showing the combined effects are cumulative which is helpful for tough matrices [74]. Hawthorne et al. (1992) [31] studied removal of PCBs from sediment and PAHs from a petroleum waste sludge and railroad bed soil and effect of various modifiers examined. Regarding the extraction of PCBs from sediment samples, the lower extraction recovery (an average of 62% recovery) was related to supercritical extraction with CO_2 alone and higher extraction recovery was obtained using modified CO_2 with methanol (an average of 90% recovery) [31]. In another study by Hartonen et al. (1997) [75] removal of chlorinated and brominated organic contaminants from nine sediments using consecutive extractions indicate presence of modifier enhances the recovery and sample matrix affects the efficiency of modifier according to various recoveries achieved for different sediments [75]. Remediation of PCB contaminated sediments by SFE with various combinations of CO_2 with modifiers conducted by Langenfeld et al. (1994) [33]. It was indicated the effect of modifier nature on increasing the recovery was higher than the concentration of modifier. Generally, raising modifier concentration from 1 to 10 vol. % does not highly change the extraction percentage of PCB and PAH [33].

2.11 Solubility studies of compounds in SCFs

One of the many factors involved in SFE is the solubility of a target contaminant in SCF [4]. Performing studies about the solubility is very useful in determining how much pollutants have potential to be removed (capacity) and under what conditions the extraction system can be optimized (selectivity). If there are enough solubility data available at different temperatures and pressures, models could be developed to anticipate the solubility at any situations [11,36]. The dissolution of solute in a SCF is controlled by various parameters such as the thermodynamic and structural properties of the solute and SCF including the solute's vapor pressure, polarity, critical pressure and temperature values, solute-solvent and solute-solute interactions [4,11,76]. Solute's vapor pressure and SCF density are regarded as the major parameters that have high effects on the solubility [11].

The changes in solubility caused by temperature depend on the solute's vapor pressure, fluid density and molecular interactions in the supercritical state [76]. When the pressure is low (close to the critical pressure), rise in temperature leads to reduction in solubility owing to lower density of SCF. In fact, a small rise in temperature leads to a large reduction in SCF density, when it does not increase solute volatility very high that cannot make up for a high decrease in density. Therefore, the final outcome results in reduction in solubility due to increase in temperature. On the other hand, at condition where pressure is high (pressure is greater enough than the critical pressure), a rise in temperature leads to an increase in solubility of solute since temperature does not affect the density of SCF considerably. In this situation, a rise in temperature leads to a small reduction in SCF density, when it increases solute volatility that makes it the controlling factor. Therefore, the final outcome results in increase in solubility due to increase in temperature [36,77]. Use of modifiers enhances the solubility of SCF. In fact, interactions between modifiers and the intended solute are formed by hydrogen bonding, acid-base interactions or dipole-dipole interactions [36].

The challenging effects between factors such as density of SCF and solute volatility are related to "crossover pressure". As a matter of fact, if pressure is below the crossover pressure, rise in temperature leads to reduction in solubility. When pressure is above the crossover pressure, rise in temperature leads to rise in solubility. Crossover pressure has been discovered by several researchers who investigated the dissolution of hydrocarbons in SCFs. For example, Reverchon et al. (1993) [78] defined a crossover pressure around 11 MPa for the solubility of solid octacosane ($C_{28}H_{58}$) in supercritical CO_2 which is shown in Figure 2.3 [77,78].

Some correlations such as empirical and fundamental-basis ones used to predict the solubility. However, they mainly require experimental values to define several parameters. Therefore, enough data at various density, temperature and pressure values should exist [4]. On the other hand, collections of experimental data are costly, time-consuming and hard to be trustworthy. Therefore, some models are proposed according to existing data in the literature to predict the solubility at any situation. These models usually use on following approaches: (1) an equation of state (EOS) (2) semi empirical approach (3) a density-based approach (4) a solubility parameter approach [79,80]. In general, in order to collect enough solubility data of different substances, some methods are proposed which are static and dynamic methods [14]. The quasi-static is a later method which is placed between the static and dynamic methods [81]. Thermodynamic equilibrium of the solute–SCF–matrix is not highly affected by low amounts of SCF flow rate, but more information about solubility data in a short period of time can be obtained at this condition. Although, some empirical correlations based on experimental results have been used for solute solubilities, but development of models are requested, since they are more precise [11].

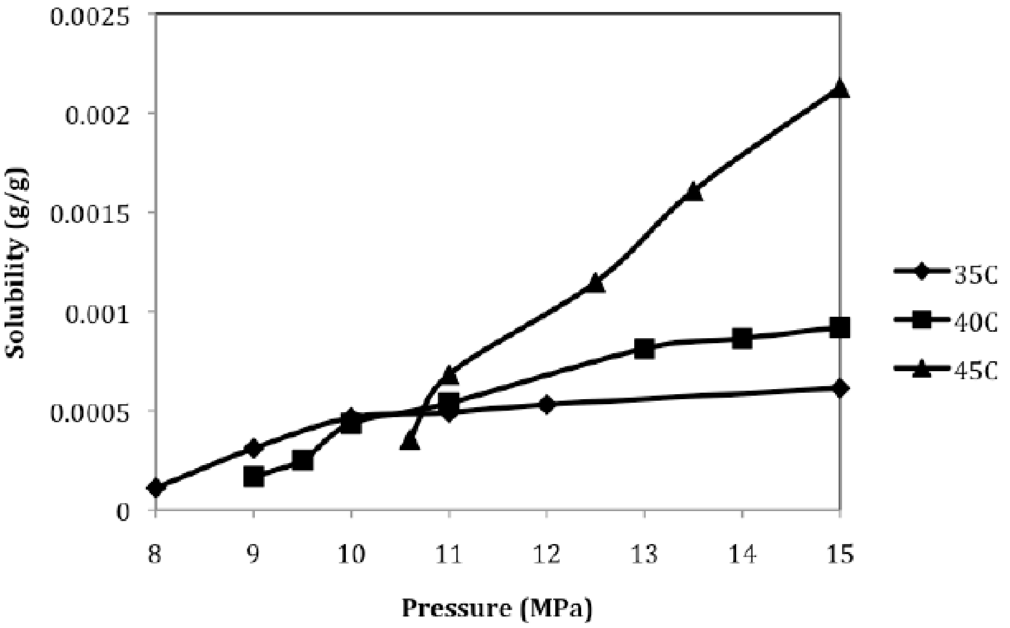


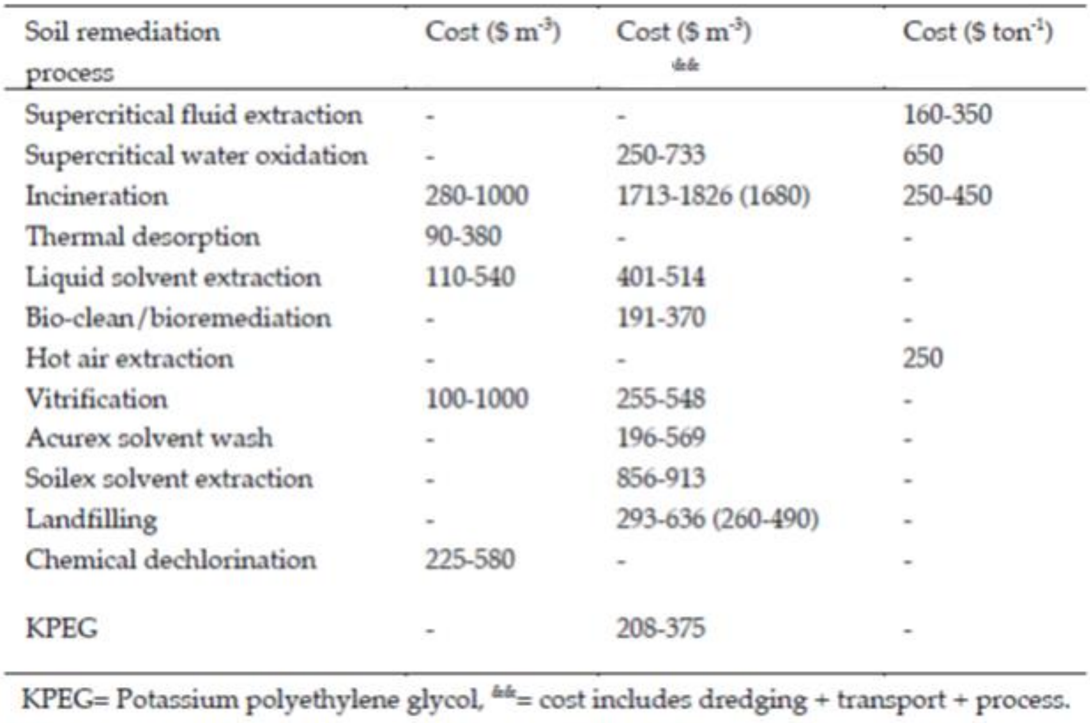
Figure 2.3. Example of crossover pressure for solubility of octacosane in supercritical CO_2 [77]

2.12 Cost analysis

Saldana et al. (2005) [36] presented cost analyses for extraction of different pollutants from soil by semi-continuous SFE pilot-scale systems using CO_2 as solvent. The pollutants included PCBs, naphthalene, 1,2,4-trimethylbenzene, phenanthrene, hexachlorobenzene and pentachlorophenol. According to the information presented, the cost of SFE can vary from \$64 m^{-3} to \$318 m^{-3} (with CO_2 recycle) or \$567 m^{-3} (without CO_2 recycle). The parameters considered for the estimations of costs are: (1) excavation of the polluted soil, (2) move of the excavated materials to the reactor, and (3) costs required to run the SFE system [36]. Among the cost analyses done, the majority of them pointed out the greatest part of costs are related to the cost of SFE operation [82,83], while two cases stated the main part is the cost of excavation and movement of wastes [84,85].

Comparison of SFE with other soil remediation techniques, which is presented in Table 2.2, shows SFE is fairly comparable to other techniques including incineration, thermal desorption, bioremediation and liquid solvent extraction [36].

Table 2.2. Economic analysis comparison of SFE to other soil remediation processes [36]



Soil remediation process	Cost ($\$ m^{-3}$)	Cost ($\$ m^{-3}$) $^{\&\&}$	Cost ($\$ ton^{-1}$)
Supercritical fluid extraction	-	-	160-350
Supercritical water oxidation	-	250-733	650
Incineration	280-1000	1713-1826 (1680)	250-450
Thermal desorption	90-380	-	-
Liquid solvent extraction	110-540	401-514	-
Bio-clean/bioremediation	-	191-370	-
Hot air extraction	-	-	250
Vitrification	100-1000	255-548	-
Acurex solvent wash	-	196-569	-
Soilex solvent extraction	-	856-913	-
Landfilling	-	293-636 (260-490)	-
Chemical dechlorination	225-580	-	-
KPEG	-	208-375	-

KPEG= Potassium polyethylene glycol, $^{\&\&}$= cost includes dredging + transport + process.

Although SFE has the ability to treat the polluted soils quickly with high recovery percentages, more pilot-scale and full-scale SFE works need to be performed to provide significant information that are helpful in economic analysis of the SFE system. Despite the cost of SFE is not low, it would be reduced by advancement of the SFE system to a larger scale and its utilization in industry. Having enough information about pilot- or full-scale SFE system may imply SFE is comparable to other treatment techniques from economic viewpoints [36].

2.13 Summary

In order to choose a suitable soil treatment method, some factors including cost, the duration of treatment (slow vs. quick), the size of equipment and social acceptance (cleaner technologies which have less negative impacts on the environment are requested) are considered [11]. SFE is a practical choice that can be applied for the treatment of soils, sludges and sediments polluted with non-volatile heavy mixtures including PAHs, PCBs, pesticides, and dioxins [10]. SFE has been developed noticeably owing to the need for a quick and selective extraction that also uses lower amounts of solvents. Advancements of this process have led SFE to be applied for the extraction of more types of contaminants and soils. While SFE is mainly applied for the extraction of fairly non-polar compounds, polar compounds (and also metals) can be treated by the addition of modifiers, derivatizing reagents and chelating reagents that shows the broad area of the SFE usage [18]. Although valuable improvements of SFE performed for treatment of many mixtures, commercial application of SFE still lags behind [4]. In order for SFE to compete with other treatment technologies, associated costs should be decreased; that may be possible through more advancement of SFE at a large-scale and more investigation of a continuous SFE system for treatment [36].

Although there is information reported in the literature for remediation by SFE, some information is contradictory, and some findings are reported for specific types of soil and contamination. Thus, there is a lack of information on the systematic analysis of SFE operational parameters which are supported by statistical analysis.

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Chapter 3: Optimization of Operational Parameters of Supercritical Fluid Extraction for PHCs Removal from a Contaminated Sand using Response Surface Methodology

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Abstract

Supercritical fluid extraction (SFE) was applied to investigate the removal of petroleum hydrocarbons (PHCs) from a contaminated soil. The sand spiked with diesel fuel with a ratio of 5 wt% was used for this study. The effects of SFE operational parameters including fluid pressure, fluid temperature, time duration and mode of extraction on the removal efficiency of PHCs were investigated. SFE experiments were performed at different levels of pressure (15, 33 and 50 MPa) and temperature (30, 75 and 120 °C). Static mode alone and combination modes at various time duration were performed. Among them, the combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles for a total time of 60 min resulted in the highest PHCs removal percentages. In addition, factorial design and response surface methodology (RSM) were applied to optimize the effect of pressure and temperature. According to RSM, the optimum pressure and temperature were found to be 50 MPa and 69.3 °C, respectively. The optimum combination of pressure and temperature based on experimental results was determined to be at 33 MPa and 75 °C; which resulted in 99.2%, 91.7% and 86.1% removal for PHC F2, F3 and F4 fractions, respectively. Increasing pressure at constant temperature resulted in higher PHC removal percentages, however, increasing temperature at constant pressure did not necessarily lead to higher PHC removal percentages and there was an optimum range for temperature.

Keywords: petroleum hydrocarbon; supercritical fluid extraction; contaminated soil; sand; response surface methodology; optimization

3.1Introduction

Many contaminated sites and brownfields exist in different countries around the world. These contaminated sites are polluted with various materials including petroleum products, organic compounds, metals and radioactive elements which can cause problems to human health and the environment when entering the human food chain, groundwater and surface water resources, or air [1]. In Canada, about 60% of contaminated sites involve petroleum hydrocarbon (PHC) contamination accounting for multibillions of dollars in environmental liabilities and remediation costs [2,3]. Generally, treatment methods for polluted soils are restricted due to costs, time and efficiencies [4,5]. Extraction of contaminants from soil and sediment can be carried out through treatment technologies such as incineration, thermal desorption, solvent extraction, chemical remediation, and bioremediation [4,6]. Supercritical extraction (SCE) is considered as a solvent extraction method in the class of physical/chemical treatment technologies [7,8]. There is limited literature on economic feasibility of SFE at large scale. A previous study reported that SFE was economically competitive compared to other soil treatment techniques including incineration, thermal desorption, bioremediation and liquid solvent extraction. It also reported that the cost of the SFE unit was 53%-68% of the total treatment cost [4]. Favorable and flexible characteristics of SCFs such as density (liquid-like), viscosity (gas-like) and also their high diffusion property make supercritical fluid extraction (SFE) a potentially viable option as a solvent extraction treatment [8–10]. In addition, having zero surface tension allows SCFs to readily move into various matrices [7–9,11,12]. Other advantages of SFE compared to conventional solvent extraction methods include extraction selectivity of the target contaminant from the soil matrix, low solvent requirement and consequently less waste products [4,9] and no detrimental effects on the soil fabric [13,14]. The most commonly used fluid (about 90% of all analytical SFE applications) is carbon dioxide (CO_2) [15]. This is due to favourable CO_2 characteristics: non-poisonous, non-flammable (or non-explosive), chemically inactive, and having fairly low critical points (31 °C and 7.4 MPa). Since CO_2 is a non-polar solvent, it works efficiently for non-polar organic compounds such as hydrocarbons and is suitable for lipophilic compounds as well [15–20].

Pressure and temperature are the most important factors when it comes to supercritical state and the efficiency of SCE process. By changing pressure and temperature, it is possible to control the extraction of a substance from a matrix [7,21,22]. Increasing pressure at a temperature neighbouring the critical temperature results in a significant increase in density of SCF [23]. Both density and solvent capacity increase by increasing pressure and drop by increasing temperature. However, the increase of temperature can lead to an increase in the vapor pressure of the target compounds to be extracted, and consequently increases the transport of these target compounds in the fluid phase [18]. In fact, the volatility of the target compound and the solvation strength of SCF control the dissolution of a material into a SCF [23]. On the one hand, this implies that for substances having high vapor pressure, the dissolution can be increased noticeably by increasing temperature while pressure remains unchanged. On the other hand, raising temperature can lead to a reduction of solubility for compounds having insufficient vapor pressures since the density is reduced [10,24]. Therefore, the optimum range of pressure and temperature depends on the type of target compounds [18].

Hawthorne and Miller [25] extracted chlorophenols, S- and N-heterocycles, and pesticides from soil, and polycyclic aromatic hydrocarbons (PAHs) from soil and soot by SFE and soxhlet extraction. Supercritical carbon dioxide (SC-CO_2) at 40.5 MPa pressure and 50 °C temperature resulted in much lower percentages of extraction than soxhlet extraction. However, SFE at 40.5 MPa pressure and 200 °C temperature in 30 min showed comparable removal percentages with soxhlet extraction operated for 18 hours. Additional increase in temperature up to 350 °C did not change recoveries noticeably. They deduced that if there were strong interactions between contaminants and the matrix, temperature would have more significant effects on reaching higher removal percentages than pressure. Also, they concluded that increasing temperature could be applied instead of using modifiers to improve extraction efficiency [25]. Considering practical feasibility and operational costs, SFE technology seems to be a potentially viable option for temperatures less than 150 °C [15]. Low and Duffy [26] extracted diesel fuel and total petroleum hydrocarbons (TPHs) from soils using SFE. Spiked soils were treated with combinations of static and dynamic modes without using any modifier. They studied the effect of pressure (in the range of 10.1 to 36.5 MPa) and temperature (two values of 40 and 80 °C). When temperature was increased from 40 °C to 80 °C, pressure was required to increase from 17.5 MPa to 36.5 MPa to keep the density of SC-CO_2 constant (at 0.8 g/ml). Also, the increase of temperature from 40 °C to 80 °C at 15.2 MPa resulted in hydrocarbons with a higher molecular mass to be extracted more effectively than those hydrocarbons with a lower molecular mass while density decreased [26]. Firus et al. [27] extracted diesel fuel and PHCs from a field-contaminated clayey loam and a loamy sand spiked with diesel fuel. Only dynamic-mode was applied in SFE without the use of any modifier. Temperatures of 50, 80 and 100 °C at 20 MPa pressure were investigated. The efficiency was 21% for the field-contaminated soil and 95% for the spiked soil [27]. Hawthorne et al. [28] investigated the extraction of polychlorinated biphenyls (PCBs) from a sediment, PAHs from a petroleum waste sludge and PAHs from railroad bed soil by SFE using different SCFs including $CHClF_2$, N_2O and CO_2. Increasing the temperature of CO_2 extraction from 50 °C to 100 °C at constant pressure of 40.5 MPa led to an increase in the extraction of PAHs from railroad bed soil, especially for the most volatile PAH (i.e. phenanthrene) [28].

SFE is a relatively newer technology compared to most conventional soil remediation technologies and as such has not been as thoroughly studied as other soil treatment methods. There is a need to study the effect of pressure and temperature and their optimum range under different conditions for SCE of different types of contaminants. In addition, there is limited literature on the impact of these operational parameters on the removal efficiency of PHC fractions. Considering above, the main objective of this study is the systematic assessment of the application of SFE for treatment of petroleum contaminated sand using statistical analysis and response surface methodology (RSM). The specific objectives are: the investigation of the effect of operational parameters for SCE including pressure, temperature and time duration; the effect of static and dynamic modes of operation on the extraction of PHCs; and to apply a factorial experimental design and RSM to optimize the effect of pressure and temperature.

3.2 Materials and methods

Figure 3.1 presents the general experimental procedure and steps that were followed in this study. After preparation of the spiked soil samples, the initial concentrations of PHCs were measured. Then, a soil sample was taken to conduct the SFE test. After the SFE test was finished, the final concentrations of PHCs were measured. The initial and final PHCs measurements were used to calculate the PHCs removal percentages. Four consecutive steps were used for PHCs measurement including ultrasonic extraction, silica gel column cleanup, Kuderna-Danish (K-D) concentration and gas chromatography (GC) analysis. These steps are explained in more details in a later section.

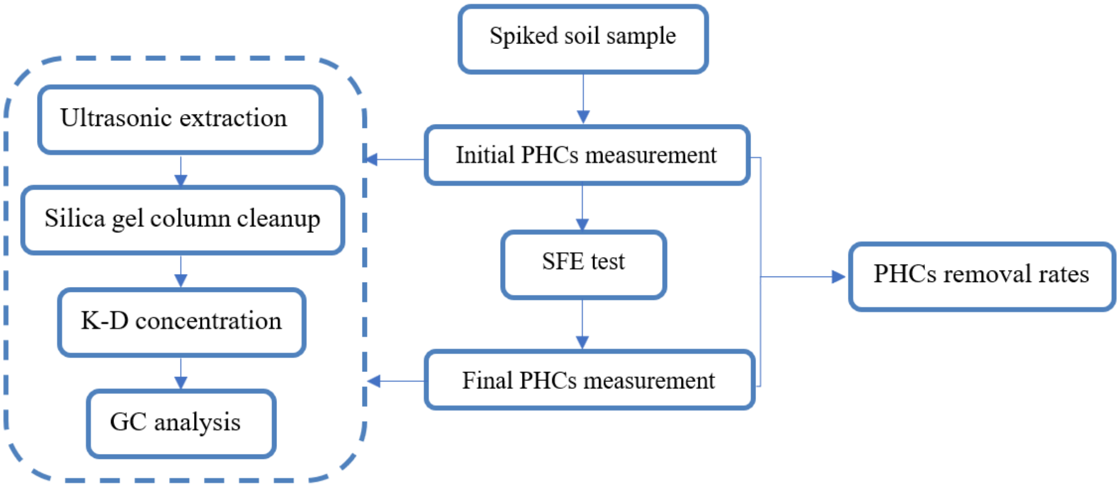


Figure 3.1. Flowchart of the experimental procedure [29]

3.2.1 Soil samples

The soil used for these experiments was a poorly graded sand (classified as SP according to the unified soil classification system), which had 99.9% sand and 0.1% fine particles (silt and clay). This sand, which comprised silica sand with quartz minerals, was purchased from a Canadian company offering geotechnical laboratory supplies. The sand was classified as medium size sand that had particle sizes mostly in the range between 0.425 mm and 2 mm. The soil was spiked with diesel fuel with a ratio of 5 wt%. The soil was dried at the start and had a moisture content of 0.28% ± 0.05%. Diesel fuel which was used for spiking soil samples was obtained from a gas station. The required amounts of soil and diesel fuel based on 5 wt% were mixed thoroughly to achieve a homogenous state. The spiked soil samples were then placed in amber color glass jars with Teflon-lined caps to minimize any potential degradation due to light. All prepared soil samples were stored in a refrigerator for one month at a temperature of 4 °C ± 0.5 °C until used for experiments. The initial concentrations of PHCs were measured after one month of storage time.

3.2.2. PHCs measurement

PHC F2, F3 and F4 fractions were analyzed according to Canada-Wide Standard requirements. The concentrations of the PHCs fractions were compared with regulatory standards to check if the soil met the acceptable criteria for different applications [30]. Based on designated ranges of equivalent carbon number, PHCs fractions are defined as: PHC F2 ($>nC_{10}$ to nC_{16}), PHC F3 ($>nC_{16}$ to nC_{34}) and PHC F4 ($>nC_{34}$ to nC_{50+}) [31]. Prior to and following SFE tests, the concentration of PHC F2, F3 and F4 fractions in a soil were measured by conducting four consecutive steps (ultrasonic extraction, silica gel column cleanup, K-D concentration and GC analysis) as explained in the following sections. For quality control, several spiked soil samples (before and after the SFE test) were also sent to an external accredited laboratory to analyze PHCs measurement. The differences of the concentrations of PHC fractions between the external laboratory and this study were less than 10%; which shows the accuracy of analytical methods adopted in this study.

3.2.2.1 Ultrasonic extraction

Ultrasonic extraction can be used to extract non-volatile and semi-volatile organic compounds from soils [32]. Ultrasonic irradiation produces oscillating cavitation bubbles and shockwaves that can break the soil particle aggregates and enhance separation of target contaminants from the soil surface; and can consequently reach the inner space of the soil structure. As a result, the separation of contaminants such as PHCs which are attached to soil particles is feasible by ultrasonic extraction [33]. Method 3550C of US EPA (United States Environmental Protection Agency) [32] for medium/high concentration organic contaminants (expected to have concentrations greater than 20 mg/kg) was adopted for this study.

According to method 3550C of US EPA for medium/high concentration process, a 1/8-inch tapered microtip, which was supplied from “Crystal Electronics Inc.”, was connected to the bottom of a 1/2-inch horn [32]. The digital sonifier model by “Branson Ultrasonics Corporation” with 450 watts power supply was used in this research. The soil was thoroughly mixed to form a homogenous sample. Approximately 2 g of soil was taken and placed in a 20-mL glass vial. To prevent any cross-contamination, the vial’s cap (e.g. PTFE-lined screw caps) should be put on. Anhydrous sodium sulfate (granular), Na_2SO_4, was heated at 400 °C for 4 hours in the furnace to be purified prior to use. Anhydrous sodium sulfate (about 2 g) was added to soil samples which were wet (gummy) and did not have a free-flowing texture. The final volume of mixture of was brought to 10 mL by addition of a sufficient volume of solvent (acetone and hexanes with a ratio of 1:1) [32]. Acetone (C_3H_6O) and hexanes (C_6H_{14}) were purchased from “Fisher Scientific” at HPLC-grade and also met the ACS (American Chemical Society) specifications. Ultrasonic extraction was then performed. A set of preliminary tests was conducted to determine the optimum conditions for ultrasonic extraction [29]. Considering the above settings, the output power applied to soil samples was approximately 45 watts. After completion of sonication, the sample was kept in a refrigerator until it was used in the next step.

3.2.2.2 Silica gel column cleanup

If present in a sample, naturally occurring non-hydrocarbon polar organics can interfere with measurements. It is recommended to selectively separate these compounds from PHCs by silica gel column cleanup [30]. A small amount of glass wool was put at the bottom of a glass chromatographic column to retain the adsorbent. 5 g of activated silica gel (60-200 mesh size obtained from “Acros Organics”) was added to the top of the glass wool. Silica gel was activated by heating over 101 °C overnight before being used in the silica gel column cleanup procedure [34]. Anhydrous sodium sulfate (approximately 10 mm) was then added. 10 mL of hexane: dichloromethane (with a ratio of 50:50) was used as an eluting solvent to wash and moisten the column. Dichloromethane (methylene chloride, CH_2Cl_2) was supplied by "Fisher Scientific at an Optima-grade and also met the ACS specifications. The sample extract was then passed through the column and eluant collected. Finally, the column was eluted with at least 20 mL of hexane: dichloromethane and the whole eluant was collected [30].

3.2.2.3 Kuderna-Danish concentration technique

K-D is commonly used for the concentration of materials dissolved in organic solvents. K-D is a helpful device where a significant portion of the solvent should be removed, but the compounds of interest dissolved in that solvent must be retained. Prior to GC analysis, the sample was concentrated using K-D to a lower volume (around 2 mL) and then analyzed by GC. Since toluene is a compatible solvent for the GC apparatus used in this study, toluene (around 1 mL) was added to the sample. In fact, during concentration of the sample, other solvents rather than toluene are removed because of their lower boiling points from toluene's boiling point.

The 500-mL evaporation flask was connected to the concentrator tube (10 mL graduated glass tube) by a clamp. The liquid extract which was collected in the silica gel column, was transferred to the K-D with an additional 20 mL of solvent, a mixture of acetone and hexanes with a ratio of 1:1. One or two boiling chips were added to the flask [35]. Boiling chips with approximately 10-40 mesh from "VWR Scientific, Inc." were used. Boiling chips are added to liquids to make them boil more calmly and prevent bumping [36]. The (3-ball macro) Snyder column were joined to the flask with a clamp. Approximately 1 mL of solvent (acetone/hexane with a ratio of 1:1) was used to moisten the column. The whole K-D set-up was placed in a hot water bath in a fume hood. The flask was positioned at a level such that the lower surface of the flask could be bathed in steam. The temperature of water bath was adjusted to approximately 85 °C so that it could vaporize solvents. Around 1 mL of exchange solvent (toluene) was added to the flask by removing the

Snyder column instantly [35]. Toluene ($C_6H_5CH_3$) was purchased from "Fisher Scientific" at an Optima-grade and also met the ACS specifications. The concentration rate can be modified with the water's temperature compared with the boiling point of solvents. The final volume of extract around 2 mL can be reached after a few hours [30]. At the end, the K-D device should be removed from the water bath to be cooled down. Then, the final extract can be collected for further analysis.

3.2.2.4 Gas chromatography (GC)

An Agilent GC- 6890 series with flame ionization detector (FID) was used to measure the concentration of PHCs. The column was HP-1 crosslinked methyl siloxane (30m × 0.32mm × 0.25 µm film thickness). 2 µL of sample (dissolved in toluene) was injected into the GC. The oven temperature was held at 40 °C for 1 min, and then ramped from 40 to 325 °C at 15 °C/min. The injector and detector temperatures were both set at 340 °C. Standards which had identical amounts of n-decane (C_{10}), n-hexadecane (C_{16}) and n-tetratriacontane (C_{34}) hydrocarbons dissolved in toluene and also n-pentacontane (C_{50}) dissolved in toluene were used to obtain the calibration curves and determining retention times [30]. The area under the chromatogram from GC was analyzed with regards to the peak of nC_{10}, nC_{16}, nC_{34} and nC_{50} to give the PHC fractions. The area under chromatogram for each fraction was then converted to concentration according to the calibration curve which was prepared before.

3.2.3 Experimental setup and procedure of SFE

SCE can be conducted in three modes: *Static-mode* (SCF is kept in the extraction vessel for a certain duration and then released), *Dynamic-mode* (a pump flows the SCF into the extraction vessel steadily), and *Combination-mode* (combinations of static- and dynamic-modes are performed such that the static-mode is conducted for a certain duration and then the dynamic-mode is started) [9].

The apparatus for performing supercritical fluid extraction was acquired from "Supercritical Fluid Technologies Inc.". The apparatus specifications are summarized in Table 3.1 [37].

Table 3.1. Properties of SFT-110 apparatus [37]

Parameter	Range
Pressure	0 to 10,000 psi (68.9 MPa)
Temperature	Ambient to 200 °C
Flow rate	0.01 to 24.00 mL/min liquid CO_2
Extraction vessel	100 mL
Dimensions	29cm Width, 57cm Depth, 76cm Height

Figure 3.2 shows a schematic of the lab-scale SFT-110 apparatus which was used for performing SFE experiments. A liquid CO_2 cylinder (99.99%) with a dip tube that sucks the liquid CO_2 from the bottom of cylinder was used for CO_2 supply. The dual piston pump provides high pressures required for SFE and this pump pressurizes the CO_2. The pump has safety measures to avoid over-pressure conditions. Moreover, a rupture disk is supplied to act mechanically against incidental over-pressure conditions. The apparatus has a 100-mL extraction vessel (reactor or extraction cell) where the polluted soil is contained and exposed to SCF. The extraction vessel is surrounded by a heating unit. The oven has a pre-heater to control the temperature. In order to maintain a high pressure in the extraction line, a restrictor is required. The restrictor valve is the point in the system where the CO_2 and dissolved contaminants are stepped down from supercritical to atmospheric pressure. In the static mode, both static/dynamic valve and restrictor valve are closed. To switch from static mode to dynamic mode, first the static/dynamic valve is opened and then the restrictor valve is opened slightly. In dynamic mode, flow rate can be adjusted accurately with a restrictor valve (back pressure regulator). As a more accurate control of CO_2 flow rate, a flow meter was installed to measure the flow rate of the expanding CO_2 gas [37]. SCF is carried into the extraction

vessel and dissolves/extracts contaminants from the solid phase. The SCF containing contaminants is then released from the extraction vessel to a collection vial through a restrictor valve. Restrictor valve is also resistant to blockage. When the fluid is depressurized (fluid is not in supercritical state any more), the extracted contaminants are separated from the fluid due to the reduction in their solubility [9,38]. The contaminants that are extracted can be gathered in a collection vial. The rupture disk and collection vial are both connected to a fume hood for ventilation purposes [37]. Once the extraction vessel is depressurized, the soil sample is then removed from the extraction vessel for the analytical procedure.

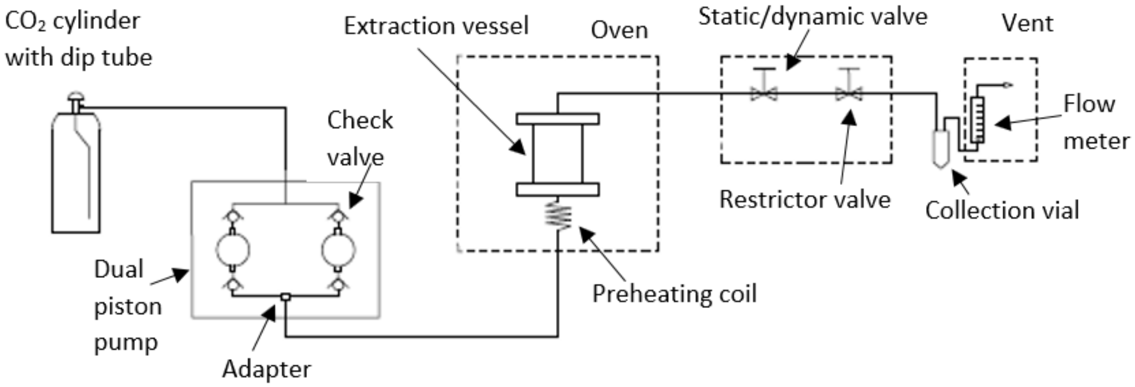


Figure 3.2. SFT-110 apparatus [37]

3.2.3.1 SFE extraction mode and time duration

An initial set of tests was carried out to determine the optimum extraction mode and time duration for performing SFE tests. Different combinations of static cycles (10 and 20 min) and dynamic cycles (5 and 10 min) were investigated as summarized in Table 3.2. S and D represents static and dynamic modes of extraction, respectively.

Table 3.2. Initial tests for determination of SFE mode and time duration

Extraction mode	Static cycle duration (min)	Dynamic cycle duration (min)	No. of cycles	Total time (min)
Static mode (10S)	10	0	1 2 3	10 20 30
Static mode (20S)	20	0	1 2 3	20 40 60
Combination mode (10S+5D)	10	5	1 2 3	15 30 45
Combination mode (10S+10D)	10	10	1 2 3	20 40 60

S: static mode, D: dynamic mode

3.2.4 Statistical method and data analysis

Factorial design and response surface methodology (RSM) were used to determine the optimum pressure and temperature levels in order to achieve the highest removal of PHC fractions from the contaminated soil. Two independent variables P (pressure) and T (temperature) at three levels were chosen for the response surface model. The ranges of these factors which were coded between -1 and +1 are presented in Table 3.3. The ranges of each variable were selected based on the related information available in the literature that led to the highest recovery of contaminants and also the specifications of SFT-110 apparatus which was used in this study for performing SFE tests.

Table 3.3. Experimental design and the levels of independent variables

Independent variable	Symbol	coded levels		
		-1	0	+1
Pressure (MPa)	P	15	33	50
Temperature (^{o}C)	T	30	75	120

Design-Expert® software (version 10) was used to perform statistical analysis and RSM [39]. Three outcome responses including PHC F2 removal percentage, PHC F3 removal percentage and PHC F4 removal percentage were defined. Each outcome response as a removal percentage was calculated using the Eq. (3.1).

$$PHC\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq. (3.1)}$$

Where C_i and C_f are the initial (before SFE test) and final (after SFE test) PHC concentrations (mg/kg), respectively; that were measured for each PHC fraction separately (i.e. PHC F2 to F4). The behavior of the system could be described by the quadratic equation as shown in Eq. (3.2) [40,41].

$$Y = A_0 + \sum_{i=1}^{n} A_i X_i + \sum_{i=1}^{n} A_{ii} X_i^2 + \sum_{i \neq 1\ j=1}^{n} A_{ij} X_i X_j + \varepsilon \qquad \text{Eq. (3.2)}$$

Where Y is the outcome response; X_i and X_j are the independent variables; A_0 is the value of the fixed response at the center point of the design; A_i, A_{ii} and A_{ij} represents the interaction coefficients of linear, quadratic and second-order terms, respectively; n is the number of independent variables; and ε is the random error.

3.3 Results and discussion

3.3.1 Determination of SFE extraction mode and time duration

SFE can be performed in static, dynamic and combined modes. The mode as well as time duration in each mode can affect the PHCs removal by SFE. Therefore, an initial set of tests was carried out to determine the optimum extraction mode and time duration of SFE that would achieve the highest PHCs removal percentages from a contaminated soil. The following conditions were applied for this set of experiments: 25 MPa pressure, 55 °C temperature, flow rate of 24 ml/min of liquid CO_2 (for dynamic mode), sand spiked with diesel fuel with a ratio of 5 wt% (aged for 3 months) and approximately 105 g soil was used to fill the extraction vessel of the SFE apparatus. The concentration of PHCs before and after conducting SFE tests were measured and compared to determine the effect of extraction mode and time duration on the removal efficiency of PHCs from a contaminated soil.

