A simple strategy based on fibers coated with surfactant-functionalized multiwalled carbon nanotubes to improve the properties of solid-phase microextraction of phenols in aqueous solution

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Abstract

A functionalized multiwalled carbon nanotube (MWCNT)-coated solid-phase microextraction (SPME) fiber was developed for concentrating analytes in aqueous samples. Sodium deoxycholate(NaDC) was used as a wrapping layer for non-covalent modification of MWCNTs. Non-covalent bonding between the MWCNTs and sodium deoxycholate changed the electrical and steric resistance of the MWCNTs, and improved their solubility and dispersibility. To investigate the capability of this MWCNTs/NaDC SPME fiber, it was applied to the analysis of phenols in aqueous solution. After extraction, the analytes were desorbed in an acetonitrile–water solution and analyzed using high-performance liquid chromatography. The MWCNTs/NaDC fiber exhibited a response two to six times that of a commercial fiber for phenols. The hydrogen interactions with the analytes and the large surface area of the MWCNTs facilitated analyte adsorption with good selectivity and reproducibility. Under the optimum extraction conditions, the MWCNTs/NaDC fiber had a good linear range (1−100 ng/mL), repeatability for the extractions (relative standard deviation = 4.9%−7.1%, n = 3), low limits of detection (0.15−0.30 ng/mL), and satisfactory recoveries (80.3%−95.4%). This is an accurate and cost-effective pretreatment method.

Introduction

Phenols are persistent contaminants that are soluble in water. [1-3] Contamination with organic pollutants such as phenols is a common environmental problem. To determine these compounds at ultratrace levels, suitable enrichment procedures are needed. Liquid–liquid extraction and solid-phase extraction are well-established procedures for concentrating analytes in aqueous samples.[4] However, they are time-consuming and require medium to large volumes of high-purity organic solvents that are potentially toxic and expensive. [5]

In the past few years, solvent-minimized, membrane-based extraction techniques, such as solid-phase microextraction (SPME), have been developed for the extraction of phenols.[6-9] SPME has several obvious merits: simplicity of operation; a short extraction time; solvent-free process; and the possibility of full automation, which reduces contamination of the original sample and loss of analytes.[10, 11] In addition, using SPME, samples can be collected in situ, and reliable results can be obtained for analytes present in trace quantities.[12] In these methods, commercial fibers such as 50 μm carbowax/templated resin and 60 μm polydimethylsiloxane (PDMS)/divinylbenzene are widely used for analysis of environmental water samples.[13,14] However, these commercial fibers have some drawbacks as they show thermal instability, can be stripped off from the substrate, are easily broken, and swell in organic solvents.[15] The stationary phase coated onto the fiber is critical in improving the SPME performance.[16] To obtain high extraction efficiencies for these compounds, various types of SPME coatings have been investigated, including molecularly imprinted polymers,[17] ionic liquids,[18] metal−organic frameworks,[19] and carbon materials.[20-23]

Multiwalled carbon nanotubes (MWCNTs) have unique electronic, mechanical, and chemical properties and have attracted attention in recent years.[24−28] MWCNTs contain internal cavities that are large enough to allow analytes to penetrate, and their surfaces and interspaces within nanotube bundles provide excellent sorption.[29] Because of their unique properties and their hydrophobic character, MWCNTs are superior adsorbents for aliphatic hydrocarbons,[30] alkylphenols,[31] phthalates,[32] and volatile organic compounds.[33, 34] Non-covalent modification of the outer walls of MWCNTs with surfactants or natural macromolecules can increase their solubility and dispersibility, which may alter the adsorption selectivity from that of the original MWCNTs.

In this study, a new approach was applied to prepare coated MWCNTs for use in SPME of phenols from environmental samples. The combination of SPME with high-performance liquid chromatography (HPLC) provides a rapid and sensitive method for the determination of phenols in aqueous solution, and was applied to seawater samples from the South China Sea and Wastewater.

Experimental

2.1 Reagents and Materials.

Phenol, *p*-nitrophenol (4-NP), *o*-nitrophenol (2-NP), 2, 4-dimethylphenol (2,4-DMP), and 2,4-dichlorophenol (2,4-DCP) standards were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrogen nitrate (AR grade, purity 65%−68%) and sulfuric acid were purchased from Guangzhou Chemical Reagents (Guangzhou, China). HPLC-grade acetonitrile (ACN), methanol, isopropanol, and formic acid were from Thermo Fisher Scientific Co. (Waltham, MA). Fused-silica fibers (120 μm i.d.) were obtained from Ruifeng Chromatographic Device Co. Ltd (Yongnian, China). MWCNTs (20−30 nm, purity > 98% mass fraction) were purchased from Sigma−Aldrich (St. Louis, MO). SPME hand shank and PDMS fiber (Supelco, USA) were purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China). Acrylic ester was obtained from Guangzhou Chemical Reagents. Sodium deoxycholate (NaDC), Triton X-100, and 3-aminopropyltriethoxysilane were purchased from Aladdin Chemistry (Shanghai, China). Ultrapure water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA). All other chemicals were of analytical grade.

