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Preconcentration of benzene and phenolic compounds in water sample by adsorption on Carbon nanotubes coated fiber

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A simple method has been developed for the preconcentration of benzene and phenolic compounds (BPC) by the adsorption of its carbon nanotubes (CNTs). The preconcentration of benzene and phenolic compounds (BPC) are ubiquitous pollutants, and many of them are carcinogenic or mutagenic. Carbon nanotubes (CNTs) are a kind of novel and interesting carbon material which can be used for separation and purification. In this investigation, commercial solid-phase microextraction (SPME) fibers (PDMS) were coated with single-wall nano tubes (SWNTs) and multi-wall nano tubes (MWNTs) to study the adsorption and extraction ability of hydrophobic BPC. While MWNTs adsorbed more hydrophobic BPC than SWNTs, the fibers coated with CNTs had advantages over traditional SPME fibers in selectivity and sensitivity. They could be used to separate hydrophobic BPC. The results show that the selectivity, sensitivity and reproducibility of this method are good for real sample analysis.

Key words: Carbon nanotubes (CNTs), Solid-phase microextraction (SPME), preconcentration of benzene and phenolic compounds (BPC).

INTRODUCTION

Many organic pollutants, such as phenol, o-chlorophenol, and benzene, are present in the environment in trace amounts. Due to their high toxicity (Zhang et al., 2001) and capability of accumulating in the environment, these pollutants are hazardous to living organisms (Bianchi et al., 2002). Due to their toxicity, persistence, and unpleasant organoleptic properties, both the US Environmental Protection Agency (EPA) and the European Union (EU) have classified several phenols and chlorophenols as priority pollutants (Kovacs et al., 2008; Puig and Barcelo, 1996). Phenol is a pollutant widely occurring in surface waters, in which it originates mainly from sewage effluents of chemical, pharmaceutical, and dye industries (Cernakova and Zemanovicova, 1998). Phenol derivatives, (Cernakova and Zemanovicova, 1998; Li et al., 2008) including chlorophenols, show genotoxic, mutagenic, and carcinogenic properties, and are characterized by high stability (Saitoh et al., 2008).

Benzene can naturally occur in crude oil; therefore, it can be found in refinery products (Schnatter, 2007; Roma-Torres et al., 2006). Since it has been classified as a first class carcinogenic factor (Eining and Dehnen, 1995) targeting bone marrow, more and more limits are

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being placed on its use. The above-mentioned pollutants are commonly present in surface waters. Since surface waters, are used by humans and in animal breeding after their treatment, (Manini et al., 2006) it is necessary to control the levels of organic pollutants (Michaowicz and Duda, 2007), particularly those that are present in trace amounts and show toxic and carcinogenic activities. Therefore, research on efficient methods for purification and preconcentration of analytes before their determination by means of an appropriate analytical technique is of great importance (Fattahi et al., 2007).

Among the many techniques developed for the isolation and preconcentration of different organic compounds and metal ions, solid phase extraction (SPE) is the most frequently used (Rendle, 2000). The extraction process to the solid phase is based on the retention of an analyte on a sorbent (Pic´o et al., 2007). Originally, the SPE application area was usually restricted to preconcentration of analytes showing strongly hydrophobic properties, whereas the recovery rates for polar compounds were not satisfactory (Saitoh et al., 2004). In our previous papers, a successful application of silica modified with ketoimine to the determination of trace amounts of bisphenol-A (BPA) in mineral water and powdered milk samples was reported (Rykowska et al., 2008; Rykowska 2007). The packing of ketoimine groups bonded with complexes of transition metals was also studied (Rykowska et al., 2004).

Carbon nanotubes (CNTs) are a kind of novel and interesting carbon material first found in 1991 by Iijima. CNTs are divided into single-wall nanotubes (SWNTs) and multi-wall nanotubes (MWNTs) according to their numbers of graphite sheets. The unique electrical, mechanical, and chemical properties of CNTs have aroused great interest among research workers (Pic´o et al., 2007; Saitoh et al., 2004; Rykowska et al., 2004). CNTs have a curved surface (composed of two fullerene halves and a cylinder made of a rolled up graphite sheet), and are thus expected to show a stronger binding affinity for hydrophobic molecules compared with a planar carbon surface. Furthermore, the internal pores of the CNTs are large enough to allow molecules to penetrate. The adsorption can occur on the inner hollow cavity of CNTs, on the outside surface, and on the interstitial spaces between the nanotube bundles. All these indicate that CNTs have strong physical adsorption ability to hydrophobic compounds. With the great process in the methods of preparing CNTs, large efforts have been devoted to the fields of application, such as gas storage (Rykowska, 2007), preconcentration of volatile organic compounds (Rykowska et al., 2004), removal of chemical and toxic wastes from water (Moghimi, 2013) and GC (Moghimi et al., 2009) to name but a few. It is therefore conceivable that CNTs may have great analytical potential as an effective solid-phase microextraction adsorbent for some suitable compounds. It is known that the interaction between BPC and surfaces are complex, involving many types of noncovalent forces that are electrostatic, hydrogen bonding, hydrophobic, or entropic in nature related to surfaces as well as surrounding water molecules (Mrksich et al., 1997; Brash, 1991). Nevertheless, this is a topic crucial to many areas of biological and medical science and technology. It is reported that the internal surface of CNTs interacts strongly with the enzyme BPC and the CNTs appear to act as a benign host to encapsulate protein molecules in their internal tube cavity.

