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Analysis of perfluorooctane sulfonate and perfluorooctanoic acid with a mixed-mode coating-based solid-phase microextraction fiber

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ABSTRACT

A novel mixed-mode coating-based solid-phase microextraction (SPME) fiber was prepared by chemical bonding dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride and 3-(trimethoxysilyl)-1-propanamine, the sol–gel precursors, on an anodized Ti wire, aiming to effectively adsorb perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). The anodized Ti wire with uniform TiO_2 nanotube arrays provides high mechanical strength and strong adhesion to the mixed-mode coating. The prepared fiber shows excellent organic solvent stability due to the covalent bonding between the coating and the fiber, and significantly higher extraction efficiency than the commercial fibers, 100 μm polydimethylsiloxane and 85 μm polyacrylate fiber, due to the synergistic extraction effects of the coating functional groups. Good linearity (R^2=0.9994 for PFOS, R^2=0.9992 for PFOA) was obtained with detection limits of 2.5 and 7.5 pg mL^{-1} for PFOS and PFOA, respectively. Recoveries were in the range of 88%–102%. The proposed method was successfully applied in the analysis of PFOS and PFOA in a local river with the results of 0.05 and 0.06 ng mL^{-1}, respectively.

1. Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) consisting of a hydrophobic fully fluorinated alkyl chain and a hydrophilic sulfonate group or carboxylic group belong to the family group of perfluorinated compounds (PFCs). The molecular structures provide PFOS and PFOA unique properties such as chemical stability and both water and oil repellency. PFOS and PFOA have been widely used in the manufacture of textiles, papers, carpets, food packaging and firefighting foams [1]. However, PFOS and PFOA are very persistent in the environment and resistant to degradation by physical or chemical mechanisms, and thus can be accumulated in biotic environment and show potential toxic effects on organisms [2–4]. The widespread occurrence of PFOS and PFOA has been reported in a variety of environmental and biological samples including water, sediment, wildlife, and human samples at different concentration levels [5–8].

The analytical methods for the trace analysis of PFOS and PFOA in various environmental matrices have been developed since 1960s [9], including fluorine nuclear magnetic resonance (^{19}F NMR) [10], attenuated total reflected Fourier transform infrared spectroscopy (ATR-FTIR) [11], capillary zone electrophoresis (CZE) [12], gas chromatography–mass spectrometry (GC–MS) [13,14] and liquid chromatography–mass spectrometry (LC-MS) [5,15]. There are some intrinsic drawbacks for most of the developed methods. For example, ^{19}F NMR method is nonspecific because it determines the presence of CF_2 and CF_3 moieties in a sample; CZE method coupled with indirect photometric detection possesses low sensitivity with LODs of 0.6–2.4 ppm as it determines analytes through the decrease in the background absorbance resulting from the displacement of a chromophore probe ion added in the background electrolyte with an analyte ion; GC–MS method requires derivatization procedure before analysis. On the other hand, LC–MS and LC–MS/MS methods have become the most intensively applied methods for the analysis of PFOS and PFOA. In particular, LC–electrospray ionization-MS/MS (LC-ESI-MS/MS) method has been reported in a majority of researches due to its superior advantages of high selectivity and sensitivity, wide linear range and high precision. However, the high purchase and maintenance costs have become the limitation to routine analyzes for LC–ESI-MS/MS method [16]. LC with single-quadrupole MS method has lower selectivity than LC–ESI-MS/MS method but is also considered to be a sensitive method, just requiring thorough clean-up of the sample [6]. In addition, matrix constitutes of complicated samples such as waste water, sewage sludge and biological tissues may cause the enhancement or suppression of analyte signals in the quantification process for LC–ESI-MS and LC–ESI-MS/MS methods. Therefore, sample extraction and clean-up procedures are very essential prior to analysis for the elimination of interferences from sample matrices.

