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Supercritical fluid extraction/ γ -radiolysis of PCBs from contaminated soil

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Abstract

Off-line supercritical fluid extraction (SFE) followed by γ -radiolysis as an alternative treatment technique for PCB-contaminated soil was investigated in this study using BZ #54 (2,2',6,6'-tetrachlorobiphenyl) as the model compound. The preliminary results indicate that removal of BZ #54 from spiked sand and soil using SFE at 150°C and 20 MPa is 98% and 93%, respectively. The reduction efficiency of 864 mg/l BZ #54 in isooctane by γ -radiolysis is 99.8% at an absorbed dose of 500 kGy. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Owing to their extraordinary chemical stability, PCBs are persistent environmental contaminants. This persistence, combined with their complex toxicological effects and omnipresence, make remediation research in PCBs an important task in environmental chemistry. In light of this concern, many techniques had been developed to solve the PCB-contamination dilemma. In a 1992 critical review [1], the authors identified seven techniques, which include incineration, in-situ vitrification, destruction using quicklime, bioremediation, chemical dechlorination, solvent extraction, and stabilization. Of these seven techniques quoted above, only incineration has been applied to large-scale operations. The disadvantages of thermal treatment are the high costs associated with

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construction and operation and the problematic acceptance of incineration by the public. By 1992, there were less than 10 Toxic Substance and Control Act (TSCA)-approved commercial PCB incinerators in the USA [1]. Although destruction of PCBs using quicklime was listed as one of the potential techniques by this 1992 review, it was found in the subsequent years that quicklime actually volatilizes the PCBs rather than destroys them [2], thus, shortening the list of viable techniques down to six.

The list of useful techniques becomes more abbreviated when the PCB matrix to be treated is a porous solid such as soil or harbor sludge. The use of incineration, stabilization or in situ vitrification is certainly possible for these matrices, but less than ideal since a great deal of energy is wasted in destroying the soil in order to attack the PCBs. These techniques are probably practical only for small sites such as spills associated with transformer pads. It is also less environmentally intrusive to decontaminate the soil, and return a healthy soil to its native location.

The remaining techniques, bioremediation, chemical dechlorination and solvent extraction are more viable possibilities. However, bioremediation is generally limited to low PCB concentrations and requires longer treatment times than chemical methods. Chemical methods require the use of solvents and hazardous reagents such as metallic sodium. The drawbacks with both bioremediation and chemical treatments become more severe as the scale of the remediation effort increases. Both also require treatment of the entire soil volume.

Only solvent extraction allows a separation that preconcentrates the PCBs for treatment. Thus, precious energy and reagents are not wasted on the massive inert volumes. Recently, Curry et al. [3] showed that PCB contaminated soils could be cleaned using extraction with oil-based solvents, which were then floated from the soil with water. Their extraction method allowed for a factor of three preconcentration in PCBs, which were then also decomposed by radiolysis. An advantage of Curry et al.'s method is that certain soils may be treated in-situ using grout containment walls around the spill site, and portable electron generators to produce the radiation.

Supercritical fluid extraction (SFE) of organic compounds from solid matrices has become an acceptable alternative to conventional solvent extraction processes. Carbon dioxide is the fluid of choice for SFE because of its moderate critical constants ($T_c = 31^\circ\text{C}$ and $P_c = 7.3$ Mpa), non-toxic nature, and availability in purified form. The advantages of SFE over conventional solvent extraction include elimination of waste solvent production and use of hazardous reagents, better penetration in porous materials, and tunable solvation power with respect to density (temperature and pressure) of the fluid phase. Extraction of PCBs from contaminated soil and sediments with supercritical (Sc) CO_2 has been reported by several groups of researchers including van der Velde et al. [4], Lee and Peart [5], Fernandez et al. [6], and Langenfeld et al. [7]. The extracted PCBs are usually trapped in a solvent or adsorbed on a solid phase for subsequent analytical purposes. In this manner, SFE greatly preconcentrates the bulk of PCBs randomly distributed in a massive volume of matrix, particularly soil or sludge, into a small volume, making destruction treatments much more energy-efficient, and thus more cost-efficient. This method of preconcentration is especially useful in large-scale operation such as harbor sludge and river sediments, where thousands of tons of soil have to be treated.

Recently, Arbon et al. [8] and Mincher [9] reported that PCBs in organic solvents could be degraded to biphenyl by high intensity γ -radiation. The dechlorination process is initiated by free electrons produced by interactions between the solvent and γ -radiation. With the selection of appropriate solvent, the SFE process may be hyphenated with subsequent γ -radiolysis to destroy the PCBs removed from contaminated sources. This approach may provide an effective and economic way of remediating PCB contaminated solid materials. The initial results concerning SFE and subsequent γ -radiolysis for remediation of PCBs from a contaminated soil are presented in this discussion.

