



Removing perfluorooctane sulfonate and perfluorooctanoic acid from solid matrices, paper, fabrics, and sand by mineral acid suppression and supercritical carbon dioxide extraction

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HIGHLIGHTS

- ▶ PFOX can be easily removed from solid matrix by Sc-CO₂ extraction.
- ▶ Nitric acid and methanol are used to enhance the solubility of PFOX in Sc-CO₂.
- ▶ Both reagents suppress the polarities of PFOX and Sc-CO₂, respectively.
- ▶ This method is simple, rapid, green, and low-cost for PFOX remediation.

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ABSTRACT

The removal of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from solid matrices has received considerable attention because of the environmental persistence, bioaccumulation, and potential toxicity of these compounds. This study presents a simple method using concentrated HNO₃ as a suppression agent, and methanol-modified supercritical carbon dioxide (Sc-CO₂) extraction for removing PFOS and PFOA from solid matrices. The optimal conditions were 16 M HNO₃ and 20% (v/v) methanol containing Sc-CO₂, under a pressure of 20.3 MPa and a temperature of 50 °C. Extraction time was set at 70 min (40 min for static and 30 min for dynamic extraction). PFOA and PFOS were identified and quantitated by liquid chromatography/mass spectrometry. The extraction efficiencies (with double extractions) were close to 100% for PFOA and 80% for PFOS for both paper and fabric matrices. The extraction efficiencies for sand were approximately 77% for PFOA and 59% for PFOS. The results show that this method is accurate, and effective, and that it provides a promising and convenient approach to remediate the environment of hazardous PFOA and PFOS contamination.

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1. Introduction

Perfluorinated compounds (PFCs) are organic molecules with all hydrogen atoms replaced by fluorine atoms on the carbon backbone. Chemicals in the PFC group include perfluorooctane sulfonate (PFOS; C₈F₁₇SO₃) and perfluorooctanoic acid (PFOA; C₈F₁₅O₂H) (also known as C8). The chemical structure of PFOX (X = A and S) makes them highly resistant to breakdown in the environment. PFOX possess the unique properties of chemical stability, thermal resistance, and high surface activity. Therefore, they have been used widely in industrial and con-

sumer products such as textile, paper, packaging, pesticides, carpets, leather, cosmetics, and fire-fighting foams (Hansen et al., 2002; Moody et al., 2002; Harada et al., 2003), as well as in the semiconductor industry (Hori et al., 2006). Both PFOS and PFOA are hazardous materials and persistent organic pollutants (POPs). PFOA has an average half-life of approximately 3 yr (Steenland et al., 2010) and has been found scattered throughout global environmental and biological media (Betts, 2007). Because of its ubiquity and long half-life, PFOA can potentially enter the body through the food chain, and a high concentration can accumulate in the body (Kannan et al., 2005). PFOX have been detected in numerous matrices: house dust (Moriwaki et al., 2003), water (Ju et al., 2008; Jin et al., 2009; Yu et al., 2009), soil (Washington et al., 2008), animals (Dorneles et al., 2008; Shi et al., 2010), human blood and breast milk (Reagen et al., 2008; Yeung et al., 2008; Zhang et al., 2010), and even in the atmosphere (Dorneles et al., 2008; Jin et al.,

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2009). The harmful effects of PFCs include growth inhibition in birds and aquatic invertebrates, liver and thyroid damage in mammals, lethality in fish (USEPA, 2000a) and saltwater invertebrates (USEPA, 2000b), and changes in biodiversity (Sanderson et al., 2002; Boudreau et al., 2003).

PFCs do not degrade through any natural processes, and they resist hydrolysis, photolysis, biodegradation, and metabolism (Kissa, 2001). Because of this and the difficulty of removing PFOA from industrial wastewater using current treatments, an effective treatment system must be developed. Although various destructive technologies have been proposed, the removal of PFOX under mild conditions is still lacking. A number of studies have developed strategies and technologies for removing PFCs from sludge and wastewater (Guo et al., 2008; Saito et al., 2010). Filtration and sorption, or other physicochemical technologies, now offer the most promising methods for removing PFOA from aqueous waste streams (Schröder et al., 2010; Li et al., 2011). Solvent extraction is a traditional method for removing various contaminants from liquid and solid matrices. Its application to the treatment of perfluoroalkylated substances such as PFOS and PFOA has been reported (Berger and Haukås, 2005; Dorneles et al., 2008). However, this method consumes a large quantity of organic solvents, which are often expensive and potentially harmful. Solid phase extraction is also used for the treatment of PFOS and PFOA before measurement (Inoue et al., 2004; Enevoldsen and Juhler, 2010), but the solvent used for desorption is potentially harmful. Therefore, finding a suitable method of treatment remains a challenge (Rayne and Forest, 2009). Recently, supercritical fluid extraction (SFE) has received attention as a separation technology. Nonetheless, efficient SFE techniques for the extraction of PFOX have yet to be reported.