Static mode was employed for 10 and 20 min with the cycles repeated three times. The SCF was kept in the extraction vessel for 10 or 20 min and then the treatment was stopped (the pump turned off). The extraction vessel was opened, and the first soil sample was taken (10S × 1C). Then, second cycle was started with increasing pump pressure to the target value. The SCF was kept in the extraction vessel for the required time duration and then the treatment was stopped. The extraction vessel was opened, and the second soil sample was taken (10S × 2C). Similarly, after third cycle of 10 min, the third soil sample was taken (10S × 3C). In other words, three soil samples at 10, 20 and 30 min after the start of the test were collected and analyzed. The same process was followed for 20 min static time cycles. Consequently, three soil samples after 20, 40 and 60 min from the start of the test were collected and analyzed. Combinations of static and dynamic modes were also investigated. In the combination mode, static mode was conducted for 10 min followed by a dynamic mode cycle of 5 or 10 min with the cycles repeated three times. For example, for the case of combination of 10 min static and 5 min dynamic modes, three soil samples after 15, 30 and 45 min from the start of the test were collected and analyzed. It should be noted that “S”, “D” and “C” denote static mode, dynamic mode and cycle number, respectively.

Figure 3.3 shows removal percentages of PHC F2 fraction for all investigated modes of operation. As it was expected, the remaining PHC concentrations for each mode decreased with each cycle of treatment. For 10 min static cycles, the percentage removal percentage observed for PHC F2 increased from 68.3% at the end of cycle #1 to 80.5% at the end of cycle #2 and further to 93.3% at the end of cycle #3 (total time of 30 min). Similar trend was observed for the case of 20 min static cycles, where the highest percentage removal of 89% was obtained at the end of cycle #3 (total time of 60 min). When a combination of 10 min static and 5 min dynamic modes was used, the removal percentage of PHC F2 increased from 72.5% at the end of cycle #1 to 92.5% at the end of cycle #2 and further to 98% at the end of cycle #3 (total time of 45 min). This shows that using a combined mode and alternating between static and dynamic modes was more effective than using a single static mode. For the case of combination of 10 min static and 10 min dynamic modes, the highest percentage removal of 97.6% was obtained at the end of cycle #3 (total time of 60 min) The extraction of PHC F3 and F4 fractions showed roughly similar trends as F2 fraction.

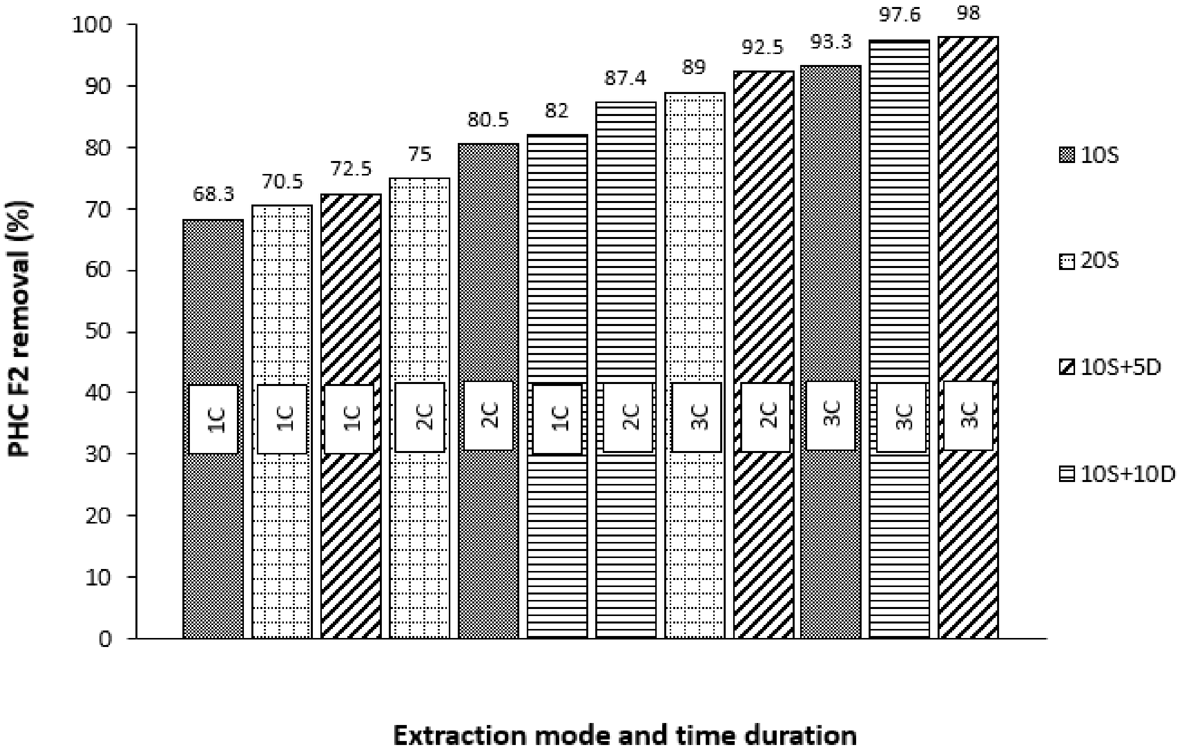


Figure 3.3. PHC F2 removal percentages for different SFE extraction modes and time durations (S: static mode, D: dynamic mode, C: cycle)

In order to compare the combined mode with static mode alone, the same time duration and cycle number should be considered. For example, "10S+10D × 3C" and "20S × 3C", both at the end of cycle #3 with the total time of 60 min, resulted in 97.6% and 89.0% removal of PHC F2, respectively, showing that combined mode performed better than static mode. The same trend was observed for "10S+10D × 2C" vs. "20S × 2C". In dynamic mode, the SCF flows through the soil and could flush the extracted contaminants out of the extraction vessel and would enhance the removal of PHCs. This shows that using a combined mode was more effective than using a single static mode. Comparing all static and combination modes shows that the 10S+5D × 3C and 10S+10D × 3C combinations resulted in the highest removal percentage of PHC F2, F3 and F4 fractions. 10S+5D × 3C mode resulted in 98%, 85.5% and 76.3% removal of PHC F2, F3 and F4 fractions, respectively. 10S+10D × 3C mode led to 97.6%, 89.8% and 86.3% removal of PHC F2, F3 and F4 fractions, respectively. For the subsequent tests (i.e. effect of pressure and temperature), 10S+10D × 3C mode (combination of 10 min static followed by 10 min dynamic mode, repeated for 3 cycles for a total time of 60 min) was adopted and performed. Low and Duffy (1995) [42] studied different SFE extraction modes including static, dynamic and combination modes for a clay soil spiked with 7.5% w/w of diesel. According to their results, combination of static and dynamic mode at 20.3 MPa pressure, 40 °C temperature, 1 g/min flow rate and 45 g CO_2 used was selected among the extraction mode studied, which led to the highest extraction (i.e. 99%) of diesel from soil [42]. It should be mentioned that the conditions such as soil type, spiking ratio, time duration, SFE operational parameters in this study and a study by Low and Duffy (1995) [42] were different; while the combination mode was selected in both.

The results of PHC extractions can be compared with the Ontario Ministry of Environment (MOE) - Canada, “Table 2- under Industrial/Commercial/Community property use” as presented in Table 3.4 [43]. Comparison of PHC concentrations at the end of cycle #3 of SFE for both two cases of combination modes of 10S+5D × 3C (F3: 1480.5 mg/kg; F4: 260.3 mg/kg) and 10S+10D × 3C (F3: 1241 mg/kg; F4: 383.5 mg/kg) with Table 2 of MOE shows that F3 and F4 fractions were below the standard limits (i.e. 1700 mg/kg for F3 and 3300 mg/kg for F4) indicated for a soil that was considered clean and can be used for appropriate land uses. Only PHC F2 was slightly above the table limit and should be treated more. Concentration of PHC F2 for combination of 10S+5D × 3C (382.8 mg/kg) was about 153 mg/kg above the table limit (i.e. 230 mg/kg). Concentration of PHC F2 for combination of 10S+10D × 3C (499.1 mg/kg) was about 269 mg/kg above the table limit (i.e. 230 mg/kg). However, PHC concentrations were greater for static modes alone and did not meet the limits stated in the Table 2 of MOE. Therefore, it may be concluded that combination of static and dynamic modes shows better results than static mode alone.

Table 3.4. Petroleum Hydrocarbons values based on “Table 2” of MOE [43]

Contaminant	Industrial/Commercial/Community property use (mg/kg)
PHC F2	230 (250)
PHC F3	1700 (2500)
PHC F4	3300 (6600)

() standard in bracket applies to medium and fine textured soils

3.3.2 Effect of pressure and temperature

The ranges of pressure and temperature reported in the literature for SFE treatment of contaminated soils (that were mostly contaminated with PHC and/or PAH) were 6-66 MPa and 20-200 °C, respectively, with the highest extraction obtained for a pressure range of 12-55 MPa and a temperature range of 30-150 °C [4,5,9,44–50]. As can be seen, the range for both parameters is quite wide. The laboratory SFT-110 apparatus used in this study can maintain pressures up to 69 MPa and temperatures up to 200 °C. As presented in Table 3.3, three levels for pressure and temperature were studied based on the factorial design, which resulted in 9 experiments in total. The tests at low levels (-1) and high levels (+1) of pressure and temperature were triplicated while the remaining tests at the medium level (0) of pressure (i.e. 33 MPa) and/or medium level of temperature (i.e. 75 °C) were performed only once. Considering all tests and their replicates, 17 tests were performed. The orders of conducting experiments were randomly selected to reduce the bias for the outcome response. In this manner, the effects of some unknown and uncontrolled factors on the results would be the least possible.

The following parameters were fixed for all experiments to negate their effects and only allow pressure and temperature to influence results. The time duration was the combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles (60 min in total) and flow rate was 24 ml/min of liquid CO_2. Approximately 120 g of the spiked sand (with diesel fuel with a ratio of 5 wt%) was placed in the extraction vessel.

Figure 3.4 shows PHC removal percentages for different pressures at a fixed temperature. High PHC F2 removal percentages (ranged from 92.3% to 99.4%) were observed for all cases, which were greater than removal percentages obtained for PHC F3 and F4 fractions. At 30 °C, PHC F2 and F3 extraction yield showed a general increasing trend with increase in pressure while PHC F4 extraction yield reached the maximum at the medium pressure level (i.e. 33 MPa). The same trend for PHC F3 and F4 extraction yield was observed at 75 °C, however the increase of pressure from 15 MPa to 50 MPa at this temperature did not affect the extraction of PHC F2 considerably. At 120 °C, no trend was observed for PHC F2 extraction yield. PHC F3 extraction yield increased as pressure reached the medium level (i.e. 33 MPa) and remained unchanged with further increase in pressure; while PHC F4 extraction yield showed a slight decrease followed by an increase with increasing pressure. Since replicates were available for low and high levels of pressure (i.e. 15 and 50 MPa), the results were statistically compared. At 30 °C, PHC F2 and F4 extraction yield at 15 and 50 MPa were significantly different at $p<0.05$, however, PHC F3 extraction yield were not significantly different. The extraction of PHC fractions were not statistically different at $p<0.05$ at pressures of 15 MPa and 50 MPa at temperature of 120 °C. In general, increasing pressure from 15 MPa to 50 MPa at constant temperature resulted in higher extraction of PHC fractions except at 120 °C.

As expected, removal of PHC F2 from soil would be easier than F3 and F4 fraction because of PHC F2 fraction is considered as light extractable PHCs in soil and has lower molecular weight than F3 and F4 fractions. Interactive forces between hydrocarbon components and the soil matrix could be different. For example, higher molecular weight alkanes may have greater Van der Waals sorption forces with the clay matrix [42]. As a result, there might be strong interactions between the soil and PHC F4 fraction compared to other fractions. In conclusion, the increase in pressure from 15 MPa to 50 MPa led to higher extraction of PHC F2 and F4 fractions at 30 °C and PHC F3 and F4 fractions at 75 °C. In this case, an increase in pressure at a fixed temperature resulted in an increase in CO_2 density that can improve the solubility of PHC fractions and consequently, led to higher PHC removal percentages. Furuya and Teja (2004) [51] investigated the solubility of high molecular weight n-alkanes including n-tetracosane (n-$C_{24}H_{50}$), n-pentacosane (n-$C_{25}H_{52}$), n-hexacosane (n-$C_{26}H_{54}$), n-heptacosane (n-$C_{27}H_{56}$) and n-nonacosane (n-$C_{29}H_{60}$) in SC-CO_2 at the pressure range of 10 to 50 MPa. The solubility of n-tetracosane increased from $8.7 \times 10^{+4}$ mole fraction to $10.4 \times 10^{+4}$ mole fraction by increasing pressure from 15.6 to 45.9 MPa at a constant temperature of 36.9 °C, which resulted in an increase in the density of CO_2 from 18.4 to 22.4 mol/L. Also, increasing pressure from 15.2 to 32.3 MPa at constant temperature of 39.9 °C led to the increase in the solubility of n-pentacosane from $8.6 \times 10^{+4}$ mole fraction to $9.3 \times 10^{+4}$ mole fraction, which was accompanied by an increase in the density of CO_2 from 17.8 to 20.9 mol/L [51].

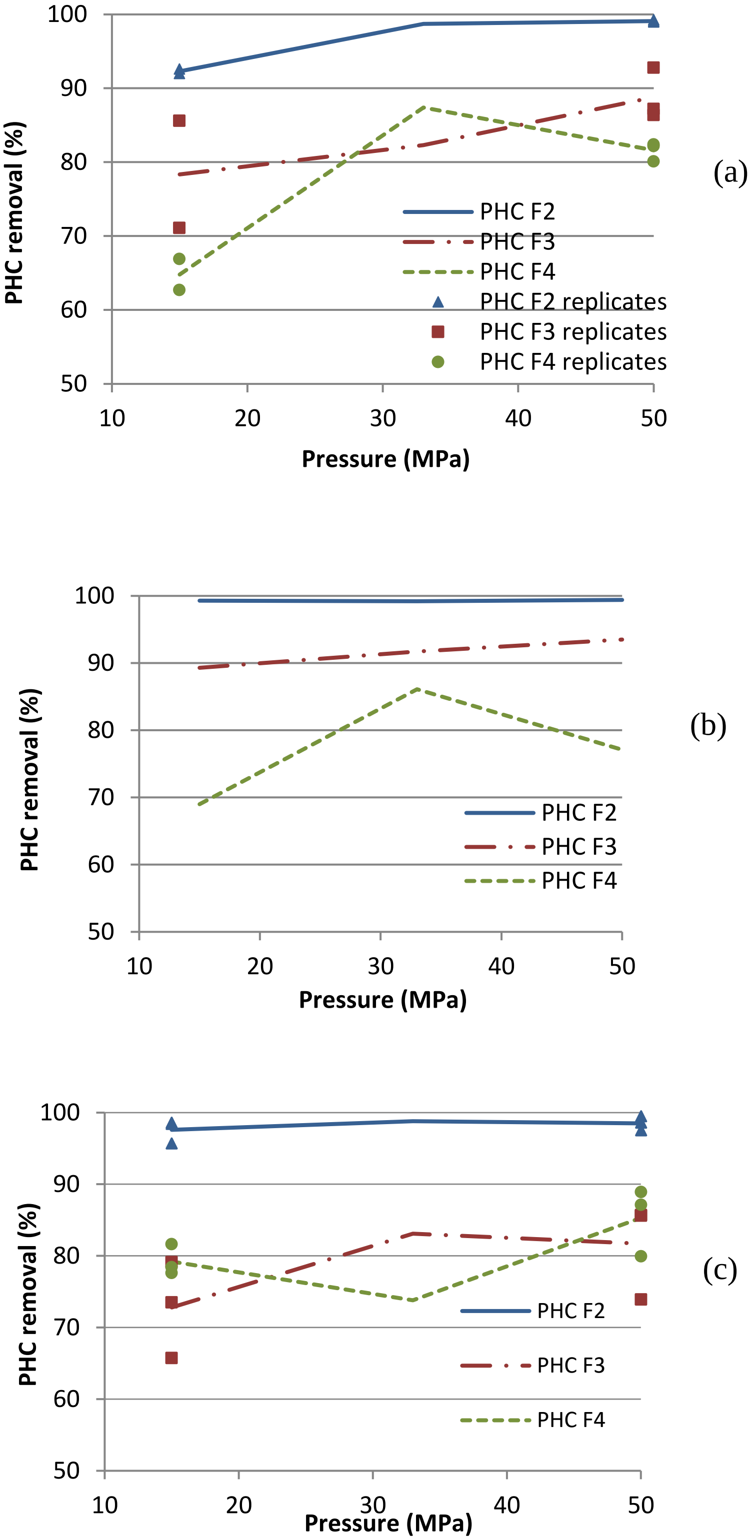


Figure 3.4. PHC fractions removal percentages for different pressures at (a) 30 °C (b) 75 °C (c) 120 °C

Figure 3.5 shows PHC removal percentages for different temperatures at a fixed pressure. At constant pressure of 15 MPa, removal percentages of PHC F2 and F4 increased with increasing temperature from 30 °C to 120 °C while PHC F3 removal percentages were not statistically different ($p < 0.05$). The increase of temperature from 30 °C to 120 °C at 33 MPa pressure did not affect the extraction of PHC F2 considerably. Increasing temperature from 30 °C to 120 °C at 33 MPa pressure resulted in an increase and a decrease in the removal percentage of PHC F3 and F4 fractions, respectively. In general, removal percentages of PHC fractions were not statistically different ($p < 0.05$) at temperature of 30 °C and 120 °C at constant pressure of 50 MPa.

The effect of temperature on the extraction of contaminants is a sum of the temperature effects on fluid density, volatility (solute vapor pressure), and the adsorption of the contaminant onto the soil matrix [52]. On the one hand, a rise in temperature could cause higher PHC removal percentages despite a decrease in density. The increase of PHC removal percentage by increasing temperature could be because of an increase in the volatility and/or an increase in the desorption of the contaminants from the soil [15,26]. Consequently, solute volatility and/or desorption of a pollutant from the soil are dominant factors over a small decrease in density. Therefore, in this state, a rise in temperature led to higher PHC removal percentages. This is the case for the increase of PHC F2 and F4 removal percentages at 15 MPa and PHC F3 removal percentage at 33 MPa because of a rise in temperature. On the other hand, for some cases, a rise in temperature at a constant pressure could lead to a reduction in solubility due to a remarkable decrease in density [15,26]. Therefore, in this case, a rise in temperature led to lower PHC removal percentages. This might be a reason for a decrease of PHC F4 removal percentage because of the rise in temperature from 30 °C to 120 °C at 33 MPa. Shi et al. (2015) [53] studied the solubility of n-alkanes (C_6H_{14}-$C_{18}H_{38}$) in SC-CO_2

at the temperature range of 44.9-69.9 °C. The solubility of $C_{16}H_{34}$ decreased from 114.3 to 19.1 kg/m^3 by increasing temperature from 44.9 to 69.9 °C at constant pressure of 15.1 MPa, which resulted in a decrease in the density of CO_2 from 745.3 to 515.6 kg/m^3. Also, increasing temperature from 44.9 to 64.9 °C at constant pressure of 16.2 MPa led to the decrease in the solubility of $C_{18}H_{38}$ from 53.5 to 21.4 kg/m^3, which was accompanied by a decrease in the density of CO_2 from 764.8 to 600.8 kg/m^3 [53]. Increasing temperature by 25 °C resulted in a noticeable decrease in density of CO_2 by 229.7 kg/m^3 and 95.2 kg/m^3 decrease in solubility of $C_{16}H_{34}$. The decrease in density of CO_2 (by 164 kg/m^3) and decrease in solubility (by 32.1 kg/m^3) of $C_{18}H_{38}$ due to 20 °C increase in temperature were observed.

PHC F4 removal showed a different behaviour at 15 MPa and 33 MPa due to an increase in temperature. This behaviour of PHC F4 might be related to complicated interactions between soil-pollutant-fluid. Interactive forces between hydrocarbon components and the soil matrix could be different that may lead to selective extraction of hydrocarbon components [26]. There might be strong interactions between the soil and PHC F4 fraction. In addition, a certain amount of energy should be provided to desorb a compound from the soil matrix [45]. Therefore, a specific energy was required to disrupt the strong interactions between F4 fraction and the soil to improve the desorption process. The required energy may not be provided when temperature changed from 30 °C to 120 °C at 33 MPa. Another possible reason for a decrease of PHC F4 removal at 33 MPa might be related to the level of pressure (15 MPa vs. 33 MPa) which might also influence the effect of temperature on the PHC F4 extraction. Furthermore, the highest PHC F3 removal percentage was observed at the medium temperature (75 °C) at constant pressure of 33 MPa.

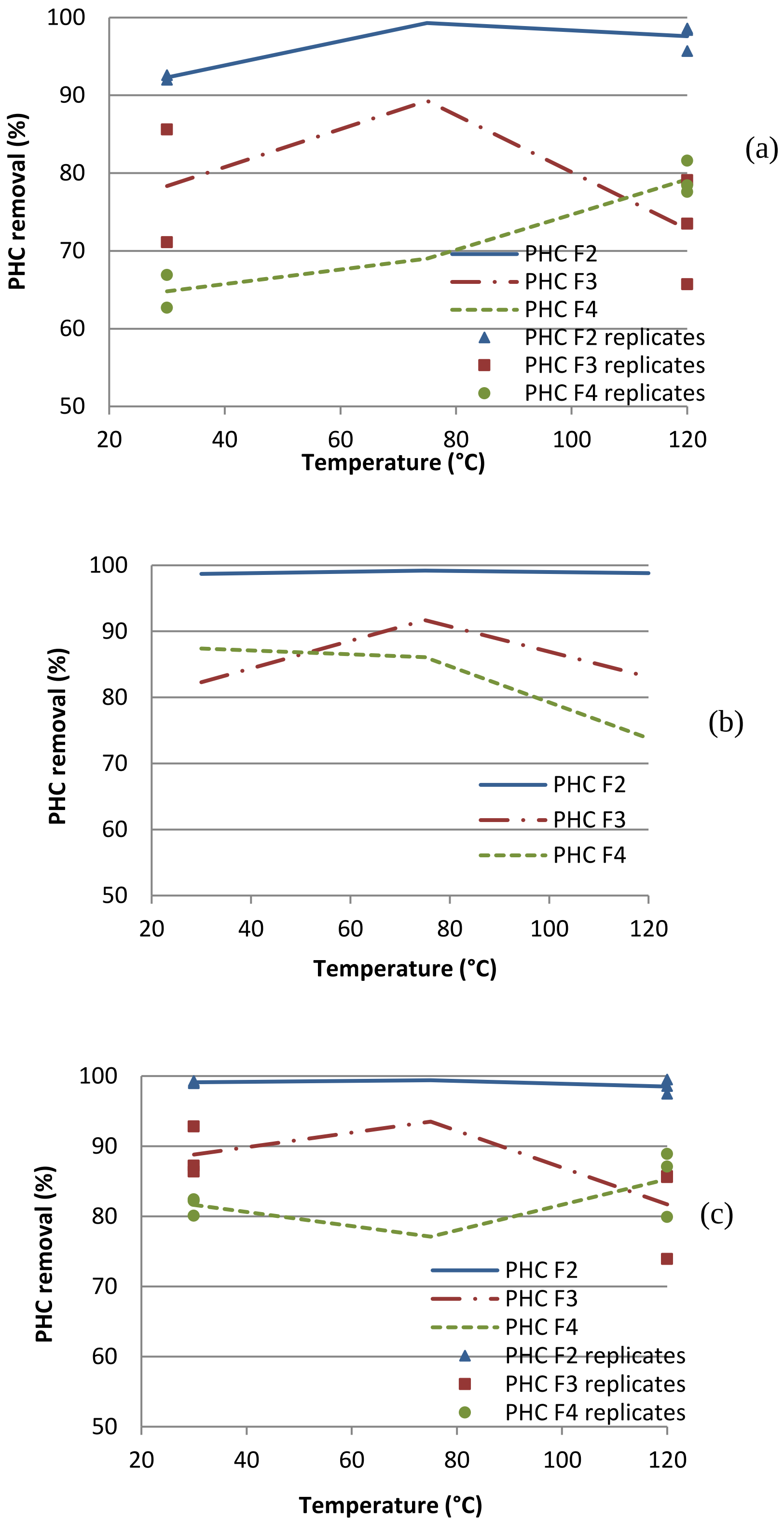


Figure 3.5. PHC fractions removal percentages for different temperatures at (a) 15 MPa (b) 33 MPa (c) 50 MPa

Considering the obtained results for all the combinations of pressure and temperature, it can be stated that the lowest extraction was related to the combination of low pressure and low temperature and combination of low pressure and high temperature. The highest removal percentage was observed for medium values for both pressure and temperature and combination of high pressure and medium temperature. Comparison between these two latter conditions for the highest removal percentages shows that PHC F2 and F3 removal percentages were about the same, however, PHC F4 removal percentage was higher for medium pressure and medium temperature combination (86.1%) than high pressure and medium temperature combination (77.1%). In addition, the difference between these two conditions is the pressure level. From a practical point of view, reaching medium pressure (33 MPa) is easier, safer and more economical than high pressure (50 MPa). Therefore, the best combination for pressure and temperature which resulted in the highest extraction of PHCs based on the experimental results was selected for medium values for both pressure and temperature (33 MPa and 75 °C). This combination resulted in 99.2%, 91.7% and 86.1% removal percentage for PHC F2, F3 and F4 fractions, respectively.

3.3.3 Statistical analysis and modeling

Based on a factorial design of two independent variables (i.e. pressure and temperature) at three levels, a total of 17 runs for the extraction of each PHC fraction were obtained. One data point out of 17 experimental values was considered as an outlier and eliminated. Therefore, 16 data points were considered for statistical analysis and modeling. Regression analysis was applied to develop the best-fit model for the collected data. Two responses including PHC F2 removal percentage and PHC F3 removal percentage were fitted for quadratic models, which are shown in Eq. (3.3) and Eq. (3.4), respectively [39].

$$PHC\ F2 = 81.680 + 0.494P + 0.217T - 0.0018PT - 0.0041P^2 - 0.0009T^2 \qquad \text{Eq. (3.3)}$$

$$PHC\ F3 = 52.656 + 0.659P + 0.729T - 0.0005PT - 0.0057P^2 - 0.0052T^2 \qquad \text{Eq. (3.4)}$$

Where PHC F2 and F3 are the removal percentage of PHC fractions, P and T are pressure and temperature, respectively. It should be noted that an attempt was made for modeling the PHC F4 fraction removal, however, the regression model for PHC F4 removal percentage was not significant accompanied with a significant lack of fit and a low R-squared value (below 0.5). Therefore, no results for statistical analysis for PHC F4 removal percentage were presented.

F-test was conducted for analysis of variance (ANOVA) to evaluate the statistical significance of quadratic models. The ANOVA test results for PHC F2 model are presented in Table 3.5. According to Table 3.5 (a), the F-value of 7.62 and the "Prob>F" value of 0.0034 indicated that the model was statistically significant for PHC F2 removal percentage. For PHC F2 model, the "Prob>F" value for the P^2 term (0.174) was greater than 0.05 implying that this term was an insignificant and could be eliminated from the model [39]. The ANOVA test results for the reduced form of the PHC F2 model are shown in Table 3.5 (b). All terms in the reduced model had the "Prob>F" values less than 0.05 and were significant. The "adjusted R-squared" (0.656) and "predicted R-squared" (0.456) values in reduced model were within a reasonable agreement (the difference was not greater than 0.2) in the reduced model; however, the difference between the "adjusted R-squared" (0.688) and "predicted R-squared" (0.404) values in the full model was more than 0.2. This shows that the model was improved by eliminating the insignificant term. The difference between other parameters for the reduced model and full model were not considerable.

Coefficient of determination (R-squared), adjusted R-squared (R^2_{adj}) and predicted R-squared (R^2_{pred}) values were used to evaluate the fitness of the model. Adjusted R-squared is a modification of R-squared, which adjusts for the number of explanatory terms in a model relative to the number of data points [54]. The predicted R-squared indicates how well a regression model predicts responses for new observations [55]. The reduced model was simpler (less terms) than the full model and was considered to be appropriate to model the PHC F2 removal percentage. The reduced quadratic model for PHC F2 removal percentage is shown as Eq. (3.5) [39].

$$PHC\ F2 = 84.695 + 0.224P + 0.232T - 0.0018PT - 0.001T^2 \qquad \text{Eq. (3.5)}$$

According to Table 3.5 (b), the model F-value of 8.15 implied the model was significant and there was only a 0.26% chance that a F-value this large could occur due to noise. The lack of fit compares residual error with pure error from replicated design points. The lack of fit F-value of 3.19 implied the lack of fit was not significant relative to the pure error. Adequate precision measures the signal to noise ratio. Adequate precision of 9.834 indicated an adequate signal (a ratio greater than 4 is desirable) and this model can be used to navigate the design space.

Table 3.5. ANOVA for PHC F2 (a) full and (b) reduced quadratic model parameters [39]

(a)

Source	Sum of squares	df	Mean square	F value	p-value Prob>F	
Model	66.24	5	13.25	7.62	0.0034	significant
P	33.56	1	33.56	19.31	0.0013	
T	11.56	1	11.56	6.65	0.0274	
PT	21.15	1	21.15	12.17	0.0058	
P^2	3.72	1	3.72	2.14	0.1742	
T^2	8.12	1	8.12	4.67	0.0560	
Residual	17.38	10	1.74			
Lack of Fit	9.90	3	3.30	3.09	0.0991	not significant
Pure Error	7.48	7	1.07			
Total	83.62	15				
$R^2=0.792$, $R^2_{adj}=0.688$, $R^2_{pred}=0.404$, *Adequate precision=9.252*						

(b)

Source	Sum of squares	df	Mean square	F value	p-value Prob>F	
Model	62.52	4	15.63	8.15	0.0026	significant
P	32.84	1	32.84	17.12	0.0017	
T	11.14	1	11.14	5.81	0.0346	
PT	20.54	1	20.54	10.71	0.0074	
T^2	10.49	1	10.49	5.47	0.0393	
Residual	21.10	11	1.92			
Lack of Fit	13.62	4	3.41	3.19	0.0864	not significant
Pure Error	7.48	7	1.07			
Total	83.62	15				
$R^2=0.748$, $R^2_{adj}=0.656$, $R^2_{pred}=0.456$, *Adequate precision=9.834*						

The ANOVA test results for PHC F3 model is presented in Table 3.6. According to Table 3.6 (a), the F-value of 3.74 and the "Prob>F" value of 0.036 indicated that the model was statistically significant for PHC F3 removal percentage. For PHC F3 model, the "Prob>F" values for PT (0.84) and P^2 (0.662) terms were greater than 0.05 implying that these terms were insignificant and could be eliminated from the model [39]. The ANOVA test results for the reduced form of the PHC F3 model is shown in Table 3.6 (b). All terms in the reduced model were significant ("Prob>F" value less than 0.1 was considered marginally, which is close to 0.05).

The “adjusted R-squared” (0.554) and “predicted R-squared” (0.381) values were within a reasonable agreement (the difference was less than 0.2) in the reduced model; however, the difference between the “adjusted R-squared” (0.478) and “predicted R-squared” (0.115) values in the full model was more than 0.2. This shows an improvement achieved in the reduced model by eliminating insignificant terms. The difference between other parameters for the reduced model and full model were not considerable. The reduced model was simpler (less terms) than the full model and was considered to be appropriate to model the PHC F3 removal percentage. The reduced quadratic model for PHC F3 removal percentage is shown as Eq. (3.6) [39].

$$PHC\ F3 = 58.081 + 0.252P + 0.733T - 0.0053T^2 \qquad \text{Eq. (3.6)}$$

According to Table 3.6 (b), the model F-value of 7.22 implied the model was significant and there was only a 0.5% chance that a F-value this large could occur due to noise. The lack of fit F-value of 0.2 implied the lack of fit was not significant relative to the pure error. There was a 95.15% chance that a lack of fit was not significant. Adequate precision of 8.15 indicated an adequate signal (a ratio greater than 4 is desirable) and this model can be used to navigate the design space. The R-squared value of 0.643 showed that the model could fit the experimental data properly. The predicted R-squared of 0.381 was in a reasonable agreement with the adjusted R-squared of 0.554 (the difference was less than 0.2) [39].

Table 3.6. ANOVA for PHC F3 (a) full and (b) reduced quadratic model parameters [39]

(a)

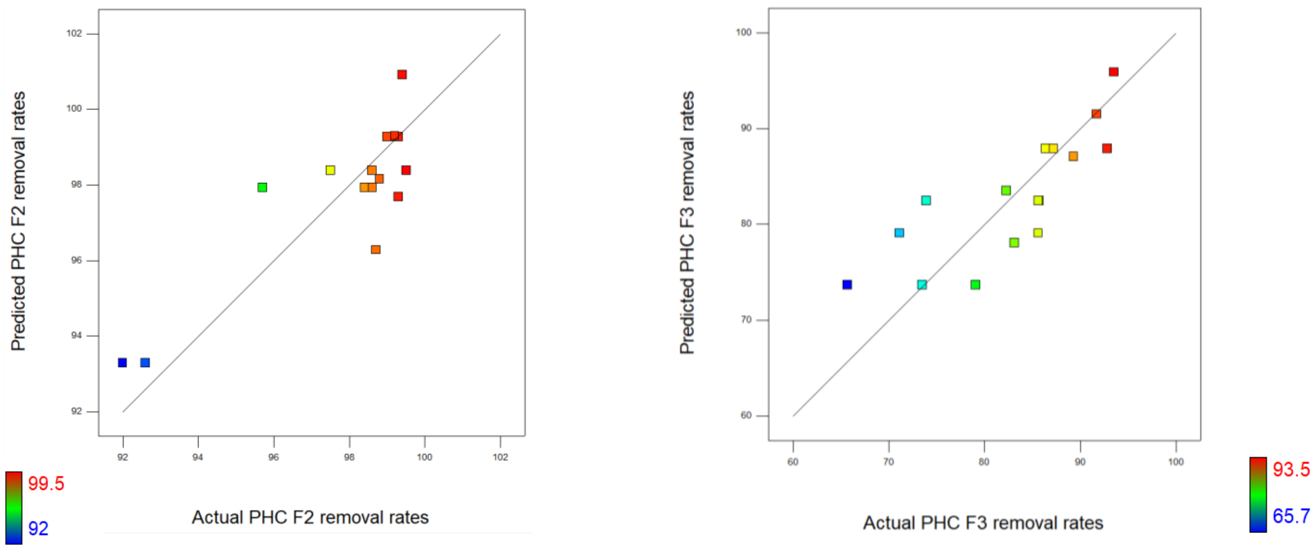
Source	Sum of squares	df	Mean square	F value	p-value Prob>F	
Model	652.48	5	130.50	3.74	0.0360	significant
P	252.99	1	252.99	7.25	0.0226	
T	89.13	1	89.13	2.56	0.1410	
PT	1.51	1	1.51	0.043	0.8395	
P^2	7.07	1	7.07	0.20	0.6621	
T^2	256.05	1	256.05	7.34	0.0219	
Residual	348.73	10	34.87			
Lack of Fit	36.65	3	12.22	0.27	0.8424	not significant
Pure Error	312.08	7	44.58			
Total	1001.21	15				
R^2=0.652, R^2_{adj}=0.478, R^2_{pred}=0.115, *Adequate precision=5.983*						

(b)

Source	Sum of squares	df	Mean square	F value	p-value Prob>F	
Model	644.12	3	214.71	7.22	0.0050	significant
P	249.33	1	249.33	8.38	0.0135	
T	94.01	1	94.01	3.16	0.1008	
T^2	278.80	1	278.80	9.37	0.0099	
Residual	357.09	12	29.76			
Lack of Fit	45.01	5	9.00	0.20	0.9515	not significant
Pure Error	312.08	7	44.58			
Total	1001.21	15				
R^2=0.643, R^2_{adj}=0.554, R^2_{pred}=0.381, *Adequate precision=8.150*						

Figure 3.6 illustrates the observed (actual) response values versus the predicted response values for removal of PHC F2 and F3 fractions. Actual values were collected from the experimental data and predicted values were calculated by the model. This graph helps to detect observations that were not well predicted by the model. The coefficient of determination (R^2) provides a measure of the goodness of the fit for the predicted outcomes by the model and the observed data within the ranges of experiments. The R-squared (R^2) values for PHC F2 and F3 removal percentages were 0.748 and 0.643, respectively. The R^2 values indicated a good correlation between the actual and

predicted values for the PHC F2 and F3 models, and there was a good agreement between adjusted and predicted R-squared values.


(a)

(b)

Figure 3.6. Predicted versus actual values for removal rates of (a) PHC F2 (b) PHC F3 [39]

Figure 3.7 presents the normal probability plots of externally studentized residuals. The figure shows an adequate fit of the externally studentized residuals versus normal probability percentage, confirming that the statistical assumptions suited the analytical data, which represents that the model predictions statistically fitted the observed results. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. A non-linear pattern (such as a S-shaped curve) indicates non-normality in the error term, which may be corrected. Externally studentized residuals (sometimes referred to as outlier t-value) are calculated by leaving the run in a question, one at a time, out of the analysis and estimating the response from the remaining runs. It checks whether the run in a question follows the model with coefficients estimated from the rest of the runs, that is, whether this run is consistent with the rest of the data for this model. A value greater than the calculated limits means that this point should be examined as a possible outlier. Externally studentized residuals based on a deletion method are recommended due to being more sensitive for finding problems with the analysis [39].