2. Experimental

2.1. Reagents and analytical techniques

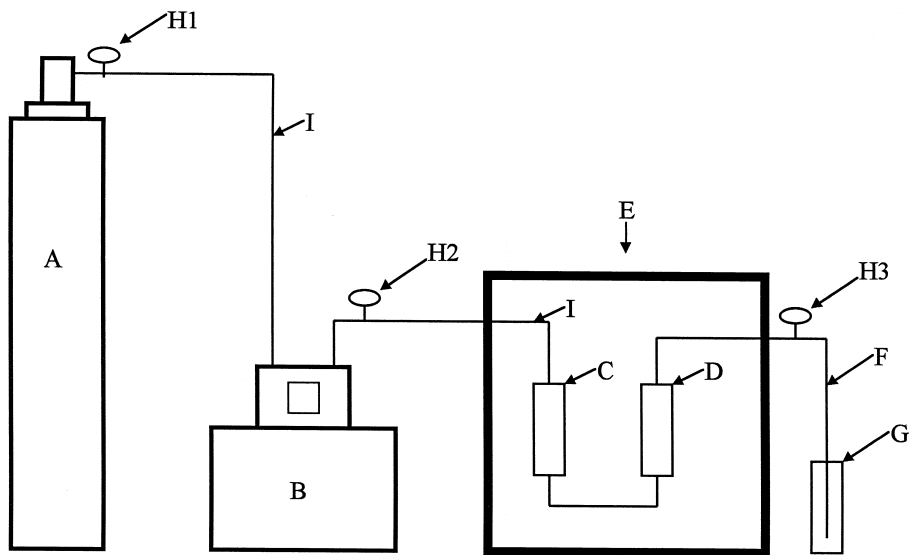
BZ #54 (2,2',6,6'-tetrachlorobiphenyl) and BZ #153 (2,2',4,4',6,6'-hexachlorobiphenyl) were purchased from Ultra Scientific (North Kingston, RI) and reagent grade isooctane from Fisher Scientific (Fair Lawn, NJ). SFE grade CO₂ was purchased from Scott Specialty Gases (Plumsteadville, PA). Analyses of PCBs were done on a HP 5890 Series II Plus Gas Chromatograph and a HP 5972 Series Mass Spectrometer. A 30 m \times 0.25 mm I.D. HP 5 MS column with 0.25 μ m film thickness was used, with helium flowing at 24.8 cm/s. The initial oven temperature was 60°C, with the first ramp at 20°C/min until 140°C, then from 140°C to 220°C at 4.0°C/min and held at 220°C for 25 min.

2.2. Preparation of spiked soil

A soil sample (20 g) was weighed out in a glass beaker and isooctane was added until the soil was submerged in the solvent. A total of 10 ml of 1000 μ g/ml (10 mg) BZ #54 in isooctane was added to the mixture. The soil was dried with a 75-W table lamp with occasional stirring to produce 0.5 mg of BZ #54 per gram of soil before being stored in a glass vial. Another 20 g of the same batch of soil was taken as the blank without any spiking.

2.3. Supercritical fluid extraction

The set-up of the SFE in this experiment is shown in Fig. 1. Before the experiment, the Isco 260 syringe pump **B** is filled with liquid CO₂ from a tank of SFE grade CO₂ **A** and brought up to the desired pressure. The extraction cell **D** is filled with a known amount of soil and then completely filled with glass beads to minimize the void volume in the cell. After **D** was secured tightly into the circuit, the GC-oven **E** was brought up to the desired temperature with both high-pressure valves **H2** and **H3** closed. The oven temperature was thermostated to $\pm 1^\circ\text{C}$. Upon reaching the desired temperature, **H2** is opened and CO₂ is allowed to flow through the preheat unit **C**, where it is converted to Sc state, before it reaches **D** and stalls at **H3**. Timing of static, or no-flow, extraction starts when the temperature stabilizes. After the desired amount of time had lapsed, **H3** was opened and timing of dynamic, or continuous flow, extraction was started. The



- A = SFE grade CO₂
- B = Isco 260 Syringe Pump
- C = CO₂ Preheat Unit
- D = Stainless-steel Extraction Cell
- E = Thermostated Oven
- F = Fused-silica Restrictor
- G = Collection Vessel
- H(1,2,3) = High-pressure Valves
- I = Stainless-steel Tubings

Fig. 1. A schematic of SFE apparatus.

extractant was collected in 10 ml of isooctane placed in a collection vessel **G** via a 50- μ m restrictor **F**, which also regulates the back pressure of the system. The final volume of the collection solvent was brought to 5-ml in a volumetric flask. Half of this volume is used for irradiation and the other half as the control. Destruction efficiency was calculated based on the ratio of the amount of BZ #54 present in the irradiation sample to the non-irradiated control.

