Simultaneous determination of bifenox, dichlobenil and diclofop methyl by hollow carbon nanospheres enhanced magnetic carboxylic multi-walled carbon nanotubes

Wen-kui Li [a, b], Hai-xia Zhang [c], Yan-ping Shi [a, *]

[a] CAS Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
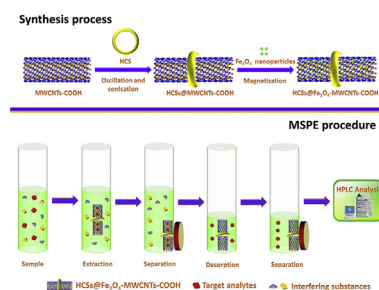[b] University of Chinese Academy of Sciences, Beijing 100039, PR China
[c] College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

HIGHLIGHTS

- An efficient MSPE-HPLC-DAD method was established for three herbicides simultaneous determination.
- A novel composite of HCSs enhanced Fe_3O_4-MWCNTs-COOH was employed for the herbicides determination.
- The extraction mechanisms for the herbicides were attributed to hydrogen bonding and π-π EDA interactions.
- The potential application of the proposed method was evaluated by MSPE of DCB, BFO and DCM from wheat flour.

GRAPHICAL ABSTRACT

ABSTRACT

A novel analytical method based on magnetic solid-phase extraction (MSPE) coupled with high performance liquid chromatography-diode array detection (HPLC-DAD) was established for three herbicides simultaneous determination. The key of the method was the explored extractant, which was a composite of hollow carbon nanospheres (HCSs) enhanced magnetic carboxylic MWCNTs (HCSs@Fe_3O_4-MWCNTs-COOH). MWCNTs-COOH was inserted in the pores of HCSs by oscillation and sonication with the capillary forces, making the carboxylic groups and structure intervals of the composite increase as compared to MWCNTs-COOH, therefore the extractant exhibited enhanced hydrophilicity, dispersibility, adsorptivity and selectivity. The extractant was sensitive to analytes with the structure of multi-aromatic ring, more hydrogen bond acceptor and large molecular polar surface area, which can be attributed to hydrogen bonding and π-π electron-donor-acceptor (EDA) interactions. The morphology, structure and magnetic property of the extractant were characterized. Then the explored extractant based MSPE-HPLC-DAD method was applied for bifenox (BFO), dichlobenil (DCB) and diclofop methyl (DCM) determination from wheat flour samples. Prior to real sample analysis, critical extraction parameters such as solution pH, extraction time, salt addition and temperature were investigated and optimized, and the analytical method was evaluated. It was indicated that the method had satisfactory linearities with the linear coefficients above 0.99, good precision with the RSD less than 3.5%, desirable recoveries ranged from 88.8% to 96.6%, and low limits of detection (LOD) that were 0.39, 0.24, and 0.68 ng/g for DCB, BFO and

* Corresponding author.
E-mail address: shiyp@licp.cas.cn (Y.-p. Shi).

DCM, respectively. The established MSPE-HPLC-DAD method has great potentials for trace polar herbicides selective determination from complex matrix samples.

1. Introduction

Bifenox (BFO), dichlobenil (DCB) and diclofop methyl (DCM) are three well-known herbicides. They are widely used in agriculture activities and their toxicity gradually attracts increasing public concerns for their extensive uses and their residues in agricultural areas. Therefore, for the protection of human health and control of the environment, it is crucial to develop accuracy, sensitive, rapid and selective methods for determination of these herbicides [1–3]. Various analytical techniques including liquid or gas chromatography and mass spectrometry have been used for determination of herbicides in environmental and food samples [4–6]. However, a sample preparation procedure is indispensable prior to this technique in consideration of the low concentration of the herbicides and the complex matrix of the samples.

As a classical sample preparation technology, solid-phase extraction (SPE) has been widely explored and applied in the analytical science, which based on the explored sorbent for sorption and desorption of analytes and aims for cleaning up, isolating, and concentrating the needed analytes [7]. As the SPE technology increasingly used, various materials were explored. Among them, magnetic materials based magnetic solid-phase extraction (MSPE) technology has received considerable attention in recent years, which was introduced for easy and rapid sample extraction, and overcame the tedious operations of conventional SPE, such as packing of materials into the cartridge, time-consuming loading of large-volume samples, tedious filtration and centrifugation procedures and so on [8,9]. Various magnetized sorbents were explored for MSPE, including magnetic retrieval of graphene [10], magnetic carbon nanotubes (CNTs) [11], magnetic metal organic frameworks (MOFs) [12], and other iron-oxide nanoparticles coated or modified materials [9].