There are many ways to separate the target protein from the sample matrix (Johansson et al., 2008), and few research papers focus on the subject of solid phase extraction of acidic and basic BPC using CNTs, CNTs immobilization, or CNTs functionalization (Hu et al., 2009). However, to the best of our knowledge, there is hardly any research on the SPME process of BPC using CNTs. The purpose of our present work was to develop a novel SPME technique using CNTs (SWNTs and MWNTs) as fiber coating for the extraction of two important hydrophobic also, the concentration of hydrophobic BPC was roughly determined using our method. It presents many advantages, that is, it is relatively inexpensive and is a parallel fabrication technique, allowing the production of a large number of samples during the same process.

MATERIALS AND METHODS

Reagents and instrumentation

Phenol, o-chlorophenol, and benzene were obtained from Fluka (Buchs, Switzerland). Individual stock solutions at concentrations of 100 mg/ml each were prepared in dichloromethane–acetone (50:50). The working standard solution was prepared by mixing each of the PAH stock solutions and diluting with dichlorome thane–acetone (50:50) for a final concentration of 2 mg/ml. *p*-Terphenyl (analytical-reagent grade) from Tokyo Kasei was used as internal standard (I.S.) in gas chromatography–mass spectrometry (GC–MS) analysis. The standard solution for this compound was prepared in benzene at a concentration of 8 µg/ml. All the standard solutions were stored in the dark at 4°C to prevent photolysis of the compounds.

Raw SWNTs and MWNTs were purchased from Shenzhen Nanotech Port Co. Ltd and used without further purification. The specific surface area of SWNTs and MWNTs are 450 m^2/g and 40-300 m^2/g, were obtained from E.Merck, Darmstat, Germany respectively. A commercial 30 µm PDMS fiber and SPME holder were purchased from Supelco (Bellefonte, PA, USA). Other materials were of analytical grade and used as purchased without further treat. The SEM images were taken by Field Emission Scanning Electron Microanalyser JSM-6700F (JEOL, Japan). The UV-Vis spectra were determined by a UV-Vis spectrophotometer TU-1901. The mixtures of BPC were separated by SDS-polyacrylamide gel electrophoresis (SDSPAGE) and detected by a fluorescence spectrometer.

The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

Preparation of CNTs fiber for SPME

First, 0.5 g of SWNTs was dispersed in 125 ml of 1,2- dichloroethane

Table 1. Retention times and quantitative ions for GC–MS (SIM) analysis of BPC.

Compound	Retention time (min)	Quantitative ion (*m/z*)
Phenol	7.24	128
o-chlorophenol	9.92	152
Benzene	10.24	153

[a] Internal standard BPC from a sample of 500 ml of pond water.

by ultrasonic agitation for 30min. Then, 7.5 g of organic binder, made up of 90% terpineol, 5% ethylcellulose, and 5% dibutyl phthalate (by mass), was added to the solution and sonicated for another 30 min. This mixture was filtered through a 300-mesh net to remove big clusters. Finally, it was heated to 90°C to totally evaporate the 1,2-dichloroethane and obtain a sticky paste.

The used SPME fiber was a PDMS fiber (30 µm diameter) which was stuck in the SPME holder. It was coated with SWNTs paste by carefully spinning the fiber on a sheet of sticky SWNTs paste. After it was dried by hot air (about 150°C), the thickness of the coated layer was a few micrometers. The above procedure was repeated three times, so the final thickness of the coated SWNTs layer was about 15 µm (determined by SEM). The diameter of the coated SPME fiber was about 45 µm. Finally, the coated fiber was sintered at 400°C for 30 min in a nitrogen atmosphere to remove the organic binder. The coated SPME fiber was used directly in the extraction process. The MWNTs coated SPME fiber was fabricated in exactly the same way.

Preparation of hydrophobic BPC solutions

Different volumes of K_2HPO_4 solution (0.1 mol L^{-1}) and KH_2PO_4 solution (0.1 mol L^{-1}) were mixed to get 0.1 mol L^{-1} phosphate buffer of various pH (standard method). Then, the pH meter was used to adjust the pH to exactly the required value (NaOH or HCl was used). 5 mg of hydrophobic BPC were dissolved in 10 ml of various phosphate buffers with different pH, and the prepared solutions were all stored in a refrigerator until use.

