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# Hyper-crosslinked polymer nanoparticles as the solid-phase microextraction fiber coating for the extraction of organochlorines

Wenchang Wang, Wenjin Wang, Shuaihua Zhang\*, Zhi Li, Chun Wang, Zhi Wang\*

Department of Chemistry, College of Science, Hebei Agricultural University, Baoding 071001, China

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## ABSTRACT

A hyper-crosslinked polymer benzenedimethanol (HCP-BDM) was synthesized and explored as a solid-phase microextraction (SPME) fiber coating material. To prepare the HCP-BDM, 1,4-benzenedimethanol monomer was self-condensed *via* a simple Friedel-Crafts alkylation reaction. The physical-chemical properties of the HCP-BDM material were characterized by infrared spectroscopy, scanning electron microscopy, thermogravimetric and analysis nitrogen adsorption-desorption isotherms. The HCP-BDM coated fiber demonstrated excellent adsorption performance for some organochlorine pesticides (OCPs). An effective HCP-BDM fiber-based SPME method combined with gas chromatography-micro electron capture detector was established for the analysis of the OCPs from various vegetable samples. The linear ranges were observed from their corresponding limits of quantification (LOQs) to 50 ng g<sup>-1</sup> for the OCPs, with correlation coefficients varied from 0.9952 to 0.9992. Their limits of detection at S/N=3 ranged from 0.058 to 0.14 ng g<sup>-1</sup>. The single fiber repeatability and fiber-to-fiber reproducibility, expressed as the relative standard deviations (RSDs), were from 3.4% to 8.8% and from 6.7% to 9.6%, respectively. The established method was finally applied to the analysis of the OCPs from cucumber, Chinese cabbage and tomato samples with satisfactory recoveries and repeatability.

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## 1. Introduction

As a kind of persistent organic pollutants, organochlorine pesticides (OCPs) were once employed in great amount as the main agricultural insecticides worldwide. These pesticides have been found to be carcinogenic, highly resistant to natural degradation, and able to bioaccumulate in both the environment and some high trophic level animals through the food chains. Although most of them have been banned for decades, OCPs can still be found in milk [1], human serum [2], cabbage [3], peppers [4], yogurt and cheese [5], water [6] and soil [7] due to their persistence and huge historical use [8]. Therefore, to develop facile and effective methods to monitor the OCPs in food and environmental samples is of great significance [9].

Currently, the separation and analysis of OCPs from various sample matrices have been mainly performed by gas chromatography (GC) or GC-mass spectrometry (GC-MS) with the help of some sample pretreatment methods including Soxhlet extraction [10], liquid-liquid microextraction (LLME) [11], solid-phase extrac-

tion (SPE) [12], micro-solid-phase extraction ( $\mu$ -SPE) [13], matrix solid phase dispersion [14], solid-phase microextraction (SPME) [15] and QuEChERS method [16]. Among them, SPME, which was firstly introduced by Pawliszyn and Arthur [17], combines sampling, enrichment and injection into a single step. Owing to its diverse merits such as simplicity, sensitivity, being solvent-free and easy coupling with chromatographic detection apparatus, SPME has shown extensive utilizations in the analysis of biological [18], environmental [19], pharmaceutical [20] and food samples [21]. In SPME, the composition and structure of the coating materials play an essential role since this technique is based on the analytes distribution between the sample matrix and the sorbent coating material which is generally deposited onto the metal wire or quartz fiber. To date, in addition to the limited variety of commercial fibers from Supelco [22,23], diverse advanced materials such as metal oxide nanoparticles [9], carbon nanotubes [24], graphene [25], ionic liquids or polymeric ionic liquids [26] and metal-organic frameworks (MOFs) [27] have been employed as new coatings for the preconcentration of various analytes from different samples.

Porous organic polymers (POPs) [28] are newly emerging porous materials which integrate the organic monomers together to form 2D- or 3D- porous architectures *via* the covalent bonds between the low-weight elements, e.g., C, B, O, N and Si. These materials have the intrinsic features of excellent acid- or alkali-resistance,

\* Corresponding authors.