2.2 Instruments and conditions

Sample analyses were carried out using a Waters (Milford, MA) e2695 system equipped with a 2998 photodiode array detector. A C18 column (250 mm × 4.6 mm i.d., 5 μm particle size, Agela) was used for the chromatographic separation. The mobile phase was a mixture of 0.2% acetic acid (A) and acetonitrile (B) at a flow rate of 1.0 mL/min. We used the following gradient elution: 0−5 min, A = 70% and B = 30%; 20 min, A = 20% and B = 80%; 21 min, A = 10% and B = 90%; 25 min, A = 10% and B = 90%; and 26−30 min, A = 70% and B = 30%. The column temperature was 30 °C and the wavelength was 280 nm.

Transmission electron microscope (TEM) images were recorded using a JEM 2100 instrument (JOEL, Tokyo, Japan). SEM observation was executed using a Hitachi S-3000N(Japan) scanning electron

microscope after fixing the samples on a brass holder and coating them with gold. Fourier transform infrared (FT-IR) spectra of the materials were obtained on a TENSOR 27 spectrometer (Bruker, Ettlingen, Germany). The freeze-dried samples were mixed with KBr compressed into semitransparent KBr pellets before the measurement. XRD spectra were recorded on a D8 Advance X-ray diffractometer ((Bruker, Germany) with Cu-K a radiation(λ= 0.154 nm). The XRD was operated at 40 kV and 40 mA in a step scan mode. The scanning speed was 0.025°/s. XRD measurements were performed over a 2θrange of 10-40°.

2.3 Synthesis of functionalized MWCNTs.

Functionalized MWCNTs (MWCNTs/NaDC) were synthesized as follows. First, 2 g of pristine MWCNT powder was added to 100 mL of a mixture of HNO_3 and H_2SO_4 (1:3, v/v). The mixture was then heated in a water bath at 80 °C for 3 h with stirring. The processed MWCNTs were collected by filtration and washed with deionized water until the pH approached neutral, and then dried at 60 °C for further use. Second, the processed MWCNTs were modified respectively by cetyl pyridinium chloride monohydrate (CPC), sodium deoxycholic acid (NaDC), polyethylene glycol octyl phenyl ether(tritonx-100), with a mass ratio of 1:1.The suspension was ultrasonic for 30 min in the ultrasonic crushing instrument, and then by magnetic stirring for 12h. The resulting solution was filtered, washed with ultrapure water, and dried at 60 °C for 24 h. Two other surfactants were investigated for comparison and method optimization (see Supplementary Material). Figure 1 presents the synthetic strategy for the MWCNTs/NaDC.

2.4 Preparation of the MWCNTs/NaDC SPME fiber.

The MWCNTs/NaDC SPME fiber was fabricated using the following processes. First, a silica fiber was cut to 10 cm. Then, one end (2.0 cm) was burned on an alcohol blast burner to remove the protecting polyimide layer. Subsequently, the fiber was washed thoroughly with 10mL of water and 10mL of acetonitrile in sequence, and dried at 60°C for 12h. Next, the fiber was parallelly dipped in epoxy glue for 30 s, and then coated. The unnecessary epoxy glue was removed with a tweezers to generate a homogeneous film of glue. And the equal in quality of MWCNT/NaDC was immobilized on every silica fiber by silicone glue. The coated section was 2.0 cm long. Finally, the proposed SPME fiber was heated to 200 °C for 5 h to remove any contaminants.

2.5 SPME procedure.

For phenol analysis, all extraction experiments were carried out in a 10-mL working solution, which was introduced to a 20-mL amber vial capped with a polytetrafluoroethylene-coated septum. The solution was agitated at 1100 rpm by magnetic stirring with a Teflon-coated stir bar. To perform the extraction, the MWCNTs/NaDC-coated SPME fiber or a commercial PDMS fiber was immersed in a water sample for a certain time. After extraction, the fiber was removed and placed in a 5-mL vial. Then, the analytes were desorbed in a 2 mL solution of 70% ACN solvent, and 10 μL of the stripping solvent was used for HPLC analysis. The chromatographic peak area was used to evaluate the extraction efficiency under different conditions. The MWCNTs/NaDC SPME fiber could be reused after rinsing with the 70% ACN solvent. To

avoid memory effects, the SPME fibers were desorbed in a 70% ACN solvent after extraction until the desorption solution had a flat baseline on injection into the HPLC.