Solid-phase microextraction process

20 ml glass vial was used as a sample container, and 5 ml of sample solution was placed into it. The SPME holder was fixed at a suitable height above the sample vial so that the coated SPME fiber was totally immerged in the solution and then the bottle was sealed. It was shaken for a required time at ambient temperature. After extraction, the fiber was removed from the sample vial and immediately inserted into the desorption buffer. The desorption process was conducted in various buffers in the same way as the SPME process. A commercial SPME fiber (PDMS) was conducted as a SPME process in the same way for comparison.

Recovery calculations

Extraction efficiency (E_{ex}) was calculated from the hydrophobic BPC concentrations before (C_0) and after extraction (C_1).

$$E_{ex} = (C_0\text{-}C_1)/C_0 \times 100\%$$

Recovery yield (E_r) was calculated from the hydrophobic BPC concentration in the desorption buffer (C_2) and the adsorbed BPC.

$$(C_0\text{-}C_1).\ E_r = C_2/(C_0\text{-}C_1) \times 100\%$$

Concentrations were determined from the maximum absorbance around 200 nm by UV-Vis spectra.

Gas chromatography mass spectrometry (GC–MS) analysis

A Shimadzu QP-5000 GC–MS system equipped with a Model AOC-17 auto sampler was used for analysis. Chromatographic separation of the 16 BPC and the internal standard was accomplished with a DB-5 (J & W, Folsom, CA, USA) fused-silica capillary column (30 m × 0.32 mm I.D., 0.25 mm film thickness). Helium was the carrier gas at a flow-rate of 2.0 ml/min, and an inlet split ratio of 1:20 was used. Sample injection was in the splitless mode with an injection volume of 2 µl and an injection time of 2 min. The GC oven temperature was programmed as follows. An initial temperature of 50°C was held for 2 min and then ramped at 15°C/min to 220°C followed by another ramp of 58°C/min to 300°C, held for 1 min. The temperatures of the injection port and the interface with the MS system were set at 300°C. For selected ion monitoring (SIM), the voltage of the detector was 1.5 kV, and for each compound, one ion was chosen for quantification while two other ions were for identification. The retention times and quantitative ions for the analytes and I.S. are listed in Table 1. Linear calibration curves could be obtained for all the PAH components across a 50-fold concentration range; typically, R^2 0.999. The instrumental detection limit was measured to be from 2 (for the two-ring and three-ring BPC) to 10 pg/ injection (for five-ring and six-ring BPC).

Sample analysis

Our method was firstly applied to pond water. To prove the feasibility of our method in real samples, 1 ml pond water was diluted to 10 ml by phosphate buffer (0.1 mol L^{-1}) and various amounts of BPC were added to it to get various BPC concentrations (such as 0.1, 0.2 and 1 mg mL^{-1} and so on). Then the SPME experiments were conducted in 5 ml of these prepared samples under optimized conditions. 1 ml BPC was diluted to 10 ml by phosphate buffer (0.1 mol L^{-1}), and then 5 ml was taken to conduct the SPME procedure under optimized conditions. The concentration of BPC was determined by the obtained concentration curve.

RESULTS AND DISCUSSION

Characterization of CNTs and CNTs coated SPME fiber

The diameters of the MWNTs were within 10 to 30 nm and the lengths were in the range of 5 to 15 µm. The Raman spectra of both were also studied (Figure 1). There were three major lines of MWNTs, which were around 1360 cm^{-1} (D line), 1570 cm^{-1} (G line) and 2930

