2012 2nd International Conference on Environmental and Agriculture Engineering
IPCBEE vol.37 (2012) © (2012) IACSIT Press, Singapore

Purification of Two Regional PAHs Contaminated Soil Using Subcritical Water

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Abstract. The remediation of PAHs contaminated soils has been investigated by extraction using continuous flowing subcritical water. Water temperature ranging from 100 to 300 ^oC, extraction time ranging from 15 to 60 min, and flow rate ranging from 0.5 to 2.0 mL/min were investigated to determine their effects on removal efficiencies of target PAHs (naphthalene, phenanthrene, fluoranthene and pyrene) from two different regional (‘A’;Jeju Island and ‘B’;Gwangju, Korea) contaminated soils. Removal rates of two soils were gradually increased up to over 90% with temperature increased from 100 to 300 ^oC. Removal rates of PAHs from soil ‘A’ and ‘B’ had shown different trends as a function of extraction time. There was no significant effect of flow rate on removal efficiency of PAHs was observed in this study. Overall, the higher removal rate was observed at different condition from soil ‘B’ than soil ‘A’. It suggests that the soil property is one of the factors for remediation of PAHs.

Keywords: Extraction, Subcritical Water, PAHs, Removal Efficiency

1. Introduction

Subcritical water that refers to water of which temperature ranges from 100 ^oC (ambient temperature) to 374 ^oC (critical temperature of water) under a moderate pressure (<221 bar) to maintain the liquid phase. It has unique characteristics such as dramatically decreased dielectric constant, surface tension, and viscosity with increasing temperature. If temperature increase, the hydrogen bonding network of water molecules is weaken and it cause the decrease of dielectric constant(Ɛ) and polarity [1]. For example, the dielectric constant of water decreases from 73 to 2 by increasing the temperature from 25 ^oC to 315 ^oC at 100 bar of pressure. Pressure has much weaker influence on dielectric constant of water as compared to temperature and extraction time. Therefore, solubility of nonpolar compounds is increase as temperature increases in this range. For example, dielectric constant (Ɛ) of superheated water is 27 at temperature of 250 ^oC and 50 bar of pressure. This value is between those of organic solvent ethanol (Ɛ=24) and methanol (Ɛ=33) at 25 ^oC. It’s indicating that superheated water acts like organic solvent [2-3]. So that, subcritical water extraction have been suggested as alternative cleaning technologies, instead of using organic solvents or toxic and strong aqueous liquid media [4-6]. Dielectric constants of the subcritical water and organic solvents are shown on Table 1. These characteristics of water can be applied to extraction of PAHs (Polycyclic Aromatic Hydrocarbons), PCBs, BTEX, and other nonpolar matter in soils.

PAHs remediation process has been under researched. There have some techniques, such as; solvent extraction, biological remediation, phytoremediation, chemical oxidation, photocatalytic, electrokinetic remediation, and thermal process for PAHs remediation. Subcritical water extraction can be categorized into solvent extraction [7]. In this study, continuously flowing subcritical water extraction process was studied for two different regional contaminated soils to test the factors and soil properties effect on

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removal rate. Removal efficiency of PAHs was evaluated at different temperature, extraction time and flow rate.

Table1: Dielectric constant (ε) depends on temperature in subcritical water at 100 bar

Subcritical water Dielectric constant (Temperature, °C)	Common organic solvent at 25°C Dielectric constant (solvent)
39 (175)	1.9 (n-hexane)
35 (200)	21 (acetone)
20 (300)	33 (methanol)
2 (315)	39 (Acetonitrile)

2. Materials and Method

2.1. Subcritical Water Extractor

Lab-scale subcritical water extractor has shown in Figure 1. It was composed of water tank, high pressure pump, preheater, main reactor, chiller, separator, and back pressure regulator.

