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One-pot fabrication of magnetic fluorinated carbon nanotubes adsorbent for efficient extraction of perfluoroalkyl carboxylic acids and perfluoroalkyl sulfonic acids in environmental water samples

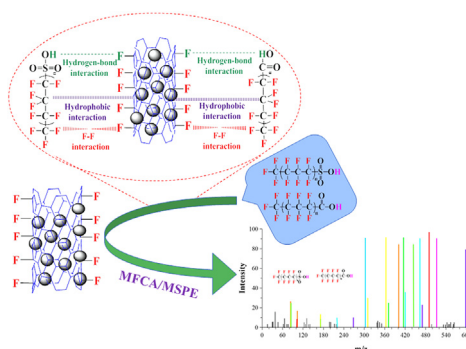
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HIGHLIGHTS

- A new magnetic fluorinated carbon nanotubes adsorbent was facily synthesized.
- The MFCA/MSPE extracted PFSAs and PFCAs effectively by means of multi-interactions.
- Extraction parameters were optimized in detail.
- The practical applicability of MFCA/MSPE-HPLC-MS/MS approach was investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Efficient extraction of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) is challenging due to their highly fluorinated property. Based on the particular characters of PFCAs and PFSAs, a new type of magnetic fluorinated carbon nanotubes adsorbent (MFCA) for magnetic solid phase extraction (MSPE) was fabricated facily using one-pot hydrothermal approach. The morphology, structure and magnetic properties of the prepared MFCA were investigated by Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy and vibrating sample magnetometry. It was observed that the resultant adsorbent possessed satisfactory superparamagnetism and saturation magnetism. Furthermore, the MFCA exhibited excellent enrichment performance for target PFCAs and PFSAs by means of fluorous-fluorous, hydrophobic and hydrogen bonding interactions. Under the most favorable preparation and extraction conditions, the proposed MFCA/MSPE was combined with high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) to quantify ultra trace target analytes in environmental water samples. The limits of detection ($S/N = 3$) of PFCAs and PFSAs were 0.010–0.036 ng/L and 0.024–0.50 ng/L, respectively. In addition, the introduced approach also displayed other features such as quick extraction procedure, wide linear dynamic ranges, excellent method precision and eco-friendliness. Finally, the concentrations of PFCAs and PFSAs in tap, river, lake and waste water samples were successfully measured by isotope internal standard calibration curve method.

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1. Introduction

Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) consisted of perfluorinated alkyl chains and acidic functional groups. They are a large group of perfluorinated compounds. In the past 6 decades, perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs) have been extensively used in industrial production because of their unique high surface activity, amphiphilic property, chemical and thermal stabilities [1]. However, PFCAs and PFSAs can be released into environmental waters during the production and application procedure. Studies have evidenced that most of PFCAs and PFSAs are toxic, extremely resistant to degradation, and have long half-life period [2–4]. As a result, some of PFCAs and PFSAs such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been listed as persistent organic pollutants by the Stockholm Convention in 2009 [5]. At the same time, a lifetime health advisory level of 70 ng/L for PFOA and PFOS in ground water and drinking water was regulated by the Drinking Water Health Advisories of Environmental Protection Agency [6]. Considering these implications, developing highly sensitive method for the monitoring of ultra trace PFCAs and PFSAs in environmental waters has received wide attention.

So far, high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) has become the popular technology to identify and quantify PFCAs and PFSAs in water samples [7–10]. However, direct determination of PFCAs and PFSAs is difficult due to their low contents and the complex matrices in real samples. Accordingly, prior to chromatographic analysis, suitable sample pretreatment procedure should be performed to realize the enrichment of analytes and matrix removal. Currently, a few of sample pretreatment approaches such as liquid-phase microextraction (LPME) [11,12], solid-phase extraction (SPE) [13–15], solid-phase microextraction (SPME) [16,17], multiple monolithic fiber solid-phase microextraction (MMF-SPME) [10], stir bar sorptive extraction (SBSE) [18], and magnetic solid-phase extraction (MSPE) [19–21] have been developed to extract PFCAs and PFSAs in various samples. Among these technologies, MSPE affords various attractive merits such as simple operation, fast extraction procedure, low consumptions of sample and organic solvent. Based on the advantages, several studies that using MSPE to extract PFCAs and PFSAs have been reported [19–22]. Yao et al prepared 3-fluorobenzoyl chloride functionalized magnetic nanoparticles ($\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{FBC}$) and used it to enrich PFCAs in river water under the MSPE format [19]. Expected extraction performance was obtained, but the synthesized procedure of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{FBC}$ was time-consuming and inconvenient. Recently, covalent triazine-based frameworks (CTFs) was anchored on the surface of magnetic core and obtained $\text{CTF}@ \text{Fe}_2\text{O}_3$ composites for MSPE of PFCAs [22]. The $\text{CTF}@ \text{Fe}_2\text{O}_3$ -MSPE was applied to monitor low levels of PFCAs in environmental waters. However, the temperature used in the preparation of $\text{CTF}@ \text{Fe}_2\text{O}_3$ composites was as high as 500–550 °C. At the same time, the extraction capacity for target PFCAs should be further improved. As other sorbent-based extraction formats [23–25], the extraction phase is the core of MSPE. According to the extraction performance of existing adsorbents for MSPE of PFCAs and PFSAs, developing new adsorbent materials with simple preparation procedure, high extraction performance and good dispersibility in aqueous matrix is highly desired.

Carbon nanotubes (CNTs) firstly reported by Iijima et al [26], are cylindrical nanostructures, with covalent sp^2 bonds between carbon atoms. Due to the unique mechanical, thermal and electrical properties, CNTs have been applied in many fields such as environmental sensing, renewable energy and biotechnology [27]. In addition, according to the high surface area and π - π stacked architectures, CNTs have become good adsorbents for the extraction or the removal of pollutants [28]. To enhance extraction selectivity and improve the dispersion of CNTs in aqueous media, the surface of CNTs may be modified through mechanical, physicochemical and irradiation technologies [29]. The

reported studies well prove that CNTs and modified CNTs have superior potential in sample pretreatment. However, to the best of our knowledge, the utilization of CNTs or modified CNTs as extraction phase of MSPE to capture PFCAs and PFSAs has rarely been reported.