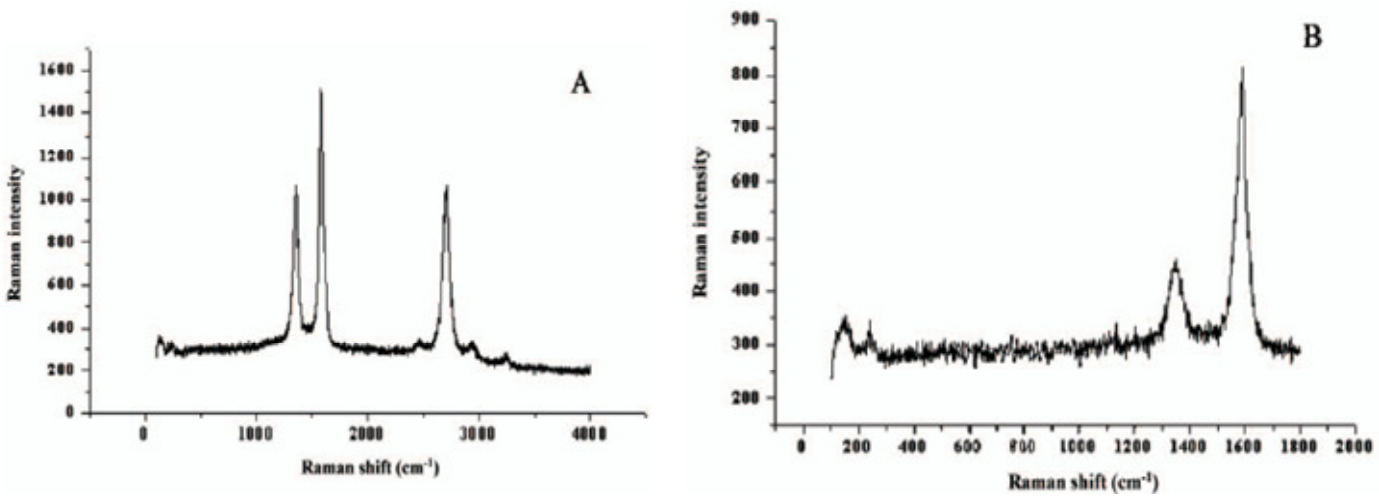

Figure 1. Raman spectra of MWNTs (A) and SWNTs (B).

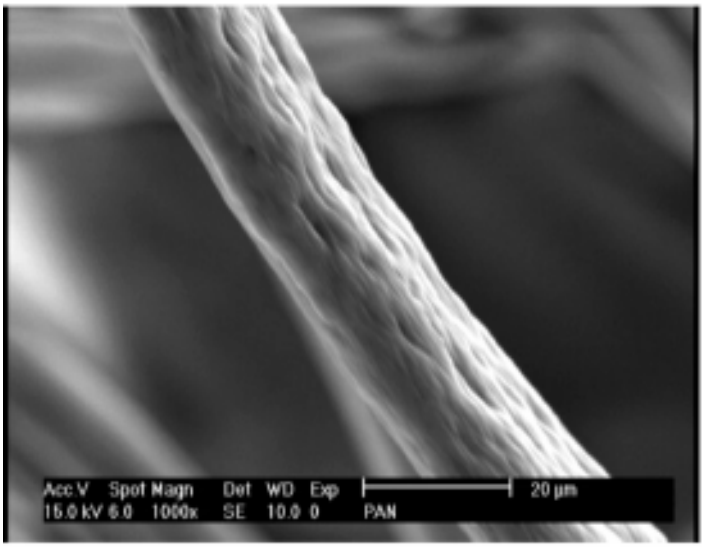

Figure 2. SEM images of coated MWNTs (lower magnification); Acceleration voltages and magnifications were indicated on the images.

cm^{-1} (D+G line). There were two major lines of SWNTs, which were around 1350 and 1600 cm^{-1}. In order to examine the coating state of CNTs on the SPME fiber using our method, the SEM images of MWNTs-coated fiber were studied (Figure 2). It demonstrated the presence of CNTs as a homogenous coating on the surface of the fiber and the coating possessed a rough surface, which resulted in larger surface areas and higher extractive capacity than conventional polymeric phases. The film thickness of the carbon nanotubes coating was proven to be about 15 µm by SEM. Also, it showed that the MWNTs were cut short by sonication, which might affect the extraction efficiency. However, the sonication step was necessary for dispersion.

Optimization of SPME procedure

It is known that SPME is an equilibrium process. The principle behind SPME is the partitioning of analytes between the sample matrix and the extraction medium. In order to obtain good sensitivity, several experimental parameters related to both extraction and desorption steps needed to be optimized.

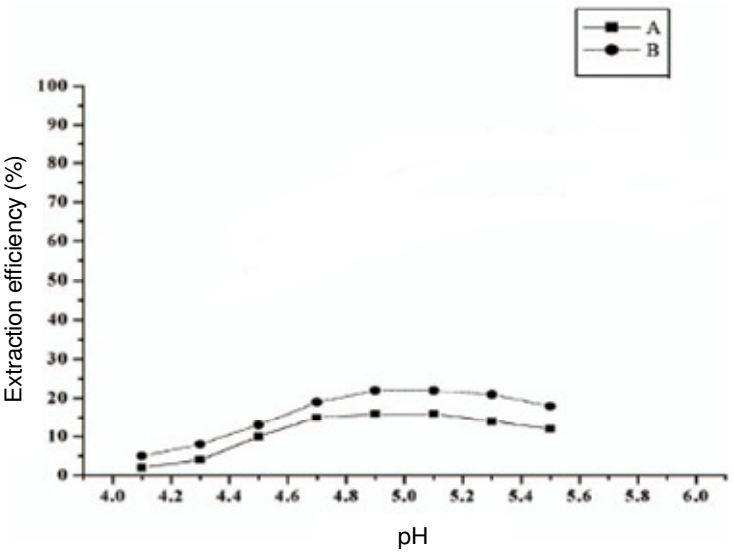

Figure 3. Effect of pH value of the extraction buffer on extraction efficiency (A: MWNTs extraction of BPC; B: SWNTs extraction of BPC). Other extraction conditions: phosphate concentration of extraction buffer: 0.1 mol L^{-1}; extraction time: 120 min for BPC 5 ml; BPC concentration: 0.5 mg mL^{-1}.

