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Efficient extraction of perfluorocarboxylic acids in complex samples with a monolithic adsorbent combining fluorophilic and anion-exchange interactions

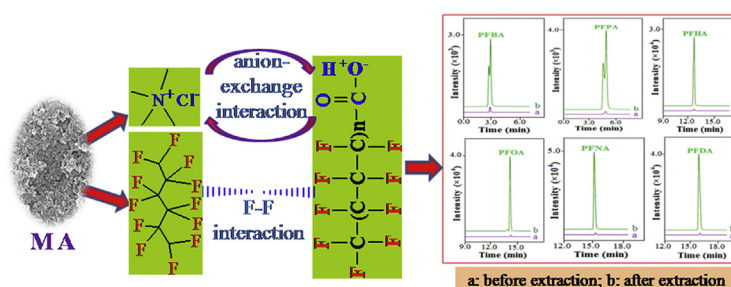
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HIGHLIGHTS

- A new monolithic adsorbent was synthesized facilely.
- The adsorbent was utilized as the extraction phase of MMF-SPME.
- Fluorophilic and anion-exchange interactions involved in the extraction of PFCAs.
- MMF-SPME-HPLC-MS/MS was developed for the determination of PFCAs in complex samples.

GRAPHICAL ABSTRACT



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ABSTRACT

Efficient extraction of perfluorocarboxylic acids (PFCAs) is a key step for the accurate and sensitive determination of PFCAs due to their low concentration and the complexity of sample matrices. Herein, according to the chemical characteristics of PFCAs, a new adsorbent based on poly(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl acrylate)/(vinylbenzyl)trimethylammonium chloride-co-divinylbenzene/ethyl-methacrylate) monolith was fabricated and utilized as the extraction medium of multiple monolithic fiber solid-phase microextraction (MMF-SPME). Results well indicated that the prepared monolithic adsorbent (MA) could efficiently extract PFCAs through fluorophilic and anion-exchange interactions. Under the optimal conditions, the MA/MMF-SPME was combined with HPLC-MS/MS for the sensitive monitoring of ultra-trace PFCAs in water and milk samples. The limits of detection ($S/N = 3$) of the target PFCAs in water and milk samples were 0.40–4.40 ng/L and 0.9–12.1 ng/L, respectively. Furthermore, the proposed method also exhibited some merits including wide linear dynamic ranges, satisfactory sensitivity, good method precision and low consumption of sample and organic solvent. Isotope internal standard calibration curve method was used to quantify the concentration of PFCAs in real samples, and trace levels of PFCAs in tap water and milk samples had been successfully detected.

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1. Introduction

Due to the unique characteristics such as surface activity, satisfactory chemical and thermal stability, superhydrophobicity and oleophobicity, perfluorocarboxylic acids (PFCAs) and their salts

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have been widely utilized in many fields in the last decades. However, the PFCAs may be released to environment during manufacture and application. As a result, PFCAs have become ubiquitous pollutants and commonly found in different sample matrices such as environmental waters and food of animal origin. Studies have indicated that PFCAs present a potential risk to humans and may cause some toxic effects such as endocrine disruption, hepatotoxicity, carcinogenicity and immunotoxicity [1,2]. To protect the humans' health, several governments and organizations have regulated the guidelines for PFCAs in waters. For example, office of water in Environmental Protection Agency issued a lifetime health advisory level of 70 ng/L for the combined perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) concentration in drinking water [3]. Furthermore, to assess the risk associated with dietary exposure of PFCAs, the European Food Safety Authority recommended that further data on their levels in foods such as milk would be desirable [4]. Herein, there is a necessary to develop an accurate and sensitive method for the monitoring of trace PFCAs in environmental waters and food such as milk.

Nowadays, high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) has become the robust method for the monitoring of trace or ultra-trace level PFCAs due to its high sensitivity and selectivity. Considering the low content of PFCAs in real sample and the complex interferences in actual matrices, suitable sample preparation is indispensable before chromatographic analysis. Typically, the reported sample preparation methods can be divided into solvent-based extraction (SBE) and adsorbent-based extraction (ABE). Comparing with SBE, ABE is more attractive because of less consumption of organic solvent, abundant adsorbents and cost-effectiveness. So far, several ABE methods such as solid phase extraction (SPE) [5,6], solid phase microextraction (SPME) [7,8], matrix solid-phase dispersion extraction (MSPDE) [9] and in-tube solid-phase microextraction (IT-SPME) [10] have been developed and applied to extract PFCAs in complex samples. The commercial adsorbents for the extraction of PFCAs mainly include silica gel, C18, HLB, WAX, Florisil, ENVI-Carb™. However, the reported ABE methods for the extraction of PFCAs still suffer from some dilemmas such as inconvenient operation, low extraction capacity, unacceptable repeatability and the necessary of complicated devices. For commercial adsorbents, some disadvantages limit their wide application. For example, when using HLB to extract PFCAs, low recoveries were encountered for short-chain PFCAs [11]. WAX adsorbent had good extraction efficiency for a wide range of range of neutral and acidic perfluorinated compounds, but the high price increased the cost of testing. Therefore, developing multiply functional adsorbent and combining suitable extraction format is highly desired for the extraction of PFCAs.

