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Diesel recovery from extraction of contaminated soils using subcritical water

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Abstract

The effective water temperature range of 250~300℃ was evaluated to remediate and get recovery of diesel from six different contaminated soils. More than 90% of diesel removal and 70% of recovery was observed in most cases when contaminated soil was extracted at 275^{0}C.

Keywords—recovery, diesel, subcritical water, TPH, soil

Introduction

Subcritical water that refers to water of which temperature ranges from 100 ^{0}C (ambient temperature) to 374 ^{0}C (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 ^{0}C to 315 ^{0}C 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 ^{0}C and 50 bar of pressure. This value is between those of organic solvent ethanol (Ɛ=24) and methanol (Ɛ=33) at 25 ^{0}C. 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 could be effect to extract of oil compounds, PAHs (Polycyclic Aromatic Hydrocarbons), PCBs, BTEX, and other nonpolar matter in soils.

Thermal desorption is effective process to remediate oil-contaminated soil, but it was impossible to recover the diesel from spilled contaminated soil. Also soil washing is effective, but it only works to restoration of sand particles (> 0.05 mm).

Slurry (mostly clay) from separated soil washing process is not usually treated, and it shows a high water content and high TPH (Total petroleum hydrocarbons) concentration. In Korea, this contaminated slurry is discharged to hazardous-landfill site to date. In this study, subcritical water extraction process for the removal and recovery of TPH (Total petroleum hydrocarbons) from the contaminated soil and slurry was evaluated.

TABLE I.
DIELECTRIC CONSTANT(Ɛ) OF ORGANIC SOLVENT AND SUBCRITICAL WATER.

Dielectric constant(Ɛ)	
Subcritical water at 10 MPa (Temperature, ℃)	*Organic solvent at 25℃ (solvent)*
39 (175)	39 (Acetonitrile)
35 (200)	33 (Methanol)
20 (300)	21 (Acetone)
2 (315)	1.9 (n-Hexane)

Material and Method

Six different contaminated soils were used in this study, as shown Table 2.

A 10g of contaminated soil was packed into the reactor and distilled water was flowed through preheater and reactor at 2 mL/min under pressure of 10 MPa (100bar). Extracted water was collected in 20 mL vial for every five minutes during operation of the system. The counting of extraction time was started after the reactor temperature reached the set temperature. After extraction, pump and heater were stopped and pressure was released to atmospheric pressure. The reactor was cooled down to 50~60℃ for 1 hour and packed soil was then collected to analyze the remaining TPH concentration. Also scale-up experiment was carried out using the soil of 1.65 kg with the water flow of 25~30 mL/min at pressure of 6 MPa (Fig 1).

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TABLE II.
PROFILE OF DIESEL CONTAMINATED SOILS.

Soil	Properties of contaminated soils		
	Collection site	***Initial TPH concentration (mg/kg)***	***Soil texture***
A	Spiked in lab.	10,000	Silty loam
B	Industrial complex (busan, korea)	1,466	Sandy loam
C	US army base (dongducheon, Korea)	1,701	Sandy loam
D	Slurry obtained from soil washing	142,965	Slurry (silt and clay)
E	Farm-land site, spiked (Hwa-soon, Korea)	12,447	Silty loam
F	Sand (purchase), spiked	8,968	Sand