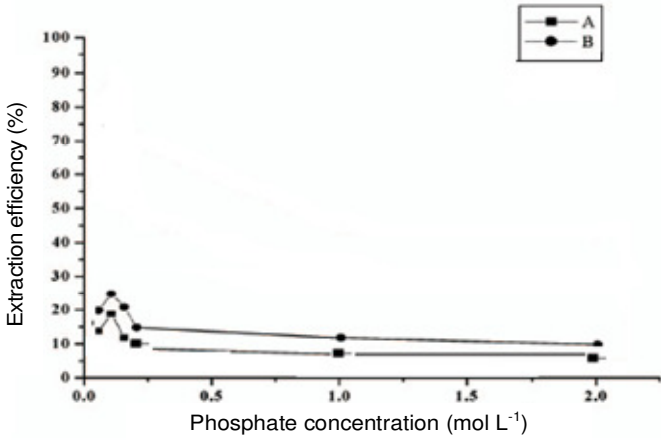

Figure 4. Effect of extraction buffer ionic strength on extraction efficiency (A: MWNTs extraction of BPC; B: SWNTs extraction of BPC). Other extraction conditions: pH of extraction buffer: 5.0 for BPC; extraction time: 120 min for BPC; extraction buffer volume: 5 ml; BPC concentration: 0.5 mg mL^{-1}.

The electrical property of BPC is dependent on the pH value of the solution. First of all, the pH value of the extraction buffer was optimized (Figure 3). As can be seen from Figure 3, MWNTs and SWNTs adsorbed BPC most strongly between a pH of 4.9 and 5.1. It is known that the pI value of BPC is around 4.7. When the pH value of the buffer is around the pI value of the BPC, the BPC is nearly neutral and more hydrophobic than at other pHs. Also, CNTs are hydrophobic and they are inclined to adsorb hydrophobic compounds. That is to say CNTs adsorb BPC most strongly around the pI value of the BPC. A pH of 5.0 for BPC was chosen in the next experiments. Other literatures report that the ionic strength of the extraction buffer also has some impact on the extraction efficiency (Mrksich et al., 1997; Brash, 1991). Thus, the effect of ionic strength of the extraction buffer is investigated (Figure 4). When the concentration of phosphate increased, the extraction efficiency

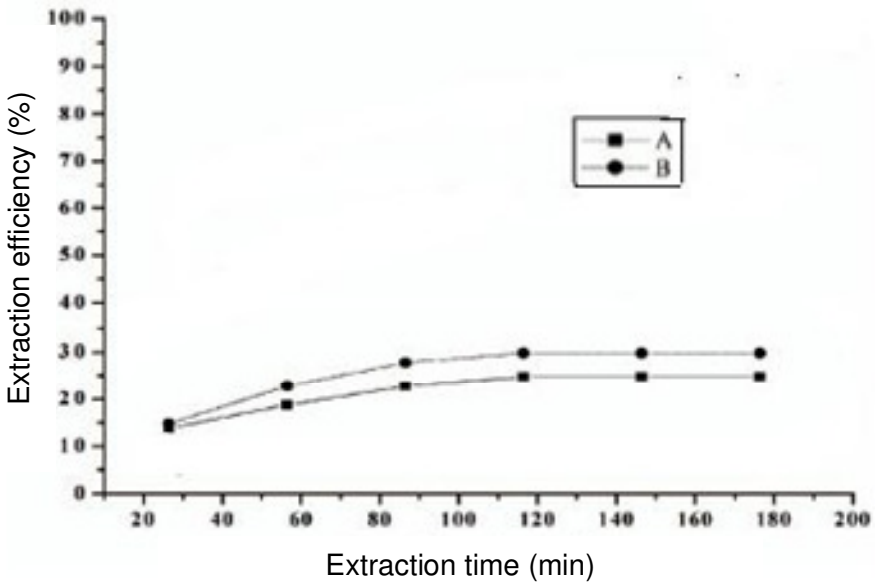

Figure 5. Effect of extraction time on extraction efficiency (A: MWNTs extraction of BPC; B: SWNTs extraction of BPC). Other extraction conditions: pH of extraction buffer: 5.0 for BPC; phosphate concentration of extraction buffer: 0.1 mol L^{-1}; extraction buffer volume: 5 ml; BPC concentration: 0.5 mg mL^{-1}.

Table 2. Effect of coating times on extraction efficiency BPC, concentration: 0.5 mg mL-1; pH of extraction buffer: 5.5; phosphate concentration of extraction buffer: 0.1 mol L^{-1}; extraction time: 150 min; extraction buffer volume: 5 ml).

Coating times	1	2	3	4	5	6
MWNTs' E_{ex} for BPC (%)	78.2	84.1	88.8	92.7	97.6	98.3
SWNTs' E_{ex} for BPC (%)	60.2	62.9	66.9	68.0	73.5	76.1

increased accordingly at first and reached a maximum value. But then, the extraction efficiency dropped. This may be explained as follows. On the one hand, an increase of phosphate can reduce the amount of water available to dissolve analyte molecules due to the formation of hydration spheres around the ionic salt molecules (Boyd-Boland and Pawliszyn 1995), which improved the extraction efficiency for the investigated compounds. Thus, phosphate anions can interact with a positive charge on BPC molecules and form "ionic atmosphere", which increases with phosphate concentration.

