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Supercritical Fluid Extraction of 1,2,4-Trichlorobenzene from DOE Job Control Wastes

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ABSTRACT

At U.S. Department of Energy (DOE) sites, significant amounts of job control waste (JCW) need to be disposed. This JCW is generated and contaminated with polychlorinated biphenyls (PCBs) during cleanup operations. A commercial, plant-based absorbent material, “Toxi-dry,” is used extensively for decontamination and decommissioning of DOE waste sites and is classified a hazardous JCW after use. In this investigation, 1,2,4-trichlorobenzene (TCB) was chosen as the surrogate for PCBs. As a promising separation technology, supercritical fluid extraction (SFE) was investigated for removing and recovering PCBs from contaminated of JCW. TCB was extracted from Toxi-dry using both pure and modified supercritical carbon dioxide. It was found that at

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constant pressure, increasing temperature from 40 to 80°C greatly improved the recoveries, while the pressure effect of SFE was not as clear as the temperature effect. With 5wt% acetone or ethanol added as cosolvent, the efficiency of SFE of TCB was also significantly improved.

Key Words: Supercritical fluid extraction; Job control waste; Polychlorinated biphenyls; 1,2,4-Trichlorobenzene.

INTRODUCTION

Due to their high chemical and biological stability and high lipophilicity, persistent organic pollutants, like polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), chlorobenzenes, and pesticides, cause serious environmental problems.[1–5] These pollutants leach into soil, sediment, and groundwater and, finally, contaminate the food chain. At U.S. Department of Energy (DOE) sites across the country, large quantities of PCB-contaminated wastes exist and will continue to be generated during decontamination and decommissioning (D&D) operations. DOE sites, including the Savannah River Site (SRS), need a promising technology to isolate and then destroy PCBs that contaminate certain solid waste forms. Conventional methods of remediating these wastes are costly, time-consuming, and generate large amounts of secondary waste. No proposed process for the recovery and/or destruction of these persistent pollutants has emerged as the preferred choice for DOE cleanup.

In this work, supercritical fluid extraction (SFE) using carbon dioxide (CO_2) has been investigated for the decontamination of PCBs from DOE wastes. During this first stage of process research, the feasibility of using SFE with CO_2 to remove and recover PCBs was tested in an analytical-scale apparatus on a representative DOE matrix. This article focuses on our analytical scale extraction results. The objectives of this study are to find the optimal supercritical CO_2 extraction conditions, reveal the mechanisms of extraction from porous DOE wastes, and provide reliable benchmarks for further decontamination investigations.

BACKGROUND

Job Control Waste at DOE Sites

From 1929 to 1979, approximately 1.4 million pounds of PCBs were produced worldwide and caused serious contamination problems.[6] At DOE sites across the country, PCBs are found in many solid matrices, as well as in trace levels in contaminated water. D&D activities generate PCB-contaminated job control waste, tank/basin sediments, and paint chips. Frequently, these wastes are also contaminated with HTO (tritiated water) or other species, resulting in a PCB-contaminated, low-level radioactive waste (LLW). Such wastes contain constituents regulated under the Toxic Substances and Control Act (TSCA) regulations and, thus, are also mixed low-level wastes (MLLW). Incineration is the only approved disposal path for certain PCB wastes. The TSCA incinerator at Oak Ridge is the only incinerator in the nation that is permitted to burn radioactive PCB waste. In addition to the problem of inadequate incinerator capacity, disposal by incineration produces secondary atmospheric emissions and ash that require control and treatment. A significant potential benefit of this research is the development of alternative technologies that do not produce secondary pollution similar to incineration.

The solid waste forms encountered are classified as homogeneous inorganic debris (e.g., scrap metals and concrete), organic debris (e.g., paper, cloth, plastic, rubber), heterogeneous debris, slurries (defined as having total suspended solids (TSS) between 1% and 30% by weight), and sludges (defined as having TSS greater than 30%). A specific example of PCB-contaminated radioactive waste in storage at SRS is waste generated by cleanup activities, named "job control waste" (JCW). The majority of these wastes include materials such as "Toxi-dry" and "spill pillows" used to absorb liquid wastes resulting from PCB spills within process facilities. Toxi-dry, a plant-based absorbent, was the solid matrix used during this investigation.

