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Remediation of polycyclic aromatic hydrocarbons from soil using superheated water extraction

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ABSTRACT

In this study, superheated water extraction (SWE) was used for remediation of polycyclic aromatic hydrocarbons (PAHs) incl. naphthalene, phenanthrene, anthracene and pyrene from contaminated soil. The effect of two parameters including the water temperature and extraction time on remediation efficiency was investigated. Water temperature was varied from 100 to 180 °C and extraction time ranging from 5 to 20 min. A two-phase mathematical model was developed to evaluate the behavior of superheated water extraction process and to simulate the remediation of PAHs from contaminated soils. The results showed that the remediation efficiency depends strongly on water temperature. Also, the capability of superheated water as a green solvent for remediation of PAHs from soil was proven.

1. Introduction

A new alternative extracting technique that has attracted the attention of many researchers is superheated water extraction (SWE) [1]. SWE is a powerful technique based on use of water as a solvent instead of organic solvents [2]. Superheated water is liquid water at temperatures ranging from100 to 374 °C and enough pressure to maintain its liquid state [3]. Water is an unrivaled solvent because of its high dielectric constant, high polarity and its highly hydrogen-bonded structure that lead to excessively high boiling point at ambient conditions. If the water temperature rises, its properties change dramatically [4]. Under standard conditions, 25 °C and 101 kPa, water is a polar solvent with dielectric constant (ε) of about 80, but when temperature is increased to around 200 to 350 °C, the dielectric constant fall to about 20 to 30, which is similar to the dielectric constants of solvents like methanol, ethanol and acetone at ambient temperature [5]. The effect of increasing temperature means that superheated water can have a permittivity very similar to organic solvents and it can dissolve a wide range of medium including low polarity components [1]. Also, viscosity and surface tension of water decreases with increasing temperature [6]. Furthermore, water as a green solvent is environmentally friendly, easily available, non-toxic and it can easily be obtained and disposed of. Therefore, SWE can be considered as a low cost and efficient method of extraction for low polar organic components from soil, sediments and plant materials [7].

SWE has been reported for the remediation of organic pollutants such as PCBs [8], pesticides [9] and PAHs [10–13] from contaminated soils. Polycyclic aromatic hydrocarbons (PAHs) are among most common and major classes of organic environmental pollutants [14]. PAHs are micro pollutants that because of their toxicity and their mutagenic properties have been listed as priority pollutants, and because of their hydrophobic nature, PAHs are highly resistant to environmental degradation [12,15]. Because of their persistence in the environment through contamination of water, soils and sediments, remediating these pollutants is important [2]. However, the remediation of PAHs contaminated soil by extraction using superheated water for commercial applications has not been sufficiently studied.

In this research work, a dynamic superheated water extraction process in lab-scale was carried out for soil remediation from some frequently encountered PAHs such as naphthalene, phenanthrene, anthracene and pyrene. Two factors including water temperature and extraction time were selected to investigate the extraction process. The second aim is to introduce modifications to the model described in our previous work [13] to describe the behavior of superheated water extraction system and to simulate the remediation of contaminants from soil.

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Nomenclature

b_B	parameter of the He–Yu equation
c_{fi}	concentration of each solute in the bulk fluid phase (kg/m^3)
c_{si}	concentration of each solute in the surface of particle(kg/m^3)
c_i^*	concentration of each solute in the fluid phase at the particle surface (kg/m^3)
D_{AB}	binary diffusion coefficient of each solute in superheated water (m^2/s)
d_b	bed diameter (m)
D_l	axial dispersion coefficient (m^2/s)
d_p	particle diameter (m)
k_{fi}	external mass transfer coefficient for each solute
k_{pi}	Volumetric partition coefficient of the solute between the solid and the fluid phase for each solute
M_A	molar mass of solute (kg/mol)
M_B	molar mass of solvent (kg/mol)
Pe	Peclet number
P_{cB}	critical pressure (Pa)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
T	Temperature (K)
t	time (s)
u_z	superficial velocity (m/s)
V_A	molar volume of the solute at its normal boiling point (m^3/mol)
V_B	limiting volume of water (m^3/mol)
V_{cB}	critical volume of water (m^3/mol)
z	bed height (m)
α	specific surface (m^2/m^3)
β	parameter of the He–Yu equation
ε	void volume fraction
ρ	density of water (kg/m^3)
ρ_r	reduced density of the pure solvent at system temperature
φ	association factor for the solvent
γ	parameter of the He–Yu equation
μ	viscosity (Pa s)