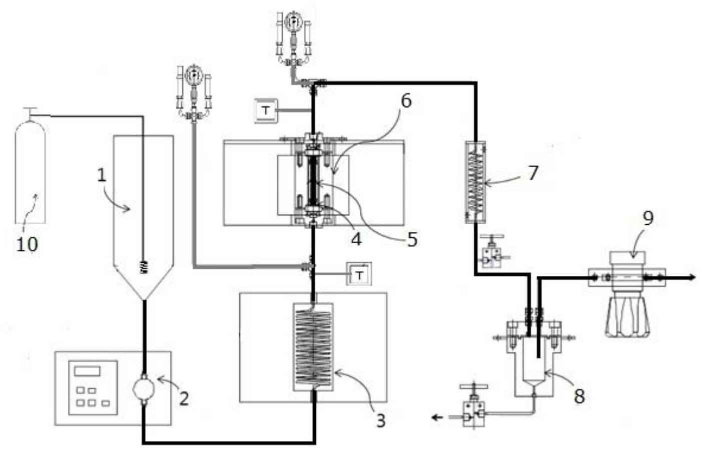

Fig. 1: Schematic of superheated water extraction system. (1) water tank, (2) high pressure pump, (3) preheater, (4) reactor filter, (5) soil, (6) reactor, (7) chiller, (8) separator, (9) pressure regulator, (10) helium gas cylinder.

2.2. Contaminated Soil

Two types of soils were used in this remediation study. Soil A was collected from Jeju Island and soil B was collected from Gwangju city of South Korea which were historically and regionally different. The soil properties have shown in Table 2. Naphthalene, phenanthrene, fluoranthene, and pyrene (all contaminants purity was more than 98%) have been spiked into soil A and B to make a contaminated soil. 0.3g of each contaminant was inserted into 200g n-Hexane to make a spiking solution that was added into the each soil and mixed on rotating mixture for 24hrs. After that, contaminant soil was dried for 12 hours and kept it for 14 days.

Table 2: Soils properties and origin contaminant level

Soil \ content	SOM, %	Sand, %	Silt, %	Clay, %	Soil texture	Parent material[a]	Location
Soil A	13.4	3.3	76.8	19.9	Silt loam	Volcanic ash	Jeju island, Korea
Soil B	9.5	62.5	37.1	0.4	Sandy loam	Quaternary soil & Acidic rock	Gwangju city, Korea

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2.3. Subcritical Water Extraction Process

8g of contaminated soil was packed into the extractor and purged distilled water was flowed through pre-heater and extraction cell. To investigate the temperature effect on contaminant extraction, the reactor was heated at a temperature of 100, 150, 200, 250, and 300 °C; to investigate the time effect, extraction was operated 15, 30, 45, and 60 min; and to investigate the flow rate effect on removal rate of PAHs, water flow was changed at 0.5, 1.0, 1.5, and 2.0 mL/min at desired condition. The counting of extraction time was started after the reactor temperature reached the set temperature. After the desired extraction, pump and heater were stopped and pressure was released to atmospheric pressure. The reactor was allowed to cool to room temperature and packed soil was collected to analyze the remaining contaminant concentration. Contaminant concentration in the methanol (methanol extraction) was analyzed using HPLC with UV_{254nm} (Younglin M730D) and fluorescent detectors with flowing acetonitrile solution (8:2) at 2.0 ml/min.

3. Results and Discussion

The PAHs concentrations at initial and extracted soil have shown in Table 3. As shown in Figure 2, the PAHs removal efficiency was greatly affected by elevated water temperature. The removal efficiency was gradually increased with an increasing the water temperature from 100 °C to 300 °C for soils 'A' and 'B'. However, more than 97% removal efficiency of naphthalene was obtained at only 150 °C for 30 min extraction for both soils. It is possibly due to the lower molecular weight and higher solubility properties contaminant. The other three PAHs (phenanthrene, flouranthene and pyrene) removal rates from soil 'A' have shown gradually increases with temperature increase, but soil 'B' have shown dramatically increase from 200℃ to 250℃. Removal rate of soil A was higher than soil B at 100 °C, 150 °C and 200 °C. This means that contaminants had a lower interaction potential with soil A than soil B, due to the different soil properties. However, similar extraction efficiency was observed for all PAHs from both of soils at a higher temperature of 250 °C and 300 °C. All of PAHs removal rate were found over 93% at 300 °C. Compared this study result with other PAHs remediation processes, subcritical water has higher removal rate than soil washing (50%), ozonation (50-60%), and biological treatment (30%) [9].

