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Remediation of soil contaminated with lubricating oil by extraction using subcritical water

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ABSTRACT

The remediation of lubricating oil contaminated soil was investigated by extraction using subcritical water. The effects of temperature and time on extraction efficiency were studied by performing eight individual extractions and varying the subcritical water temperature (200, 225, 250, and 275 °C) and extraction time (90, 120, 180, and 240 min) in a dynamic mode. Also, a comparison was carried out of the feasibility of two operational modes, namely, dynamic and static-dynamic mode. Of the 25,088 mg/kg of lubricating oil as the total petroleum hydrocarbon (TPH) concentration in untreated soil, the residual concentration was found to be ~500 and 235 mg/kg for after 120 min extraction in a lab-scale apparatus and 150 min extraction in a 30-fold scale-up experiment, respectively, at 275 °C in static-dynamic mode. The result of this study showed the significant effect of the static-dynamic mode on extraction efficiency. The time and volume of water needed for the static-dynamic mode were much lower than those needed for the dynamic mode. These results are of practical interest in developing the subcritical water extraction technology for extraction of lubricating oil and, in a broad sense, petroleum hydrocarbons contaminated soil.

1. Introduction

Subcritical water extraction (SCWE) has become a green extraction method for the remediation of different classes of compounds contaminated soil and is a technique based on the use of superheated water ($100\,^{\circ}\mathrm{C} \leq T \leq 374\,^{\circ}\mathrm{C}$ and pressure < 22.1 MPa) as a solvent instead of organic chemicals. The unique characteristics of subcritical water have been described in the literature [1–3]. Lagadec et al. [4] were among the first to fully exploit the feasibility of SCWE technology to remediate the organic contaminated sites. Their pilot scale study of hot water extraction of polycyclic aromatic hydrocarbons (PAHs) and pesticides from soils was unique in one respect; hot water extraction was compared to bioremediation and supercritical CO_2 extraction. Removal rates during one year of bioremediation were much lower even for low molecular weight PAHs than those obtained after 60 min of hot water extraction. The PAHs and pesticide contaminated soils used in their study could not support plant growth prior to treatment with hot water extraction, but both soils were fertile without additional treatment after extraction. In addition, a few research groups have reported that SCWE technology can be used to treat organic contaminants such as PAHs [3,5], polychlorinated biphenyls (PCBs) [6,7], pesticides [8], and explosives [9] and have shown the feasibility of extracting contaminants from contaminated soils. These water based solvents have significant potential for beneficial use in various pollutant removal applications.

Contamination of soils by petroleum hydrocarbons (PHCs) poses a major environmental problem, especially to the soil environment, and has caused critical health defects; increasing attention has therefore been paid for developing innovative technology to clean up this contamination. A recent work by Tang et al. [10] evaluated the eco-toxicity of PHCs contaminated soil and reported that the contaminated soil greatly inhibited seed germination when the concentration of petroleum was higher than 0.1%, and that 0.5% should be considered the critical value for living microorganisms. Similar concluding remarks have been reported by other researchers [11,12].

Soil polluted with PHCs is often observed as a result of leaking fuel storage tanks, crude oil spills, and the disposal of refinery waste and railroad cars. Railroad soil or the soil near railroad junctions usually becomes contaminated with lubricant because the railroad industry uses diesel oil for fuel, lubricating oil for machinery, and waste-lubricating oil on the railroad. Such sites

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often contain organic contaminants including benzene, toluene, ethylbenzene, and PAHs originating from PHCs [13]; they thus require remediation via a clean-up to protect human health and the ecosystem.

Numerous researches have been conducted on the remediation of PHCs contaminated soil using a bioremediation process [14–18]. However, bioremediation is not suitable in treating lubricating oil contaminated sites because the oil is highly viscous and does not biodegrade easily [13]. In addition, the total petroleum hydrocarbon (TPH) removal is frequently poor because biodegradation in soil can be limited by many factors, such as microorganism types, nutrients, pH, temperature, moisture, oxygen, soil properties, and contaminant presence [19]. While supercritical ethane, supercritical argon, organic solvent, and surfactant remediation processes have proven to be an excellent technique for both extraction and chromatography [20–24], the supercritical water extraction process requires a high temperature of >374 °C and pressure of ≥22.1 MPa and is corrosive, while other processes require large volumes of organic solvents that are not only flammable but often toxic or carcinogenic, expensive, and environmentally unfriendly.