2. Experimental

2.1. Chemicals

Distilled water purified using a Milli-Q deionizing unit (Millipore, Bedford, MA) was used as solvent. Naphthalene, phenanthrene, anthracene and pyrene (purity > 98%) were purchased from Sigma Aldrich. Methanol (purity > 99%) was used to prepare samples and standards for UV analysis. Hexane (purity > 99%) was used to prepare spiking solutions.

2.2. Contaminated soil preparation

In this study, 250 g sand bath was used to simulate the soil. It was washed with distilled water and 500 mL of methanol respectively. It was dried for 24 h and then, was used to prepare spiked soil. 150 mg of each contaminant was added to 200 mL of hexane to make spiking solutions. The spiking solution was mixed with 250 g soil by using a lab mixer for 3 h. After that, the contaminated soil was dried for 24 h and maintained for 7 days. To be able to perform UV analysis correctly, all experiments were carried out on the aforementioned simulated soils. To find out how much of the solute was loaded on the soil, 5 g of the prepared sample was mixed with 60 mL of methanol. The solid-liquid mixture was mixed at 200 rpm for 3 h. The mixture was separated using filter paper and the solution was centrifuged at 2000 rpm for 1 h to assure complete separation of solid particles before UV analysis. Using calibration curves which were prepared for each contaminant, the amount of solute loading was calculated.

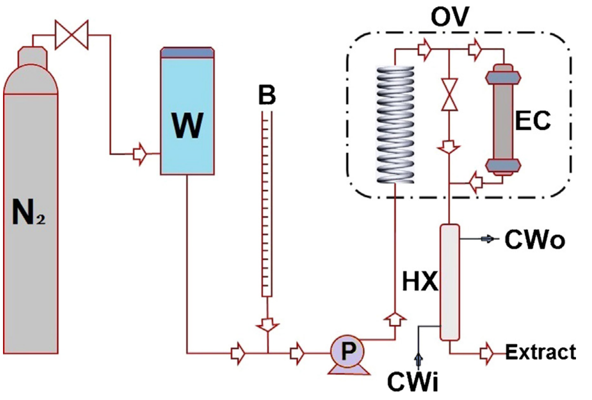

Fig. 1. Schematic diagram of the superheated water extraction system: OV: oven; HX: heat exchanger; EC: extraction cell; W:water storage; CWi: cooling water in; CWo: cooling water out; B: burette.

2.3. Superheated water extraction

Fig. 1 is a schematic diagram of SWE setup used in this study. The lab-scale superheated water extractor was described in detail in our previous work [16]. Before using the distilled water, it was purged with nitrogen for 30 min to remove dissolved oxygen. The pump (FWT, FX series, type: FXS C/A, Flow rate: max. 10 mL/min, 0.01 mL/min accuracy, max. pressure 20 bar) was operated in the constant pressure mode to supply water through the 5 L stainless steel reservoir to the extraction cell. 5 g of contaminated soil was filled into the extraction cell and it was assembled in the oven. After that, the extraction cell was placed in the oven using appropriate connections, the pump was turned on and pressure increased up to 20 bar. Then, the pump was turned off and temperature of oven was raised to the desired value. The pump was turned on and the flow rate was adjusted at the required rate. Water was passed through the extraction cell with the water flowing from top to bottom. To investigate the effect of temperature and extraction time on removal efficiency, experiments were designed and performed according Table 1. When the temperature of extraction cell was reached to the set point, recording of extraction time was started. At the end of extraction time, heater and pump were turned off and the pressure was released to the atmospheric pressure. The oven was left to cool to room temperature, the extraction cell was removed from the oven and the remediated soil was collected to

Table 1
Experimental design for remediation of PAHs from contaminated soil. All experiments were performed at 20 bar and 3 mL/min water flow rate.

Experiments	Water temperature (°C)	Extraction time (min)
Temperature	100	15
	120	
	140	
	160	
	180	
Extraction time	160	5
		10
		15
		20