



Magnetic solid-phase extraction of heterocyclic pesticides in environmental water samples using metal-organic frameworks coupled to high performance liquid chromatography determination

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ABSTRACT

A simple method of magnetic solid-phase extraction (MSPE) coupled to high performance liquid chromatography (HPLC) was developed for the simultaneous extraction and determination of four kinds of heterocyclic pesticides (carbendazim, triadimefon, chlorfenapyr and fenpyroximate) in environmental water samples. Magnetic metal-organic frameworks (MOFs) of type MOF-5 were prepared and used as adsorbents of MSPE. Several main parameters influencing MSPE efficiency were investigated, including amount of magnetic MOF-5, sample solution pH, extraction time, salt concentration, type and volume of desorption solvents and desorption time. Under optimal conditions, the MSPE-HPLC method presented fast simple separation and analysis, and excellent linearity in the range of 0.3–500.0 µg/L for carbendazim and triadimefon, and 0.1–500.0 µg/L for chlorfenapyr and fenpyroximate, with correlation coefficients (*r*) higher than 0.9992. High sensitivity with limits of detection and quantification ranging from 0.04–0.11 µg/L and 0.13–0.35 µg/L, respectively, were achieved, as well as good precision with relative standard deviations of 2.98–7.11% (intra-day) and 3.31–7.12% (inter-day). Furthermore, the method was successfully applied to reservoir and Yellow River water samples, and satisfactory recoveries at three spiked concentration levels were between 80.20% and 108.33%. The magnetic MOF-5 composites based MSPE followed by HPLC proved promising for convenient and efficient determination of heterocyclic pesticides in environmental water samples.

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1. Introduction

Heterocyclic pesticides as a large class of pesticides are mainly used to control insects and pathogens for a variety of rice, vegetable, fruit trees, decorative plants and so on. But meanwhile, for those non-target organisms, these heterocyclic pesticides also have exhibited high toxicity or harmful side effect [1]. For example, chlorfenapyr, a kind of widely used heterocyclic pesticides, is very toxic to aquatic organisms. They can persist for a long time in the environment because the heterocyclic rings of these compounds are difficult to be broken and their biodegradability is slow. Due to extensive and inappropriate use, their residues have been

observed in vegetables, agricultural products and environmental soils or waters [2,3]. The residues of heterocyclic pesticides in environmental water may cause long-term adverse effects to the aquatic environment, and even some heterocyclic pesticides may do harm to human health. Therefore, it is extremely essential to develop convenient, sensitive and rapid methods for heterocyclic pesticides determination in environmental waters.

Besides traditionally available chromatographic technologies for separation and determination of heterocyclic pesticides [4–8], sample pretreatment procedures are crucial for the whole analysis process, which aim at enriching targeted analytes and eliminating matrix effects from complex samples. Some pretreatment techniques for the extraction of heterocyclic pesticides from water samples have been reported, such as solid-phase extraction (SPE) [9,10], solid-phase microextraction (SPME) [11], and dispersive liquid–liquid microextraction (DLLME) [12,13]. Amongst them, SPE

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technique can provide high enrichment factor to obtain lower detection limit, and has been widely used for preconcentration of trace analytes in water samples. For instance, our group has used multi-walled carbon nanotubes (MWCNTs) as SPE adsorbents combined with HPLC-DAD for enrichment and determination of pyrazole/pyrrole pesticides in water [14]. However, SPE method still has some problems, such as, the SPE columns are likely to be blocked by complicated water samples, and the extraction process is time-consuming.

As a deformation mode of SPE, magnetic SPE (MSPE) technique nowadays has attracted much interest and have been increasingly utilized in sample pretreatment of environmental water [15,16]. In MSPE mode, a small amount of magnetic adsorbents can be well dispersed in sample solution to trap target analytes and be rapidly collected under magnetic fields. Compared with traditional SPE, MSPE is time saving, and magnetic adsorbents can be easily separated from water solution without employing complicated devices [15,16]. In MSPE, it is the key to prepare and select magnetic adsorbents for different compounds to obtain high enrichment efficiency.

