

Electrodeposition of Porous Polyaniline Coating on an Etching Stainless Steel Wire as a Fiber for Solid-Phase Microextraction of Triclosan and Chlorophenols in Water Samples

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Abstract: A novel polyaniline (PANI) coating doped with perchlorate ions was prepared on a stainless steel (SS) wire by a three-electrode system. Before electrodeposition, the SS wire was etched by hydrofluoric acid to enhance its surface roughness. The prepared PANI-coated fiber was used for solid-phase microextraction (SPME) of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP) and triclosan (TCS) in water samples followed by high-performance chromatography with UV detection (HPLC-UV). The extraction procedure was optimized. The proposed SPME-HPLC-UV method provided a wide linear range. The limits of detection were 0.006 ng/mL for 2-CP, 0.005 ng/mL for 2, 4-DCP and 0.04 ng/mL for TCS, respectively. It was successfully applied to the analysis of spiked surface water samples with the recoveries from 99.6% to 109%.

Introduction

Triclosan (TCS) is an hydroxylated biphenyl ether with antimicrobial and bactericide properties included in the formulation of many personal care products, domestic and medical disinfectants, clothes and footwear. Therefore, waste water constitutes an important source of TCS in the environment. TCS itself presents a low toxicity and is removed to a considerable extent during conventional waste water treatments [1]. Also chlorophenols (CPs) are important pollutants that extensively exist in environmental waters. The main sources of CPs are effluent discharges of paper and pesticide industries. The chlorination process of phenols in water can also generate some CPs. Most of CPs are included in the priority pollutant list of the US Environmental Protection Agency because of their high toxicity and potential carcinogenicity. However an enrichment step is usually needed prior to the instrumental analysis because of their low concentration and the complexity of the environmental samples [2]. Therefore, the development of reliable, sensitive and easily operating detection methods is of great interest for the determination of these pollutants in environmental water samples. SPME is one of the most commonly used techniques for the preconcentration of TCS and CPs in environmental samples [1, 3, 4]. Various PANI coatings have been electrochemically deposited on metal supports in sulfuric acid and used as fibers for SPME of CPs coupled to GC and HPLC [5, 6]. In this work, a novel porous PANI-coated fiber was prepared on an etched SS wire in perchloric acid and employed to preconcentrate and determinate TCS and CPs in real environmental water samples.

Experimental

Reagents. HPLC-grade methanol was supplied by Yuwang Industrial Co., Ltd (Yucheng, China). Perchloric acid was supplied by Zhengcheng Industrial Co., Ltd. (Tianjin, China). Aniline

(99.5%) was purchased from Jianxin Chemical Reagent Co., Ltd. (Shanghai, China) and distilled under the vacuum. NaCl was from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Certified standard of TCS (99%), 2-CP (99%) and 2,4-DCP (99%) were purchased from AccuStandard (New Haven, USA).

Apparatus. All separations were performed on Waters 600E multi-solvent delivery system (Milford, MA, USA). A N2000 workstation (Zhejiang University, China) was used for the acquisition of data. The fiber coating was characterized by a JSM-5600LV scanning electron microscope (JEOL, Japan). Electrochemical deposition of PANI on etched SS wires (10.0cm×200μm O.D.) was performed on CHI832D electrochemical analyzer (Chenhua, China).

Preparation of PANI-coated fibers. After it was cleaned with acetone and then rinsed with water three times, the SS wire was dipped into hydrofluoric acid to be etched for 70min at 45°C. Subsequently, the etched SS wire was used as the working electrode, the platinum rod as counter electrode and the saturated calomel electrode as reference electrode for potentiostatic electrodeposition of PANI in 1.0mol/L HClO₄ containing 0.1mol/L aniline at 0.8V within 90min. After washing with distilled water and methanol, it was dried in nitrogen gas for 48h.

SPME-HPLC Procedure. A 10-mL sample solution was transferred into a 15-mL glass vial with a magnetic stirring bar inside and a Teflon septum. All sample solutions were adjust to pH=5.0 in the experiment. The fiber with PANI coating was exposed to the sample solution for 20-min extraction at 50°C at the stirring rate of 1000r/min. After extraction, The PANI-coated fiber was introduced into a SPME-HPLC interface for 10-min static desorption in the mobile phase (methanol/water, 70/30 v/v). Thereafter the valve was switched from load position to inject position and the analytes were delivered to the column at the flow rate of 1mL/min. The wavelength of UV detection was set at 282nm. Chromatographic peak area was employed to examine microextraction efficiency of PANI coating.

Results and Discussion

Morphology of PANI coating. Fig. 1 shows the scanning electron micrographs (SEM) of the SS wire before and after etching and electrodeposited PANI coating. The etching procedure significantly increases the surface area of the rough SS wire and results in strong adhesion of PANI coating onto the metal substrate. As shown in Fig. 1c, the PANI-coated fiber had a porous and relatively homogeneous structure.