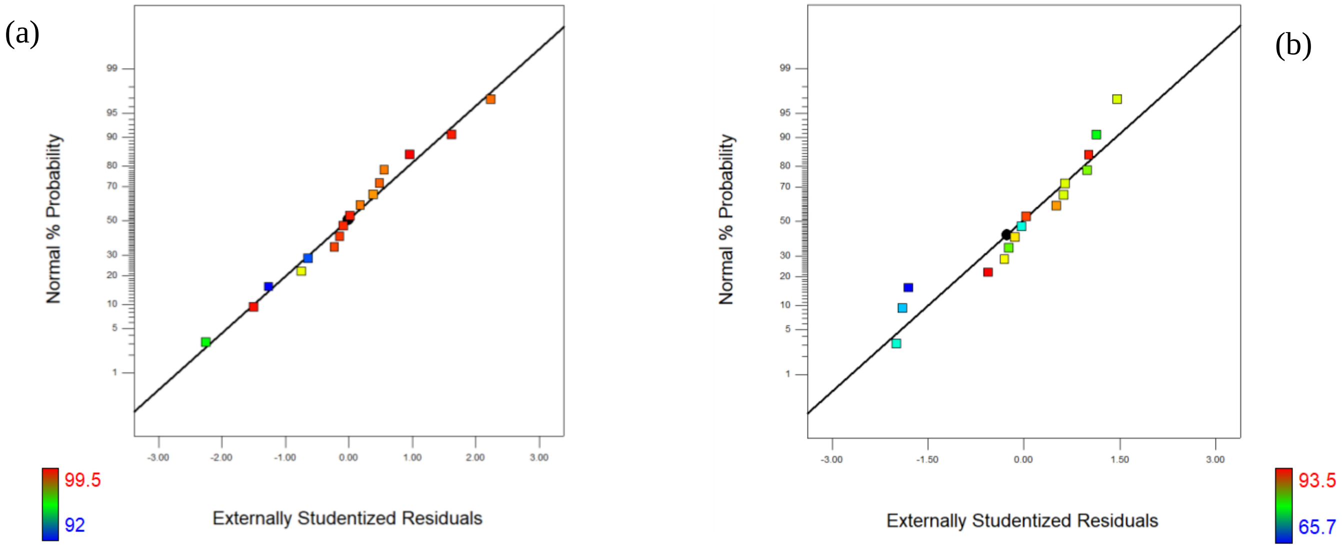


Figure 3.7. Normal probability of externally studentized residuals for removal of (a) PHC F2 (b) PHC F3 [39]

3.3.4 Response surface methodology

Numerical optimization was done by RSM to evaluate the interaction between two independent variables (pressure and temperature) and the response (PHC removal percentage). A three-dimensional surface plot and a two-dimensional contour plot for the optimization of PHC F2 and F3 fractions are shown in Figure 3.8 and Figure 3.9, respectively.

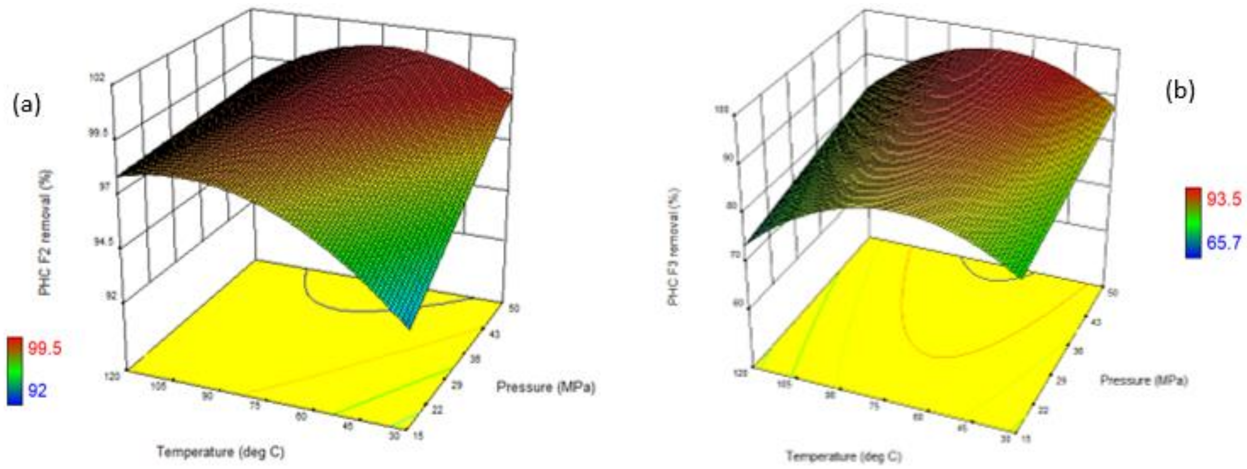


Figure 3.8. Three-dimensional surface plot by RSM for removal of (a) PHC F2 (c) PHC F3 [39]

It can be concluded from the figures that PHC extraction efficiency increased as the pressure increased. However, the effect of temperature was different and there was an optimum range for the temperature. In general, temperature around medium level (75 °C) showed better extraction results. If the extraction is to be optimized individually for PHC F2 and F3 fractions, the optimized pressure and temperature levels for each fraction would be in the ranges which are shown in Fig. 3.8. However, when PHC fractions were combined, the optimum pressure and temperature were found to be 50 MPa and 69.3 °C, respectively. These levels of pressure and temperature led to the maximum removal percentage of 100% and 96.1% for PHC F2 and F3 fractions, respectively.

Moreover, the desirability of the optimum condition was constructed at 0.897, which is an acceptable value. Therefore, responses (PHC F2 and F3 removal percentages) were combined with the goal of being simultaneously maximized to yield the highest PHC removal efficiency. Desirability varies from zero to one for any given response. A desirability value of one represents the ideal case and a zero desirability indicates that one or more responses fall outside desirable limits. Individual desirability was combined into a single number with the goal of searching for the greatest overall desirability [39].

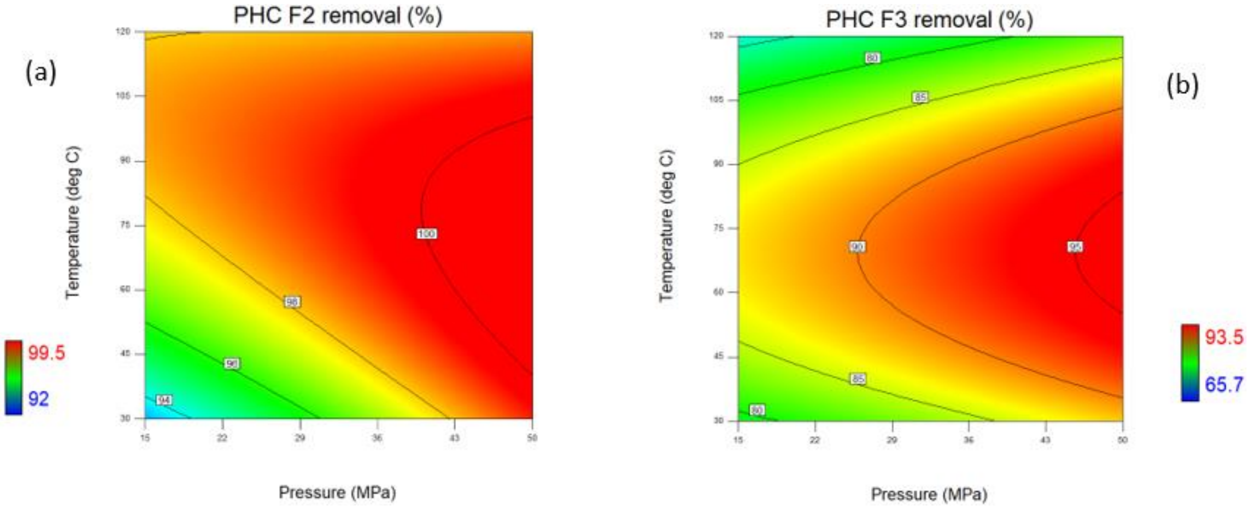


Figure 3.9. Two-dimensional contour plot by RSM for removal of (a) PHC F2 (c) PHC F3 [39]

3.4 Conclusion

This study shows that based on laboratory-scale experiments conducted, SFE is an effective treatment technology for the extraction of PHCs from contaminated soil. The following conclusions can be drawn from this study:

- Using a combined mode and alternating between static and dynamic modes is more effective for PHCs removal than using a single static mode.
- High PHC F2 removal percentages (ranged from 92.3% to 99.4%) were observed, which were greater than removal percentages obtained for PHC F3 and F4 fractions. Therefore, removal of PHC F2 from soil was easier than F3 and F4 fractions.

- Overall, an increase in pressure at constant temperature (except 120 °C) resulted in higher extraction of PHCs. PHC F2 and F4 removal percentages increased with increasing pressure from 15 MPa to 50 MPa at 30 °C while PHC F3 removal percentages were not statistically different (at $p < 0.05$ confidence level). The increase of pressure from 15 MPa to 50 MPa at 75 °C did not affect the extraction of PHC F2 considerably, however, the extraction of PHC F3 and F4 fractions increased. The extraction of PHC fractions were not statistically different (at $p < 0.05$ confidence level) with increasing pressure from 15 MPa to 50 MPa at constant temperature of 120 °C.
- At constant pressure of 15 MPa, removal percentages of PHC F2 and F4 increased with increasing temperature from 30 °C to 120 °C while PHC F3 removal percentages were not statistically different ($p<0.05$). The increase of temperature from 30 °C to 120 °C at 33 MPa pressure did not affect the extraction of PHC F2 considerably. Increasing temperature from 30 °C to 120 °C at 33 MPa pressure resulted in an increase and a decrease in the extraction of PHC F3 and F4 fractions, respectively. In general, the extraction percentages of PHC fractions were not statistically different ($p < 0.05$) with increasing temperature from 30 °C to 120 °C at constant pressure of 50 MPa.
- Increasing pressure from 15 MPa to 50 MPa at constant temperature resulted in higher extraction percentages of PHC fractions except at 120 °C. In general, increasing temperature at constant pressure did not necessarily lead to higher PHCs removal percentages and there was an optimum range for temperature.
- Based on RSM, the optimum pressure and temperature were found to be 50 MPa and 69.3 °C, respectively versus the optimum experimental results of 33 MPa and 75 °C. From a practical point of view, reaching medium pressure (33 MPa) is easier, safer and more

economical than high pressure (50 MPa) accompanied by high extraction removal percentages. Therefore, the best combination for pressure and temperature that led to the highest extraction of PHCs from the spiked sand in this study was selected at medium values for pressure and temperature (33 MPa and 75 °C); which resulted in 99.2%, 91.7% and 86.1% removal for PHC F2, F3 and F4 fractions, respectively.

Appendix: notations

ACS	American Chemical Society
ANOVA	Analysis of variance
CO_2	Carbon dioxide
FID	Flame ionization detector
GC	Gas chromatography
HPLC	High-performance liquid chromatography
K-D	Kuderna-Danish
MOE	Ontario Ministry of Environment
PHC	Petroleum hydrocarbon
RSM	Response surface methodology
SC-CO_2	Supercritical carbon dioxide
SCE	Supercritical extraction
SCF	Supercritical fluid
SFE	Supercritical fluid extraction
SFT	Supercritical Fluid Technologies Inc.
TPH	Total petroleum hydrocarbon
US EPA	United States Environmental Protection Agency

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Chapter 4: Investigation of the Effect of Water Content, pH and Modifier Addition on the PHCs Removal from a Field Contaminated Soil Using Supercritical Fluid Extraction

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Abstract

The influence of soil water content, soil pH and modifier addition on extraction of petroleum hydrocarbons (PHCs) from a field-contaminated soil using supercritical fluid extraction (SFE) was experimentally investigated. SFE experiments were performed at 33 MPa pressure and temperatures of 45 and 75 °C. Three water contents including 8%, 14% and 20% at two levels of pH 6.5 and 7.5 based on a factorial design were investigated. The extraction of total petroleum hydrocarbon fraction (TPHF), the sum of F2, F3 and F4 fractions, decreased by the increase in the water content from 8% to 20% at both pH 6.5 and 7.5. The difference of extractions of all PHC fractions at pH values of 6.5 and 7.5 were not statistically significant at a confidence level of $p < 0.05$ at all three water content levels; and pH did not have a significant influence on the PHC removal efficiency. Addition of acetone and hexanes as modifiers increased PHC removal, however, acetone (33.7% TPHF removal) was more effective than hexanes (24.3% TPHF removal) to decrease the concentrations of PHCs for the field contaminated soil.

KEYWORDS: petroleum hydrocarbon; supercritical fluid extraction; field contaminated soil; soil pH; water content; modifier addition; soil remediation

4.1Introduction

Different activities associated with production, transportation and consumption of fuels may lead to pollution of soils by petroleum hydrocarbons (PHCs) including leakage of fuel from aboveground tanks, railroad cars, underground storage tanks, pipelines, spills around production areas and unsuitable dumping of PHC contaminated wastes (e.g. refinery wastes) [1–4]. Separation-based technologies can be used to remediate contaminated soils. One such process is supercritical extraction (SCE) [5,6]. Supercritical fluids (SCFs) have the ability to extract many organic solutes from aqueous wastes (like wastewater) and solid wastes (like contaminated soils). Many choices of SCFs are available which are low-cost and non-toxic such as carbon dioxide (CO_2), nitrous oxide, H_2O and sulfur hexafluoride. Time requirement and operational costs are the main factors to determine suitability of remediation technologies, which make supercritical fluid extraction (SFE) appear as a potential viable technology for treatment of contaminated soils [5–7]. Extraction of organics from a solid matrix that contains water (soil moisture) is complicated since organic pollutants can exist in four different forms: adsorbed on dry soil, dissolved in soil moisture, adsorbed on soil such that a water layer covers them, and as a separate organic phase. The simplest phase to remove is the separate organic phase, which can be performed by dissolution. On the other hand, it is more complicated to extract other forms since there are various types of equilibrium (soil/water/SCF partitioning) associated with the extraction of different species (water and organic contaminants) [6].

Soil water content could influence the SFE operation and the contaminants removal efficiency. The water available in the soil sample may freeze in the restrictor tip of the SFE apparatus because of the Joule-Thomson cooling effect of the expanding CO_2 at the restrictor outlet. Plugging of the restrictor due to frozen water has been reported to be an issue if the water content is too high [8].

Adding a drying agent to the sample can be used as a good technique to prevent restrictor plugging, although this might result in selectively retaining some analytes. Burford et al. [8] showed that adding drying agents to dry samples (petroleum waste sludge) could retain phenols and anilines, while adding drying agents to wet samples did not retain any analytes. They suggested that drying agents can be added at the outlet end of the extraction vessel instead of mixing with the sample. This solution allowed volatile analytes to be efficiently extracted while preventing restrictor plugging [8]. The presence of low water content (e.g. 1 or 2%) is helpful by making clay surfaces wet [9] or covering areas of entrapment (or adsorption sites). However, higher water content could affect the extraction efficiency [10]. For instance, Hawthorne et al. [11] showed the efficiency of SFE of polycyclic aromatic hydrocarbons (PAHs) from a waste sludge increased when water content was reduced by drying the sample [11]. Lee and Peart [12] compared extraction efficiencies of samples which were dried completely and samples with a low water content (5%), which showed that dry samples resulted in lower extraction efficiencies. Extraction of polychlorinated biphenyls (PCBs) and chlorinated benzenes from dry sediments (zero moisture content) was low, and raising water content (from 11 to 50 wt.%) did not result in a reduction in the extraction efficiency [12].

Bielska et al. [13] compared 25 artificial soils to determine the effects of their physico-chemical properties on the extraction of phenanthrene (PAH). SFE at mild (12 MPa pressure, 50 °C temperature and 30 min extraction time) and harsh (40 MPa pressure, 150 °C temperature and 45 min extraction time) conditions were performed to measure the Phenanthrene extraction. $CaCO_3$ at 0.1 to 0.7% amounts was added to soil samples to adjust their pH to a range of 4.5 to 7.2 with the mean value of 6.1. They concluded that the various pH values had a minor impact on the behaviour of hydrophobic organic contaminants and pH should have more influence on the metals and sequestration of chemicals [13]. In another study by Spack et al. [14], SFE was conducted to extract pendimethalin (herbicide) from soils. They studied 5 different soils with pH in the range of 4.2-8.2. They found that the pH in soil (specially the acidic soil with pH 4.2) did not influence the removal percentage of pendimethalin [14].

Due to the non-polar nature of CO_2, it can be used as SCF in the extraction of non-polar organic compounds such as hydrocarbons. In order to enable CO_2 to extract more polar compounds, modifiers (co-solvents) such as methanol and water are added to enhance the polarity of the fluid. Solubility of polar substances into SCF increases by addition of modifiers and the SCF becomes more powerful to remove pollutants from a soil [10,15]. Modifiers are chosen based on the properties of the soil matrix and analytes and no definite model exists for the selection of a modifier. The polarity of a modifier plays a significant role in the efficiency of SCE [5]. Some favorable modifiers that are frequently used for extraction are methanol, acetone, toluene, hexane and methylene chloride (or dichloromethane). Modifiers can be added to the extraction fluid when using SFE in the three following ways: 1) Direct addition of a modifier to the contaminated soil; 2) Premixed fluids. In this process, the modifier is added to the CO_2 tank (cylinder); and 3) Using a separate modifier pump to add a modifier to the fluid [10].

The effects of addition of co-solvents to SCFs to remove PAHs from real soil samples were investigated by Lutermann et al. [16] and Hollender et al. [17]. In general, when co-solvents with higher concentrations (5-10%) and increased polarity were applied, greater recoveries of PAHs (especially for high molecular weight PAHs) were obtained. They also applied SFE without addition of a co-solvent and they observed that it was not effective enough to remove contaminants from polluted soils. Extraction of PAHs from a soil with high contents of humic acids was enhanced noticeably when co-solvents were used. 10 mol% of methanol was added to SCF and led to higher extractions of PAHs from a soil [16–18]. In a study by Morselli et al. [19], SCF with addition of acetone as a modifier was used to remove saturated and aromatic fractions of crude oil from a spiked sandy clay loam. SFE was conducted in combination of static and dynamic modes. Other experimental conditions were pressure of 22.7 MPa, temperature of 80 °C, 5% (v/v) acetone addition and pure CO_2 density of 0.65 g/mL which resulted in 70-100% recovery of PHCs. Adding modifier at 5% increased the recovery of aromatic fractions, while 10% concentration of modifier decreased removal of both saturated and aromatic fractions [19]. According to Langenfeld et al. [20], PAH and PCB extraction efficiencies from contaminated sediments did not differ significantly with the addition of low concentrations to high concentrations (from 1 to 10% by volume) of modifiers such as acetic acid and aniline. They indicated that the effect of modifier's nature on increasing the recovery was higher than the concentration of a modifier [20].

In summary, the optimum water content for SCE differs for various types of contaminants and conditions and the effect of pH on removal of contaminants from soils was studied to less extent, and specifically, the pH impact on the extraction of PHC fractions using SFE has not been investigated. Also, the addition of modifiers has shown to have different impacts on SCE, which depends on the soil characteristics. The main objectives of this study are the investigation of the effect of soil properties including soil pH and water content on the SFE treatment efficiency and the influence of addition of different modifiers on the PHC extraction from a field-contaminated sand.

4.2 Materials and methods

The experimental procedure is shown in Figure 4.1. After preparing the contaminated soil, a soil sample was taken to measure the PHC concentrations before SFE test as initial concentrations.

SFE test was then performed with another soil sample from the same contaminated soil. The PHC concentrations of a soil after completion of the SFE test were measured as final concentrations. Each SFE test was triplicated. The removal percentages of PHCs were calculated by comparing the initial and final concentrations of PHCs. In order to measure the concentrations of PHCs, four steps including ultrasonic extraction, silica gel column cleanup, Kuderna-Danish (K-D) concentration and gas chromatography (GC) analysis should be conducted sequentially.

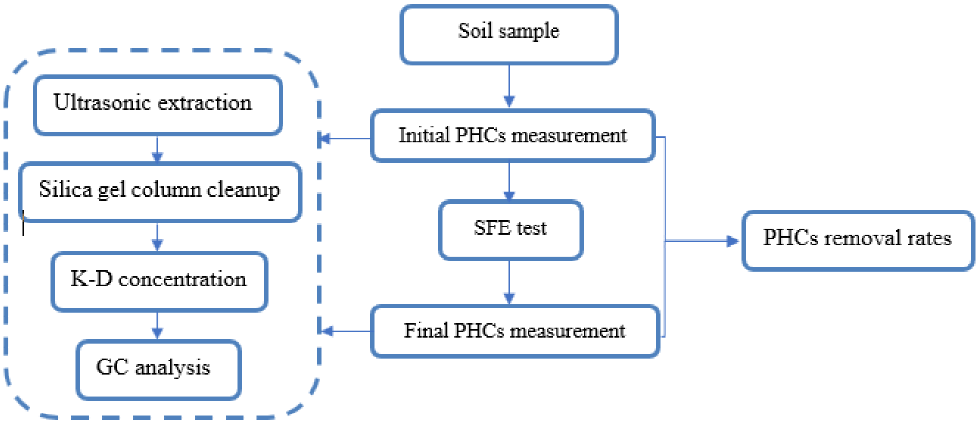

Figure 4.1. Flowchart of the experimental procedure [21]

4.2.1 Soil samples

The soil used for these experiments was a field-contaminated soil. The soil was classified as a poorly graded sand (0.4% gravel, 96.8% sand, 2.8% silt and clay) with a water content of 14% ± 0.6%. The soil was obtained from a site (a gas station) located in Ontario, Canada. The field soil was contaminated (mainly with gasoline) because of leakage from the storage tanks. Rocks and other foreign objects were discarded, and the soil was mixed thoroughly to achieve a homogenous state. The soil was then stored in a refrigerator at a temperature of 4 °C ± 0.5 °C until used for experiments.

4.2.2 PHCs measurement

PHC F2, F3 and F4 fractions were analyzed according to the requirements of Canada-Wide Standard for PHC in soil by Canadian Council of Ministers of the Environment (CCME). The concentrations of PHCs fractions were compared with standards to check if the PHCs concentrations in soil met the criteria which was regulated for different land uses [22]. Based on designated ranges of equivalent carbon number, PHCs fractions are defined as: PHC F2 (>nC_{10} to nC_{16}), PHC F3 (>nC_{16} to nC_{34}) and PHC F4 (>nC_{34} to nC_{50+}) [23]. Percentage removal of PHC fractions (i.e. F2, F3 and F4) were calculated according to Eq. (4.1) by measuring the concentration of PHC fractions before and after each SFE test.

$$PHC(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq. (4.1)}$$

Where C_i and C_f are the initial and final PHC concentrations (mg/kg), respectively. In order to measure the concentrations of PHCs in soil, four steps were conducted consecutively, which are explained briefly in the next sections. It should be noted that several soil samples (before and after SFE test) were sent to an external accredited laboratory as a quality control measure. The differences of the concentrations of PHC fractions between the external laboratory results and this study were less than 15%; which confirms the accuracy of analytical procedure used in this study.

4.2.2.1 Ultrasonic extraction

Ultrasonic is used to extract non-volatile and semi-volatile organic compounds from soils [24]. Ultrasonic irradiation can disrupt the soil particle aggregates by making oscillating cavitational bubbles and shockwaves that would result in the removal of contaminants which are attached to soil particles. Subsequently, the separation of contaminants such as PHCs from soil is facilitated [25]. There are two procedures for ultrasonic extraction according to method 3550C of US EPA (United States Environmental Protection Agency) [24]. These two procedures include low concentration procedure (for contaminants expected having less than or equal to 20 mg/kg concentration) and medium/high concentration procedure (for contaminants expected having concentration greater than 20 mg/kg). These procedures are different in terms of size of soil sample and number of extraction [24]. Medium/high concentration procedure was considered for performing ultrasonic extraction because it was expected that field contaminated soil contained more than 20 mg/kg of PHCs.

Following the medium/high concentration procedure, a 1/8-inch tapered microtip (from "Crystal Electronics Inc.") was attached to the bottom of a 1/2-inch horn. Digital sonifier (450 watts) was supplied from "Branson Ultrasonics Corporation" [24]. Field-contaminated soil was mixed well to be in a homogenous state. Around 2 g of soil was put in a 20-mL glass vial. Anhydrous sodium sulfate (granular), Na_2SO_4, was purified by heating at 400 °C for 4 hours in a shallow tray. Soil samples that were wet and did not have a free-flowing sandy texture was mixed with about 2 g of anhydrous sodium sulfate. The solvent was a mixture of acetone (C_3H6O) and hexanes (C_6H_{14}) with a ratio of 1:1 v/v that were purchased from "Fisher Scientific" at HPLC-grade and also met the ACS (American chemical society) specifications. A required quantity of solvent was added to the soil mixture until reach 10 mL final volume. The ultrasonic's probe was placed inside the vial in a position that was above the soil layer and below the solution surface. Ultrasonic extraction was performed according to a set of preliminary tests that led to the optimum conditions including 2 g soil sample, 2 min extraction duration, 50% amplitude (half power) with mode switch on pulse (no continuous) that was on 50% of time and off 50% of time. The sample was stored in refrigerator after the ultrasonic extraction was finished [24].

4.2.2.2 Silica gel column cleanup

Silica gel column cleanup is performed to selectively remove the polar compounds (naturally occurring non-hydrocarbon polar organic compounds) that might interfere with measurement without removing PHCs [22]. A glass chromatographic column was filled at the bottom with glass wool and then activated silica gel (about 5 g and more than 20 mm) was placed on top. Silica gel was activated before use by drying at a temperature greater than 101 °C overnight. 60 to 200 mesh size of silica gel was supplied from “Acros Organics” [26]. Approximately 10 mm of anhydrous sodium sulfate was placed on top of the silica gel in a column. The solvent was a mixture of hexanes (C_6H_{14}) and dichloromethane (methylene chloride, CH_2Cl_2) with a ratio of 1:1 v/v that were supplied from “Fisher Scientific” at an Optima-grade and also met the ACS specifications. The column was washed first with 10 mL of solvent (this eluant was not collected). The extract from ultrasonic step was poured into a column and then was eluted with minimum 20 mL of solvent. All eluant from the time of addition of extract was collected below the column [22].

4.2.2.3 Kuderna-Danish (K-D) concentration technique

Sample extract was concentrated to 2 mL by K-D before GC analysis by eliminating other solvents including acetone, hexanes and dichloromethane and keeping the toluene. The evaporation flask (500-mL) was attached to the concentrator tube (10 mL) using a clamp. The solvent was a mixture of acetone: hexanes with a ratio of 1:1 v/v. The extract collected in silica gel column step with 20 mL solvent was poured into the K-D [27]. One or two boiling chips (approximately 10-40 mesh) were added to make boiling calmly without bumping [28]. A three-ball Snyder column was attached to the evaporation flask by a clamp. The column was pre-wetted using about 1 mL of solvent. The K-D apparatus (placed in a fume hood) was put on a hot water bath so that the concentrator tube was partially submerged in the hot water and the lower surface of the evaporating flask was bathed with hot water. Considering the boiling point of solvents, water bath's temperature was kept at around 85 °C. Toluene ($C_6H_5CH_3$), purchased from "Fisher Scientific" at an Optima-grade with ACS specifications, was added about (1 mL) by momentarily removing the Snyder column [27]. After several hours and considering the rate of concentrating, the extract about 2 mL could be finally obtained [22]. The K-D apparatus was put away to be cooled down and then the extract can be taken.

4.2.2.4 Gas chromatography (GC)

Measurement of the concentration of PHCs was carried out using a GC (Agilent Technologies - 6890). The detector was flame ionization detector (FID) and the column was HP-1 crosslinked methyl siloxane (30 m × 0.32 mm × 0.25 µm film thickness). 2 µL of the sample dissolved in toluene was injected into the GC by auto sampler. The oven temperature was held at 40 °C for 1 min, and then ramped from 40 to 325 °C at 15 °C/min. The temperature of injector and detector were 340 °C. The GC was calibrated using standards; and calibration curves and retention times were determined accordingly. Standards included identical amounts of n-decane (C_{10}), n-hexadecane (C_{16}) and n-tetratriacontane (C_{34}) hydrocarbons dissolved in toluene and also n-pentacontane (C_{50}) dissolved in toluene but at a different concentration [22]. The chromatogram was obtained by GC as the analysis result. The area under the chromatogram for the peak of nC_{10}, nC_{16}, nC_{34} and nC_{50} correlated to the area for PHC F2, F3 and F4 fractions. According to the calibration curve, the area under chromatogram for each fraction was finally converted to PHC concentration.

4.2.3 Soil pH Measurement

The measurement of soil pH was carried out according to the ASTM D4972-13 (American Society for Testing and Materials). The soil which was used for this method was dried and sieved through a 2-mm (No. 10) sieve. This test method is not recommended for soils with particle sizes larger than 2 mm which may lead to invalid results. A "Hach" pH meter (model HQ40D) with the accuracy of ±0.002 pH was used for pH measurements in two suspensions of water and a calcium chloride solution. pH measurements in both liquids are reported. A calcium chloride stock solution (1.0 *M*) was prepared by dissolving 147 g of calcium chloride dihydrate ($CaCl_2 * 2H_2O$) in water in a 1-L volumetric flask and mixing. Then, a calcium chloride stock solution (0.01 *M*) was made by diluting 20.0 mL of stock 1.0 *M* $CaCl_2$ to 2 L with water. Approximately 20 g of dried soil was placed into a glass container and about 20 mL of water was added. Then, the solution was mixed well. In another glass container, about 20 g of dried soil was placed and was mixed with around 20 mL of the 0.01 *M* $CaCl_2$ solution. Both solutions were left for 1 hr. After this period, pH measurements in both solutions were made using the pH meter [29]. The pH electrode was positioned in the solution just above the soil layer (not inside the soil layer). After each use and before another measurement, the pH electrode was rinsed several times with water.

4.2.4 Statistical methods

Results of experiments for the investigation of the effect of pH, water content and modifier addition were statistically tested using t-tests ($p < 0.05$).

4.3 Experimental setup and procedure of SFE

Three modes of SFE operation include static-, dynamic- and combination-mode. In static-mode, SCF is kept in the extraction vessel (without flow) for a specific period. In dynamic-mode, a steady flow of SCF passes through the extraction vessel. In combination-mode, several cycles of static and dynamic modes are performed consecutively so that dynamic mode follows static mode [3].

SFE experiments were performed using SFT-110 apparatus, which was supplied from "Supercritical Fluid Technologies Inc." (Newark, DE, USA) [30]. Followings are the specifications of SFT-110: pressure and temperature can be operated up to 68.9 MPa and 200 °C, respectively. Flow rate of liquid carbon dioxide can be changed from 0.01 to 24.00 mL/min. The extraction vessel has 100 mL volume. The width, depth and height of apparatus are 29 cm, 57 cm and 67 cm, respectively [30].

The schematic diagram of the laboratory SFT-110 apparatus which was used in this research is shown in Figure 4.2. CO_2 was transferred from a cylinder (liquid state with a dip tube) pressurized by a dual piston pump. The contaminated soil was placed in the 100-mL extraction vessel (cell or reactor), which was enclosed by a heating unit. The apparatus had two main valves including a static/dynamic valve and a restrictor valve. The static/dynamic valve was used to alternate between static and dynamic mode, and the restrictor valve controlled the flow rate of CO_2 in dynamic mode. A flow meter was also used to measure the flow rate of expanding CO_2 gas. SCF extracted contaminants from soil in the extraction vessel and then SCF along with the extracted contaminants were released through the restrictor valve to a collection vial. At restrictor valve, CO_2 with dissolved contaminants were stepped down from supercritical state to atmospheric pressure [30]. At this point, because of decrease of pressure of fluid (not in supercritical state), the solubility of extracted contaminants may decrease that would result in the separation of contaminants form the fluid [3,31]. The rupture disk (acting mechanically against accidental over-pressure conditions) and collection vial were connected to a fume hood for ventilation purposes [30]. Then, the treated soil sample was analyzed for PHCs.

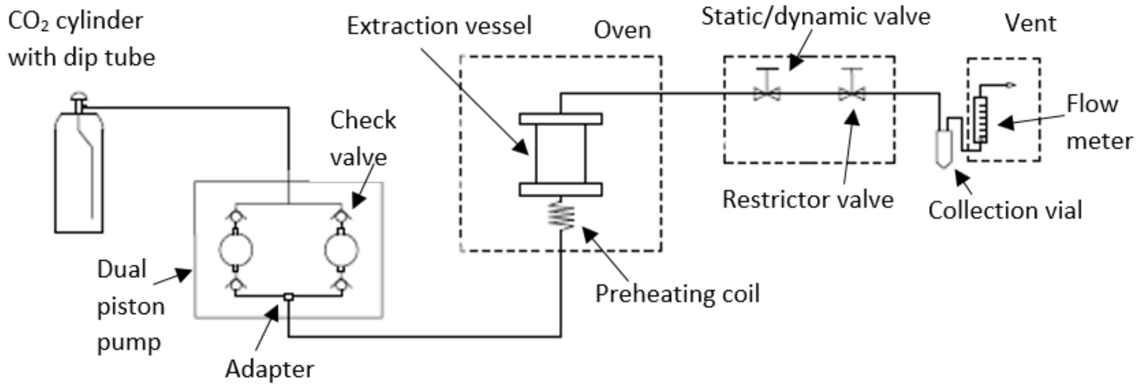

Figure 4.2. SFT-110 apparatus [30]

4.3.1 Assessment of water content and pH

To assess the effect of soil moisture on PHC extraction, three different gravimetric water contents including 8%, 14% and 20% were studied. The natural water content of the field contaminated soil was approximately 14% ± 0.6%. The other two water contents (i.e. 8% and 20%) were obtained by adding distilled water to dried samples of the field contaminated soil. The soil samples were initially dried and weighed. Then, the required quantity of distilled water was added to soil samples in order to obtain the target water content, i.e. 8% ± 0.8 and 20% ± 0.7.

The effect of pH on PHCs removal was also investigated. Common pH values for soils found in the literature were mostly in the range of 6 to 8 [13,14]. Therefore, two pH values of 6.5 and 7.5 were selected in this research. The field-contaminated soil had a pH about 6.5. The pH 7.5 was adjusted by adding calcium hydroxide, $Ca(OH)_2$, at a low percentage (less than 0.1 wt%) to the field-contaminated soil. $Ca(OH)_2$ certified ACS, was supplied from “Fisher Scientific”. The effect of water content and pH were considered together based on a factorial design as presented in Table 4.1.

Table 4.1. Combinations of pH and water content levels

pH value	Water content
6.5	8%
6.5	14%
6.5	20%
7.5	8%
7.5	14%
7.5	20%

SFE for each test was performed with the following conditions: 33 MPa pressure, 75 °C temperature and flow rate of 24 mL/min of liquid CO_2. The time duration was the combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles (60 min in total). This combination of static and dynamic mode for 60 min was the best extraction mode and time duration for PHCs extraction, which was selected based on another phase of the authors' research [21]. Approximately 100 g to 120 g field contaminated soil was placed in the extraction vessel. These conditions were fixed for all experiments to negate their effects and only allow pH and water content to influence results. All experiments were performed in triplicates (18 tests in total).

4.3.2 Assessment of modifier addition

According to the literature on the effect of modifier, the most favorable modifiers which were frequently used for the remediation of petroleum contaminated soil by SFE were: acetone, methanol, toluene and hexanes. Acetone (C_3H_6O) and hexanes (C_6H_{14}) both with HPLC-grade and methanol (CH_4O) and toluene ($C_6H_5CH_3$) at an Optima-grade were supplied by "Fisher Scientific". In a preliminary set of tests, these four modifiers were added to the field-contaminated soil by 5% volume and SFE tests were conducted at 33 MPa pressure and 45 °C temperature with 10S+10D × 3C time duration. This combination of static and dynamic mode for 60 min was the best extraction mode and time duration for PHCs extraction which was selected based on another study

[21]. Two modifiers with the highest removal percentages of PHC fractions were then selected, which were acetone and hexanes.

4.4 Results and discussion

4.4.1 Effect of pH and water content

As indicated in Table 4.1, experiments were performed based on a factorial design with 2 levels of pH and 3 levels of water contents. The initial concentrations of the field-contaminated soil over duration of the experiments changed slightly. In order to keep track of this change, regular samples were collected and analyzed to determine the contamination level of the soil before treatment. After water content and pH were adjusted and before conducting each SFE test, a soil sample was analyzed for PHC concentrations. The averages of initial PHCs concentrations of the field-contaminated soil (for 6 soil samples) were 524.3 ± 128.4 mg/kg for F2, 15320.2 ± 778.2 mg/kg for F3 and 2970.4 ± 97.7 mg/kg for F4. Comparing the initial PHCs concentrations with the Ontario Ministry of Environment (MOE), "Table 2- under Industrial/ Commercial/ Community property use" [32] shows that PHC F2 and F3 fractions were above the table limits, which are 230 mg/kg for F2 and 1700 mg/kg for F3. However, PHC F4 fraction was close to the table limit, which is 3300 mg/kg for F4 [32].

Figure 4.3 shows the effect of water content on the extraction of each PHC fractions at pH 6.5 and 7.5. The increase in water content from 8% to 20% led to a statistically significant ($p < 0.05$) reduction in the extraction of PHC F3 at both pH 6.5 and 7.5. The highest extraction percentage of PHC F3 was obtained at 8% water content for pH 6.5 (54.6%) and pH 7.5 (49.3%). When water content increased from 8% to 20%, the extraction percentage of PHC F3 decreased by 37.5% and 24.7% at pH 6.5 and 7.5, respectively. The variation and trend observed for PHC F2 and F4 fractions were not statistically significant. In other words, variations in water content did not affect the PHC F2 and F4 removal percentages significantly.

PHC F3 fraction removal percentages for 8%, 14% and 20% water contents at pH 6.5 were compared statistically and t-test results are presented in Table 4.2. According to the results, there were significant differences observed for PHC F3 removal percentages between water contents of 8% vs. 20%; 8% vs. 14%; 14% vs. 20% at pH 6.5 since p-value of two-tail for each pair was lower than 0.05 ($p < 0.05$). It should be noted that t-test results for pH 7 were not presented here, however, their effects were discussed in the context.

