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ORIGINAL RESEARCH
PAPER



Determination of organochlorine pesticides in water using GC combined with dispersive solid-phase extraction with single-walled carbon nanotubes

PENG SUN^{1,2,3*} , YANHONG CUI^{1,2}, RUI YAN^{1,2} and YONGFU LIAN^{3*}

¹ Center of Management of Laboratory Equipment, Heilongjiang Bayi Agricultural University, Daqing 163319, China

² Agricultural Products and Processed Products Supervision and Testing Center, Ministry of Agriculture, Daqing 163319, China

³ Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China

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SUMMARY

In this study, single-walled carbon nanotubes (SWNTs) were used to determine organochlorine pesticides (chlorothalonil and pentachloronitrobenzene) in water using dispersive solid-phase extraction (DSPE), followed by gas chromatography (GC). The optimal adsorption conditions were determined by analyzing the effect of adsorbent dosage, adsorption time, eluent type and volume, and elution time. Under the optimal conditions, a good linearity was obtained at concentrations from 10 to 400 $\mu\text{g L}^{-1}$ with correlation coefficients ranging from 0.9991 to 0.9986. The limits of detection (LOD) for the two organochlorine pesticides were 0.025 and 0.049 $\mu\text{g L}^{-1}$, and the limits of quantification (LOQ) were 0.080 and 0.156 $\mu\text{g L}^{-1}$, respectively. The accuracy of the proposed method was evaluated by measuring the recovery of the spiked samples, which ranged from 82.5% to 110.5% at spiking levels of 0.5–10 $\mu\text{g L}^{-1}$ with relative standard deviations lower than 5.6% ($n = 6$). This method was successfully applied to determine the target analytes in canal water, drinking water, and water taken from the inlets and outlets of a wastewater treatment plant. The results demonstrate that the developed method has great potential for determining the two organochlorine pesticides in water samples.

KEYWORDS

carbon nanotubes, dispersive solid-phase extraction, organochlorine pesticides, water samples, GC

INTRODUCTION

Organochlorine pesticides (OCPs) are highly-stable and fat-soluble synthetic insecticides that persist in the environment and pose health risks to humans and other organisms when they enter the food chain via biological enrichment [1]. To ensure environmental safety and health, it necessary to establish a convenient, fast, and accurate detection method to effectively control organic chlorine residues in the environment [2].

Currently, organochlorine pesticide detection methods mainly include gas chromatography (GC) [3, 4], GC-MS [5, 6], and HPLC-MS/MS [7, 8]. Of these, GC has been widely used for pesticide residue analysis due to its rapid analysis. Sample pretreatment is necessary when analyzing environmental samples, and the main pretreatment methods for detecting and analyzing organochlorines in water samples are liquid-liquid extraction [9, 10], solid-phase extraction (SPE) [11], and Soxhlet extraction [12]. SPE is a relatively new sample pretreatment technique that is used to separate, purify, and concentrate samples. Compared with traditional

*Corresponding author.

E-mail: byndsunpeng@sina.com

E-mail: byndkjcptk@163.com

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liquid-liquid extraction, SPE effectively separates analytes from interfering components, improves the analyte recovery rate, and simplifies the sample pretreatment process. It is widely used in food, environment, medicine, chemical, and other industries [13–15]. Dispersive solid-phase extraction (DSPE) is a novel sample preparation technique that offers advantages such as simplicity, low solvent use, safety, and automation by adding a sorbent to the extract to remove matrix contaminants. Recently, DSPE has been successfully used to purify liquid samples and extracts [16–19]. Here, single-walled carbon nanotubes (SWNTs) were prepared by an arc discharge method, and their use as a dispersive solid-phase extraction adsorbent for OCPs was studied. This is the first time single-walled carbon nanotubes was used for the dispersive solid-phase extraction; (2) chlorothalonil and pentachloronitrobenzene in water samples could be completely extracted by single-walled carbon nanotubes; (3) single-walled carbon nanotubes as adsorbents for DSPE coupled with GC were developed for determination of chlorothalonil and pentachloronitrobenzene in water sample; and (4) satisfied sensitivity and recoveries were obtained.

