



Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma



Mechanochemical synthesis of covalent organic framework for the efficient extraction of benzoylurea insecticides

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ARTICLE INFO

Article history:

Received 6 February 2018

Received in revised form 26 March 2018

Accepted 27 March 2018

Available online xxx

Keywords:

Covalent organic framework

Benzoylurea insecticides

Solid phase extraction

High performance liquid chromatography

ABSTRACT

A covalent organic framework named TpAzo was successfully fabricated by a simple and environmentally friendly mechanochemical grinding method based on the Schiff base aldehyde-amine condensation reaction between 1,3,5-triformylphloroglucinol (Tp) and 4,4'-azodianiline (Azo), with *p*-toluene sulphonic acid as a molecular organizer. The TpAzo was characterized by scanning electron microscopy, transmission electron microscopy, powder X-ray diffraction, nitrogen adsorption-desorption isotherms, and thermogravimetric analysis. The TpAzo possessed a sheet-like morphology, rich porosity and high thermal stability. The extraction performance of the TpAzo was investigated by using it as the solid phase extraction adsorbent for the extraction of benzoylurea insecticides (BUs) from juice, tomato and white radish samples prior to high performance liquid chromatographic analysis. Under the optimal conditions, a good linearity for the BUs existed in the range of 1.0–160.0 ng mL⁻¹ for juice sample and 0.5–80.0 ng g⁻¹ for tomato and white radish samples with the correlation coefficients of 0.9956–0.9999. The limits of detection for the analytes were 0.1–0.2 ng mL⁻¹ for juice sample and 0.05–0.1 ng g⁻¹ for tomato and white radish samples. The method recoveries for the analytes fell in the range of 84.1%–108.6%. The adsorption mechanism of the TpAzo was investigated by using it to extract different types of organic compounds, including phthalates, phenylurea herbicides and carbamate insecticides. The results showed that the π -stacking and hydrophobic interactions between the TpAzo and the analytes played an important role for the adsorption.

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1. Introduction

Benzoylurea insecticides (BUs) have been widely used in agriculture to control pest [1,2] because they possess some attractive properties including high selectivity, good biological activity, and rapid degradation rate [3,4]. However, the widespread application of BUs can result in their residues in food and the environment, leading to a hazard to human health due to their chronic and long-term toxicity [5,6]. Therefore, it is necessary to develop rapid, sensitive and reliable analytical techniques for their determinations in agricultural products.

To achieve a necessary level of sensitivity, sample preparations for the target analytes are essential before instrumental analysis. So far, some sample pretreatment techniques for the determination of the BUs from different samples have been developed,

such as dispersive liquid–liquid microextraction (DLLME) [1], liquid phase microextraction (LPME) [7,8], liquid–liquid extraction (LLE) [9,10], solid phase extraction (SPE) [11–13], magnetic dispersive solid phase extraction (MDSPE) [4], and solid phase microextraction (SPME) [14,15]. Among them, SPE is the most widely used method because of its high enrichment factor, ease of use and less consumption of organic solvents [16]. Since the SPE adsorbent plays an important role in achieving a high concentration factor and good extraction efficiency, great efforts have been made by scientists to develop the efficient SPE adsorbents [17].

Covalent organic frameworks (COFs) are a burgeoning type of nanoporous materials synthesized by assembling organic building blocks via covalent bonds [18,19]. Compared with other porous materials, COFs have the properties such as low mass densities [20–22], diversities of organic building blocks and synthetic reactions, high thermal and chemical stability, easy functional modification and ordered structures [23]. So far, COFs have gained widespread attention in the field of gas separation, adsorption, catalysis and photo electricity [24–31]. In terms of adsorption, the abundant phenyl rings and pore structure throughout the entire framework are beneficial to forming hydrophobic interaction, π - π

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interaction and host-guest interaction with the target compounds containing phenyl groups [32]. Therefore, COFs have a great application potential to serve as adsorbent materials. However, most of the reported COFs are fabricated under harsh solvothermal conditions, such as the reactions in sealed Pyrex tubes with inert atmosphere, high temperature/pressure and long reaction time [33]. Thus, it is desirable to develop simpler and more environmental friendly synthetic routes for the preparation of porous COFs. Some new synthetic methods for the synthesis of COFs have been developed, such as microwave heating [34,35], ionothermal [36], sonochemical [37] and mechanochemical synthesis [38,39]. The COFs fabricated by mechanochemical method under solvent-free conditions have shown to possess ordered network, high crystallinity and high porosity [40].

In this paper, a COF named TpAzo was fabricated successfully by a simple and fast mechanochemical method through the condensation reaction between 1,3,5-triformylphloroglucinol (Tp) and 4,4'-azodianiline (Azo) [40]. The resulting polymers possessed high chemistry stability, large specific surface area and porosity. Then the TpAzo was used for the first time as the SPE adsorbent for the extraction of the four BUs (diflubenzuron, triflumuron, hexaflumuron and teflubenzuron). The TpAzo showed an excellent extraction capability for the BUs and an effective SPE method for the extraction of the BUs from juice, tomato and white radish samples was established prior to their high-performance liquid chromatographic detection. Besides, the adsorption mechanism of the TpAzo for the analytes was investigated by using different kinds of compounds including the phthalates, phenylurea insecticides and carbamate pesticides as model analytes.