Table 4.2. t-test results for paired comparison of water contents (W.C.) at pH 6.5 for PHC F3 removal percentages

	W.C. 8%	W.C. 20%	W.C. 8%	W.C. 14%	W.C. 14%	W.C. 20%
Mean	54.63	17.17	54.63	41.27	41.27	17.17
Variance	27.50	78.64	27.50	16.06	16.06	78.64
Observations	3	3	3	3	3	3
Pooled variance	53.07		21.78		47.35	
Hypoth. mean difference	0		0		0	
df	4		4		4	
t Stat	6.30		3.51		4.29	
$P(T \leq t)$ two-tail	0.00325		0.02473		0.01275	
t critical two-tail	2.78		2.78		2.78	

Water can increase the extraction of contaminants by two processes: water can act like a polar modifier, or by affecting the adsorption. In the first case, water can act like a polar modifier as water is partially soluble in supercritical carbon dioxide (SC-CO_2) [14,33]. The solubility of water in SC-CO_2 at 20.26 MPa pressure and 49.85 °C temperature is 0.0102 molar fractions [34]. A part of soil water, that includes contaminants like PHCs, can be dissolved in SCF that would enhance the extraction [14]. The second mechanism represents the major effect of water as it makes contaminants more accessible to SCF so that they can be transported faster [14,33]. However, this second effect requires that the SCF penetrates into the soil matrix, which may not always be easily achievable [14]. The soil aggregate consists of individual soil mineral grains and natural organic matter and has a finite internal porosity. The desorption of contaminants from the soil into SCF is done within the internal pores of the soil that leads to the extraction of contaminants. Therefore, a certain quantity of water is required to fill the internal pores; which could enhance the extraction of contaminants. After internal pores are filled with water, the excess water forms a thin water film around soil particles. As a result, this additional layer acts as a barrier that can resist the diffusion of contaminants though it. As the water content increases, the water film around each particle starts to form a bridge between particles. In this manner, the water path for displacing contaminants would be longer and interfacial areas between SC-CO_2 and water film would be less [35]. In summary, water could improve the extraction of contaminants up to a certain quantity; beyond this point, a further increase of water content would decrease the removal percentage of contaminants.

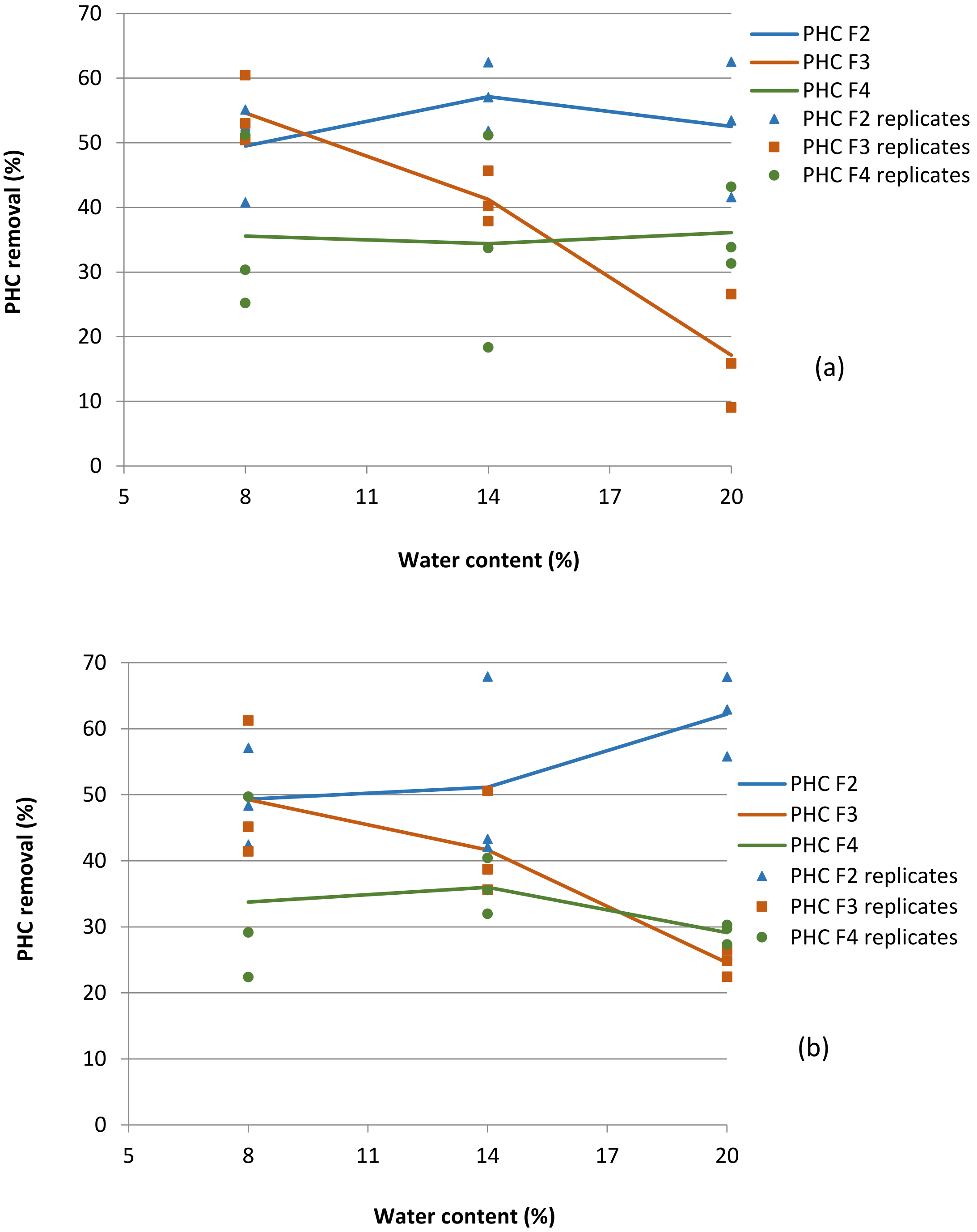

Figure 4.3. Effect of water content on the extraction of PHC fractions at (a) pH 6.5 (b) pH 7.5

As seen in Figure 4.3, the average extraction percentage of PHC F2 at pH 6.5 and 14% water content was 57.2% compared to 41.3% for F3 fraction, which was statistically different at $p < 0.05$. The extraction percentage of PHC F2 (52.5% at pH 6.5 and 62.2% at pH 7.5) was statistically ($p < 0.05$) higher than F3 fraction (17.1% at pH 6.5 and 24.6% at pH 7.5) at 20% water content. PHC F2 fractions are considered as light extractable PHCs in soil and have lower molecular weight than PHC F3 fractions. Therefore, the displacement of PHC F2 would be easier than PHC F3. In addition, PHC F2 is more soluble than PHC F3. Therefore, high water content (20%) could displace more PHC F2 than PHC F3 and led to a higher extraction of PHC F2. Furthermore, a possible explanation for lower PHC F3 removal percentage could be that PHC F3 fractions may be less accessible than F2 fractions due to different interactions with the soil matrix such as being adsorbed on a soil which is covered by a water layer, or agglomeration of the soil particles that makes the transportation of contaminants more difficult.

PHC F2 and F3 fractions removal percentages at pH 6.5 and 7.5 for 20% water content were compared statistically and t-test results are presented in Table 4.3. According to these results, there were significant differences observed for 20% water content between PHC F2 vs. F3 at pH 6.5 and 7.5 since p-value of two-tail for each pair was lower than 0.05 ($p < 0.05$). It should be noted that t-test results for other conditions were not presented here, however, their effects were discussed in the context.

Table 4.3. t-test results for paired comparison of removal percentages of PHC F2 and F3 fractions at pH 6.5 and 7.5 for 20% water content

	pH 6.5		pH 7.5	
	PHC F2	PHC F3	PHC F2	PHC F3
Mean	52.50	17.17	62.20	24.53
Variance	109.81	78.64	36.97	4.05
Observations	3	3	3	3
Pooled variance	94.23		20.51	
Hypoth. mean difference	0		0	
df	4		4	
t Stat	4.46		10.19	
$P(T\leq t)$ two-tail	0.01118		0.00052	
t critical two-tail	2.78		2.78	

Figure 4.4 shows the effect of pH on the extraction of PHC fractions at constant water content. The difference of extractions of all PHC fractions at pH values of 6.5 and 7.5 were not statistically significant ($p < 0.05$) at all three water content levels. Overall, pH did not have a significant influence on the PHC removal efficiency. This conclusion that pH could not impact the extraction efficiency of PHCs significantly was also stated by Bielska et al. for SFE of PAH from soils with pH in the range of 4.5-7.2 [13].

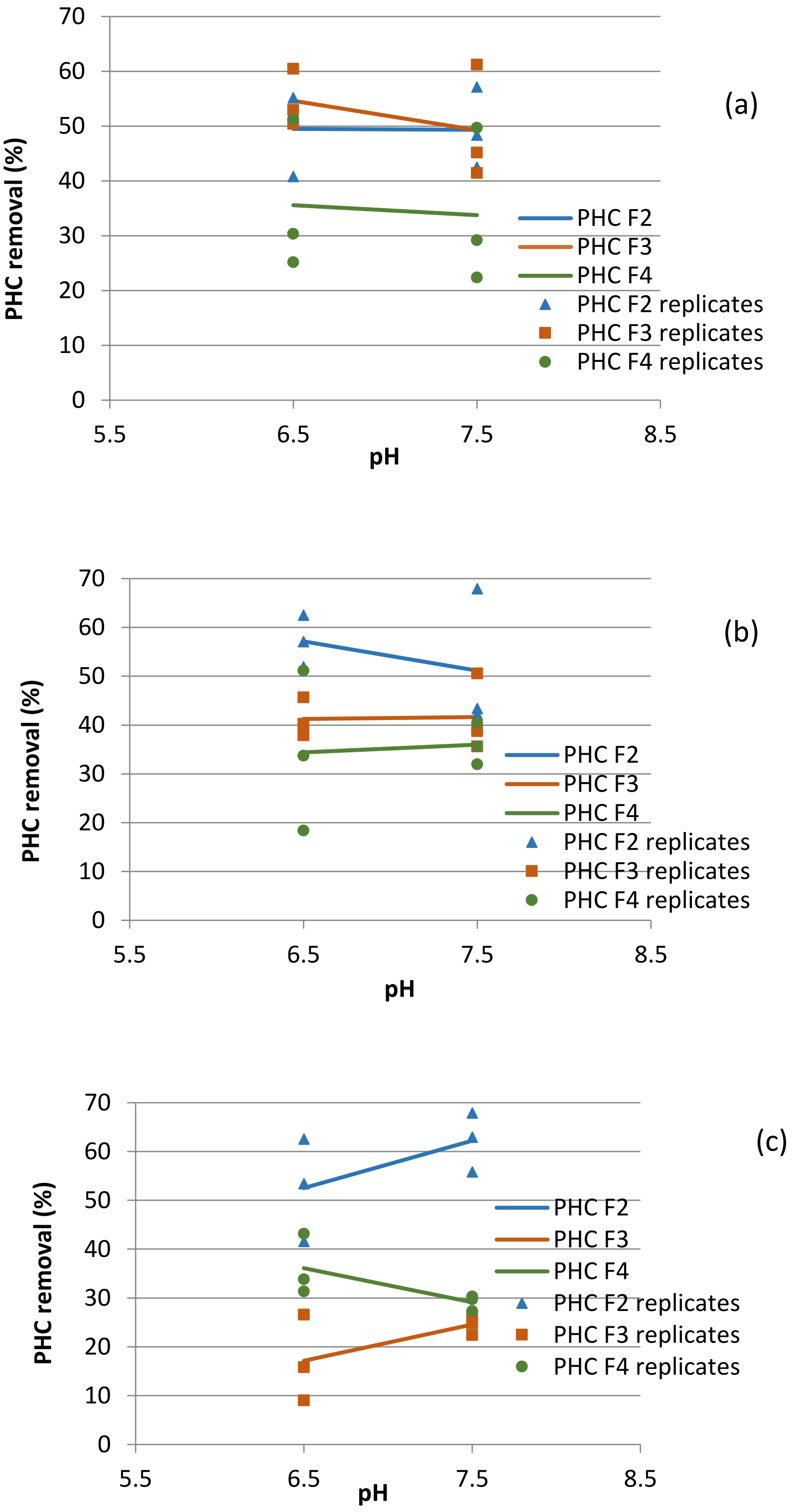

Figure 4.4. Effect of pH on the extraction of PHC fractions at constant water content (a) 8% (b) 14% (c) 20%

Total petroleum hydrocarbon fractions (TPHF) in this study is defined as the sum of PHC F2, F3 and F4 fractions. Figure 4.5 shows the effect of pH on TPHF removal percentages at different water contents. The percentage differences for the TPHF extraction by the pH variation were not statistically significant ($p < 0.05$). Therefore, the increase in pH generally did not affect the TPHF removal percentage remarkably. This conclusion that pH did not impact the extraction efficiency of contaminants was also stated by Spack et al. for SFE of herbicide from soils with pH in the range of 4.2-8.2 [14]. As for water content, the extraction of TPHF decreased by the increase in water content from 8% to 20% for both pH 6.5 and 7.5. Creation of a thin water layer around soil particles by increasing water content, can act as a barrier for separation of contaminants that would lead to a reduction in TPHF removal percentages. This also resulted in decreasing the mass transfer of the contaminants from the soil to SCF that led to lower PHC extraction. It should be noted that the differences of TPHF removal percentages between 8% and 14% water contents at pH 6.5 and 7.5 were not statistically significant ($p < 0.05$), however, TPHF removal percentages between 14% and 20% at pH 6.5 and 7.5 were statistically significant.

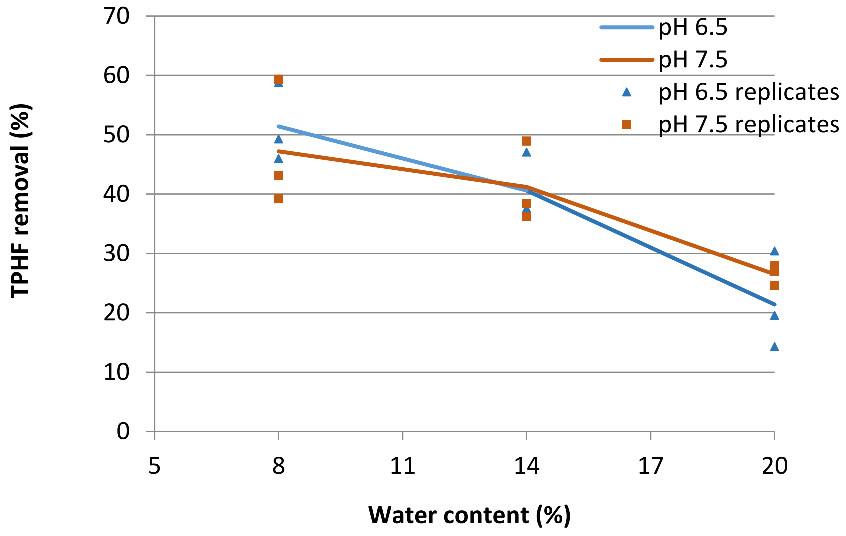

Figure 4.5. Effect of pH on TPHF removal percentages at different water contents

4.4.2 Effect of modifier

As stated before, two out of four initial modifiers with the highest PHC removal percentages were selected, which were acetone and hexanes. The results of preliminary tests for four modifiers tested are presented in Table 4.4.

Table 4.4. Results of preliminary tests (removal percentage) for selection of modifiers

Initial selection of modifiers	PHC F2 removal percentage	PHC F3 removal percentage	PHC F4 removal percentage
Acetone	46.4%	43.7%	29.4%
Methanol	37.1%	30.6%	18.2%
Toluene	47.1%	31.1%	16.3%
Hexanes	50.6%	34.6%	21.7%

There were 3 experiments (addition of acetone, hexanes and control sample without addition of a modifier) and all tests were triplicated (9 tests in total). SFE was conducted for each test with the following conditions: 33 MPa pressure, 45 °C temperature and flow rate of 24 mL/min of liquid

CO_2. The time duration was the combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles (60 min in total). Approximately 110 g field contaminated soil was placed in the extraction vessel. Modifiers (acetone and hexanes) were added directly to soil samples with a ratio of 5% by volume of a soil in the extraction vessel. Since the boiling points of modifiers are different (boiling points of acetone and hexanes are 56 °C and 69 °C, respectively), SFE tests were conducted with a temperature of 45 °C (slightly lower than 75 °C which was used for the effect of pH and water content) to be safe and being consistent.

After addition of modifier to soil and before conducting each SFE test, a soil sample was taken to measure the initial PHC concentrations. The averages of initial PHCs concentrations of the field contaminated soil (for 3 soil samples) were 514.9 ± 14.4 mg/kg for F2, 13998.9 ± 838.3 mg/kg for F3 and 2101.9 ± 107.8 mg/kg for F4.

Figure 4.6 shows how modifiers affect the removal of PHC fractions. Overall, the addition of both modifiers (acetone and hexanes) led to lower concentrations of PHCs for the field-contaminated soil. However, as can be seen, acetone was far more effective than hexanes. PHC F2 removal percentage by acetone was not statistically different (at $p < 0.05$ level) than hexanes while PHC F3 and F4 removal percentages by acetone (34.4% for F3 and 26.2% for F4) was statistically greater than hexanes (25.5% for F3 and 11% for F4). The yield obtained by acetone overall was greater than hexanes that showed acetone had more capability than hexanes to extract PHCs. The polarity (and solubility in water) of acetone is greater than hexanes [36], which may contribute to higher extraction of PHC. The difference in polarity may affect the interactions between the modifier and the soil matrix [17]. Therefore, acetone might be more capable than hexanes to break the interactions between the soil matrix and hydrocarbons that could result in separation of more hydrocarbons from a soil.

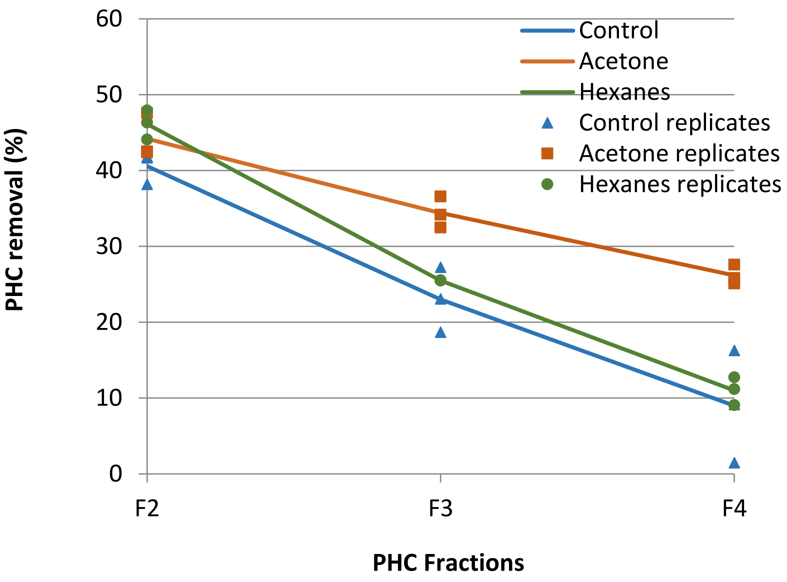

Figure 4.6. Effect of modifiers on removal of PHC fractions

PHCs removal percentages for acetone and hexanes were compared statistically and t-test results are presented in Table 4.5. According to these results, PHC F2 removal percentages between acetone vs. hexanes were not statistically different while there were significant differences observed for PHC F3 and F4 removal percentages between acetone vs. hexanes since p-value of two-tail for F3 and F4 fractions were lower than 0.05 ($p < 0.05$). It should be noted that t-test results for other conditions were not presented, however, their effects were discussed in the context.

Table 4.5. t-test results for paired comparison of acetone and hexanes for PHCs removal

	PHC F2		PHC F3		PHC F4	
	Acetone	Hexanes	Acetone	Hexanes	Acetone	Hexanes
Mean	44.17	46.10	34.43	25.50	26.17	11.03
Variance	8.84	3.64	4.24	0.00	1.66	3.44
Observations	3	3	3	3	3	3
Pooled variance	6.24		2.12		2.55	
Hypoth. mean difference	0		0		0	
df	4		4		4	
t Stat	-0.95		7.51		11.60	
P(T≤ t) two-tail	0.39691		0.00168		0.00032	
t critical two-tail	2.78		2.78		2.78	

There were not statistically significant differences (at $p < 0.05$ level) in PHC F2 extractions by acetone addition and control sample. However, removal percentages of PHC F3 (34.4%) and F4 (26.2%) by acetone were greater than removal percentage of PHC F3 (23.0%) and F4 (9.0%) in control sample. The PHC F2 removal percentage of hexanes was 5.5% greater than control sample while the removal percentages of PHC F3 and F4 fractions obtained for control sample and hexanes addition were not statistically different. As a result, hexanes as a modifier did not act successfully for the extraction of PHCs from the field contaminated soil.

Furthermore, PHC F2 and F4 showed the highest and the lowest removal percentages among all PHC fractions by addition of a modifier, respectively. Since solubility of PHC F2 is more than PHC F4 fraction, PHC F2 could be dissolved easier. Besides, PHC F4 has higher molecular mass than PHC F2 that could make their extraction more difficult. Also, there might be a possibility that the interactions between PHC F4 and soil matrix might be stronger than PHC F2 that may cause lower PHC F4 removal percentages than PHC F2 fraction.

The enhancement in recoveries of PHC fractions and TPHF using modifiers are shown in Table 4.6. The enhancement in recovery was calculated as the ratio of the amount of PHC concentration extracted with addition of a modifier divided by the amount of PHC concentration extracted without addition of a modifier (control sample). Since acetone showed higher ratios of recovery enhancement than hexanes (except for PHC F2), acetone was overall a better modifier. In addition, acetone was a powerful modifier specifically to improve the recovery of PHC F4 (ratio 3.2), which had a high molecular weight. The extraction of TPHF was also enhanced by the addition of acetone (ratio 1.7) more than the addition of hexanes (ratio 1.2).

Table 4.6. Ratio of recovery enhancement using modifiers compared to control sample

	Modifier	
	Acetone	Hexanes
PHC F2	1.2	1.2
PHC F3	1.7	1.2
PHC F4	3.2	1.2
TPHF	1.7	1.2

Figure 4.7 shows the effect of modifiers on TPHF removal. Similar results as for PHC fractions were observed for the extraction of TPHF. Acetone showed a higher TPHF removal percentage (33.7%) than hexanes (24.3%). Addition of acetone enhanced the extraction percentage of TPHF by 11.9% compared to the control sample (without using a modifier). The extraction percentage of TPHF by hexanes was not statistically different ($p < 0.05$) than the control. Overall, the addition of a modifier to the contaminated soil increased the extraction of PHCs. Modifiers can improve the extraction of contaminants from soil by two processes. Firstly, some modifiers can enhance the process of extraction since they would enhance the mass transfer of some contaminants [6,37]. Consequently, the diffusion of those contaminants inside the pores of a soil may be simplified [38]. Secondly, some modifiers would help the removal of some contaminants from the soil matrix [39,40]. As a result, the interactions between hydrocarbons and soils might be broken due to the presence of modifiers [17,37].

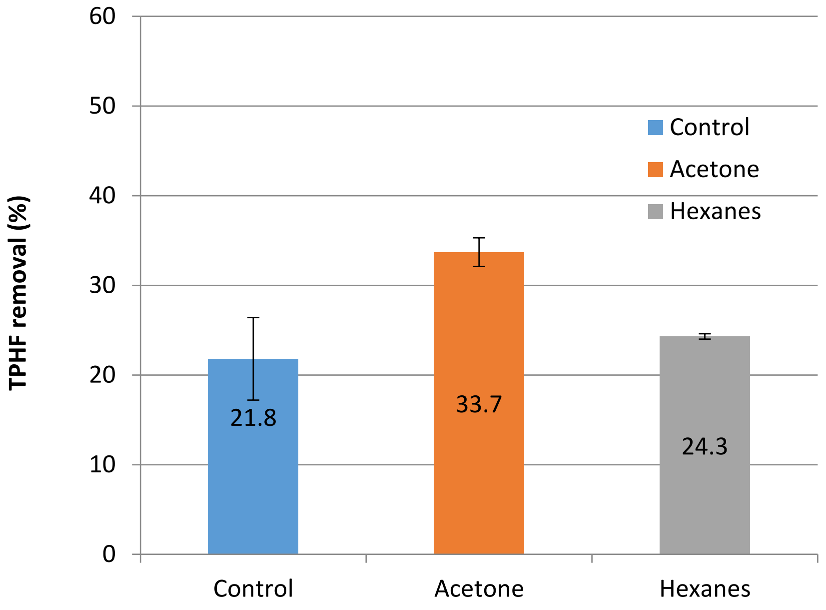

Figure 4.7. Effect of modifiers on TPHF removal

4.5 Conclusion

The following conclusions can be drawn from this study:

- The increase in water content from 8% to 20% led to a statistically significant reduction in the extraction percentage of PHC F3 at both pH 6.5 and 7.5. The highest extraction of PHC F3 was obtained at lowest water content (8%) for both pH levels. However, variations in water content did not affect the PHC F2 and F4 removal percentages significantly. The extraction percentage of PHC F2 was statistically higher than F3 fraction at 20% water content for both pH levels.

- The extraction of TPHF decreased by the increase in water content from 8% to 20% for both pH 6.5 and 7.5.
- The differences in the extractions of PHC fractions and TPHF at pH values of 6.5 and 7.5 were not statistically significant at all three water content levels. Therefore, pH variation overall did not have a significant influence on the PHC and TPHF removal efficiency within the studied range of pH.
- Acetone was more effective than hexanes. PHC F2 removal percentage by acetone was not statistically different than hexanes while PHC F3 and F4 removal percentages by acetone was much greater than hexanes.
- The removal percentages obtained for F3 and F4 fractions for control (without addition of a modifier) and hexane addition were not statistically different. As a result, hexanes as a modifier did not act successfully for the extraction of PHCs from this field contaminated soil.
- Addition of acetone enhanced the extraction percentage of TPHF by 11.9% compared to the control sample (without using a modifier). Acetone showed a higher TPHF removal percentage than hexanes. The extraction percentage of TPHF by hexanes was not statistically different than the control. PHC F2 and F4 showed the highest and the lowest removal percentages among all PHC fractions by addition of a modifier, respectively.

Appendix: notations

ACS	American Chemical Society
ASTM	American Society for Testing and Materials
CO_2	Carbon dioxide
FID	Flame ionization detector
GC	Gas chromatography
HPLC	High-performance liquid chromatography
K-D	Kuderna-Danish
PAH	Polyaromatic (polycyclic aromatic) hydrocarbon
PCB	Polychlorinated biphenyl
PHC	Petroleum hydrocarbon
SC-CO_2	Supercritical carbon dioxide
SCE	Supercritical extraction
SCF	Supercritical fluid
SFE	Supercritical fluid extraction
SFT	Supercritical Fluid Technologies Inc.
TPHF	Total petroleum hydrocarbon fractions
US EPA	United States Environmental Protection Agency

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Chapter 5: Assessment and Comparison of PHCs Removal from Three Types of Soils (sand, silt loam and clay) using Supercritical Fluid Extraction

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Abstract

Supercritical fluid extraction (SFE) was applied to investigate the removal of petroleum hydrocarbons (PHCs) from contaminated soils. Per an initial set of tests for different extraction modes and time durations, the combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles for a total time of 60 min resulted in the highest PHCs removal percentages. SFE experiments were performed at 33 MPa pressure and 75 °C temperature to investigate the influence of soil texture and grain size. Three types of soils were formed and then were spiked with diesel fuel with a ratio of 5 wt%. Soil A, B and C had different particle sizes and were categorized as sand, silt loam and clay, respectively. Soil A (sand) which had the largest particle size resulted in the highest total petroleum hydrocarbon fractions (TPHF), sum of PHC F2, F3 and F4 fractions, removal percentage (90.4%) while soil C (clay) with the smallest particle size and the highest clay content led to the lowest TPHF removal percentage (47.4%). PHC F2 removal percentage for soil A (sand) was 27.3% greater than soil B (silt loam), and the removal efficiency for soil B was 20.4% higher than soil C (clay). While the similar trend was observed for the extraction of PHC F3, the extraction efficiency of PHC F4 for soil A, B and C were not statistically significant. Regarding soil A (sand), the extraction efficiency for PHC F2, PHC F3 and PHC F4 were 98.4%, 92.7%, and 50.2%, respectively. For soil C (clay), the removal efficiency of all PHC fractions were not statistically different.

Keywords: petroleum hydrocarbon; supercritical fluid extraction; contaminated soil; soil grain size; statistical analysis

5.1 Introduction

Approximately 300,000 contaminated sites existed in the United States [1,2] and about 30,000 brownfields have also been reported in Canada that need to be managed and/or treated in the early 2000s [3]. In Canada, petroleum hydrocarbon (PHC) contamination is the primary source of pollution in about 60% of these contaminated sites [4,5]. PHCs have been classified as priority environmental pollutants by the US Environmental Protection Agency (US EPA) due to their impact on human health and environment, representing a huge concern for the general public [2,6]. Some of these contaminated sites have been abandoned because of pollution. This implies major costs related to decreasing productivity and monetary depreciation of the impacted sites for future use. If they are remediated, they will have positive effects on the economy and society. Therefore, remediation techniques have been considered to decontaminate these polluted sites [3]. Despite the fact that there are various techniques to treat contaminated sites, their applications may be limited due to different parameters such as costs, time and efficiency [2,7]. Some treatment technologies are only suitable for a specific pollutant and they do not work well for other sources of contaminations. Similarly, some treatment technologies may be effective for some soil types, but they may not be applicable for other soil types [8]. Among current technologies for soil remediation, supercritical fluid extraction (SFE) is a recent and promising method, which is considered a solvent extraction method in the class of physical/chemical technologies [9,10]. When a compound is in supercritical state, it shows properties similar to both gases and liquids and in fact it intermediates between those properties [2,11]. However, it stands as a single fluid phase [2,12]. Mass transfer is quick within the supercritical state. In addition, changes in pressure and temperature may change the viscosity and diffusivity. In other words, the solvating power of the fluid can be tuned by applying different pressures and temperatures [9,13,14].

Characteristics of a soil that can influence the extraction are the soil type and particle size distribution (i.e. quantities of sand, silt and clay that form the soil), mineralogy, particle's shape and surface area, porosity, organic matter content and soil moisture content [2,15–20]. Although some researchers expressed that the effect of soil type could not be determined properly due to complicated interactions between soil particles and pollutants, soil type could have an effect on the extraction efficiency of polluted soil [8]. If there are specific interactions between solutes and matrix active sites, it may affect the extraction process noticeably [19,20]. Soil components (especially clay) are able to interact with analytes [21]. The nature of analyte-matrix interactions between pollutants and heterogeneous soil is not well understood, and it seems that there could be potentially various types of interactions with regards to composition of individual matrix components. Therefore, pollutants may be associated with inorganic (e.g. alumina, silica) and/or organic (e.g. humic and fluvic) active sites of soil, each with different binding strengths [22] that may lead to a different extraction recovery [2]. The analyte-soil interactions can be Van der Waals forces, electron donor-acceptor interactions and hydrogen bonding [21]. In addition, some physical obstructions can hinder extraction, for example pollutants could be located between clay surfaces, or pollutants may be masked by organic matter or water which limits their exposure [22]. In general, removal of contaminants by SFE process from solid matrices (specifically from porous materials like soil) can be assumed to involve the following phases: (1) penetration of supercritical fluid (SCF) into internal structure of porous material, (2) dissolution of solute into supercritical matrix, (3) diffusion of the mixture of solute and supercritical matrix to solid interface, and (4) diffusion of mixture to bulk SCF [12]. Therefore, solid matrix properties such as pore size and connectivity are critical, due to SCF need to be distributed in the solid matrix during SFE. Particle size also affects the SFE significantly. Particle size in the solid matrix (specifically porous materials like soil) influences the SFE of contaminants because of changing the diffusion path [12]. Sample size is one of the characteristics of the solid matrix that would affect the SFE as well. Some factors should be considered to determine the sample size required for extraction including the detection limit of the analytical method and the size of the extraction vessel [22,23]. Soil samples required for performing SFE on the laboratory scale are commonly small [24], however, the application of SFE at large scale needs to be investigated as well. For example, removal of polychlorinated biphenyls (PCBs) from contaminated harbor sediments in pilot-scale SFE unit was conducted by CF Systems Corporation [25].

Chen et al. (1997) [26] studied PCBs removal from contaminated soils and sediments by SFE. They investigated three soil types including sand, till and clay. Sand and clay had the lowest and the highest percentages of clay, respectively. In addition, total organic carbon (TOC), which is related to organic matter content, was the lowest for sand and the highest for clay. Till was composed of 81.2% sand, 12.5% silt and 6.3% clay. Till had the clay percentage and TOC quantities between those of sand and clay. Based on the obtained results, sand had the fastest PCBs removal among these three soil types. They also compared the PCBs removal for air-dried clay and till samples. The desorption rates of PCBs in clay was lower than till since clay had higher clay and organic matter contents. Higher organic matter and clay contents led to a decrease of PCBs extraction rates. The authors concluded that extraction of pollutants from soils that had lower percentages of clays was easier than those soils having higher amounts of clays; i.e. SFE of clay soil is more difficult than sandy soil [26]. Also, higher organic contents in soil led to lower recovery compared to the soils contain lower organic matter [26,27]. In addition, SFE recovery can be affected by the clay type (swelling vs. non-swelling) if water is available [20,24]. Chen et al. (1997) [26] also compared PCBs removal from real samples and spiked samples. Spiked samples showed greater and faster extraction rates than real field-contaminated samples. Their results indicated that PCBs were bound stronger to real field-contaminated samples than spiked samples [26].

The soil grain size has great importance on supercritical fluid extraction of petroleum contaminated soils and there is a need to further investigate their impacts on the extraction of PHC fractions, which has not been reported before. Thus, the main objective of this study is the investigation of the effect of soil particle sizes on SFE treatment efficiency for PHC removal using statistical analysis

5.2 Materials and methods

Figure 5.1 presents the general experimental procedure and steps that were followed in this study. After preparation of the spiked soil samples, the initial concentrations of PHCs were measured. Then, a soil sample was taken to conduct the SFE test. Each test was replicated three times. After the SFE test was finished, the final concentrations of PHCs were measured. The initial and final PHCs measurements were used to calculate the PHCs removal percentages. Four consecutive steps were used for PHCs measurement including ultrasonic extraction, silica gel column cleanup, K-D concentration and gas chromatography (GC) analysis.

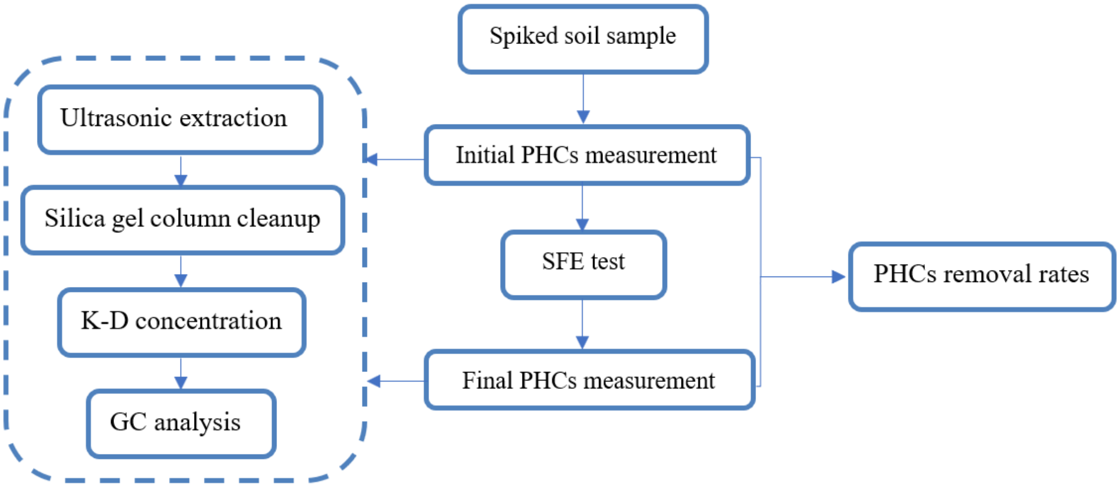


Figure 5.1. Flowchart of the experimental procedure

5.2.1 Soil samples

Three initial sources of soils including sand, silt and clay were chosen. These soils were mixed with various percentages to form three types of soils with different grain size distributions. Each soil was then spiked with diesel fuel with a ratio of 5 wt%. Diesel fuel which was used for spiking soil samples was obtained from a gas station. The required amount of soil and diesel fuel based on 5 wt% were mixed thoroughly to achieve a homogenous state. The spiked soil samples were then placed in amber color glass jars with Teflon-lined caps to minimize any potential degradation due to light. All prepared soil samples were stored in a refrigerator for one month at a temperature of 4 °C ± 0.5 °C until used for experiments. One-month storage time was considered to give enough time for binding diesel fuel to soil matrix.

5.2.2 PHCs measurement

PHC F2, F3 and F4 fractions were analyzed according to Canada-Wide Standard requirements. The concentrations of the PHCs fractions were compared with regulatory standards to check if the soil met the acceptable criteria for different applications [28]. Based on designated ranges of equivalent carbon number, PHCs fractions are defined as: PHC F2 (>nC_{10} to nC_{16}), PHC F3 (>nC_{16}

to nC_{34}) and PHC F4 ($>nC_{34}$ to nC_{50+}) [29]. Percentage removal (or percentage decrease) of PHC fractions for each SFE test were calculated according to Eq. (5.1).

$$PHC(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq. (5.1)}$$

Where C_i and C_f are the initial and final PHC fraction concentrations (mg/kg), respectively. In order to measure the concentration of hydrocarbons in a soil, the following four steps were conducted consecutively: ultrasonic extraction, silica gel column cleanup, K-D concentration and GC analysis. A brief procedure for each step is presented in the following sections.

5.2.2.1 Ultrasonic extraction

Non-volatile and semi-volatile organic compounds can be separated from solids including soils by ultrasonic extraction [30]. Ultrasonic irradiation produces oscillating cavitation bubbles and shockwaves that can break the soil particle aggregates and enhance separation of target contaminants from the soil surface; and can consequently reach the inner space of the soil structure. As a result, the separation of contaminants such as PHCs which are attached to soil particles is feasible by ultrasonic extraction [31]. US EPA SW-846 Test Method 3550C [30] defines two procedures of ultrasonic extraction for low concentration (concentrations less than or equal to 20 mg/kg) and medium/high concentration (concentrations greater than 20 mg/kg) organic contaminants. While a bigger sample and three sequential extractions are used for low concentration process, medium/high concentration process applies one extraction with a smaller sample [30]. Since contaminated soils which were used in this research had PHC concentrations of more than 20 mg/kg, the medium/high concentration process was followed for ultrasonic extraction.