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Solid-phase extraction (SPE) has been the most commonly used sample preparation techniques for the enrichment and clean-up of analytes in various sample matrices because of its high preconcentration factors, low consumption of organic solvents and ease of operation [17]. However, the multi-step SPE procedures have some drawbacks such as time-consuming, labor-intensive, and high relative standard deviation, which limit its further applications. Considering the limitations of SPE, other extraction techniques have been applied as the alternative extraction methods for the analysis of PFOS and PFOA in aqueous matrices such as ion pair extraction (IPE) [18,19] and vortex-assisted liquid–liquid microextraction (VALLME) [20]. In recent years, solid-phase microextraction (SPME), as a simple, rapid, and solvent-free sample preparation technique, has been successfully applied in the analysis of a wide range of organic compounds [21–23]. Nonetheless, few papers related to determination of anionic compounds have been published. Saito et al. developed an in-tube SPME method to determine PFOS and PFOA by using an open tubular fused-silica capillary with an inner surface coating as the SPME device [24]. However, it is not suitable for the extraction of complicated samples by in-tube SPME method because the capillary used for the extraction is prone to be clogged.

In this work, a SPME method for the determination of PFOS and PFOA in environmental samples was developed by sol–gel deposition of a mixed-mode coating to an anodized Ti wire support. The mixed-mode coating is composed of 3-(trimethoxysilyl)-1-propanamine and dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride which provide a synergistic effect of hydrophobic interactions and electrostatic interactions, enhancing the selectivity and the extraction capability toward PFOS and PFOA. The anodized Ti wire has high mechanical strength and rich Ti–OH groups. The use of anodized Ti wire as support can not only overcame the fragile drawback of commonly used fused-silica rod but also can form stable coating through strong covalent bonding with the Ti–OH groups.

2. Experimental

2.1. Chemicals and reagents

Ti wire (Φ 0.28 mm, 99.9% in purity) was purchased from Lihua Non-ferrous Metals Co., Ltd. (Baoji, China). Hydrofluoric acid (40.0%) was purchased from Tianjin Fuyu Fine Chemicals Co., Ltd (Tianjin, China). 3-(Trimethoxysilyl)-1-propanamine (APTES) was purchased from Acros Organics (NJ, USA). Dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (C_{18}-TMOS) and trifluoroacetic acid (TFA) were purchased from Aladdin-reagent (Shanghai, China). Perfluorooctane sulfonic acid potassium salt (PFOS-K) and perfluorooctanoic acid (PFOA) were obtained from Fluka (Milwaukee, MI, USA). HPLC grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). Ultrapure water was prepared by MilliQ system (Bedford, USA). Stock solutions containing 1 mg mL^{-1} PFOS and PFOA were prepared using methanol as the solvent and stored at 4 °C in darkness. Aqueous working standard solutions were prepared by diluting the stock solutions with methanol and then further diluting with ultrapure water to the required concentration.

2.2. LC–ESI-MS analysis

The determination of PFOS and PFOA was performed with a Waters 600 series liquid chromatograph, equipped with a Waters ZQ4000 mass detector (Milford, Mass, USA). A XB-C_{18} column (150 mm × 4.6 mm, particle size 5 μm; Welch Materials Inc., USA) was used for the separation of PFOS and PFOA. Methanol (A) and 10 mM ammonium acetate buffer solution (B) (pH = 6.0) were employed as mobile phase. The elution gradient was: 0–4 min, from 72% to 95% (A) linearly at flow rate of 1.0 mL min^{-1}; 4–7 min, from 95% to 72% (A) linearly at flow rate of 1.0 mL min^{-1}; 7–10 min, retain in 72% (A). The injection volume was 20 μL. The MS analysis was operated at the negative mode under the conditions as follow: capillary voltage: 3.0 kV, cone voltage: 30 V, temperature of desolvation and electrospray source were 300 and 120 °C, respectively; nitrogen was used as both nebulizing gas and desolvation gas at flow rates of 5 and 350 L/h, respectively; mass scan range, m/z 100–550; selected ion recording (SIR), m/z 499 (PFOS) and 369 (PFOA).