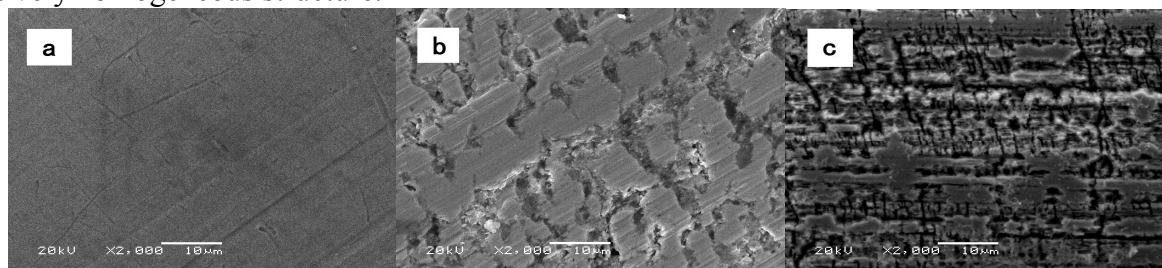


Fig. 1 SEM micrographs of the bare SS wire (a), etched SS wire (b) and PANI coating (c).

Effect of Extraction Time and Desorption Time. Fig. 2 shows the effect of time on the extraction efficiency for CPs and TCS. The extraction efficiency for all analytes increased with extending extraction time and more than 90% of adsorption is achieved within the initial 20 min. Since SPME allows precise determinations at non-equilibrium conditions when extraction time and mixing conditions are controlled, 20 min was employed in subsequent experiment. After extraction, CPs and TCS extracted onto PANI-coated fiber were desorbed in the SPME-HPLC interface. The results showed 10 min is needed for the desorption of CPs and TCS.

Effect of Temperature. The extraction temperature is rather important in SPME because it can affect the rate and the equilibrium of extraction. At elevated temperature, the diffusion of targeted analytes is a predominant factor for SPME. However, the extraction efficiency of CPs and TCS decreased at higher temperature than 50°C. According to these results, the extraction temperature was kept at 50°C.

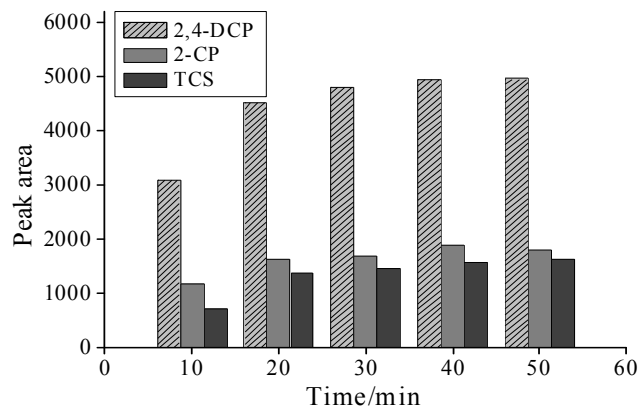


Fig. 2 Effect of extraction time on the extraction efficiency of CPs and TCS.

Effect of Stirring. Stirring is a common procedure to shorten the extraction time because it is usually a diffusion-controlling step in SPME. However the extraction efficiency decreased when the stirring rate exceeded 1000r/min. As a result, 1000r/min was used in further experiment.

Salt Addition. NaCl was added into the sample solution to investigate the effect of the salt concentration on the extraction and to improve the extraction efficiency. The results show that the extraction efficiency increased with the NaCl concentration up to 0.3g/mL, followed by a equilibrium with further increasing of NaCl concentration for three analytes.

Analytical Performance of the Method. Table 1 shows the linearity with correlation coefficient (r^2) of CPs and TCS for the novel PANI fiber under the optimized conditions. Their recovery (R), relative standard deviations (RSD) and limits of detection (LODs) was determined by five replicate analyses of spiked water samples with 10ng/mL standards. These data shows that this novel PANI fiber exhibited high sensitivity for three analytes. Extraction performance of the PANI-coated fiber is still acceptable after 250 times of extraction and desorption.

Table 1 Analytical data for the SPME-HPLC-UV of CPs and TCS

Analytes	Linearity [ng/mL]	r^2	R	RSDs [%]	LODs [ng/mL]
2-CP	0.01-200	0.9998	98.72-102.1	3.01	0.006
2,4-DCP	0.01-150	0.9998	99.46-101.9	2.20	0.005
TCS	1.00-200	0.9996	98.83-103.2	5.04	0.040

Analysis of Real Samples. To evaluate the applicability of the proposed method, water samples were collected from the Yellow River (Lanzhou, China), rain and tap water in September 2013. Furthermore real water samples were spiked with CPs and TCS to examine the matrix effect. As shown in Table 2, good recovery and precision were obtained. These results demonstrated that the proposed SPME-HPLC method was suitable for trace CPs and TCS in real water samples.

Table 2 Analytical results of CPs and TCS in real water samples

Water	Analytes	Original water			Spiked water at 5ng/mL		
		Detected [ng/mL]	R [%]	RSD [%]	Detected [ng/mL]	R [%]	RSD [%]
River water	2-CP	0.25	—	4.50	5.23	99.6	3.63
	2,4-DCP	11.62	—	3.31	17.99	108	3.24
	TCS	0.09	—	5.89	5.50	108	5.47
Rain water	2-CP	ND*	—	—	5.10	102	3.47
	2,4-DCP	23.15	—	3.44	30.59	109	3.75
	TCS	ND	—	—	5.14	103	5.41
Tap water	2-CP	ND	—	—	5.05	101	3.92
	2,4-DCP	ND	—	—	5.12	103	3.40
	TCS	1.00	—	5.44	6.29	105	5.32

* ND not detected.

Conclusions

In the study, a novel PANI fiber doped with perchlorate ions was prepared on an etched SS wire. The results showed this novel PANI fiber had good extraction capability for CPs and TCS. Furthermore, the PANI fiber had quicker adsorption. Extraction performance is still very stable after 250 times of extraction.

Acknowledgments

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