2.6 Analysis of real samples.

Water samples were collected from the South China Sea near Baishamen, Yangpu, and Holiday Beach. Wastewater sample were collected from a chemical plant. These samples were analyzed immediately after sampling without any pretreatment.

2.7 Enrichment factor of SPME.

For the equilibrium adsorption experiments, the enrichment factor of SPME depended on the interactions (i.e., π−π, hydrogen bonding, and electrostatic) between the analytes and MWCNTs/NaDC. The enrichment factor (EF) was defined as the ratio of the target-analyte sensitivity after extraction with regard to the initial amount. And the chromatographic peak area was used for quantification of the final analyte concentration after extraction, which was obtained by direct injection of 10 μL of standard solution.

Results And Discussion

3.1 Preparation and characterization of modified MWCNTs

The TEM image of the original MWCNTs (Figure 2a) showed an aggregated structure, whereas the MWCNTs/NaDC (Figure 2b) was more hydrophilic than their pristine counterparts and well-dispersed in the ethyl alcohol solution. SEM image reveal the presence of MWCNTs/NaDC homogenously coating the surface of the silica fiber in Figure 2c. The coating thickness was approximately 20 μm(Figure 2d). Three types of surfactant-modified MWCNTs are compared in Figure S1. The functionalized MWCNTs with NaDC(Figure S1d) were more hydrophilic than their pristine MWCNTs (Figure S1a) and the other two surfactants processing(Figure S1b and Figure S1c), and showed a better dispersibility structure. It has been reported that the surfactant is mainly combined with the surface of carbon nanotubes by micelles, semi-micelles or random adsorption in a non-covalent modification way and the dispersion of carbon nanotubes is achieved by overcoming the strong *van der Waals force* between carbon nanotubes through electrostatic or spatial repulsion effect.[35−37] And the performance of MWCNT-coated SPME fiber can be enhanced by the complete dispersion and proper assembly of the nanotubes.

According to the FT-IR spectrum of the MWCNTs (Figures 3), the absorption peak associated with the stretching vibration of the carboxyl group can be seen in the spectral curve of ($\sim$1720 cm^{-1}), which was on the curve of MWCNTs/NaDC. The absorbance peaks at approximately 1169 cm^{-1}assigned to the C-OH stretch. After NaDC modification, because of the stronger interaction between NaDC with MWCNTs, the stretching vibration of C=C ($\sim$1620 cm^{-1}) peak move higher wavenumber.[38] The result showed that NaDC is mainly combined with the surface of MWCNTs−COOH by random adsorption in a non-covalent modification way.

X-Ray Diffraction(XRD) tests were performed to further demonstrate the functionalization of surfactant modified MWCNTs. Because of the amorphous structure of NaDC, no new characteristic peaks appeared in the XRD pattern. According to the Figure 4, 26.2°is the characteristic peak of MWCNTs, when NaDC modified MWCNTs, its characteristic peak has been little significant change. This probably because of the adsorption interaction between NaDC and MWCNTs, that it will not disturb the crystal lattice of MWCNTs, which agreed with the FT-IR data.

3.2 Effect of experimental conditions on the extraction efficiency with the MWCNTs/NaDC SPME fiber.

To evaluate the performance of the MWCNTs/NaDC SPME fiber, five phenols were selected as target compounds for SPME. Different experimental parameters that could affect extraction efficiency, including the extraction time, the inorganic salt concentration, the composition of the elution solvent, and desorption time, were investigated and optimized.

3.2.1 Extraction Time. Because SPME is an equilibrium-based technique, the extraction efficiency depends on the amount of analyte transferred from the sample solution to the MWCNTs/NaDC, and there is a correlation between the extraction amount and the extraction time. Extraction profiles for the five phenols are shown in Figure 5a. The results indicated that the extraction efficiency increased with the exposure time, and the extraction equilibrium was reached in 20 min for 2,4-DCP, 30 min for 2,4-DMP, 40 min for phenol and 4-NP, and 50 min for 2-NP. All phenols reached extraction equilibrium within 50 min. Therefore, 50 min was chosen as the preferred extraction time.

3.2.2 Ionic Strength Ionic strength is another parameter influencing the extraction efficiency of analytes in an aqueous solution. Addition of inorganic salt can decrease the solubilities of analytes in an aqueous sample and enhance their concentrations in the adsorbent. Therefore, the influence of ionic strength was investigated by adding different proportions of NaCl (0%−36% w/v) as a salting-out agent (Figure 5b). The results showed that most compounds had higher extraction efficiencies with high salt concentrations than with low salt concentrations, and 36% (w/v) NaCl was chosen for subsequent extractions.