E-mail addresses: [zhangshuaihua@hebau.edu.cn](mailto:zhangshuaihua@hebau.edu.cn) (S. Zhang), [wangzhi@hebau.edu.cn](mailto:wangzhi@hebau.edu.cn) (Z. Wang).

high porosity and large surface area. According to the polymerization reactions used for their synthesis, POPs have been divided into several categories such as hyper-crosslinked polymers (HCPs) [28], covalent-organic frameworks (COFs) [29], covalent triazine-based organic frameworks (CTFs) [30], polymers of intrinsic microporosity (PIMs) [31] and conjugated microporous polymers (CMPs) [32], etc. Among the above mentioned POPs, HCPs are a subclass of low-cost POPs with permanent microporosities, easy functionalization, and diverse synthetic methods under mild conditions [28]. Their applications in gas storage [33], carbon dioxide capture [34], removal of benzene [35] and separation of alkylbenzenes [36] have been intensively explored. Due to their physicochemical characteristics, there will be a great potential for the HCPs to serve as good SPME fiber coating materials.

In the current work, a hyper-crosslinked polymer benzenedimethanol (HCP-BDM) was synthesized by the self-condensation of 1,4-benzenedimethanol monomer *via* a simple anhydrous iron (III) chloride-catalyzed Friedel-Crafts alkylation reaction [37]. Then, the newly-prepared HCP-BDM material was simply coated onto the surface of a stainless steel wire *via* physical coating method for the fabrication of a SPME fiber. This HCP-BDM coated fiber was subsequently utilized for the SPME of five organochlorine pesticides (OCPs) including aldrin, endosulfan, hexachlorobenzene (HCB), *p,p'*-dichlorodiphenyldichloroethane (*p,p'*-DDD), and trans-heptachlor epoxide (THCE) from various vegetable samples. The main experimental parameters affecting the extraction efficiency, including extraction conditions (ionic strength, extraction temperature, stirring rate, and extraction time) and desorption conditions, were optimized. In the end, a HCP-BDM fiber based SPME method coupled with gas chromatography/micro-electron capture detection (GC- $\mu$ ECD) was established for the determination of OCPs from different vegetable samples including cucumber, Chinese cabbage and tomatoes.

## 2. Experimental

### 2.1. Instruments

The chromatographic analysis of the OCPs was carried out by using a 7820A GC System (Agilent Technologies, CA, USA) equipped with a  $\mu$ ECD detector and a HP-5 GC column (30 m long  $\times$  0.32 mm i.d., the phase layer 0.25  $\mu$ m). The column temperature program: initial at 80 °C during 2 min, then heating at 30 °C min<sup>-1</sup> to 220 °C (held for 1 min), and finally increased to 260 °C at 3 °C min<sup>-1</sup> (held for 3 min). The carrier gas (1.2 mL min<sup>-1</sup>) and the make-up gas (25 mL min<sup>-1</sup>) was nitrogen (purity 99.999%). All the GC analyses were carried out in splitless mode with the injector temperature being set at 270 °C and the detector temperature at 290 °C.

The nitrogen adsorption isotherm (77.3 K), surface area and pore size of the HCP-BDM were measured on a V-Sorb 2800P surface area and pore size distribution analyzer (Gold APP Instruments, Beijing, China) based on the Brunauer, Emmet and Teller (BET) method. A Henven HCT-2 thermal gravimetric analyzer (Beijing, China) was used for thermogravimetric analysis (TGA). The scanning electron microscopy (SEM) images of the HCP-BDM coated fiber were recorded by a FEI F400 field emission electron microscope (FEI, Netherland). A Bruker Alpha spectrometer (Ettlingen, Germany) was used to measure the Fourier transform infrared (FT-IR) spectra.