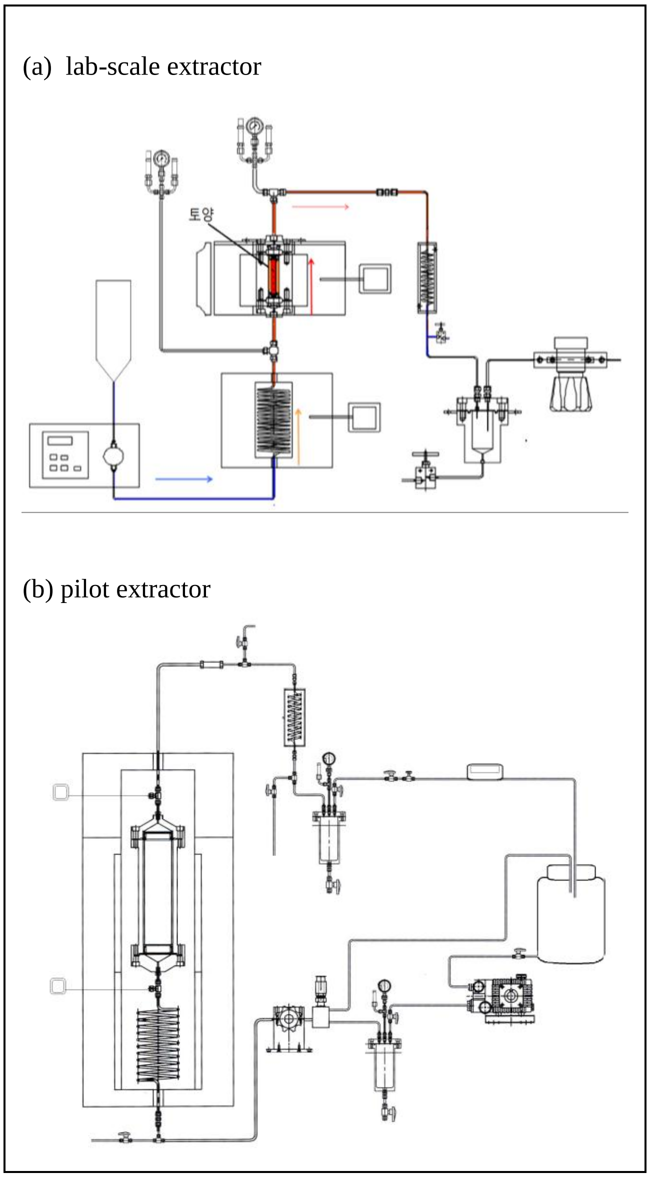

Figure 1. Schematic of subcritical water extraction system. (a) Lab-scale extractor, (b) pilot-scale extractor.

The method of determining the amount of diesel (as TPH) in the corresponding soil samples was based on the Korean Standard Test Method: 10 g of soil was mixed with anhydrous sodium sulfate and was then ultrasonically extracted twice with 200 mL of dichloromethane in 100 mL dichloromethane

for 3 min each time. The extract was filtered and extractant was concentrated using a rotary evaporator and purified with silica gel(60mesh) column. The amount of TPH in the final solution was analyzed using gas chromatography fitted with a flame ionization detector (HP-6890, Agilent Tech., USA). The amount of diesel in the effluent water was determined by extraction followed by liquid-liquid extraction with Dichloromethane.

Mass balance was evaluated using the initial and final concentrations of diesel in soil and collected water. Lab scale of mass balance was calculated extracted soil and extraction water samples (collected every 5 minutes). Pilot scale of mass balance was sum of extracted soil, oil/water separator, and effluence water for total recovery.

The water retention time in lab- and pilot-scale system was 7 and 35 min, respectively, which was calculated by considering the reactor cell volume, pipeline volume, and water flow rate condition.

Result and Discussion

Subcritical water extraction was the effective remediation process of contaminated soils. Soils A to D were extracted using lab-scale equipment (10 g), and Soil E and F were subjected to pilot-scale apparatus (1.65 kg). Removal percentage of diesel in pilot-scale experiment was usually lower than the lab-scale experiments.

Removal percentage of diesel from soil A, B, and C was 100% when water temperature was 300℃, flow rate was 2 mL/min, extraction time was 30 min, and system pressure was 10Mpa. About 99.8% of diesel was removed from soil D at 275℃ and 6MPa for 120 min extraction, and flow rate of 1 mL/min under static-dynamic (20 min – 20 min) condition, and that of 76.5% for soil E at 250℃, 25 mL/min, and 120 min. In case of soil F, the removal percentage of diesel was 95.9% at 275℃, 25 mL/min, 40 min, and 6MPa.

