



Use of a hypercrosslinked triphenylamine polymer as an efficient adsorbent for the enrichment of phenylurea herbicides

Xinyu Liang^{a,1}, Juntao Wang^{b,1}, Qiuhua Wu^a, Chun Wang^{a,*}, Zhi Wang^{a,b,*}

^a College of Science, Hebei Agricultural University, Baoding 071001, Hebei, China

^b College of Food Science and Technology, Hebei Agricultural University, Baoding 071001, China



ARTICLE INFO

Article history:

Received 20 December 2017

Received in revised form 13 January 2018

Accepted 15 January 2018

Keywords:

Hypercrosslinked triphenylamine polymer

Solid-phase extraction

Phenylurea herbicides

High performance liquid chromatography

ABSTRACT

A hypercrosslinked triphenylamine polymer (HCTPA) was prepared through a simple one-step Friedel-Crafts alkylation reaction. The HCTPA had an extended π -conjugated system, large specific surface area and high micropore volume. In order to evaluate its extraction performance, the HCTPA was used as the adsorbent for the solid-phase extraction of the phenylurea herbicides (monuron, chlortoluron, isoproturon, monolinuron and buturon) from watermelon, tomato and cucumber samples. The main parameters that could affect the extraction efficiency including the sample volume, sample solution pH, sample solution loading rate and desorption conditions were investigated and optimized. Under the optimized conditions, the HCTPA showed a good extraction performance for the target analytes. The linear range for the quantification of the analytes was in the range of 0.4–160.0 ng g⁻¹ with the correlation coefficients of 0.9996–0.9999. The limits of detection (S/N = 3) of the analytes by the method ranged from 0.06 to 0.12 ng g⁻¹ for watermelon and tomato, and 0.06–0.15 ng g⁻¹ for cucumber samples. The recoveries of the analytes for the method were between 83.1% and 112.5% with the relative standard deviations below 5.5%. These results indicate that the HCTPA can be used for the enrichment of phenylurea herbicides from complex matrix samples like watermelon, tomato and cucumbers.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Phenylurea herbicides (PUHs) are widely applied in a variety of crops to selectively control the growth of weeds by inhibiting their photosynthesis [1]. However, PUHs have shown residual activity in the surrounding environment or even the crops [2]. Due to their toxicity and possible carcinogenic properties [3], PUHs and their degradation products can affect human health through environment and the food chain [4]. Hence, it becomes an important task to develop simple and sensitive analytical methods for the quantitative determination of trace PUHs in crops samples [5].

So far, high performance liquid chromatography (HPLC) [6] and gas chromatography (GC) [7] are the commonly used means for the determination of PUHs. Nevertheless, due to the thermal instability of the PUHs, prior derivatization is necessary for their analysis by GC [8]. Therefore, HPLC is favorable for their direct and rapid deter-

minations. However, sample preparation prior to final instrumental detection is generally needed for the sensitive determination of the trace target analytes in real samples because the pesticides residues often exist at low concentrations in the sample. Several different sample preparation techniques including solid-phase extraction (SPE) [9], solid-phase microextraction (SPME) [10], liquid phase microextraction (LPME) [11], and dispersive liquid-liquid microextraction (DLLME) [12] have been developed. Among them, SPE is the most widely used one [13] since it has the advantages of high enrichment factor and simple operation [14]. In SPE, the adsorbent packed in the cartridge plays a vital role for an efficient extraction. So the development of effective SPE adsorbents is highly desirable for the enhancement of the extraction efficiency for some compounds.

In the past decades, microporous organic polymers (MOPs) have attracted an increasing interest due to their tunable pore sizes, excellent stability, lightweight and high surface areas [15]. The types of the MOPs include the polymers of intrinsic microporosity (PIMs) [16], covalent organic frameworks (COFs) [17], conjugated microporous polymers (CMPs) [18] and hypercrosslinked polymers (HCPs) [19]. In contrast to most of the MOPs that are often prepared by using high cost catalysts or starting materials, which makes them expensive and limits their practical applications [20], HCPs are a

* Corresponding authors at: College of Science, Hebei Agricultural University, Baoding 071001, Hebei, China.