Metal organic frameworks (MOFs) are new functional materials with various transition metal ions interconnected by a variety of organic ligands. MOFs have some excellent characteristics such as enormous surface area, ultrahigh porosity, and tuneable pore size, and they have demonstrated great application potentials in gas storage [17–19], drug delivery [20,21], heterogeneous catalysis applications [22,23], and sample pretreatment [24,25]. As for sample pretreatment, MOFs have often been used as adsorbents of SPE [24–28] and SPME [24,25,29,30]. However, not all MOFs can be used in environmental water samples, because some MOFs have limitations in liquid phase adsorption due to their relatively low stability in water and hydrophilic nature [31,32]. Recently, several magnetic MOFs as MSPE adsorbents for water analysis have been reported, and they exhibit good dispersibility in water together with good adsorption efficiencies. For example, magnetic MIL-101 has been used for MSPE of polycyclic aromatic hydrocarbons (PAHs) [33] and pyrazole/pyrrole pesticides [34] in environmental water samples. Magnetic HKUST-1 based MSPE has been used in determination of

palladium in environmental samples [35], as well as $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ microspheres for MSPE enrichment of phthalate esters [36]. The magnetic MOFs materials have been demonstrated to be stable in water samples. However, the metal center (Cr) of this material is toxic. MOF-5 (Zn) material synthesized by solvothermal method has been proved to be water stable and eco-friendly. For instance, MOF-5 has been utilized for SPE of thiols from wastewater [37]. Also, magnetic MOF-5 has been used for MSPE. For example, MOF-5- Fe_3O_4 nanoparticles have been synthesized for the enrichment of colchicine in root of colchicum extracts and plasma samples [38]. Amino functionalized Fe_3O_4 nanoparticles have been combined with MOF-5 and then presented effective MSPE of PAHs and gibberellic acids from environmental, food and plant samples [39]. However, in those reports magnetic MOF-5 is not used in environmental water samples.

Taking account of the advantages of MOF materials and MSPE procedures, in this study, we prepared magnetic MOF-5 composites and used them for MSPE of four widely used heterocyclic pesticides, namely carbendazim, triadimefon, chlorfenapyr and fenpyroximate, in environmental water samples. Several main factors that possibly influenced the MSPE efficiency were systematically optimized. Then the developed MSPE-HPLC method was validated and applied to real water samples.

2. Experimental

2.1. Chemical reagents and solutions

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, hydrochloric acid (HCl) and terephthalic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). *N,N*-Dimethylformamide (DMF) and glycol were purchased from Fuyu Fine Chemical Co. Ltd. (Tianjin, China). Sodium acetate was obtained from Aibi (Shanghai, China). Choline was supplied by Sanaishi (Shanghai, China). All organic solvents are of HPLC grade. Methanol, acetonitrile and acetone were purchased from TEDIA (USA). Ethyl acetate was obtained from Tianjin Guangfu Fine

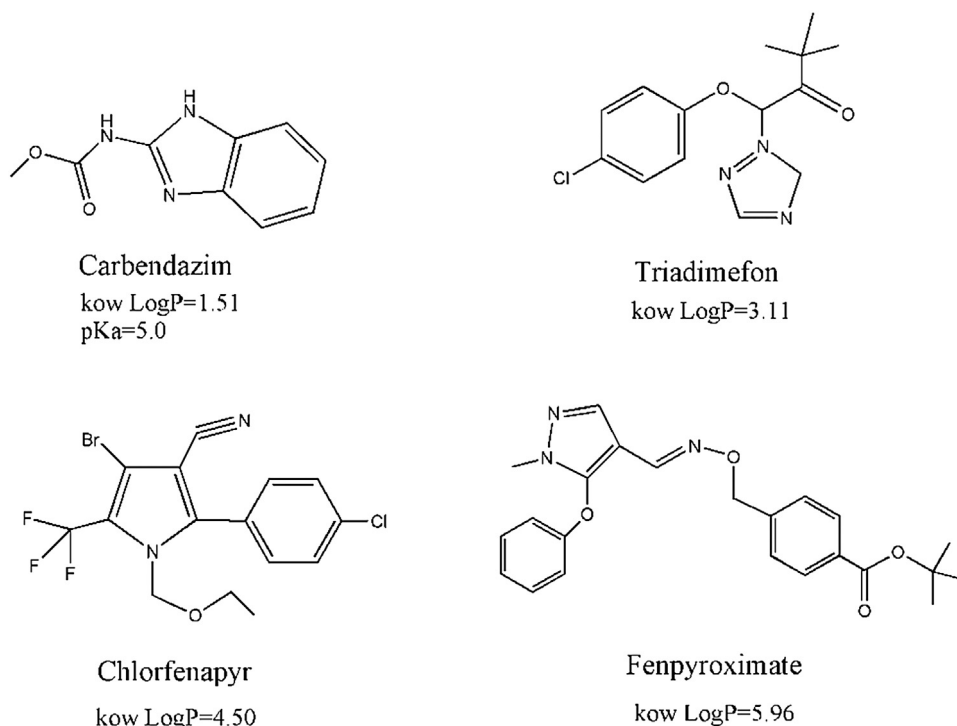


Fig. 1. Structural formulas of the four analyzed heterocyclic pesticides.

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