According to the principle of "similarity dissolves similarity", to extract PFCAs effectively with an adsorbent, multiply interactions between the adsorbent and PFCAs should be involved in the extraction procedure. Typically, there are abundant fluorinated (*F*-) alkyl chains and dissociable carboxyl groups in the molecules of PFCAs. In this connection, utilizing an adsorbent which can produce special interactions with *F*-alkyl chains and carboxyl groups may achieve expected enrichment effect for PFCAs. In this work, a novel monolith-based adsorbent (MA) was synthesized using 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl acrylate (DFHA) and (vinylbenzyl)trimethylammonium chloride (VTAC) as mixed functional monomers. The new MA contains ample *F*-alkyl and quaternary amine groups. As a result, the MA can produce fluorophilic and anion-exchange interactions with PFCAs. Therefore, it is reasonable to expect the efficient extraction of PFCAs with the new MA. Apart from the adsorbent, considering the operation simplicity

and usability, selection of suitable extraction format is important to realize the efficient enrichment of PFCAs in complex samples. Recently, a new extraction method named multiply monolithic fiber solid-phase microextraction (MMF-SPME) was proposed in our group [12,13]. The MMF-SPME has the same extraction mechanism as conventional SPME, but MMF-SPME possesses higher extraction capacity because it contains of four thin monolithic fibers. Additionally, the MMF-SPME possesses other merits such as simple operation, fast mass-transfer, low cost and environmental friendliness. Therefore, the combination of MA with MMF-SPME (MA/MMF-SPME) will supply an efficient and simple sample preparation method for the analysis of PFCAs in complex samples.

In this study, six PFCAs including perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA), perfluoroheptanoic acid (PFHA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) were selected as target analytes to evaluate the extraction performance of proposed MA/MMF-SPME for PFCAs. After optimization of the fabrication conditions and extraction parameters, the MA/MMF-SPME was combined with HPLC-MS/MS to sensitively monitor ultra-trace PFCAs in environmental waters and milk samples.

2. Experimental

2.1. Chemical reagents

The functional monomers of DFHA ($\geq 95\%$) and VTAC (98%) were bought from Sigma-Aldrich (St. Louis, MO, USA) and Cheng Jie Chemical Co. LTD (Shanghai, China). Cross-linkers of ethylenedimethacrylate (ED, 97%) and divinylbenzene (DB, 80%) were purchased from Alfa Aesar Ltd. (Tianjin, China). 1-Propanol (97%), 1,4-butanediol (98%), azobis (isobutyronitrile) (AIBN) (97%) and trifluoroacetic acid (TFA) were obtained from Xilong Chemical Co. (Guangzhou, China). Acetonitrile (ACN) and methanol HPLC-grade are all HPLC-grade and were purchased from Tedia Company (Fairfield, USA). A Milli-Q water purification system (Millipore, USA) was employed to prepare the ultrapure water which was utilized throughout the present study. Fused-silica capillary (530 μm i.d.) was supplied by Ruifeng Instrumental Co. (Hebei, China).

The standards of PFBA (98%), PFPA (97%), PFHA (99%), PFOA (96%), PFNA (97%) and PFDA (98%) were supplied by Sigma-Aldrich (St. Louis, MO, USA). The internal standard (IS) $^{13}\text{C}_8$ -PFOA ($\geq 99\%$) which was used in the internal calibration of HPLC-MS/MS analysis was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The chemical properties of these PFCAs were shown in Supporting Information (Table S1). Individual stock solutions of each PFOA at a concentration of 10.0 mg/L were prepared in HPLC-grade methanol for up to one month. Working solutions (containing a standard mixture for each PFOA) were prepared at a concentration of 10.0 $\mu\text{g}/\text{L}$ (20.0 $\mu\text{g}/\text{L}$ for PFBA and PFPA) to validate the method. All samples were stored at -4°C before use.

2.2. Instruments and chromatographic conditions

The HPLC-MS/MS analysis of PFCAs were performed using an Agilent 1290 Infinity LC system equipped with an auto sampler and coupled to an Agilent 6400 triple quadrupole mass spectrometer (MS/MS). The Agilent Masshunter Workstation software (Foster City, CA, USA) was used to control the whole HPLC-MS/MS system.

The HPLC system 1290 from Agilent Technologies (Foster City, CA, USA) comprising the LC column Phenomenex Kinetex C₁₈ (100 mm \times 3.0 mm, 2.6 μm particle size) with guard from Phenomenex (Aschaffenburg, Germany). The HPLC separation was performed with a binary mobile phase consisted of ultrapure water

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