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Remediation of Naphthalene and Phenanthrene Contaminated Soil by Extraction Using Superheated Water

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Abstract. The water solubility of a nonpolar chemical increases as water temperature increases. In this study, remediation of PAHs contaminated soil has been investigated by extraction using continuously flowing superheated water. Prepared contaminated soil by naphthalene and phenanthrene for 2 years has been used. 8g of contaminated soil was packed into extractor and 2ml/min of water flowed through the packed extractor for 30 minutes under pressure of 100bar. Water temperature was changed into 100, 150, 200, 250, and 300℃. Initial concentrations of naphthalene and phenanthrene in soil were 22 and 43 ppm, respectively. The removal rate of both contaminants increased as water temperature increased. Especially, naphthalene was extracted efficiently at relatively low temperature of 150℃. However, the removal of phenanthrene increased gradually as temperature increased until 300℃. These results suggest that soils contaminated by persistent organic chemicals can be remediated by extraction using pure water as solvent.

Keywords: superheated water, PAHs, continuously, extraction

1. Introduction

Superheated water(subcritical water) is liquid water existed between 100 and 374℃ under high pressure(<221bar). water properties change with 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]. Specially, dielectric constant decreases from 73 for 25 ℃ to 2 for 315 ℃ at 100 bar. Therefore, solubilities of nonpolar compounds increase as temperature increases in this range. For example, dielectric constant(Ɛ) of superheated water is 27 at 250℃ and 50bar. This value is between those of ethanol (Ɛ=24) and methanol (Ɛ=33) at 25℃. Superheated water acts like organic solvent [2,3]. Dielectric constants of the superheated 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.

Table1. Dielectric constant(Ɛ) depends on temperature in superheated water at 100 bar. [4]

Superheated water Dielectric constant (Temperature)	Common organic solvent at 25℃ Dielectric constant (solvent)
39 (175℃)	1.9 (n-hexane)
35 (200℃)	21 (acetone)
20 (300℃)	33 (methanol)
2 (31℃)	39 (Acetonitrile)

PAHs are produced when fuels such as coal, oil, gas, and garbage are burned incompletely. They have been used to make dyes, plastics, pesticides, even medicines. PAHs are concern chemicals because they are toxic and persistent, that is, stay in the environment for long period of time. Exposure to PAHs can be occurred through skin contacts with PAH contaminated soil or products like heavy oil, coal tar, roofing tar,

or creosote. And once in your body, PAHs can spread and target fat tissues. Target organs include the kidneys and liver [5].

PAHs remediation process has been researched. There are solvent extraction, biological remediation, phytoremediation, chemical oxidation, photocatalytic, electrokinetic remediation, and thermal process [6]. Superheated water extraction can be categorized into solvent extraction [7,8]. GC oven as heater has been used for most lab scale extraction study [9]. In this study, continuously flowing superheated water extraction process was utilized for soil remediation without any chemical reagent. Removal efficiency of PAHs was evaluated at different temperature.

2. Material and Method

2.1. Superheated water extractor

superheated water extractor design has been shown on Figure 1. It is composed of water tank, high pressure pump, preheater, reactor, thermometer, back pressure regulator, and separator.

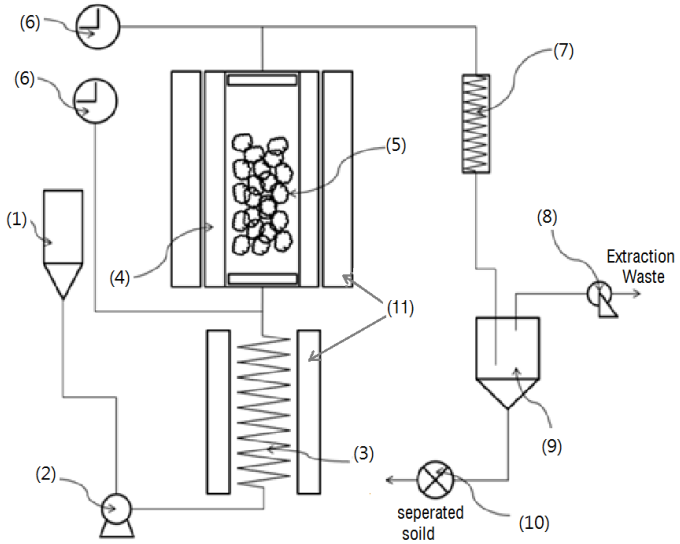

Figure 1. Schematic of superheated water extraction system. (1) Water Tank, (2) High pressure pump, (3) Preheater, (4) Extractor, (5) Soil, (6) Safety valve and gauge of temperature and pressure, (7) Chiller, (8) Back pressure regulator, (9) Separator, (10) separator valve.

2.2. Contaminated soil

Heukeumgi soil, which was collected from Jeju island in korea, has been used in this study. Heukeumgi soil properties are shown on Table 2. Naphthalene and phenanthrene have been spiked into Heukeumgi soil to prepare contaminated soil. Contaminant properties are shown on Table 3. The prepared contaminant soil was placed into 100 ml vial and 20ml of methanol was added to determine contaminant concentration by methanol extraction. The vial was mixed on 200rpm for 24hrs using shaking incubator. After 24hrs, the mixture was separated using centrifuge at 2000rpm for 10min. Contaminant concentration in the supernatant was analyzed using HPLC.

Table 2. Soil properties.