Supercritical Fluid Extraction of Job Control Waste

As an analytical-scale extraction method, supercritical CO_2 extraction is more efficient than conventional techniques, giving higher recoveries than liquid extraction and with no need for the cleanup steps required in Soxhlet extraction.[1,7] Furthermore, SFE is faster and requires less sample handling. In commercial-scale SFE, the solvent power of the fluid can be manipulated by changing pressure and temperature, or by adding a small amount of a cosolvent, such as alcohol or water. Compared to liquid solvents, SCF CO_2 has lower viscosity and surface tension and has higher solute diffusivities; therefore, it can penetrate into porous solid materials more effectively and give superior mass-transfer rates. Moreover, extracts can be easily separated by depressurizing the SCF.[8] These advantages have prompted research on supercritical CO_2 as a basis for large-scale decontamination of contaminated soils, sediments, and other solids. Supercritical carbon dioxide (SC-CO_2) is particularly attractive for the extraction of organic-contaminated wastes, because CO_2 is nontoxic, nonflammable, and environmentally acceptable. It is also cheap and available in large quantities. CO_2 has a low-critical temperature (31°C) and a moderate-critical pressure (1078 psia), so that equipment development is entirely feasible within the current state of the art. In addition, CO_2 can dissolve numerous nonpolar and moderately polar compounds due to its Lewis base characteristics, induced dipole interactions, and quadrupole interactions.[9]

There are several possible factors that influence the mechanism of a particular SFE: (1) thermodynamic factors, such as the solubility of the extract in the SCF; (2) kinetic factors, such as slow desorption of the analyte from the surface, diffusion of the analyte through the organic matrix of the sample, matrix swelling, and the extraction time; and (3) physical factors, such as the influence of the solid matrix on diffusion and the complex solvent-solute-matrix interaction.[9–11]

Thermodynamics properties, such as analyte solubility, are useful to understand the SFE process.[12] Vapor pressure, polarity, molecular weight, and chemical composition of the solute are the most important factors affecting solubility of compounds in supercritical fluid. At fixed temperature, the density of SC-CO_2 increases with pressure. When the density of a supercritical fluid is increased, the solubility of a solid solute in this supercritical fluid is also increased.[8] If the supercritical fluid extraction is solubility controlled, increasing extraction pressure will result in increasing extraction recovery. On the other hand, if the supercritical fluid extraction is kinetically or desorption controlled, the structure of the matrices will have much more effect on recovery, and the density effect will be small. Extraction of trace amounts of aged organic contaminates, like PCBs, from environmental samples usually is kinetically controlled.[5]

The effect of extraction temperature is complex and is a combination of the effects on thermodynamic properties (solute vapor pressure, fluid density, and desorption isotherm), as well as dynamic properties (viscosity, desorption kinetics, mass-transfer coefficients). Usually, the extraction is more efficient at higher temperatures if the solute is volatile. If the solute vapor pressure does not increase significantly with temperature, a decrease of extraction efficiency will result from increasing temperature due to the decreased density.[13] For SFE of PCBs, some studies found insignificant temperature effects,[1,14] while others claim a beneficial effect of temperature.[15]

Previous studies indicated that the solvent power of pure dense CO_2 is not strong enough to extract persistent pollutants from environmental samples. When the pressures for extraction are much above the critical pressure of CO_2, or the polarity of the fluid is not suitable for the targeted solute, the use of cosolvents is necessary to enhance recoveries in SFE.[16] Although numerous modifiers with different chemical characteristics have been employed in SFE, choice of a modifier for an application has been highly empirical. The choice of modifier is highly matrix dependent, and the characteristics of the analyte have a pronounced effect on the efficiency of modifiers.

