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Electropolymerized multiwalled carbon nanotubes/polypyrrole fiber for solid-phase microextraction and its applications in the determination of pyrethroids

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ABSTRACT

A novel solid-phase microextraction (SPME) fiber coated with multiwalled carbon nanotubes/polypyrrole (MWCNTs/Ppy) was prepared with an electrochemical method and used for the extraction of pyrethroids in natural water samples. The results showed that the MWCNTs/Ppy coated fiber had high organic stability, and remarkable acid and alkali resistance. In addition, the MWCNTs/Ppy coated fiber was more effective and superior to commercial PDMS and PDMS/DVD fibers in extracting pyrethroids in natural water samples. Under optimized conditions, the calibration curves were found to be linear from 0.001 to 10 μg mL^{-1} for five of the six pyrethroids studied, the exception being fenvalerate (which was from 0.005 to 10 μg mL^{-1}), and detection limits were within the range 0.12–0.43 ng mL^{-1}. The recoveries of the pyrethroids spiked in water samples at 10 ng mL^{-1} ranged from 83 to 112%.

1. Introduction

Since its introduction in 1990 [1], solid-phase microextraction (SPME) has proved to be an effective and powerful tool for the analysis in environmental samples. This technique is based on the distribution effect of analytes between samples and the SPME coating. Therefore, the fiber coating is the key factor in SPME because the extraction efficiency primarily depends on the coating characteristics. In recent years, several fiber coating approaches, including sol–gel technology [2–5], physical deposition [6,7], direct use of uncoated fibers [8–10], epoxy-glued solid sorbents [11,12], electrochemical procedures [13–15], and molecular imprinting polymers [16,17] have been developed.

Polypyrrole (Ppy) has been widely used for many applications because of the interaction between Ppy and the target analytes [16]. Since Ppy can be prepared on a metal surface by electrodeposition from an aqueous solution, fine stainless steel wire could be selected as a supporting fiber in SPME. A microextraction fiber coated with Ppy as an extraction phase is capable of concentrating analytes from complex matrices. Ppy coatings can be used for the analysis of peptides, indicating that Ppy coatings can be taken as an extraction phase for both small molecules and peptides [17]. Polyphosphate-doped Ppy coated on a steel fiber can be used for SPME of organochlorine pesticides in water [18]. The detection limits were 0.015–0.06 ng mL^{-1}.

Multiwalled carbon nanotubes (MWCNTs) are a kind of wide application carbon material that was first discovered in 1991 [19]. Recent electrochemical studies reveal that the unique properties of MWCNTs make them very promising in the design of electrochemical sensors and biosensors [20–22]. The application of MWCNTs for solid phase extraction of organic pollutants in water has been demonstrated [23] and, recently, MWCNTs have been used as a new SPME coating material for the determination of polybrominated diphenyl ethers [24,25].

The desirable merging of CNTs and conduction polymer properties in a composite form presents new opportunities to produce superior materials for novel applications. To date, electrochemically grown CNTs-conduction polymer films using Ppy have been given great attention, since Ppy offers a greater degree of electrochemical processing flexibility than most other commercially available conducting polymers. Nano size CNTs have been considered as the surface-enhancing component for Ppy film. An open porous structure of Ppy-CNTs with high surface area is reported [26]. Compared to Ppy, Ppy-CNTs are of better thermal stability and have higher charge delocalization properties. Nano-porous

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composite films of MWCNTs and either Ppy were grown using an electrochemical polymerization technique in which the nanotubes and conducting polymer were deposited simultaneously [27]. The electrochemical growth of MWCNTs-conducting polymer composites offers the ability to produce 3-dimensional nano-structured films that combine the redox pseudo-capacitive charge storage mechanism of conducting polymers with the high surface area and conductivity of MWCNTs [28]. Such films should be very useful in the fabrication of micro-SPE cartridges. It is noteworthy that composites of polyaniline and CNTs prepared similarly using electrodeposition are reported [29] and, more recently, results of a study have been presented regarding an electrochemical deposited CNTs-polypyrrole composite for the determination of phthalate esters in aqueous samples [30].