3.2.3 Composition of the elution solvent The effect of the composition of the elution solvent on extraction efficiency was also investigated (Figure 5c). A mixture of ACN and water gave good solubility for the phenols on the modified MWCNTs fiber. Generally, as the water volume fraction increased, the extraction efficiency also increased for most phenols. The optimum desorption was achieved with an ACN volume fraction of 70%. Consequently, 70% ACN was used in subsequent experiments.

3.2.4 Desorption Time. The effect of desorption time was investigated with ultrasonication for between 1 and 10 min (Figure 5d). All the phenols were desorbed almost completely within 8 min. Increasing the time above 8 min did not considerably increase the desorption efficiency. Therefore, 8 min was chosen as the optimum desorption time.

The optimum conditions for SPME of phenols were an extraction time of 50 min, NaCl content of 36% (w/v), ACN volume fraction of 70%, and desorption time of 8 min.

3.3 Comparison of the MWCNTs/NaDC fiber with a commercial PDMS fiber.

The extraction performance of the MWCNTs/NaDC fiber was compared with a commercial 100-μm PDMS fiber. PDMS fiber was employed in the applicable conditions recommended by the manufacturer. The SPME using the MWCNTs/NaDC and PDMS fiber was carried out with a phenol concentration of 10.0 ng/mL. The results are represented in Table 1 (see Supplementary Files) and Figure 6. The enrichment factor (*EF*) was defined as the ratio of the analyte concentration after extraction to that in the original sample. The relative response of the MWCNTs/NaDC fiber was roughly two to six times that of the commercial fiber for phenols. Obviously, the MWCNTs/NaDC showed a completely different adsorption mechanism for phenols than PDMS. As phenols are polar compounds, polar oxygen-containing groups such as carboxyl and carbonyl were existed on the MWCNTs/NaDC fiber, thus, the extraction efficiency of polar compounds was improved. Furthermore, the surface and interspaces of MWCNTs/NaDC changed with the electrical and steric resistance, and excellent sorption was achieved.

3.4 Comparison of MWCNTs/NaDC Fiber with MWCNTs Fiber.

To evaluate the usefulness of the MWCNTs/NaDC Fiber, the adsorption efficiency of MWCNTs/NaDC with pristine MWCNTs were compared. The SPME analysis of the aqueous sample was executed by testing the sample spiked with phenols at 10.0 ng/mL. As presented in Figure 7, the peak area of the fiber with MWCNTs/NaDC increased additionally as compared to the pristine MWCNTs fiber, so that the better performance of the MWCNTs/NaDC fiber was achieved. At each HPLC analysis, three measurements were repeated.

3.5 The lifetime of the coating

The lifetime of a coating is very important for practical applications. Coatings are mainly damaged by exposure to high temperatures, organic solvents, strong acids, or strong bases. The reproducibility of the MWCNTs/NaDC fiber extraction was investigated (Figure 8). After repeating phenol extraction and elution 20 times, the peak areas in the SPME chromatograms did not change remarkably. These results prove that the coating is quite stable and fabrication of the MWCNTs/NaDC coating by chemical bonding is reproducible.

3.6 Method validation and application to real samples

Under the optimized conditions, calibration curves were constructed for phenols analysis (Table 2 in the Supplementary Files). The linear ranges for all tested analytes were 1–100 ng/mL with good correlation coefficients (R^2 > 0.9997). The limits of detection (LODs) were calculated at a signal-to-noise ratio of three, and the LOD ranges were 0.15-0.30 ng/mL. The LOQ were estimated from the S/Ns of 10, and LOQ values were in the range of 0.60-1.20 ng/mL. The results showed that the RSD range between 4.9 and 10.2% from single fiber, and range between 5.7 and 11.9% from fiber to fiber with three replicates.

The developed method with other analytical SPME methods were compared as well(Table 3 in the Supplementary Files). Our method is comparable to existing methods and allows for trace analysis in real samples. For a repeatability study, three parallel experiments were conducted with one fiber on an aqueous sample containing 100 ng/mL phenols, and the relative standard deviation was below 10%.

Then, the optimized method was applied to the determination of phenols in samples from the South China Sea and Wastewater. 10 mL of aqueous solution was extracted by this novel MWCNTs/NaDC fiber without any pretreatment, the results indicated that P was detected in the wastewater(3.64 ng/mL), while the concentrations of 2-NP, 4-NP, 2,4-DMP and 2,4-DCP were below the LODs. No phenolic compounds were found in South China Seawater. Spiking experiments were then performed to evaluate the accuracy of the established method, and the samples were spiked with phenols at 10.0 and 100.0 ng/mL. Figure 9 showed the chromatograms of phenols extracted by the MWCNTs/NaDC fiber from real water sample and spiked samples. As listed in Table 4 (see Supplementary Files) , the recovery ranges were 85.6% –93.1% (relative standard deviation < 7%) for seawater samples from the Yangpu area, 88.6%–95.4% for samples from the Baishamen area, 80.3%–87.3% for samples from the Holiday Beach area, and 82.6% –90.5% for wastewater samples. The precision and accuracy of the present method were acceptable.

