A Supercritical Fluid Extraction Based Closed Loop System For Decontamination Of Soil

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INTRODUCTION

Supercritical fluid extraction (SFE) is receiving increasing attention as a decontamination technique. Considerable data have been presented in the literature indicating that high desorption efficiency can be achieved with SFE for a variety of non-polar and moderately polar contaminants. The advantages of SFE lie in rapid equilibration and the ease with which the contaminants can be separated from the critical fluids, thus allowing the reuse of the fluids. Separation of the solute from the critical fluid is accomplished by lowering the density of the fluid, by either reducing the pressure or raising the temperature. The most common approach is to decrease the density by lowering the pressure (decompression). This approach, while simple, is unsatisfactory for large scale decontamination operations due to the fact that a substantial energy input is required for fluid compression prior to reuse; furthermore, a separate detoxification step is necessary for ultimate disposal of the contaminants. The energy cost of decompression can be reduced by use of adsorbents. The use of carbon for this purpose is being investigated in our laboratory. The system utilizes an oxidative regeneration process for regeneration of carbon through destruction of adsorbed contaminants without energy input from external sources.

The objective of the present study was to explore the applicability of SFE coupled counterflow oxidative regeneration (COR) process for decontamination of low level contaminants in solid matrices.

EXPERIMENTAL

The study involved four sets of experiments:

a. Partition and solubility experiments
b. Breakthrough experiments
c. Carbon regeneration experiments
d. Setup and evaluation of bench scale integrated systems.

a. Partition and solubility experiments

The objective of the experiments was to optimize extraction parameters for removal of organochlorine contaminants from soil. These experiments were carried out with a static SFE system which was interfaced directly to a gas chromatograph (GC) or a liquid

chromatograph (LC). The details of the system have been provided elsewhere[1-4]. Experiments were carried out with soil fortified with selected contaminants; concentrations of contaminants ranged from 1-500 ppm. Extraction parameters such as fluid density, pressure, temperature and equilibration period were optimized. The effect of matrix parameters such as moisture content, surface area, texture and organic matter content on removal of organic contaminants was also examined.

b. Breakthrough experiments

One of the critical questions in the reuse of the fluid is related to the efficiency with which contaminants are removed from the critical fluid. To assess the efficiency of the process with granular activated carbon (GAC), a serial adsorbent trap configuration was used. A schematic of the experimental setup is shown in Figure 1. Analytes of interest were dispersed on glass beads. The amounts were varied depending on the saturation

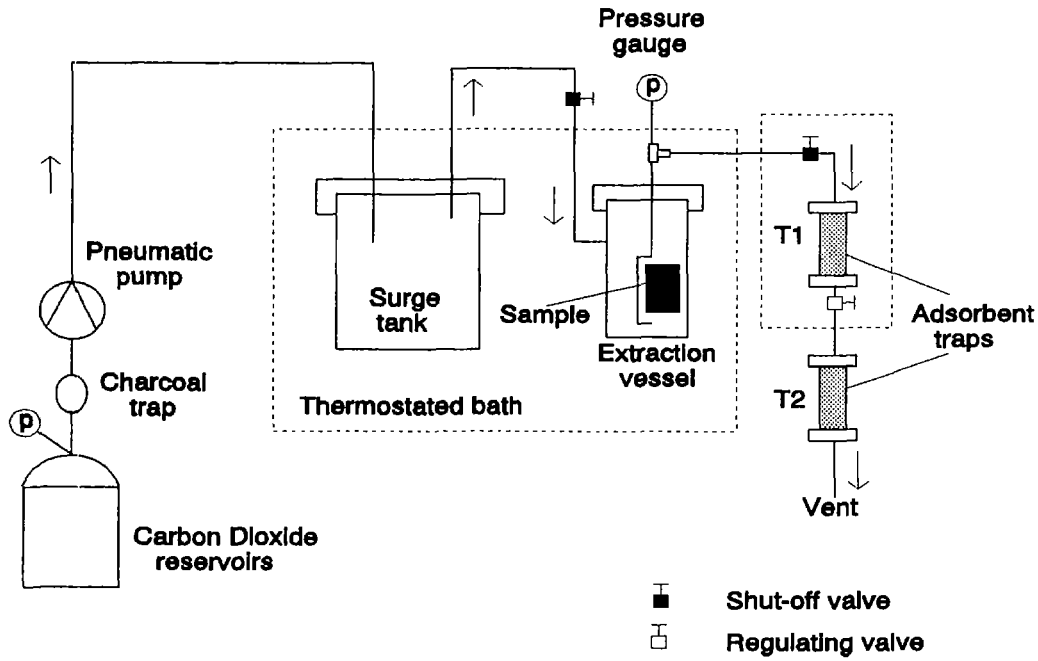

Figure 1: Schematic diagram of the SFE/adsorbent trap system.

solubility limits of the solutes. The saturation limits were determined experimentally and verified with literature values where possible. The system with coated glass beads was allowed to equilibrate for 1 hr. The pressurized fluid was allowed to pass through the adsorbent trap. Pressure in the first trap was maintained above critical pressure by placing a restrictor after the trap. Pressures in the extraction vessel and in the trap were measured independently. A mass balance approach was used to calculate adsorption efficiency.

c. Carbon regeneration experiments

An oxidative carbon regeneration processes was used for detoxification/destruction

of contaminants in the adsorbent trap. This process termed COR has been investigated in our laboratory. The details of these studies have been reported earlier[5,6].

