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Short communication

Multi-walled carbon nanotubes as a solid-phase extraction adsorbent for the determination of chlorophenols in environmental water samples

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Abstract

Multi-walled carbon nanotubes (MWCNs) are used as adsorbent for solid-phase extraction (SPE) of several chlorophenols (CPs). CPs were adsorbed on MWCNs cartridge, then desorbed with pH 10.0 methanol, finally determined by HPLC. Under the optimized conditions, detection limits of 0.08–0.8 ng mL^{-1} were obtained. The method had been applied to analyze the five CPs in tap water and river water.

Keywords: Multi-walled carbon nanotubes; Solid-phase extraction; HPLC; Chlorophenols; Water samples

1. Introduction

Carbon nanotubes, repeatedly discussed in the literature for the SPE of several organic contaminants [1–4] and trace metal ions [5], are now tested for the SPE of a limited number of CPs.

2. Experimental

2.1. Reagents and water samples

4-Chlorophenol (4CP) and 3-chlorophenol (3CP) (1.00 mg/mL) were purchased from the Institute for Reference Materials, Beijing, China. 2,4-Dichlorophenol (DCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) were obtained from China State Research Center for Reference Materials, Beijing, China. LC-grade methanol and acetonitrile were purchased from Siyou Biomedical Technology Co. Ltd. (Tianjing, China). The physical characterization of MWNTs used was described elsewhere [1].

Tap and river water were collected from the water tap in our laboratory and the Jingmi Canal, respectively, filtered through a 0.20 μm cellulose membrane and then stored at a temperature of 4 °C.

2.2. Chromatographic system and conditions

The HPLC instrument included a P680A gradient pump, an AS50 autosampler, a LC30 chromatography oven set at 30 °C and an AD25 absorbance detector (Dionex, Sunnyvale, USA) set at 285 nm. The separation was performed on a polar-enhanced C_{16} silica column (150 mm × 4.6 mm I.D., 5 μm, 120 Å, Dionex, Sunnyvale, USA) at a flow rate of 1 mL/min. The gradient elution was performed with a mixture solution of acetonitrile and water (20 + 80, v + v) containing 1% acetic acid (A) and acetonitrile containing 1% acetic acid (B). The gradient program was as follows: started at 10% B, increased B to 55% in 15 min, increased B to 100% in 5 min and kept for 5 min, then decreased B to 10% in 1 min and kept for 2 min to equilibrate the column.

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2.3. Extraction procedure

The SPE cartridge packed 0.3 g MWCNs was prepared and pretreated by the method described elsewhere [1]. The solutions adjusted to pH neutral were loaded at a flow rate of 5 mL min^{-1}. Then, CPs were eluted with 6 mL of pH 10.0 methanol. Under a gentle stream of nitrogen gas, the eluate was evaporated to about 0.5 mL, then its pH was adjusted to 3.0 and its volume was increased to 1.0 mL with methanol. Finally, 25 μL of the solution was injected for the HPLC determination.

3. Results and discussion

3.1. Evaluation of MWCNs as SPE sorbents

3.1.1. Choice of the kind and the volume of eluent

Five types of eluents including methanol, acetonitrile, tetrahydrofuran, ethyl acetate and pH 10.0 methanol were tested and the results are shown in Fig. 1. It is difficult to elute CPs quantitatively with methanol, acetonitrile, tetrahydrofuran and ethyl acetate alone. Of all five CPs, PCP was the most difficult one to be eluted. The experiments showed that pH 10.0 methanol was the most effective eluent.

For extraction of 4CP, 3CP, DCP and TCP, when eluent volume was in the range of 1–2 mL, the recoveries increased with increase of eluent volume; but when eluent volume was increased further, the recoveries leveled off. For extraction of PCP, only when eluent volume amounted to 5–6 mL, did the recovery get to a higher level and level off. So, 6 mL of pH 10.0 methanol was adopted. In this case, recoveries of 92%, 91%, 91%, 87% and 84% were achieved for 4CP, 3CP, DCP, TCP and PCP, respectively.

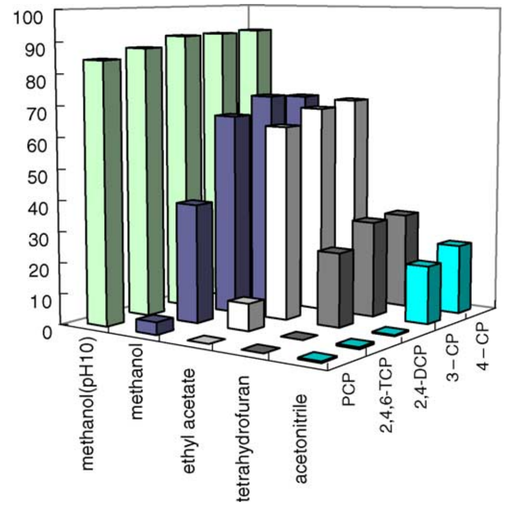

Fig. 1. Effect of types of eluents on the recoveries of five CPs. Volume of solutions: 50 mL; concentration of five CPs: 400 ng mL^{-1}.