	Kd	TOC	pH	Sand	Silt	Clay
Heukyemji	10.3	13.4%	5.1%	3.3%	76.8%	19.9%

Table 3. Contaminant Properties

contaminant	Molecular weight	Melting point	Boiling point	Solubility in water (at 25℃)
Naphtalene	128.2	80.26	218	30mg/L
Phenanthrene	178.2	99.15	340	insoluble

2.3. Superheated water extraction process

Distilled water was purged by Helium gas for 30 minutes to remove dissolved Oxygen. 8g of contaminated Heukeumgi soil was packed into the extractor and purged distilled water was flowed through preheater and extractor in 2 ml/min under pressure of 100 bar (10 Mpa). To investigate temperature effect on contaminant extraction, the flowing water temperature was changed to 100, 150, 200, 250, and 300℃. Extraction time was 30 minutes at each temperature. After extraction, pump and heater were stopped and pressure was released to atmospheric pressure. The extractor was cooled down to 50~60℃ for 1hr and packed soil was removed to analyze the remained contaminant concentration

The remained contaminant was extracted from removed soil using 20ml of methanol. The soil was placed into 100 ml vial and 20ml of methanol was added. The vial was mixed on 200rpm for 24hrs using shaking incubator. After 24hrs, the mixture was separated using centrifuge at 2000rpm for 10min. Contaminant concentration in the supernatant was analyzed using HPLC.

2.4. HPLC analysis

The supernatant samples were analyzed using HPLC with UV_{254nm} (Younglin M730D) and fluorescent detectors (Waters 2475) at 2ml/min of acetonitrile solution (8:2) with LC-PAH column.

3. Result and discussion

Initial concentrations of naphthalene and phenanthrene in soil were 22 (±1.7) and 43 (±5.3) ppm, respectively. Figure 2 shows the extraction result using continuously flowing superheated water. Remained naphthalene concentrations at 100, 150, 200, 250, and 300°C were 29, 1.8, 1.9, 0, and 0 ppm, respectively. That is, remained naphthalene concentration in soil at 100°C was a little higher than the initial soil, and then the concentration was dramatically decreased to below 2 ppm above 150°C. It suggest that soil sorbed naphthalene is persistent, not desorbable and extractable below 100°C. however, it can be easily desorbable and extractable from soil at water with above 150°C. A couple of reasons are considered for the higher remained concentration observed at 100°C. One is that soil physical properties are changed due to heating up to 100°C under water with pressure of 100bar and the change affect on the methanol extraction from the soil increasing the extraction efficiency of remained naphthalene. The other one is the heterogeneity of soil, and the soil used for 100°C might have high concentration initially.

Remained phenanthrene concentration decreased gradually from 30 ppm at 100℃ to 0.74 ppm at 300°C in figure 2. Phenanthrene extraction required higher temperature than naphthalene which can be speculated from the characteristics that phenanthrene has lower solubility, higher molecule weight and melting point than naphthalene.

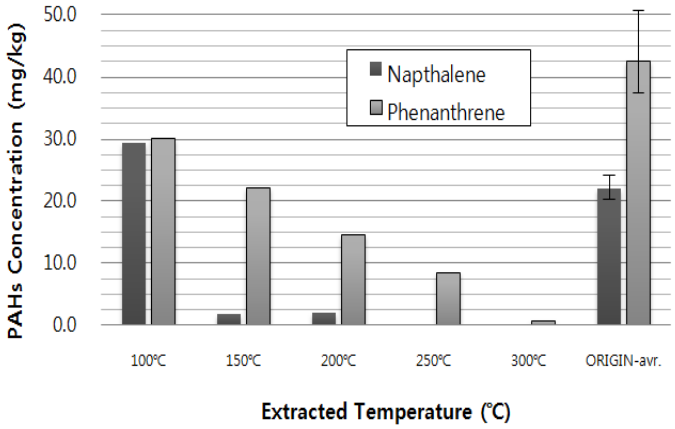

Figure 2. Naphthalene and phenanthrene Concentrations in initial and remediated soils. Experimental condition: water flow rate of 2 ml/min, extraction time of 30 min, and pressure of 100bar (10Mpa).

Figure 3 shows the removal percent of contaminants at different temperature. To remediate naphthalene contaminated soil, 150°C is enough for the extraction temperature of water. However, if soil contaminated

with mixture of PAHs such as phenanthrene, anthracene, acenatphalene, etc., above 250°C of water is required to remediate it.

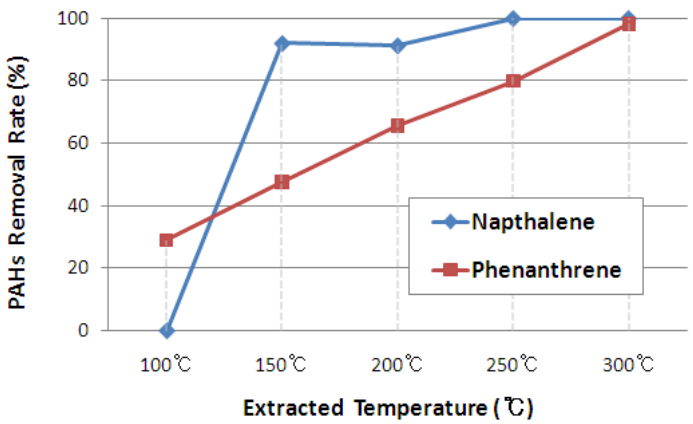

Figure 3. Removal percent of naphthalene and phenanthrene at each extraction temperature.

4. Acknowledgements

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5. References

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