



# Carboxylated carbon nanospheres as solid-phase extraction adsorbents for the determination of perfluorinated compounds in water samples by liquid chromatography–tandem mass spectrometry

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## ABSTRACT

This work demonstrates the extraction potential of carboxylated carbon nanospheres (CNSs-COOH) for solid-phase extraction of perfluoroalkyl acids (PFAAs) for the first time. Six PFAAs, including perfluorohexanesulfonate (PFHxS), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorooctanoic sulfonic (PFOS), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA), were quantitatively adsorbed on a CNSs-COOH-packed cartridge; then, the PFAAs retained on the adsorbent were quantitatively eluted with an optimized volume of acetone (pH = 10). Finally, the desorbed PFAAs were determined by liquid chromatography–tandem mass spectrometry. Important relevant factors, such as the eluant and its volume, sample pH, amount of CNSs-COOH, sample flow rate and sample volume were optimized in detail. Under the optimized conditions, low limits of detection (0.01–1.2 ng L<sup>-1</sup>), wide linear range (0.50–200 ng L<sup>-1</sup>) and good repeatability (2.4–5.1%) and good reproducibility (3.7–8.8%) were obtained. The proposed method was applied to analyze the six PFAAs in real environmental water samples, and satisfactory results were achieved. All of these results showed that CNSs-COOH will be a good choice for the pre-concentration and analysis of target PFAAs at trace levels in environmental water samples in the future.

## 1. Introduction

Perfluorinated compounds (PFCs) are a large group of organic compounds that are characterized by the presences of fully or partially fluorinated hydrophobic and lipophobic carbon chain attached to one or more hydrophilic functional groups [1]. They have been used widely in many consumer-related and industrial applications because of their unique chemical and thermal stabilities. Two major PFCs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), were on the list of new persistent organic pollutants by the Stockholm Convention in 2009 due to their persistence, bioaccumulation and potential toxicity [2]. These chemicals have attracted considerable attention all over the world because they have frequently been detected in environmental samples and often occur at high concentrations [3,4]. Therefore, it is important to develop sensitive techniques to monitor PFCs in the environment at trace levels.

Liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) is an often-used analytical method because of its high sensitivity and selectivity towards PFCs. However, direct analysis is

usually difficult due to their low concentrations and complexity of environmental matrix. Suitable sample preparation techniques are often required prior to LC-MS/MS analysis. Fortunately, various sample pretreatment techniques, such as liquid-liquid extraction [5], solvent extraction [3], liquid-liquid microextraction [6], solid-phase extraction (SPE) [7] and so on, have been used to pretreat PFCs in environmental samples. Among these techniques, SPE is the most commonly used pretreatment technique for environmental water samples because it has many obvious advantages, such as high enrichment factors, low organic solvent consumption and simple operation [7,8]. As the cartridge adsorbent plays an important role in SPE, it is essential to develop novel adsorbents to extract PFCs from environmental samples. Many adsorbents, such as surfactant-templated ordered mesoporous material, magnetic core-mesoporous shell microspheres with decyl-perfluorinated interior pore-walls, functionalized multi-walled carbon nanotubes, 3-fluorobenzoyl chloride functionalized magnetic nanoparticles and surfactant-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles [4,9–12], have been used in SPE for PFCs. However, high-enrichment efficiency and selectivity remain a challenge due to the strong interactions

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between polar PFCs and aqueous samples.

Currently, carbon spheres (CSs) have attracted great attention from both scientific and practical points of view due to their potential applications as reinforcing agents, lubricants, electrode materials, catalyst supports and hydrogen storage media [13–16]. However, this type of material is limited by its inert surface properties and non-polarity [16]. The new generation of CS products, including carboxylated carbon spheres (CNSs-COOH), overcome these disadvantages while maintaining the original advantages, including a low price as well as high thermal and chemical stabilities [15,17].

In this paper, the adsorptive potential of using CNSs-COOH for SPE of perfluoroalkyl acids (PFAAs) was investigated for the first time. Related important factors, such as the eluant and its volume, sample pH, amount of CNSs-COOH, sample flow rate and sample volume, were investigated and optimized in detail. Finally, the proposed method was applied to analyze PFAAs in real environmental water samples.

## 2. Experimental

### 2.1. Reagents

CNSs-COOH was obtained from Nanjing JCNANO Tech Co. Ltd. (Nanjing, China). Perfluorohexanesulfonate (PFHxS) ( $\geq 98\%$ ), perfluoroheptanoic acid (PFHpA) ( $\geq 98\%$ ), perfluorooctanoic acid (PFOA) ( $\geq 98\%$ ), perfluorooctanoic sulfonic (PFOS), perfluorononanoic acid (PFNA) ( $\geq 98\%$ ) and perfluorodecanoic acid (PFDA) ( $\geq 98\%$ ) were purchased from Anpu Shiyuan Tech Co. Ltd. (Shanghai, China). Standard stock solutions ( $100 \text{ mg L}^{-1}$ ) containing these compounds were prepared in methanol and stored at  $4^\circ\text{C}$ . Methanol (MA) and acetone (ACE) were of HPLC grade. Unless otherwise stated, all other reagents were of analytical grade.