Herein, we aim to prepare a novel magnetic fluorinated carbon nanotubes adsorbent (MFCA) for MSPE of PFCAs and PFSAs in water samples. The MFCA was fabricated by means of simple one-pot synthesized strategy. Various characterized technologies including infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) were employed to investigate the surface morphology, spectroscopic and magnetic properties. Parameters influencing the extraction performance of MFCA/MSPE for target analytes were checked and optimized in detail. The possible enrichment principle was also discussed. Finally, the prepared MFCA/MSPE was coupled with high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) to measure low levels of PFCAs and PFSAs in environmental water samples.

2. Experimental

2.1. Reagents and materials

Fluorinated multiple-walled carbon nanotubes (F-MWNTs) were purchased from XFNANO Co. Ltd. (Nanjing, China). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (98%), ethylenediamine ($\geq 99\%$), isopropanol ($\geq 99.7\%$) and trifluoroacetic acid (TFA) were obtained from Xilong Chemical Co. Ltd. (Guangzhou, China). HPLC-grade acetone and methanol were purchased from Tedia (Fairfield, USA). Sample pH value was adjusted by HCl (1.0 mol/L) or NaOH (2.0 mol/L). The other reagents were at least analytical grade. Ultrapure water was used throughout the study (Milli-Q system, Millipore, USA).

The following PFSAs standards and internal standard (IS) were purchased from ANPEL Laboratory Technologies (Shanghai, China): perfluoro-1-butanefulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHXS), perfluoroheptanesulfonic acid (PFHPS), perfluorooctanesulfonic acid (PFOS), hexacosafuorodecanesulfonic acid (PFDS), sodium perfluoro-1-[1,2,3- ^{13}C]-hexanesulfonate ($^{13}\text{C}_3$ -PFHXS). Perfluoroheptanoic acid (PFHA) (99%), perfluorooctanoic acid (PFOA) (96%), perfluorononanoic acid (PFNA) (97%) and perfluorodecanoic acid (PFDA) (98%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). The IS, sodium perfluoro-1-[1,2,3,4,5,6,7,8- ^{13}C]-octanoic acid ($^{13}\text{C}_8$ -PFOA) ($\geq 99\%$) was provided by Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). The basic properties of target analytes were listed in [Supplementary data \(Table S1\)](#). Each of PFSAs standard solution (5.0 mg/L) and PFCAs standard solution (2.0 mg/L) were prepared in methanol and stored at 4 °C in the refrigerator.

2.2. Instruments

The morphology and size of MFCA were characterized by SEM (IEISS SUPRA 55, German) and TEM (JEM-1400, Japan). The FI-IR (Shimadzu, Japan) and PPM-9 VSM (QUANTOM, USA) were used to analyze the chemical structure and magnetic properties of prepared MFCA. The contents of carbon and hydrogen in MFCA were measured by elemental analysis (EA) (PerkinElmer-Model PE 2400, USA). The SHZ-82 oscillator (Jiangshu, China) was employed to perform MSPE process.

The separation and quantification of target analytes were realized on the Agilent 1290 Infinity HPLC coupled to Agilent 6460 triple quadrupole mass spectrometer (HPLC-MS/MS) (Foster City, CA, USA), which equipped with an automatic sample injector and a binary pump. The triple quadrupole system was performed in negative electrospray ionization (ESI) and under the mode of multiple reaction monitoring (MRM).

2.3. Hplc-Ms/Ms

A Phenomenex Kinetex C18 (2.6 μm particle size, 100 \times 3.0 mm, USA) was employed to separate PFCAs and PFSAs. The mobile phase used for the HPLC consisted of ACN with 0.2% FA (v/v) (A) and ultrapure water with 0.2% FA (v/v) (B). The elution gradient procedure started at 30% A and lasted for 5.0 min, then rose to 50% A in 1.0 min and held for 3.0 min, and then increased to 80% A in 1 s and kept to 15 min. Finally, the mobile phase returned to initial proportion in 1.0 min and maintained for 12 min. The flow rate, injection volume and column temperature were 0.25 mL/min, 10 μL and 40 $^{\circ}\text{C}$, respectively.

The source parameters of mass spectrometer were as follows: drying gas supplied by a nitrogen generator was at the rate of 11 L/min; drying gas temperature was 300 $^{\circ}\text{C}$; atomizer pressure and capillary voltage were 15 psi and 4.0 kV, respectively; the temperatures of MS1 and MS2 were both 100 $^{\circ}\text{C}$. Other detailed parameters were shown in Table S2.

2.4. Synthesis of MFCA

In the present study, the MFCA was facilely fabricated by one-pot synthesized approach. Typically, F-MWNTs (0.3 g), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.2 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.0 g) were dispersed in 100 mL 50% (v/v) isopropanol solution. Subsequently, the solution was transported into a three-necked flask which was placed in a thermostat water bath with mechanical stirring (300 rpm) at 80 $^{\circ}\text{C}$. Under nitrogen gas protection, 10 mL of ethanediamine was dropwise added into the above solution and the solution was vigorous stirred (500 rpm) for 2.0 h. After the reaction, the resulting particles were collected from the solution by an external magnetic field, and the particles were washed with water and methanol in turn. Finally, the prepared particles were dried in at 70 $^{\circ}\text{C}$ for 1.0 h to obtain the final MFCA. It can be seen that the current one-pot approach is simple and time-saving, and the synthesized conditions is milder than reported methods [19,22]. Fig. 1 shows the schematic illustration of the one-pot preparation approach of MFCA.

2.5. MFCA/MSPE procedure

Before extraction, the MFCA particles were activated by methanol and ultrapure water in turn both for 15 min. After that, 30 mg MFCA was placed in a 100 mL vial, 50 mL sample solution contained 20.0 $\mu\text{g/L}$ IS was added into the vial. The pH value was adjusted to 4.0 and the adsorption procedure was carried out at thermostat oscillator for 9.0 min (250 rpm). Subsequently, the adsorbent was separated from the sample with a magnet. The supernatant was discarded, and 0.5 mL desorption solvent (acetone/TFA = 96/4.0, v/v) was added and oscillated for 2.0 min (250 rpm) to release the retained analytes from the adsorbent. To enhance the sensitivity, the desorption solution was dried with nitrogen gas. The dried residue was dissolved with 0.2 mL methanol, and 10 μL of the final solution was injected into HPLC-MS/MS for analysis. The used MFCA was washed in turn with acetone and

ultrapure water for next application. Fig. S1 displays the whole MFCA/MSPE procedure.