In this study, 1,2,4-trichlorobenzene (TCB) was spiked onto the Toxi-dry. It is believed that results obtained from recently spiked samples cannot be used to predict the behavior of aged samples, especially not for heterogeneous environmental samples.[5] Adsorption and desorption of contaminants from a specific matrix can give insight in verifying validation of the spiking method. Cornelissen et al.[17] determined desorption kinetics for 1,2,4-trichlorobenzenze in sediment at various concentrations. They also studied how a large amount of freshly added 1,2,4-trichlorobenzene affects the desorption behavior of field-aged chemicals (PCBs and HCB) and found that the freshly added compounds were able to compete with aged ones for active adsorption sites in matrix. The investigators stated that several weeks of incubation are sufficient for solutes to reach slow-sorption sites. They demonstrated that the longer a spiked organic chemical was allowed to interact with the matrix, the stronger the absorption became.[18]

The effect of the solid matrix on extraction of PCBs is still not understood on a fundamental basis. While organic content of the matrix has been frequently implicated as a major factor affecting desorption of organic pollutants, other matrix characteristics, such as type of organic matter and particle size, also need to be considered.[12] This question is particularly critical for D&D operations within DOE, because the physical chemistry of PCB absorption will be markedly different in the types of matrices important to SRS and the rest of the DOE weapons complex (absorbents, fibers, concrete, paint, and metal). In the current investigation, our focus was on a particular matrix, Toxi-dry, identified by Savannah River Site (SRS) collaborators. The matrix is a porous, lipophilic, plant-based material that is used to absorb spills, wash solutions, and solvent solutions generated during D&D activities.There have been no studies on PCB extraction from this commonly used absorbent, and clearly the characteristics of this lipophilic-organic matrix are quite different from soils and sediments that have been widely studied. Because the effects of solid matrix, cosolvent, temperature, and pressure are still not understood in a fundamental level, and phase equilibrium and mass-transfer rate are usually not available in SFE process, experimental SFE data are indispensable for process design.

METHODOLOGY

Materials

For these preliminary laboratory studies, 1,2,4-trichlorobenzene (TCB) was the chosen surrogate for PCBs. Chlorobenzenes are found on many lists of priority pollutants and are present in significant amounts in the environment.

Toxi-dry absorbent was obtained from Mt. Pulaski Products (Mt. Pulaski, IL, USA) and was used without further treatment. The product specifications are crude fiber (34%), nitrogen-free-extraction (55%), moisture (8%), and protein (3%). Its extractables are 9% with water and 5.6% with alcohol. The 1,2,4-trichlorobenzene (purity $> 99\%$) and acetone (purity $> 99.8\%$) were obtained from Fluka. Ethanol (purity $> 99.6\%$) was obtained from Sigma. SFE grade CO_2 (purity $> 99.99\%$) was obtained from Air Products.

Spiked Samples

A spiked sample can be useful in developing a preliminary SFE method for complex environmental samples. Because of the difficulty in working with radioactive PCB-contaminated waste and strict EPA regulations in handling MLLW, we spiked 1,2,4-trichlorobenzene into clean Toxi-dry matrix and extracted these samples. In the spiking procedure, 0.1 g of 1,2,4-trichlorobenzene and 500-mL acetone were added to a 1-L beaker with a magnetic stirrer and mixed vigorously. Toxi-dry absorbent (42.5 g) was added to the beaker to form a slurry. Stirring was continued for 12 hours to give an even loading. The mixture was placed in a fume hood for two days to evaporate acetone. The spiked Toxi-dry was stored in sealed bottles for at least two weeks before extraction. No water was loaded into the samples during extraction.

Supercritical Fluid Extraction

Figure 1 gives a schematic of the ISCO supercritical CO_2 extraction system. An ISCO 260D pump was used as the CO_2 pump to provide liquid CO_2 and control the system pressure. A 1-g sample was packed into a 10-mL extraction cell. Membrane filters (five micron) were placed at each end inside the cell to prevent small particles from reaching the capillary-tube restrictor. After the extraction cell was placed in the extractor, the temperature was set using the temperature controller of the extractor. The outlet valve of