2.3. Preparation of mixed-mode SPME fiber coating.

The anodized Ti wire was prepared according to our previous work [25]. The sol solution was prepared by mixing 100 μL of APTES, 100 μL of C_{18}-TMOS, 47 μL of methanol, 19.3 μL of H_2O, and 25 μL of TFA in a polypropylene tube. This mixture was stirred for 12 h, and then used for fiber coating. The anodized Ti wire was vertically dipped into the sol solution for 20 min at room temperature and then taken out to be dried. This coating procedure was repeated for ten times. Finally, the resulted anodized Ti (SPME fiber with mixed-mode coating) wire was placed in a desiccator for overnight at room temperature. The SPME fiber was conditioned at 120 °C for 2 h before use. Surface structure and composition characterization of the SPME fiber and anodized Ti wire were obtained using scanning electron microscope (JSM 6700F; JEOL, Tokyo, Japan) and Fourier transform infrared spectrophotometer (WQF-410; Braic Crop, China).

2.4. SPME procedure

The SPME fiber was assembled to a commercial SPME device (Supelco, Bellefont, CA) and was conditioned for 30 min in methanol. The extraction was performed in a 25 mL glass vial with PTFE-coated septa containing 20 mL sample solution. The SPME fiber was immersed in the sample solution through the septa for 60 min under stirring. The ionic strength and pH value were adjusted with sodium chloride and phosphate buffer. After extraction, the SPME fiber was immediately dipped in 100 μL of methanol for solvent desorption, and 20 μL of the desorption solution was injected to the HPLC system for analysis.

2.5. Environmental water samples

Environmental water samples (surface water) were collected from Xiangjiang River (Changsha, Hunan province), filtered through a 0.45 μm membrane and stored in an amber glass bottle at 4 °C prior to analysis.

3. Results and discussion

3.1. Characterization of the proposed SPME fiber

Ti wire has been reported as SPME fiber support because of its high mechanical strength and ease of functionalization via Ti–OH groups provided by the oxidation layer on the surface of Ti wire [26–28]. However, the spontaneous oxidation layer is usually very thin and irregular. In this work, TiO_2 nanotube arrays were in situ fabricated on the surface of Ti wire by anodization of Ti. The surface morphology of the anodized Ti wire before and after sol–gel coating is shown in Fig. 1. The inset of Fig. 1a shows that perpendicularly orientated and uniform TiO_2 nanotubes with a pore size of ~100 nm are formed on the Ti surface, which results in

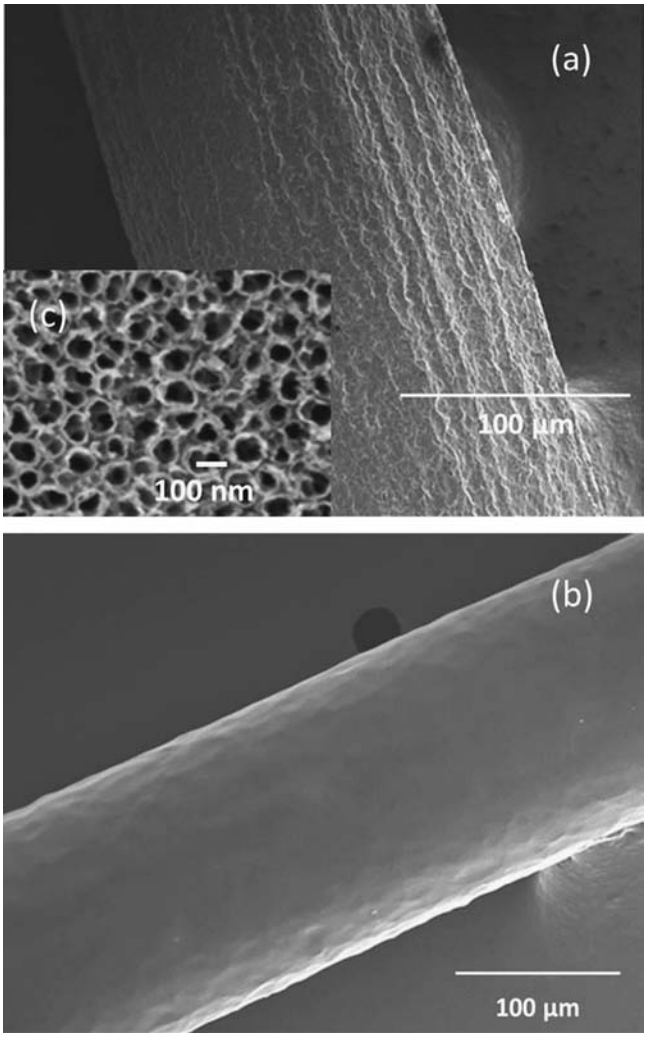

Fig. 1. SEM images of the anodized Ti wire before (a) and after (b) being modified with the mixed-mode coating, and the morphology of TiO_2 nanotube formed on the anodized Ti wire (c).