Conclusions

A HPLC method using a MWCNTs/NaDC SPME fiber for trace analysis of phenols has been developed and its application in aqueous solution coupled with HPLC. The MWCNTs/NaDC fiber exhibited high extraction efficiencies, a wide linear range, low LODs and satisfactory reproducibility for phenols. The high adsorption capacity was attributed to hydrogen bonding between the hydroxyl and carboxyl groups of the MWCNTs/NaDC surface and capacity for dissociation of phenols. The proposed fiber has much better detection sensitivity than commercial PDMS fibers. The LOD range of the proposed method for phenols analysis was 0.15−0.30 ng/mL. These results broaden the potential for application of MWCNTs in the analysis of trace compounds in aqueous samples.

Declarations

Availability of data and material

Supplementary material.

Competing interests

The authors declare no competing interest.

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Authors' contributions

Not applicable.

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Tables

Due to technical limitations, tables are only available as a download in the supplemental files section.

Figures
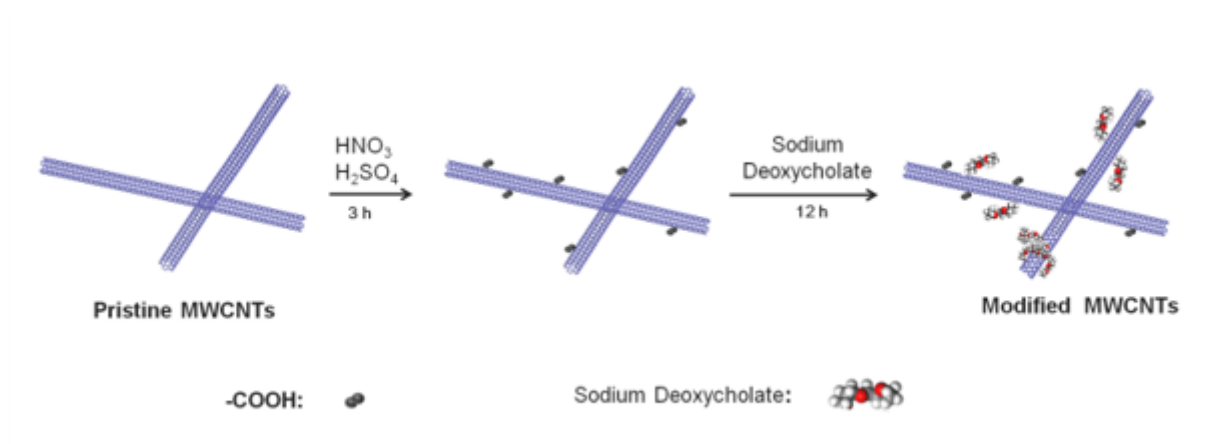
Figure 1

Synthesis of the MWCNTs/NaDC.
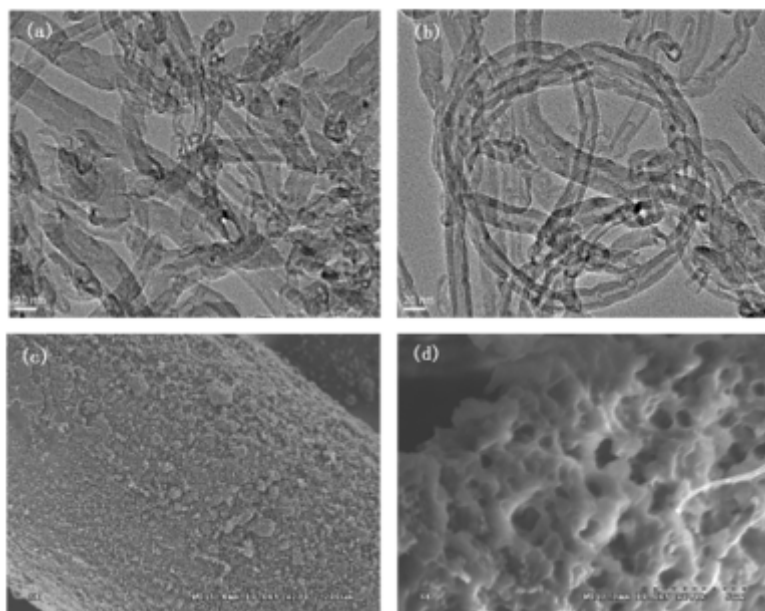
Figure 2

TEM image of the original MWCNTs (a), TEM image of the modified MWCNTs after processing with NaDC (b), and SEM image of the MWCNTs/NaDC coating surface of the silica fiber(c,d).
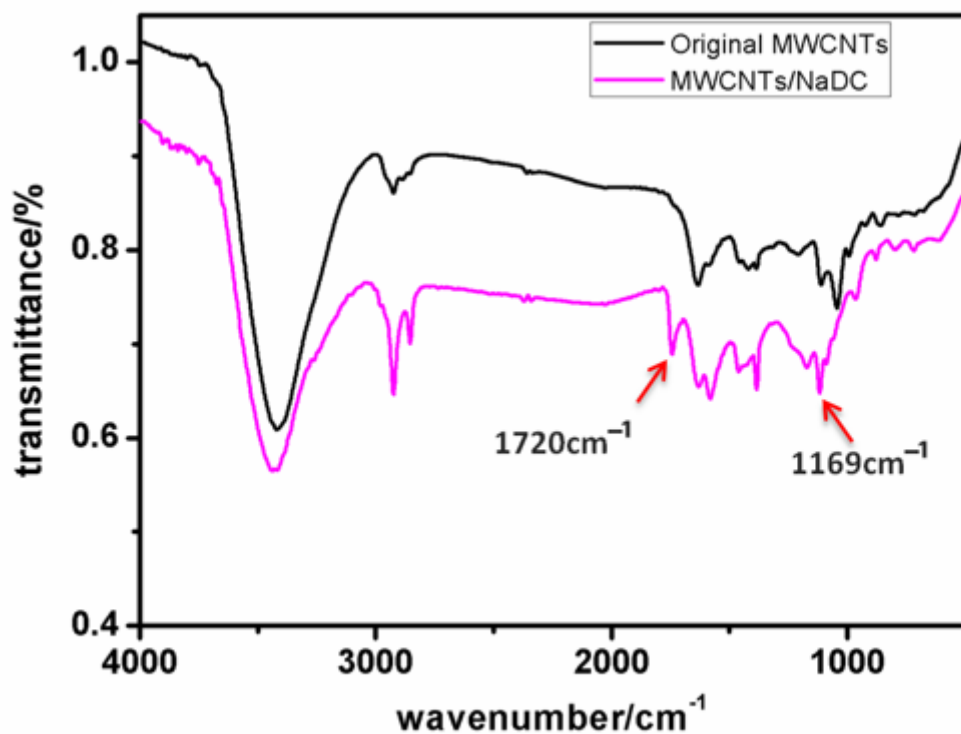
Figure 3

The FT-IR spectrum of the MWCNTs/NaDC and original MWCNTs.
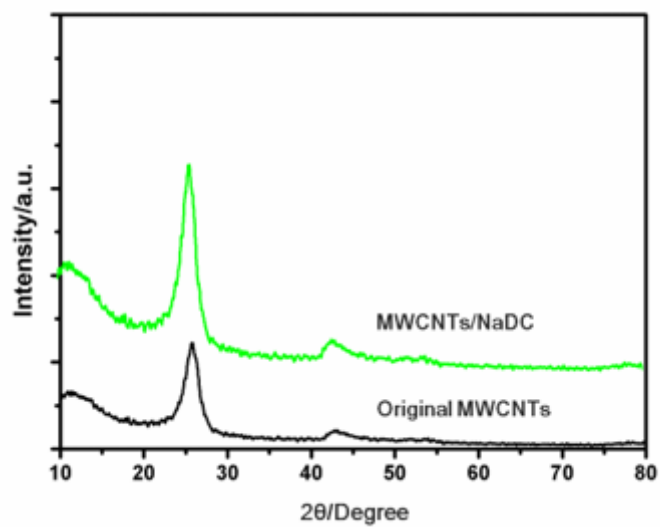
Figure 4

