Remediation of Soil Contaminated with Crude Oil using Supercritical CO2

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ABSTRACT

Soil and sediment contamination with hydrocarbons is an environmental concern, which demands for more efficient remediation techniques. Pure and modified supercritical carbon dioxide (SC CO_2) was used for the extraction of petroleum hydrocarbons from soil contaminated with crude oil. Effect of CO_2 flow rate (1 and 4 ml/min), temperature (80 and 160 °C), pressure (250 and 350 bar), and addition of 5% (v/v) organic solvent (heptane or toluene) on the extraction efficiency and on the composition of extracted hydrocarbons were investigated.

The maximum extraction efficiency (92.26%) was obtained at 80 °C and 350 bar corresponding to a modified CO_2 with 5% (v/v) heptane. Extraction efficiency of CO2 increased with pressure and decreased with temperature. Chemical modification of CO2 by adding heptane increased the extraction efficiency. Analysis of the soil after the extraction process shows that pure SC CO_2 was able to remove up to 92.86% of TPH in the contaminated soil. In addition, a significant reduction in PAH level was observed. Supercritical fluid extraction proved to be an efficient method for the remediation of hydrocarbon-contaminated soil.

Keywords: Remediation, Contaminated Soil, Crude Oil, Supercritical CO2

1. INTRODUCTION

Soil contamination with crude oil and petroleum products is often observed at industrial sites, causing environmental pollution, which can be hazardous to the health of plants, animals, and humans [1-4]. The hydrocarbon molecules may contain hazardous complex chemical mixtures such as total petroleum hydrocarbons (TPH), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Removal of such compounds from contaminated sites is an important and challenging problem. The most important and widely used remediation methods are incineration, thermal desorption, biological remediation, chemical treatment and solvent extraction [5]. Conventional techniques such as landfill disposal, thermal desorption, incineration and liquid solvent extraction are expensive and involve risks associated with air and residual pollution. Biological remediation is a rather slow process, with possible logistic and practical disadvantages.

Despite great efforts and expenditure of resources to develop both technically and economically effective cleanup processes for contaminated soils, no widely accepted method has been found and further research is still needed. New methods are therefore being investigated in order to improve the remediation efficiency and lower the costs or the remediation time. Since three decades ago, supercritical fluids (SCFs) have been used as extraction media to remove various types of substances from solid matrices. The unique properties of SCFs that make them technically attractive are their enhanced ability to dissolve organic compounds, an ability, which can be easily tuned by changing temperature and/or pressure, thus changing the fluid properties from gas-like to liquid-like. Such properties allow the SCFs to dissolve and carry away materials like a liquid but also enter very small pores like a gas. The most popular fluid is supercritical carbon dioxide (SC CO_2) because it is non-toxic, non-flammable, chemically stable, readily available, inexpensive, environmentally acceptable, and can easily be separated from the products. Although SCF technology has been successfully realized for environmental remediation in the laboratory, its commercialization still lacks the significant technological improvement required in order to reach economic feasibility. Like other new technologies, SFE technology, utilizing CO_2 as a fluid has its specific problems. One of these problems is the limited ability of SC CO_2 to dissolve and separate polar or high molecular weight organic compounds even at very high densities. To increase the efficiency of the SFE process for such compounds, the selectivity and solubilizing power of SC CO_2 can be enhanced by the addition of polar organic compounds, known as modifiers.

Significant research has been carried out in order to study various aspects of contaminant removal by SC CO_2. Comprehensive presentations of various aspects on the use of this technology for extraction purpose are available in several critical reviews [1,6-8] and hundreds of other scientific articles. Supercritical CO_2 has been successfully used for extracting a variety of organic compounds such as polycyclic aromatic hydrocarbons (PAHs) [9-12], polychlorinated biphenyls (PCBs) [1,11,13-16], pesticides [17-18], and hydrocarbons [11,19-23]. However, data for CO_2 extraction at extremely high pressures and temperatures are scarce in the literature, especially for soil contaminated with crude oil. Al-Marzouqi et al. [23] showed that SC CO_2 at 300 bar and 120 °C is able to extract about 70% of hydrocarbons from a typical UAE soil contaminated with crude oil. The objective of the present study was to investigate the ability of pure and modified CO_2 under supercritical conditions to remediate soil contaminated with crude oil and achieve higher extraction efficiencies.