According to method 3550C of US EPA for medium/high concentration process, a 1/8-inch tapered microtip, which was supplied from Crystal Electronics Inc. (Newmarket, ON, Canada), was connected to the bottom of a 1/2-inch horn [30]. The Branson digital sonifier model by Branson Ultrasonics Corporation (Danbury, CT, USA) with 450 watts power supply was used in this research. The soil was mixed thoroughly using a stainless-steel spatula to form a homogenous sample. Approximately 2 g of soil was taken and placed in a 20-mL glass vial. Anhydrous sodium sulfate (granular), Na_2SO_4, was heated at 400 °C for 4 hours in the furnace to be purified prior to use. Anhydrous sodium sulfate (about 2 g) was added to soil samples which were wet (gummy) and did not have a free-flowing texture. Soil samples should be then in a free-flowing state that shows a good mixing was done. The final volume of mixture of soil and sodium sulfate was brought to 10 mL after addition of a sufficient volume of solvent, which was acetone and hexanes with a ratio of 1:1. Acetone (C_3H_6O) and hexanes (C_6H_{14}) were purchased from Fisher Scientific (ON, Canada) at HPLC-grade (high-performance liquid chromatography) and also met the ACS (American Chemical Society) specifications. The vial was placed below the ultrasound's probe while the horn tip was located between the solution surface and sample layer. Ultrasonic extraction was then performed. A set of preliminary tests was conducted to determine the optimum conditions for ultrasonic extraction. These conditions were a sample size of 2 g, a time duration of 2 min at amplitude of 50% (half power) with the mode switch on pulse (no continuous) and percent duty cycle at 50% (energy on 50% of time and off 50% of time). After completion of sonication, the sample was kept in a refrigerator until it was used in the next step [30].

5.2.2.2 Silica gel column cleanup

Naturally occurring non-hydrocarbon polar organics can be present in samples and interfere with measurements. These compounds can be selectively separated from PHCs by silica gel column cleanup [28]. A small amount of glass wool was put at the bottom of a glass chromatographic column to retain the adsorbent. Approximately 5 g of activated silica gel was added on top of the glass wool. Silica gel with 60-200 mesh size was procured from Acros Organics (NJ, USA). Silica gel was activated by heating over 101 °C overnight before being used in the silica gel column cleanup procedure [32]. Anhydrous sodium sulfate (approximately 10 mm) was then added. 10 mL of hexane: dichloromethane (with a ratio of 50:50) was used as an eluting solvent to wash and moisten the column. Dichloromethane (methylene chloride, CH_2Cl_2) was supplied by Fisher Scientific (ON, Canada) at an Optima-grade and also met the ACS specifications. The sample extract was then poured into a column. All eluant from this time were collected at the bottom of the column. Finally, the column was eluted with at least 20 mL of hexane: dichloromethane and the whole eluant was collected [28].

5.2.2.3 Kuderna-Danish (K-D) concentration technique

K-D is typically used for the concentration of materials dissolved in organic solvents. Prior to GC analysis, the sample was concentrated using K-D to a lower volume (around 2 mL) and then analyzed by GC. Since toluene is a compatible solvent for the GC apparatus used in this study, toluene (around 1 mL) was added to the sample. In fact, while the sample concentration is in progress, solvents should be exchanged to toluene based on their boiling points.

The 500-mL evaporation flask was connected to the concentrator tube (10 mL graduated glass tube) by a clamp. The liquid extract which was collected in the silica gel column, was transferred to the K-D with an additional 20 mL of solvent, a mixture of acetone and hexanes with a ratio of

1:1. One or two boiling chips were added to the flask [33]. Boiling chips with approximately 10-40 mesh from VWR Scientific, Inc. (ON, Canada) were used. Boiling chips are added to liquids to make them boil more calmly and prevent bumping [34]. The (3-ball macro) Snyder column were joined to the flask with a clamp. Approximately 1 mL of solvent (acetone/hexane with a ratio of 1:1) was used to moisten the column. The whole K-D set-up was placed in a hot water bath in a fume hood. The flask was positioned at a level such that the lower surface of the flask could be bathed in steam. The temperature of water bath was adjusted to approximately 85 °C so that it could vaporize solvents. Around 1 mL of exchange solvent (toluene) was added to the flask by removing the Snyder column instantly [33]. Toluene ($C_6H_5CH_3$) was purchased from Fisher Scientific (ON, Canada) at an Optima-grade and also met the ACS specifications. The concentration rate can be modified with the water's temperature compared with the boiling point of solvents. The final volume of extract around 2 mL can be reached after a few hours [28]. At the end, the K-D device should be removed from the water bath to be cooled down before collection of the final extract.

5.2.2.4 Gas chromatography (GC)

A 6890 series GC with flame ionization detector (FID) from Agilent Technologies (CA, USA) was used to measure the concentration of hydrocarbons. The column was HP-1 crosslinked methyl siloxane (30 m × 0.32 mm × 0.25 µm film thickness). The auto sampler was used to inject 2 µL of the sample dissolved in toluene into the GC and the carrier gas was Helium. The oven temperature was held at 40 °C for 1 min, and then ramped from 40 to 325 °C at 15 °C /min. The injector and detector temperatures were both set at 340 °C. Standards which had identical amounts of n-decane (C_{10}), n-hexadecane (C_{16}) and n-tetratriacontane (C_{34}) hydrocarbons dissolved in toluene and also n-pentacontane (C_{50}) dissolved in toluene but at a different concentration were used for obtaining calibration curves and determining retention times [28]. The area under the chromatogram from GC should be analyzed to give the PHC fractions. The area under chromatogram for each fraction was then converted to concentration according to the calibration curve which was prepared before.

5.2.3 Experimental setup and procedure of SFE

SFE can be conducted in three modes: *Static-mode* (SCF is kept in the extraction vessel for a certain duration and then released), *Dynamic-mode* (a pump flows the SCF into the extraction vessel steadily), and *Combination-mode* (combinations of static- and dynamic-modes are performed such that the static-mode is conducted for a certain duration and then the dynamic-mode is started) [12].

The apparatus for performing supercritical fluid extraction was acquired from Supercritical Fluid Technologies (SFT) Inc. (Newark, DE, USA). The SFT-110 apparatus specifications are as follows: SFT-110 can operate pressures up to 68.9 MPa and temperatures up to 200 °C. Flow rates can range from 0.01 to 24 mL/min (0.008 to 18 g/min) of liquid CO_2. The volume of the extraction vessel is 100 mL [35].

Figure 5.2 shows a schematic of the lab-scale SFT-110 apparatus which was used for performing SFE experiments. A liquid CO_2 cylinder (99.99%) with a dip tube that sucks the liquid CO_2 from the bottom of cylinder, supplied by Linde Canada Ltd. (ON, Canada), was used for CO_2 supply. The dual piston pump provides high pressures required for SFE and this pump pressurizes the CO_2. The apparatus has a 100-mL extraction vessel (reactor or extraction cell) where the polluted soil is contained and exposed to SCF. The extraction vessel is surrounded by a heating unit. The oven has a pre-heater to control the temperature. In order to maintain a high pressure in the extraction line, a restrictor is required. The restrictor valve is the point in the system where the CO_2 and dissolved contaminants are stepped down from supercritical to atmospheric pressure. In the static mode, both static/dynamic valve and restrictor valve are closed. To switch from static mode to dynamic mode, first the static/dynamic valve is opened and then the restrictor valve is opened slightly. In dynamic mode, flow rate can be adjusted accurately with a restrictor valve (back pressure regulator). As a more accurate control of CO_2 flow rate, a flow meter was installed to measure the flow rate of the expanding CO_2 gas [35]. SCF is carried into the extraction vessel and dissolves/extracts contaminants from the solid phase. The SCF containing contaminants is then released from the extraction vessel to a collection vial through a restrictor valve. Restrictor valve is also resistant to blockage. When the fluid is depressurized (fluid is not in supercritical state any more), the extracted contaminants are separated from the fluid due to the reduction in their solubility [12,36]. The contaminants that are extracted can be gathered in a collection vial. The rupture disk and collection vial are both connected to a fume hood for ventilation purposes [35].

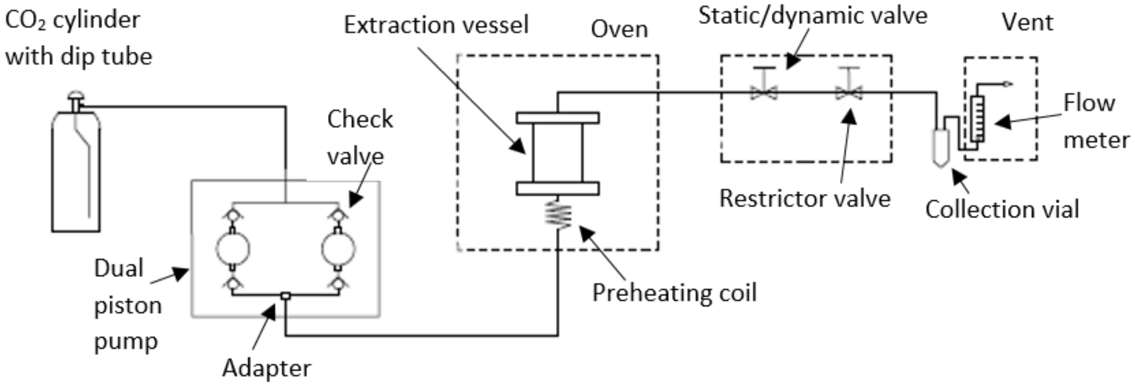


Figure 5.2. SFT-110 apparatus [35]

5.2.3.1 SFE extraction mode and time duration

An initial set of tests was carried out to determine the optimum extraction mode and time duration for performing SFE tests. Different combinations of static cycles and dynamic cycles were investigated as summarized in Table 5.1. “S” and “D” represents static and dynamic modes of extraction, respectively.

Table 5.1. Initial tests for determination of SFE mode and time duration

Extraction mode	Static cycle duration (min)	Dynamic cycle duration (min)	No. of cycles	Total time (min)
Static mode (10S)	10	0	1 2 3	10 20 30
Static mode (20S)	20	0	1 2 3	20 40 60
Combination mode (10S+5D)	10	5	1 2 3	15 30 45
Combination mode (10S+10D)	10	10	1 2 3	20 40 60

5.2.4 Soil mineralogy

The powder x-ray diffraction (PXRD) method was used for soil mineralogy analysis. PXRD is a versatile, non-destructive analytical technique for the identification of crystalline materials in powdered or solid compounds. Crystalline phase identification is the most common application and is performed by comparison of the diffraction pattern with that of a known substance or by search-match analysis using a database such as the International Centre for Diffraction Database (ICDD). Mineralogy analysis of a soil sample was performed using a Rigaku Ultima IV powder x-ray diffractometer instrument available at the “X-ray Core Facility” of the University of Ottawa (Ottawa, ON, Canada). The detector was scintillation counter and continuous scan mode had a scan speed/duration time of 4 degree/min. Step width, scan axis and scan range were 0.0300 deg., 2 theta/theta, and 5.0000-100.0100 deg., respectively [37].

5.2.5 Statistical methods

One-way ANOVA test was performed to determine if significant differences existed among the removal efficiency (%) of PHC fractions in the three different soil types (soil A, B and C). Once the ANOVA test showed there was a significant difference among the groups of data, t-tests ($p<0.05$) were then performed to compare PHC removal percentages statistically for each pair of groups.

5.3 Results and discussion

5.3.1 Determination of SFE extraction mode and time duration

The following conditions were applied for all SFE experiments: 25 MPa pressure, 55 °C temperature, flow rate of 24 ml/min of liquid CO_2 (for dynamic mode), a sandy soil spiked with diesel fuel with a ratio of 5 wt% (aged for 3 months) and approximately 105 g soil was used to fill the extraction vessel of the SFE apparatus.

Static mode for 10 and 20 min with the cycles repeated three times was employed for some experiments. The SCF was kept in the extraction vessel for 10 or 20 min and then the treatment was stopped (the pump turned off). The extraction vessel was opened, and the first soil sample was taken (10S × 1C). Then, second cycle was started with increasing pump pressure to the target value. The SCF was kept in the extraction vessel for the required time duration and then the treatment was stopped. The extraction vessel was opened, and the second soil sample was taken (10S × 2C). Similarly, after third cycle of 10 min the third soil sample was taken (10S × 3C). In other words, three soil samples at 10, 20 and 30 min after the start of the test were collected and analyzed. The same process was followed for 20 min static time cycles. Combinations of static and dynamic modes were also investigated. In the combination mode, static mode was conducted for 10 min followed by a dynamic mode cycle of 5 or 10 min with the cycles repeated three times.

For example, for the case of combination of 10 min static and 5 min dynamic modes, three soil samples after 15, 30 and 45 min from the start of the test were collected and analyzed. It should be noted that “S”, “D” and “C” denote static mode, dynamic mode and cycle number, respectively.

Figure 5.3 shows percentage removal of PHC F3 fraction for all modes investigated. For 10 min static cycles, the percentage removal observed for PHC F3 increased from 55% at the end of cycle #1 to 60.5% at the end of cycle #2 and further to 84.2% at the end of cycle #3 (total time of 30 min). For the case of 20 min static cycles, similar trend was observed with the highest percentage removal of 73.9% at the end of cycle #3 (total time of 60 min). For the case of combination of 10 min static and 5 min dynamic modes, the highest percentage removal of 85.5% was obtained at the end of cycle #3 (total time of 45 min). When a combination of 10 min static and 10 min dynamic modes used, the removal percentage of PHC F3 increased from 67.8% at the end of cycle #1 to 80.3% at the end of cycle #2 and further to 89.8% at the end of cycle #3 (total time of 60 min). The extraction of PHC F2 and F4 fractions showed roughly similar trends as F3 fraction.

In order to compare the combined mode with static mode alone, the same time duration and cycle number should be considered. For example, “10S+10D × 3C” and “20S × 3C”, both at the end of cycle #3 with the total time of 60 min, resulted in 89.8% and 73.9% removal of PHC F3, respectively, showing that combined mode performs better than static mode. The same trend was observed for “10S+10D × 2C” vs. “20S × 2C”. In dynamic mode, the SCF flows through the soil and could flush the extracted contaminants out of the extraction vessel and would enhance the removal of PHCs. These results indicated that using a combined mode and alternating between static and dynamic modes was more effective than using a single static mode. Comparing all static and combination modes shows that the “10S+10D × 3C” resulted in the highest removal percentage of PHC F2, F3 and F4 fractions. For the subsequent tests, “10S+10D × 3C” mode (combination of 10 min static followed by 10 min dynamic mode, repeated for 3 cycles for a total time of 60 min) was performed.

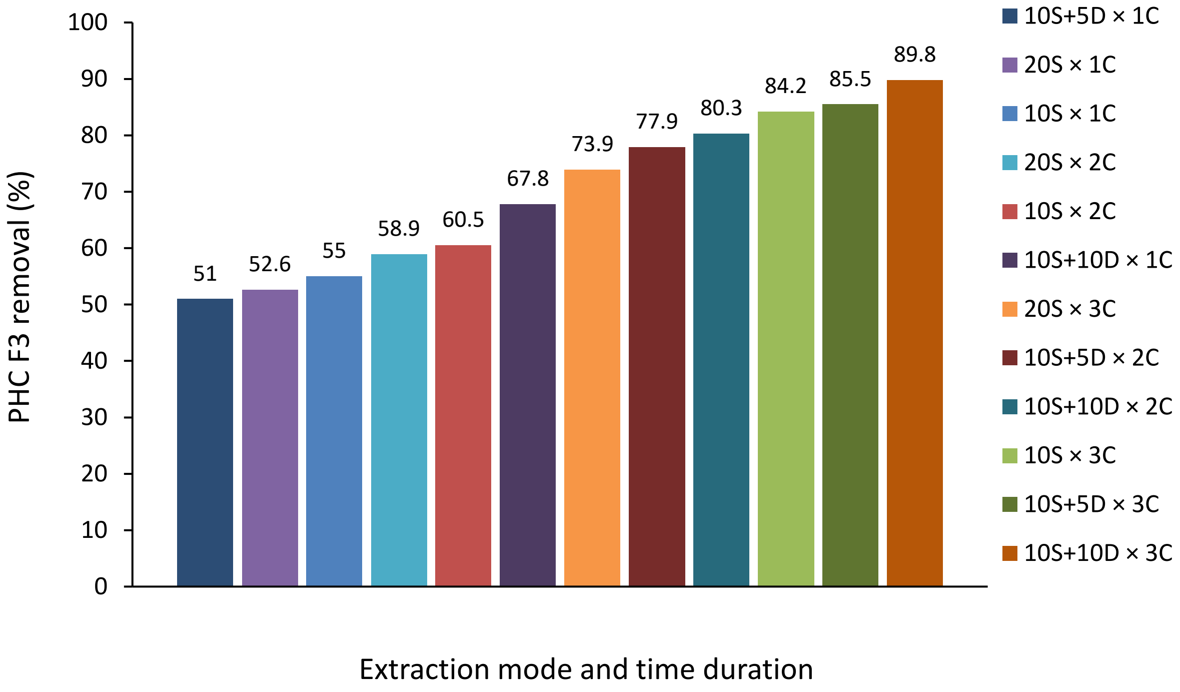


Figure 5.3. PHC F3 removal percentages for different SFE extraction modes and time durations (S: static mode, D: dynamic mode, C: cycle)

5.3.2 Soil characterization and mineralogy analysis

Three initial sources of soils were sand, silt and clay. Sand was a silica sand that had quartz (SiO_2) minerals (about 99.6%) with white to off white colour and sub-angular grain shape. Sand had particle sizes mostly in the range of #16 mesh (1.19 mm) to #50 mesh (0.297 mm) [38]. Silt had microcrystalline forms of quartz (SiO_2) and clay had mainly kaolinite ($Al_2Si_2O_5(OH)_4$) minerals

[37]. Silt and clay had particle sizes mostly in the range of #400 mesh (0.038 mm) to #325 mesh (0.045 mm) [38].

To have an accurate control over soil particle sizes, spiked soils were used as contaminated soils. Various ratios of the initial sources were mixed thoroughly to form different soils. In this way, soils had the same sources and the properties of them did not change significantly. The most important parameter that changed among these soils was particle size. Soil A had 90% sand, 10% silt and 0% clay. Soil B had 20% sand, 60% silt and 20% clay. Soil C had 40% sand, 20% silt and 40% clay. The water contents of soil A, B and C were 3.9%, 4.3% and 4.7%, respectively. According to the soil texture triangle, different compositions of each soil resulted in the three soils which are shown in Figure 4 (left). Therefore, sand, silt loam and clay were the types of soil A, B and C, respectively; and it was tried to select the soil types that were distinctly different in terms of particle size. In addition, Figure 4 (right) shows particle size distributions of the three soil types, which was established by mechanical sieving and hydrometer test. In general, the equivalent particle size (diameter) of soil A was by far larger than both soil B and soil C. Particles sizes of soil B and C were slightly different. Coarse-grained fraction (larger than 0.075 mm) of soil B was smaller than soil C since soil B had lower quantity of sand. Fine-grained fraction (smaller than 0.075 mm) of soil C was smaller than soil B since soil C had higher quantity of clay.

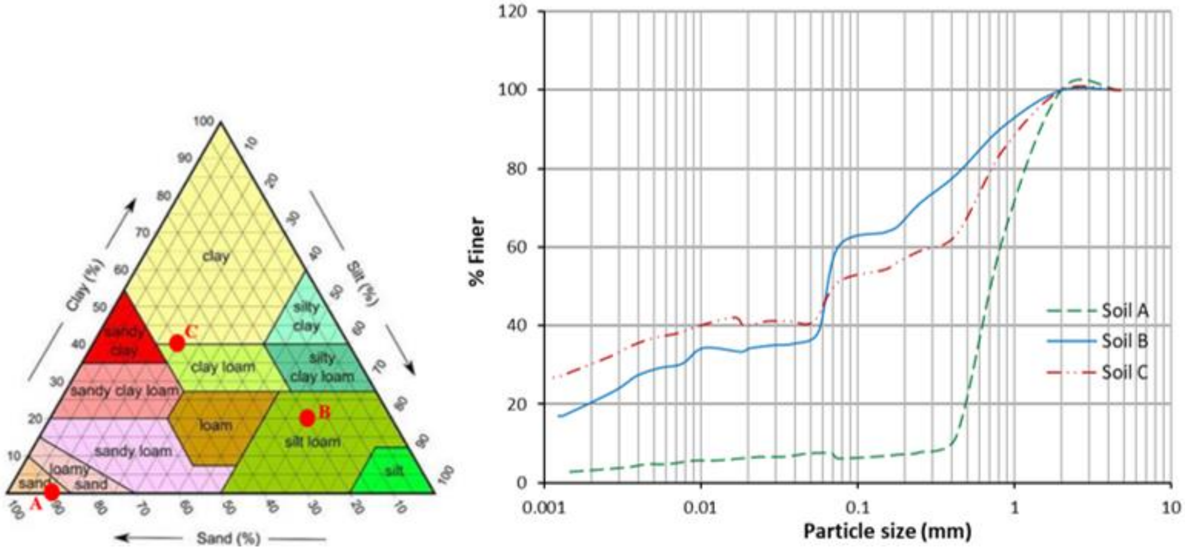
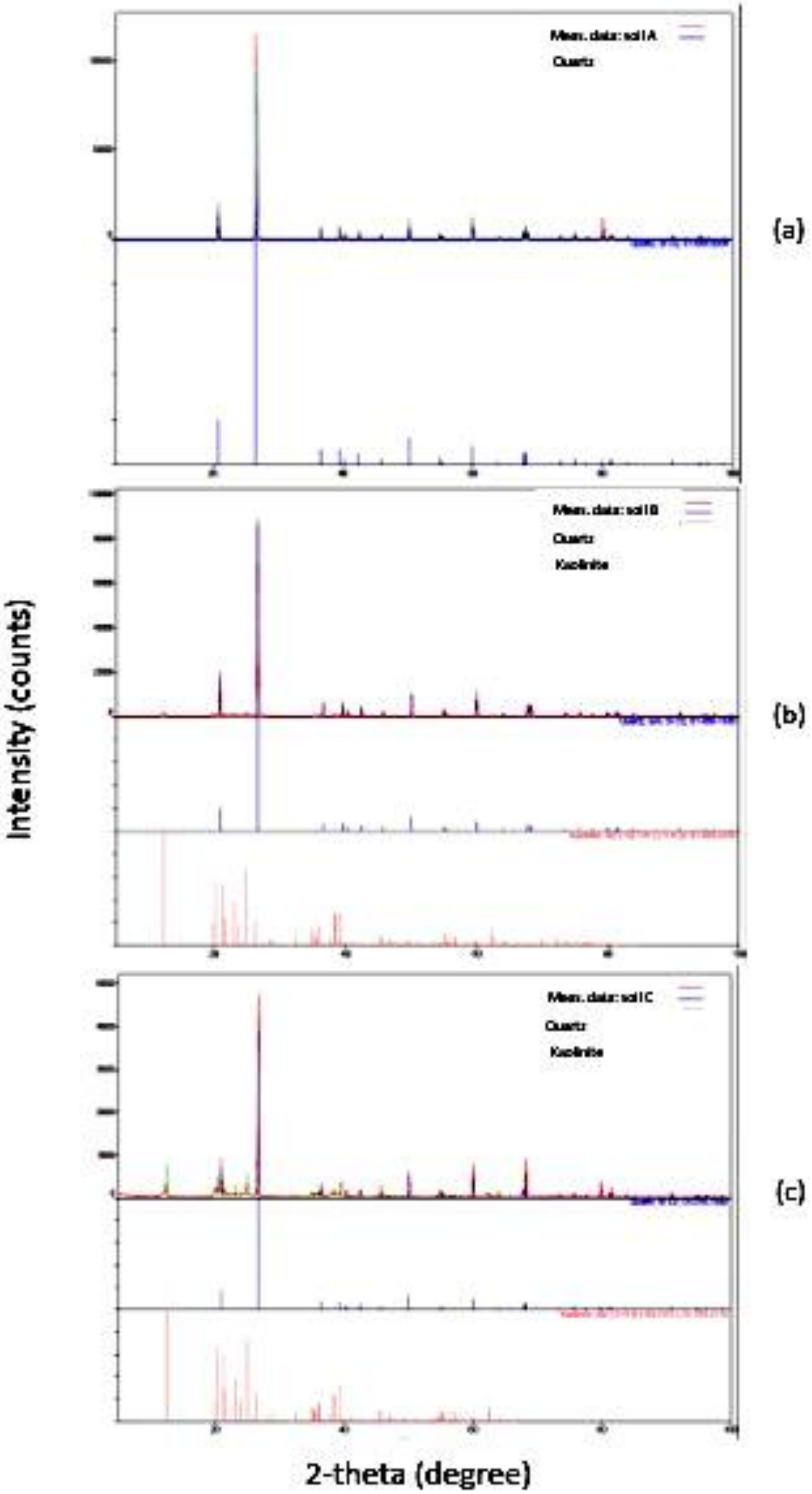


Figure 5.4. Soil texture triangle (left) and particle size distribution curves (right)

Mineralogy analyses of soil samples were performed at the “X-ray Core Facility” of the University of Ottawa and results are presented in Figure 5.5. The analysis was performed by comparison of the diffraction pattern with that of a known substance or by search-match analysis using a database such as ICDD [37]. According to mineralogy analyses, soil A had quartz (SiO_2) minerals (about 99.6%). Soil B constituted quartz (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$) with approximate contents of 64.5% and 35.1%, respectively. Soil C had quartz (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$) minerals with approximate contents of 34.4% and 65.2%, respectively [37]. Per the information given for the minerals of initial sources of soils and considering their mixing ratios, the results of mineralogy analyses for soil A, B and C can be confirmed.

Figure 5.5. Mineralogy results for (a) Soil A (b) Soil B (c) Soil C [37]



5.3.3 Effect of soil grain size

SFE was performed for each soil with the following conditions: 33 MPa pressure, 75 °C temperature and flow rate of 24 ml/min of liquid CO_2. The time duration was the combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles (60 min in total). Approximately 100 g of soil A, B and C was placed in the extraction vessel. These conditions were fixed for all experiments to negate their effects and only allow soil grain size to influence results. There were 3 replicates for each SFE test. In other words, the complete procedure (i.e. SFE, ultrasound extraction, silica gel column cleanup, K-D concentration and GC analysis) for each experiment were repeated three times. The averages of PHCs concentrations of soil A, B and C (i.e. three samples) before treatment are presented in Table 5.2.

Table 5.2. Average of initial concentrations of all soils before treatment

PHC fraction	Average concentration ± standard deviation (mg/kg)
PHC F2	17742.6 ± 2217.4
PHC F3	8761.6 ± 813.3
PHC F4	4690.3 ± 187.5

Total petroleum hydrocarbon fractions (TPHF) in this study is defined as the sum of PHC F2, F3 and F4 fractions. TPHF removal percentage for each soil type is shown in Figure 5.6. As can be seen in this figure, the highest and the lowest TPHF removal percentages were obtained for soil A (90.4% removal) and soil C (47.4% removal), respectively. The extraction of TPHF from soil B was 65.3%, which was about 18% higher than TPHF removal percentage of soil C. SFE was successfully capable for TPHF removal from soil A with 90.4% efficiency, which was 43% greater than that of soil C. Eckert-Tilotta et al. [17] determined removal of total petroleum hydrocarbons (TPHs) from real-world fuel-spill contaminated soil samples using SFE. Three spiked soils including Ottawa sand, kaolinite clay and silty-clay loam (which was composed of 8% sand, 46% silt, 46% clay) were also studied. SFE experiments at 40 MPa and 65 °C for at least 2 h on spiked soil samples with jet-diesel fuel led to the TPH recovery above 90% from sand and below 60% from loam and below 55% from clay [17]. It should be mentioned that the SFE operational parameters (pressure, temperature and time), soil type and the type of contamination in this study were different than the previous study which was discussed.

The important parameters relating to soil texture that affect the removal of contaminants (PHCs) are particle size, the clay, silt and sand content and the structure of pores. SCF should first contact the organic contaminants so that it can then transport them. The diffusion pathway of SCF through soil particles is important for the extraction efficiency. As SCF penetrates the soil specimen and can distribute easily within the soil structure, the more contaminants could be removed [39]. Therefore, pore size and connectivity of particles are critical since SCF needs to be distributed in the soil matrix during SFE [12]. In general, the equivalent particle size of soil A was by far larger than both soil B and soil C. Greater particle sizes in soil A (sand) might lead to the bonding force between organic contaminants (PHCs) and sand particles that may not be very strong, which could potentially result in higher TPHF removal. As for soil C, which had the highest clay content, fine particle sizes would have large surface areas. In addition, fine soils have smaller pore sizes that may cause more PHCs would be trapped in the pore spaces within the structure of soil C that could make the extraction of PHCs more difficult. Also, the flow of SCF within the fine pore size structure might be more restricted compared to a coarse pore size structure. Therefore, large surface areas of fine particles and the complexity of structure of soil C (with multiple layers of micro-pores) could cause lower extraction of TPHF in soil C [31].

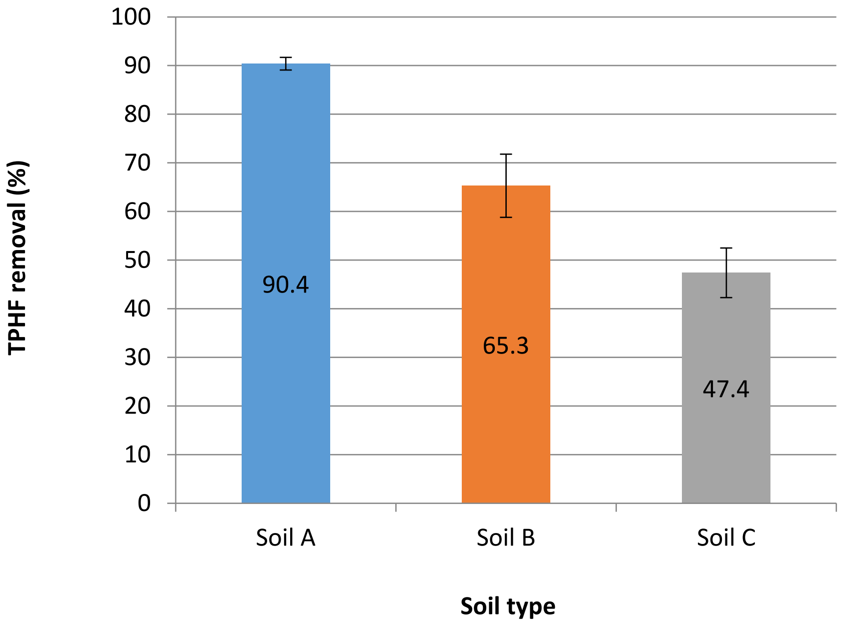


Figure 5.6. Effect of soil type on the TPHF removal percentage

Table 5.3 shows the result of statistical analysis performed using single factor ANOVA. According to this table, the p-value was lower than 0.05 ($p < 0.05$); indicating there were significant differences between the TPHF removal efficiency in these three soil types (A, B and C).

Table 5.3. Single factor ANOVA test for TPHF removal percentages

Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	2803.962	2	1401.981	60.384	0.000106	5.143
Within Groups	139.307	6	23.218			
Total	2943.269	8				

The one-way ANOVA test did not provide further information on differences between the groups of data. Therefore, TPHF removal percentages in each pair of soil types were compared statistically and results are presented in Table 5.4. According to these results, there were significant differences observed between the removal percentages for soil A vs. soil B; soil A vs. soil C; and soil B vs. soil C since p-value of two-tail for each pair was lower than 0.05 ($p < 0.05$). As a result, the contribution of each soil type was significant on the TPHF removal percentage.

Table 5.4. t-test results for paired comparison of soil types for TPHFs removal percentages

	Soil A	Soil B	Soil A	Soil C	Soil B	Soil C
Mean	90.43	65.30	90.43	47.40	65.30	47.40
Variance	1.66	42.51	1.66	25.48	42.51	25.48
Observations	3	3	3	3	3	3
Pooled variance	22.09		13.57		34.00	
Hypoth. mean difference	0		0		0	
df	4		4		4	
t Stat	6.55		14.31		3.76	
$P(T \leq t)$ two-tail	0.00281		0.00014		0.01977	
t critical two-tail	2.78		2.78		2.78	

Figure 5.7 shows the effect of soil type on the extraction of PHC fractions. Regarding PHC F2, the removal percentage of soil A was 27.3% greater than soil B and the removal percentage of soil B was 20.4% higher than soil C. The similar trend was observed for the extraction of PHC F3. In other words, soil A and soil C had the highest (92.7% removal) and the lowest (42% removal) extraction efficiency of PHC F3, respectively. The extraction percentage of PHC F4 for soil A, B and C were not statistically significant. The clay content in soil A, B and C ranged from minimum to maximum, respectively. In general, the PHC F2 and F3 removal percentages ranged from higher to lower from soil A to soil C, respectively. This fact showed that the higher clay content would result in lower extraction percentage of PHC F2 and F3 fractions. The same effect of higher clay

content resulting in a lower extraction percentage of contaminants was also reported by Chen et al. (1997) for PCBs removal from contaminated soils [26]; and Elektorowicz et al. [39] for removal of polycyclic aromatic hydrocarbon (PAH), phenanthrene, from soils [39]; and Eckert-Tilotta et al. [17] for TPH removal from real field fuel-spill soil samples [17]; and Montero-Vazquez et al. [40] for the extraction of PAH (pyrene) from spiked soils [40].

Regarding soil A, the extraction efficiency of PHC F2 (98.4% removal) was higher than PHC F3 (92.7% removal) and the extraction efficiency of PHC F3 (92.7% removal) was greater than PHC F4 (50.2% removal). For soil B, the removal percentage of PHC F2 was 19.2% greater than PHC F4 while the extraction percentages of PHC F2 and F3, PHC F3 and F4 were not statistically different. Regarding soil C, the removal efficiency of all PHC fractions were not statistically different. In addition, among all the studied conditions, the highest extraction efficiency of PHC F2 and F3 was observed for soil A. Furthermore, soil C showed the lowest extraction efficiency of PHC F2 and F3 fractions. PHC F2 fractions are considered as light extractable PHCs in soil and have lower molecular weight than PHC F3 fractions. As a result, displacement of PHC F2 would be easier than PHC F3. Also, since solubility of PHC F2 is more than PHC F3 fraction, PHC F2 can be dissolved easier in SCF. Similarly, the extraction of PHC F3 would be less difficult than PHC F4.

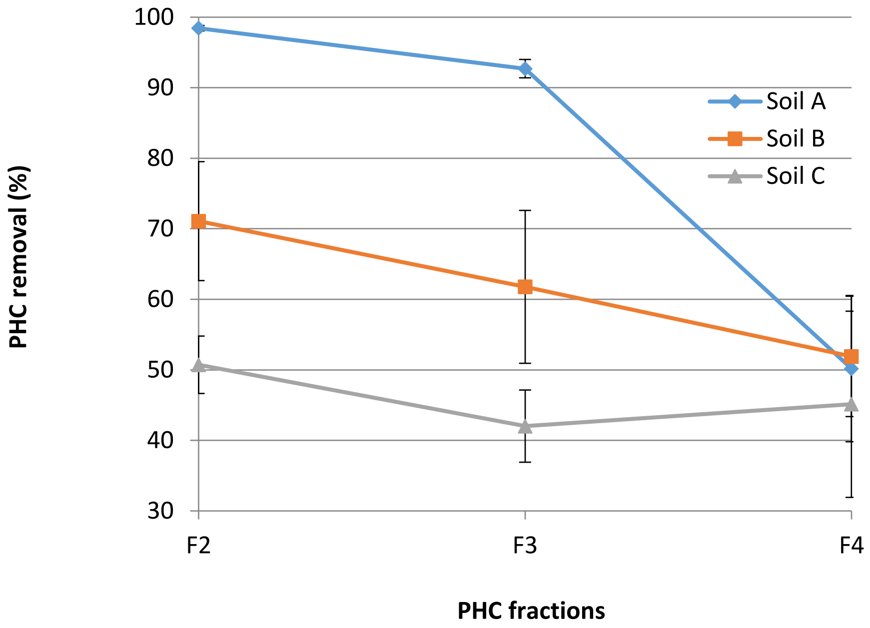


Figure 5.7. Effect of soil type on the extraction rate of PHC fractions

PHC fractions removal percentages for soil A were compared statistically and results are presented in Table 5.5. According to these results, there were significant differences observed for soil A between the removal percentages for PHC F2 vs. PHC F3; PHC F2 vs. PHC F4; and PHC F3 vs. PHC F4 since p-value of two-tail for each pair was lower than 0.05 ($p < 0.05$). As a result, the contribution of each PHC fraction was significant. It should be noted that t-test results for other soil types (B and C) were not presented, however, their effects were discussed in the context.

Table 5.5. t-test results for paired comparison of PHC fractions removal rates for soil A

	PHC F2	PHC F3	PHC F2	PHC F4	PHC F3	PHC F4
Mean	98.43	92.7	98.43	50.2	92.70	50.2
Variance	0.14	1.69	0.14	107.13	1.69	107.13
Observations	3	3	3	3	3	3
Pooled variance	0.92		53.64		54.41	
Hypoth. mean difference	0		0		0	
df	4		4		4	
t Stat	7.33		8.07		7.06	
P(T≤ t) two-tail	0.00184		0.00128		0.00213	
t critical two-tail	2.78		2.78		2.78	

PHC F4 removal percentages in each pair of soil types were compared statistically and results are presented in Table 5.6. According to these results, there were not significant differences observed between the PHC F4 removal percentages for soil A vs. soil B; soil A vs. soil C; and soil B vs. soil C since p-value of two-tail for each pair was greater than 0.05. As a result, the contribution of each soil type was not significant. It should be noted that t-test results for other PHC fractions (F2 and F3) were not presented; however, their effects were discussed in the context.