In our study, we prepared a new SPME fiber coating MWCNTs/Ppy on a stainless steel wire. The performance of the MWCNTs/Ppy-coated fiber was evaluated using pyrethroids as test compounds. Good adsorptive properties of this novel coating were obtained due to the fiber having a high surface-to-volume ratio and a nano-structured surface. The optimized SPME method was applied to the analysis of pyrethroids in water samples, and the primary results of both the analytical evaluation and water sample analysis showed that the proposed MWCNTs/Ppy-coated fiber was a promising alternative for SPME applications.

2. Experimental

2.1. Reagents and chemicals

Pyrethroids (fenpropathrin, cyhalothrin, permethrin, cypermethrin fenvalerate and deltamethrin, 100 μg mL^{-1}, GSB B-230232-92) were purchased from the Agro Environmental Protection Institute of the Ministry of Agriculture (Tianjin, China). MWCNTs of less than 5 nm in diameter and 5–15 μm in length were obtained from Shenzhen Nanotech Port (Shenzhen, China). The specific surface area of the MWCNTs was larger than 400 m^2 g^{-1}. Pyrrole (≥98%) and sodium dodecyl benzene sulfonate were supplied by National Medicines Corporation (Shanghai, China). All the other solvents were of analytical reagent grade. The stock solutions of pyrethroids were prepared by diluting a 100 μg mL^{-1} solution of each compound to 10 μg mL^{-1} with acetone. The working standard solutions for SPME procedures were prepared by diluting the mixed standard solution with pure water to the required concentrations. These solutions were stored at 4 °C in the dark before use.

2.2. Apparatus

Surface characteristic studies of the prepared MWCNTs/Ppy-coated fiber were performed using scanning electron microscopy (SEM, model LEO1530, Oberkochen, Germany).

For the experiment, a home-made SPME device was prepared as follows: a 0.15 mm-diameter × 17.0 cm-long prepared stainless steel wire was mounted into the SPME device and the exposed fiber was trimmed to 1.5 cm. In the preparation, stainless steel wire was selected due to its excellent flexibility and electrical conductivity. A Branson 200 ultrasonicator (Danbury, CT, USA) was used to mix various solution ingredients thoroughly. An electrochemical analyzer (LabNet VA5021, China) was used for the electrodeposition of MWCNTs/Ppy films. The pure water for solution preparation was from a Millipore autopure WR600A system (USA), and was used throughout. A gas chromatograph (model GC-2010, Shimadzu, Japan), equipped with an ECD detection system, was employed in the SPME experiments. Commercial manual sampling SPME devices with 100 μm polydimethylsiloxane (PDMS) and 65 μm PDMS/divinylbenzene (PDMS/DVB) were obtained from Supelco (Bellefonte, PA, USA).

2.3. Gas chromatography conditions

An Rtx-1 capillary, 30 m × 0.25 mm × 0.25 μm film thickness (J&W Scientific, Folsom, CA, USA), was selected as the separation column. Nitrogen (99.999%) was used as the carrier gas and kept at a flow rate of 2.3 mL min^{-1}. Temperature control in the experiment was as follows: initial temperature 160 °C; increased at the rate of 10 °C min^{-1} to 240 °C and held for 2 min; and finally increased by 5 °C min^{-1} to 300 °C. The ECD and injector temperature was kept at 300 °C and 270 °C, respectively.

2.4. Preparation of MWCNTs/Ppy-coated fiber

Before being coated, the stainless steel wire was cleaned with acetone and ethanol in an ultrasonicator for 10 min, washed with pure water, and finally air dried at room temperature. In the pre-polymerization mixture with pure water as the solvent, 0.1 mol L^{-1} Py and sodium dodecyl benzene sulfonate (SDS) were selected. Although the larger amount of MWCNTs used in the preparation of the SPME fiber would yield higher extraction efficiency, the preparation reproducibility of the fibers decreased owing to the coating flaking. In the experiment, about 0.75% by weight of suspended MWCNTs was used when Py was electropolymerized onto the stainless steel wire, which served as the working electrode. A saturated calomel electrode was selected as the reference electrode and a platinum wire as the counter electrode. The cyclic voltammogram (CV) method was used to investigate the electrochemical behavior of Py in SDS–HCl solution, and a suitable potential selected for the pyrrole electropolymerization. Based on the CV results, Py could be oxidized at a potential of +450 mV. In the pyrrole electropolymerization, an electrochemistry analyzer was used to apply a constant potential of +0.6 V for 30 min. In order to compare the extraction ability of acid-treated MWCNTs/Ppy-coated fiber to that made by commercially purchased (untreated) MWCNTs/Ppy, acid-treated MWCNTs were obtained by treating MWCNTs with nitric acid and sulphuric acid. Acid-treated and untreated MWCNTs/Ppy composite films were grown using the selected electrochemical method in which Ppy and untreated or acid-treated MWCNTs were simultaneously deposited on a stainless steel wire. A Ppy coated fiber was prepared for the comparison using the identical procedure to that described above, but without the addition of MWCNTs. The prepared fibers were conditioned at 180 °C for 30 min in the GC-2010 injector. The coating length of each fiber was kept at 1.5 cm.