This interaction could cause the reduction of BPC adsorption on CNTs. 42 0.1 mol L^{-1} was chosen as the extraction buffer concentration. The equilibration time in SPME for given analytes was determined by constructing an adsorption-time profile by exposing the fiber to the same analytes concentration solution for different times (Figure 5). As can been seen from Figure 5, MWNTs and SWNTs extraction could reach equilibrium at the same time (after 120 min) when BPC was the analyte. For further experiments, 120 min for BPC was chosen as extraction time. The coating thickness of CNTs could also affect the extraction efficiency (Table 2). As can be seen from Table 2, when coating times increased, the extraction efficiency also increased a little. When the coating times increased, the coating thickness also increased which made the coating surface area increase accordingly. Therefore, more BPC could be adsorbed on the coating. Coating carried out three times was sufficient in our study.

Some reports show that increasing the ionic strength and decreasing the pH value of the extraction buffer can wash off the adsorbed BPC (Mrksich et al., 1997; Brash, 1991). The pH value of the desorption buffer would not affect the recovery yield if it was low enough. That might be because the ionic strength effect was dominant and much larger than the pH effect. Desorption time is also an important parameter (Figure 6). As can be seen from Figure 6, MWNTs and SWNTs could reach their highest recovery yield at the same time (after 60 min) when BPC was the analyte. Similarly, MWNTs and SWNTs could

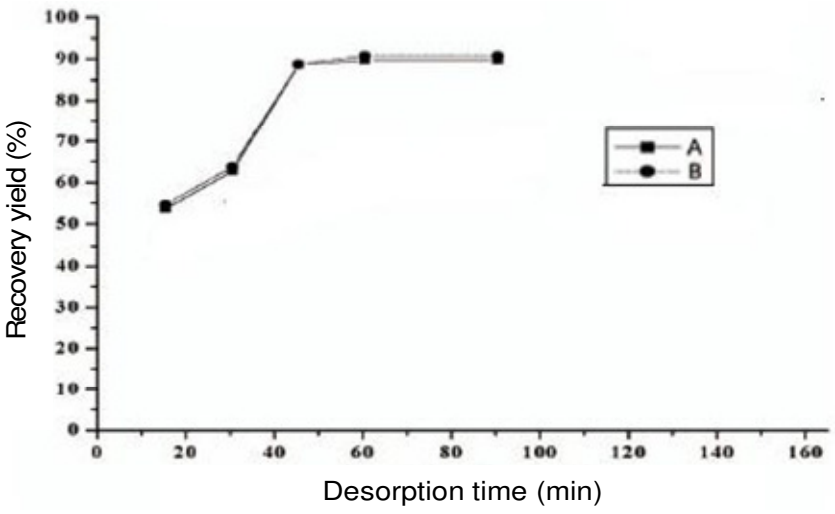

Figure 6. Effect of desorption time on recovery yield (A: MWNTs extraction of BPC; B: SWNTs extraction of BPC). Extraction conditions: pH of extraction buffer: 5.0 for BPC; phosphate concentration of extraction buffer: 0.1 mol L^{-1}; extraction time: 120 min for BPC; extraction buffer volume: 5 ml; BPC concentration: 0.5 mg mL^{-1}. Other desorption conditions: pH of desorption buffer: 2.0; NaCl concentration of desorption buffer: 3 mol L^{-1}; desorption buffer volume: 5 ml.

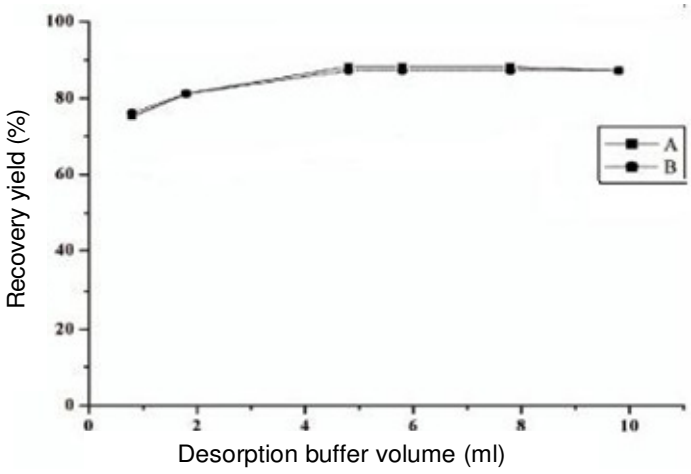

Figure 7. Effect of desorption buffer volume on recovery yield (A: MWNTs extraction of BPC; B: SWNTs extraction of BPC). Extraction conditions: pH of extraction buffer: 5.0 for BPC; phosphate concentration of extraction buffer: 0.1 mol L^{-1}; extraction time: 120 min for BPC; extraction buffer volume: 5 mL; BPC concentration: 0.5 mg mL^{-1}. Other desorption conditions: pH of desorption buffer: 2.0; NaCl concentration of desorption buffer: 3 mol L^{-1}; desorption time: 120 min for BPC.