Table 5.6. t-test results for paired comparison of soil types for PHC F4 removal percentages

	Soil A	Soil B	Soil A	Soil C	Soil B	Soil C
Mean	50.20	51.9	50.20	45.13	51.90	45.13
Variance	107.13	73.17	107.13	174.96	73.17	174.96
Observations	3	3	3	3	3	3
Pooled variance	90.15		141.05		124.07	
Hypoth. mean difference	0		0		0	
df	4		4		4	
t Stat	-0.22		0.52		0.74	
P(T≤ t) two-tail	0.83716		0.62892		0.49819	
t critical two-tail	2.78		2.78		2.78	

The percentage differences among removal percentages of PHC F2 and F3 fractions were calculated according to Eq. (5.2). Table 7 presents the differences in PHC F2 and F3 removal percentages for each soil type. The highest differences in PHC F2 (64%) and F3 (75.2%) removal percentages were observed for soil A and C. The lowest percentage difference of PHC F2 (32.3%) was related to soil A and B and the lowest percentage difference of PHC F3 was observed for soil B and C (38%).

$$Percentage\ difference = \left| \frac{(X_1 - X_2)}{(X_1 + X_2)/_2} \right| \times 100 \qquad \text{Eq. (5.2)}$$

Where X_1 and X_2 are two values of PHC removal percentages.

Table 5.7. Percentage differences among extraction of PHC fractions

	Percentage difference (%)		
	Soil A and B	Soil B and C	Soil A and C
PHC F2	32.3	33.4	64.0
PHC F3	40.1	38.0	75.2

The standard limits for concentrations of PHC fractions according to the Ontario Ministry of Environment (MOE), “Table 2- under Industrial/Commercial/Community property use” is presented in Table 8 [41].

Table 5.8. Petroleum Hydrocarbons values based on “Table 2” of MOE [101]

Contaminant	Industrial/Commercial/Community property use (μg/g)
PHC F2	230 (250)
PHC F3	1700 (2500)
PHC F4	3300 (6600)

() standard in bracket applies to medium and fine textured soils

Comparison of PHC concentrations after SFE treatment for each soil type with Table 2 of MOE is shown in Figure 5.8. According to this figure, none of PHC F2 concentrations met the table limit, however, PHC F2 concentration in soil A was slightly above the table limit (less than 70 mg/kg). Regarding PHC F3, only concentration in soil A was below the table limit. For the case of PHC F4, all soil types met the table limit. Therefore, it could be concluded that soil A could be considered almost clean and can be used for the appropriate land use (which is industrial, commercial, community) since concentrations of PHC fractions in soil A were below the standard limits (except PHC F2). Furthermore, variations of PHC F2 replicates were 78.2-1429.4 mg/kg. Variations of PHC F3 replicates were 123.1-973.6 mg/kg and variations of PHC F4 replicates were 418.5-607.5 mg/kg.

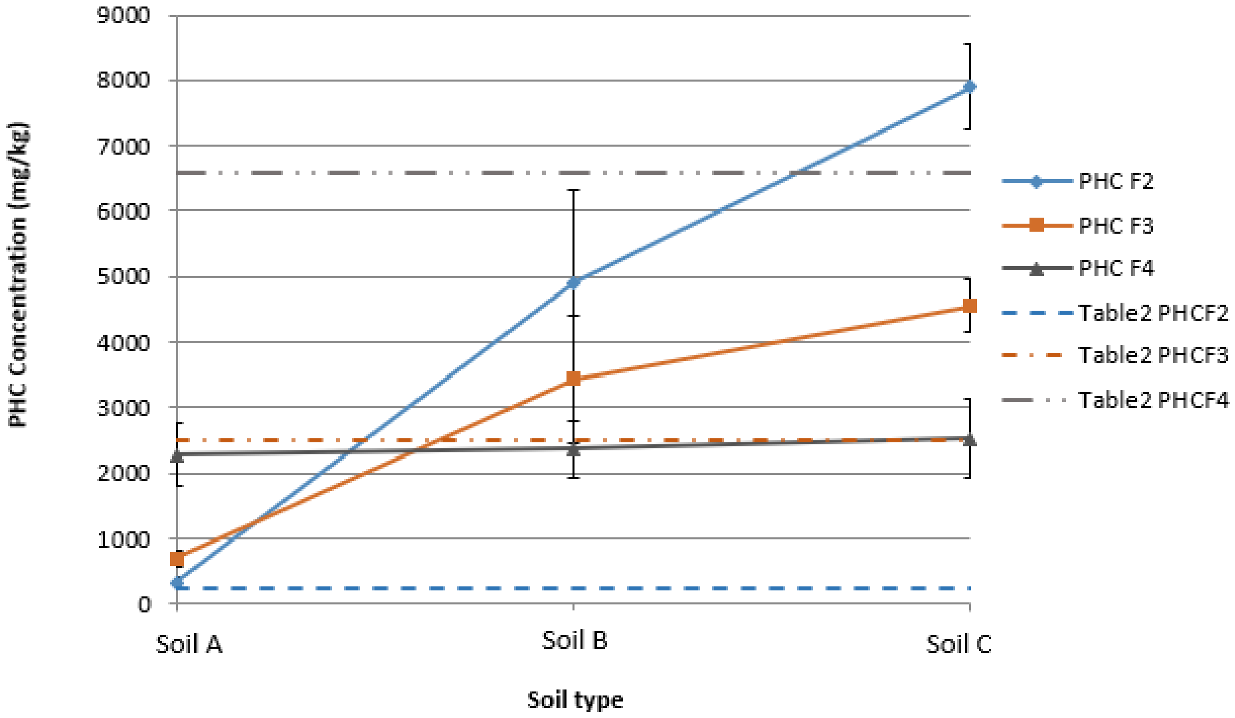


Figure 5.8. Concentrations of PHC fractions for different soil types after SFE treatment

5.4 Conclusion

The following conclusions can be drawn from this study:

- It may be concluded that using a combined mode and alternating between static and dynamic modes is more effective than using a single static mode for PHCs removal.
- The highest (90.4% removal) and the lowest (47.4% removal) TPHF removal percentages were obtained for soil A (sand) and soil C (clay), respectively; showing larger particle sizes would result in a higher TPHF removal percentage.
- PHC F2 removal percentage of soil A (sand) was 27.3% greater than soil B (silt loam) and the removal percentage of soil B (silt loam) was 20.4% higher than soil C (clay). Similarly, soil A (sand) and soil C (clay) had the highest (92.7%) and the lowest (42%) extraction efficiency of PHC F3, respectively. The extraction percentage of PHC F4 for soil A, B and C were not statistically significant.
- Regarding soil A (sand), the extraction efficiency of PHC F2 (98.4%) was higher than PHC F3 (92.7%) and the extraction efficiency of PHC F3 (92.7%) was greater than PHC F4 (50.2%). For soil B (silt loam), the removal percentage of PHC F2 was 19.2% greater than PHC F4 while the extraction percentages of other fractions were not statistically different. Regarding soil C (clay), the removal efficiency of all PHC fractions were not statistically different.
- Among all studied conditions, the highest and the lowest extraction efficiency of PHC F2 and F3 was observed for soil A (sand) and soil C (clay), respectively. A higher clay content in soil C (clay) resulted in lower extraction percentage of PHC F2 and F3 fractions.

- Soil A could be considered almost clean after SFE treatment and can be used for the appropriate land use since the concentrations of PHC fractions for soil A (sand) were below the standard limits of MOE, Table 2 (except PHC F2, which was slightly, 70 mg/kg, above the Table 2 limit). However, the concentrations of PHC F2 and F3 fractions for soil B (silt loam) and C (clay) were above the MOE, Table 2 limits and they should be treated more.

Appendix: notations

ACS	American Chemical Society
CO_2	Carbon dioxide
FID	Flame ionization detector
GC	Gas chromatography
HPLC	High-performance liquid chromatography
ICDD	International centre for diffraction database
K-D	Kuderna-Danish
MOE	Ontario Ministry of Environment
PAH	Polyaromatic (polycyclic aromatic) hydrocarbon
PCB	Polychlorinated biphenyl
PHC	Petroleum hydrocarbon
PXRD	Powder x-ray diffraction
SCF	Supercritical fluid
SFE	Supercritical fluid extraction
SFT	Supercritical Fluid Technologies Inc.
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
TPHF	Total petroleum hydrocarbon fractions
US EPA	United States Environmental Protection Agency

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Chapter 6: Investigation of the Effect of Supercritical Fluid Extraction Operational Parameters on the Petroleum Hydrocarbons Removal from a Clay Soil and their Optimization

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Abstract

Supercritical fluid extraction (SFE) was applied to investigate the removal of petroleum hydrocarbons (PHCs) from a clay soil which was spiked with diesel fuel with a ratio of 5 wt%. The effects of the most important SFE operational paraments including pressure and temperature on the extraction of PHC fractions (i.e. F2, F3 and F4) were experimentally investigated. SFE experiments were performed at three levels of pressure (15, 33 and 50 MPa) and temperature (30, 75 and 120 °C). In addition, factorial design and response surface methodology (RSM) were applied to optimize the effect of pressure and temperature. The optimum combination for pressure and temperature based on the experimental results was selected for 33 MPa pressure and 120 °C temperature that led to 70.3%, 58.4% and 32.6% removal of PHC F2, F3 and F4 fractions, respectively. According to RSM, the optimum pressure and temperature were found to be 42.8 MPa and 120 °C that resulted in 74.9% removal of PHC F2 and 65.6% removal of PHC F3. In general, the increase of pressure from 33 MPa to 50 MPa did not result in a greater extraction of total petroleum hydrocarbon fractions (TPHF) and an additional rise of temperature beyond 75 °C would be effective for achieving a greater extraction of TPHF while no significant improvements were observed at a lower temperature of 30 °C.

Keywords: petroleum hydrocarbon; supercritical fluid extraction; contaminated soil; clay; statistical analysis

6.1 Introduction

A huge number of polluted sites have been reported in many places to be contaminated with various materials such as petroleum hydrocarbons. Most of these pollutants have high chemical and biological stability which makes them harmful to the environment [1]. These pollutants can be threatening in different ways; they may be absorbed by plants and animals and enter the food chain; they may be discharged into groundwater and surface water; or released into the air and result in subsequent exposure. Consequently, many of these contaminated sites have been abandoned because of pollution [2]. In Canada, petroleum hydrocarbon (PHC) contamination is the primary concern in about 60% of contaminated sites [3]. Over the past years, many technologies have been developed and applied as remediation technologies to decontaminate such sites [1]. Solvent extraction is one of the treatment technologies which is used for the extraction of contaminants from a soil [4]. One promising method which could be applied in industry is supercritical extraction (SCE) [1], which is considered as a novel solvent extraction method in the class of physical/chemical treatment technologies [4,5]. The target contaminant, which is extracted from the soil matrix in supercritical fluid extraction (SFE), can be separated from the supercritical fluid (SCF). Other conventional solvent extraction methods may need further extraction of solvents to completely collect and separate the contaminants. In addition, the solvent usage for SFE is low and consequently, SFE produces less waste. There are no hazardous residues remaining in the soil which was treated by SFE. Furthermore, conventional solvent extraction methods which use organic solvents may result in low removal percentages of contaminants [1,6]. In general, the applicability of the common solvent extraction is more restricted than SFE [7]. When it comes to treatment of biodegradable contaminants such as petroleum compounds, bioremediation is not very costly and would not result in other pollutions; but the main drawback is that bioremediation is a very time-consuming process where the treatment can last even for several years in some cases [8]. On the other hand, compared to bioremediation, SFE is a fast technology [6]. A solvent in supercritical state shows specific physical properties. The density of supercritical fluids is greater than that of normal gases and less than that of organic liquids; they are approximately close to liquids (liquid-like). Considering viscosity, SCFs have obviously less values than liquids, similar to gases (gas-like). Diffusivity of SCFs is higher than liquids and less than gases, which leads to SCFs showing promising transport characteristics (high diffusivity like gases). Considering these specific properties, SCFs are considered as good choices as solvents for the extraction. In addition, having zero surface tension allows SCFs to move into various matrices readily [1,4,5,9–11].

Various densities of SCF can be achieved by slight alteration of temperature and pressure that defines the solubility strength of a solvent. Thus, through changing temperature and pressure, SFE would be able to selectively extract different substances [5,12,13]. If substances are sufficiently distinctive, they can be fractionated with SCF and the extraction would be performed selectively [14]. Therefore, SCE is highly affected by pressure and temperature levels.

Treatment of contaminated soils consisting of large contents of clay is often problematic. Since clay soils have specific characteristics including fine sizes of particles, cohesion, presence of different minerals and swelling behaviour, the extraction of contaminants from clay soils could be challenging [15]. Elektorowicz et al. (2007) [15] investigated the extraction of phenanthrene (a polycyclic aromatic hydrocarbon (PAH) compound) from clay soils and various mixtures of illite and fine pure silica sand using SFE technique. Four pressures including 34, 40.8, 47.6 and 54.4 MPa and four temperatures including 70, 80, 100 and 120 °C were tested. The extraction efficiency increased by increasing the pressure for pure clay soils including bentonite, kaolinite and illite. A similar effect of pressure on the PAH recovery from illite-sand samples was also observed. The effect of temperature varied with the type of the soil. The extraction of phenanthrene from pure clay soils decreased by an increase of temperature while increasing the temperature (from 80 to 120 °C) led to a remarkable rise in the recovery of illite-sand mixtures [15]. Nagpal and Guigard (2005) [16] studied the application of SFE for PHCs removal from two flare pit soils including a sandy soil (FP1) and a loam soil (FP2). They considered pressures ranging from 11 to 24.1 MPa and temperatures ranging 40 to 80 °C in their study. They achieved higher PHC extraction efficiencies by increasing pressure at a fixed temperature. However, when temperature increased at a constant pressure, the removal percentage decreased. They concluded that the density of SCF had a more significant effect on the removal of PHCs from FP1 than contaminant volatility and desorption of contaminants from the soil. Therefore, their experimental results showed the SFE efficiency was solvent density dependent. The highest PHC removal percentage from both soils (FP1 and FP2) were obtained at 24.1 MPa and 40 °C [16]. Eckert-Tilotta et al. (1993) [17] determined removal of total petroleum hydrocarbons (TPHs) from real-world fuel-spill contaminated soil samples using SFE. Three spiked soils including Ottawa sand, kaolinite clay and silty-clay loam were also studied. Most SFE experiments were performed at 40 MPa and 65 °C, however, high-temperature tests at 40 MPa and 150 °C and high-pressure tests at 68 MPa and 65 °C were conducted as well. Although the extraction efficiency of loam increased by a pressure rise, low TPH removal yielded at high pressures for the clay soil. On the other hand, increase in temperature resulted in a higher recovery for both loam and clay soils [17].

The influence of the most important SFE operational parameters, i.e. pressure and temperature, on the removal of contaminants from clay soils have been studied to less extent, and specifically, for the removal of PHC fractions. As such there is a need for more investigations for the effect of temperature and pressure on the application of SCE process for PHCs removal from clay soils, which is the main objective of this study. This was implemented through a factorial experimental design and response surface methodology (RSM) to assess and optimize the effect of pressure and temperature.

6.2 Materials and methods

Figure 6.1 presents the general experimental procedure that were followed in this study. After spiked soil samples were prepared, the initial concentrations of PHCs were measured. Then, a required amount of soil sample (around 90 g) was taken to conduct the SFE test. Each test was replicated three times. The final concentrations of PHCs were measured. The initial and final PHCs measurements were used to calculate the PHCs removal percentages. Four consecutive steps including ultrasonic extraction, silica gel column cleanup, Kuderna-Danish (K-D) concentration and gas chromatography (GC) analysis were used for PHCs measurement.

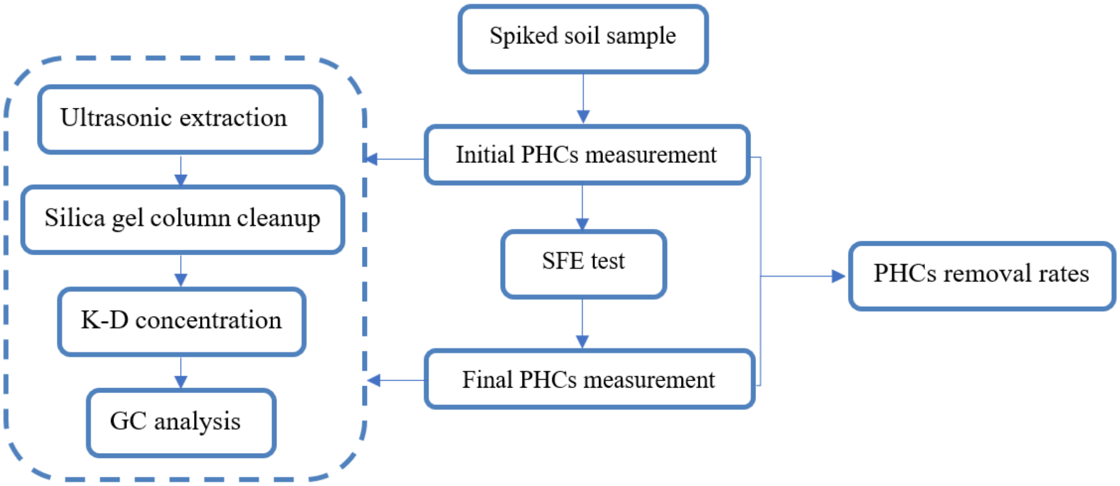

Figure 6.1. Flowchart of the experimental procedure [18]

6.2.1 Soil samples

The clay soil, which was used for this study, was composed of 40% sand, 20% silt and 40% clay with a water content of 4.3%. After soil characterization, the clay soil was spiked with diesel fuel with a ratio of 5 wt%. The desirable amounts of soil (in a natural condition with 4.3% water content) and diesel fuel based on 5 wt% were mixed thoroughly to achieve a homogenous state. The spiked soil samples were then placed in amber color glass jars with Teflon-lined caps to minimize any potential degradation due to light. All prepared soil samples were stored in a refrigerator for one month at a temperature of 4 °C ± 0.5 °C until used for experiments.

6.2.2 PHCs measurement

PHC F2, F3 and F4 fractions were analyzed according to Canada-Wide Standard for PHC in soil requirements by Canadian Council of Ministers of the Environment (CCME). The concentrations of PHCs fractions were compared with regulatory standards to check if the PHC concentrations in soil were below the acceptable criteria set for different land applications so that soil can be re-used [19]. Based on designated ranges of equivalent carbon number, PHCs fractions are defined as: PHC F2 ($>nC_{10}$ to nC_{16}), PHC F3 ($>nC_{16}$ to nC_{34}) and PHC F4 ($>nC_{34}$ to nC_{50+}) [20]. Concentration of PHC F2, F3 and F4 fractions in soil were measured according to the steps presented in the following sections.

6.2.2.1 Ultrasonic extraction

Non-volatile and semi-volatile organic compounds can be separated from soil by ultrasonic extraction [21]. Ultrasonic irradiation produces oscillating cavitation bubbles and shockwaves that can break the soil particle aggregates and would enhance the separation of contaminants from soil surface. As a result, the separation of contaminants such as PHCs which are attached to soil particles is feasible by ultrasonic extraction [22]. Method 3550C of US EPA (United States Environmental Protection Agency) [21] defines two procedures of ultrasonic extraction including low concentration (concentrations less than or equal to 20 mg/kg) and medium/high concentration (concentrations greater than 20 mg/kg). The amount of soil sample and number of extraction stages differ from low concentration process to medium/high concentration process [21]. Since contaminated soils that were used in this research expected to have PHC concentrations more than 20 mg/kg, the medium/high concentration process was followed for ultrasonic extraction.

According to method 3550C of US EPA for medium/high concentration process, a 1/8-inch tapered microtip, which was supplied from "Crystal Electronics Inc.", was attached to the bottom of a 1/2-inch horn [21]. A digital sonifier from "Branson Ultrasonics Corporation" with 450 watts power was used in this research. The soil was mixed thoroughly, and 2 g of soil was taken and placed in a 20-mL glass vial. Anhydrous sodium sulfate (granular), Na_2SO_4, was heated at 400 °C for 4 hours in the furnace to be purified prior to use. Anhydrous sodium sulfate (about 2 g) was added to soil samples that were wet (gummy) and did not have a free-flowing sandy texture. The volume of soil and sodium sulfate mixture was increased to 10 mL after addition of a required volume of solvent, which was acetone and hexanes with a ratio of 1:1 v/v. Acetone (C_3H_6O) and hexanes (C_6H_{14}) were purchased from "Fisher Scientific" at HPLC-grade and also met the ACS (American Chemical Society) specifications. The vial was placed below the ultrasound's probe while the horn tip was located between the solution surface and soil layer. Ultrasonic extraction was then performed. A set of preliminary tests was conducted to determine the optimum conditions for ultrasonic extraction were a sample size of 2 g, a time duration of 2 min at amplitude of 50% (half power) with mode switch on pulse (no continuous) and percent duty cycle at 50% (energy on 50% of time and off 50% of time). After completion of ultrasonic extraction, the sample was kept in a refrigerator [21].

6.2.2.2 Silica gel column cleanup

Naturally occurring non-hydrocarbon polar organic compounds can be available in contaminated soil samples and may interfere with PHC measurements. These polar compounds can be separated from PHCs by silica gel column cleanup [19]. A small amount of glass wool was put at the bottom of a glass chromatographic column to retain the adsorbent. Approximately 5 g of activated silica gel was added on top of the glass wool. Silica gel with 60-200 mesh size was procured from “Acros Organics; and was activated by drying over 101 °C overnight before being used in the silica gel column cleanup procedure [23]. Anhydrous sodium sulfate (approximately 10 mm) was then added on top of the silica gel. 10 mL of hexane: dichloromethane (with a ratio of 50:50 v/v) was used as an eluting solvent to wash and moisten the column. Dichloromethane (methylene chloride, CH_2Cl_2) was supplied by “Fisher Scientific at an Optima-grade and also met the ACS specifications. The sample extract from ultrasonic step was then poured into a column. All of eluant from this time was collected. Finally, the column was eluted with minimum 20 mL of hexane: dichloromethane and the whole eluant was collected [19].

6.2.2.3 Kuderna-Danish (K-D) concentration technique

K-D is typically used for the concentration of materials dissolved in organic solvents. Prior to GC analysis, the sample extract was concentrated to a lower volume (around 2 mL) using K-D. Since toluene is a compatible solvent for the GC apparatus used in this study, toluene (around 1 mL) was added to the sample. Through concentrating the sample, other solvents rather than toluene (i.e. acetone, hexanes and dichloromethane that were used in other analytical steps) were removed because of their lower boiling points from toluene’s boiling point.

The 500-mL evaporation flask was attached to the concentrator tube (10 mL graduated glass tube) by a clamp. The solvent was a mixture of acetone and hexanes with a ratio of 1:1 v/v. The liquid extract which was collected in the silica gel column, was transferred to the K-D with an additional 20 mL of solvent. One or two boiling chips were added to the flask to prevent bumping [24,25]. The Snyder column (3-ball macro) was attached to the flask by a clamp. Approximately 1 mL of solvent (acetone/hexane) was used to moisten the column. The whole K-D set-up was placed in a hot water bath in a fume hood. The flask was positioned at a level such that the concentrator tube was partially submerged in the hot water and the lower surface of the evaporating flask was bathed with hot water. The temperature of water bath was adjusted to approximately 85 °C so that it could vaporize solvents except toluene. Around 1 mL of exchange solvent (toluene) was added to the flask by momentarily removing the Snyder column [24]. Toluene ($C_6H_5CH_3$) was purchased from "Fisher Scientific" at an Optima-grade and also met the ACS specifications. The rate of concentrating can be adjusted by water's temperature compared with the boiling point of solvents. The final volume of extract around 2 mL can be reached after a few hours [19]. At the end, the K-D device should be removed from the water bath to be cooled down. Then, the final extract can be collected for further analysis.

6.2.2.4 Gas chromatography (GC)

A 6890 series GC with flame ionization detector (FID) from "Agilent Technologies" was used to measure the concentration of PHCs. The column was HP-1 crosslinked methyl siloxane (30 m × 0.32 mm × 0.25 µm film thickness). The auto sampler was used to inject 2 µL of the sample dissolved in toluene into the GC and the carrier gas was Helium. The oven temperature was held at 40 °C for 1 min, and then ramped from 40 to 325 °C at 15 °C/min. The temperature of injector and detector were set at 340 °C. Calibration curve and retention times were obtained using standards which had identical amounts of n-decane (C_{10}), n-hexadecane (C_{16}) and n-tetratriacontane (C_{34}) hydrocarbons dissolved in toluene and also n-pentacontane (C_{50}) dissolved in toluene but at a different concentration [19]. The area under the chromatogram from GC was analyzed with regards to the peak of nC_{10}, nC_{16} nC_{34} and nC_{50} to give the PHC fractions. The area under chromatogram for each fraction was then converted to concentration of PHC fractions according to the calibration curve which was prepared before.

6.2.3 Experimental setup and procedure of SFE

SFE can be conducted in three modes: *Static-mode* (SCF is kept in the extraction vessel for a certain duration), *Dynamic-mode* (a pump flows the SCF into the extraction vessel continuously), and *Combination-mode* (combinations of static- and dynamic-modes are performed and repeated for few cycles such that the static-mode is conducted for a certain duration followed by a dynamic mode) [1].

The apparatus for performing SFE experiments (i.e. SFT-110) was acquired from Supercritical Fluid Technologies Inc. The apparatus specifications are summarized in Table 6.1 [26].

Table 6.1. Properties of SFT-110 apparatus [26]

Parameter	Range
Pressure	0 to 10,000 psi (68.9 MPa)
Temperature	Ambient to 200 °C
Flow rate	0.01 to 24.00 mL/min liquid CO_2
Extraction vessel	100 mL
Dimensions	29cm Width, 57cm Depth, 76cm Height

Figure 6.2 shows a schematic diagram of the lab-scale SFT-110 apparatus which was used for performing SFE experiments. A liquid CO_2 cylinder (99.99% purity) with a dip tube that sucks the liquid CO_2 from the bottom of cylinder, was supplied by Linde Canada Ltd. The dual piston pump pressurized the CO_2. A rupture disk was supplied to act mechanically against incidental over-pressure conditions. The apparatus had a 100-mL extraction vessel (reactor or cell) where the

polluted soil was contained. The extraction vessel was surrounded by a heating unit, which had a pre-heater to control the temperature. In static mode, both static/dynamic valve and restrictor valve were closed. To switch from static mode to dynamic mode, first the static/dynamic valve was opened and then the restrictor valve was opened slightly. In dynamic mode, flow rate can be adjusted with a restrictor valve. A flow meter was installed to measure the flow rate of the expanding CO_2 gas. SCF was carried into the extraction vessel and extracted contaminants from soil. The SCF containing contaminants was then released from the extraction vessel to a collection vial through a restrictor valve. The restrictor valve is the point in the system where the CO_2 and dissolved contaminants are stepped down from supercritical to atmospheric pressure [26]. When the fluid was depressurized (fluid is not in supercritical state any more), the extracted contaminants were separated from the fluid due to the reduction in their solubility [1,27]. The contaminants that were extracted can be gathered in a collection vial. The rupture disk and collection vial were both connected to a fume hood for ventilation purposes [26]. Once the extraction vessel was depressurized, the soil sample was then removed from the extraction vessel.

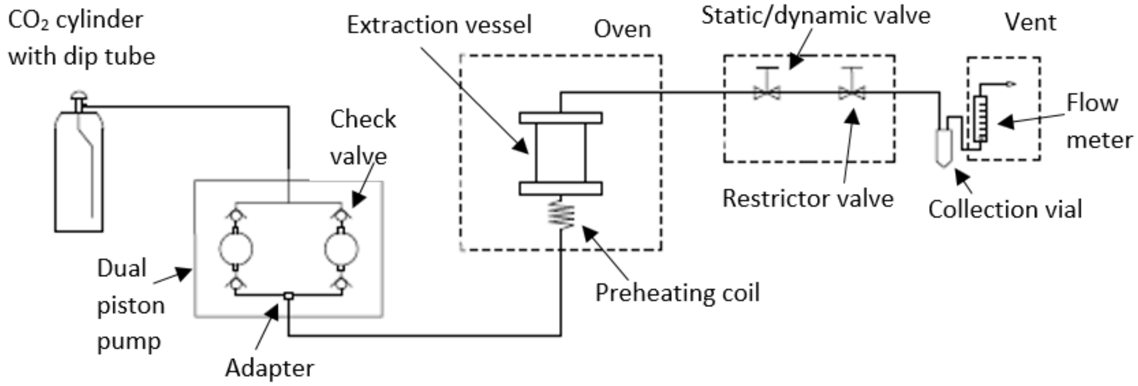

Figure 6.2. SFT-110 apparatus [26]

6.2.4 Soil mineralogy

The powder x-ray diffraction (PXRD) method was used for soil mineralogy analysis using a Rigaku Ultima IV powder x-ray diffractometer instrument at the “X-ray Core Facility” of the University of Ottawa. The detector was scintillation counter and continuous scan mode had a scan speed/duration time of 4 degree/min. Step width, scan axis and scan range were 0.0300 deg., 2 theta/theta, and 5.0000-100.0100 deg., respectively [28]. The diffraction pattern obtained by PXRD method was compared either with that of a known substance or by search-match analysis using a database such as the International Centre for Diffraction Database (ICDD).

6.2.5 Statistical method and data analysis

Factorial design and response surface methodology (RSM) were applied to set up experiments and to determine the optimum pressure and temperature levels. Two independent variables including pressure (P) and temperature (T) at three levels were selected. The ranges of changes of these variables which were coded between -1 and +1 are presented in Table 6.2. The selected values were based on the related information available in the literature that led to the highest extraction of contaminants [1,6,15,29–35] and also considering the specifications of SFT-110 apparatus used in this study. All tests were conducted three times.

Table 6.2. Experimental design and the levels of independent variables

Independent variable	Symbol	Coded levels		
		-1	0	+1
Pressure (MPa)	P	15	33	50
Temperature (°C)	T	30	75	120

Design-Expert® software (version 10) was used to perform the statistical analysis and RSM [36]. Three outcome responses including PHC F2, PHC F3 and PHC F4 removal percentages were calculated using the Eq. (6.1).

$$PHC\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{Eq. (6.1)}$$

Where C_i and C_f are the initial (before SFE test) and final (after SFE test) PHC concentrations (mg/kg), respectively; that were measured for each PHC fraction separately (i.e. PHC F2 to F4). The behavior of the system could be described by the quadratic equation as shown in Eq. (6.2) [37,38].

$$Y = A_0 + \sum_{i=1}^{n} A_i X_i + \sum_{i=1}^{n} A_{ii} X_i^2 + \sum_{i \neq 1\ j=1}^{n} A_{ij} X_i X_j + \varepsilon \qquad \text{Eq. (6.2)}$$

Where Y is the outcome response; X_i and X_j are the independent variables; A_0 is the value of the fixed response at the center point of the design; A_i, A_{ii} and A_{ij} represents the interaction coefficients of linear, quadratic and second-order terms, respectively; n is the number of independent variables; and ε is the random error.

The following parameters were fixed for all SFE experiments to negate their effects and only allow pressure and temperature to influence results. The time duration was the combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles (60 min in total) and flow rate was 24 mL/min of liquid CO_2. This combination of static and dynamic mode for 60 min was the best extraction mode and time duration for PHCs extraction, which was selected based on another phase of the authors' research [18]. Approximately 90 g of the spiked clay soil was placed in the extraction vessel.

6.3 Results and discussion

6.3.1 Effect of pressure and temperature on a clay soil

The ranges of pressure and temperature reported in the literature for SFE treatment of contaminated soils are 6-66 MPa and 20-200 °C, respectively, that from these studied values a pressure range of 12-55 MPa and a temperature range of 30-150 °C led to the highest extraction of contaminants [1,6,15,29–35]. As can be seen, the range for both parameters is quite wide. The laboratory SFT-110 apparatus used in this study could handle pressures up to 69 MPa and temperatures up to 200 °C. Various combinations of pressure and temperature were studied based on the 3-level factorial experimental design as presented in Table 6.2. All tests were triplicated.

The results of mineralogy analyses are presented in Figure 6.3. The analysis was performed by comparison of the diffraction pattern with that of a known substance or by search-match analysis using a database such as ICDD [28].

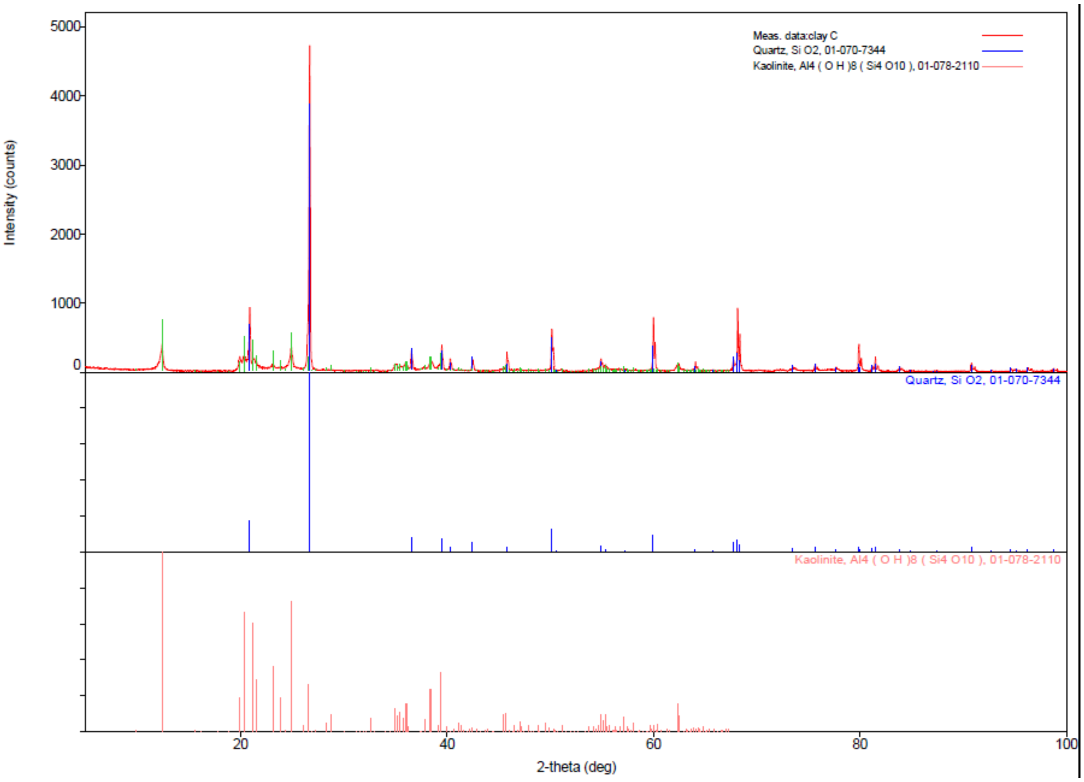

Figure 6.3. Mineralogy results for a clay soil [28]

According to the mineralogy analysis, the clay soil had quartz (SiO_2) minerals with an approximate content of 34.4% and kaolinite ($Al_2Si_2O_5(OH)_4$) minerals with an approximate content of 65.2% [28].

The averages of initial PHCs concentrations of the soil were 15285.4 ± 334.5 mg/kg for F2, 7679.3 ± 193.0 mg/kg for F3 and 3757.1 ± 392.1 mg/kg for F4. Total petroleum hydrocarbon fractions (TPHF) in this study is defined as the sum of PHC F2, F3 and F4 fractions. Figure 6.4 shows the changes in TPHF removal percentages at different pressures at constant temperature. TPHF removal percentages increased by the pressure rise from 15 MPa to 33 MPa at 75 °C and 120 °C temperatures. However, TPHF removal percentages were not statistically different ($p < 0.05$) by increasing pressure from 15 MPa to 33 MPa at 30 °C temperature. Further increase of pressure from 33 MPa to 50 MPa resulted in the reduction of TPHF removal percentage by 23.7% at 30 °C temperature. The rise in pressure from 33 MPa to 50 MPa did not affect the TPHF removal percentage at 75 °C and 120 °C significantly. In conclusion, no general trend was observed in TPHF removal percentages with changes in pressure at the low temperature of 30 °C. However, the extraction of TPHF increased with increasing pressure from 15 MPa to 33 MPa at constant temperatures of 75 °C and 120 °C. Overall, an additional rise of pressure from 33 MPa to 50 MPa did not result in a greater extraction of TPHF.

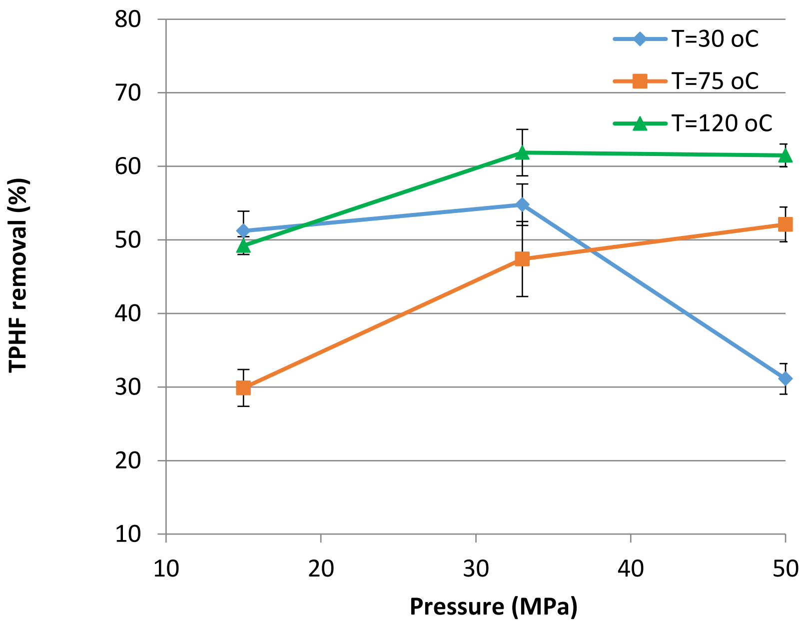

Figure 6.4. TPHF removal percentages with different pressures at a constant temperature

Figure 6.5 shows the changes in TPHF removal percentages at different temperatures at constant pressure. When temperature increased from 30 °C to 75 °C, the extraction of TPHF decreased at constant pressures of 15 MPa and 33 MPa while TPHF removal percentage increased at 50 MPa pressure. TPHF removal percentages increased by increasing temperature from 75 °C to 120 °C at all constant pressures. Besides, 120 °C temperature led to the highest TPHF removal percentage at constant pressures of 33 MPa and 50 MPa. Overall, an additional rise of temperature beyond 75 °C would be effective for achieving a greater extraction of TPHF while no significant improvements were observed at a lower temperature of 30 °C.