2.6. Sample collection and preparation

Lake water, river water, tap-water and waste water were selected as real environmental samples. The above-mentioned waters were originated from Siming campus of Xiamen University, our lab, Xiamen University at Xiang'an campus and Zhangzhou city, respectively. Prior to analysis, the water samples were filtered through 0.22 μm filter membranes, and the pH values were adjusted to 4.0. After that, all samples were placed in brown glass vials in refrigerator (4 $^{\circ}\text{C}$).

3. Results and discussion

3.1. Characterization of MFCA

EA results revealed that the C and H contents in MFCA were 14% and 6.6% (w/w), respectively. Fig. 2a-I, Fig. 2a-II and Fig. 2a-III show the FT-IR spectra of Fe_3O_4 , F-MWNTs and MFCA, respectively. Clearly, the characteristic absorption bands of F-MWNTs and MFCA can be found in MFCA (Fig. 2a-III). The band located at 571 cm^{-1} belongs to the Fe-O-Fe stretching vibration of Fe_3O_4 , and the band appeared at 1205 cm^{-1} is attributed to C-F vibration. Two weak bands appeared at 1637 cm^{-1} and 1550 cm^{-1} are assigned to the stretching vibrations of C=O and C=C groups of F-MWNTs, respectively. The morphologies of the prepared MFCA were investigated by SEM and TME. The Fe_3O_4 particles and the CNTs can be observed clearly from the SEM at 50000 \times magnification (Fig. S2). The particle size of Fe_3O_4 and the diameter of CNTs are around 30 nm and 40 nm, respectively. Furthermore, the Fe_3O_4 magnetic cores twined by CNTs can be seen clearly from the TEM (Fig. 2b). Fig. 3 displays the field-dependent magnetization curves of MFCA and Fe_3O_4 at room temperature. The MFCA displays a typical paramagnetic behavior due to the nearly zero coercivity and remanence. The magnetic saturation values (MSVs) of MFCA and Fe_3O_4 are 47.7 emu g^{-1} and 79.4 emu g^{-1} , respectively. Obviously, the decrease of MSV of MFCA is due to the coating of F-MWNTs on the magnetic cores. However, the MSV is enough for MFCA to keep satisfying magnetic responsiveness and perform magnetic separation quickly. As the inset of Fig. 3, the dispersive MFCA could be collected quickly within 10 s from sample solution by an external magnet. According to the above-mentioned characterizations, the MFCA was successfully synthesized with one-pot approach. The obtained MFCA exhibits high saturation magnetization and super paramagnetic property.

3.2. Optimization of MFCA/MSPE parameters

Various parameters that can influence the extraction performance of MFCA/MSPE for target PFCAs and PFSAs were investigated in detail. These parameters including the MFCA amount, desorption solution,

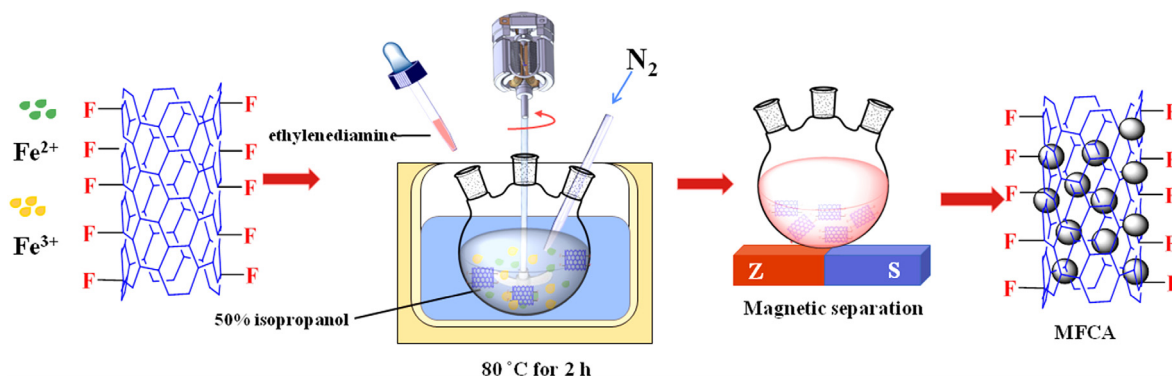


Fig. 1. Scheme for the one-pot fabrication of MFCA.

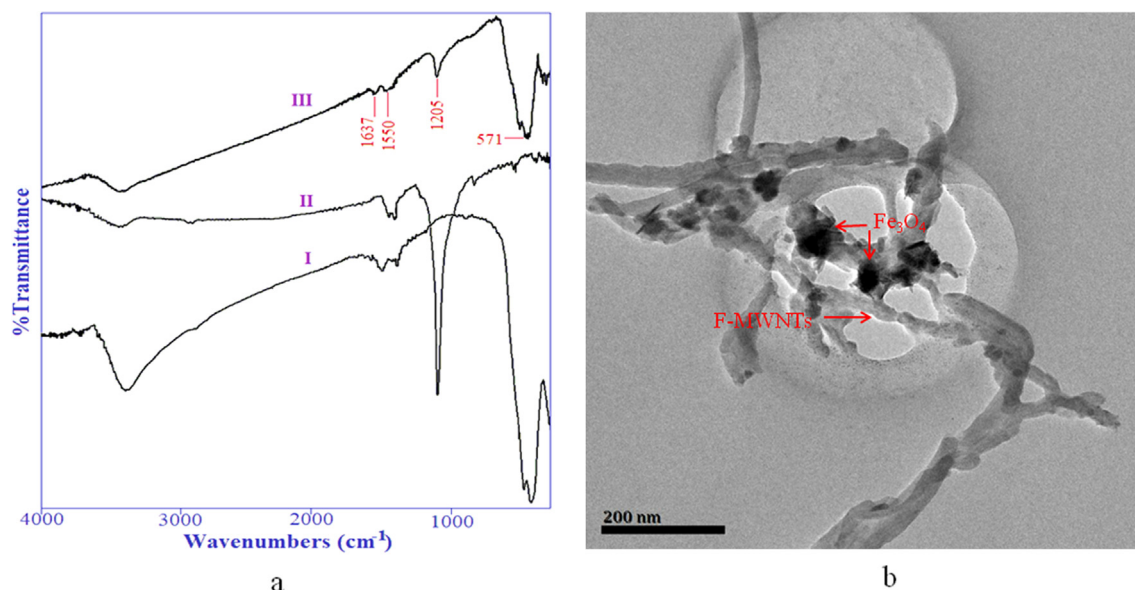


Fig. 2. The FT-IR spectra (a) for Fe_3O_4 (I), F-MWNTs (II) and MFCA (III), and TEM image (b) of MFCA.

adsorption and desorption time, pH value of sample solution and salinity in sample matrix. The optimization experiments were performed using spiked standard analytes aqueous solution containing $2.0 \mu\text{g/L}$ of each PFCAs and $5.0 \mu\text{g/L}$ of each PFSA. Each experiment was carried out in triplicate.