2. EXPERIMENTAL

Materials

Carbon dioxide (purity of 99.995%) was supplied by Abu Dhabi Oxygen Company. Crude oil (average molecular weight = 281.5 g/mole and density = 0.8634 g/ml) was obtained from Bu Hasa oil field (Abu Dhabi, UAE). The chemical modifiers (n-heptane and toluene) and the organic solvents (dichloromethane and methanol) were of analytical grade with purity ≥99% and were supplied by Sigma Aldrich. Soil samples (bulk density = 1.6 g/ml and average particle size = 150 μm) were collected from Sahel oil field in the UAE. The porosity and permeability of the soil were 35% and 20.15 Darcy, respectively.

Experimental design

Extraction of hydrocarbons with SCFs from contaminated soil was carried out by following the full factorial experimental design with four factors: pressure (250 and 350 bar), temperature (80 and 160 °C), flow rate (1 and 4 ml/min) and fluid type (pure SC CO_2, modified SC CO_2 with 5% (v/v) toluene and modified SC CO_2 with 5% (v/v) n-heptane). Each experiment was repeated twice, resulting in a total number of 48 experiments. Experiments were run in random order to eliminate various types of biases due to uncontrolled nuisance factors. The statistical analysis was performed using the statistical package SPSS (SPSS inc., Version 15.0). All the statistical analyses of the effects of variables on the extraction efficiency were performed using a multi-way analysis of variance (ANOVA) with two replications per cell.

Experimental apparatus

The experimental setup consisted of a 260-ml capacity syringe pump and a controller system (ISCO 260D), a 100-ml stainless steel extraction chamber (DBR-JEFRI 100-10-BE), and a cold trap as described earlier (Al-Marzouqi et al., 2007). The extraction chamber was kept in an air-circulating oven (Memmert ULE 400) with a temperature control ranging from 30-250 °C. Pressure within the extraction chamber was measured and controlled by the ISCO system. A micrometering valve (HIP 15-12AF1-V) was used as the expansion valve at the exit of the extraction chamber to achieve a good control of the flow rate. Circulating methanol at -15 ^oC was used as a cold trap to separate CO_2 from other components of the mixture.

Experimental procedures

Soil samples were spiked with 10 w/w% crude oil and placed in the extraction chamber. The extraction chamber was kept in the oven at the desired temperature until thermal equilibrium was reached (30-60 min). The chamber was then pressurized with CO_2 to the desired pressure and kept for another 30 minutes to reach equilibrium. In the case of modified CO_2, the second syringe pump was used to deliver the cosolvent (heptane or toluene), which was mixed with the CO_2 stream at desired ratio. Pure and modified carbon dioxide at supercritical condition was then added to the ISCO SCF Extraction system (SFX system) and equilibrated for about 15 minutes. The SCF was allowed to flow through the coil of tubing and enter the extraction chamber from the bottom. The fluid was equilibrated with the spiked soil sample for at least 30 minutes. The supercritical solution was then allowed to flow into a vial and the extract was separated from the supercritical fluid by depressurizing the system in the cold trap. The residual hydrocarbons in the soil, after SFE process, were also analyzed for concentration of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbons (PAHs).

3. RESULTS AND DISCUSSIONS

The CO_2 extraction efficiency (the ratio of extracted hydrocarbons to the initial amount of crude oil in place) is used throughout this study to evaluate the capacity of CO_2 to extract hydrocarbons from the soil. The average extraction efficiencies obtained at each of the investigated operating conditions are tabulated in Table 1. The lowest value of extraction efficiency (68.38% ± 1.99) was obtained for modified SC CO_2 (with an addition of 5 % toluene) at 250 bar and 160 °C, while the maximum efficiency (92.26 % ± 5.40) was found for SC CO_2 (with an addition of 5 % n-heptane) at 350 bar and 80 °C. The highest efficiency obtained by SC CO_2 alone (without modifier) was 78.51 % ±0.46, which was obtained at 350 bar and 160 °C. The complexity of crude oil mixture containing many compounds with significantly different physico-chemical properties that vary with temperature and pressure are believed to cause such a large variation in the extraction capacity of SC CO_2.