EXPERIMENTAL

Instrumentation

Chromatographic analysis was performed using a Shimadzu GC instrument coupled with an electron capture detector (ECD) (Shimadzu Co., Japan). An Extrapid SPE apparatus from Beijing Labtech Instruments Co., Ltd. was used. Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 500/VP SEM. FT-IR spectra (4000–400 cm^{-1}) were recorded on a 1,600 series Perkin-Elmer FTIR Spectrometer (MA, USA) using KBr pellets. Nitrogen adsorption/desorption isotherms were obtained using an Autosorb-iQ-MP automatic gas adsorption analyzer.

Chemicals and reagents

SWNTs were purchased from Beijing Deke Daojin Science and Technology Co., Ltd., China, its specific surface area of SWNTs is $96.9 \text{ m}^2 \text{ g}^{-1}$, the pore volume is $0.42 \text{ cm}^3 \text{ g}^{-1}$, and the average pore size is 14.7 nm. SWCNTs was ultrasonic dispersion in 12 mol L^{-1} HCl for 30 min, the lower layer sample was washed with deionization for several times and $\text{pH} = 6\text{--}7$ of the supernatant. The black flake sample was obtained at $60 \text{ }^\circ\text{C}$ vacuum drying for experimental, 50 mg of dried sample was measured and added with 40 mL of 8 mol L^{-1} HNO_3 and 9.2 mol L^{-1} HSO_4 . The above operation was repeated to obtain SWCNTs purified by mixed acid.

Chlorothalonil (CTL) and pentachloronitrobenzene (PCNB) with a 99.5% purity and a concentration of 100 mg L^{-1} were purchased from the Agro-Environmental Protection Institute, Ministry of Agriculture, China. Methanol, ethanol, acetone, tetrahydrofuran, and acetonitrile were purchased from Fisher Scientific, USA. Microporous membranes ($0.22 \text{ }\mu\text{m}$) were obtained from Dikma Technologies (Beijing, China).

Standard curve configuration

Standard solution configuration: 1 mL of CTL standard solution with a concentration of $1,000.0 \text{ mg L}^{-1}$ was diluted to 100 mL with *n*-hexane and the concentration was 1 mg L^{-1} . The standard solution of PCNB with a concentration of 1 mg L^{-1} was prepared using the same method. The CTL and PCNB standard solutions were mixed and used on-site.

Sample preparation

A natural water sample (20 mL) was placed in a 50 mL centrifuge tube. Then, 160 mg of SWNTs were added, and the mixture was vortexed for 5 min, centrifuged for 5 min at $10,000 \text{ r min}^{-1}$, and then the supernatant was discarded. 5 mL ethyl acetate was added into the centrifuge tube, shaken for 5 min, and centrifuged at $10,000 \text{ r min}^{-1}$ for 10 min. 1 mL of the supernatant was extracted and blown dry with nitrogen in a water bath at $20 \text{ }^\circ\text{C}$. The resulting residue was re-dissolved in 1 mL *n*-hexane, then passed through a $0.22 \text{ }\mu\text{m}$ microporous membrane filter for GC analysis.

DISCUSSION

Adsorption of OCP pesticides by SWNTs

First, 5 mL of mixed standard solutions of CTL and PCNB with concentrations of $5 \text{ }\mu\text{g L}^{-1}$ were prepared, and various amounts of SWNTs were added. After vortex oscillation and centrifugation, 1 mL of the supernatant was extracted and dried with nitrogen in a water bath at room temperature. Then, 1 mL of *n*-hexane was used to re-dissolve the residue and was then filtered through a $0.22 \text{ }\mu\text{m}$ microporous membrane for GC analysis.