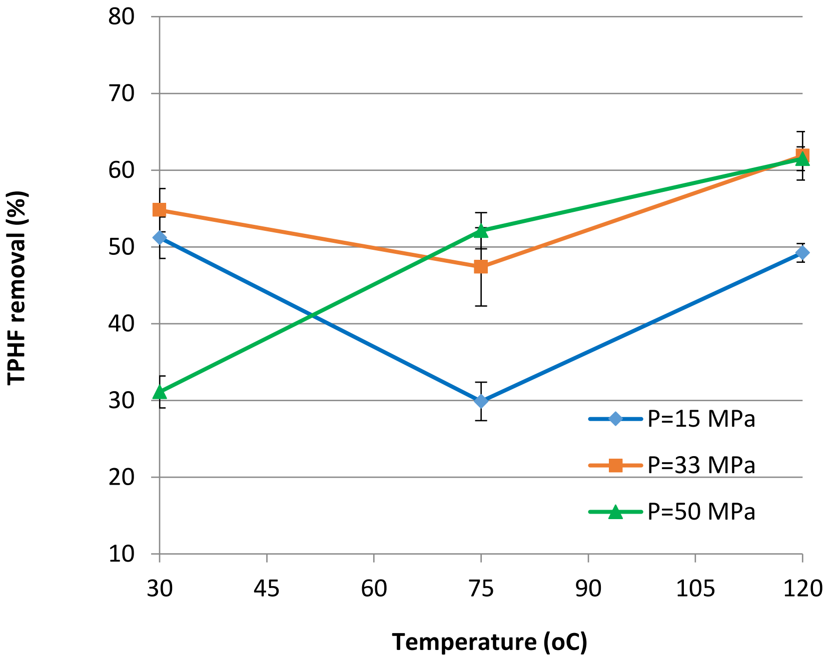

Figure 6.5. TPHF removal percentages with different temperatures at a constant pressure

Figure 6.6 shows the changes in removal percentages of PHC fractions at different pressures at constant temperature. Increase in pressure from 15 MPa to 33 MPa led to higher extraction of PHC F2 and F3 fractions at 75 °C and 120 °C temperatures (statistically significant at $p < 0.05$), however, no significant effect was observed for PHC F2 and F3 fractions at 30 °C. Further increase of pressure from 33 MPa to 50 MPa did not result in significant changes in PHC F2 and F3 removal percentages at 120 °C while a significant drop in PHC F2 and F3 removal percentages was observed at 30 °C. At 75 °C, increasing pressure from 33 MPa to 50 MPa led to an increase in PHC F2 removal percentage while PHC F3 removal percentage did not change significantly. For PHC F4, no significant change was overall observed by an increase in pressure at all three levels of temperatures tested. In general, the extraction of PHC F2 and F3 increased with increasing pressure (from 15 to 33 MPa) at higher temperatures.

PHC F2 had the highest removal percentages than other PHC fractions in the most studied conditions. The same result for a greater removal of F2 fraction than F3 and F4 fractions was stated by Nagpal and Guigard (2005) [16] for PHC removal from flare pit soils using SFE [16]. Removal of PHC F2 from soil would be easier than F3 and F4 because of PHC F2 fraction is considered as light extractable PHCs in soil and has lower molecular weight than F3 and F4 fractions. In addition, the interactions between F2 fraction and the soil matrix may be weaker than the interactions between F3 and F4 fractions and soil. An increase in pressure at a fixed temperature would increase the solvating power of CO_2 due to a higher density. Consequently, the solubility of PHC fractions would be improved which resulted in higher PHC removal percentages [15,17]. This effect of improving the extraction of PHCs owing to an increase in pressure at a constant temperature was observed for most PHC F2 and F3 fractions. A reduction in the extraction of PHC F2 and F3 fractions was observed when pressure increased from 33 MPa to 50 MPa at 30 °C. This different behaviour may be related to mass transfer limitations and a higher resistance to mass transfer at a lower temperature (30 °C). Interactive forces between hydrocarbon components and the soil matrix could be different [39]. Thus, the soil might have a stronger interaction for PHC F4 fraction compared to other fractions and SCF could not overcome that strong interaction. If there was a strong interaction between a contaminant and the soil matrix; temperature could have more significant effects on reaching higher removal percentages than pressure [40]. This might be a reason that no significant change was overall observed for the extraction of PHC F4 by an increase in pressure.

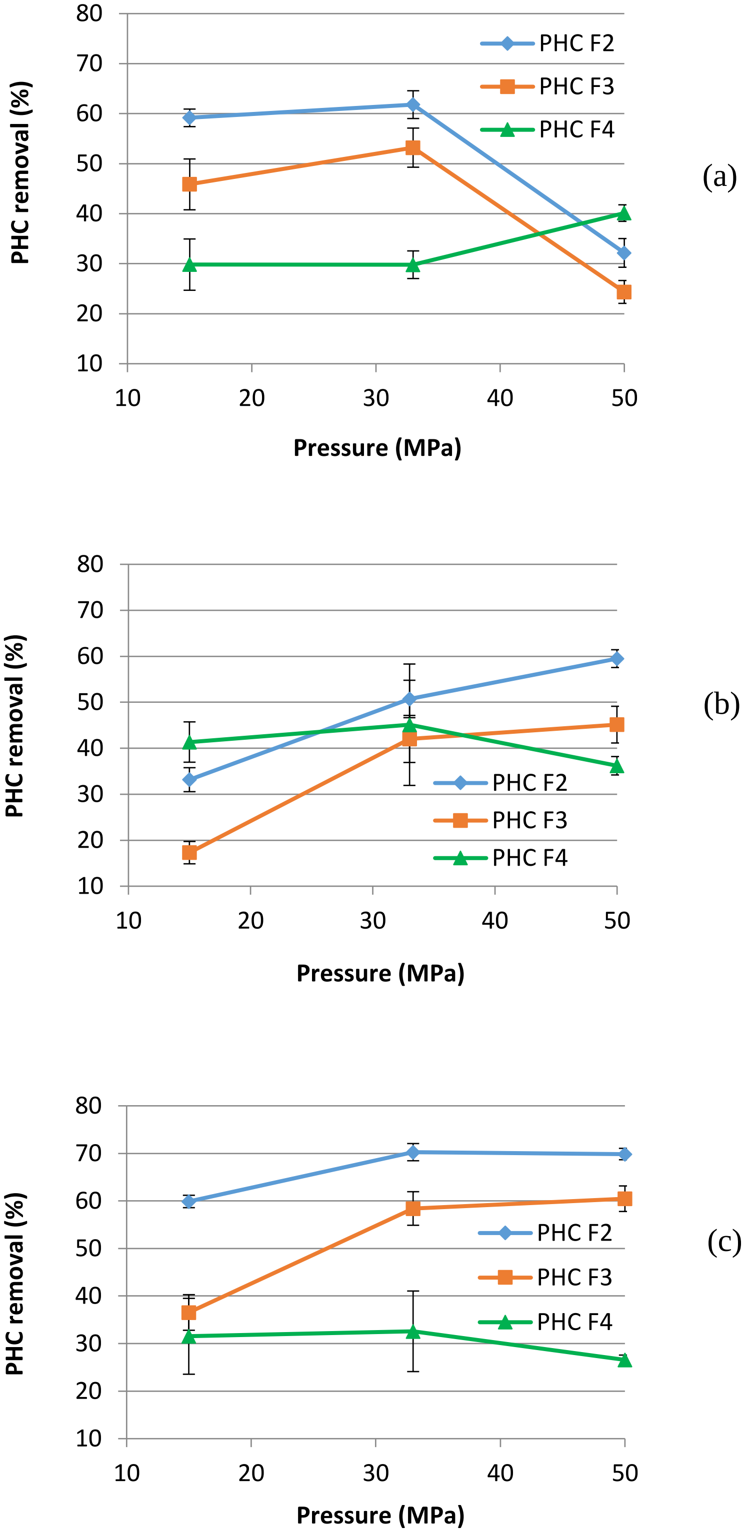

Figure 6.6. Removal percentages of PHC fractions with different pressures at (a) 30 °C (b) 75 °C (c) 120 °C

Figure 6.7 shows the changes in removal percentages of PHC fractions at different temperatures at constant pressure. The extractions of PHC F2 and F3 declined when temperature changed from 30 °C to 75 °C at constant pressures of 15 MPa and 33 MPa. The increase in temperature from 30 °C to 75 °C at a constant pressure of 50 MPa led to an increase in PHC F2 and F3 removal percentages. Further increase of temperature from 75 °C to 120 °C resulted in an increase in PHC F2 and F3 removal percentages at all constant pressures. Regrading PHC F4 fraction, no general trend was observed. At constant pressure of 15 MPa, PHC F4 removal percentage increased by increasing temperature from 30 °C to 75 °C and did not change significantly by increasing temperature from 75 °C to 120 °C. At constant pressure of 33 MPa, PHC F4 removal percentages were not statistically significant with increasing temperature from 30 °C to 75 °C and from 75 °C to 120 °C. At constant pressure of 50 MPa, increasing temperature from 30 °C to 75 °C and from 75 °C to 120 °C resulted in a decrease in PHC F4 removal percentage. High temperature of 120 °C led to the highest extraction of PHC F2 and F3 at the constant pressures of 33 MPa and 50 MPa. As expected, PHC F2 had the highest removal percentages than other PHC fractions in the most studied conditions.

In conclusion, the effect of temperature on the extraction of contaminants is a sum of the temperature effects on fluid density, volatility (solute vapor pressure), and the adsorption of the contaminant onto the soil matrix [41]. A rise in temperature could cause higher PHC removal percentages despite a reduction in density. The increase of PHC removal percentage by increasing temperature could be because of an increase in the volatility and/or an increase in the desorption of the contaminants from the soil [14,39]. Consequently, solute volatility and/or the desorption of a pollutant from the soil are dominant factors over a small decrease in density. Therefore, in this state, a rise in temperature caused higher PHC removal percentages. This is the case for an increase in PHC F2 and F3 removal percentages because of the rise in temperature from 75 °C to 120 °C at all constant pressures and increasing temperature from 30 °C to 75 °C at 50 MPa. There are different reasons for a decrease of PHC F2 and F3 removal percentages by the increase of temperature from 30 °C to 75 °C at 15 MPa and 33 MPa, which are explained subsequently. First, a rise in temperature at a constant pressure could lead to a reduction in solubility due to a remarkable decrease in density [14,39]. Therefore, in this case, a rise in temperature led to lower PHC removal percentages. Second, at a low-pressure level (e.g. 15 MPa), the rate of reduction in density (which led to a lower PHC extraction) due to an increasing temperature is expected to be higher than the rate of decrease of density due to an increasing temperature at a high-pressure level (e.g. 50 MPa). Therefore, PHC extraction efficiencies would be lower at a low-pressure level than a high-pressure level. Based on the presented results, the average of PHC F2, F3 and F4 removal percentages at 15 MPa were 50.7%, 33.2% and 34.2%, respectively. Whereas, the average of PHC F2, F3 and F4 removal percentages at 50 MPa were 53.8%, 43.3% and 34.3%, respectively; which were approximately higher than those at 15 MPa. This comparison showed that the level of pressure might also be important to investigate the effect of temperature on the extraction of PHCs; which may cause a difference in the extraction of PHC F2 and F3 at 15 MPa and 50 MPa. Third, since the soil had a high content of clay, it might happen that some PHCs were trapped within pore spaces in clay surfaces and consequently, PHCs were less accessible that caused the transportation of those PHCs (PHC F2 and F3) more difficult. In this situation, the pressure and temperature levels may also have an effect on the diffusion of contaminants. Fourth, another reason for a decrease of PHC F2 and F3 removal percentages due to the increasing temperature from 30 °C to

75 °C at 15 MPa and 33 MPa could be because of diffusion of SCF through the soil structure may be affected by the temperature level [15].

Considering PHC F4, the extraction of PHC F4 decreased while PHC F2 and F3 removal percentages increased at 50 MPa. PHC F4 removal percentages behaved differently than PHC F2 and F3 fractions. This different behaviour might be related to some factors such as complicated interactions between soil-pollutant-fluid. Interactive forces between hydrocarbon components and the soil matrix could be different [39]. The soil might have had a strong interaction with PHC F4 fraction. Therefore, more energy was required to disrupt the strong interactions between F4 fraction and the soil to improve the desorption process [15]. The required energy could be provided or could not be provided which may depend on the various pressure and temperature levels.

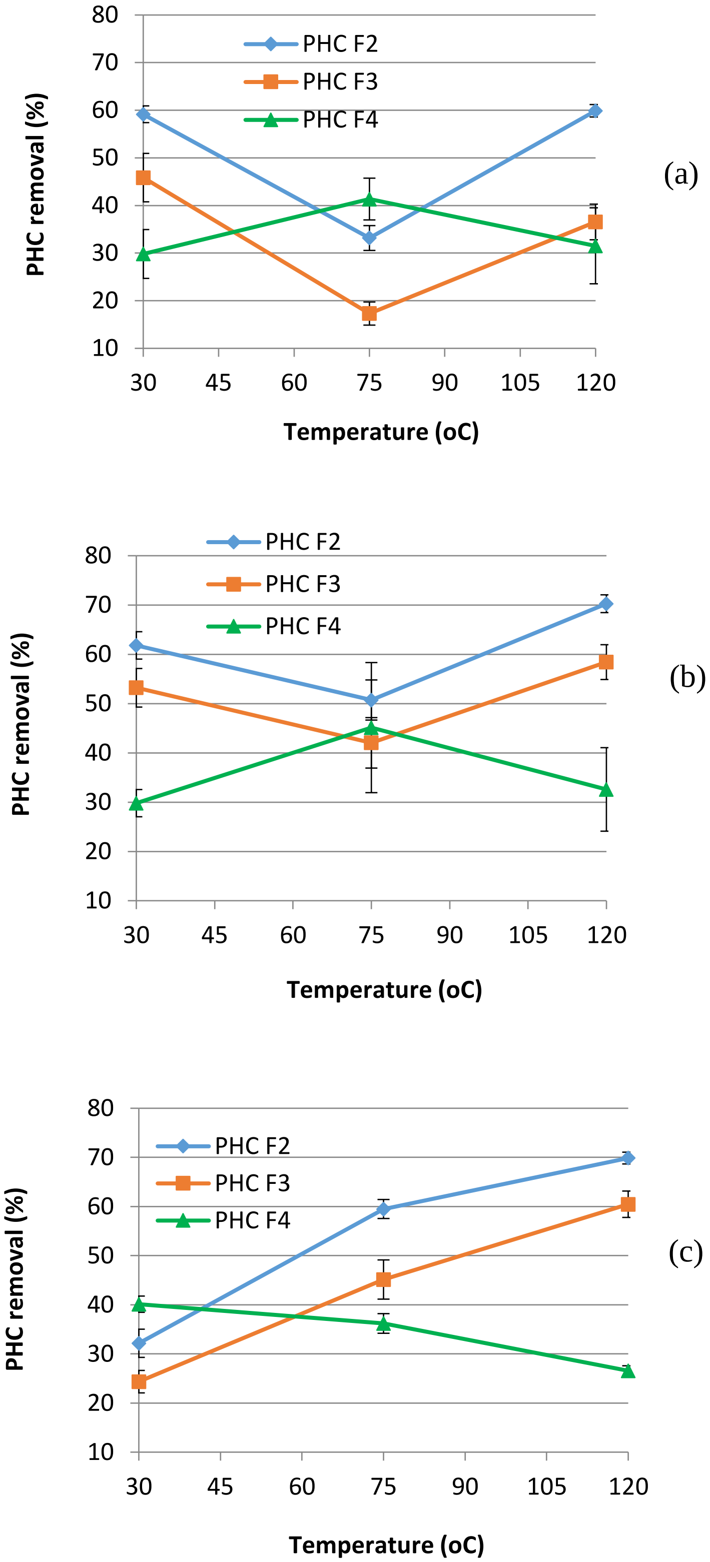

Figure 6.7. Removal percentages of PHC fractions with different temperatures at (a) 15 MPa (b) 33 MPa (c) 50 MPa

In summary, based on all the conditions studied here, the lowest extraction percentage was related to the combination of low pressure and medium temperature and the combination of high pressure and low temperature. The highest extraction percentage was observed for the combination of medium pressure and high temperature and the combination of high pressure and high temperature. Comparison between these two latter conditions shows that PHC F2 and F3 removal percentages were roughly close to each other, however, PHC F4 removal percentage was higher for medium pressure and high temperature than high pressure and high temperature. On the other hand, the difference between these two conditions was the pressure level. From the practical point of view, reaching medium pressure (33 MPa) is easier, safer and more economical than high pressure (50 MPa). Therefore, the best combination for pressure and temperature which resulted in the highest extraction of PHCs from the soil studied here was selected for medium value for pressure (33 MPa) and high value for temperature (120 °C). This combination resulted in 70.3%, 58.4% and 32.6% removal percentage for PHC F2, F3 and F4 fractions, respectively.

6.3.2 Statistical analysis and modeling

Based on a factorial design of two independent variables (pressure and temperature) at three levels with three replicates, a total of 27 runs for the extraction of each PHC fraction were obtained. Regression analysis was applied to develop the best-fit model for the collected data. Two responses including PHC F2 removal percentage and PHC F3 removal percentage were fitted for quadratic models, which are shown in Eq. (6.3) and Eq. (6.4), respectively [36].

$$PHC\ F2 = 67.233 + 1.04P - 1.028T + 0.0117PT - 0.0282P^2 + 0.0055T^2 \qquad \text{Eq. (6.3)}$$

$$PHC\ F3 = 48.11 + 1.951P - 1.213T + 0.0144PT - 0.0422P^2 + 0.0058T^2 \qquad \text{Eq. (6.4)}$$

Where PHC F2 and F3 are the removal percentage of PHC fractions, P and T are pressure and temperature, respectively. It should be noted that an attempt was made for modeling the PHC F4 fraction removal, however, the regression model for PHC F4 removal percentage was not significant accompanied with a significant lack of fit and a low R squared value (below 0.5). Therefore, no results for statistical analysis for PHC F4 removal percentage were presented.

F-test was conducted for analysis of variance (ANOVA) to evaluate the statistical significance of quadratic models. The ANOVA test results for PHC F2 model are presented in Table 6.3. According to Table 6.3 (a), the F-value of 9.45 and the “Prob>F” value of <0.0001 indicated that the model was statistically significant for PHC F2 removal percentage. For PHC F2 model, the “Prob>F” value for the P term (0.442) was greater than 0.05 implying that this term was insignificant and could be eliminated from the model [36]. The ANOVA test results for the reduced form of the PHC F2 model are shown in Table 6.3 (b). All terms in the reduced model had the “Prob>F” values less than 0.05 and were significant. The reduced model was simpler (less terms) than the full model and was considered to be appropriate to model the PHC F2 removal. The reduced quadratic model for PHC F2 removal percentage is shown as Eq. (6.5) [36].

$$PHC\ F2 = 83.109 - 1.068T + 0.013PT - 0.014P^2 + 0.0055T^2 \qquad \text{Eq. (6.5)}$$

According to Table 6.3 (b), the model F-value of 11.87 implied the model was significant and there was only a 0.01% chance that a F-value this large could occur due to noise. The lack of fit compares residual error with pure error from replicated design points. The lack of fit F-value of 60.84 implied the lack of fit was significant. Adequate precision measures the signal to noise ratio. Adequate precision of 9.501 indicated an adequate signal (a ratio greater than 4 is desirable) and this model can be used to navigate the design space. The R-squared value of 0.683 showed that the model could fit the experimental data properly. The predicted R-squared of 0.558 was in a reasonable agreement with the adjusted R-squared of 0.626 (the difference was not greater than 0.2) [36]. Coefficient of determination (R-squared), adjusted R-squared (R^2_{adj}) and predicted R-squared (R^2_{pred}) values were used to evaluate the fitness of the model. Adjusted R-squared is a modification of R-squared, which adjusts for the number of explanatory terms in a model relative to the number of data points [42]. The predicted R-squared indicates how well a regression model predicts responses for new observations [43].

Table 6.3. ANOVA for PHC F2 (a) full and (b) reduced quadratic model parameters [36]

(a)

Source	Sum of squares	df	Mean square	F value	p-value Prob>F	
Model	3350.58	5	670.12	9.45	< 0.0001	significant
P	43.56	1	43.56	0.61	0.4419	
T	1098.24	1	1098.24	15.49	0.0008	
PT	1026.75	1	1026.75	14.48	0.0010	
P^2	447.21	1	447.21	6.31	0.0203	
T^2	734.83	1	734.83	10.37	0.0041	
Residual	1488.70	21	70.89			
Lack of Fit	1383.18	3	461.06	78.65	< 0.0001	significant
Pure Error	105.52	18	5.86			
Total	4839.28	26				
$R^2=0.692$, $R^2_{adj}=0.619$, $R^2_{pred}=0.501$, *Adequate precision=8.597*						

Table 6.3. ANOVA for PHC F2 (a) full and (b) reduced quadratic model parameters [36]

(b)

Source	Sum of squares	df	Mean square	F value	p-value Prob>F	
Model	3307.03	4	826.76	11.87	< 0.0001	significant
T	1098.24	1	1098.24	15.77	0.0006	
PT	1026.75	1	1026.75	14.74	0.0009	
P^2	447.21	1	447.21	6.42	0.0189	
T^2	734.83	1	734.83	10.55	0.0037	
Residual	1532.25	22	69.65			
Lack of Fit	1426.73	4	356.68	60.84	< 0.0001	significant
Pure Error	105.52	18	5.86			
Total	4839.28	26				
R^2=0.683, R^2_{adj}=0.626, R^2_{pred}=0.558, *Adequate precision=9.501*						

The ANOVA test results for PHC F3 model is presented in Table 6.4. As can bee seen in the table, all terms in the full model were significant (“Prob>F” value less than 0.05) and there was no need to reduce the model for PHC F3 removal percentage.

According to Table 6.4, the model F-value of 17.39 implied the model was significant and there was only a 0.01% chance that a F-value this large could occur due to noise. The lack of fit F-value of 18.54 implied the lack of fit was significant. Adequate precision of 11.539 indicated an adequate signal (a ratio greater than 4 is desirable) and this model can be used to navigate the design space. The R-squared value of 0.805 showed that the model could fit the experimental data properly. The predicted R-squared of 0.682 was in a reasonable agreement with the adjusted R-squared of 0.759 (the difference was less than 0.2) [36].

Table 6.4. ANOVA for PHC F3 full quadratic model parameters [36]

Source	Sum of squares	df	Mean square	F value	p-value Prob>F	
Model	4335.19	5	867.04	17.39	< 0.0001	significant
P	456.02	1	456.02	9.14	0.0065	
T	513.07	1	513.07	10.29	0.0042	
PT	1548.14	1	1548.14	31.04	< 0.0001	
P^2	1003.63	1	1003.63	20.13	0.0002	
T^2	814.33	1	814.33	16.33	0.0006	
Residual	1047.24	21	49.87			
Lack of Fit	791.18	3	263.73	18.54	< 0.0001	significant
Pure Error	256.06	18	14.23			
Total	5382.43	26				
$R^2=0.805$, $R^2_{adj}=0.759$, $R^2_{pred}=0.682$, *Adequate precision=11.539*						

Figure 6.8 illustrates the observed (actual) response values versus the predicted response values for removal of PHC F2 and F3 fractions. Actual values were collected from the experimental data and predicted values were calculated by the model. This graph helps to detect observations that were not well predicted by the model. The coefficient of determination (R^2) provides a measure of the goodness of the fit for the predicted outcomes by the model and the observed data within the ranges of experiments. The R-squared (R^2) values for PHC F2 and F3 were 0.683, and 0.805, respectively. The R-squared (R^2) values indicated a good correlation between the actual and predicted values for the PHC F2 and F3 models.

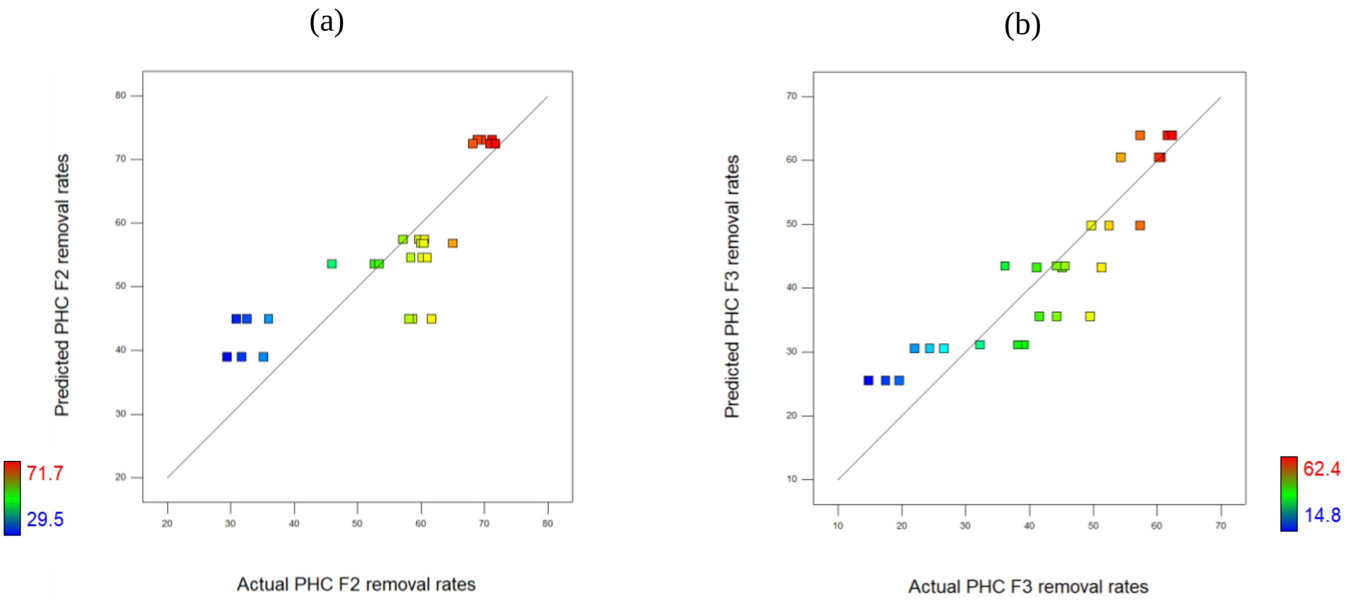

Figure 6.8. Predicted versus actual values for removal rates of (a) PHC F2 (b) PHC F3 [36]

Figure 6.9 presents the normal probability plots of externally studentized residuals. The figure shows an adequate fit of the externally studentized residuals versus normal probability percentage, confirming that the statistical assumptions suited the analytical data, which represents that the model predictions statistically fitted the observed results. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. A non-linear pattern (such as a S-shaped curve) indicates non-normality in the error term, which may be corrected. Externally studentized residuals (sometimes referred to as outlier t-value) are calculated by leaving the run in a question, one at a time, out of the analysis and estimating the response from the remaining runs. It checks whether the run in a question follows the model with coefficients estimated from the rest of the runs, that is, whether this run is consistent with the rest of the data for this model. A value greater than the calculated limits means that this point should be examined as a possible outlier. Externally studentized residuals based on a deletion method are recommended due to being more sensitive for finding problems with the analysis [36].

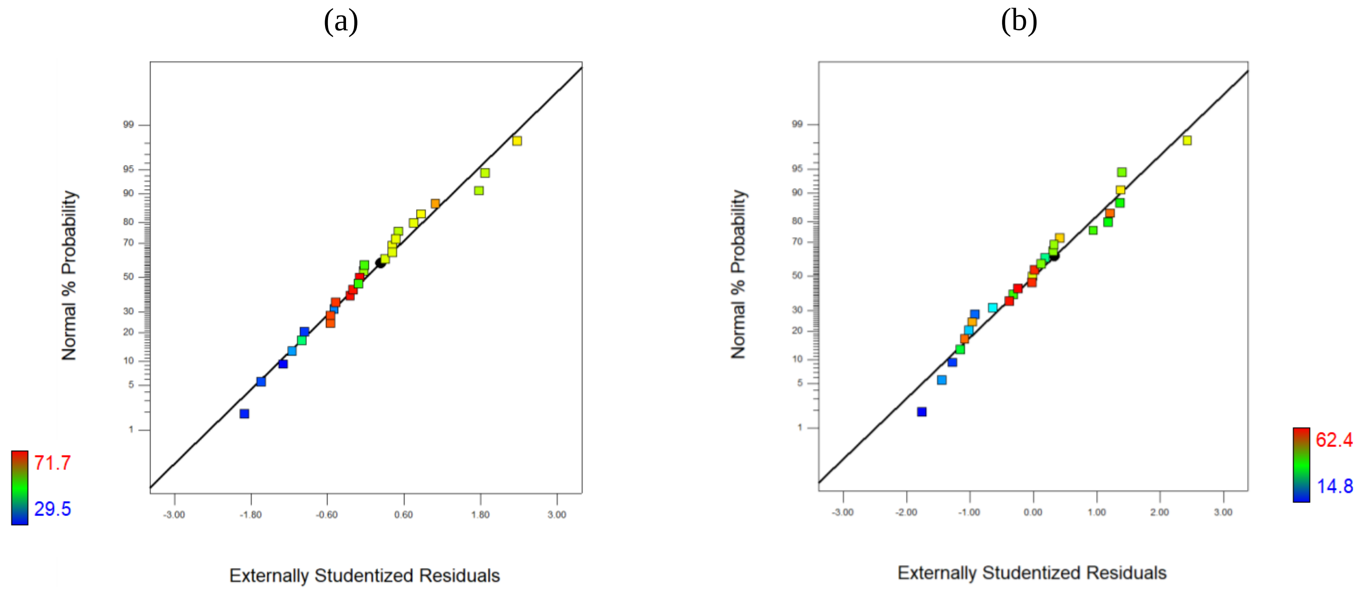

Figure 6.9. Normal probability of externally studentized residuals for removal of (a) PHC F2 (b) PHC F3 [36]

6.3.3 Response surface methodology

Numerical optimization was done by RSM to evaluate the interaction between two independent variables (pressure and temperature) and the response (PHC removal percentage). A three-dimensional surface plot and a two-dimensional contour plot for the optimization of PHC F2 and F3 fractions are shown in Figure 6.10 and Figure 6.11, respectively.

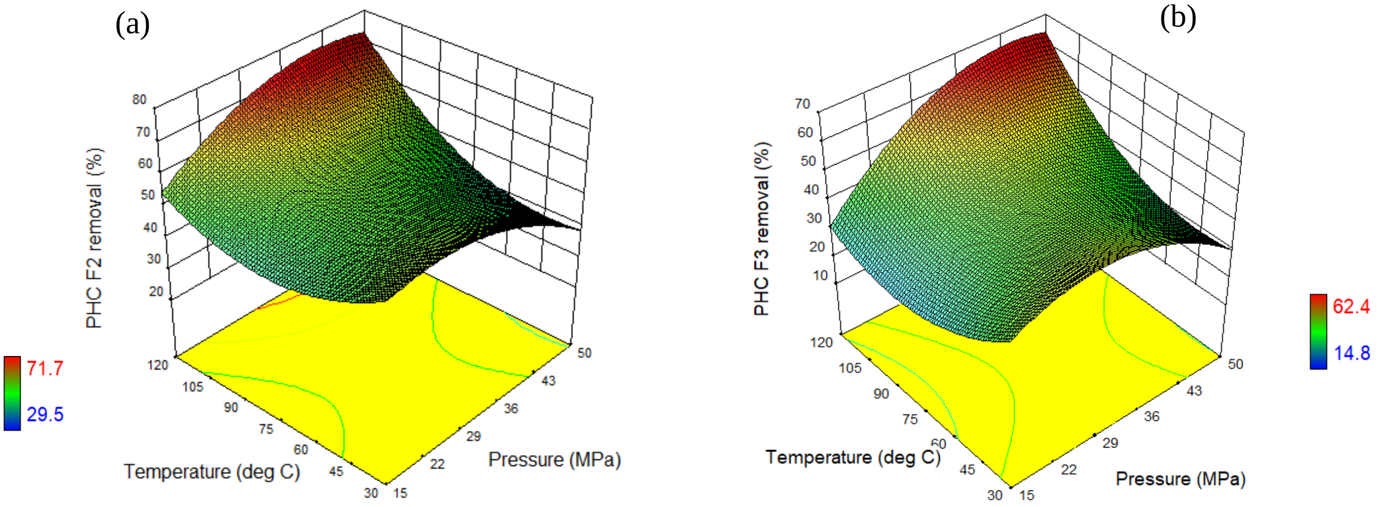

Figure 6.10. Three-dimensional surface plot by RSM for removal of (a) PHC F2 (c) PHC F3 [36]

It can be concluded from the figures that temperatures above 75 °C overall increased the PHC extraction efficiency. However, the effect of pressure was different and there was an optimum range for the pressure. In general, pressure around medium level (33 MPa) showed better extraction results. If the extraction is to be optimized individually for PHC F2 and F3 fractions, the optimized pressure and temperature levels for each fraction would be in the ranges which are shown in Fig. 6.10. However, when PHC fractions were combined, the optimum pressure and temperature were found to be 42.8 MPa and 120 °C, respectively. These levels of pressure and temperature led to removal percentages of 74.9% and 65.6% for PHC F2 and F3 fractions, respectively.

Moreover, the desirability of the optimum condition was constructed at 0.434. Therefore, responses (removal percentages of PHC fractions) were combined with the goal of being maximized to yield the highest PHC removal efficiency. Desirability varies from zero to one for any given response. A desirability value of one represents the ideal case and a zero desirability indicates that one or more responses fall outside desirable limits. Individual desirability was combined into a single number with the goal of searching for the greatest overall desirability [36].

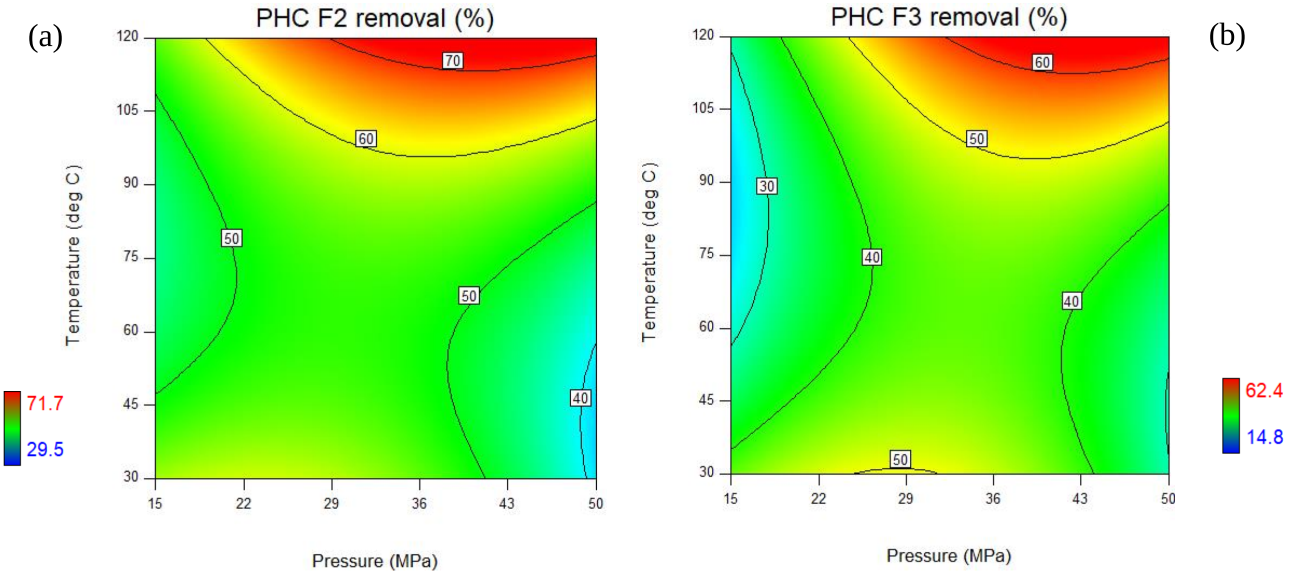

Figure 6.11. Two-dimensional contour plot by RSM for removal of (a) PHC F2 (c) PHC F3 [36]

6.4 Conclusion

The following conclusions can be drawn from this study:

- No general trend was observed in TPHF removal percentages with changes in pressure at the low temperature of 30 °C. However, the extraction of TPHF increased with increasing pressure from 15 MPa to 33 MPa at constant temperatures of 75 °C and 120 °C. An additional rise of pressure from 33 MPa to 50 MPa at 75 and 120 °C temperature did not result in a greater extraction of TPHF.

- The changes in pressure at 30 °C temperature did not result in any obvious trend on the removal of PHC F2 and F3 fractions. The extraction of PHC F2 and F3 fractions increased with increasing pressure from 15 to 33 MPa at higher temperatures (i.e. 75 and 120 °C). Increasing pressure from 33 to 50 MPa at 75 and 120 °C did not lead to an obvious effect on removal of PHC F2 and F3 fractions. Considering PHC F4, no significant change was overall observed by an increase in pressure at all three levels of temperatures tested.
- PHC F2 had the highest removal percentages than other PHC fractions in the most studied conditions. In other words, removal of PHC F2 from soil was overall easier than F3 and F4 fractions. Despite the fact that there are differences in molecular weight of extractable PHC fractions in soil, the interactions between each PHC fraction and the soil matrix could be different.
- When temperature increased from 30 °C to 75 °C at constant pressures of 15 MPa and 33 MPa, the extraction of TPHF and PHC F2 and F3 fractions decreased while at 50 MPa pressure, removal percentages of TPHF and PHC F2 and F3 fractions increased. Removal percentages of TPHF and PHC F2 and F3 fractions increased by increasing temperature from 75 °C to 120 °C at all constant pressures. Regrading PHC F4 fraction, no general trend was observed.
- 120 °C temperature led to the highest TPHF removal percentage at constant pressures of 33 MPa and 50 MPa. An additional rise of temperature beyond 75 °C would be effective for achieving a greater extraction of TPHF while no significant improvements were observed at a lower temperature of 30 °C.
- The optimum combination of pressure and temperature based on the experimental results was selected for medium pressure and high temperature (i.e. 33 MPa and 120 °C) that led

to 70.3%, 58.4% and 32.6% removal of PHC F2, F3 and F4 fractions, respectively. According to RSM, the optimum pressure and temperature were found to be 42.8 MPa and 120 °C that resulted in 74.9% removal of PHC F2 and 65.6% removal of PHC F3.

