油類污染土壤之中尺度污染評估模式研究及處理開發 **(II): Study of Meso-Scale Pollution Assessment Model of Petroleum-Polluted Soil and Development of Treatment Technology (II). (Optimization of the supercritical fluid extraction parameters for studying the sorption behavior of Toluene, Ethylbenzene and p-Xylene)**

1. Abstract (Supercritical fluid extraction, volatile organic contaminants)

Supercritical fluid extraction has shown to be an efficient technique to analyze the various organic contaminants from the environmental matrices. In order to study the vapor phase sorption behavior of the volatile petroleum hydrocarbons (VOCs) such as toluene, ethylbenzene, and p-xylene (TEX) in the present work three important parameters such as fluid pressure, chamber temperature and fluid flow rate were optimized. The results reveal that the fluid pressure of 121 bar, chamber temperature of 98 °C and the fluid flow rater of 2 ml/min was the optimal condition with the equilibration time of 5 min and extraction time of 25 min. Under the optimal condition the amount of TEX extracted was higher compared with other conditions. The results also indicates that the adsorbed amount of TEX was in the order that toluene > p-xylene > ethylbenzene.

2. Introduction

The presence of organic contaminants in the soil results in a great problem since many of them are toxic and harmful to the health of humans, other organisms, or to the environment. The most commonly observed contaminants in the waste product of petroleum refineries and industrial solvents are volatile organic compounds (VOCs) such as toluene, ethylbenzene, xylene (TEX) benzene and chlorobenzenes. The waste materials include explosive, flammable, volatile, radioactive, and pathological wastes. Literature survey reveals that petroleum refineries presently generate over one million tons of total waste materials per year nationally (Bonner and Authenrieth, 1989).

Supercritical fluid extraction (SFE) technique has been gaining much attention in recent years since it is found to be a better alternative over the conventional liquid solvent extraction methods (Soxhlet and sonication) for the extraction of environmental samples. SFE has several advantages such as less extraction time, low solvent requirement, low cost, and higher efficiency, less laborious and no environmental pollution (Tena *et al.* 1994).

Supercritical fluids such as N_2O, SF_6, CH_3OH, H_2O, $CHClF_2$, and CO_2 possess unique physio-chemical properties that make them as attractive extraction solvent (Camel *et al.* 1993).

The most popular fluid for SFE has been CO_2 because of its low critical properties ($T_c = 32°C$, $P_c = 72$ atm), high purity, low toxicity and cost, chemical inertness, and its ability to solvate a wide range of organic compounds including those having higher molecular weight.

3. Materials and Methods

Toluene ($C_6H_5CH_3$, OSAKA, 95%), p-Xylene ($C_6H_4C_2H_6$, OSAKA, 95%), Ethylbenzene ($C_6H_5C_2H_5$, OSAKO 95%) were obtained from Osaka Chemical Industries and Pentane ($CH_3(CH_2)_3CH_3$) was obtained from Fisons, (99.35% pure). Supercritical fluid extraction grade of carbon dioxide without a helium head pressure obtained from Air Products (Nepean, Canada).

The sorbent used in the present study was clean soil collected from a farm located at Southern Taiwan. Then the soil was homogenized by passing the entire sample through the 30-mesh sieve. The soil was also tested to verify whether it contains any TEX.

3.1 Sorption Apparatus

The experimental apparatus set up used in the study was taken from David *et al.* (1996). It consists of 120 ml glass vials with Teflon rubber screw caps, 5ml glass tubes, and 0.1 ml pipettes.

3.2 Methods

About 0.5 gm of the air-dried soil was taken in the glass vial and spiked with a TEX mixture containing 100 mg of each toluene, ethylbenzene, p-xylene and capped tightly and

allowed to equilibrate for 48 h at 20 °C. After the equilibration period the 0.5 gm of the soil sample was taken in the extraction thimble and the extraction was carried out with the conditions mentioned in the following SFE section. Triplicate experiments were carried and an average of the best two results was taken.

3.2.1 Supercritical fluid extraction

SFE experiments were performed using a Hewlett-Packard 7680T supercritical fluid extractor. The supercritical extraction pressure range was 80-164 bar, temperature was 40–80 °C, flow rate was 3 ml/min, static extraction time was 5 min and the dynamic extraction time was 25 min.