d. Bench scale SFE-COR system

An integrated bench scale system is being fabricated in the laboratory. The system is designed to permit operation in static as well as dynamic modes. A schematic of the system is given in Figure 2. It consists of an extractor, a trap and a reciprocating piston pump. The liquified fluid is pumped to a heating coil where its temperature is brought above

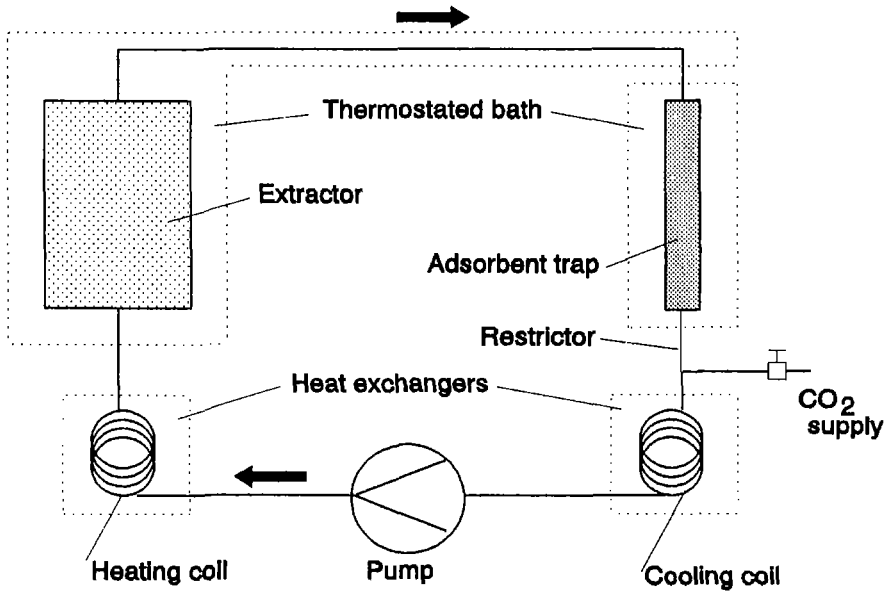

Figure 2: Schematic diagram of a bench scale SFE-COR system.

the critical condition. Supercritical fluid is then made to pass through matrices held in the extraction vessel housed in a thermostated bath. The fluid, along with extracted contaminants, passes through the GAC trap. The contaminants are adsorbed on the carbon and the "clean" fluid is liquified for reuse.

RESULTS AND DISCUSSION

The results of desorption experiments for several chlorinated organics are summarized in Table I. Extractions were carried out using carbon dioxide or nitrous oxide as the extraction fluid. The extractions were optimized in the near-critical region of both fluids. Extraction efficiencies ranging up to 75% were achieved with carbon dioxide, and a marked improvement was brought about by introduction of polar modifiers. Methanol was the modifier of choice; its introduction even at relatively low levels (1-2%) improved extraction efficiencies to $\geq$90-95%. The exact role of modifiers in SFE has not been elucidated so far; however, it is generally believed that polar modifiers improve extraction efficiencies by improving the wettability of the surface and by weakening the electrostatic interactions between contaminant molecules and polyphenolic matrices of soil organic matter. The results clearly demonstrate that high extraction (decontamination) efficiencies can be achieved

Table I: Extraction Efficiency of Selected Xenobiotics from Soil.

Solute	Conc. Range	Ext. Temp (k)	Ext. Presence (Atm)	Density (g/ml)	Percent Extracted		
					CO_2	CO_2-MeOH	CO_2-Toluene
PCBs[1]	2-250	313	122	0.73	81.0	93.0	92.0
	2-250	323	177	0.75	84.0	100.0	95.0
2 Chlorphenol[2]	50-250	323	177	0.75	63.0	76.0	63.0
2,4 Chlorophenol[2]	50-250	323	177	0.75	60.0	81.0	62.0
Trichlorophenols[2]	50-250	323	177	0.75	37.0	85.0	51.0
2,3,4,5 Tetrachlorophenol[2]	50-250	323	177	0.75	25.0	83.0	39.0
Pentachlorophenol[3]	1-500	323	177	0.75	22.0	83.0	36.0

[1]Extractions were completed in two 30 min. cycles.
[2]Extractions were completed in one 60 min cycles.

with SFE in the near-critical region.

Breakthrough studies with pentachlorophenol as a model compound showed that all of the compound extracted with supercritical carbon dioxide was adsorbed on the GAC in the first trap (T1) at critical conditions. Consequently, no breakthrough was observed in the second trap (T2). Complete detoxification of chlorinated contaminants adsorbed on GAC was achieved by the COR process, which required no external source of energy.

REFERENCES

1 Nam KS, Kapila, S, Viswanath DS, Clevenger TE, Johansson J, Yanders AF. *Chemosphere*, 1989;19(1-6):33-38.

2 Nam KS, Kapila S, Yanders AF, Puri RK. *Chemosphere*, 1990;20(7-9):873-880.

3 Liu MH, Kapila S, Yanders AF, Clevenger TE, Elseewi AA. *Chemosphere*, 1991;23(8-10):1085-1095.

4 Liu MH, Kapila S, Nam KS, Elseewi AA. Submitted to the *Journal of Chromatography*, 1992.

5 Cady CC, Kapila S, Manahan SE, Larsen BW, Yanders AF. *Chemosphere*, 1990;20(10-12):1959-1966.

6 Cady CC, Kapila S, Viswanath DS. Submitted to the *Environmetnal Science and Technology*, 1992.