Electrokinetic (EK) soil remediation has attracted interest among researchers over the last decade. Since 1996, when the first EK remediation was introduced in Korea for soil contaminated with heavy metals, many researchers have investigated different EK system configurations to achieve enhanced performance [25]. In recent, modified EK system, namely EK-Fenton remediation has been reported as a promising technique to remediate diesel contaminated soil [26,27]. Pazos et al. [26] reported that the TPH removal efficiency of 90% was obtainable by surfactant EK-Fenton process after 15 days of treatment. However, this technique is not suitable for remediation of high range hydrocarbons (heavy oil) as well as requires a long treatment time. For example, Park et al. [13] documented the feasibility of EK technology on the remediation of railroad soil contaminated by lubricating oil and zinc; and the removal efficiency of lubricating oil was only ~50% after 17 days of operation.

As a result, a suitable remediation method is needed to treat PHCs contaminated soils. A study by Kim and Kweon [28] showed that oily lubricating materials were effectively removed from the parts of a lubricating machine by SCWE at a relatively low operating temperature. But, so far, the remediation of used lubricating oil contaminated soil by extraction using subcritical water has not been studied. Therefore, the main objective of this research was to exploit the possibility of the SCWE of lubricating oil as an excellent remediation technique to treat soils contaminated with PHCs. A secondary aim of this study was to optimize the extracting process using subcritical water for the pilot scale application.

2. Experimental

2.1. Soil characterization

The main properties assessed in the soil were the pH, the organic matter content and the particle size distribution. The non-polluted soil was collected from Hwasun in South Korea and a soil sample was air-dried, homogenized, and sieved using a 10-mesh sieve. The physicochemical properties of the soil are summarized in Table 1.

2.2. Soil contamination procedure

A <2 mm fraction of 5 kg of non-polluted soil sample was contaminated by mixing the soil with used lubricating oil (density = 0.8364 g/cm^3) that was collected from a car repairing centre nearby our university campus. Lubricating oil was selected since it is known as the most difficult contaminant to extract from soil due to its high boiling point fractions (>350 °C). Used lubricating oil was previously dissolved in dichloromethane before it was spiked into the soil. 135 g of used lubricating oil, dissolved in 3 L dichloromethane, was added to 5 kg soil sample. The soil–dichloromethane mixture was shaken overnight and subsequently the dichloromethane was evaporated by air-drying the soil for about 6 h. The contaminated soil was kept in a closed aluminium container at room temperature for 3 week to allow the dispersion and sorption of the contaminant in the soil matrix. The average initial concentration of lubricating oil after contamination was 25,088 mg/kg, in terms of TPH. It should be noted that the hydrocarbon components of lubricating oil are classified within the chromotographable hydrocarbon range of C_{24}–C_{36}.

Table 1
Physicochemical properties of used silt loam soil.

Properties	Values
pH	6.62
Total organic matter (%)	9.23
Particle distribution (%)	
Sand	38
Silt	59
Clay	3
Initial concentration[a]	
Lubricating oil (mg/kg) as TPH	25,088

[a] Initial concentration was based on the analysis of three 10-g subsamples of a homogenized soil sample.

2.3. SCWE equipment and extraction process

One semi-pilot and one lab-scale SCWE apparatus were used in this work to carry out the extractions of the lubricant contaminated soil, in which a lab-scale apparatus previously used for PAHs [5] is described in Fig. 1. In the case of the lab-scale apparatus, the stainless steel tube (1 mm o.d., 0.6 mm i.d.), which is part of the equipment, was used as a heating coil and a water flow line through the pre-heater, main-heater, and condenser to the outer chamber. A high pressure pump (Series II, Chrom Tech, Inc.) was used to deliver water to the pre-heater, followed by a 9.5 mL extraction cell (17.0 mm o.d., 10.0 mm i.d., and 108.7 mm long; made of stainless steel) and the cell was capped at the inlet and outlet with a 2 μm stainless steel microfilter.

In the case of scale-up extraction, 254 mL of the extraction cell was constructed from stainless steel (30.0 mm o.d., 70.9 mm i.d., and 359.0 mm long) with end cap (20 μm stainless steel microfilter). An Annovi Reverberi pump (RC-M.01.10, made in PR China) was used in the dynamic flow mode to pump water through the preheating coil of 2.0 mm i.d. (4.1 mm o.d.) stainless steel tubing and extraction cell. For both extractions, the soil sample was weighed and inserted into the extraction cell which was placed into the main heating chamber. The extraction cell was then closed tightly and connected to the water and contaminant mass flow tube. Thereafter, the water was pumped at a desired flow rate for a desired period through the pre-heating coil and extraction cell. The temperature in the preheating coil and extraction cell was observed by a thermocouple connected to a West 6100+ temperature controller (Ise, Inc., USA). Superheated water has a decreased dielectric constant, surface tension, and viscosity, thus making it an efficient solvent for extracting soluble poor or non-soluble organic contaminants while passing through the extraction cell. A system pressure regulator valve was used to control and allow the pressure to build up. The extraction cell was heated to the desired temperature. After the desired extraction, the pump and heater were stopped and the pressure was released to atmospheric pressure. The reactor was left to cool to room