a rough surface of the anodized Ti wire with a high surface area benefiting the sol–gel coating. The treatment of the anodized Ti wire in alkaline solution formed Ti–OH groups by which APTES and C_{18}-TMOS, the sol–gel precursors, were chemically bonded on the Ti surface. The as-prepared fiber is therefore with high mechanical strength and stable coating. Fig. 1b shows the SEM image of the resulting sol–gel coated fiber. An integrated and uniform coating is obtained on the surface of the anodized Ti wire. The thickness of the coating is ~5 μm estimated from the SEM image. The coating bears several kinds of functional groups including aminopropyl group, octadecyl group and quaternary amine group. These functional groups can provide various interactions between the target compounds and the coating, such as hydrophobic interaction, electrostatic interaction, and hydrogen bonding, making the coating a mixed-mode adsorbent that can selectively bind PFOS and PFOA.

The formed coating was further characterized by FT-IR spectra as shown in Fig. 2. The adsorption bands at 3436 cm^{-1} corresponds to the combination of N–H stretching of amino groups and O–H stretching of silanol groups. The N–H bending vibration of amino groups appeared at 1604 cm^{-1}. The characteristic features of C_{18}-TMOS were the absorption bands corresponding to C–H stretching vibrations of methyl and methylene groups at 2933 cm^{-1} and 2860 cm^{-1} respectively, and corresponding to C–H bending

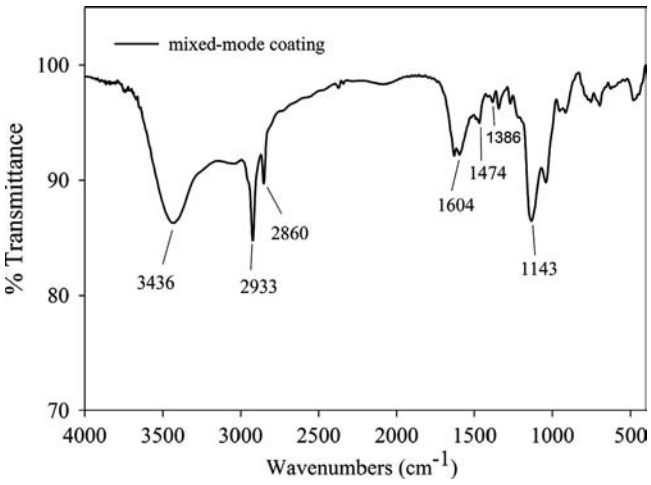

Fig. 2. The FTIR spectrum of the mixed-mode coating.

vibrations of methyl and methylene groups at 1474 cm^{-1} and 1386 cm^{-1}, respectively. The absorption bands at 1143 cm^{-1} are ascribed to Si–O–Si stretching vibrations. These characteristic adsorption peaks further confirm the successful binding of the mixed-mode coating to the fiber substrate.

3.2. Optimization of SPME procedure

The adsorption ability of the SPME fiber toward PFOS and PFOA are affected by extraction conditions such as sample volume, extraction time, sample solution pH, ionic strength, and desorption conditions. The extraction conditions were optimized firstly to achieve the best extraction efficiency.

Since SPME is an equilibrium extraction technique, the maximum analytes extracted to the coating are obtained when the distribution equilibrium of anlytes between sample matrix and fiber coating is achieved. The extraction time profiles of PFOS and PFOA are shown in Fig. 3a. The extracted amounts (corresponding to peak area) of both PFOS and PFOA increase with increasing the extraction time, and the equilibrium arrives at about 60 min. Therefore, 60 min was chosen as the extraction time for the subsequent experiments.