3.2.1. The amount of MFCA

The amount of MFCA is an important parameter influencing the extraction efficiency. In the present study, 20.0, 30.0, 40.0, 50.0 and 60.0 mg MFCA particles were utilized to investigate the influence of adsorbent amount on extraction performance. As shown in Fig. 4a, the peak areas for all target analytes enhance with the increase of MFCA amount from 20.0 to 30.0 mg, and decline when increasing the usage of MFCA from 30.0 to 60.0 mg. The changed profiles can be explained that the distribution coefficients (K) of target PFCAs and PFSA between

sorbent and aqueous were constant when the MFCA/MSPE was carried out under the same conditions. The extraction capacity of MFCA for PFCAs and PFSA would be enhanced when increasing the sorbent amount. However, the more MFCA was used, the more it retained target analytes due to the volume of desorption solvent and the K values were kept constant in desorption procedure. As a result, the recoveries of targeted PFCAs and PFSA decreased when more MFCA was employed. Based on this finding, 30.0 mg of MFCA was used to extract PFCAs and PFSA in the subsequent experiments.

3.2.2. Desorption solution

In the preliminary study, the retained analytes could not be released from MFCA completely when using pure organic solvent as eluent. Considering the fluorophilic and hydrogen bonding interactions may take part in the extraction, addition of TFA in eluent can interrupt the

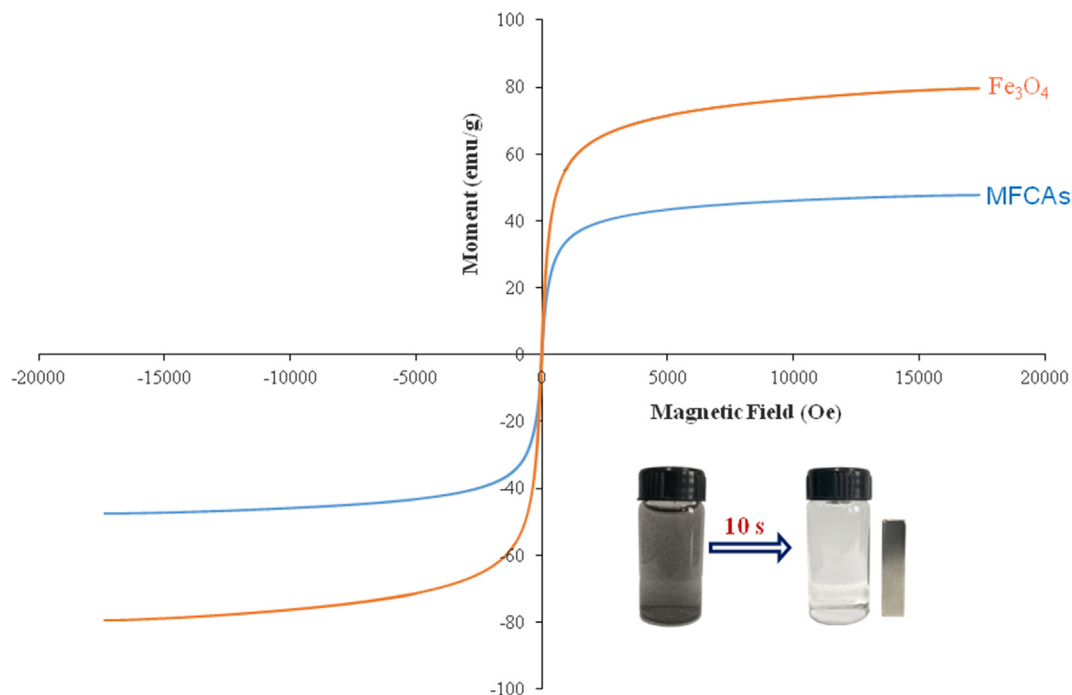


Fig. 3. The magnetization curves of MFCA and Fe_3O_4 at room temperature.