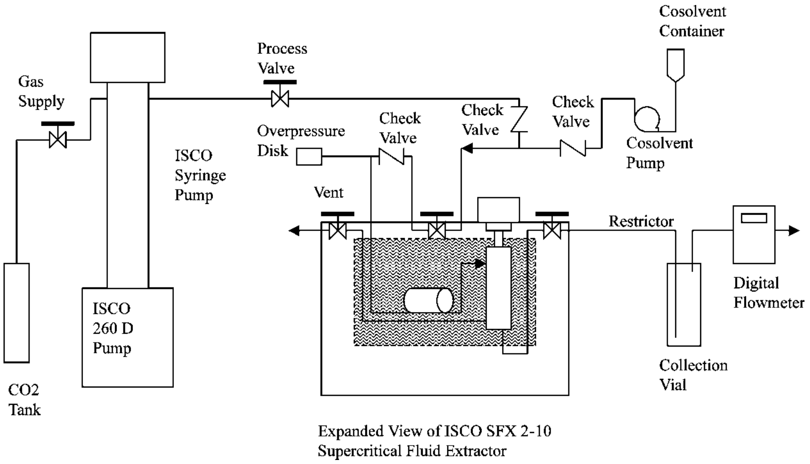

Figure 1. Extraction apparatus.

the syringe pump was then opened. Pure or cosolvent-modified CO_2 passed through the preheater, where it was heated up to the extraction temperature before flowing to the extraction cell. Static pressure was maintained for 20 minutes, after which, the outlet valve was opened and dynamic extraction was conducted. To collect the TCB extract, we used solvent trapping with chilled acetone as the solvent. The TCB-impregnated Toxi-dry samples were extracted for 2 h. Flow rates were controlled by an ISCO integral restrictor. The experimental pressures were 2000, 4000, or 6000 psia, and the temperature was either 40°C or 80°C.

Since 1 mL/min of supercritical CO_2 extractant at extraction conditions can expand to 500 mL/min of gaseous CO_2 during sample collection, volatile and semivolatile organics extracted can easily be lost during the collection step, while the depressurized fluids pass through collection solvent at high-flow rate. It is clear that the more volatile the chlorinated benzene is, the more likely it was lost during collection. For example, Sweetman et al.[1] indicated that chlorobenzenes were partially lost during transfer from the vaporizing carbon dioxide as it bubbled through the hexane. We cooled the collection vial to 3°C and extracted the TCB samples for 2 hours under a low-flow rate of CO_2 (0.2- to 0.3-ml liquid CO_2 per minute) to reduce the loss of TCB from the collection solvent during extraction.

In this work, both acetone and ethanol were used as the cosolvents at approximately 5 wt%. There are three common ways to introduce the cosolvents: use a cosolvent pump; use premixed fluids from a cylinder, and directly spike cosolvent on the matrix before extraction. In this study, cosolvent was introduced with an Eldex (Apple valley, MN, USA) metering pump (Model A-30 -VS) and was mixed with CO_2 before the preheater. Thus, the sample was continuously extracted by the cosolvent-modified CO_2 of constant composition. The extraction results with modified solvent are compared with SFE results using pure CO_2.

Soxhlet Extraction and Sonication

Soxhlet extraction was used to quantify the amount of TCB on Toxi-dry before and after CO_2 extraction. For the purpose of defining an "extraction efficiency," it is assumed that Soxhlet extraction removes 100% of the impregnated 1,2,4 TCB. The amount of TCB extracted by supercritical CO_2, or CO_2 + cosolvent, was then compared to the amount removed by Soxhlet extraction. For all Soxhlet extractions, about 5 g of the sample were weighed into a cellulose extraction thimble, and the sample was extracted with 150 mL of acetone for 24 hours. After the extraction was completed, the solvent was evaporated to a volume of 10 mL for gas chromatographic analysis. Sonication is another traditional analytical technique in environmental sample analysis. In addition to Soxhlet extraction, some samples of TCB-spiked Toxi-dry were extracted using sonication in acetone. This gave a second method to verify SFE recoveries. For sonication, the SFE residues were mixed with 15-mL acetone in a 30-mL vial and sonicated for 12 hours.