Selection of adsorbent dosage

Adsorbent dosage is one of the main factors that affects DSPE. Different amounts of SWNTs (100, 120, 140, 160, 180, and 200 mg) were added to 5 mL of a mixed standard solution containing $50 \text{ }\mu\text{g L}^{-1}$ organochlorine, then subjected to vortex oscillation for 3 min and centrifugation for 5 min at $10,000 \text{ r min}^{-1}$. The supernatant was extracted and passed through a $0.22 \text{ }\mu\text{m}$ microporous membrane filter, and then analyzed by GC. The GC analysis results (Fig. 1) show that when the amount of adsorbent was between 100 and 140 mg, the removal rate of organochlorine in the mixed standard solution gradually increased with an increasing amount of SWNTs, but OCPs were still detected. When the adsorbent dosage was increased to 160 mg, the removal rate of CTL reached 88%, and the removal rate of quintozene reached 73%. The removal rate of the two OCPs remained unchanged when the adsorbent dosage was further increased, indicating that 160 mg SWNTs was the optimal adsorbent amount. Therefore, 160 mg SWNTs was used for subsequent DSPE experiments.

Selection of pH

CTL and PCNB can slowly hydrolyze in alkaline solution, so the effect of pH (3, 4, 5, 6, 7) on the removal rate of the two OCPs was investigated (Fig. 2). When pH was between 3 and



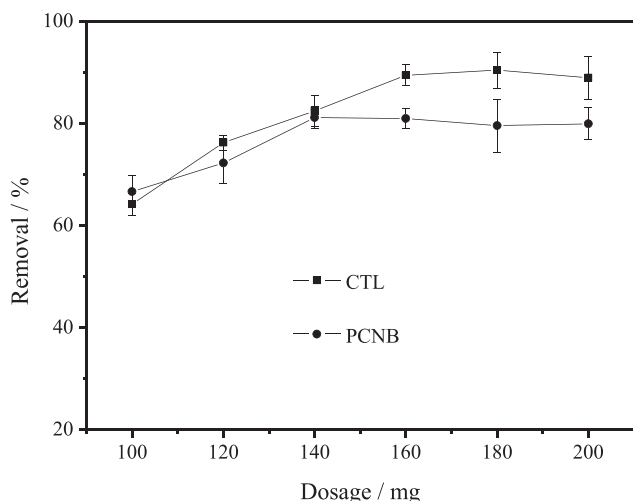


Fig. 1. Effect of different amounts of SWCNTs on removal of two OCPs

5, the removal rate of CTL and PCNB in the mixed standard solution gradually increased with the solution pH. When the pH increased to 5, the removal rate of CTL and PCNB reached a maximum and began to slowly decline when it further increased to 7. SWNTs readily accept protons at low pH values that competitively bind to the adsorbent. As the pH increased, the positive charge density on the surface of SWNTs gradually decreased, thus increasing the electrostatic attractions between the adsorbent and CTL, as well as PCNB. The adsorption rapidly increased, showing that the optimal pH was 5.

Effect of adsorption time

Using the optimized test conditions, the effects of adsorption time (1, 3, 5, 7, 9 min) on the removal of target compounds was investigated. Fig. 3 shows that the removal rate of CTL and PCNB gradually increased with the shaking time from 1 to 3 min. At 3 min, the removal rate of PCNB reached 89.4%, and continuing to increase the shaking time did not further increase the removal rate of PCNB. When the shaking time was 5 min, the removal rate of CTL reached 95.6%, and

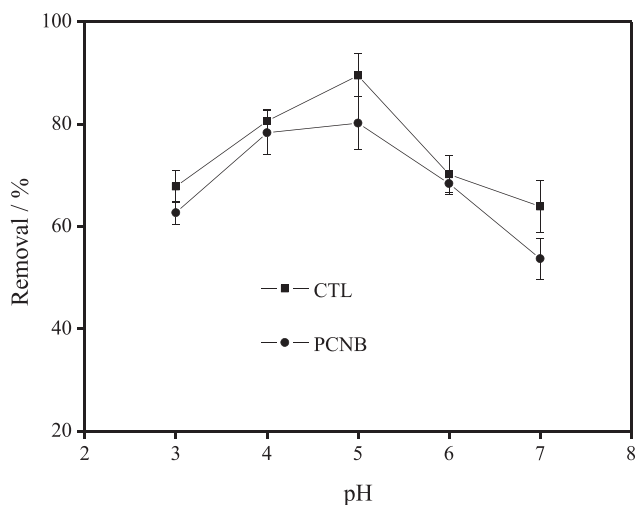


Fig. 2. Effect of pH on removal of two OCPs

further increasing the adsorption time did not increase the CTL adsorption amount. When 160 mg SWNTs was used as the adsorbent, equilibrium adsorption of PCNB was reached in 3 min, while that of CTL was reached at 5 min.