2.5. Solid-phase microextraction

Prior to extraction, the fiber was conditioned at 270 °C for 30 min to remove any possible contaminants. The MWCNTs/Ppy-coated fiber was assembled in a homemade SPME device for the applications based on our previous work [5]. A 5-mL glass vial was used as a sample container, and 5 mL of standard solution or water sample was placed into the sample vial with a spin bar. After homogenizing the vial solution, the SPME fiber was passed through the septum. The syringe was fixed at a suitable height above the sample vial and thus the section of coated fiber was completely immersed into the sample solution for 15 min at ambient temperature. After extraction, the fiber was removed from the sample vial and introduced into the GC injector maintained at 270 °C for 4 min desorption.

3. Results and discussion

3.1. MWCNTs/Ppy-coated SPME fiber and its extraction ability

In the experiments, six pyrethroids (fenpropathrin, cyhalothrin, permethrin, cypermethrin fenvalerate and deltamethrin) were

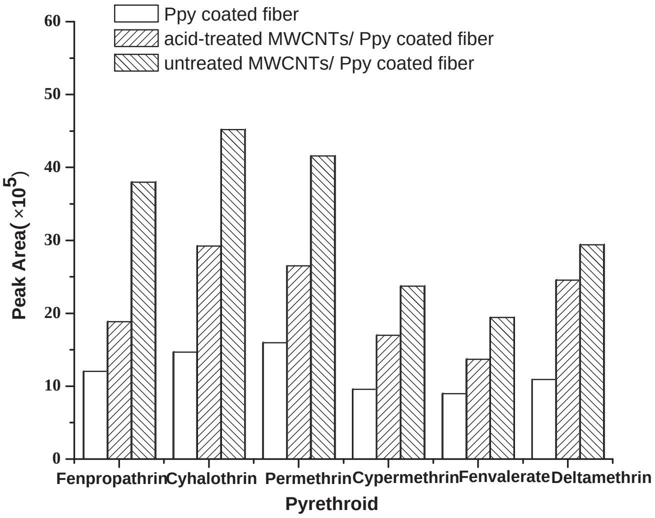

Fig. 1. Comparison of extraction amounts using a Ppy coated fiber, an acid-treated MWCNTs/Ppy coated fiber and an untreated MWCNTs/Ppy coated fiber. Sample volume, 5 mL; extraction time, 15 min; stirring rate, 1000 rpm; desorption temperature, 270 °C; desorption time, 3 min. Concentration of each pyrethroid, 10 ng mL^{-1}.

used as model compounds to investigate the extraction performances of MWCNTs/Ppy-coated fibers. The extraction abilities of the prepared fibers were initially evaluated by comparing them with a Ppy coated fiber under the same experimental conditions. The results (Fig. 1) indicate that the Ppy coated fiber exhibited some degree of extraction for the pyrethroids, but it was lower than that obtained using acid-treated MWCNTs/Ppy or untreated MWCNTs/Ppy-coated fiber. Among the three fibers, the untreated MWCNTs/Ppy-coated fiber exhibited the highest extraction ability for the pyrethroids, which might result from its special morphology. Generally, after acid treatment, the surface area of MWCNTs was increased due to the broken-bend folds of the MWCNTs. In the MWCNTs/Ppy coated fiber as shown in the SEM images (Fig. 2b and c), we were able to find that the MWCNTs were covered by Ppy. In the coating, MWCNTs might partially be taken as a skeleton. The coating appearance showed that the surface of the untreated MWCNTs/Ppy coated fiber appeared to have homogeneous folds or protuberances, but aggregative protuberances could be found from the acid treated MWCNTs/Ppy coated fiber, as shown in Fig. 2c, resulting in a lower surface area than that of untreated MWCNTs/Ppy coated fiber. Since the spherical protrusion surfaces of the untreated MWCNTs/Ppy-coated fiber exhibited the highest extraction efficiency for the pyrethroids and the fibers were easily prepared, in all subsequent experiments, the untreated MWCNTs/Ppy-coated fiber was selected.