3.2.2 Gas Chromatographic Analysis

Extracts were analyzed using a gas chromatograph equipped with a mass spectrometry detector (HP 1800A GCD, USA). Separation is performed using a 30 m × 0.25 mm i.d. HP-1 capillary column (J & W Scientific, Folsom, CA, U.S.A.).

4. Results and Discussions
4.1 Optimization of pressure

Initially the experiments supercritical extraction was carried out for the extraction pressure of 81 bar, chamber temperature of 40 C, flow rate of 3 mg/ml with the equilibration time of 5min and extraction time of 25 min. In order to optimize the extraction conditions and to study the effect of pressure on the TEX recovery the extraction was carried out for different pressures such as 121, 164 and 265 bar respectively. The recovery of TEX under various pressures is presented in Table 1. It is observed from the Table 1 that the recovery of TEX is higher for the pressure of 121 bar compared with the higher and lower pressures and hence 121 bar is considered as the optimal pressure. The lower recovery at 81 bar can be explained by the fact that the solvating power of the supercritical fluid is low at low pressures since it depends on the density. At low pressures the density is low and hence the recovery is low (Reindl and Höfler, 1994). When the pressure is increased to 121 bar the recovery increases but when the pressure is increased to 164 bar there was a decrease in the recovery and when the pressure is further increased to 265 bar there was a very significant decrease in the recovery. This shows at low pressure and at very high pressures the recovery is less. The increase in the recovery at 121 bar is due to the increase in the solvating power with an increase in the density. If that is the case the recovery should be higher at 164 and 265 bar. The results

indicate that there was a slight decrease in the recovery at 164 bar and a significant decrease in the recovery at 265 bar respectively. With increasing density the solvating power is increased, but at higher densities the diffusion coefficients are decreased (Lee and Markides, 1990). The decrease in the diffusion coefficients can cause lower recoveries as a result of the kinetics of the extraction process. This may the reason why there is a slight decrease in the recovery at 165 bar. However, the dramatic decrease in the recovery at 265 bar is owing to the reason that the solubility of the solute is higher at elevated pressures and thus the extract become very complex and the analysis becomes very difficult. This reason accounts for the lower recovery at 265 bar (Camel *et al.*, 1993). Reindl and Höfler observed a similar trend, when they increased the extraction pressure from 8.5 to 60 Mpa during the extraction of polynuclear aromatic hydrocarbons from soil samples. Considering the above results 121 bar is taken as the optimal pressure. Though the spiking amount of all the three VOCs are same, it is also observed from the Figure 1 that the amount of toluene adsorbed by the soil is greater at all the pressures followed by *p*-xylene and ethlylbenzene. Since the vapor pressure of toluene is about 3-fold higher than that of ethylbenzene and *p*-xylene and hence the volatility is higher than the other two volatile organic compounds and hence it get vaporized easily and occupies the available adsorption sites before ethylbenzene and *p*-xylene. It is also observed that it is ethylbenzene that shows the marked decrease in the adsorption and not *p*-xylene. There was only a slight decrease in the amount of *p*-xylene adsorbed compared with toluene.

4.2 Effect of temperature on the extraction

At a constant pressure the density of carbon dioxide decreases with an increase in temperature. In this study, experiments were carries out in the temperature range of 40 to 100 °C with a static extraction time of 5 min and dynamic extraction time of 25 min. When the temperature was increased from 40 to 60 °C the result obtained was nearly the same as the 40 °C results. But a dramatic decrease in the recovery was observed when the temperature was 80 °C. When the temperature was increased to 98 °C there was a marked increase in the recovery. It is apparent from Table 2 that increasing the extraction temperature is much more effective for obtaining higher recovery comparing with the increase in the fluid pressure. The increase in the recovery at 98 °C is due to the reason that at higher temperatures the vapor pressure is

increased and hence boiling off the pollutant molecules. Figure 2 shows the influence of temperature on the extraction of TEX. The reason for the decrease in the adsorption at 80 C can be explained by the reason that for a volatile solute there is competition between its solubility, which decreases as the temperature increases and its volatility, which rises as the temperature increases (Camel et al. 1993). At 80 °C the solubility effect is more pronounced and hence there was a decrease in the amount of TEX extracted. Whereas at 98 °C the other effect is well dominated and hence the amount of TEX extracted was significantly greater.