Gas Chromatographic Analysis

Gas chromatography coupled with flame ionization (FID), electron capture (ECD), or multiple ion-detection-mass spectrometer (MID-MS) has been used to analyze trace TCB in environmental samples.[14] For this work, an HP model 5890 series II GC (Hewlett-Packard, Palto Alto, CA) with FID was used for analyzing the extracted fractions. The GC column was an AT-1 from Alltech (Deerfield IL). A l-μL sample was injected at an oven temperature of 70°C (held for 1 minute) followed by temperature programming to 200°C with a rate of 15 °C/minute. Quantitations were based on an eight-point linear calibration curve from gravimetrically prepared standards. Pure 1,2,4-trichlorobenzene was used for the calibration standards. Identification of analytes was based on comparison of retention times with those obtained from standard solutions.

RESULTS AND DISCUSSION

Table 1 gives representative results for extraction of spiked Toxi-dry with pure CO_2, $CO_2 + 5$ wt% acetone, and $CO_2 + 5$ wt% ethanol. All extractions lasted 2 hours. The metric is the percentage recovery of TCB from the Toxi-dry matrix, where 100% recovery is defined by 24-hour Soxhlet extraction using acetone. Table 1 shows how the TCB extraction efficiency changes with temperature, pressures and cosolvent. These results are graphed and discussed in the following sections.

Figure 2 highlights the effect of pressure on TCB recovery at different conditions. Increasing pressure at 40°C was found to have only a small effect on recovery, regardless of whether cosolvent was used. For pure CO_2 extraction at 80°C, in contrast, the extraction yield increased significantly when extraction pressure was increased. At 40°C, increasing the pressure from 2000 psi to 6000 psi increases the density of pure CO_2, from 0.771 g/mL to 0.978 g/mL. At 80°C, the same pressure change increases the density from 0.413 g/mL to 0.861 g/mL.[19] It is a common observation that the logarithm of the solubility is linearly dependent on the density or the log of the density of the supercritical fluid. Increasing solubility favors the partitioning of TCB molecules from the internal sites in the matrix into the bulk supercritical fluid. If the extraction efficiency were only controlled by solubility, one would expect the extraction efficiency to increase noticeably both at 40°C and at

Table 1. Supercritical fluid extraction results with pure or modified CO_2.

T (°C)	P (psia)	Cosolvent	Extraction time (min)	Percentage TCB recovered
40	2000	0	120	33
40	4000	0	120	31
40	6000	0	120	42
80	2000	0	120	60
80	4000	0	120	75.6
80	6000	0	120	96.3
40	2000	5% acetone	120	56.1
40	4000	5% acetone	120	58.3
40	6000	5% acetone	120	61.6
80	2000	5% acetone	120	96.3
80	4000	5% acetone	120	100.4
80	2000	5% ethanol	120	94.7
80	4000	5% ethanol	120	109.7

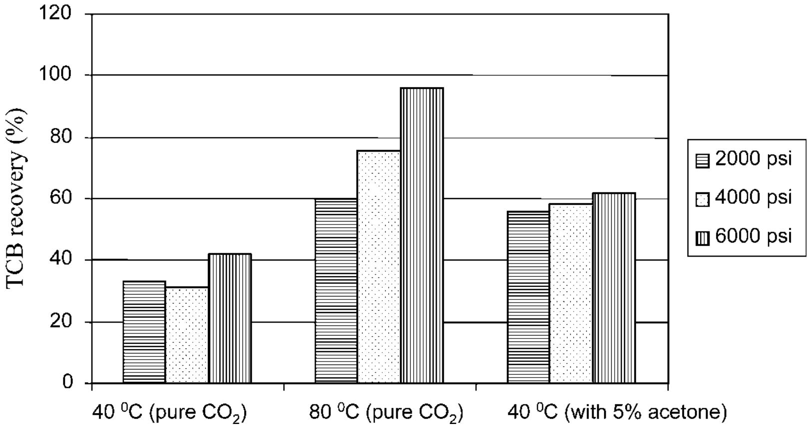

Figure 2. Pressure effect on SFE of TCB from Toxi-dry.