2. Experimental

2.1. Chemicals and reagents

The BU standards of diflubenzuron, triflumuron, hexaflumuron and teflubenzuron, the phthalates (PAEs) standards of diallyl phthalate (DAP), butyl benzyl phthalate (BBP) and dibutyl phthalate (DBP), the phenylurea herbicides standards of monolinuron, isoproturon and chlortoluron, and the carbamates standards of propoxur, isoprocarb and bassa were all purchased from Aladdin Reagent (Shanghai, China.). The HPLC-grade acetonitrile, acetone and methanol were bought from Huaxin Chemical Regent Company (Baoding, China). The distilled water used throughout the work was double-distilled on a SZ-93 automatic double-distiller supplied by Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China). The juice, tomato and white radish samples were purchased from a local supermarket (Baoding, China).

The respective mixture stock solutions for the four groups of the compounds (BUs, PAEs, phenylurea herbicides and carbamates) were separately prepared in methanol at a concentration of $40.0 \mu\text{g mL}^{-1}$. Low concentration of the BU standard solution was prepared by diluting an appropriate amount of high concentration solution with methanol in a 10.0 mL volumetric flask as required. All the standard solutions were protected from light and stored at 4 °C.

For the optimization experiments, the aqueous mixture solution of the analytes at the concentration of 80 ng mL^{-1} was prepared by diluting 0.2 mL of the standard solution ($40.0 \mu\text{g mL}^{-1}$) with water to 100 mL.

2.2. Synthesis of 1,3,5-triformylphloroglucinol (Tp)

1,3,5-triformylphloroglucinol (Tp) was synthesized according to the reported method [41] with some modifications. The process includes the following steps: firstly, hexamethylenetetramine

(7.55 g, 53.9 mmol) and phloroglucinol (3.0 g, 23.8 mmol) were added into a 250 mL three-necked flask, and then 45 mL TFA was added slowly under nitrogen atmosphere. The solution was heated at 80 °C in a water bath for 3 h, and then 75 mL HCl (3 mol L^{-1}) was added into the solution. The mixture was kept at 80 °C for another 1 h. After being cooled down to room temperature, the mixture was filtered through celite, and the filtrate was extracted with dichloromethane. Magnesium sulfate (5 g, 41.5 mmol) was added into the extract to remove moisture and the solution was concentrated on a rotary evaporator to obtain the Tp.

2.3. Synthesis of p-azobenzene

p-Azobenzene (Azo) was synthesized according to the literature with some modifications [42]. p-Nitroaniline (14.5 mmol, 2.0 g), NaOH (5 mmol, 0.2 g) and 22 mL of ethanol were taken into round-bottomed flask with magnetic stirring. After the solution was heated in water bath to 50 °C, 24 mL aqueous solution of D-glucose (86.0 mmol, 15.5 g) was added dropwise. Then the mixture was heated at 60 °C for 8 h. After the solvent in the flask was removed on a rotary evaporator, the solid was collected by filtration and washed with water, followed by crystallization with anhydrous ethanol twice, and finally a yellow Azo crystal was obtained.

2.4. Synthesis of the TpAzo

TpAzo was synthesized according to the reported methods with some modifications [40]: p-toluene sulphonic acid (PTSA, 12.5 mmol, 2.377 g) was put in a mortar followed by the addition of Azo (2.25 mmol, 477.5 mg). The mixture was thoroughly ground with a pestle for 5 min. Then Tp (1.5 mmol, 315 mg) was added to the mortar and the mixture was ground for another 10 min until a color change appeared. Then water (500 μL , 27.5 mmol) was added dropwise to the mixture and the mixture was ground again for another 5 min. The mixture was transferred into a surface dish and heated in a muffle stove at 170 °C for 60 s to obtain a deep reddish powder. After being cooled down to room temperature, the product was washed with water to remove the excess PTSA. Then, the product was washed for 3 times with N,N-dimethylacetamide, acetone and water sequentially, and then dried under reduced pressure for further use. The scheme for the synthesis of the TpAzo is shown in Fig. 1.

2.5. Characterization of the TpAzo

The Brunauer-Emmett-Teller (BET) surface areas were determined from the N_2 adsorption at 77 K using V-Sorb 2800P (Jinaipu, China). The texture of the TpAzo was observed by transmission electron microscopy (TEM) using a JEOL model JEM-2011(HR) (Tokyo, Japan) and scanning electron microscopy (SEM) with an S-4800 instrument (Hitachi, Japan). The powder X-ray diffraction (PXRD) measurements were carried out with Cu K α radiation on a Bruker D8 ADVANCE (Bruker, Germany). The infrared spectra (IR) were measured with a WQF-510A spectrometer (Ruili, China). The thermal stability of the material was measured from room temperature to 900 °C under a N_2 atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ on a thermo gravimetric analyzer (TGA) (Henvon HCT-2, Beijing, China).

2.6. Samples preparation

Fifty mL of juice sample was diluted with 50 mL of double-distilled water, and the resulting solution was centrifuged and filtered through 0.45 μm membrane prior to the following SPE. The tomato or white radish samples were chopped and homogenized in a laboratory homogenizer. About 50.0 g of the homogenized samples was weighed and placed into two 50-mL centrifugal tubes with

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