Table 3: Contaminant concentration (mg kg^{-1}) in initial and extracted samples

Soil	PAHs	Initial soil conc.	Water temperature (°C)					Water flow rate (mL/min)				Extraction time (min)			
			100	150	200	250	300	0.5	1.0	1.5	2.0	15	30	45	60
A	Naphthalene	380.2	186	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Phenanthrene	354.9	260	212.9	172.7	63.9	6.7	66.2	101.4	44.6	63.9	123.6	44.6	36.1	13.4
	Fluoranthene	494.4	266	224.4	164.2	85.1	18.6	81.1	113.7	76.0	85.1	164.5	76.0	72.8	21.2
	Pyrene	392.5	248	208.1	150.8	86.8	23.3	91.4	114.7	88.9	86.8	60.0	88.9	55.2	8.2
B	Naphthalene	585.4	507	17.1	9.2	0.0	0.0	0	0	0	0	0	0	0	0
	Phenanthrene	409.0	384	315.1	224.3	30.0	0.0	0	0	30.0	0	8.0	30.0	0	0
	Fluoranthene	679.4	616	530.6	433.2	106.2	4.2	22.9	2.8	106.2	56.1	88.4	106.2	44.6	11.2
	Pyrene	572.9	533	467.4	393.7	117.9	2.4	28.9	4.5	117.9	71.4	92.4	117.9	61.4	17.5

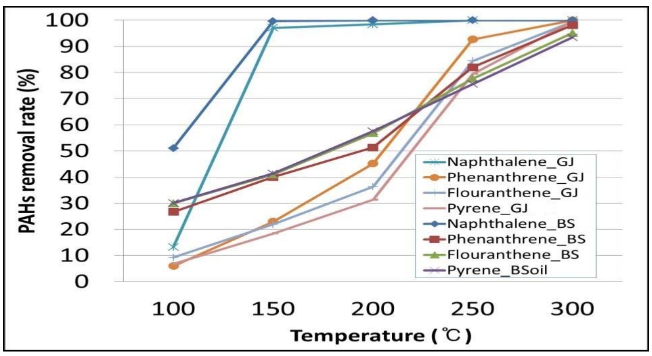

Fig. 2: Removal rates of PAHs from soil A(GJ) and soil B(BS) at different temperatures (extraction time was 30min and water flow rate of 1.5mL/min).

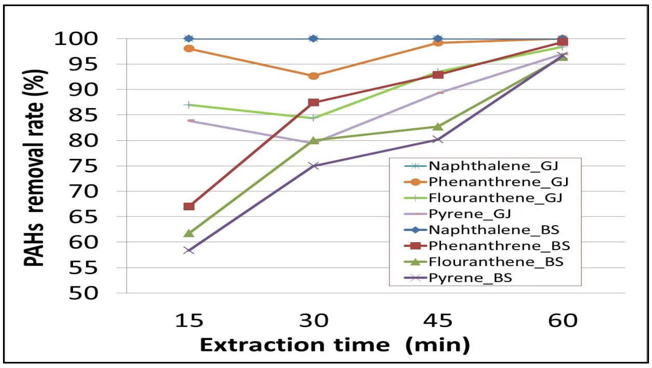

Fig. 3: Removal rates of PAHs from soil A(GJ) and soil B(BS) at different extraction times (water temperature was 250 ^{0}C and flow rate of 1.5mL/min).