80°C. This is clearly not the case, as shown in Fig. 2. Therefore, we conclude that there are other factors besides solubility of TCB that control the extraction process. A possible explanation for this observation is that after 2 weeks' storage of spiked samples, the majority of TCB molecules diffuse into the interior of the Toxi-dry and were adsorbed at the internal matrix surface. Therefore, kinetic factors, such as the desorption rate of the TCB molecules from the internal matrix surface and diffusion rate through the porous matrix, could control factors of the extraction process. In this scenario, enhancing the solubility of TCB in the bulk supercritical fluid is not sufficient to yield high-extraction efficiencies. It is possible that at 80°C, the majority of TCB molecules exists as a separate phase within the matrix and could be removed by simple dissolution, so the desorption control was weak, and pressure/density effect was clear. Figure 2 also illustrates that acetone improves the TCB recovery at 40°C compared to using pure CO_2 solvent. Again, though, the effect of pressure on the recovery using the mixed solvent is small. The cosolvent effect is discussed in more detail subsequently.

From Fig. 3, it is clear that the recoveries of TCB from the Toxi-dry samples are greatly affected by the extraction temperature. Increasing temperature from 40 to 80°C at the same pressure increased the extraction efficiency about 30 to 40%. As previously noted, the extraction temperature affects the solute vapor pressure, solvent density, and desorption of solute molecules from matrix surface.[20] At constant pressure, increasing temperature will increase solute vapor pressure and decrease density of CO_2. For example, at 25 MPa, for a temperature increase from 40 to 80°C,

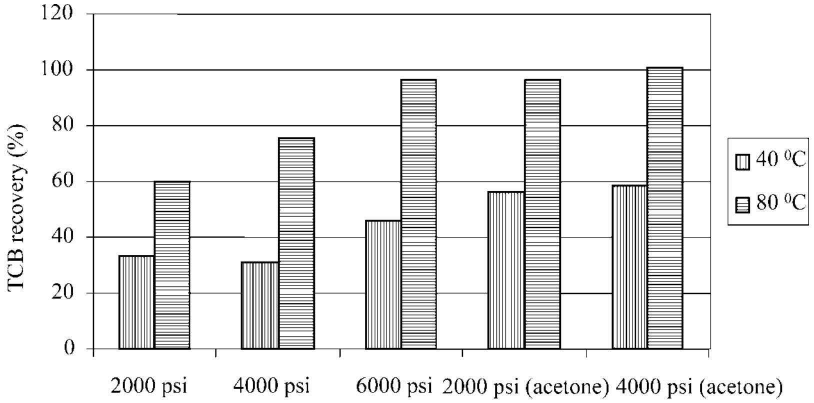

Figure 3. Temperature effect on SFE of TCB.

the vapor pressure of 1,2,4-trichlorobenzene changes from 102.4 to 1038 Pa, while the density of CO_2 decreases from 0.880 to 0.687 g/mL. The solubility of TCB in CO_2 is dependent on its vapor pressure and density of CO_2. The solute-vapor pressure increases significantly, and the density decrease of supercritical fluid is relatively small, so the positive effect of temperature is clear. Besides the thermodynamic considerations mentioned above, extraction temperature also affects extraction process kinetically. According to Dupeyron et al,[21] temperature enhances the diffusion coefficients and reduces solvent viscosity and interfacial tensions. These two effects allow better penetration of the solvent into the matrix and result in faster mass transfer. Sweetman et al also found that increasing temperature appeared to increase the recoveries of chlorinated benzenes in some cases.[1]

Figure 4 illustrates that the efficiency of TCB extraction from Toxi-dry absorbent is improved with the addition of a small amount of acetone or ethanol as cosolvent. At 80°C, TCB recoveries in excess of 90% and approaching 100% (within experimental uncertainty) are obtained at pressures as low as 2000 psi. This is a significant benefit because both capital costs and operating costs will be substantially lower if the extraction process can be operated at lower pressures. Based on these results, the most favorable extraction condition should is 80°C, 2000 psi, and 5% ethanol as cosolvent.