CNTs have gained significant popularity in SPE as promising sorbents due to their unique structures and properties such as high surface area, rich in π electrons, easy to be functionalized with covalent and non-covalent forms, ability to sorption of aromatic compounds, and so on [13]. Magnetized CNTs have been explored for widely application in MSPE procedure [11,14]. Our group has prepared magnetic hydroxylated multi-walled carbon nanotubes (MWCNTs) for the determination of aconitines in human serum samples [15], and we also fabricated magnetic carboxylated MWCNTs for the determination of caffeine in carbonated beverage samples. Hydroxylated or carboxylated function apparently enhanced the adsorptivity and selectivity of CNTs. However, the content of the functionalized groups was relatively low, especially for carboxyl, which was only 0.73% on our purchased MWCNTs-COOH. The low content of carboxyl on the CNTs imposed restriction on their adsorptivity and selectivity.

Our group has established a physical entrapment method for the preparation of CNTs reinforced macroporous adsorption resin with enhanced selective extraction performance, which was achieved by capillary forces and sonication [16]. In this work, we prepared hollow carbon nanospheres (HCSs) with hollow pore sizes ranging from 30 to 50 nm under hydrothermal conditions, which was abundant of carboxyl. With the physical entrapment strategy, carboxylic MWCNTs (OD, 30–50 nm) were inserted in the pores of HCSs. The obtained composite was washed and uncombined HCSs

were suspended in the upper solution and then were removed. The carboxyl content of the obtained HCSs enhanced MWCNTs-COOH was effectively improved, which was up to 3.16 wt%. Besides, the dispersibility of the prepared composite was apparently improved as compared to MWCNTs-COOH. The improved carboxyl content and dispersibility of the composite enhanced its adsorptivity for polar aromatic analytes. Furthermore, iron-oxide nanoparticles were prepared and coated on the surface of the prepared composite and then made it a novel MSPE extractant, which was applied for the MSPE of trace BFO, DCB and DCM prior to high performance liquid chromatography-diode array detection (HPLC-DAD) analysis. The composite was sensitive to these herbicides due to their benzene rings and electron withdrawing groups contained structure. Related MSPE procedure was established and the influence factors including pH, extraction time, salt addition and temperature were investigated and optimized. Then the established MSPE-HPLC method was applied for the determination of three herbicides from wheat flour samples after the method was validated.

2. Experimental

2.1. Reagents and materials

BFO, DCB and DCM were purchased from J&K Chemical Technology (Beijing, China). 4-Methylbenzoic acid (TLA), 4-chlorobenzoic acid (CBA), 4-nitrobenzoic acid (NBA), anthrone (ATO), formaldehyde, 2, 4-dihydroxybenzoic acid, oleic acid and ammonia solution (25%) were gained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Benzophenone (BPO) was gained from Kishida Chemical Co. Ltd. (Hangzhou, China). 1-Naphthaleneacetic acid (NAA) was gained from Aladdin Industrial Corporation (Shanghai, China). Chloranil (CLA) was purchased from Aldrich Chemical Co., Ltd. (Shanghai, China). MWCNTs-COOH (OD, 30–50 nm; length, 10–20 μm; −COOH content, 0.73 wt%; purity >95 wt%) was purchased from Chengdu Organic Chemical Co., Ltd. (Chengdu, China). Ethylene glycol, polyethylene glycol and anhydrous sodium acetate were purchased from Li'anlong Bohua Pharmaceutical Chemical Co., Ltd (Tianjin, China). Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) was supplied by Beijing Chemicals Corporation (Beijing, China). All reagents were of analytical reagent grade. Standard stock solutions of BFO, DCB, DCM, CLA, TLA, NAA, ATO, BPO, CBA and NBA (40.0 μg/mL) were prepared in brown flasks with a solution of 80% methanol and stored at 4 °C. All the working solutions were freshly prepared by appropriate diluting of the stock solutions to the required concentrations with the solution of 80% methanol.

2.2. Instruments

Transmission electron microscope (TEM) image was obtained on a Tecnai-G2-F30 field TEM instrument (FEI, USA). Fourier transform infrared (FTIR) spectrum was obtained on an IFS120HR spectrometer (Bruker, Germany). Magnetic property was performed on a 3473−70 vibrating sample magnetometer (VSM) (Gmw Associates, USA). X-ray diffraction (XRD) measurement was accomplished on an X'pert PRO X-ray diffraction (Philips, Netherlands). HPLC system consisted of Waters 1525 HPLC system, 2998 diode array detection