The percent of diesel recovery from the collected effluent water over an operating time was presented in Fig. 2. Soil B and soil C were collected from the field contaminated site, but soil A was spiked with diesel. The trend of diesel recovery for each soil was similar over a period of extraction, except at 40 ~ 45 min. Accumulations of extracted TPH mass were over 97% at 50~55 min.

Process effluent water (EW) was collected in every 10 minutes when the slurry(soil D) sample was extracted (Fig. 3). A thin oil layer was appeared in the water sample, EW-10. TPH mass in EW-10 was 707.98 mg, which the diesel recovery corresponding to 66.03% of the mass present in contaminated slurry.

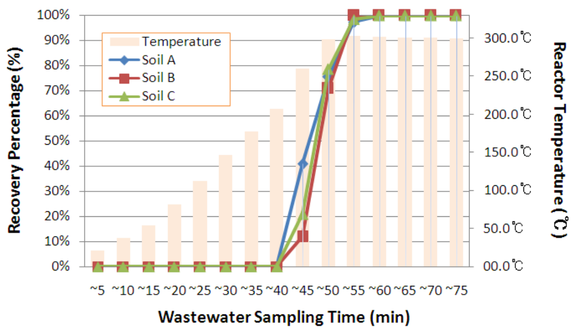

Figure 2. Accumulation of Recovery mass percentage of extracted TPH from collected water during subcritical water extraction for Soil A, B, C (300℃, 2 mL/min, 30 min, 10 MPa).

Diesel recovery at other water samples (EW 1~9) were found to be 0.04 ~ 18.48 mg (0 ~ 1.72% of initial mass). The total mass of diesel was found 765.62 mg (71.3%) in process effluent water including EW-10. Considering the recovery from treated soil, the total diesel recovery was calculated to be 92.6%.

The recovery of diesel at pilot scale by subcritical water extraction was investigated for soil E and F. In case of soil E, the removal efficiency of TPH was increased from 76.9 to 80.8% when the extraction time was increased from 120 to 160 min at 250℃ and the total recovery of TPH mass was obtained 73.8% at 250℃ for 120 min extraction. The mass of diesel (4.82 mg) was still remained in the treated soil (23.5%). The recovery of diesel (as TPH mass) was found 71.6% at 275^{0}C and 40 min for the contaminated soil F. It should be noted that the higher removal efficiency of diesel was observed at higher temperatures.

Over 70% recovery was found at both lab- and pilot-scale experiments when operated at 275 ^{0}C for soil D and F. Most effective conditions for diesel extraction and recovery recommended were 275 ^{0}C and static-dynamic extraction.

Figure 3. Extraction water of contaminated soil D (collect samples in every 10mins after 40min).

Conclusion

The effective water temperature range of 250~300℃ was evaluated to remediate and get recovery of diesel from six different contaminated soils. More than 90% of diesel removal and 70% of recovery was observed in most cases when contaminated soil was extracted at 275^{0}C.

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TABLE Ⅲ. MASS BALANCE OF DIESEL IN SOIL SUBCRITICAL WATER EXTRACTION SYSTEM (SOIL AND EXTRACTION WATER).

Soil	*Experimental Condition*	TPH Mass (mg)			TPH recovery (%)		
		initial soil	*extracted soil*	*extraction water*	*Extracted Soil*	*Extraction Water*	*Total (Soil + water)*
A	300^{0}C, 30minm 10g-scale, sity loam	115.99	0	60.23	0	51.6	51.6
B	300^{0}C, 40min, 10g-scale, silty loam	7.88	0	4.19	0	53.2	53.2
C	300^{0}C, 30min, 10g-scale, sity loam	20.41	0	12.89	0	63.1	63.1
D	275^{0}C, 10g-scale, 120min, slurry of soil washing, static-dynamic	1072.20	2.28	765.62	0.2	71.4	71.6
E	250^{0}C, 1.65kg, 40min, silty loam	20.54	4.82	5.52	23.5	50.3	73.8
F	275^{0}C, 1.65kg, 120min sand, static-dynamic	14.98	0.60	8.78	4.0	69.6	66.6

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