E-mail addresses: chunwang69@126.com (C. Wang), zhiwang2013@aliyun.com, wangzhi@hebau.edu.cn (Z. Wang).

¹ These authors contributed equally to this work.

class of low-cost porous organic materials [21] which can be synthesized by simple Friedel–Crafts alkylation reaction and can be easily scaled up [22]. HCPs have been widely researched [23,24] and used in the fields like gas storage and separation [25], heterogeneous catalysis [26], energy storage [27], adsorbent [28] and carbon capture [29].

Triphenylamine is a low-cost monomer with three-dimensional (3D) rigid structure. With triphenylamine as the monomer, the obtained HCPs possess large Brunauer–Emmett–Teller (BET) surface areas, high micropore volumes and good thermal stability. These triphenylamine-based HCPs have been mainly used as catalyst [30], sensors [31] and adsorbent of CO₂ [32]. For example, Mondal et al. have reported the synthesis of a highly porous polytriphenylamine (PPTPA-1) by a simple one-step oxidative self-polycondensation of triphenylamine [33]. The PPTPA-1 was sulfonated and employed as a solid acid catalyst for direct conversion of sugar to 5-hydroxymethylfurfural. Zhang et al. have synthesized hypercrosslinked porous polytriphenylamine networks (PTPAs) via using external crosslinkers [34]. The PTPAs have demonstrated a potential capability for applications in gas uptake. More recently, Jiang et al. reported a new synthesis method by using *p*-dimethoxybenzene as an external crosslinker to construct the hypercrosslinked triphenylamine (HCTPA) networks. The HCTPA has been explored for the application in gas storage and supercapacitors. The HCTPA not only has a large specific surface area and high micropore volume, but also has a more extended π -conjugated system than either PPTPA-1 or PTPAs [35]. The extended π -conjugated system in the HCTPA can form a strong π -interaction with aromatic compounds, and therefore it can possibly serve as an effective adsorbent for the extraction of aromatic compounds [36]. However, the application of HCTPA as the adsorbent to extract aromatic pollutants from real sample has been little explored.

In this study, the HCTPA material was prepared through a one-step Friedel–Crafts alkylation of *p*-dimethoxybenzene and triphenylamine [37]. Then, it was explored as the adsorbent for the extraction of some PUHs (monuron, chlortoluron, isoproturon, monolinuron and buturon) from watermelon, tomato and cucumber samples before their high performance liquid chromatography–diode array detection (HPLC–DAD). The main extraction conditions that affect the extraction efficiencies were optimized. The HCTPA gave a satisfactory extraction recovery for the PUHs compounds.

2. Materials and methods

2.1. Reagents and materials

Chromatography-grade acetonitrile and methanol were purchased from Huaxin Chemical Reagent Company (Baoding, China). The standards of the PUHs (monuron, chlortoluron, isoproturon, monolinuron and buturon), the benzoylurea insecticides (diflubenzuron, triflumuron and teflubenzuron), the phthalate esters (diethyl phthalate, diallyl phthalate, diisobutyl phthalate, dimethyl phthalate and dibutyl phthalate) and the estrogens (oestrone, diethylstilbestrol and estriol), triphenylamine, *p*-dimethoxybenzene and anhydrous ferric chloride (FeCl₃) were purchased from Aladdin–Reagent (Shanghai, China). Hydrochloric acid (HCl), sodium hydroxide (NaOH), acetone, sodium chloride (NaCl) and all other reagents were bought from Boaxin Chemical Reagents Company (Baoding, China). The double-distilled water used throughout the work was obtained from an SZ-93 automatic double-distiller (Yarong Biochemistry Instrumental Factory, Shanghai, China).