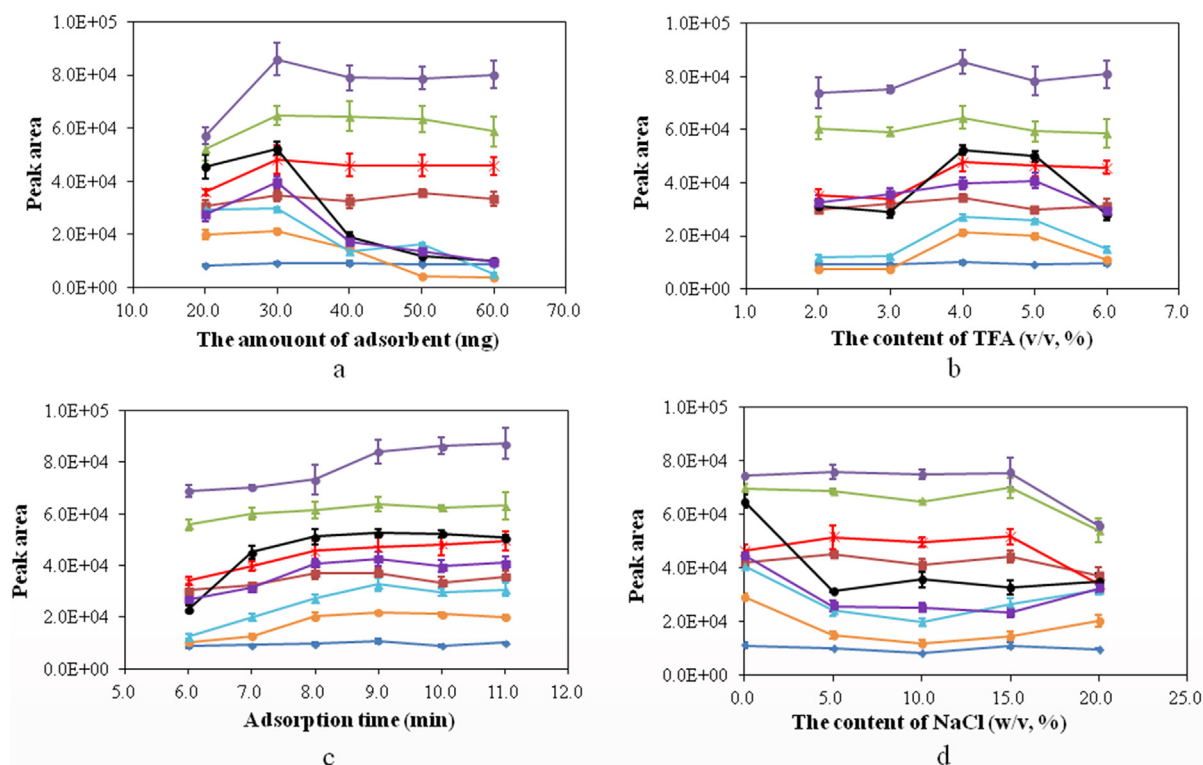


Fig. 4. The effect of the amount of adsorbent (a), desorption solution (b), adsorption time (c) and ionic strength (d) on the extraction performance of MFCA/MSPE for PFCAs and PFSAs. Conditions: adsorption time and desorption time were 10.0 min and 5.0 min, respectively; desorption solution was the mixture of 500 μ L acetone/TFA (94/6, v/v); sample pH value and ionic strength of sample matrix did not be adjusted; (b) the amount of MFCA was 30.0 mg; the other conditions were the same as in Fig. 4(a); (c) 500 μ L acetone/TFA (94/6, v/v) was used as desorption solution; the other conditions were the same as in Fig. 4(b); (d) adsorption time and desorption time were 9.0 min and 2.0 min, respectively; the other conditions were the same as in Fig. 4(c). Symbols: ◆PFBS; ■PFHXS; ▲PFHPS; ●PFOS; *PFDS; ●PFNA; ●PFHA; ▲PFOA; ■PFDA.

related interactions between MFCA and analytes. Therefore, the effect of addition of different amount of TFA in acetone on desorption performance was evaluated. It can be seen from Fig. 4b that addition of 4.0% (v/v) in acetone favors the elution of adsorptive analytes from MFCA. Based on the results, the mixture of acetone/TFA (96/4.0, v/v) was selected as the most favorable desorption solution in the following experiments.

3.2.3. Adsorption and desorption time

As other sorbent-based extraction methods, the extraction performance of MSPE relates to adsorption time. The influence of adsorption time was evaluated by varying the time from 6.0 to 11.0 min with an interval of 1.0 min (Fig. 4c). As shown, the adsorption amounts of PFCAs and PFSAs on the MFCA enhance with the increase of adsorption time from 6.0 to 9.0 min, and there is no remarkable change from 9.0 to 11.0 min. The effect of desorption time on extraction performance was also optimized. As shown in Fig. S3, 2.0 min desorption time is enough to release the retained analytes from MFCA when the adsorption time is 9.0 min. According to the results, the 9.0 min and 2.0 min were selected as the optimal adsorption and desorption time in the following studies.

3.2.4. Sample pH value and salinity

Fig. S4 displays the profiles of the effect of sample pH value on the extraction performance. It can be found that the extraction performance for all analytes enhances slightly when the pH value increases from 2.0 to 4.0. The reason is that the enhancement of pH value favors the formation of F-F and hydrogen-bond interactions between MFCA and analytes. Therefore, hydrophobic, fluorophilic and hydrogen-bond co-contribute the extraction. However, the extraction performance for PFCAs declines when the pH value increases continuously. The changed profiles may be that the carboxyl groups of PFCAs and hydroxyl groups

of MFCA dissociated when sample pH value increased. The electrostatic repulsion weakened the interactions between MFCA and PFCAs, resulting in the decline of extraction performance. For target PFSAs (except for PFOS), there is no obvious change when the sample pH enhances from 4.0 to 10.0. The phenomenon may be explained that the extraction of PFSAs on MFCA mainly related to hydrophobic, fluorophilic and hydrogen-bond interactions. Balancing the extraction performance, pH 4.0 was selected as the favor sample pH value.

Salinity is another critical factor in MSPE assay due to the opposite effects, salting-out and salting-in effects when sample salinity is changed [29]. Salting-out effect benefits the transfer of analytes to sorbent, and thus enhancing extraction performance. However, salting-in effect results from electrostatic interaction between analytes with ions in the solution will make against the extraction. To explore the influence of salinity on the extraction performance, the salt concentration (NaCl) was ranged from 0.0% to 20.0% (m/v). As indicated in Fig. 4d, for target PFCAs, the extraction performance declines with the increase of salinity. For PFSAs, there is no apparent change in extraction performance when the concentration of NaCl increase from 0.0% to 15.0% (m/v), but decline rapidly when the salinity enhances continuously. Thereby, the salinity did not be adjusted in the further experiments.

Under the optimized extraction conditions, the developed MFCA/MSPE exhibits satisfying extraction performance for target analytes. As displayed in Fig. 5, the peaks for target PFCAs and PFSAs are difficult to be identified before enrichment. However, the peak heights for the all analytes increase apparently after treatment with MFCA/MSPE. The enrichment factors (EFs) (the ratio of chromatographic peak area of analyte after MFCA/MSPE to that before extraction) for PFCAs and PFSAs were in the ranges of 93–112 and 130–187, respectively. Herein, better sensitivity can be achieved after treatment with MFCA/MSPE. At