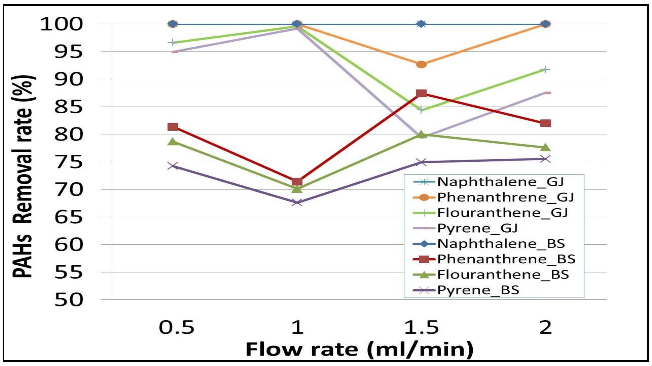

Fig. 4: Removal rates of PAHs from soil A(GJ) and soil B(BS) at different water flow rate (extraction time was 30min and water temperature of 250 ^{0}C).

To test the extraction time effect on removal rate of PAHs, experiments were performed at 250 ^{0}C and flow rate of 1.5 mL/min with increasing the time from 15 min to 60 min. Extraction time effect on removal rate through subcritical water extraction process for soil A and soil B have presented in Figure 3. Extraction efficiency was increased as increased the extraction time from 15 min to 60 min. Naphthalene removal rates of two soils were 100% at even after 15 min. There was little difference of removal rate of soil B at 15 and 30 min extraction and increasing removal rate was observed from 30 to 60min. However, removal rate of soil A has gradually increased with extraction time increases from 15 min to 60 min, suggesting that there was a significant effect of extraction time on removal rate of PAHs with causes of different soil properties (Figure 3). To get the satisfactory extraction, 60 min is recommendable for PAHs extraction in this study.

The flow rate effects on removal rate have shown in Figure 4. The removal rate was fluctuated with an increasing a water flow rate from 0.5 ml/min to 2.0 mL/min which indicating that there was no significant effect of flow rate in case of both contaminated soil (soil A and soil B). Overall, the PAHs extraction was faster from soil B than soil A, i.e., contaminants from sand loam soil is more easily extractable than silt loamy soil. It suggests that the soil property is one of the factors for remediation of PAHs.

4. Acknowledgement

This study was financially supported by Korea Environmental Industry and Technology Institute through the GAIA project.

5. References

[1] Y. Yang, S.E, Manahan, Environmental chemistry, p.699-700, 9thed.,CRCPress,US,2010

[2] David. J. Miller, S.B. Hawthorne, Method for determining the solubilities of hydrophobic organics in subcritical water., Anal. Chem. 1998. 70, 1618-1621

[3] D.J. Miller, S.B. Hawthorne, A.A. Clifford, Solubility of polycyclic aromatic hydrocarbons in subcritical water from 298 to 498 K, J. Chromatogr. 1998, A 810, 149,

[4] D. J. Miller and S.B. Hawthorn. Method for Determining the Solubilities of Hydrophobic Organics in Subcritical Water. *Analytical Chemistry*, 1998. 70(8): p. 1618-1621.

[5] B. Kuhlmann, E.M. Arnett, and M. Siskin. Classical Organic Reactions in Pure Superheated Water. *The Journal of Organic Chemistry*, 1994. 59(11): p. 3098-3101.

[6] Y. Yang, S.B. Hawthorne, and D.J. Miller. Class-Selective Extraction of Polar, Moderately Polar, and Nonpolar Organics from Hydrocarbon Wastes Using Subcritical Water. *Environmental Science & Technology*, 1997. 31(2): p. 430-437.

[7] S. Gan, V. Lau, and H.K. Ng. Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). *Journal of Hazardous Materials*, 2009. 172(2-3): p. 532-549.

[8] Soil Information System, *National Academy of Agriculture Science* (http://soil.rda.go.kr/webgis/webgis.jsp)

[9] Pia Haapea, Tuula Tuhkanen, Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment, *Journal of Harzardous Materials*, B136(2006), 244-250