In order to further evaluate the sensitivity and selectivity of the MWCNTs/Ppy-coated fiber in the determination of pyrethroids, two commercial fibers, 100 μm PDMS fiber and 65 μm PDMS/DVB fiber, were selected for comparison of their extraction performance. The results, as shown in Fig. 3, indicate that the MWCNTs/Ppy-coated fiber presented higher extraction efficiency for the pyrethroids than the selected commercial fibers. The fact that the MWCNTs/Ppy coating exhibited better extraction efficiency for pyrethroids might be due to some strong interactions between the MWCNTs or Ppy in the coating and the pyrethroids.

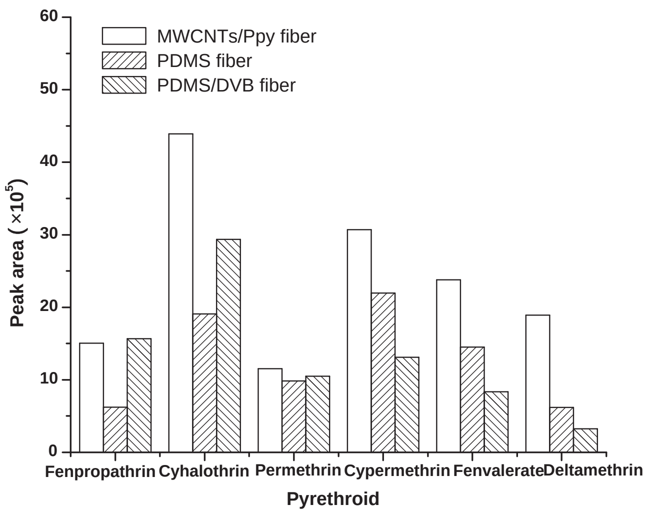

Fig. 3. Comparison of extraction amounts of a PDMS fiber, a PDMS/DVB fiber and an MWCNTs/Ppy coated fiber. Experimental conditions as in Fig. 1.

3.2. Stability of the coating

To evaluate the stability of the MWCNTs/Ppy coating towards organic solvents, the fiber was immersed into four organic solvents (hexane, ethanol, acetone and ethyl acetate) for 5 h, together with a solvent free control. After being cleaned with water, the MWCNTs/Ppy-coated fiber was conditioned at 180 °C for 30 min in an oven to remove any possible solvent residue. The fiber was then used to extract pyrethroids from water samples and subsequently transferring them to the GC apparatus. The results (Fig. 4) revealed that no measurable change of extraction quantities occurred after the fiber was dipped into any of the four organic solvents. In addition, in order to evaluate the acid and alkali resistance of the MWCNTs/Ppy-coated fiber, the fiber was dipped into hydrochloric acid and sodium hydroxide (both 2.0 mol L^{-1}) for 5 h and then cleaned with water. The MWCNTs/Ppy-coated fiber was then used to extract the analytes from the water sample. Experiment results revealed that there was no obvious change in the extraction quantities which occurred after the MWCNTs/Ppy coated fiber was dipped into hydrochloric acid or sodium hydroxide solution. The resistance of the prepared MWCNTs/Ppy-coated fiber to the four organic solvents, and a strong acid and base indicated the high chemical

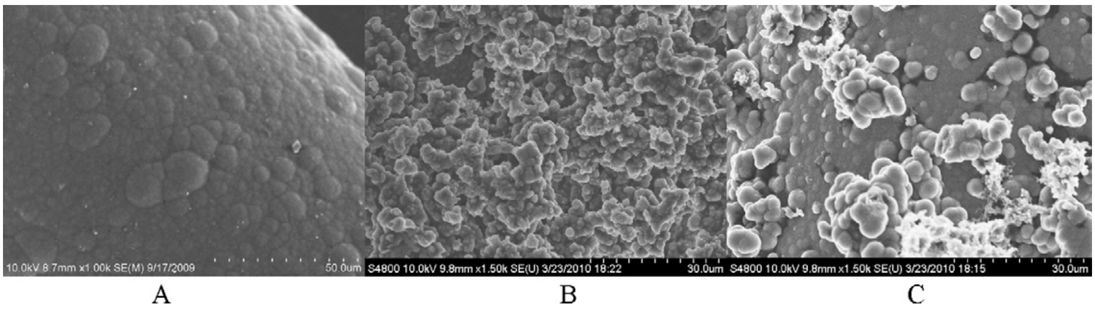

Fig. 2. SEM images of home made SPME fibers.A, Ppy coated fiber surface; B, untreated MWCNTs/Ppy coated fiber surface; C, acid-treated MWCNTs/Ppy coated fiber surface.

