One-pot polymerization of monolith coated stir bar for high efficient sorptive extraction of perfluoroalkyl acids from environmental water samples followed by high performance liquid chromatography-electrospray tandem mass spectrometry detection

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ABSTRACT

In this work, poly(1-vinylimidazole-ethyleneglycol dimethacrylate) (poly(VI-EDMA)) monolith coated stir bars were synthesized by one-pot polymerization, and they exhibited higher extraction efficiency and faster extraction dynamics for selected PFAAs than commercial ethylene glycol modified silicone (EG-silicone) and polydimethylsiloxane (PDMS) coated stir bars. Taking eleven PFAAs as target analytes, including C4-C12 perfluoroalkyl carboxylates (PFCAs) and C6, C8 perfluoroalkane sulfonates (PFSAs), a method combining monolith-based stir bar sorptive extraction (SBSE) with high performance liquid chromatography (HPLC) – electrospray tandem mass spectrometry (ESI–MS/MS) was proposed for the determination of multiplex PFAAs in environmental water samples. Under the optimized conditions, low limits of detection (0.06–0.40 ng/L) and wide linear range (0.6–400 ng/L) were obtained for target PFAAs with. The developed method was then applied for the analysis of target PFAAs in environmental water samples, and recoveries of 80.1–117% and 80.3–122% were obtained for target PFAAs in spiked Yangtze River and East Lake water samples respectively.

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1. Introduction

Perfluoroalkyl acids (PFAAs) represent a class of compounds consisting of perfluorinated alkyl chains and acidic functional groups [1]. Due to the excellent hydrophobic and oleophobic property as well as high surface activity, PFAAs have been widely applied in industrial production over the past 50 years [2,3]. During the production and application, PFAAs would enter environmental media and organism through multiple channels. With the strong carbon-fluorine (C−F) bonds, PFAAs are resistant to photolysis, hydrolysis and biological degradation [4], which results in their environmental persistence and bio-accumulative potential [5,6]. PFAAs have become a group of persistent organic pollutants (POPs) in the environment and were added to the POPs list of the Stockholm Convention in 2009. Currently, the existence of PFAAs in environmental waters [7], sediments [8], aquatic organisms [9] and even human body [10] have been found, and the potential health risks of PFAAs on human body have aroused extensive attention. It has been reported that PFAAs may affect reproductive capacity [11], lead to hepatocyte damage [12], change gene expression [13], and interfere with mitochondria functions [14]. Therefore, the monitoring of PFAAs in environment is of great significance, which would contribute to further investigation of migration as well as transformation of PFAAs in ecosystem, and systematical ecological risk assessment of pollutants of interest.

Generally, liquid chromatography (LC)-tandem mass spectrometry (MS/MS) [15–17] is commonly employed for the identification and quantification of PFAAs in various real samples because of its excellent selectivity and sensitivity. Due to the low concentration (ng/L level) of PFAAs [18,19] and the matrix interference

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in environmental samples, appropriate sample pretreatment technologies are often needed for the enrichment of target PFAAs and matrix removal before the instrumental measurement. Traditional solid-phase extraction (SPE) processes involving commercial adsorbents (e.g., hydrophilic-lipophilic balanced and weak-anion exchange stationary phases) [20] or self-made materials [21] have been applied in the determination of PFAAs in environmental samples. To further improve extraction efficiency and dynamics, novel sample pretreatment techniques, magnetic solid-phase extraction (MSPE) [22,23], solid-phase micro-extraction (SPME) [24,25] and stir bar sorptive extraction (SBSE) were applied for the analysis of PFAAs.

SBSE is an environmentally-friendly and miniaturized sample pretreatment technology, which was proposed by Baltussen on the basis of SPME in 1999 [26]. Due to the advantages of large adsorption capacity and high extraction efficiency, SBSE has been widely applied for the analysis of the environmental [27], food [28] and biological samples [29]. At present, only three kinds of coated stir bar are commercially available: polydimethylsiloxane (PDMS), ethylene glycol modified silicone (EG-silicone) and polyacrylate (PA). Martin et al. [30] evaluated the performance of PDMS and EG-silicone stir bar for the extraction of C5-C8 perfluorinated carboxylic acids (PFCAs) and perfluorooctane sulfonate (PFOS) from human milk. The results showed that EG-silicone stir bar exhibited better extraction efficiency for selected PFAAs than PDMS stir bar. Aparicio et al. [31] applied commercial EG-silicone stir bar on analysis of six PFAAs in environmental waters, low recovery was obtained for perfluorobutanoic acid (PFBA) and the extraction time for target PFAAs was up to 24 h. Besides, PFAAs with carbon chain longer than C8 have not been analyzed by using methodology based on SBSE so far. As can be seen, the present commercial stir bar coatings are not competent to high efficient and simultaneous preconcentration of multiplex PFAAs. Accordingly, new stir bar coatings with high extraction efficiency and fast extraction dynamics for multiple PFAAs with different polarity are expected urgently.