reach their highest efficiency at the same time (after 120 min) when BPC was adsorbed much stronger on CNTs. Either using MWNTs or SWNTs, BPC reached extraction equilibrium and desorption equilibrium at the same time respectively, which may demonstrate the same mechanism of MWNTs and SWNTs adsorption and desorption of BPC. Only the adsorption ability was different. 60 min for BPC was chosen as the desorption time in further experiments.

The volume of desorption buffer is also important for high recovery yield (Figure 7). As can be seen from Figure 7, all experiments could reach their highest

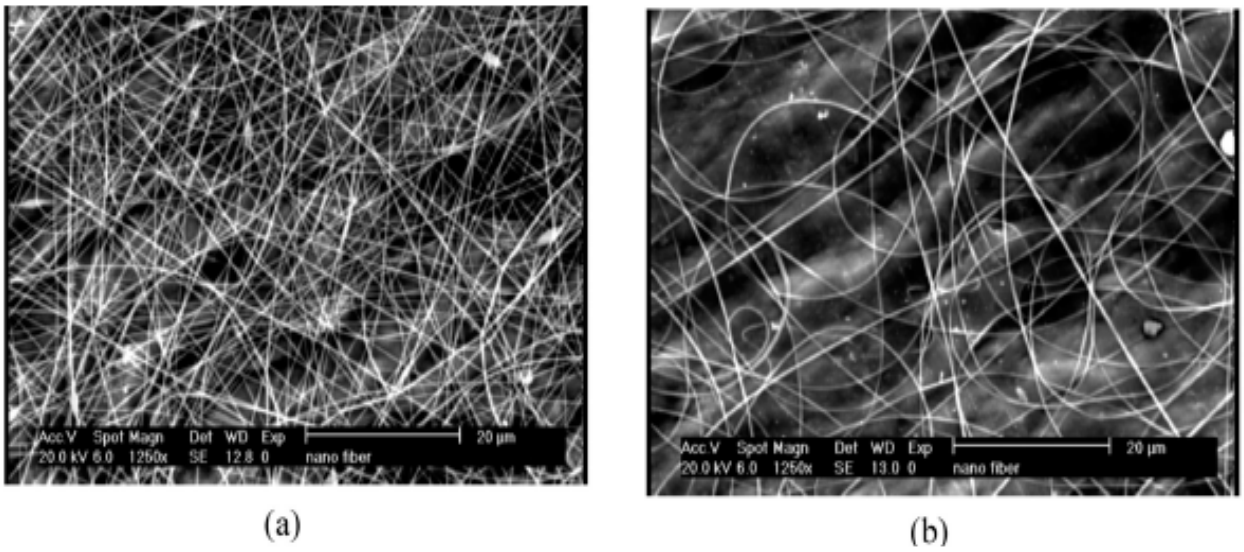

Figure 8. SEM images of BPC -adsorbed MWNTs coated fiber (A: lower magnification; B: higher magnification). Acceleration voltages and magnifications were indicated on the images.

recovery yield when using the same desorption buffer volume as the extraction buffer (5 ml). The desorption buffer volume barely had an effect, which might be because the adsorption and desorption of BPC in our experiment are determined by the amount of BPC, not the concentration. 5 ml was chosen as the desorption buffer volume in all the following experiments. The results showed that the adsorbed BPC could not be totally desorbed. The desorption process was repeated, and a little more BPC was desorbed. It was difficult to totally desorb the adsorbed BPC. This might be because the adsorbed BPC was denatured and adsorbed very strongly on the CNTs (Sandeep et al., 2004). Thus, the carry over effect was a problem in our study. However, using the coated fibers of the same fabricating process, the reproducibility was good enough. So in every experiment, a newly fabricated fiber was used to avoid the carry over effect. From these results, it is concluded that CNTs adsorbed BPC. SWNTs adsorbed more BPC than MWNTs, which might be because SWNTs have larger specific surface area than MWNTs.

Characterization of BPC adsorbed MWNTs

The surface characterization of MWNTs coated fiber that had adsorbed BPC was also investigated by the SEM technique (Figure 8). As can be seen from Figure 8, it was confirmed that BPC had been adsorbed on the MWNTs coated fiber. The MWNTs were buried in the BPC. Some reports show that the secondary structure and activity of BPC adsorbed onto nanotubes are changed as a result of the protein interaction with the nanotube surface.