Table 1
Analytical evaluation of the six pyrethroids with SPME-GC using an MWCNTs/Ppy coated fiber.

Compound	Correlation coefficient	Linear range (μg mL^{-1})	LOD (ng mL^{-1})	Repeatability (%, $n = 7$, single fiber)	Reproducibility (%, $n = 5$, fiber-to-fiber)
Fenpropathrin	0.9866	0.001–10	0.37	6.3	8.1
Cyhalothrin	0.9784	0.001–10	0.12	5.7	6.6
Permethrin	0.9931	0.001–10	0.43	5.4	9.0
Cypermethrin	0.9790	0.001–10	0.29	4.5	4.8
Fenvalerate	0.9658	0.005–10	0.33	7.1	3.9
Deltamethrin	0.9890	0.001–10	0.15	6.8	6.8

LOD—limit of detection.

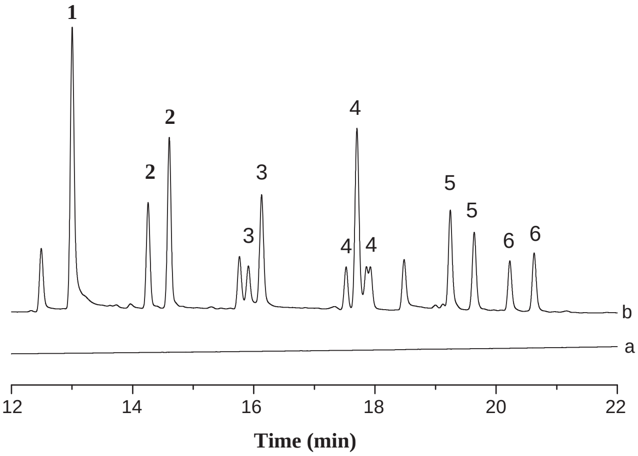

Fig. 4. Typical chromatograms of (a) seawater sample 1; and (b) spiked with the six pyrethroids (10 ng mL^{-1} each) using an MWCNTs/Ppy coated fiber. 1—fenpropathrin, 2—cyhalothrin, 3—permethrin, 4—cypermethrin, 5—fenvalerate, and 6—deltamethrin.

stability of the fiber. This remarkable chemical and organic stability of the MWCNTs/Ppy-coated fiber was attributed to the excellent chemical characteristics of MWCNTs and Ppy.

In order to use the coating in seawater samples, the effect of sodium chloride on the extraction performance was investigated using different concentrations (0, 30, 50, 100 and 200 g L^{-1}). The results indicated that the increase of sodium chloride concentration up to 100 g L^{-1} did not obviously affect the extraction amount of pyrethroids. However, further increase of sodium chloride above 100 g L^{-1} led to a decrease in the amounts extracted.

3.3. Optimization of SPME conditions

Before the proposed MWCNTs/Ppy-coated fiber was applied to analyze samples, the SPME experimental conditions, such as extraction time, stirring rate, desorption temperature and desorption time were studied and optimized.

The extraction time profile for pyrethroids was established by plotting the peak area versus the extraction time. The full equilibration period for the MWCNTs/Ppy-coated fiber was found to be longer than 60 min. The experiment results revealed that the extracted amount of analytes (corresponding to the peak areas) increased as the extraction time increased from 5 to 60 min. In routine analysis, it is not necessary to reach equilibrium if constant extracting conditions are maintained [31]. In this study, 15 min extraction time provided high enough extraction efficiencies for the six pyrethroids and an optimum time to utilize the SPME-GC application. Therefore, in subsequent studies, the extraction time of 15 min was selected.

Magnetic stirring is commonly used to improve the extraction efficiency of an SPME fiber. As expected, the chromatographic peak areas of the pyrethroids increased as the stirring rate increased from 0 to 1250 rpm. However, when stirring rates were above 1000 rpm the magneton fluttered and created an air bubble. An optimum stirring rate of 1000 rpm was therefore chosen for all subsequent experiments.