One of the many advantages of supercritical carbon dioxide (Sc-CO₂) is its readily achievable critical point ($T_c = 31.1\text{ }^\circ\text{C}$, $P_c = 7.4\text{ MPa}$). The properties of supercritical fluids can be adjusted over a wide range by changing operational conditions such as density. Furthermore, mass transfer is enhanced because of the high diffusivity and low density, viscosity, and surface tension of Sc-CO₂. It also protects extracts from thermal degradation and solvent contamination. Because of these properties, Sc-CO₂ can be used to replace various solvents traditionally used in chemical processes. The high diffusivity and the temperature and pressure dependence of the solvents are properties that make supercritical fluids highly suitable for extracting and recovering organic compounds from solid materials. However, because the sulfonic acid/sulfonate and carboxylic acid/carboxylate groups add polarity to PFOX, their solubility in Sc-CO₂ is limited. Therefore, suppressing the polarity to increase solubility in Sc-CO₂ using a simple approach is desirable.

This study attempts to establish an environmentally friendly and effective method for removing PFOX from solid matrices. This can be achieved by developing a simple acid suppression process, followed by SFE. Extraction efficiencies are then identified using liquid chromatography mass spectrometry (LC/MS). First, both PFOA and PFOS must be converted to a non-polar form that will dissolve in Sc-CO₂. Because of the acidity of PFOX (Goss, 2008) and the possibility of telomerization and polymerization, strong acids are perhaps the better agents not only to suppress the dissociation of PFOX, to keep PFOX protonated, but also to decrease their telomerization and polymerization. Second, the influences of pressure, temperature, static extraction time, as well as the modifier in the supercritical fluid and different acids on the extraction of PFOX must be investigated to achieve optimal conditions.

2. Experimental

2.1. Materials

PFOA and methanol were purchased from Aldrich (Milwaukee, WI, USA). PFOS was obtained from TCI (Tokyo Chemical Industry,

Tokyo, Japan), nitric acid was supplied by J.T. Baker (NY, USA), and ammonium acetate (CH₃COONH₄) and sea-sand were supplied by Sigma–Aldrich (Milwaukee, WI, USA). Carbon dioxide was supplied by Toyo Gas Company. Ultrapure water was prepared by pure water system (Elga, UK). Prior to use, all glassware was soaked in nitric acid (30% v/v) for 24 h and then washed with deionized water and baked at 55 °C for 24 h. Stock solutions of individual analytical standards were prepared at 1000 mg L⁻¹ in methanol. Working standards with the desired concentrations were prepared by diluting these stock solutions in methanol. All standards were kept in the refrigerator at 4 °C until use.

Samples for SFE experiments were prepared by mixing 30 µL HNO₃ (16 M) and 1 mL stock solution (1000 mg L⁻¹) in a 10-mL flask. Then, 100 µL of 100 mg L⁻¹ standard working solution was spiked on filter paper (Advantec Toyo No. 1, 110 mm) or on a small piece of lab coat (cotton fabric with size of 3 × 3 cm) (sample). The sample was dried in the hood.

2.2. Instrumentals

2.2.1. Setup for SFE

The SFE system was composed of an ISCO syringe pump (model 260D, Isco, Lincoln, NB, USA) for supplying the supercritical fluid chromatography-grade CO₂, a controller (model 260D, Isco, Lincoln, NB, USA), a thermostatic oven (HP, USA), and a homemade extraction vessel with a volume of 12 mL, maintained at the desired temperature in the thermostatic oven for extracting PFOS and PFOA from solid matrices. At the oven exit, 30 cm of stainless steel tubing (316 SS, 1.59 mm. od., 0.76 mm. id) was used as the pressure restrictor for the exit of CO₂. The schematic diagram of the SFE system is shown in Fig. 1.

2.3. Sample extraction

In dynamic extraction the supercritical fluid continuously flows through the sample in the extraction vessel and discharges to the trapping vessel. In static extraction the supercritical fluid circulates in a loop containing the extraction vessel for some period of time before releasing to trapping vessel. In the combination mode, a static extraction is performed for some period of time, followed by a dynamic extraction. Combination modes were selected for this study.

In total, 100 µL of standard solution with a concentration of 100 mg L⁻¹ (PFOS or PFOA) was spiked on the samples and placed in a hood until dried. These dry samples were then loaded in Extraction Cell 4, followed by an addition of 20% (v/v) MeOH on the samples. Filter paper free of PFOA and PFOS was installed in Cell 3, and then 20% (v/v) of MeOH solution was spiked on it.

During the first stage of extraction, Valve 2 (V2) and Valve 4 (V4) were closed. The pressure was set at 20.3 MPa and the temperature at 50 °C. Methanol-modified CO₂ flowed from the pump to Cell 4 (Valve 3 (V3) was opened), followed by static extraction (40 min) and dynamic extraction (30 min). In the second run, another 20% (v/v) of MeOH was added on the samples in Cell 4, which had immediately been subjected to the first extraction. Then, modified CO₂ was directed to Cell 3 and then to Cell 4 with V2 and V3 opened, and Valves 4 and 5 closed. When the system was ready, static extraction (40 min) was executed for the second run. After the extraction was complete, Valves 4 and 5 were reopened (V3 was closed) for depressurization and to release the extracted PFOA and PFOS.

The CO₂ flow rate was kept at approximately 0.5–1.0 mL min⁻¹ by adjusting the outlet valve manually. The extract was collected in a glass vial filled with methanol, and the gaseous CO₂ vented into the atmosphere and then prepared for LC/MS analysis.

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