EFFECT OF THERMODYNAMICS PROPERTIES OF SUPERCRITICAL FLUID ON THE EXTRACTION EFFICIENCY OF PHENANTHRENE FROM SOIL-POROUS MEDIA

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ABSTRACT

Supercritical Fluid Extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids that is CO2 as the extracting solvent. Clay soils have specific properties that cause difficulty in the assessment and remediation of contaminated sites. Furthermore, polyaromatic hydrocarbons, when present in soil, are difficult to extract due to their nonpolar, high molecular weight characterization. In this study, the supercritical fluid (carbon dioxide) extraction (SFE) technique, with methanol modifier, was used for removal of PAHs (phenanthrene) from kaolinite, illite, and mixture of soil with sand soils. The impact of thermodynamics properties of supercritical fluid enthalpy, entropy and internal energy on the removal efficiency of PAHs from clayey soils were investigated. The results of this investigation show that the extraction efficiency increases with decreasing the heat content of supercritical fluid. The recovery decreases with increasing the entropy

This is due to the soil properties such as the size of the pores, mineral content and surface area of the soil

Keywords: Clayey soil; Kaolinite; Illite; Supercritical fluid extraction (SFE); Phenanthrene; modifier ;
Extraction efficiency

INTRODUCTION

A growing concern has arisen in recent years about the fate of hazardous compounds, notably petroleum products in soils. Soil is often a receptacle of these compounds, and there is potential danger that they may reach the groundwater in their original or altered composition but still preserving toxic properties.

An assessment of the accurate content of these components is very often a challenge, especially when the contaminated sites consist of clay minerals. Therefore, the use of various extracting techniques to reach a higher removal of these contaminants from soils has been extensively researched—Soxhlet extraction [1], sonication extraction [2], water desorption [3], butanol extraction [4] are among them. However, the recovery rate of extraction from clay soil never reached 100%. Supercritical fluid extraction (SFE) has gained increasing applications for extracting and has been widely accepted as a replacement for classical extraction methods, especially for low-solubility compounds. The supercritical fluid most commonly consists of pure, nontoxic carbon dioxide or carbon dioxide with small quantities of modifiers to enhance extraction of several organic and inorganic compounds. The polyaromatic hydrocarbons (PAHs) are typical of a nonpolar, high molecular weight class of pollutants, which are difficult to extract from clayey soils. SFE can provide more advantages in recovery than classical extraction methods; it reduces the time required for extraction and it does not employ large amounts of hazardous organic solvents used in other techniques [1]. Subsequently the SFE technique could be used for more adequate analyses of contaminated soil, waste and sediments as well for its remediation. In extracting contaminants from soils, SFE would be less energy-consuming than thermal methods applied to an entire soil mass, and it leaves the soil's structure relatively intact [5].

The use of SFE to extract contaminants has been studied for various solid and soil matrices such as sand, clay, slag, and sediment (among others, [5–11]). Other researchers applied a variety of operational parameters, such as fluid pressure, fluid temperature, extraction time, cosolvent type and amount, and modifiers to optimize the recovery of organic compounds. The objectives of this paper are to present the impact of supercritical fluid extraction thermodynamics properties, and clay properties on the removal efficiency of phenanthrene from soil.

Experimental investigation

Tests were conducted on laboratory-prepared contaminated samples to assess SFE extraction efficiency of phenanthrene from clayey soils. They were performed on pure materials, namely kaolinite, illite, and montmorillonite, and sandy soils with different illite content.

Materials

In this investigation four commercial materials were used: kaolinite, illite, montmorillonite, and pure silica sand (0.06–0.2 mm). The samples consisted of pure kaolinite, illite, and mont- morillonite, and mixtures of illite and fine pure silica sand (S_4: 60% illite and 40% sand; S_5: 50% illite and 50% sand; S_6: 20% illite and 80% sand; and S_7: 100% sand). They were prepared to simulate various site conditions (i.e., dry and wet conditions). All samples were contaminated with phenanthrene to a concentration level of 200 mg/kg of dry soil.