The influence of the sample solution pH on the extraction efficiency was investigated in the pH range of 2–8. As shown in Fig. 3b, the extraction of PFOA and PFOS is pH-dependent, higher extraction efficiency is achieved in a more acidic solution. The extraction efficiency is affected by pH through two ways: one is to affect the dissociation of the target compounds; and another is to affect the surface charges of the fiber coating. According to the reports [29,30], the pKa values of PFOA and PFOS are −0.1 and −3.27, respectively. Thus, the two analytes are mainly present as anions in the tested pH solutions, and the pH effects are mainly due to the charge change in the fiber coating rather than protonation/ deprotonation of the analytes [31]. The charge of the fiber coating are pH-dependent, more positive charge in a more acidic solution, due to the protonation of amino groups and the reduced dissociation of residual silanol groups at low solution pH. Therefore, pH 2.0 was chosen as the sample solution pH in the following experiments.

The sample volume of 20 mL was chosen by referring the work by Pawliszyn [32]. Based on his work, the extraction efficiency increased with increasing the sample volume upto a plateau where the extraction was saturated. A thinner coating thickness needed a smaller sample volume to reach the equilibrium. In his work, the extraction equilibrium was built up in 20 mL sample volume for a coating thickness of 7 μm. As for a coating thickness

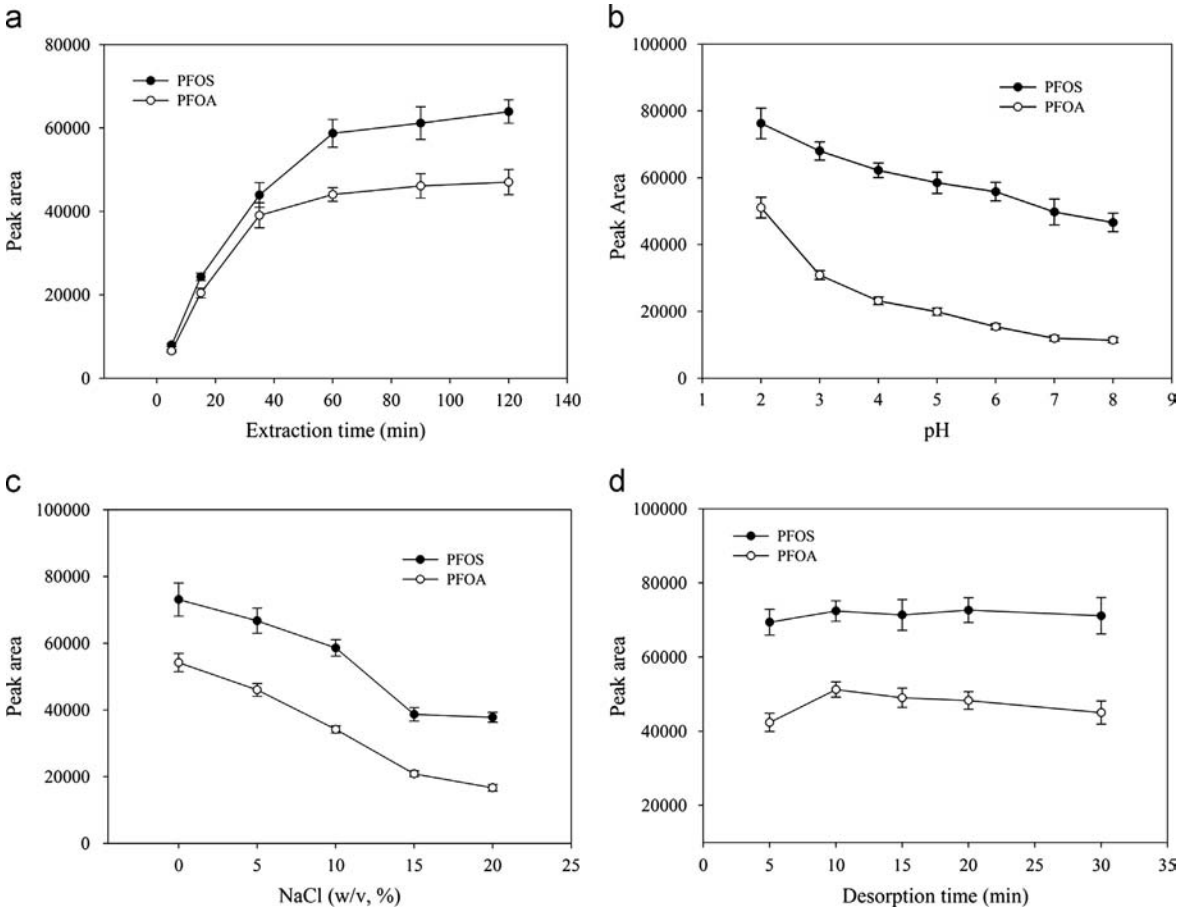

Fig. 3. Effect of (a) extraction time, (b) sample solution pH, (c) ionic strength and (d) desorption time on the extraction efficiency of the fiber for SPME of PFOS and PFOA (1 ng mL^{-1}).

of 5 μm in our work, the sample volume of 20 mL should be sufficient to reach the equilibrium, and no further optimization of sample volume was carried out.

It is known that addition of salt into the sample solution can either increase or decrease the extraction efficiency depending on the nature of the analytes and the fiber coating. For ionic compounds, increasing ionic strength of the sample solution can usually improve its activation state in water, and thus increase the solubility in water and decrease the distribution in the fiber coating. The effect of ionic strength on the extraction efficiency was investigated with addition of NaCl at concentrations ranging from 0% to 20% (w/v). As shown in Fig. 3c, the extraction efficiency for both PFOS and PFOA decreases with increasing the salt concentration. For a positively charged coating surface, increasing the ionic strength tends to screen the electrostatic attraction between the negatively charged PFOS and PFOA molecules and the surface due to the electrical double layer compression [33]. Therefore, no salt was added to the sample solution in the subsequent experiments.