3.1.2. Effects of the pH and volume of water samples on the extraction efficiency

The effect of the pH was investigated over the range of pH 1–11 and it was found that very low and high pH of solutions had a negative effect on the extractions. But when the pH of solutions varies in the range of pH 5–9, the pH nearly has no influence on the extractions. Therefore, pH 5–9 was selected as the pH of solutions.

To investigate the influence of sample volume, different volumes of purified water were spiked with 20 μg of five CPs. It was found that the recoveries decreased slightly with the increase of volume. When the volume was 200 mL, the recoveries of 83–87% were obtained for the five CPs. For some special CPs, such as 4CP and 3CP, it appears that the recoveries obtained in the present work are better than those of other research work. In report [6], polyaniline was used for

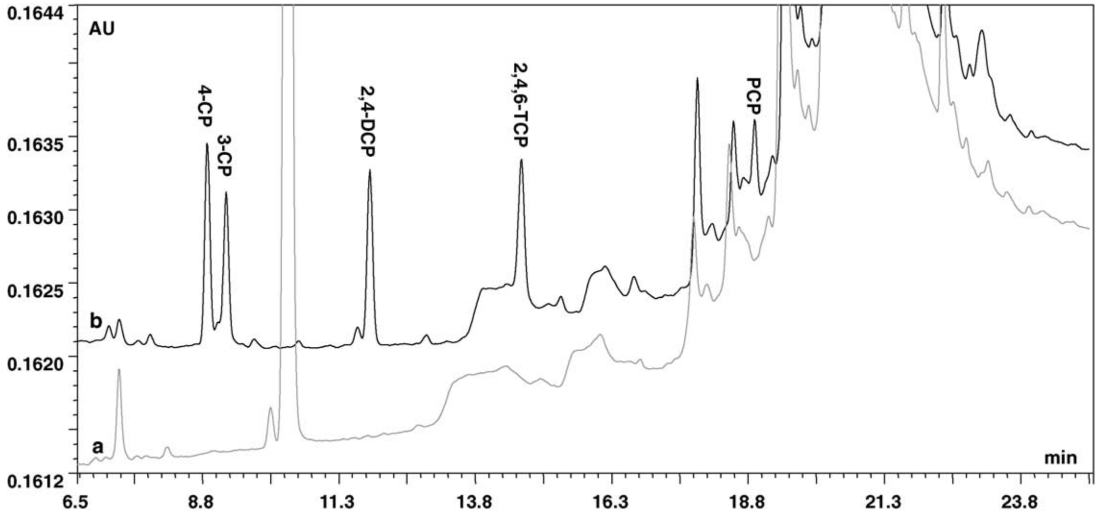

Fig. 2. SPE-LC chromatograms of tap water samples. (a) Tap water sample, and (b) tap water sample spiked with CP standards. See Table 2 for the spiked concentration level of CPs.

Table 1
Recoveries at different volumes of sample solutions ($n = 3$)

Analyte	Volume (mL)				
	50	100	200	500	1000
	Recoveries (%)				
4CP	92	90	86	76	73
3CP	91	92	87	78	73
DCP	91	93	85	83	73
TCP	87	93	84	81	76
PCP	84	87	83	82	67

SPE of several CPs, and recoveries were 45% and 55% for 2CP and 4CP, respectively. In other cases, it appears that the recoveries are as good as those obtained with some polymer adsorbents [7–9]. In the analyses of water samples, a volume of 200 mL was selected.

3.2. *Analytical performance and application*

Under the optimized conditions, the analytical performance was examined. There is a linear correlation between peak area and concentration of 1–200 ng/mL for 4CP, 3CP, DCP and TCP, 2–200 ng/mL for PCP, respectively. The detection limits (s/n = 3) of 0.08, 0.1, 0.1, 0.2 and 0.8 ng/mL were obtained for 4CP, 3CP, DCP, TCP and PCP, respectively.

The method was applied to analyses of tap and river water, and recoveries were in the range of 88–109%. The chromatograms of a tap water and its spiked standard solution are shown in Fig. 2. It is noticed that baselines of these chromatograms is rather unusual: they are not smooth after 17.5 min, but smooth before 17.5 min. The reason for this is not yet clear. In view of this case, it is very difficult to get a low detection limit for PCP. As indicated above, the detection limit for the PCP is 0.8 μg/mL, a much higher value than those of other four CPs.

4. Conclusions

MWCNs have been evaluated for SPE of trace CPs, and the recoveries were compared with those of other published reports. The results showed that MWCNs could be used as an effective SPE sorbent for CPs (Tables 1 and 2).

Table 2
Recoveries of five CPs spiked water samples ($n = 3$)

Water sample	Added (ng mL^{-1})	Recovery (%)
Tap water		
4CP	2.50	101 ± 8
3CP	2.50	103 ± 6
DCP	2.50	100 ± 7
TCP	2.50	100 ± 6
PCP	5.00	97 ± 8
River water		
4CP	2.50	100 ± 6
3CP	2.50	99 ± 5
DCP	2.50	93 ± 8
TCP	2.50	88 ± 6
PCP	5.00	109 ± 8

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