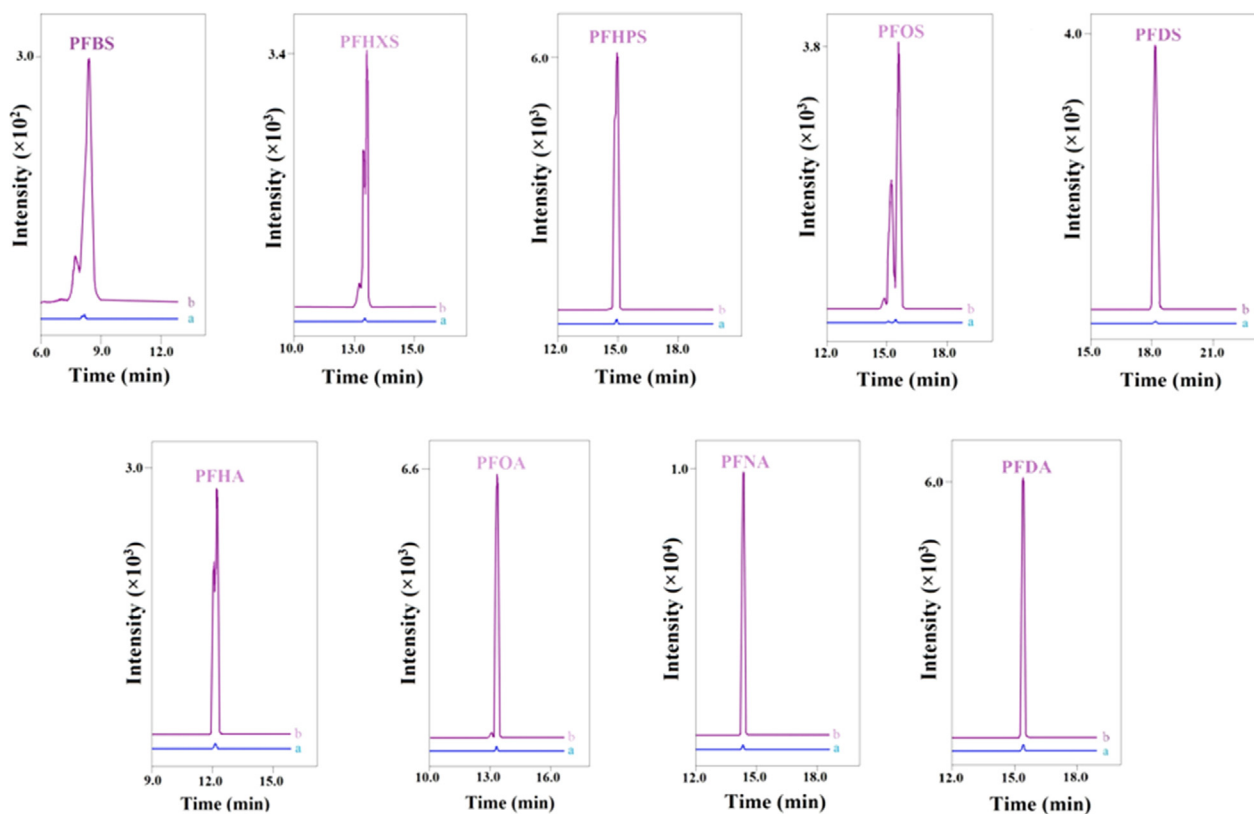


Fig. 5. TIC chromatograms of target PFSA and PFCAs. (a) Direct injection of spiked water sample at 5.0 $\mu\text{g/L}$ for PFSA and 2.0 $\mu\text{g/L}$ for PFCAs; (b) After treatment with MFCA/MSPE. Conditions: the amount of MFCA was 30.0 mg; 500 μL acetone/TFA (94/6, v/v) was used as desorption solution; adsorption time and desorption time were 9.0 min and 2.0 min, respectively; sample pH value was set at 4.0 and the ionic strength of sample matrix did not be adjusted.

Table 1

Analytical performance of the proposed approach for PFSA and PFCAs.

Compounds	Linear range ^a (ng/L)	r^2	LOD (ng/L)	LOQ (ng/L)	Intra-day assay variability (RSD, %, n = 4)		Inter-day assay variability (RSD, %, n = 4)	
					Spiked concentration (ng/L)			
					Low standard ^b	High standard ^b	Low standard ^b	High standard ^b
PFBS	5.0–10000	0.9937	0.50	1.66	6.9	2.8	6.3	3.9
PFHXS	1.0–10000	0.9996	0.043	0.14	5.6	4.7	9.8	5.3
PFHPS	1.0–10000	0.9988	0.024	0.081	3.5	6.2	9.5	6.1
PFOS	1.0–10000	0.9986	0.039	0.13	9.6	8.0	6.7	6.9
PFDS	1.0–10000	0.9948	0.039	0.13	7.1	6.0	8.2	8.4
PFHA	0.4–4000	0.9991	0.036	0.12	9.3	8.7	5.1	9.7
PFOA	0.4–4000	0.9954	0.015	0.051	9.6	9.6	4.9	10
PFNA	0.4–4000	0.9999	0.010	0.034	6.7	9.7	7.9	8.4
PFDA	0.4–4000	0.9998	0.016	0.054	9.3	7.7	6.2	1.9

^a PFSA spiked levels included 1.0, 2.5, 5.0, 10.0, 20.0, 50.0, 100, 500, 1000, 5000 and 10000 ng/L; PFCAs spiked levels included 0.4, 1.0, 2.0, 4.0, 8.0, 20.0, 40.0, 200, 400, 2000 and 4000 ng/L.

^b For PFSA: low standard assayed at 10.0 ng/L level and high standard assayed at 1000 ng/L level. For PFCAs: low standard assayed at 4.0 ng/L level and high standard assayed at 400 ng/L level.

the same time, the synthesized reproducibility of the proposed one-pot approach was evaluated. The relative standard deviations (RSDs, n = 5) of EFs varied from 2.54 to 10.1%. It is worthy of being mentioned that the prepared MFCA possesses good life-span. It could be reused to capture studied analytes more than 50 times, and there was no obvious decline in the extraction performance during continuous application. The satisfactory fabrication reproducibility and life-span will be in favor of spreading the proposed MFCA/MSPE method in the analysis of PFCAs and PFSA.

3.3. Investigation of the extraction mechanism

Typically, there are alkyl and hydroxyl groups in the CNTs, thus,

hydrophobic and hydrogen bonding interactions play the key role in the extraction of PFCAs and PFSA [30,31]. However, in the present study, F-MWNTs were utilized as functional monomer to prepare fluorine-rich MFCA. As a result, the fluorine-fluorine interaction also contributed to the capture of PFCAs and PFSA. To prove that fluorine atoms in the MFCA played an important role in the enrichment of target analytes, fluoride-free adsorbent using CNTs (MCNTs) as functional monomer was synthesized. The extraction performance of MFCA and MCNTs for PFCAs and PFSA were compared under the same condition. As shown in Fig. S5, the MFCA exhibits better extraction performance than MCNTs. The EFs achieved on MFCA are 1.1–1.9 times higher than that obtained on MCNTs. The results well evidence that fluorine-fluorine, hydrophobic and hydrogen bonding interactions co-contribute to the

Table 2
Determination results and spiked recovery of current method for target analytes in water samples.