To avoid the residual effect, complete desorption of the extracted analytes from the MWCNTs/Ppy-coated fiber was necessary. For this purpose, the desorption temperature and desorption time were optimized. Based on the results obtained, desorption at 270 °C for 3 min was selected as the optimum conditions. There were no residual effects after the fiber was desorbed using these conditions.

3.4. Analytical evaluation

The analytical performance and characteristics of the proposed SPME approach were tested at optimized conditions by extracting working standard solutions (0.001, 0.005, 0.01, 0.05, 0.1, 1.0 and 10.0 μg mL^{-1} of each pyrethroid selected). The analytical results including linearity, limits of detection, and repeatability of the method are listed in Table 1. The calibration curves were linear from 0.001 to 10 μg mL^{-1} for five pyrethroids studied, and from 0.005 to 10 μg mL^{-1} for fenvalerate. This allowed the quantification of these compounds using the standard curve method. According to the description in a reference [32], the limits of detection for the pyrethroids are in the range 0.12–0.43 ng mL^{-1}. The precision for each single fiber was determined by treating seven replicate samples with 10 ng mL^{-1} of six pyretroids under the optimum con-

Table 2
Pyrethroid concentrations in and recovery from water samples ($n = 5$).

Compound	Seawater sample 1		Seawater sample 2		Pond water sample 1		Pond water sample 2		Tap water sample	
	Concentration (ng mL^{-1})	Recovery[a] (%)	Concentration (ng mL^{-1})	Recovery[a] (%)	Concentration (ng mL^{-1})	Recovery[a] (%)	Concentration (ng mL^{-1})	Recovery[a] (%)	Concentration (ng mL^{-1})	Recovery[a] (%)
Fenpropathrin	ND[b]	91.2 ± 4.5	ND	101.1 ± 5.6	ND	103.1 ± 5.8	ND	88.9 ± 4.8	ND	107.2 ± 3.8
Cyhalothrin	ND	86.5 ± 5.6	ND	108.0 ± 6.7	ND	112.0 ± 7.9	ND	92.2 ± 3.2	ND	102.8 ± 4.2
Permethrin	ND	91.3 ± 3.2	ND	94.2 ± 5.8	ND	93.2 ± 4.1	ND	103.0 ± 4.1	ND	103.7 ± 3.1
Cypermethrin	ND	106.2 ± 6.7	ND	87.3 ± 4.5	ND	89.3 ± 3.6	ND	105.5 ± 3.6	ND	95.5 ± 2.6
Fenvalerate	ND	88.9 ± 6.0	ND	83.6 ± 5.1	ND	91.2 ± 6.5	ND	108.2 ± 5.5	ND	98.0 ± 4.5
Deltamethrin	ND	91.2 ± 5.1	ND	97.2 ± 4.6	ND	104.0 ± 4.5	ND	92.8 ± 4.5	ND	94.8 ± 3.5

[a] The spiked concentration of each compound was 10 ng mL^{-1}.
[b] ND—not detected.

ditions. The relative standard deviations were obtained in the range from 4.5 to 7.1%. The fiber-to-fiber reproducibility was evaluated using five MWCNTs/Ppy coated fibers prepared in the same batch, and the relative standard deviations were in the range from 3.0 to 9.0%.

3.5. Real sample analysis

Five water samples from Xiamen city were analyzed using the proposed method. As summarized in Table 2, the recovery of the pyrethroids with 10 ng mL^{-1} spiked in the water samples ranged from 83 to 112%. No pyrethroids were found in these water samples. These results demonstrated that the proposed MWCNTs/Ppy coating was feasible for SPME application in water sample analysis.

4. Conclusions

In this study, MWCNTs/Ppy coated fiber was prepared using an electrochemical method and employed for SPME applications. Combining the properties of MWCNTs and Ppy, the MWCNTs/Ppy coated fiber exhibited high stability and high extraction efficiency for pyrethroids. The fiber was applied to extract pyrethroids from water samples and the results demonstrated its high extraction performance with pyrethroids. The experimental results revealed that the MWCNTs/Ppy fiber had great potential for the enrichment and extraction of pyrethroids. More SPME applications using MWCNTs/Ppy coated fiber for the enrichment and determination of other pyrethroids are ongoing in our laboratory.

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