Desorption conditions including desorption solvent and desorption time were optimized to ensure a complete desorption of the analytes from the fiber coating. In consideration of the compatibility with HPLC, three water miscible organic solvents (methanol, acetonitril and acetone) were investigated as the desorption solvent and the desorption volume was 100 μL. Methanol has the maximum extraction efficiency toward PFOS and PFOA, and are thus chosen as the desorption solvent. Fig. 3d shows the desorption profiles with the desorption time ranging from 5 to 30 min. PFOS and PFOA could be completely desorbed within 10 min. In order to make sure a completely desorption of the analytes, 15 min was adopted as desorption time in the subsequent experiments.

3.3. The solvent stability of the fiber

When coupled to HPLC, the SPME fiber is required to be dipped into organic solvents to desorb the extracted analytes, thus the coating stability in solvents is very important. The fiber coating stability in methanol, acetonitrile, acetone and n-hexane was investigated as they represent various polarities. The SPME fiber was immersed into the organic solvents overnight, and then applied to extract analytes from sample solutions spiked with PFOS and PFOA. A control experiment was carried out under the same condition but without immersion of the SPME fiber in organic solvents. Compared to the control, there is no loss in the extraction efficiency after exposure to these organic solvents for overnight. The high stability of the SPME fiber towards organic solvents can be attributed to the chemical bonding between the mixed-mode coating and the anodized Ti wire.

3.4. Comparison of extraction efficiency between proposed SPME fiber and other fibers

The extraction of PFOS and PFOA from aqueous samples using the proposed fiber, C_{18}-functionalized fiber, and NH_2-functionalized fiber was carried out under their optimum condition to compare their extraction efficiencies. The results are shown in Fig. 4. As can be seen, the three fibers exhibit different affinities to

the analytes. Among these fibers, the highest extraction efficiency (expressed as peak area) is obtained using the proposed fiber. The C_{18}-functionalized fiber also shows considerable extraction capability for the analytes due to the hydrophobic interactions. The NH_2-functionalized fiber provides the smallest extraction capability among them. It can be found that both octadecyl groups and protonated amino groups on the fiber surface were favorable for the extraction of anionic PFOS and PFOA owing to the hydrophobic interactions and electrostatic attractions. Therefore, it was reasonable to conclude that the proposed fiber (C_{18}/NH_2-functionalized fiber) exhibited the highest affinity to the analytes because of the cooperation effects of hydrophobic interaction and electrostatic attractions, that is, a mixed mode mechanism dominated the extraction process with the proposed fiber.