2.4. Irradiation

The samples in this study were batch irradiated using spent reactor fuel from the Advanced Test Reactor (ATR) at the Test Reactor Area of the Idaho National Environmental and Engineering Laboratory (INEEL), ID. The extracted PCB samples (in isooctane) were contained in glass, crimp-sealed, auto-sampler vials that were placed into stainless steel capsules with threaded O-ring seals designed to prevent leakage into the irradiation facility and also to prevent radiological contamination of the sample vials. Spent nuclear fuel does not produce neutrons and hence does not result in nuclear

activation of the samples. Samples were radiologically clean following irradiation. For detailed experimental procedures, please see Ref. [9].

3. Results and discussion

The effect of temperature on the extraction of BZ #54 spiked on fine sea sand and on a local (Latahco silt loam) soil with Sc CO₂ at constant pressure is given in Table 1. The efficiency of extracting BZ #54 from sea sand is higher than that of soil under all temperature conditions chosen in this study. Quantitative extraction efficiency of BZ #54 from the silt loam soil requires a higher temperature than that observed from the sea sand experiments, probably due to abundant PCB-binding sites present on the soil. The Latahco silt loam soil used contains 41.5 g organic carbon, 159 g clay, 121 g silt, and 3.9 g total N/kg of soil, and plentiful amount of humic acids [10]. Despite the lack of understanding of the binding mechanism and location, it is certain that silt loam soil offers significantly more analyte–matrix interactions between the PCB molecules and the binding sites than sand, hence, causing the PCBs to be retained more strongly. Although methanol-modified Sc CO₂ shows higher extraction efficiency (data not included), methanol and isooctane form two distinct phases in the collection vessel that both dissolve BZ #54, hence creating an unnecessary complication. Neat CO₂ was therefore selected for this study for simplification. At 150°C and 20 MPa, the extraction efficiencies of BZ #54 using Sc CO₂ from sand and soil for 30 min of static and 30 min of dynamic extraction times are 98% and 93%, respectively. These high extraction efficiencies undoubtedly show that SFE can be used to effectively remove PCBs from various porous matrices in a relatively short period of time.

The effect of absorbed dose on the distribution of reduction products was studied by using BZ #153 and the results are presented in Fig. 2. At the absorbed dose of 50 kGy, it is observed that only 33% of the BZ #153 was reduced to penta-, tetra-, and trichlorobiphenyls; no di- and monochlorobiphenyls were observed. On the contrary, when the absorbed dose was increased to 500 kGy, only di- and monochlorobiphenyls were observed in minute quantities while none of the higher homologs were detected in the products. In the intermediate absorbed doses, all possible reduction products were observed with the general trend that the concentration of BZ #153 decreases as the

Table 1

Collection efficiencies of BZ #54 directly spiked on sand and soil at various extraction temperatures. SFE conditions are 20 MPa pressure, static and dynamic times are 30 min each, flow-rate of liquid CO₂ is ca. 1 ml/min. 210 µg of BZ #54 was spiked in each case

T (°C)	Collection efficiency (%)	
	Sand (RSD)	Soil (RSD)
60	91 (3.5)	65 (5.7)
100	97 (2.4)	65 (4.6)
150	98 (2.2)	93 (3.7)