Selection of eluent types

160 mg SWNTs powder was added to four different standard solutions (5 mL, $5 \mu\text{g L}^{-1}$) containing a mixture of CTL and PCNB. The solutions were shaken for 5 min, then centrifuged for 5 min at $10,000 \text{ r min}^{-1}$, filtered, and the supernatant was discarded. 3.0 mL acetone, *n*-hexane, ethyl acetate, and acetone + *n*-hexane (V/V = 1:1) were used as eluents, shaken for 10 min, and centrifuged. 1 mL of the supernatant was extracted and placed in a water bath at 40°C to dry. The effect of the four eluents on the recovery of the target compound was investigated, and the results are shown in Fig. 4. Hexane was used to re-dissolve the residue for GC analysis to investigate the effects of the four different eluents on the target recovery. Using ethyl acetate as the eluent showed the highest recovery rate.

Selection of eluent volume

Using the optimized conditions, the effects of different volumes of ethyl acetate eluent (1, 3, 5, 7, and 9 mL) on the recovery of the two OCPs were investigated. The results show that as the eluent volume increased, the recovery rates of the two OCPs also gradually increased. When the volume increased to 3 mL, the CTL recovery rate reached a maximum of 97.2%, and when the volume continued to increase to 5 mL, the recovery of PCNB reached a maximum. When the volume increased to 9 mL, the recoveries of the two OCPs did not increase further, so 5 mL ethyl acetate was chosen.

Selection of elution time

According to the optimized conditions, the effects of elution time (2, 4, 6, 8, and 10 min) on the recovery of the two pesticides were investigated. The results show that as the elution time increased, the recovery rate gradually increased. When the elution time was 8 min, the recovery rate reached

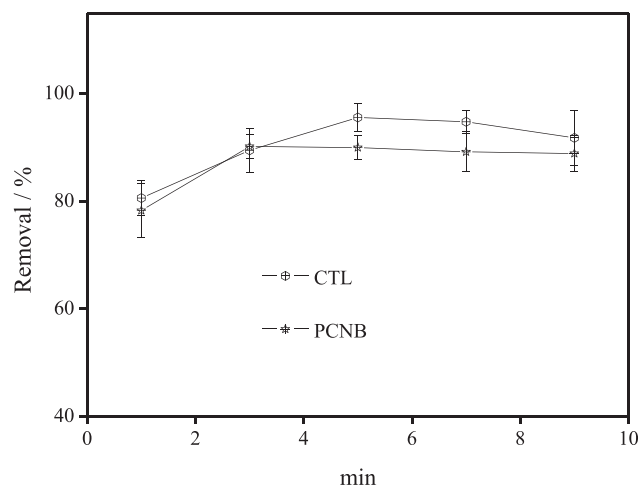


Fig. 3. Effect of different adsorption time on removal of two OCPs

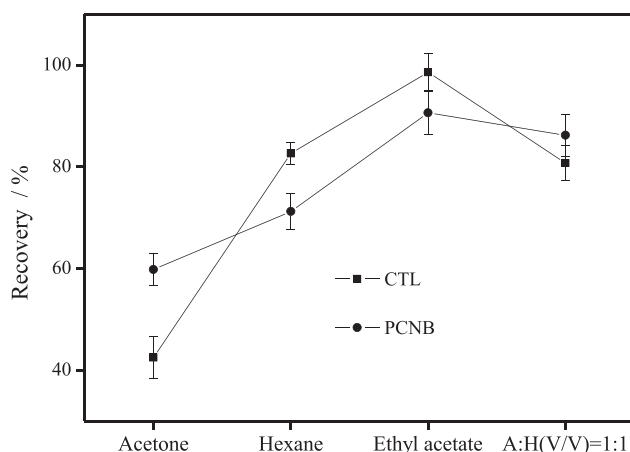


Fig. 4. Effect of different eluting solvent on recovery of two OCPs

a maximum, and further increasing the elution time did not further increase the recovery rate. Thus, an elution time of 8 min was used to maximize experimental efficiency.