XRD spectrum of the MWCNTs/NaDC and original MWCNTs.
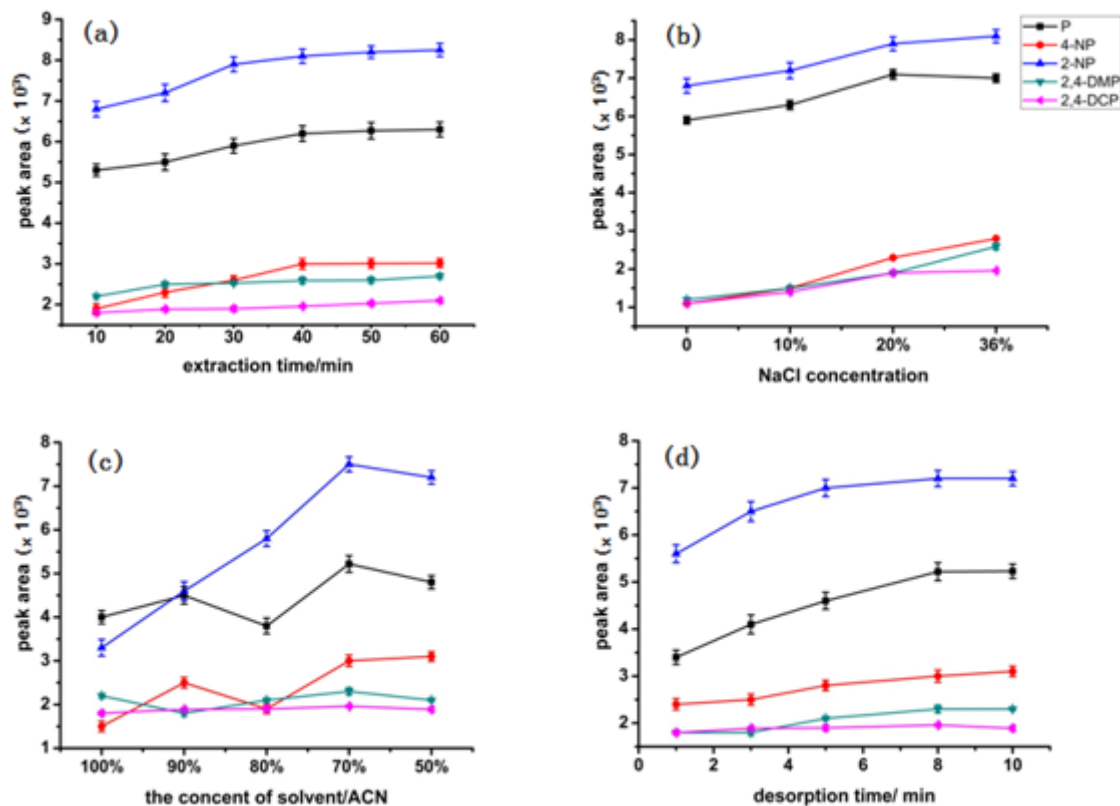
Figure 5

Effects of the experimental conditions on the extraction efficiency of the MWCNTs/NaDC SPME fiber for 100 ng/mL each analyte. (a) Extraction time, (b) ionic strength, (c) the composition of the elution solvent, and (d) desorption time. Errors bars show the standard deviation of the mean (n = 3).
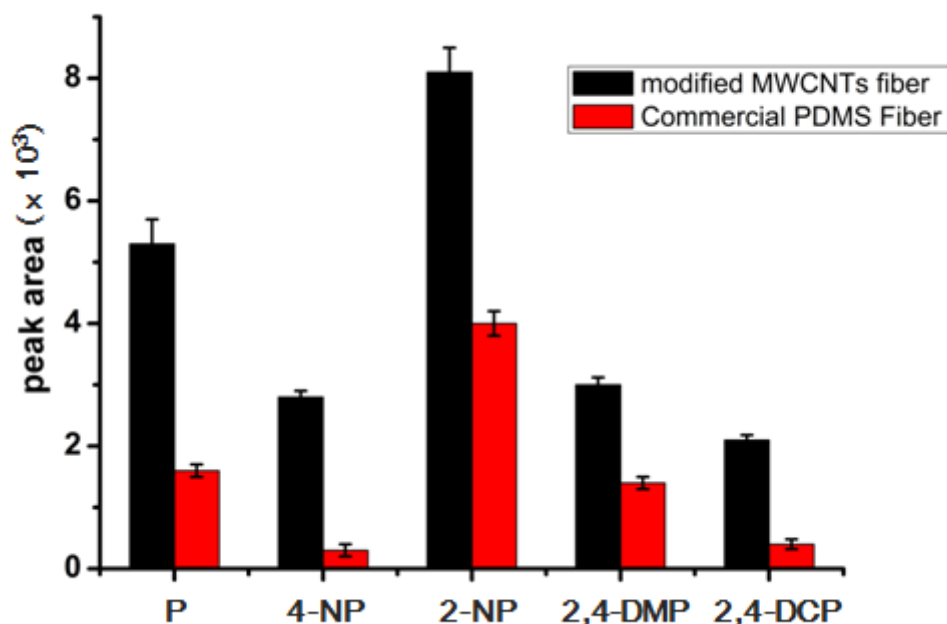
Figure 6