Supercritical fluid extraction (equipment and procedure)

All extraction experiments were performed by the SFX 220 Extraction System (ISCO, Lincoln, NE), which consists of an SFX 220 Extractor, an SFX 200 Controller, and 100-ml syringe pumps (ISCO Model 100 DX). Both the pumps and the extractor are connected to a SFX 200 Controller, which controls all pumping and extraction operations by changing the parameters such as temperature and pressure (Fig. 1). The SFX 220 Extractor is a bench top, dual chamber (cartridge filter with a 5/8-inch diameter filter element), supercritical fluid extraction device, which fits on the top of an SFX 200 Controller. The extractor incorporates six motor-actuated valves, which are controlled by the SFX 200 Controller. The fluid source for the extractor is supplied by a D-series pump and the other pump for the modifier. The devise is a pressure safe design that prevents over-pressurization or cross-contamination of chambers. Fused-silica tubing with an inner diameter of 50 µm, 30 cm long, was used as an outlet restrictor, allowing analytes to be conveniently collected in the test tubes. A vent valve allows rapid depressurization of the chamber after the extraction is completed. Extracted analyte was collected outside of the oven at room temperature by placing the outlet end of the restrictor into a 30-ml vial containing 7–10 ml of hexane.

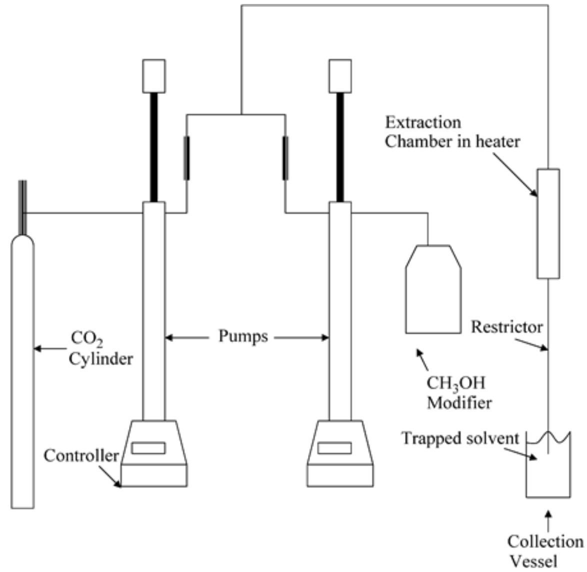


Fig. 1. Dual syringe pump system for modifier SFE.

The different extraction sequences can be described as follows: (1) 3 g of contaminated soil is placed into a 10-ml cartridge body. Valves closed, the cartridge is loaded into the extraction chamber. (2) Filters of 5/8-inch diameter are placed at the top and bottom of the cartridge. (3) The supply valve is opened and the supercritical fluid is supplied by two 100DX syringe pumps. The fluid flows into the extraction chamber, filling the cartridge upwards.

During the tests, the flow rate of CO2 was held at approximately 2.5 ml/min by a 32 µm ID × 10 cm fused-silica capillary restrictor, and the extraction volume was set to 30 ml.

Extracted analyte was collected outside of the oven at room temperature by placing the outlet end of the restrictor into a vial containing 7–10 ml of hexane. The vial was vented to the fume hood using a stainless steel needle (25 cm length of 0.023 cm ID × 40 cm OD) that was pierced through the septum. When gas ceased to exit the vent outlet, chamber depressurization was complete. The sample cartridge was removed immediately and the next sample cartridge was loaded into the chamber to begin Another extraction. In this study, extractions were performed un- der different testing conditions. Four different pressures were used: 34, 40.8, 47.6, and 54.4 MPa. The temperatures tested were 70, 80, 100, and 120 ◦ C. For pure samples, extractions were performed for 20 min.

Effect of thermodynamics properties of supercritical fluid on extraction efficiency from clays and mixture of clays and sand

The effect of enthalpy, internal energy and entropy on the extraction efficiency from the clay

For the applied pressures, the results of the tests demon- stated that pressure seems to have an impact on phenanthrene extraction from pure clays (kaolinite and illite). However, illite samples were less susceptible to the change of pressure than montmorillonite and kaolinite notably in the range 40.8–54.4 MPa (Fig. 2).