Results of the multi-way ANOVA based on the original values of extraction efficiency show that temperature, pressure and fluid type have significant effect on the extraction efficiency, but the flow rate of the CO_2 does not have a significant effect, i.e. Sig. >0.05. Moreover, pressure and fluid type interact. This means that the effect of pressure depends on which fluid is used and vice versa, which is not the case with temperature. However, by checking the validity of the ANOVA model using residual analysis, the normality assumption was found to be satisfied, i.e. the p-value was higher than 5%.

Effect of temperature

Figure 1 illustrates the effect of temperature on the extraction efficiency. Values on the figure (including bars showing the standard error of the mean) represent the mean value of extraction efficiency for 24 experiments at each temperature. Results indicate that temperature has an inverse effect on the extraction efficiency. This might be due to the increase in the kinematic viscosity and interfacial tension due to the decrease in CO_2 density with an increase in temperature.

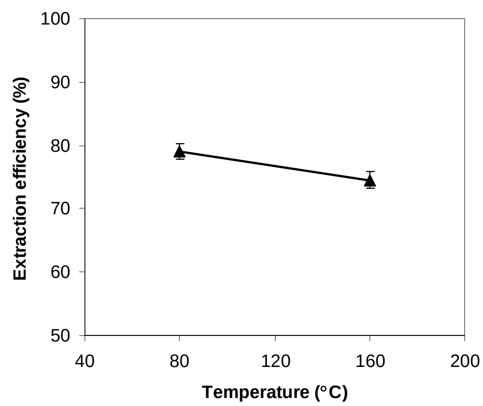

Figure 1. Effect of temperature on the extraction efficiency.

Effect of flow rate

Effect of flow rate (1 and 4 ml/min) on the extraction efficiency is shown on Figure 2. Values on the figure represent the mean value of the extraction efficiency for 24 experiments at each flow rate. Decreasing the flow rate usually ensures more contact time and results in higher extraction efficiencies for a given amount of CO_2 used. However, saturation is achieved at certain flow rates, below which the flow rate does not affect the extraction efficiency of the solvent. Results indicate that flow rate does not affect the extraction efficiency for the conditions used in this study. Therefore, the extraction process should be operated at 4 ml/min in order to reduce the extraction time.

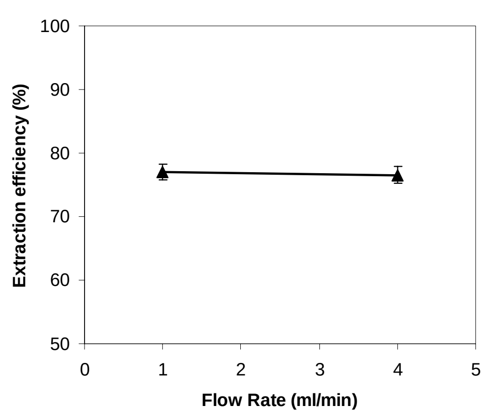

Figure 2. Effect of CO_2 flow rate on the extraction efficiency.

Table 1. Properties and average extraction efficiencies of supercritical fluids for soil samples contaminated with crude oil.