### 2.2. Instrument

In this work, a Thermo Ultimate 3000 Liquid Chromatograph (Massachusetts, USA) coupled with an AB SCIEX QTRAP 5500 mass spectrometer (Redwood, CA, USA) was used. An Agilent XDB-C18 column ( $2.1 \text{ mm} \times 150 \text{ mm}$ ,  $3.5 \mu\text{m}$  particle size) was used and held at  $40^\circ\text{C}$ . The mobile phase comprised  $5 \text{ mmol L}^{-1} \text{ NH}_4\text{Ac}$  (A) and methanol (B). The percentage of methanol varied during the chromatographic run as follows: 0–1.0 min, 10% B; 1.1–1.5 min, 10–40% B; 1.6–12.0 min, 40–95% B; 12.1–13.0 min, 95% B; and 13.1–17 min, 10% B. The flow rate of the mobile phase was  $0.4 \text{ mL min}^{-1}$ . The mass spectrometer used negative electrospray ionization (ESI) and ran in multiple reaction monitoring (MRM) mode. The source temperature was  $550^\circ\text{C}$ , and the collision gas was  $\text{N}_2$ . The ion spray voltage was  $-4500 \text{ V}$ . The curtain gas was set to 40 psi, and the ion source gases 1 and 2 were set to 55 and 60 psi, respectively. The MS parameters, including the MRM transition (parent ion  $\rightarrow$  daughter ion) and collision energies, are presented in Table 1.

The scanning electron microscopy (SEM) images were performed on a SUPPA<sup>TM</sup> 55 (Zeiss, Germany). The thermogravimetric analysis (TGA) was operated on a STA 449F3-QMS403C (Netzsch, Germany) from 25

**Table 1**  
LC-MS/MS MRM data acquisition method for PFAAs detection.

Compounds	Parent ion ( <i>m/z</i> )	Daughter ion ( <i>m/z</i> )	Declustering potential (V)	Collision energy (eV)
PFHpA	363	319, 169	- 30, - 30	14,24
PFOA	413	369, 169	- 40, - 30	14,24
PFNA	463	419, 219	- 35, - 35	16,24
PFDA	513	469, 219	- 40, - 40	18,26
PFHxS	399	79.9,99	- 90, - 90	88,72
PFOS	499	79.9,99	- 105, - 105	106,98

to  $600^\circ\text{C}$  with a ramp rate of  $10^\circ\text{C min}^{-1}$ . A direct acid-base titration method was used to determine the concentration of carboxyl group.

### 2.3. Solid phase extraction

CNSs-COOH-packed cartridges were prepared according to the literatures [8,9] by modifying an SPE cartridge ( $1000 \text{ mg}$ ,  $6 \text{ mL}$ ). After the adsorbent was removed,  $300 \text{ mg}$  of CNSs-COOH was packed in the SPE cartridge. The upper frit was reset to hold the CNSs-COOH packing in place. The cartridge inlet was connected to a PTFE suction tube, the outlet was connected to an SHB-III vacuum pump (Great Wall Company Inc., Zhengzhou, China), and the other end of the PTFE suction tube was inserted into the sample. To reduce the interference of possible contaminants, the entire SPE system was washed with purified water and acetone prior to its first use.

The CNSs-COOH column was washed with  $5 \text{ mL}$  of purified water and  $5 \text{ mL}$  of acetone ( $\text{pH} = 10$ ) prior to each SPE procedure. Then, a  $200\text{-mL}$  water sample was passed through the cartridge at  $6 \text{ mL min}^{-1}$ . After the water sample had passed through, the column was washed with  $3 \text{ mL}$  of purified water to remove the possible co-adsorbed matrix from the column. Then, the CNSs-COOH column was dried with negative pressure for  $3 \text{ min}$ . Subsequently, the target compounds retained on the CNSs-COOH were eluted with  $7 \text{ mL}$  of acetone ( $\text{pH} = 10$ ). The resulting eluent was dried with a gentle nitrogen flow at  $30^\circ\text{C}$ . Finally, the extract was redissolved in  $1.0 \text{ mL}$  of methanol ( $\text{pH} = 4$ ) and was then analyzed by LC-MS/MS with an injection of  $10 \mu\text{L}$ .

### 2.4. Water samples

In this experiment, three water samples, including barreled drinking water, tap water and pond water, were used to assess the feasibility of the developed method. Barreled drinking water samples were obtained from a local supermarket (Jinan, China). Tap water samples were collected from our lab (Jinan, China). Pond water samples were obtained from a pond located at our center (Jinan, China). Before these water samples were analyzed, they were filtered through a  $0.45\text{-}\mu\text{m}$  micropore membrane filter and stored in brown glass bottles at  $4^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Characterization of CNSs-COOH

A SEM image of the CNSs-COOH at high-magnification is shown in Fig. 1A. The general diameters of these nanospheres were between  $200\text{--}500 \text{ nm}$ . The surface area of the new material was  $248.6 \text{ m}^2 \text{ g}^{-1}$ . As shown in the collected FT-IR spectra (Fig. 1B) and compared with the raw CNSs, CNSs-COOH exhibited an absorbance peak at approximately  $1710 \text{ cm}^{-1}$  due to the carboxyl stretch of the carboxylic acid group [18]. Two absorbance peaks at approximately  $1410$  and  $1600 \text{ cm}^{-1}$  were assigned, respectively, to the symmetric and asymmetric stretching vibrations of the COO- groups [19]. The above results verified the successful introduction of carboxyl group to these CNSs. The carboxyl group content of CNSs-COOH was determined to be  $4.67\%$  by a direct acid-base titration method.

### 3.2. Optimization of the experiment parameters

To assess the extraction potential of CNSs-COOH as a SPE absorbent, six PFAAs, including PFHxS, PFHpA, PFOA, PFOS, PFNA and PFDA, were used as target pollutants. Their recoveries were used to evaluate the enrichment efficiencies of these compounds. In this work, double-distilled water spiked with  $100 \text{ ng L}^{-1}$  of the six PFAAs was used to investigate the SPE performance of CNSs-COOH under different experimental conditions. Related important parameters that affect the extraction efficiency of the SPE method, including the eluant and its volume, sample pH, amount of CNSs-COOH, sample flow rate and

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