By in- creasing the pressure from 34 to 54.4 MPa, the recovery degrees for dry condition increased respectively from 9.8 to 30% for kaolinite, from 34.7 to 51% for illite, and from 88 to 93.2% for bentonite.

This phenomenon could be caused by two factors: at first, high heat content of supercritical fluid-carbon dioxide and the soil properties such as the size of the pores, mineral content and surface area of the soil.

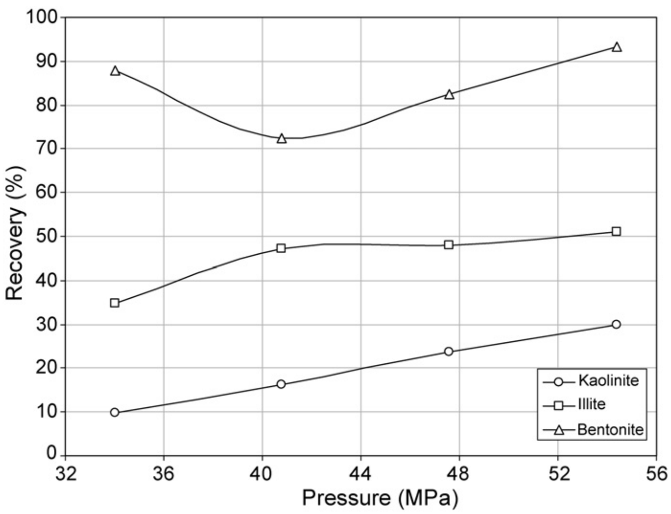


Fig. 2. Recovery versus extraction pressure (dry condition, T = 80 ◦ C).

There are several parameters which are of key importance in conducting an extraction by SFE. These are thermodynamics properties of supercritical fluid and the modifier, soil matrix properties, physical and chemical properties of the solutes that are to be extracted, etc. The analysis of an accurate extraction rate is based on the recognition of the effect of all factors in phenomena taking place in the cartridge during the extraction process.
The test results obtained in this investigation were used in the first stage to study the effect of SFE parameters on extraction efficiency. Furthermore, they were used in the second stage to investigate the effect of clay content and properties on ex- traction efficiency.

Fig.3 show that the extraction efficiency increases with decreasing the enthalpy, internal energy and entropy of carbon dioxide supercritical fluid, the percentage of extraction depends on the type of the soil. When the total heat content of supercritical fluid, the efficiency of extraction process decreases. Also it is noticed that the illite has higher efficiency than kaolinite, this is due to the properties of the soil, swelling index and surface area of illite higher than kaolinite.