Presently, the self-made coated stir bars are mainly prepared by the means of sol-gel technique, adhesion technique and monolithic technique. Polymer monolithic coatings obtained by monolithic technique involve the polymerization of monomer mixture with porogen solvent. They would provide continuous porous structures and plenty of functional groups, which may lead to good permeability and numerous adsorption sites. According to the applied monomers and crosslinking agents, the organic polymer monolith can be mainly divided into three categories, polyacrylamide, polystyrene and polyacrylate-based monoliths. Among them, polyacrylate-based monoliths have good mechanical strength, easy chemical modification, and wide application. Huang et al. [32] fabricated poly(octyl methacrylate-ethylene dimethacrylate) (MAOE-EDMA) monolith coated stir bar for the extraction of polycyclic aromatic hydrocarbons and anabolic steroids from seawater. Fast dynamics was demonstrated for poly(MAOE-EDMA) with good application potential for non-polar and polar compounds. After that, poly (vinylpyridine-ethylene dimethacrylate) [33] and poly (2-hydroxyethyl methacrylate-pentaerythritol triacrylate) [34] monolith coated stir bars were prepared and employed for the extraction of compounds with different polarities. In our previous works, molecularly imprinted polymer was introduced into polyacrylate-based monolith coated stir bar to improve the selectivity of the coatings [35]. Metal organic framework materials were also introduced into the preparation of poly (methyl methacrylate-ethyleneglycol dimethacrylate) monolith stir bar coating, and the surface area of the composite coating was obviously increased and the extraction efficiency for target phytohormones was improved [36].

The aim of this work is to prepare monolith coated stir bars for the simultaneous extraction of multiple PFAAs with large polarity differences and establish a novel method combining monolith-based SBSE-HPLC–MS/MS for the analysis of multiplex PFAAs in environmental water samples. In consideration of the hydrophobic property and anionic form of PFAAs in water samples, poly(1-vinylimidazole-ethyleneglycol dimethacrylate) (VI-EDMA) coated stir bar was prepared, and electrostatic and hydrophobic interaction are expected between target PFAAs and the monolith coating. The effect of various experimental parameters on the extraction efficiency of selected PFAAs by poly(VI-EDMA)-SBSE were investigated, and the analytical performance and application potential of the proposed method was evaluated.

2. Materials and methods

2.1. Reagents and standards

Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorododecanoic acid (PFDoA) and perfluorooctane sulfonate (PFOS) were purchased from Alfa Aesar (Ward Hill, MA, USA). Perfluorohexanoic acid (PFHxA), perfluoroundecanoic acid (PFUdA) and perfluorohexane sulfonate (PFHxS) were purchased from Sigma-Aldrich (Billerica, MA, USA). $^{13}C_3$-PFHxS, $^{13}C_4$-PFOS, $^{13}C_4$-PFBA, $^{13}C_4$-PFOA and $^{13}C_2$-PFDoDA were purchased from Wellington Laboratories (Guelph, ON, Canada). Each standard solution (1 mg/mL) of PFAAs was prepared in methanol (MeOH) and stored at 4 °C in the refrigerator.

1-Vinylimidazole, ethyleneglycol dimethacrylate and 1,4-Butanediol were obtained from Aladdin (Shanghai, China). Azodiisobutyronitrile (AIBN) was obtained from Shanghai No. 4 Reagent & H. V. Chemical Co., Ltd. (Shanghai, China). γ-(Methacryloxypropyl) trimethoxysilane (KH-570) was obtained from WD Silicone Co., Ltd. (Wuhan, China). N-Propanol, 1,4-butanediol, formic acid and ammonia were obtained from China Medicine (group) Chemical Reagent Corporation (Shanghai, China). All reagents above were of analytical grade. MeOH and ammonium acetate (NH$_4$OAc) were purchased from Fisher Scientific (Waltham, MA, USA) and Sigma-Aldrich (Billerica, MA, USA) respectively. The desorption solvents used in the experiments were all HPLC grade. High purity deionized water purified by a Milli-Q water purification system (18.2 MΩ·cm, Millipore, Molsheim, France) was applied during the whole experiments. Capillary glass bars (1.0 mm internal diameter (I.D.), 0.10 mm wall thickness) were obtained from Apparatus Factory of West China University of Medical Sciences (Chengdu, China). EG-silicone (10 mm long, 0.5 mm thick, Twister^{TM}) and PDMS (2 cm long, 0.5 mm thick, Twister^{TM}) stir bars were purchased from Gerstel GmbH (Mülheim an der Ruhr, Germany).

2.2. Instrumentation

IKA color squids magnetic stirrers (Baden-Wurttemberg, Germany), SY 1200-T ultrasound instrument (Source Ultrasonic Instruments Co., Ltd, Shanghai, China), Mettler Toledo 320 − S pH meter (Switzerland Mettler Toledo Company), Heraeus Multifuge X1R laboratory centrifuge (Thermo Fisher, Scientific, Germany) and HX-NC12 nitrogen evaporators (Wuhan Trustworthy Technology Co., Ltd, Wuhan, China) were used for the extraction and desorption process. The characterization of coated stir bar was performed by the IS10 Fourier infrared spectrometer (FT-IR, Thermal Fisher Scientific, USA) and the Zeiss Sigma scanning electron microscope (SEM, ZEISS, Germany).