Temperature (°C)	Pressure (bar)	CO_2 flow rate (ml/min)	Modifier 5% (v/v)	CO_2 density (g/ml)	CO_2 viscosity (μPa·s)	CO_2 kinematic viscosity × 10^8 (m^2/s)	Average extraction efficiency (%) ± SEM*
80	250	1	–	0.68622	56.03	8.17	72.32 ± 0.49
80	250	4	–	0.68622	56.03	8.17	75.07 ± 0.92
80	350	1	–	0.78897	70.376	8.92	77.76 ± 0.78
80	350	4	–	0.78897	70.376	8.92	77.40 ± 0.55
160	250	1	–	0.39294	33.905	8.63	68.44 ± 0.43
160	250	4	–	0.39294	33.905	8.63	69.03 ± 1.47
160	350	1	–	0.52948	43.726	8.26	78.51 ± 0.46
160	350	4	–	0.52948	43.726	8.26	77.91 ± 0.37
80	250	1	n-Heptane	–	–	–	80.40 ± 2.96
80	250	4	n-Heptane	–	–	–	79.51 ± 2.99
80	350	1	n-Heptane	–	–	–	92.26 ± 5.40
80	350	4	n-Heptane	–	–	–	87.68 ± 1.20
160	250	1	n-Heptane	–	–	–	73.03 ± 2.18
160	250	4	n-Heptane	–	–	–	78.23 ± 4.66
160	350	1	n-Heptane	–	–	–	85.07 ± 0.55
160	350	4	n-Heptane	–	–	–	82.91 ± 5.02
80	250	1	Toluene	–	–	–	76.05 ± 2.58
80	250	4	Toluene	–	–	–	71.65 ± 1.43
80	350	1	Toluene	–	–	–	77.63 ± 3.30
80	350	4	Toluene	–	–	–	81.01 ± 0.56
160	250	1	Toluene	–	–	–	72.35 ± 3.02
160	250	4	Toluene	–	–	–	68.38 ± 1.99
160	350	1	Toluene	–	–	–	70.38 ± 0.15
160	350	4	Toluene	–	–	–	70.13 ± 2.38

*SEM: Standard Error of the Mean

Effect of pressure and fluid type

Due to the interaction between pressure and fluid type, effect of these parameters cannot be shown separately, therefore, Figure 3 shows the effect of both pressure and the fluid type on the extraction efficiency. Each point on Figure 3 represents the mean value of extraction efficiency for 8 experiments for each fluid type at a given pressure. As shown in the figure, the extraction efficiency of pure and modified SC CO_2 increases as the pressure is increased. This might be due to the decrease in the kinematic viscosity due to the increase in CO_2 density with an increase in pressure. Moreover, the extraction efficiency of the modified SC CO_2 by 5% (v/v) heptane is higher than that of both pure SC CO_2 and modified SC CO_2 with 5% (v/v) toluene. The higher extraction efficiency when utilizing heptane can probably be attributed to the richness of Bu Hasa crude oil in aliphatic non-polar hydrocarbon compounds such as n-alkanes (C_6-C_{22}) as reported by Al-Marzouqi et al. (2007). However, due to the interaction between pressure and fluid type, the extraction efficiency of modified SC CO_2 with 5% (v/v) toluene is found to be higher than that for pure SC CO_2 at the low pressure (250 bar) but lower at the high pressure (350 bar).

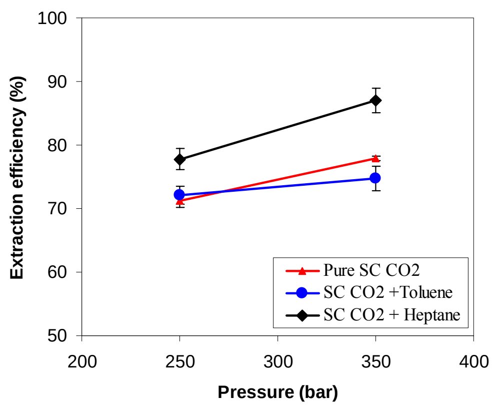

Figure 3. Effect of pressure and fluid type on the extraction efficiency.

Analysis of total petroleum hydrocarbon (TPH)

The capacity of pure SC CO_2 to extract TPH from soil saturated with Bu Hasa crude oil was investigated for selected runs (Table 2). As shown in the table, pure SC CO_2 at high pressure (350 bar) and low temperature (80 °C), is capable of extracting 92.86% of TPH from the polluted soil compared to 90.98% removal of TPH at the same pressure and higher temperature (160 °C). Removal percentage was less at the lower pressure of 250 bar (83.54% and 76.15% at 80 and 160 ^oC, respectively), which matches the results obtained from the extraction efficiency of SC CO_2. This study shows that pure SC CO_2 can effectively remediate the contaminated soil and thus reduce the harmful effects of the TPH compounds on the environment.