Adsorption mechanism

According to the experimental results, CTL and PCNB were adsorbed on the surface of SWCNTs through π - π interactions. PCNB contain a nitro group, which can easily form positively-charged ions that are adsorbed by SWCNTs. Additionally, intermolecular hydrogen bonds formed between the hydroxyl and carboxyl groups of SWCNTs, as well as between CTL and PCNB at the end of SWCNTs. These further enhanced adsorption of the target compounds.

METHOD VALIDATION

Standard curve, quantitative limit, and detection limit

A standard solution (0.1 mL) containing 100 mg L⁻¹ PCNB was placed in a 10 mL volumetric flask. A standard solution with a concentration of 1 mg L⁻¹ CTL was also prepared.

The standard solution containing CTL and PCNB was diluted with *n*-hexane, and a series of standard solutions were prepared with mass concentrations of 10.0, 20.0, 40.0, 80.0, 100.0, 200.0, and 400 $\mu\text{g L}^{-1}$. The standard solution containing CTL and PCNB was analyzed using GC using the mass concentration of the two OCPs as the *x*-axis and the instrument response as the *y*-axis to obtain a linear curve. The limits of detection (LOD) and limits of quantification (LOQ) with 3-times and 10-times signal-to-noise ratios were calculated, respectively, and the results are shown in Table 1.

Precision

A mixed standard solution (5 mL) of PCNB and CTL was prepared at a concentration of 1.0 $\mu\text{g L}^{-1}$. An actual water sample was used to prepare a standard sample with a concentration of 5 $\mu\text{g L}^{-1}$, and 6 sample solutions were prepared in parallel according to the optimized conditions. The response values of the sample were used to calculate the content, and the RSD was calculated and shown in Table 2.

Accuracy

Real water samples were used, and 20 mL of spiked samples with concentrations of 0.5, 5.0, and 10.0 $\mu\text{g L}^{-1}$ for a total of 15 samples were prepared according to the optimized conditions. The peak area concentrations of the target compounds were calculated, and the RSD of each sample was calculated six times in parallel. The results in Table 2 show that the average recoveries of CTL and PCNB were 82.5–110.5%, and the RSD ranged from 2.1 to 5.6%, respectively.

Analysis of real water samples

The optimized analysis method was used to analyze, drinking water, canal water, inlet water, and outlet water at a sewage treatment plant. Blank tests and water-recovery tests were also conducted. CTL was detected in the water sample from the sewage treatment plant at a concentration of 0.064

Table 1. Linear equation, linear range, *r*, LOD, LOQ of two OCPs

Analyte	Linear equation ($\mu\text{g L}^{-1}$)	Linear range ($\mu\text{g L}^{-1}$)	<i>r</i>	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	RSD _P	RSD _A
CTL	$Y = 12,647.613X - 83.45$	10–400	0.9991	0.025	0.080	4.6	3.9
PCNB	$Y = 6,354.512X - 36.42$	20–200	0.9986	0.049	0.156	5.1	4.8

Table 2. The average recoveries and RSDs of two OCPs spiked in environmental water samples (*n* = 6)

Analyte	Spiked ($\mu\text{g L}^{-1}$)	Drinking water	Canal water	Wastewater treatment plant	
				Inlets	Outlets
CTL	0.5	93.2(4.6)	84.6(4.4)	106.3(5.3)	86.4(3.4)
	5.0	88.9(3.6)	97.5(3.6)	95.3(2.6)	105.4(4.8)
	10.0	86.3(5.1)	103.4(5.4)	92.0(5.6)	96.5(5.1)
PCNB	0.5	105.3(4.2)	110.5(3.6)	83.2(5.0)	91.8(2.1)
	5.0	83.2(3.5)	95.7(3.5)	82.5(3.6)	102.1(3.5)
	10.0	95.6(4.4)	82.8(5.2)	87.62(3.3)	89.6(5.2)



$\mu\text{g L}^{-1}$, which was lower than the quantitative detection limit of the method. The concentration of the added sample was $1.0 \mu\text{g L}^{-1}$, and the calculated recovery rate was 96.8%. The results are satisfactory and indicate that the established method was accurate and reliable and can be used to detect and analyze OCPs in environmental water samples. The chromatogram of the mixed standard solution (a), spiked samples (b), and real water samples (c) are shown in Fig. 5.