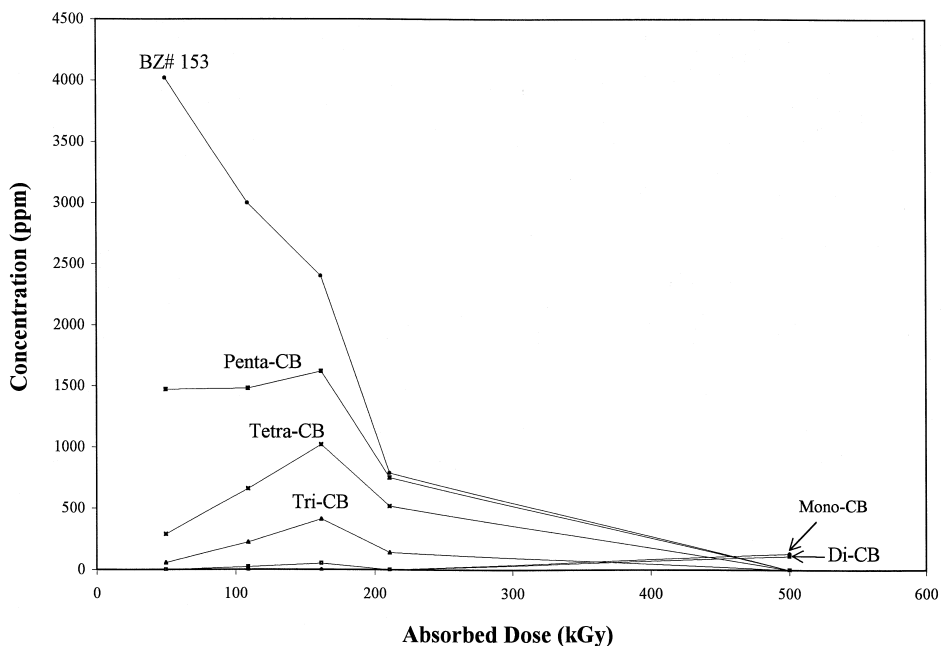


Fig. 2. Effect of absorbed dose on the distribution of reduction products. Starting material is 6000 ppm of BZ #153. CB is the acronym for chlorobiphenyl. Reduction products are identified by GC-MS as homologs rather than congeners.

absorbed dose increases. The presence of these products strongly suggests that this radiolytic reduction process occurs stepwise, with each chlorine atom on the PCB molecule being sequentially replaced by a hydrogen atom. The final carbonaceous reduction product in this process is biphenyl.

The trap solution in the collection vessel is important for this process as not only must it be effective for collecting the extracted PCBs, it should also serve as an effective solvent medium for subsequent radiolytic dechlorination. The radiation chemistry of PCBs has been studied in a number of solvents, including water [11], alkaline isopropanol [12–14], neutral isopropanol [15–17], cyclohexane [18], and petroleum ether [19,20]. In this study, isooctane was chosen as the collection solvent, or “trap solution”, because it is a common solvent for analytical work with PCBs, and because its PCB radiation chemistry has been well-characterized [21].

The results of dechlorination of BZ #54 in isooctane by γ -radiolysis are given in Table 2. It can be seen that at an absorbed gamma dose of 500 kGy, greater than 99% of the PCB was decomposed, regardless of the initial PCB concentration. The result that 864 mg/l and 84.2 mg/l of BZ #54 both showed similar dechlorination efficiencies indicates that γ -radiolysis can be applied effectively to a range of PCB concentration in isooctane. This result is not unexpected and demonstrates that SFE may be hyphenated with radiolysis, using an appropriately selected solvent (in this case isooctane) for the trap solution.

Table 2

Reduction efficiency by γ -radiolysis of BZ #54 in isooctane used as trap solution following Sc CO₂ extraction from soil. Absorbed dose is 500 kGy

Initial concentration (mg/l)	Final concentration (mg/l)	Reduction efficiency (%)
864	1.5	99.8
89.8	< 0.4	> 99.6
84.2	< 0.4	> 99.5

Of the solvents for which PCB radiation chemistry has been studied, the one showing the greatest efficiency for PCB destruction has been alkaline isopropanol. The chain-reaction dechlorination, which results when PCBs are irradiated in this solvent, is well known [12–14]. Use of alkaline isopropanol as a trap solution may increase PCB destruction efficiency by up to four orders of magnitude, suggesting a required γ -ray dose of only 0.05 kGy, had it been used here. In addition to increased radiolysis efficiency, this will allow use of methanol as a phase modifier for SFE because it will not form a second phase in the collection vessel. Thus, SFE efficiency will also be increased.

4. Conclusion

It has been shown here in benchscale tests that Sc CO₂ extraction of PCBs may be combined with radiolytic PCB dechlorination to decontaminate soils and destroy the PCB fraction. This is accomplished by collecting the PCBs in a suitable trap solution following extraction, which facilitates the presentation of the PCBs to the radiation source in a matrix of optimum chemistry for efficient PCB dechlorination. SFE has the advantages of preconcentrating the PCBs prior to treatment while avoiding the use of hazardous solvents and reagents. In this way, the treatment technique need only to treat the PCBs, and not a large inert volume of soil.

The advantages of radiolysis include selective decomposition of the PCBs, which assures a recyclable trap solution. Furthermore, since radiolysis in organic solvents such as isopropanol and isooctane is a reductive process, hazardous byproducts such as dioxins and dibenzofurans cannot be generated. These byproducts are a major concern during PCB incineration. Thus the combination of SFE and radiolysis offers an attractive option for remediation of PCB-contaminated soils, sludge, and debris.

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