Acetone is a polar organic cosolvent and a hydrogen bond acceptor, and ethanol is a self-associating polar organic cosolvent. Both of them are capable of strong intermolecular interaction with the solute. Of the two cosolvents investigated, ethanol is the DOE-preferred cosolvent, because DOE does not place health or safety restrictions on use of ethanol as a process solvent

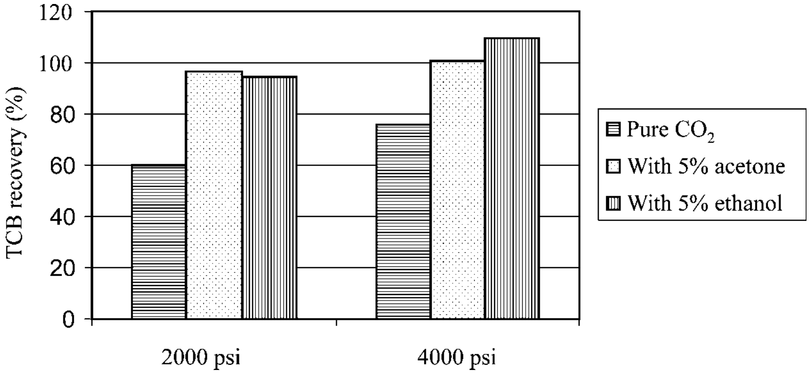

Figure 4. Cosolvent effect on SFE of TCB at 80°C.

(unlike acetone, methanol, or other common cosolvents). Jeong and Chesney[22] also indicated that ethanol, though not as polar as methanol, could be a better choice because of its low toxicity. Therefore, it would be much simpler, faster, and less expensive from a permitting standpoint to use ethanol as cosolvent. In addition, according to the phase equilibrium data provided by Chang et al,[23] the mixed solvent, acetone + CO_2 or ethanol + CO_2, will be totally miscible under the extraction conditions.

The mechanism of cosolvent–analyte–matrix interaction is a key point to understand the effect of pressure, temperature, and cosolvent on SFE. Although different potential interactions, including dipole interactions, hydrogen-bonding interaction, dispersion interactions, and different modifier properties such as polarizablity, acidity/basicity, and dipole moment, have been considered in previous studies; there is still insufficient information for drawing a general conclusion. In this investigation, the organic matrix, Toxi-dry, has not previously been extracted with supercritical CO_2. The large solubility of Toxi-dry in solvent (Toxi-dry is 5.6% soluble in alcohol) makes the situation even more complicated. The color of the collection solvent after extraction is pale yellow, which indicates that components of Toxi-dry are dissolved and extracted during SFE. Amador-Hernandez and Luque De Castro pointed out that the appropriate cosolvent increases the effective polarity of the supercritical fluids, which increases the bulk solubility of solutes and results in favorable partitioning into the supercritical fluid.[24] The second effect occurs due to the wetting properties of a solvent causing more intimate solvent/solute contact. Moreover, it was believed that cosolvents could interact with the analyte/matrix complex and lower the activation energy barrier of desorption.[15]

CONCLUSION

This work explored the optimal conditions for supercritical fluid extraction of chlorinated aromatics from DOE job control wastes. In this preliminary study, 1,2,4-trichlorobenzene (TCB) was used as a surrogate for PCBs in spiked Toxi-dry samples. Spiked Toxi-dry samples were extracted with pure supercritical carbon dioxide and modified supercritical carbon dioxide (with 5 wt% acetone or ethanol), and the efficiency of SFE was compared with Soxhlet extraction and sonication. The extraction results indicate that the supercritical fluid extraction of TCB from Toxi-dry is controlled primarily by kinetic factors. The effects of temperature, pressure, and cosolvent on extraction efficiency were studied. It was found that increasing temperature from 40 to 80°C greatly improved the recoveries of TCB. Increasing pressure at 80°C increased TCB recoveries, while increasing pressure did not have clear effect on TCB recoveries at 40°C. Addition of 5 wt% cosolvent also substantially improved the efficiency of SFE of TCB. Based on these results, as well as safety and environmental regulations at DOE sites, ethanol is the preferred cosolvent for extraction of chlorinated organics from solid job control wastes.

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