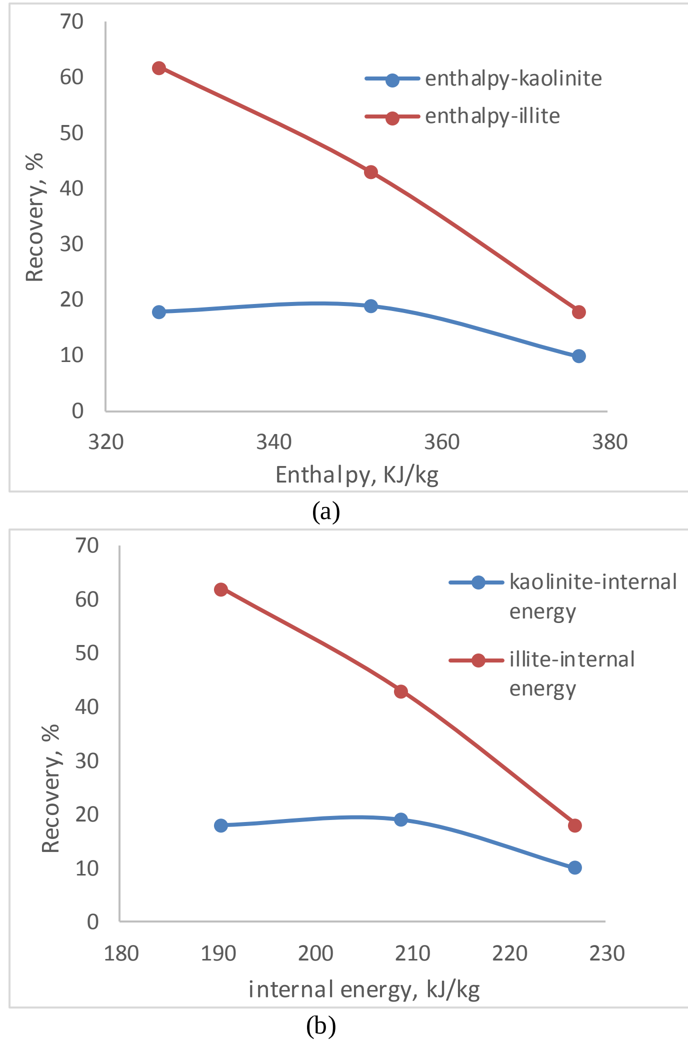


Fig. 3. The relation between enthalpy (a) and internal energy (b) on the extraction efficiency of phenanthrene from kaolinite and illite, P=54.4 MPa

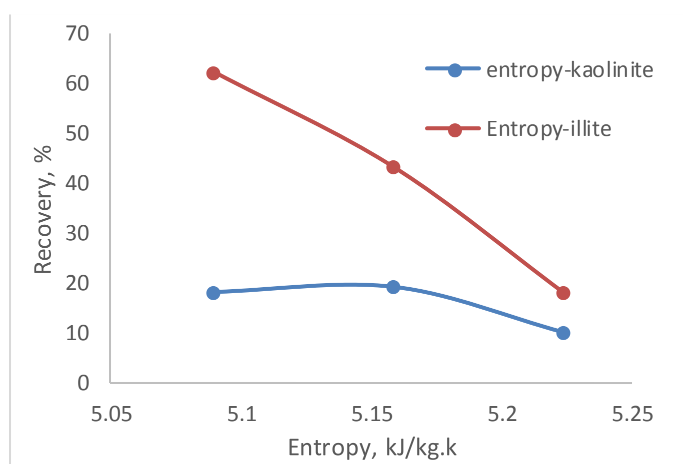
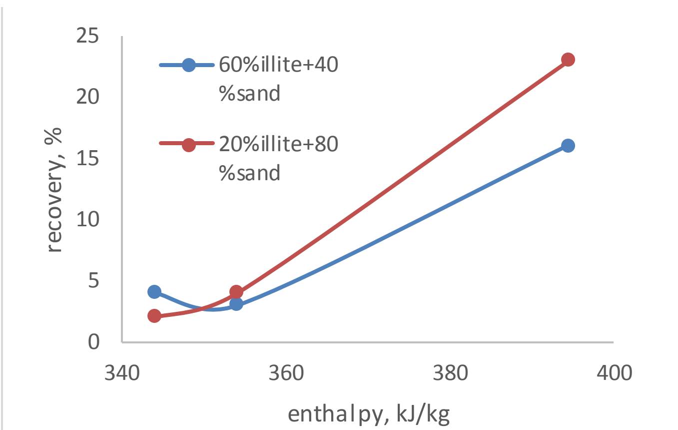


Fig. 4. The relation between entropy on the extraction efficiency of phenanthrene from kaolinite and illite, P=54.4 MPa

Fig. 4 shows that the extraction efficiency of contaminant from illite is inversely proportional with the entropy. However for kaolinite, the change of extraction efficiency of contaminant is insignificant vs. the entropy at high pressure 54.4 MPa. It is due to the porosity, the porosity of illite is 30+0.01 %, and the porosity of kaolinite is 2+0.01%.

The effect of enthalpy and internal energy on the extraction efficiency from the mixture of clay and sand

Fig. 5 (a) and (b) show that the for sandy illite soils, increasing the enthalpy of supercritical fluid up to 395 kJ/kg and decreasing the pressure of the system up to 34 kPa increases the efficiency removal of phenanthrene from the soil. This is due to the void ratio of sand is big, 0.74-0.9. Therefore the mixture of illite and sand change the properties of the soil, the results show that the combination of the thermodynamics properties and the type of media such as (porous media) affect on the extraction efficiency.