Analysis of polycyclic aromatic hydrocarbons (PAHs)

The PAHs measurement was conducted for selected runs to investigate the efficiency of SC CO_2 in extracting PAHs from soil samples contaminated with Bu Hasa crude oil. Concentration of 16 PAHs in the selected soil samples after the SFE process is tabulated in Table 3. Results show that the modified SC CO_2 with 5% (v/v) heptane at low temperature (80 °C) and high pressure (350 bar) was not able to completely remove some of the PAHs from the contaminated soil. Also, the extraction by pure SC CO_2 at the same pressure and temperature was the worst among all other conditions. However, pure SC CO_2 at 160 °C and 350 bar resulted in a better extraction of the 16 PAHs. This might be attributed to the effect of high temperature, which increases the volatility of the PAHs and thus increases their solubility in the fluid.

4. CONCLUSIONS

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

Table 2. TPH analysis of the clean soil, soil spiked with crude oil before SFE and treated soil after the SFE process.

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

Table 3. PAHs analyses of the clean soil, spiked soil with crude oil before SFE and treated soil after the SFE process. Removal efficiencies (%) are shown in parenthesis. Removal efficiency was assumed 100% for PAH concentration < LOD*.

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

* LOD: limit of detection.

5. REFERENCES

[1] G. Anitescu, and L.L. Tavlarides, "Supercritical extraction of contaminants from soils and sediments", **The Journal of Supercritical Fluids**, Vol. 38, No. 2, 2006, pp. 167–180.

[2] E.W. Liebeg and T.J. Cutright, "The investigation of enhanced bioremediation through the addition of macro and micronutrients in a PAH contaminated soil", **International Biodeterioration and Biodegradation**, Vol. 44, 1999, pp. 55–64.

[3] D. Sarkar, M. Ferguson, R. Datta, S. Birnbaum, "Bioremediation of petroleum hydrocarbons in contaminated soils: comparison of biosolids addition, carbon supplementation, and monitored natural attenuation", **Environmental Pollution**, Vol. 136, No. 1, 2005, pp. 187–195.

[4] N. Vasudevan and P. Rajaram, "Bioremediation of oil sludge contaminated soil", **Environment International**, Vol. 26, No. 5–6, 2001, pp. 409–411.

[5] S. Paria, "Surfactant-enhanced remediation of organic contaminated soil and water", **Advances in Colloid and Interface Science**, Vol. 138, 2008, pp. 24–58.

[6] P.K. Wong and J. Wang, "The accumulation of polycyclic aromatic hydrocarbons in lubricating oil over time - a comparison of supercritical Fluid and liquid-liquid extraction methods", **Environmental Pollution**, Vol. 112, 2001, pp. 407–415.

[7] B.T. Bogolte, G.A.C. Ehlers, R. Braun, A.P. Loibner, "Estimation of PAH bioavailability to Lepidium sativum using sequential supercritical fluid extraction e a case study with industrial contaminated soils", **European Journal of Soil Biology**, Vol. 43, 2007, pp. 242–250.

[8] A.S. Pimenta, B.R. Vital, J.M. Bayona, R. Alzaga, "Characterisation of polycilic aromatic hydrocarbons in liquid products from pyrolysis of Eucalyptus grandis by supercritical fluid extraction and GC/MS determination", **Fuel**, Vol. 77, No. 11, 1998, pp. 1133–1139.

[9] C. Lutermann, W. Dott, J. Hollender, "Combined modifier/in situ derivatization effects on supercritical fluid extraction of polycyclic aromatic hydrocarbons from soil", **Journal of Chromatography A**, Vol. 811, 1998, pp. 151–156.