The mixture stock solution containing monuron, chlortoluron, isoproturon, monolinuron and buturon each at 40.0 $\mu\text{g mL}^{-1}$ was

prepared in methanol. The mixture stock solution was further diluted with methanol in a 10.0 mL volumetric flask to prepare the standard solutions of lower concentrations (0.1, 0.5, 1.0, 5.0, 10.0 and 20.0 $\mu\text{g mL}^{-1}$). They were used to prepare the calibration samples. All the standard solutions were protected from light and stored at 4 °C.

The watermelon, tomato and cucumber samples were purchased from a local market (Baoding, China).

2.2. Instrumentation

Chromatographic separations were performed on an InertSustain C18 column (250 mm \times 4.6 mm I.D., 5.0 μm) from GL Sciences Inc (Tokyo, Japan). The HPLC was a LC-20AT system (Shimadzu, Japan) which consists of a SPD-M20A diode array detector (DAD) and two LC-20AT pumps. The sample injection volume was 20.0 μL . The ultraviolet detection monitoring wavelength was chosen at 244 nm. The mobile phase was a mixture of acetonitrile–water (41:59, v/v) at a flow rate of 1 mL min⁻¹.

The N₂ adsorption/desorption isotherms of the HCTPA were measured at liquid nitrogen temperature (77 K) with a V-sorb-2800 instrument (Jinaipu, China). Prior to the measurement, the samples were dried under vacuum at 120 °C for 4 h. The Fourier transform infrared (FT-IR) spectra were obtained by using a WQF-510 FT-IR spectrometer (Ruili, China). The morphology of the material was studied with the scanning electron microscopy (SEM) on an S-4800 instrument (Hitachi, Japan). The X-ray diffraction (XRD) patterns of the samples were recorded at room temperature (300 K) on a Bruker D8 ADVANCE (Germany).

2.3. Synthesis of the hypercrosslinked triphenylamine

The synthesis of the hypercrosslinked triphenylamine was as follows [37]: under a N₂ atmosphere, anhydrous ferric chloride (18.0 mmol, 3.0 g) was added to a solution of *p*-dimethoxybenzene (7.5 mmol, 1.1 g) and triphenylamine (0.6 mmol, 0.15 g) in nitrobenzene (22.5 mL), and the mixture was stirred at 80 °C for 5 h and then at 120 °C for 24 h. After being cooled down to room temperature, the mixture was filtered and the precipitate was washed with hydrochloric acid and methanol. The black precipitate was further purified by Soxhlet extraction in methanol for 24 h. The final product was dried under vacuum at 60 °C for 24 h.

2.4. Sample preparation

For the following SPE, the watermelon, tomato and cucumber samples were pretreated as follows. Each sample was well homogenized using a stainless steel blender and 25.0 g of the homogenized sample was then placed into a 50.0-mL centrifugation tube to centrifuge at 4000 rpm for 10 min. The supernatant was transferred to a clean 150.0-mL conical flask. Then, 10.0 mL double-distilled water was added to the sediment. The mixture was vortexed for 3 min and then centrifuged at 4000 rpm for 10 min. The supernatant was combined with the first supernatant in the 150.0-mL conical flask. All the supernatant was filtered through a 0.22 μm membrane and transferred to a 100-mL volumetric flask to which double-distilled water was added to the mark. Then, the resulting sample solution was used for the subsequent SPE.

2.5. Procedures of SPE

15.0 mg of the HCTPA was packed in an empty SPE cartridge (3.0 mL). Thereafter, the packed cartridge was conditioned with 5.0 mL acetonitrile and 5.0 mL double-distilled water. Then, 100.0 mL of sample solution was loaded through the packed cartridge at a flow rate of 5.0 mL min⁻¹. After sample loading, the

Download English Version:

<https://daneshyari.com/en/article/7608772>

Download Persian Version:

<https://daneshyari.com/article/7608772>

[Daneshyari.com](https://daneshyari.com)