4.3 Effect of fluid flow rate on the extraction

To investigate the effect of flow rate three different flow rates were taken into comparison. The effect of flow rate can be negligible or important depending upon the process that controls the overall extraction of the sample. In this study the effect of flow rate was seemed to be very important. The extractions were carried out for the flow rates of 1 ml/min, 2 ml/min and 3 ml/min for the extraction pressure of 121 bar and the extraction temperature of 98 °C. The results are presented in Table 3. It is clear from the Table 3 that the extracted amount of TEX was greater for the flow rate of 2 ml/min in comparison to 3 ml/min and 1 ml/min. Hence the flow rate of 2 ml/min is the optimal flow rate for the extraction of TEX. In the present study decreasing the flow rate from 3 ml/min increased the amount of TEX extracted. While further decrease in the recovery to 1 ml/min decreased the amount of TEX extracted. Decreasing the flow rate results in a lower linear velocity and usually increased extraction recoveries (as a result of the extended contact between the supercritical fluid and the sample) (Camel *et al.*, 1993). This is the reason why there was an increase in the amount of TEX extracted while decreasing the flow rate from 3 ml/min to 2 ml/min. In contrast to the above statement the decrease of flow rate from 2 ml/min to 1 ml/min.

5 References

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6.Figures and Tables

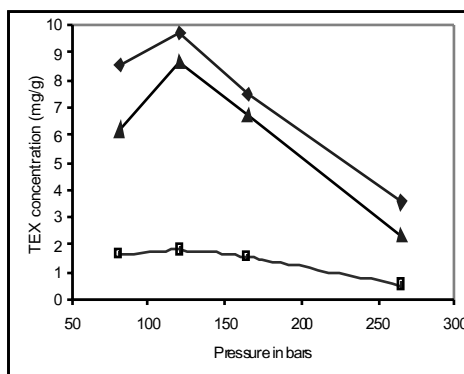Figure 1 Effect of pressure on the extraction of toluene, ethylbenzene, *p*-xylene with the extraction temperature of 40 C, flow rate 3 ml/min, equilibration time 5 min and extraction time 25 min.
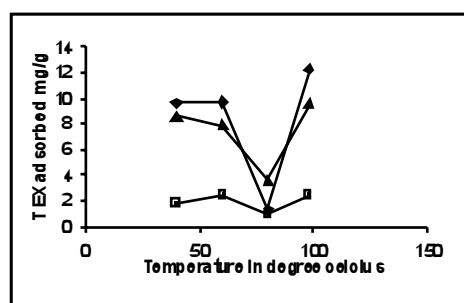

Figure 2 Effect of temperature on the TEX extraction

Table 1 Effect of pressure on VOCs recovery. Extraction conditions: temperature 40 °C, flow rate 3 ml/min, equilibration time 5 min and extraction time 25 min.

VOCs (mg/g)	Pressure (bar)			
	81	121	164	265
Toluene	8.52	9.68	7.44	3.54
Ethyl benzene	1.62	1.79	1.54	0.52
p-Xylene	6.17	8.63	6.69	2.33

Table 2 Effect of Temperature on the TEX recovery Extraction conditions: pressure 121 bar, flow rate 3 ml/min, equilibration time 5 min and extraction time 25 min

VOCs (mg/g)	Temperature (°C)			
	40	60	80	98
Toluene	9.68	9.47	1.30	12.26
Ethyl benzene	1.79	2.44	0.89	2.47
p-Xylene	8.63	7.89	3.63	9.57

Table 3 Effect of fluid flow rate on the TEX extraction Extraction conditions: pressure 121 bar, flow rate 3 ml/min, equilibration time 5 min and extraction time 25 min

VOCs (mg/g)	Flow rate (ml/min)		
	1	2	3
Toluene	6.65	17.73	12.26
Ethyl benzene	1.56	2.98	2.47
p-Xylene	6.28	13.29	9.57