Analytical figures of merit

As can be seen from the former work, CNTs adsorbed BPC. When the concentration of BPC reached some degree, CNTs could only adsorb BPC, which was useful for real sample analysis. BPC is a much larger hydrophobic molecule. Since CNTs are hydrophobic, they adsorb hydrophobic compounds more strongly than hydrophilic compounds. As a result of more BPC being adsorbed on CNTs, it was used as the experimental protein in a further study. The fiber to-fiber reproducibility was investigated on five replicate experiments using CNTs coated fibers prepared in the same way under the optimized conditions. MWNTs' E_{ex} for BPC was 87.8 ± 1.20% (n = 5, RSD = 2.15%) and SWNTs' E_{ex} for BPC was 69.8 ± 1.94% (n = 5, RSD = 2.16%). All these results indicated that our method was feasible and reliable.

Comparison of the SPME efficiency of the coated fiber with PDMS fiber

To prove the advantage of our method to extract BPC, our method was compared with commercial SPME fibers (PDMS). PDMS fiber is relatively a blank reference to the proposed CNTs coating fiber because CNTs in this study were coated on it. The PDMS fiber's E_{ex} was 35.5 ± 0.90% (n = 3) for BPC under optimized SPME conditions. The results showed that PDMS adsorbed less BPC but more BPC than CNTs. The selectivity between BPC was

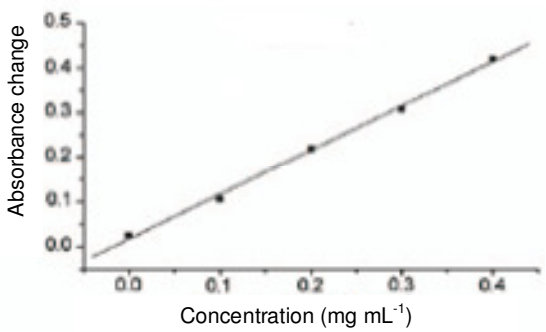

Figure 9. Absorbance change of different spiked BPC concentrations in bovine serum. The inserted figure is the liner relation of BPC concentration and absorbance change. Extraction conditions: pH of extraction buffer: 5.0; phosphate concentration of extraction buffer: 0.1 mol L^{-1}; extraction time: 120 min; extraction buffer volume: 5 ml.

not as obvious as that of CNTs. This might be because PDMS are less hydrophobic than CNTs. Thus, CNTs have some advantages in BPC analysis as compared to PDMS.

Sample analysis

Our method was applied to the analysis of pond water to study the substrate effect. The extraction efficiency of the BPC water sample was a little lower than in the phosphate buffer, around 80% when using MWNTs. And the recovery yield of BPC in the desorption buffer was 65 to 75%. The results showed that when the concentration of BPC was under 0.49 mg mL^{-1} (5 ml sample), the absorbance change was linear to the concentration (Figure 9). The regression equation is $y = 0.025 + 0.97x$ ($R^2 = 0.99884$, SD = 0.00956, N = 5, $p < 0.0001$). Thus, the amount of BPC can also be determined in these samples, and our method is applicable to water samples of various concentrations. The detection limit of this method in water was 0.078 mg mL^{-1} determined according to 3 S_b/m (S_b is the blank standard deviation and m is slope of the linear fit line). Finally, our method was applied to determine the BPC concentration in a pond water sample. The results showed that the concentration of BPC was 2.64 ± 0.18 mg mL^{-1} (n = 3, RSD = 2.99%). This data was about 3.0 mg mL^{-1} determined by the method of GC-MS. This result demonstrated the feasibility of our method to roughly determine the concentration of BPC in the water sample.

Conclusion

In this paper, SWNTs and MWNTs were coated on commercial SPME fibers to study the adsorption effect of BPC on CNTs. First, raw CNTs and CNTs coated with SPME fiber were characterized. The results showed that the surface of CNTs coating was propitious to BPC adsorption. The SEM image of BPC adsorbed MWNTs coated fiber confirmed this assumption. Then, the SPME procedure was optimized. From the results, it was observed that both MWNTs and SWNTs had much stronger adsorption ability than BPC. SWNTs have larger specific surface area, so their adsorption ability is stronger than MWNTs. However, in the situation of BPC, the much larger size relative to the diameter of SWNTs is dominant, which creates small interaction area with the nanotubes. Thus, MWNTs have stronger affinity for BPC. Also, the reproducibility is good for real sample analysis. From our sample analysis, the concentration of BPC was linear to the absorbance change when the concentration of BPC was under 0.49 mg mL^{-1} (5 ml sample). When compared with commercial SPME fiber (PDMS), our method was more selective and sensitive.

In conclusion, our method is advantageous for BPC extraction from the water sample. It is simple, inexpensive and time-saving, which may make it a good way to determine BPC concentration. The method developed was simple, reliable, and precise for determining BPC in water. Also, the proposed method was free of interference compared to conventional procedures to determine copper (Zhang et al., 2001; Manini et al., 2006; Bianchi et al., 2002). The method can be successfully applied to the separation and determination of BPC in binary mixtures.

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