Peak areas obtained with the MWCNTs/NaDC fiber and commercial PDMS fiber for phenols. Error bars show the standard deviation of the mean (n = 3).
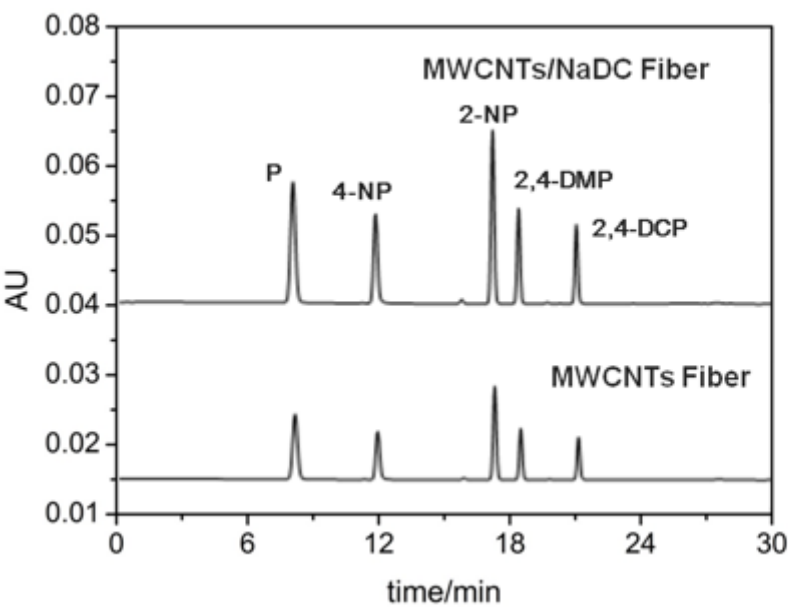
Figure 7

Chromatograms of the phenols standard solution containing 10 ng/mL obtained with the MWCNTs/NaDC and the pristine MWCNTs fibers.
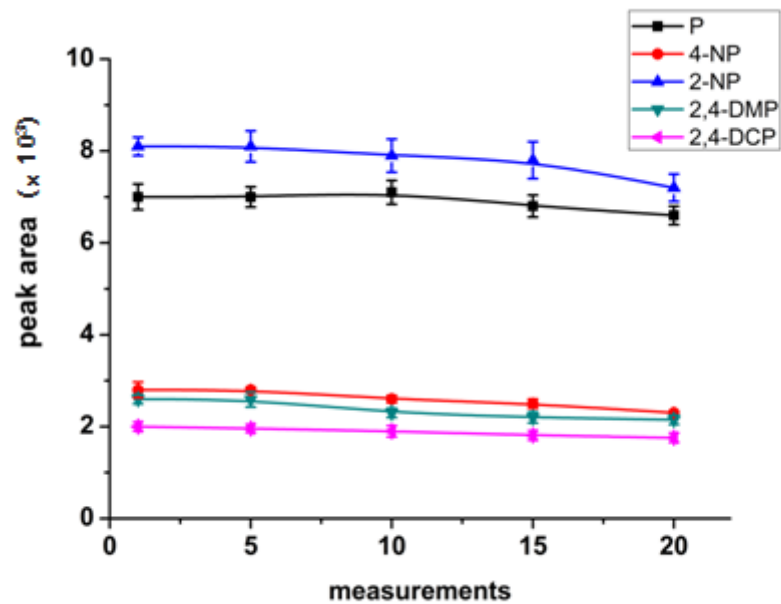
Figure 8

Peak areas of the phenols as the function of the number of measurements performed with a single MWCNTs/NaDC fiber
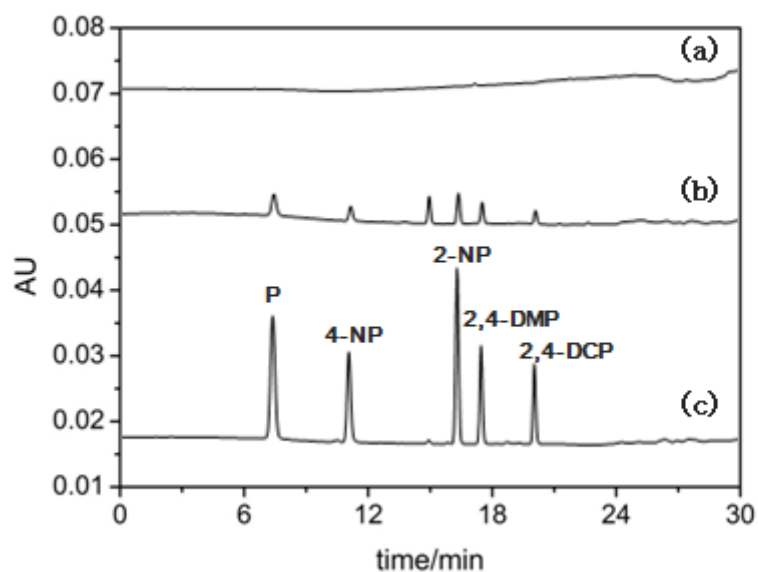
Figure 9

Chromatograms of phenols extracted by the MWCNTs/NaDC fiber from (a) a blank Yangpu seawater sample and (b) the same seawater sample spiked with a phenols standard solution at 10.0 ng/mL. (c) The 100.0 ng/mL phenols standard solution used for spiking.