### 2.2. Chemicals and reagents

1,4-Benzenedimethanol (99%) and anhydrous iron (III) chloride (FeCl<sub>3</sub>,  $\geq$ 99.9%) were provided by Aladdin Chemistry (Shanghai,

China). Analytical grade sodium chloride (NaCl), anhydrous 1,2-dichloroethane (CH<sub>2</sub>Cl<sub>2</sub>), methanol (CH<sub>3</sub>OH) and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. The stainless steel wires (type 304, 350  $\mu$ m o.d.) and GC microsyringes (5  $\mu$ L) were supplied by Shanghai High Pigeon Industrial and Trade Co., Ltd., China. The double-distilled water for all the experiments was prepared with an SZ-93 automatic double-distiller system (Shanghai, China). The neutral silicone sealant was used as a physical adhesion agent for the preparation of the HCP-BDM coated fiber (Guangzhou Baiyun Chemical Industry Co., Ltd., Guangzhou, China).

The standards of the five OCPs, HCB (99%), aldrin (analytical standard), THCE (analytical standard), endosulfan (analytical standard) and *p,p'*-DDD (analytical standard), were procured from Shanghai Macklin Biochemical Co., Ltd., China. The standard mixture solution (100  $\mu$ g mL<sup>-1</sup>) of the OCPs was prepared in acetone. To prepare various concentrations of working mixture solutions, the standard mixture solution was appropriately diluted with double-distilled water and stored at 4 °C.

### 2.3. Synthesis of HCP-BDM nanoparticles

The HCP-BDM nanoparticles were synthesized *via* the Friedel-Crafts reaction using iron (III) chloride as the catalyst [37] with some modifications. Briefly, 1,4-benzenedimethanol (2.76 g, 20 mmol) and anhydrous FeCl<sub>3</sub> (6.69 g, 40 mmol) were added to the anhydrous 1,2-dichloroethane (20 mL) in a 50 mL round flask. The above mixture solution was then heated at 80 °C in a thermostatic oil-bath for 24 h. The resulting product was recovered by filtration and thorough washing with methanol for several times until the supernatant turned clear. Then, the product was further purified *via* the Soxhlet extraction with methanol for 24 h. After being dried at 60 °C under vacuum overnight, the desired HCP-BDM nanoparticles were obtained.

### 2.4. Fabrication of HCP-BDM coated SPME fiber

Before the fiber coating, one end of the stainless steel wire (1.5 cm) was precleaned thoroughly with 1.0 mol L<sup>-1</sup> NaOH solution and double-distilled water, respectively. After drying, the pretreated section of the wire was etched in a mixed acid (HNO<sub>3</sub>: HCl = 1: 3, v/v) to generate roughness of the surface with an approximate diameter of 180  $\mu$ m, followed by ultrasonically washing with double-distilled water, methanol and acetone each for 10 min. Subsequently, the pretreated section was dipped into the diluted neutral silicone sealant (500 mg silicone sealant was diluted with 1 mL toluene) in an Eppendorf tube (1.5-mL). The gummed part was subsequently inserted into another Eppendorf tube filled with the HCP-BDM nanoparticles, rotated for several cycles, pulled out carefully, and then heated at 80 °C for 30 min in an air oven. To obtain the desired homogeneous coating thickness (about 30  $\mu$ m), the above-mentioned operations were repeated two more times. At last, the HCP-BDM coated fiber was equipped with a 5  $\mu$ L GC syringe. Before the first extraction, the as-prepared fiber must be conditioned in the GC inlet at 270 °C under nitrogen atmosphere until a stable chromatographic baseline was obtained. Meanwhile, for comparison, the pure silicone sealant SPME fiber was also fabricated by the same procedures only without the HCP-BDM nanoparticles.

### 2.5. Sample pretreatment and direct-immersion SPME procedures

Real vegetables samples (tomato, cucumber and Chinese cabbage) were obtained from a local market in Baoding (Hebei, China). The fresh vegetable samples (about 100.0 g) were firstly chopped into small pieces and homogenized with a food blender. Then, one gram aliquot of the above vegetable homogenate was accurately weighed, put into a 10 mL centrifuge tube with 1.0 mL aceton-

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