CONCLUSION

This is the first time single-walled carbon nanotubes as adsorbents was used for the dispersive solid-phase extraction coupled with GC were developed for determination of CTL and PCNB in water sample; CTL and PCNB in water samples could be completely extracted by single-walled carbon nanotubes; satisfied sensitivity and recoveries were

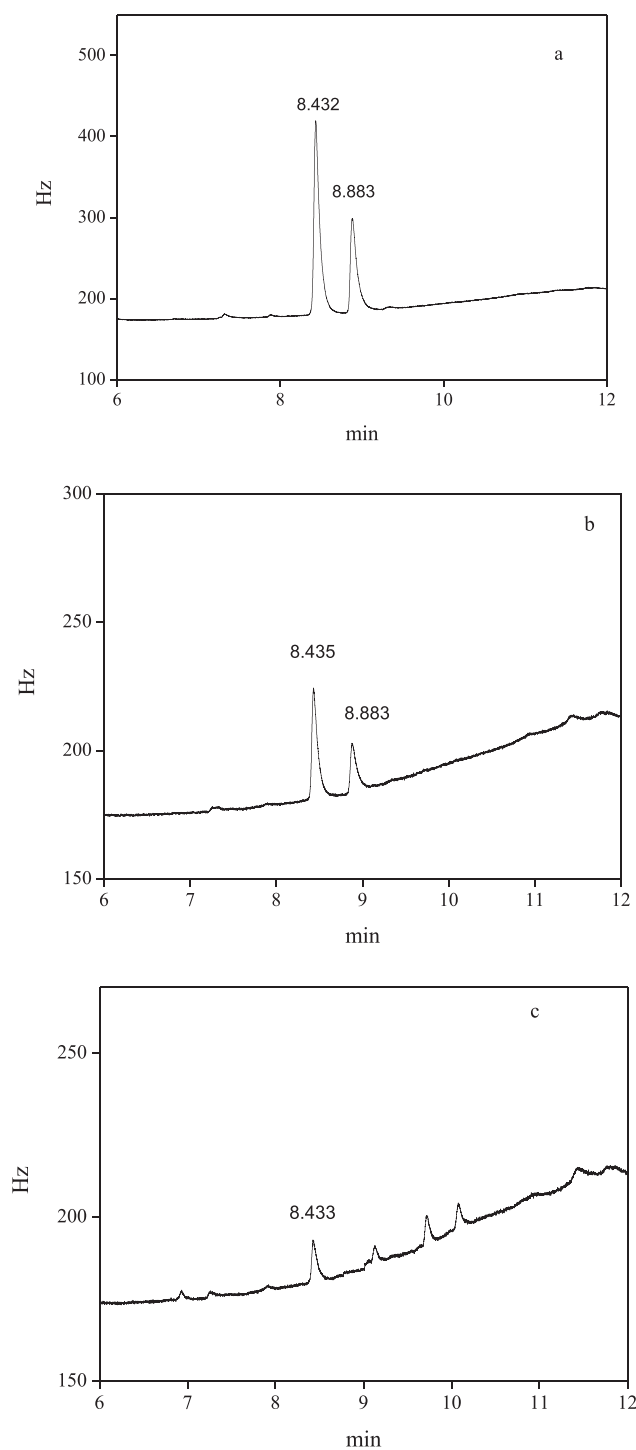


Fig. 5. GC chromatogram of the target in mixed standard solution(a), spiked samples (b) and real water samples(c) CTL ($t_R = 8.43$), PCNB ($t_R = 8.88$)

obtained. These results indicate that the proposed method can be used for the efficient determination of trace organochlorine pesticides in various water samples.

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Conflict of interest: The authors declare that they have no conflict of interest.

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