(a)

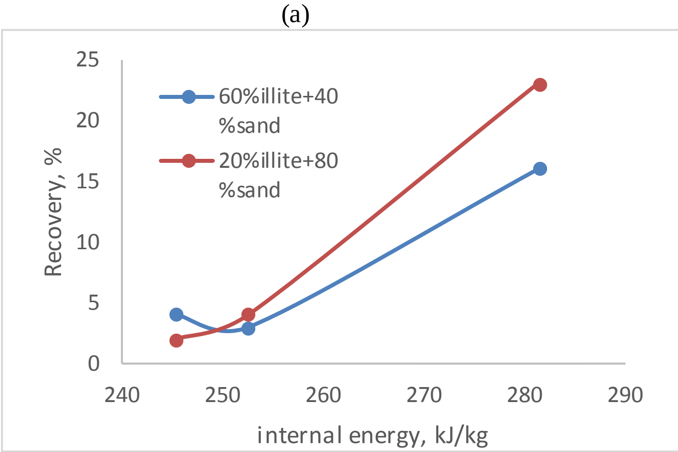


Fig. 5. The relation between enthalpy (a) and internal energy (b) on the extraction efficiency of phenanthrene from 60%illite+40%sand and 20%illite+80%sand, P=34 kPa

The effect of entropy on the extraction efficiency from the mixture of clay and sand

Fig. 6 shows the entropy vs. recovery of Sand, mixture of 60%illite+40%sand, and mixture of 20%illite+80%sand. It is noticed that the recovery of mixture of clay and sand and sand is increasing with increasing the entropy at low pressure. This is due to the effect of the properties of supercritical fluid on the extraction efficiency and the porosity of mixture of clay and sand and 100% is higher than the clay, also it is noticed that 100%sand has higher recovery than the mixture.

The extraction efficiency of contaminant from sand is directly proportional with the entropy at low pressure. The porosity of sand is 79%. It is concluded that increasing the porosity of porous media is inversely proportional with the entropy at high pressure. However at low pressure the extraction efficiency is directly proportional with the Entropy. In the future, Dimensionless parameters will be developed to minimize the number of variables and it will simplify the analysis.

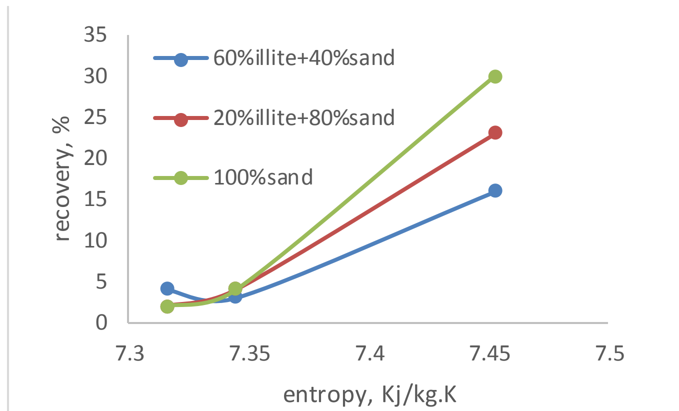


Fig. 6. Comparison of Entropy vs. recovery of sand, 20%illite+80%sand, 60%illite+40%sand at P =34 kPa

Conclusion

A series of laboratory tests were conducted [12] in order to evaluate the influence and the impact of thermodynamics properties of carbon dioxide supercritical fluid (enthalpy, entropy, and internal energy) and the effect of the soil structure and porosity on the extraction efficiency. The results obtained showed that the percentage of extraction efficiency is related to the amount of heat content of supercritical fluid and the void ratio of the soil (porous media). Increasing the void ratio of porous media and the enthalpy, internal energy and entropy of supercritical fluid will increase the percentage of extraction efficiency at low pressure. Also adding the modifier to the supercritical fluid will improve the extraction efficiency. On the other hand, at high pressure and small porosity the extraction efficiency are inversely proportional with the enthalpy, internal energy and entropy

It is concluded that the combination of thermodynamics properties of supercritical fluid and the soil properties affect on the extraction efficiency of the nonpolar, high molecular weight class of pollutants from the soil

In the future, different types of supercritical fluid and modifiers will be carried out.

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