In addition, the extraction performance of the proposed SPME fiber was also compared with those of 100 μm PDMS and 85 μm PA commercial fibers, two commercial fibers suitable for extraction of non-polar and polar compounds, respectively (shown in Fig. 4). The PA fiber shows little extraction efficiency toward both PFOS and PFOA, while the PDMS fiber exhibits a higher extraction efficiency toward PFOS and PFOA than PA fiber. The reason is likely because the PDMS fiber is more hydrophobic than PA, and has a higher affinity to PFOS and PFOA. The proposed SPME fiber shows a significantly higher extraction efficiency than PDMS and PA fibers. The absolute recoveries (determined as the ratio of the amount extracted by SPME versus total amount of standard which was initially spiked in sample) obtained using the proposed fiber were calculated as (8.67 ± 0.52)% for PFOS and (12.39 ± 0.51)% for PFOA, respectively. The extraction efficiency of the proposed SPME fiber is four times that of PDMS and 55 times that of PA. The significant enhancement in extraction efficiency can be attributed to the cooperative effects of hydrophobic interaction and electrostatic interaction which originated from a variety of functional groups of the mixed-mode coating leading to strong adsorptions toward PFOS and PFOA.

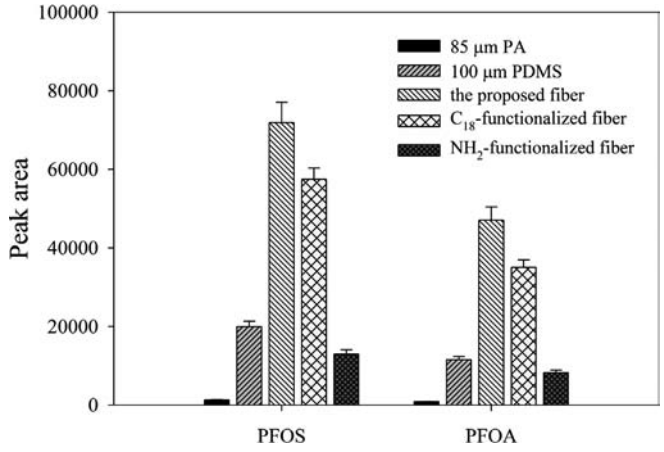

Fig. 4. Comparison of the extraction efficiencies of SPME fiber with other fibers.

Table 1
Analytical parameters of the proposed SPME-LC–MS method for the determination of PFOS and PFOA.

Compounds	Linear range (ng mL^{-1})	R^2	LODs[c] (pg mL^{-1})	Repeatability (n=5, %) (single fiber)	Reproducibility (n=3, %) (fiber to fiber)
PFOS	0.01–10	0.9994	2.5	3.6	6.5
PFOA	0.05–5	0.9992	7.5	4.2	8.3

3.5. Analytical evaluation

Under the optimized conditions, analytical performances of the SPME-LC-MS method for the determination of PFOS and PFOA including linear range, correlation coefficient and limits of detections (LODs) were studied. The results are shown in Table 1. The linear range is 0.01–10 ng mL^{-1} with a good correlation coefficient larger than 0.999. The LODs, calculated as three times of signal-to-noise (n=3), are 2.5 and 7.5 pg mL^{-1} for PFOS and PFOA, respectively. The repeatability of a single fiber was evaluated by determination of standard solutions spiked with PFOS and PFOA at 1 ng mL^{-1} with 5 replicates. The relative standard deviations (RSDs) are 3.6% for PFOS and 4.2% for PFOA. The fiber to fiber reproducibility of three different fibers prepared in the same way was also studied, giving RSDs of 6.5% for PFOS and 8.3% for PFOA.