Samples	Spiked ^a	Detected (µg/L)/Recoveries (%RSD, n = 3)									
		PFBS	PFHXS	PFHPS	PFOS	PFDS	PFHA	PFOA	PFNA	PFDA	
River water	Blank	ND	ND	ND	0.016	0.059	ND	0.0078	0.0033	0.059	
	Low	0.046 92.2 (4.3)	0.048 96.6 (8.3)	0.054 108 (8.9)	0.074 115 (9.4)	0.10 83.7 (7.6)	0.018 90.0 (1.1)	0.024 81.8 (6.8)	0.021 87.2 (8.3)	0.079 97.7 (8.1)	
	Medium	0.40 80.4 (6.3)	0.56 111 (3.6)	0.52 104 (6.7)	0.56 109 (5.3)	0.59 107 (1.0)	0.18 90.0 (4.5)	0.18 84.8 (9.9)	0.20 100 (6.9)	0.26 102 (6.6)	
Lake water	High	4.2 83.8 (9.8)	5.7 113 (5.8)	5.2 104 (6.4)	6.0 119 (4.0)	5.9 116 (3.9)	2.1 105 (6.5)	1.9 96.7 (7.2)	2.0 102 (9.9)	2.0 97.7 (7.4)	
	Blank	ND	0.0090	0.052	0.052	0.10	ND	0.0048	ND	0.026	
	Low	0.047 94.7 (9.5)	0.063 107 (8.5)	0.096 87.1 (7.1)	0.11 107 (5.8)	0.15 91.7 (7.7)	0.019 95.0 (1.7)	0.021 82.4 (8.0)	0.027 103 (9.8)	0.042 80.4 (8.5)	
Waste water	Medium	0.41 82.7 (6.7)	0.60 118 (9.8)	0.54 98.7 (8.7)	0.63 116 (3.3)	0.68 115 (8.9)	0.18 90.0 (9.3)	0.21 103 (9.4)	0.21 105 (3.2)	0.20 87.0 (6.7)	
	High	4.8 95.2 (7.3)	5.9 118 (6.5)	5.6 111 (10)	4.6 90.8 (8.3)	5.9 116 (8.7)	1.7 85.0 (7.4)	2.2 109 (6.1)	5.0 100 (7.2)	2.4 119 (7.7)	
	Blank	ND	ND	ND	0.0091	0.016	ND	0.0092	0.023	0.055	
Tap water	Low	0.054 108 (8.6)	0.058 116 (6.6)	0.048 95.2 (5.1)	0.050 82.2 (4.8)	0.075 117 (7.7)	0.020 100 (6.8)	0.029 101 (1.7)	0.045 109 (8.0)	0.072 86.2 (4.5)	
	Medium	0.40 80.2 (8.7)	0.60 119 (4.4)	0.57 114 (3.1)	0.60 118 (3.9)	0.59 115 (9.2)	0.02 84.7 (9.1)	0.20 93.4 (3.7)	0.22 98.2 (0.84)	0.28 110 (3.2)	
	High	3.9 78.7 (5.0)	5.9 118 (2.8)	5.8 115 (8.0)	5.4 107 (9.1)	5.9 117 (5.9)	1.6 79.1 (3.8)	2.1 105 (5.7)	2.1 105 (8.5)	2.1 101 (9.7)	
Tap water	Blank	ND	0.026	0.013	0.017	ND	ND	0.0047	ND	ND	
	Low	0.044 87.7 (5.1)	0.048 115 (0.39)	0.070 113 (4.5)	0.071 108 (7.9)	0.054 108 (7.1)	0.017 86.9 (1.5)	0.024 94.3 (3.1)	0.021 105 (9.1)	0.022 112 (8.4)	
	Medium	0.39 78.9 (8.7)	0.40 80.8 (6.7)	0.55 107 (4.6)	0.57 110 (5.7)	0.56 112 (3.1)	0.18 92.2 (7.7)	0.23 111 (7.4)	0.17 85.0 (5.6)	0.22 110 (7.5)	
Tap water	High	3.9 77.5 (7.2)	4.5 89.2 (5.0)	0.6 114 (6.4)	5.8 116 (3.3)	5.8 116 (6.4)	2.2 111 (7.1)	2.3 117 (9.1)	2.1 105 (9.1)	2.2 110 (8.8)	

^a For PFBS: low standard spiked at 0.05 µg/L, medium standard spiked at 0.5 µg/L and high standard spiked at 5.0 µg/L. For PFCAs: low standard spiked at 0.02 µg/L, medium standard spiked at 0.2 µg/L and high standard spiked at 2.0 µg/L.

extraction of MFCA for PFCAs and PFSAs.

3.4. Approach validation

To validate the introduced MFCA/MSPE-HPLC-MS/MS approach, various experiments with regard to linearity, limits of detection (LODs), limits of quantification (LOQs) and precision were carried out under the most favorable conditions. The linear range was determined by spiking ultrapure water in the concentration range of 1.0–10000 ng/L for PFSAs and 0.4–4000 ng/L for PFCAs, and fixed the IS concentration of 20 µg/L. Calibration curves were plotted by the ratio of each analyte peak area to the peak area of its corresponding IS. The related data are presented in Table 1. As listed, the quantitative approach exhibits good linearity in the range of 5.0–10000 ng/L for PFBS, 1.0–10000 ng/L for PFHXS, PFHPS, PFOS and PFDS, 0.4–4000 ng/L for target PFCAs, with coefficient of determination (r^2) ranging from 0.9937 to 0.9999. The developed method also yielded satisfactory sensitivity. The limits of detection (LODs) calculated at a signal-to-noise ratio of 3 (S/N = 3) are in the ranges of 0.024–0.50 ng/L and 0.010–0.036 ng/L for PFSAs and PFCAs, respectively. The limits of quantification (LOQs) (S/N = 10) vary from 0.034 to 1.66 ng/L. At the same time, the approach precision was inspected according to the intra-day and inter-day assay variability. It can be seen from the Table 1 that the RSDs are in the ranges of 3.5–10%, depending on the analytes and fortified concentrations.