[10] S.B. Hawthorne, C.B. Grabanski, E. Martin, D.J. Miller, "Comparisons of Soxhlet extraction, pressurized liquid extraction, supercritical fluid extraction and subcritical water extraction for environmental solids: recovery, selectivity and effects on sample matrix", **Journal of Chromatography A**, Vol. 892, No. 1–2, 2000, pp. 421–433.

[11] P. Hallgren, R. Westbom, T. Nilsson, S. Sporring, E. Björklund, "Measuring bioavailability of polychlorinated biphenyls in soil to earthworms using selective supercritical fluid extraction", **Chemosphere**, Vol. 63, No. 9, 2006, pp. 1532–1538.

[12] S. Sporring, S. Bøwadt, B. Svensmark, E. Björklund, "Comprehensive comparison of classic Soxhlet extraction with Soxtec extraction, ultrasonication extraction, supercritical fluid extraction, microwave assisted extraction and accelerated solvent extraction for the determination of polychlorinated biphenyls in soil", **Journal of Chromatography A**, Vol. 1090, No. 1–2, 2005, pp. 1–9.

[13] T. Nilsson and E. Björklund, "Selective supercritical fluid extraction as a tool for determining the PCB fraction accessible for uptake by chironomid larve in a limnic sediment", **Chemosphere**, Vol. 60, No. 1, 2005, pp. 141–146.

[14] W. Zhou, G. Anitescu, L.L. Tavlarides, "Polychlorinated biphenyl (PCB) partition equilibrium between St. Lawrence River sediments and supercritical fluids", **The Journal of Supercritical Fluids**, Vol. 29, No. 1–2, 2004, pp. 31–42.

[15] E. Reverchon and I. De Marco, "Supercritical fluid extraction and fractionation of natural matter", **The Journal of Supercritical Fluids**, Vol. 38, No. 2, 2006, pp. 146–166.

[16] C. Gonçalves, J.J. Carvalho, M.A. Azenha, M.F. Alpendurada, "Optimization of supercritical fluid extraction of pesticide residues in soil by means of central composite design and analysis by gas chromatography–tandem mass spectrometry", **Journal of Chromatography A**, Vol. 1110, No. 1–2, 2006, pp. 6–14.

[17] C. Quan, S. Li, S. Tian, H. Xu, A. Lin, L. Gu, "Supercritical fluid extraction and clean-up of organochlorine pesticides in ginseng", **The Journal of Supercritical Fluids**, Vol. 31, No. 2, 2004, pp. 149–157.

[18] R. Jaffé, D. Diaz, K.G. Furton, E. Lafarg, "High Temperature Supercritical Carbon Dioxide Extractions of Geological Samples: Effects and Contributions from the Sample Matrix", **Applied Geochemistry**, Vol. 15, No. 1, 2000, pp. 79–89.

[19] M.O.P. Crespo and M.A.L. Yusty, "Comparison of supercritical fluid extraction and Soxhlet extraction for the determination of aliphatic hydrocarbons in seaweed samples", **Ecotoxicology and Environmental Safety**, Vol. 64, No. 3, 2006, pp. 400–405.

[20] A. Akinlua, N. Torto, T.R. Ajayi, "Supercritical fluid extraction of aliphatic hydrocarbons from Niger Delta sedimentary rock", **The Journal of Supercritical Fluids**, Vol. 45, No. 1, 2008, pp. 57–63.

[21] I. Okamoto, X. Li, T. Ohsumi, "Effect of supercritical CO2 as the organic solvent on cap rock sealing performance for underground storage", **Energy**, Vol. 30, No. 11–12, 2005, pp. 2344–2351.

[22] R.J. Hwang and J. Ortiz, "Mitigation of Asphaltics Deposition during CO_2 Flood by Enhancing CO_2 Solvency with Chemical Modifiers", **Organic Geochemistry**, Vol. 31, No. 12, 2000, pp. 1451–1462.

[23] A.H. Al-Marzouqi, A.Y. Zekri, B. Jobe, A. Dowaidar, "Supercritical Fluid Extraction for the Determination of Optimum Oil Recovery Conditions", **JPSE**, Vol. 55, 2007, pp. 37–47.