In order to evaluate the applicability in the analysis of environmental water samples, the fiber was applied in the extraction of PFOS and PFOA from water samples collected from Xiangjiang River (Changsha, China). Both PFOS and PFOA were detected in Xiangjiang River water with concentrations of 0.05 and 0.06 ng mL^{-1}, respectively. The typical chromatograms of river water samples spiked with and without PFOS and PFOA are shown in Fig. 5. Recovery experiments were performed with real water samples spiked at three concentration levels (0.1, 0.5, and 1 ng mL^{-1}) to evaluate the reliability of the proposed SPME-HPLC–MS method. The analytical results are summarized in Table 2. The recoveries for the spiked samples are in the range

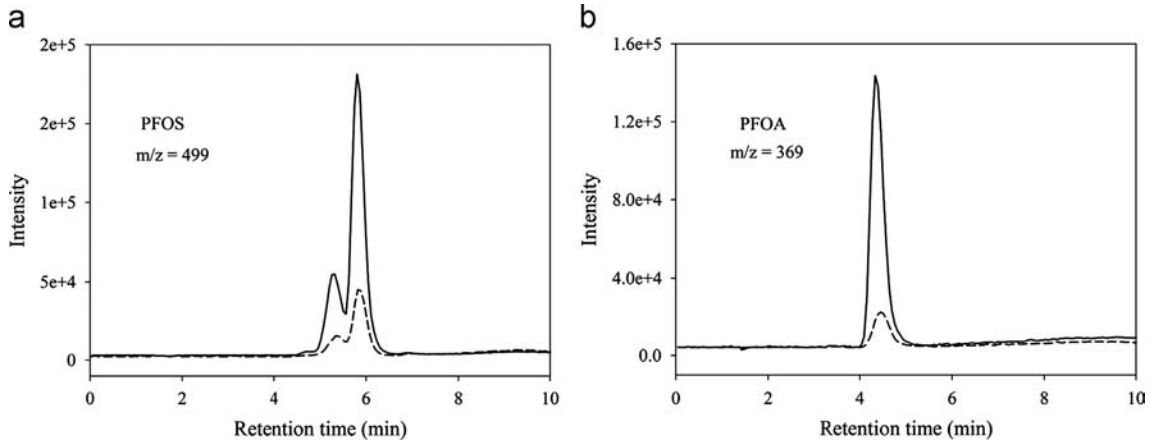

Fig. 5. LC–MS chromatograms of PFOS (a) and PFOA (b) obtained in the SIR mode for the SPME of spiked (solid line) and unspiked (dashed line) river water samples. Spiked concentration is 1 ng $mL^{-1}$for each compound.

Table 2
Analytical results for the determination of PFCs in real water samples.

Compounds	Founded in water samples (ng mL^{-1})	RSD (%)	Spiked (ng mL^{-1})	Recovery[a] (%)
PFOS	0.05	4.8	0.1	92 ± 3.2
		–	0.5	102 ± 6.8
		–	1.0	95 ± 4.7
PFOA	0.06	5.2	0.1	91 ± 5.2
		–	0.5	88 ± 4.8
		–	1.0	95 ± 7.3

[a] Standard deviation for three determinations.

of 92%–102% for PFOS and 88%–95% for PFOA with RSDs less than 7.3%.

4. Conclusions

A SPME fiber was prepared by covalently bonding a designed mixed-mode adsorbent to a TiO2 NTs/Ti wire through sol–gel process aiming to the determination of PFOS and PFOA in water samples. The TiO_2 NTs/Ti wire provides high strength, large surface area, and rich Ti–OH groups benefiting the chemical bonding of the coating. The proposed SPME fiber exhibits high organic solvent stability and significantly higher extraction efficiency than the commercial extraction fibers, 100 μm PDMS and 85 μm PA. Low LODs (2.5 pg mL^{-1} for PFOS and 7.5 pg mL^{-1} for PFOA) and good linearity ($R^2=0.9994$ for PFOS, $R^2=0.9992$ for PFOA) were achieved. The proposed SPME-LC-MS has been successfully applied in the analysis of PFOS and PFOA in local river water samples, with the content of 0.05 and 0.06 ng mL^{-1} for PFOS and PFOA, respectively.

Acknowledgments

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