To evaluate the MFCA/MSPE procedure, matrix effect (ME) was also investigated. According to previous studies [32], matrix standard solutions and reagent standard solutions of 0.5, 5.0 and 50.0 µg/L were prepared and utilized to inspect the ME. As shown in Table S3, the %ME values for analytes varied from –16.6 to 19.3, which well suggested that there was no apparent ME after the treatment of MFCA/MSPE.

The above-mentioned results well imply that the established MFCA/MSPE-HPLC-MS/MS approach has super-sensitivity, good precision and negligible ME. Thus, it can be apply to monitor trace levels of PFCAs and PFSAs in water samples.

3.5. Assay of real samples

Based on the distinguished merits, the proposed MFCA/MSPE-HPLC-MS/MS method was applied to quantify trace levels of PFCAs and PFSAs in tap water, river water, waste water and lake water. As listed in Table 2, some of target analytes were detected in the four water samples. Although the concentrations are ng/L level, the pollution of PFCAs and PFSAs in waters should be attracted attention. To investigate the accuracy of current approach, recoveries with low, medium and high fortified levels were tested. The data displayed in Table 2 clearly indicate that recoveries are 80.4–116%, 80.4–119%, 78.7–118% and 77.5–117% for river water, lake water, waste water and tap water, respectively, depending on the spiked concentrations and analytes. Furthermore, the RSDs for repeatability vary from 1.0 to 9.8% for all target analytes in all samples. These results well evidence that the established MFCA/MSPE can effectively extract PFCAs and PFSAs in complex environmental matrices, and the proposed MFCA/MSPE-HPLC-MS/MS method is dependable and applicable in the monitoring of trace analytes in environmental water samples.

3.6. Comparison with previously reported approaches

To further illustrate the merits of the established method, the analytical features of the MFCA/MSPE-HPLC-MS/MS were compared with previously published analytical procedures (Table 3). As shown, the total extraction time (including adsorption and desorption time) spent in the current method is 11 min which lower than reported approaches [10,18,19,22,30,33–39]. The consumed organic solvent in the developed method is at the same level of SBSE/HPLC-MS/MS [18], micro-SPE (µ-SPE)/HPLC-MS/MS [33], MMF-SPME/HPLC-MS/MS [10] and LPME/HPLC-MS/MS [39], and less than other approaches

Table 3
Comparison of proposed method with reported methods for the analysis of PFSA and PFCAs in water samples.

Methods	Adsorbent	Extraction time (min)	Organic solvent consumption	LODs (ng/L)	Recoveries (%)	Ref.
SBSE/HPLC-MS/MS	VI-EDMA	70	0.3 mL methanol	0.06–0.40	80.1–122	18
μ -SPE/HPLC-MS/MS	porous polypropylene	45	0.2 mL acetone	0.02–0.08	64.0–127	33
SPE/HPLC-MS/MS	CNSs-COOH	35	7 mL acetone	0.01–1.2	82.2–113	30
SPE/HPLC-MS/MS	bamboo charcoal	44	12 mL acetone	0.01–1.15	83.4–117	34
SPE/HPLC-MS/MS	OASIS HLB	50	4 mL methanol	0.03–1.9	97.3–113	35
SPE/LC-MS/MS	fluorous sorbent	> 30	1 mL methanol	0.02–1.67	92.0–104	36
MMF-SPME/HPLC-MS/MS	MA/MMF	65	0.4 mL acetonitrile	0.40–4.40	80.8–119	10
MSPE/HPLC-MS/MS	Fe ₃ O ₄ @SiO ₂ -NH ₂ &F ₁₃	30	0.7 mL acetonitrile	0.029–0.099	90.0–106	37
MSPE/HPLC-MS/MS	(CTF)/Fe ₂ O ₃	18	3 mL acetone	0.62–1.39	84.1–105	22
MSPE/GC-MS	F ₁₇ Fe ₃ O ₄ @mSiO ₂	35	0.6 mL acetonitrile	55–86	93.0–107	38
MSPE/HPLC-MS/MS	Fe ₃ O ₄ @SiO ₂ @FBC	12	0.84 mL acetonitrile	0.01–0.06	89.3–111	19
LPME/HPLC-MS/MS	BHF	45	0.2 mL methanol	0.4–6.48	8.72–68.7	39
MSPE/HPLC-MS/MS	MFCAs	11	0.5 mL acetone	0.010–0.50	77.5–119	Proposed method

VI-EGDMA: poly (1-vinylimidazole-co-ethyleneglycol dimethacrylate) monolith.

CNSs-COOH: carboxylated carbon nanospheres.

(CTF)/Fe₂O₃: covalent triazine-based framework.

MA/MMF: monolithic adsorbent/multiple monolithic fiber.

[19,22,30,33–38]. At the same time, the proposed method exhibits better sensitivity than previously reported approaches except for SBSE/HPLC-MS/MS [18] and MSPE/HPLC-MS/MS [19]. What's more, the recoveries got in this study are better than μ -SPE/HPLC-MS/MS [33] and LPME/HPLC-MS/MS [39], and at the same level as other studies [10,18,22,30,33–39]. The comparison well suggests that the established MFCA/MSPE-HPLC-MS/MS approach presents some merits including quick and simple extraction procedure, high sensitivity and eco-friendliness in the measurement of trace levels of PFCAs and PFSA.

4. Conclusion

In this work, fluorine-rich magnetic CNTs were successfully and facilely prepared and were utilized as the reusable adsorbent for MSPE of PFCAs and PFSA in environmental water samples. The prepared MFCA exhibited good dispersibility in aqueous samples and satisfactory paramagnetic behavior. Most importantly, the MFCA/MSPE displayed excellent extraction performance for PFCAs and PFSA due to the multi-interactions such as fluorine-fluorine, hydrophobic and hydrogen bonding interactions co-contributed to the enrichment. Under the optimal conditions, the introduced MFCA/MSPE-HPLC-MS/MS method achieved wider linearity, low LODs/LOQs and good precision. Finally, the proposed method was successfully applied to quantify trace levels of target analytes in various environmental water samples. Satisfying spiked recovery (77.5–119%) and repeatability (RSDs were in the range of 1.0–9.8%) were achieved. Based on the prominent advantages such as facile fabrication of adsorbent, quick extraction procedure, high sensitivity and low consumption of organic solvent, the current MFCA/MSPE-HPLC-MS/MS approach will be useful and reliable in the monitoring of trace levels of PFCAs and PFSA in waters and other samples.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2019.122392>.

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