Appendix: notations

ACS	American Chemical Society
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
CO_2	Carbon dioxide
FID	Flame Ionization Detector
GC	Gas Chromatography
HPLC	High-performance liquid chromatography
ICCD	International centre for diffraction database
K-D	Kuderna-Danish
PAH	Polyaromatic (Polycyclic aromatic) hydrocarbon
PHC	Petroleum hydrocarbon
PXRD	Powder x-ray diffraction
RSM	Response surface methodology
SCE	Supercritical extraction
SCF	Supercritical fluid
SFE	Supercritical fluid extraction
SFT	Supercritical Fluid Technologies Inc.
TPH	Total petroleum hydrocarbon
TPHF	Total petroleum hydrocarbon fractions
US EPA	United States Environmental Protection Agency

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Chapter 7: Synthesis, Integration and General Discussion of Results

The application of supercritical fluid extraction (SFE) for treatment of petroleum hydrocarbon (PHC) contaminated soil was investigated. The effect of pressure, temperature, time duration, mode of extraction, soil water content, soil pH, modifier addition, soil type and soil grain size were assessed through laboratory scale experiments. PHCs are categorized into fractions according to the requirements of Canada-Wide Standard for PHC in soil by Canadian Council of Ministers of the Environment (CCME). The main findings of this research are synthesized and discussed below.

7.1 Effect of pressure and temperature for sand

The effects of SFE operational parameters including fluid pressure, fluid temperature, time duration and mode of extraction on PHC removal from a sand spiked with diesel fuel with a ratio of 5 wt% were investigated. A combined mode of operation and alternating between static and dynamic modes through repeated cycles was more efficient than using a single static mode due to the fact that in dynamic mode, supercritical fluid (SCF) flows through soil and could flush the extracted contaminants out of the soil matrix and would enhance the removal of PHCs. A combination of 10 min static mode followed by 10 min dynamic mode, repeated for 3 cycles (10S+10D × 3C) for a total time of 60 min resulted in the highest PHC removal percentages. The concentrations of PHC fractions at the end of cycle #3 of SFE for the case of 10S+10D × 3C were compared with the Ontario Ministry of Environment (MOE)- Canada, “Table 2- under Industrial/Commercial/Community property use”. This comparison shows that only PHC F2 concentration was slightly above the standard limit while the concentrations of PHC F3 and F4 fractions were below the standard limits; indicated that soil was considered almost clean and can be used for appropriate land uses.

The diesel fuel can be overall available in four different phases in soil. Diesel can be adsorbed on soil surface, dissolved in soil water content, available in gaseous phase and as a separate pure phase. Since water content of the soil used in this study was low (around 1% by weight) and also solubility of PHC F2-F4 fractions in water relatively is low, the amount of diesel dissolved in water content should not be significant. The soil used for this set of experiments was silica sand that may have little adsorption capacity and the amount of diesel adsorbed on soil particles expected to be low. Therefore, it is expected that the diesel fuel would be present mostly in pure phase. The pure phase overall in not very difficult to be extracted and consequently, high removal percentage of diesel from soil was achieved using SFE.

The effect of pressure and temperature on SFE of PHC fractions was investigated based on a factorial design involving three levels of pressure (15, 33 and 50 MPa) and three levels of temperature (30, 75 and 120 °C) with the experiments that the low and high ends replicated 3 times. PHC F2 removal percentages in the range of 92.3% to 99.4% were observed. Removal percentages of PHC F3 and F4 were in the range of 72.8%-93.5% and 64.8%-87.4%, respectively. PHC F2 removal from spiked sand was easier than F3 and F4 fractions due to the fact that F2 fraction is considered as light extractable PHCs in soil and has lower molecular weight than F3 and F4 fractions. An increase in pressure between 15 and 50 MPa at constant temperature of 30 and 75 °C (except at 120 °C) resulted in an increase in PHC removal percentage. This could be due to the fact that an increase in pressure at a fixed temperature resulted in an increase in CO_2 density that could improve the solubility of PHC fractions and consequently, led to higher PHC removal percentages. Increasing temperature between 30 and 120 °C at constant pressure (except at 50 MPa) did not necessarily lead to higher PHCs removal percentages and there was an optimum range for temperature. The effect of temperature on the extraction of PHCs is a sum of the temperature effects on fluid density, volatility (solute vapor pressure), and desorption of contaminants from soil matrix. The increase in temperature could result in an increase in the volatility and/or an increase in desorption of the contaminants from the soil that led to an increase in PHC removal percentage. In some cases, it could happen that the increase in temperature may result in a remarkable decrease in density that would led to a decrease in PHC removal percentage.

The best combination of pressure and temperature based on experimental results was determined to be at 33 MPa and 75 °C; which resulted in 99.2%, 91.7% and 86.1% removal of PHC F2, F3 and F4 fractions, respectively. The results were also analyzed using response surface methodology (RSM), which indicated an optimum pressure of 50 MPa and a temperature of 69.3 °C which could result in 100% removal of PHC F2 and 96.1% removal of PHC F3 fraction.

7.2 Effect of water content, pH and modifier addition

The influence of soil properties including soil water content and soil pH on PHC removal from a field-contaminated sand was investigated using SFE experiments at 33 MPa pressure and 75 °C temperature. Three water content levels of 8%, 14% and 20% and two pH values of 6.5 and 7.5 were assessed based on a factorial design. The increase in water content between 8% and 20% led to statistically significant ($p < 0.05$) PHC F3 removal reduction of 37.5% and 24.7% at pH 6.5 and 7.5, respectively. However, variations for PHC F2 and F4 fractions were not statistically significant by changing water content between 8% and 20%. Furthermore, increasing water content between 8% and 20% led to a decrease in removal of total petroleum hydrocarbon fractions (TPHF) (defined as the sum of F2, F3, and F4 fractions) at both pH 6.5 and 7.5. Excess water content in soil can create a thin water layer around soil particles that could act as a barrier for transportation of PHCs by SCF, which would lead to a decrease in PHC removal percentage. Differences among the extraction of PHC fractions (and TPHF removal) by changing pH 6.5 to 7.5 were not statistically significant at all three water content levels. Consequently, it is concluded that pH did not have a significant influence on PHC removal percentage.

The influence of modifier addition (5% by volume of a soil in the extraction vessel) on PHC removal from a field-contaminated sand was assessed using SFE experiments at 33 MPa pressure and 45 °C temperature. Preliminary tests indicated that acetone and hexanes were more effective than methanol and toluene. Addition of modifiers overall led to an increase in PHC removal since modifiers can help the removal of contaminants from the soil matrix, which may break the interactions between PHC and soil. Addition of acetone and hexanes resulted in 33.7% and 24.3% removal of TPHF, respectively, which showed acetone was more effective than hexanes for PHCs extraction. Addition of acetone enhanced the extraction of TPHF by 11.9% compared to the control sample (field-contaminated sand without addition of modifier). Hexanes was not effective for the extraction of PHCs compared to control sample since the differences of TPHF removal by hexanes were not statistically significant than control sample. The polarity of acetone is greater than hexanes and the difference in polarity may affect their performance.

7.3 Effect of soil grain size

The effect of soil type and soil grain size on PHC removal using SCE was investigated by assessment of PHC removal from three types of soil, sand, silt and clay, spiked with diesel fuel with a ratio of 5 wt%. Soil A (sand) was composed of 90% sand, 10% silt and 0% clay; soil B (silt) was composed of 20% sand, 60% silt and 20% clay; and soil C (clay) was composed of 40% sand, 20% silt and 40% clay. The equivalent particle size (diameter) of soil A was by far larger than both soil B and soil C. Particles sizes of soil B and C were slightly different. Coarse-grained fraction (larger than 0.075 mm) of soil B was smaller than soil C since soil B had lower quantity of sand. Fine-grained fraction (smaller than 0.075 mm) of soil C was smaller than soil B since soil C had higher quantity of clay. According to mineralogy analyses, soil A had quartz (SiO_2) minerals (about 99.6%). Soil B constituted quartz and kaolinite ($Al_2Si_2O_5(OH)_4$) with approximate contents of 64.5% and 35.1%, respectively. Soil C had quartz and kaolinite minerals with approximate contents of 34.4% and 65.2%, respectively.

SFE experiments at 33 MPa pressure, 75 °C temperature and combination of 10 min static mode and 10 min dynamic mode for three cycles were conducted. The highest and the lowest TPHF removal percentages were observed for soil A (90.4% removal) and soil C (47.4% removal), respectively. Greater particle sizes in soil A (sand) might lead to the bonding force between organic contaminants (PHCs) and sand particles that may not be very strong, which could potentially result in higher TPHF removal. Removal of PHC F2 and F3 fractions for soil A were (27.3% for F2 and 30.9% for F3) greater than soil B, and removal of PHC F2 and F3 fractions from soil B were (20.4% for F2 and 19.8% for F3) higher than soil C. However, the differences among PHC F4 fraction removal percentages for soil A, B and C were not statistically significant. Large surface areas of fine particles and the complexity of the structure of soil C (with multiple layers of micro-pores) could cause lower extraction of TPHF in soil C. As a result, higher clay content would result in a lower PHC removal percentage. PHC concentrations of each soil type after SFE treatment were compared with Table 2 of MOE. This comparison shows that soil A could be considered almost clean and can be used for the appropriate land use (which is industrial, commercial, community) since concentrations of PHC fractions in soil A were below the standard limits (except PHC F2). However, soil B and C overall did not meet the standard limits.

It should be noted that the three types of soil may differ in other characteristics rather than soil grain size such as organic matter content and soil chemical properties (such as surface charges). These properties might affect the process of PHCs extraction from soil. However, the focus of this study was to investigate the impact of soil grain size and thus, other soil properties (except than soil grain size) were not considered.

7.4 Effect of pressure and temperature for clay

Treatment of contaminated soils containing considerable amounts of clay is often problematic, which has been studied to lesser extent, specifically for the extraction of PHC fractions. The application of SFE for PHCs extraction from clay spiked with diesel fuel with a ratio of 5 wt% was investigated. Clay was composed of 40% sand, 20% silt and 40% clay; and had quartz (approximately 34.4% content) and kaolinite (approximately 65.2% content) minerals.

SFE experiments were performed based on a factorial design at 3 levels of pressure (15, 33 and 50 MPa) and 3 levels of temperature (30, 75 and 120 °C), with 3 replicates for each test. PHC F2 removal percentages in the range of 32.2% to 70.3% were observed. Removal percentages of PHC F3 and F4 were in the range of 17.3%-60.5% and 26.6%-45.1%, respectively. Increasing pressure from 15 to 33 MPa led to an increase in TPHF removal by 17.5% and 12.7% at constant temperatures of 75 and 120 °C, respectively. Also, the extraction of PHC F2 and F3 fractions increased by increasing pressure from 15 to 33 MPa at 75 and 120 °C temperature, probably due to an increase in density of CO_2 and may led to higher solubility. An additional rise of pressure from 33 to 50 MPa did not result in a greater extraction of TPHF as well as PHC F2 and F3 fractions. Regarding PHC F4, no statistically significant (at $p < 0.05$ confidence level) change was observed overall by increasing pressure at constant temperature.

Increasing temperature beyond 75 °C (i.e. from 75 to 120 °C) at constant pressure led to an increase in TPHF removal by 19.3, 14.5 and 9.4% at 15, 33 and 50 MPa pressure. Temperature of 120 °C led to the highest TPHF removal percentage of 61.9% and 61.5% at constant pressures of 33 MPa and 50 MPa, respectively. Also, extraction of PHC F2 and F3 fractions increased by increasing temperature from 75 to 120 °C at all constant pressures, which may be because of an increase in the volatility and/or an increase in the desorption of the contaminants from the soil. No significant improvements were observed for TPHF removal by increasing temperature from 30 to 75 °C (except at 50 MPa). Increasing temperature from 30 to 75 °C resulted in a decrease (at 15 and 33 MPa pressure) and an increase (at 50 MPa pressure) in PHC F2 and F3 fractions. No general trend was overall observed for PHC F4 fraction by changing temperature at constant pressure.

Application of RSM indicated that the optimum combination of pressure and temperature were 42.8 MPa and 120 °C; which resulted in 74.9% and 65.6% removal of PHC F2 and F3 fractions, respectively. The optimum combination of pressure and temperature based on experimental results was determined to be at 33 MPa and 120 °C; which resulted in 70.3%, 58.4% and 32.6% removal of PHC F2, F3 and F4 fractions, respectively.

7.5 Comparison the effect of pressure and temperature for sand and clay

In this study a poorly graded sand (composed of 99.9% sand and 0.1% silt and clay) was investigated in Chapter 3 while a clay (composed of 40% sand, 20% silt and 40% clay) was assessed in Chapter 6. Both clay and sand were spiked with diesel fuel with a ratio of 5 wt% and were tested at three levels of pressure and temperature under 10S+10D × 3C time and flow rate of 24 ml/min of liquid CO_2. For both sand and clay, PHC F2 removal was easier than F3 and F4 fractions. Removal percentage of PHC F2 for sand and clay were in the range of 92.3-99.4% and

32.2-70.3%, respectively. This comparison showed that removal percentage of PHC F2 from sand was obviously greater than clay.

Overall, higher pressure (50 MPa vs. 15 MPa) at constant temperature (except at 120 °C) for sand resulted in an increase in PHC removal percentage. With regards to the effect of pressure for clay, increasing pressure from 15 to 33 MPa at constant temperatures of 75 and 120 °C led to an increase in TPHF (as well as PHC F2 and F3 fractions) removal while increasing pressure from 33 to 50 MPa did not result in a greater extraction of TPHF (as well as PHC F2 and F3 fractions). In other words, there was an optimum range for the effect of pressure for clay. Regarding the effect of temperature for sand, increasing temperature between 30 and 120 °C at constant pressure (except at 50 MPa) did not necessarily lead to higher PHCs removal percentage and there was an optimum range for temperature. For the effect of temperature for clay, increasing temperature from 75 to 120 °C at constant pressure led to an increase in TPHF (as well as PHC F2 and F3 fractions) removal while no significant improvements were observed for TPHF removal (as well as PHC F2 and F3 fractions) by increasing temperature from 30 to 75 °C (except at 50 MPa).

The best combination of pressure and temperature for sand based on experimental results was 33 MPa and 75 °C; which resulted in 99.2%, 91.7% and 86.1% removal of PHC F2, F3 and F4 fractions, respectively. The best combination of pressure and temperature for clay based on experimental results was 33 MPa and 120 °C; which resulted in 70.3%, 58.4% and 32.6% removal of PHC F2, F3 and F4 fractions, respectively. Comparing the best combination between sand and clay based on experimental results shows that the pressure level is the same (33 MPa) and higher temperature (120 °C) for clay was more effective compared to sand (75 °C). In addition, the removal percentage of all PHC fractions were higher for sand compared to clay. A summary of the comparison of different parameters between sand and clay is presented in Table 7.1.

Table 7.1. Comparison of different parameters for sand and clay

Parameter	Sand	Clay
PHC F2 removal percentage range	92.3-99.4 %	32.2-70.3 %
Effect of pressure on PHC removal	increase	optimum range
Effect of temperature on PHC removal	optimum range	increase
Optimum experimental combination of pressure and temperate	33 MPa and 75 °C	33 MPa and 120 °C
Removal percentage for optimum experimental combination	99.2% F2, 91.7% F3, 86.1% F4	70.3% F2, 58.4% F3, 32.6% F4
Optimum RSM combination of pressure and temperate	50 MPa and 69.3 °C	42.8 MPa and 120 °C
Removal percentage for optimum RSM combination	100% F2, 96.1% F3	74.9% F2, 65.6% F3

Chapter 8: Conclusions and Recommendations for Future Work

8.1 Conclusions

The following conclusions can be drawn from this study for the application of SFE for treatment of petroleum contaminated soil:

- Using a combined mode and alternating between static and dynamic modes is more effective for PHCs removal than using a single static mode.
- PHC F2 removal percentages from spiked sand were observed in the range of 92.3% to 99.4%. PHC F2 removal from sand was easier than removal of PHC F3 (in the range of 72.8%-93.5% removal) and PHC F4 (in the range of 64.8%-87.4% removal).
- In the case of spiked sand, increasing pressure between 15 MPa and 50 MPa at constant temperature (except at 120 °C) resulted in an increase in removal percentages of PHC fractions. Increasing temperature between 30 and 120 °C at constant pressure (except at 50 MPa) did not necessarily lead to higher PHCs removal percentages and there was an optimum range for temperature.
- The optimum combination for pressure and temperature for spiked sand based on experimental results of three levels of pressure and temperature was determined to be at 33 MPa and 75 °C; which resulted in 99.2%, 91.7% and 86.1% removal of PHC F2, F3 and F4 fractions, respectively. According to response surface methodology (RSM), the optimum pressure and temperature were found to be 50 MPa and 69.3 °C that led to 100% removal of PHC F2 and 96.1% removal of PHC F3 fraction.

- An increase in water content between 8% and 20% led to a decrease in removal of total petroleum hydrocarbon fractions (TPHF) (defined as the sum of F2, F3, and F4 fractions) as well as PHC F3 fraction at both pH 6.5 and 7.5.
- Differences among the extraction of PHC fractions and TPHF from a field-contaminated sand by changing pH 6.5 to 7.5 were not statistically significant at all three water content levels. Therefore, pH variation did not have a significant influence on PHC and TPHF removal percentage within the studied range of pH.
- Addition of acetone and hexanes to field contaminated sand resulted in 33.7% and 24.3% TPHF removal, respectively that showed acetone was more effective than hexanes. Hexanes as a modifier did not act successfully for the extraction of PHCs compared to control sample (i.e. field contaminated sand without addition of modifier) since differences of TPHF removal by hexanes were not statistically significant than control sample.
- Soil A, B and C were composed of various percentages of coarse-grained and fine-grained particles that had different particle sizes. According to soil texture triangle, sand, silt loam and clay were the names of soil A, B and C, respectively. The highest and the lowest TPHF removal percentages were observed for soil A (90.4% removal) and soil C (47.4% removal), respectively. This shows that extraction of PHCs from soil C (clay) was more difficult than soil A (sand). Therefore, large particle size would lead to an increase and high clay content would result in a decrease in PHC removal percentage.
- Considering spiked clay, increasing pressure from 15 to 33 MPa led to an increase in TPHF (as well as PHC F2 and F3) removal at constant temperatures of 75 and 120 °C while an additional rise of pressure from 33 to 50 MPa did not result in a greater extraction of TPHF (as well as PHC F2 and F3). There was an optimum range for pressure. Increasing

temperature from 75 to 120 °C at constant pressure led to an increase in TPHF removal by 19.3, 14.5 and 9.4% at 15, 33 and 50 MPa pressure, respectively. 120 °C temperature led to the highest TPHF removal percentage at constant pressures of 33 MPa and 50 MPa.

- PHC F2 removal percentages from spiked clay were observed in the range of 32.2% to 70.3%. Removal percentages of PHC F3 and PHC F4 were in the range of 17.3%-60.5% and 26.6%-45.1%, respectively.
- The optimum combination of pressure and temperature based on RSM was selected at 42.8 MPa and 120 °C; which resulted in 74.9% and 65.6% removal of PHC F2 and F3 fractions, respectively. The optimum combination of pressure and temperature based on experimental results was determined to be at 33 MPa and 120 °C; which resulted in 70.3%, 58.4% and 32.6% removal of PHC F2, F3 and F4 fractions, respectively.

8.2 Recommendations for future work

Despite the fact that much information and significant outcomes were obtained in this research, there are still a number of other aspects that can be considered for future research to improve the application of SFE. These recommendations are summarized below:

- Co-contamination. Extraction of both organic and inorganic contaminants from a soil using SFE can be implemented in one process. If acceptable recoveries are achieved, the application of SFE will be then extended over a wide range.
- Although SFE is able to extract contaminants from soils quickly with a high removal percentage, the associated costs with the SCE operation may be high. Performing pilot-scale and full-scale SFE systems can provide significant information that would be helpful

for the economic analysis. Consequently, the development of SFE at a large-scale and the investigation of a continuous system would be beneficial.

- SFE can be integrated with other remediation techniques as a pre-treatment or post-treatment. Due to SCE only removes the contaminants from the sample, contaminants can be treated in another step after SCE using a suitable remediation method.
- Various ways of addition of modifiers to soil samples rather than the direct addition (which was used in this research) including premixed fluids and using a separate modifier pump should be utilized and compared to determine their differences on the extraction results.
- SFE should be compared with another soil remediation technique with regards to ease of run, operation time, costs, extraction efficiency and reproducibility under similar conditions.
- Analytical models can be developed to correlate the extraction efficiency with SFE operational parameters.
- Extraction of other types of contaminants including dioxins, furans, phenols, pesticides, metals and perfluorinated compounds (PFCs) from soils using SFE should be investigated. In addition, SFE can be used for treatment of other matrices such as wastewater and sludge.

Appendices

Appendix A: Laboratory Equipment used for PHCs measurement

1. Ultrasonic extraction

The ultrasonic device which was used in this research is shown in Figure A.1.

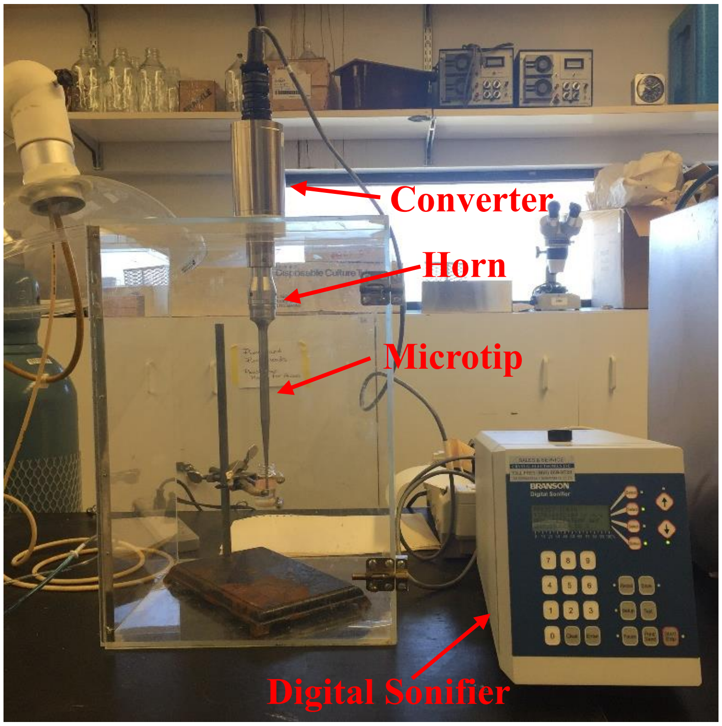

Figure A.1. Ultrasonic device

2. Silica gel column cleanup

Figure A.2 shows the set-up used for performing the silica gel column cleanup.

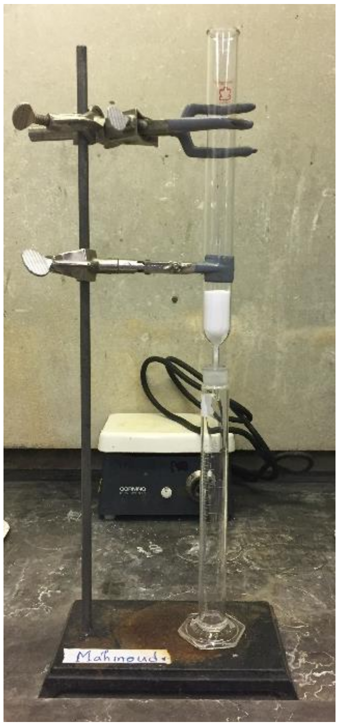

Figure A.2. Chromatographic column used for the silica gel column cleanup

3. Kuderna-Danish (K-D) concentration

K-D is typically developed for the concentration of materials dissolved in organic solvents. Steam is heat source which is used to evaporate the solvents, and the upper Snyder columns are used to condense heavier fractions back into the vessel. The column is designed to speed evaporation with reduced hold-up. The K-D apparatus which was used in this research is shown in Figure A.3. The K-D apparatus consisted of the following parts:

- Concentrator tube: 10-mL graduated glass tube
- Evaporation flask: 500-mL
- Snyder column: 3-ball macro

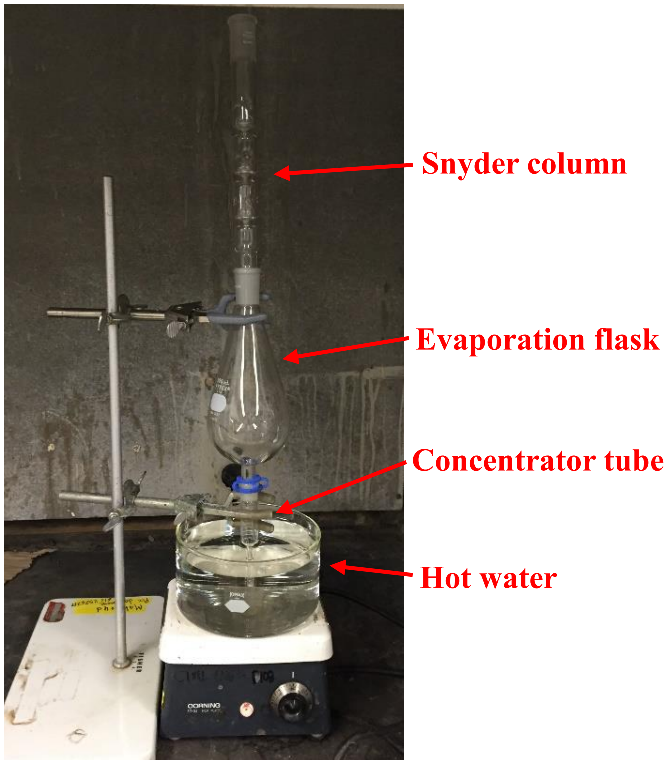

Figure A.3. K-D apparatus

4. Gas chromatography (GC)

Figure A.4 shows the GC apparatus which was used in this research for measuring the PHC concentration.

Figure A.4. GC apparatus used for measuring the PHC concentration

5. Supercritical fluid extraction

The SFT-110 apparatus for performing SFE tests is shown in Figure A.5. In addition, Figure A.6 shows the extraction vessel where the soil sample was placed. The extraction vessel is located inside the oven.

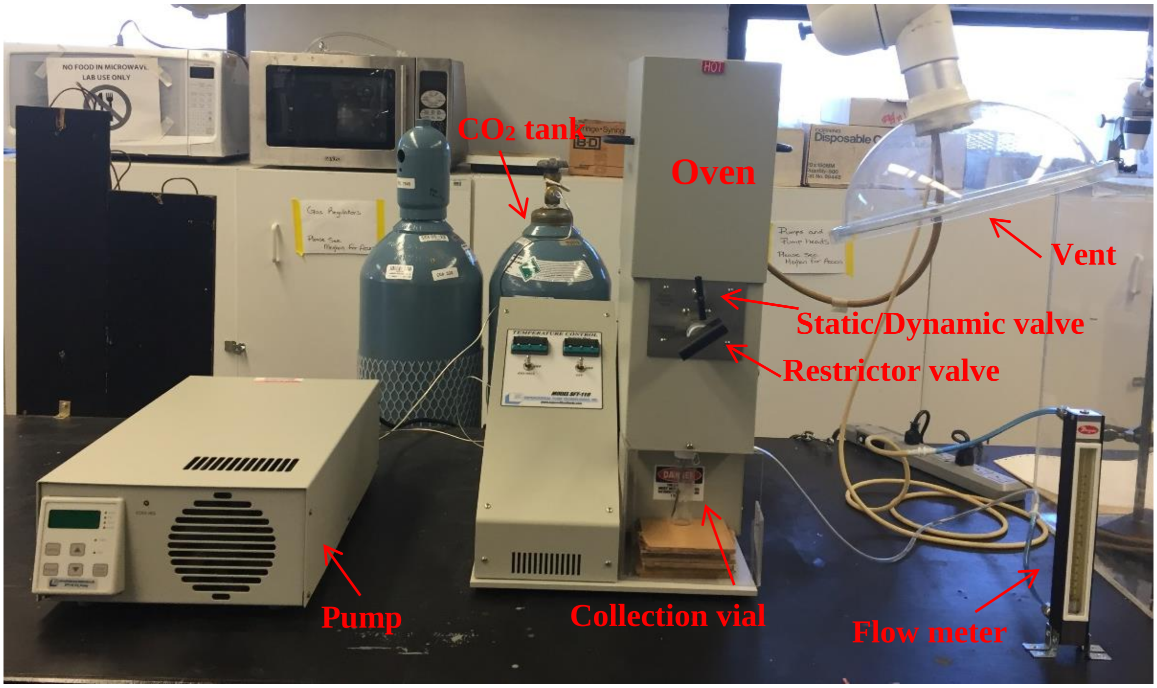

Figure A.5. SFT-110 apparatus

Figure A.6. Extraction vessel used in the SFT-110 apparatus

Appendix B: Preliminary Results for Ultrasonic Extraction

Ultrasonic extraction

Ultrasonic extraction plays an important role in the analytical procedure for the PHC measurement. Since the contact time between the solvent and the sample is not that long in this step and it could affect the PHC measurement, it was decided to run some preliminary tests to investigate the effect of ultrasonic extraction so that the highest PHC extraction percentages are obtained from the ultrasonic extraction.

1. Effect of time duration on ultrasonic extraction

Various ultrasonic extraction times were used to determine what time duration would result in the best result for the extraction of PHCs from a soil. Four extraction times of 1, 2, 4 and 10 min were chosen. A poorly graded sandy soil which was spiked with diesel fuel with the ratio of 5wt % and aged for 1 month was used as the contaminated soil. The soil samples were treated by the SFE procedure. After sonication, silica gel column cleanup, K-D concentration and GC analysis were done for each soil sample. Each test was duplicated and the results of the average of duplicates are presented in Table B.1.

Table B.1. PHC values (mg/kg) for different ultrasonic extraction times

	1min	2min	4min	10min
PHC F2	1952.4	2054.5	2008.4	1870.2
PHC F3	1484.8	1620.5	1562.3	1589.3
PHC F4	265.5	322.8	276.3	252.6

According to the Table B.1, two (2) min sonication gave the highest concentrations for all PHC fractions. Therefore, 2 min was selected as the best time duration for performing ultrasonic extraction. It should be noted that this is in agreement with the 2min ultrasonic time stated by US EPA (US EPA 2007).

2. Effect of sample size on ultrasonic extraction

In addition to ultrasound extraction time duration, it was decided to investigate the effect of sample size on the extraction. Two different soil sample sizes were selected to determine if sample size has any effect on the ultrasonic extraction. 2g and 5g soil samples were taken from the same contaminated soil as used in the previous section. The soil samples were treated by the SFE procedure explained earlier. Both samples were sonicated for 2 min. After sonication, silica gel column cleanup, K-D concentration and GC analysis were done on the samples. Each test was duplicated and the results of the average of duplicates are presented in Figure B.1.

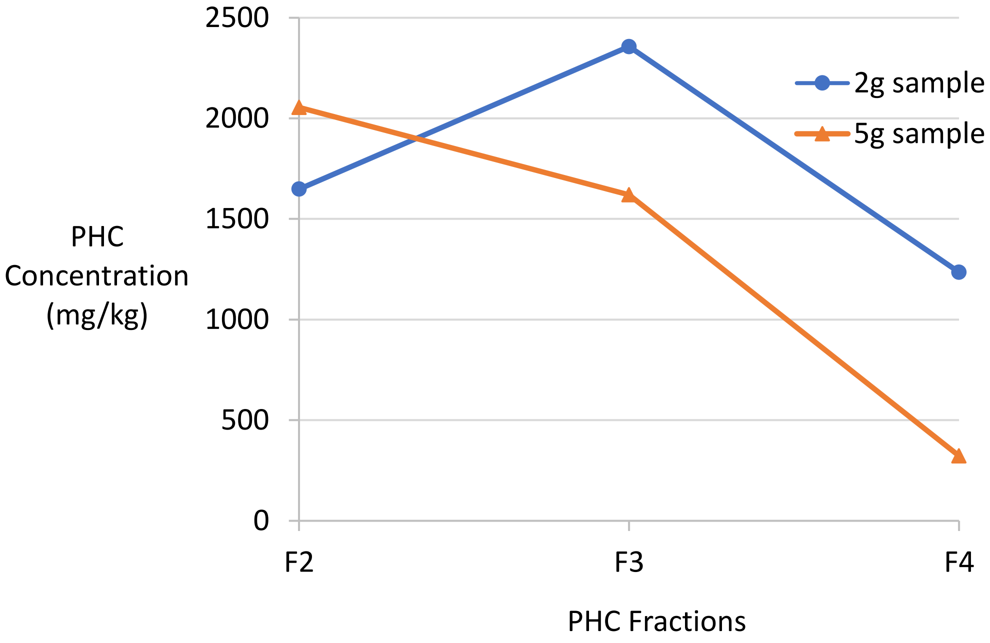

Figure B.1. Effect of sample size on ultrasonic extraction

Except for F2 fraction, 2g soil sample showed a little higher PHC concentrations than 5g soil sample. Therefore, it was decided to choose 2g as the soil sample size for the sonication step, which is in agreement stated by US EPA (US EPA 2007).

3. Effect of pulse time on ultrasonic extraction

The pulse time is another parameter that should be set for the ultrasonic extraction. Since duty cycle is 50%, times for pulse on and off are equal. In pulse on mode, ultrasonic probe vibrates for a certain period time and in pulse off ultrasonic probe does not vibrate for the same period of time. Two pulse times of 30 s and 60 s were investigated. A soil sample which was spiked with diesel fuel with the ratio of 5 wt% and aged around 6 months was used as the contaminated soil. In one case, a soil sample was sonicated for a pulse time of 30 s and another soil sample was sonicated for 60 s pulse time. Other conditions of the ultrasonic extraction for both cases were equal. These conditions included 2min sonication time and the use of about 2g soil sample. Similar analytical procedures after sonication (i.e. silica gel column cleanup, K-D concentration and GC analysis) were done for both cases. Each test was duplicated and the results of the average of duplicates are presented in Figure B.2. 60 s pulse time showed similar results as 30 s pulse time. 60 s pulse time was selected for the ultrasonic extraction.

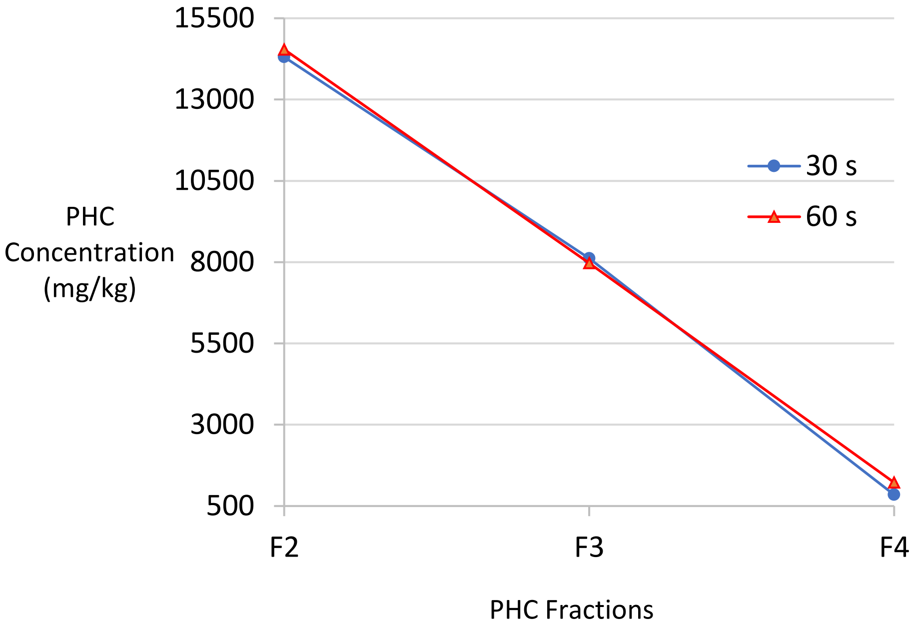

Figure B.2. Effect of ultrasonic pulse time

4. Verification of ultrasonic extraction

One possible control that can be done in the procedure of PHC measurement is to check the effect of ultrasound. To do that, two spiked soil samples contaminated with diesel fuel (5wt %) were selected. These samples were stored in the refrigerator more than 4 months. One sample was analyzed completely (i.e. ultrasound extraction, silica gel column cleanup, K-D concentration and GC analysis). The other sample was analyzed without the ultrasound extraction (i.e. silica gel column cleanup, K-D concentration and GC analysis). The extraction conditions were similar and comparable. It should be mentioned that none of these two samples were treated with SFE and their conditions before treatment were considered. In addition, each sample was duplicated and the results of the average of duplicates are presented in Table B.2. Also, the percentage difference of PHCs between these two samples were calculated according to Eq. 1:

$$Percentage\ difference = \left| \frac{(X_1 - X_2)}{(X_1 + X_2)/_2} \right| \times 100 \qquad \text{Eq. (1)}$$

Where X_1 and X_2 are the first and second PHC concentrations, respectively.

Table B.2. PHC concentrations of control samples with/without ultrasound extraction

	With ultrasound (mg/kg)	Without ultrasound (mg/kg)	Difference %
PHC F2	19643.1	14928.3	27.3
PHC F3	9914.8	7737.4	24.7
PHC F4	2252.9	1866.3	18.8

According to Table B.2, PHC concentrations were higher when ultrasonic extraction is performed. In other words, ultrasonic resulted in more contaminants from the soil matrix to be extracted. Therefore, the need to have the ultrasonic extraction step was verified and confirmed.