



Magnetic solid-phase extraction of triazine herbicides from rice using metal-organic framework MIL-101(Cr) functionalized magnetic particles

Li Liang, Xinghua Wang, Ying Sun, Pinyi Ma, Xinpei Li, Huilan Piao, Yanxiao Jiang, Daqian Song*

Department of Analytical Chemistry, College of Chemistry, Jilin University, Qianjin Street 2699, Changchun 130012, PR China

ARTICLE INFO

Keywords:

Magnetic solid-phase extraction
MOF
Triazine herbicides
Rice samples

ABSTRACT

The metal-organic framework (MOF) functionalized magnetic graphene oxide/mesoporous silica composites ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-GO/MIL-101(Cr)}$) were synthesized and utilized as magnetic solid-phase extraction (MSPE) adsorbent for the extraction of seven triazine herbicides (terbuthylazine, secbumeton, terbumeton, atraton, atrazine, prometon and trietazine) in rice samples. Several experimental parameters, including type and volume of extraction solvent, amount of MIL-101(Cr), extraction time, volume of desorption solvent and desorption time were investigated and optimized. The limits of detection (LODs) of seven triazine herbicides obtained by using the proposed MSPE method combined with high performance liquid chromatography (HPLC) were in the range of $0.010\text{--}0.080\ \mu\text{g kg}^{-1}$. The recoveries of the triazine herbicides in spiked rice samples ranged from 83.9–103.5% with the relative standard deviations lower than 8.7%. The intra and inter-day ($n = 6$) precisions for all triazine herbicides at the spiked level of $100.0\ \mu\text{g kg}^{-1}$ were 1.4–5.9% and 2.6–7.8%, respectively.

1. Introduction

Triazine, a kind of selective pre- and postemergence herbicide, is frequently used in agricultural processes to prevent the growth of weeds [1]. In East and Southeast Asia, extensive usage of herbicides for protecting rice-crops from weeds is associated with the rice-farming to ensure the sustained production of rice. However, the residues of the triazine herbicides would trigger potential health-hazards such as cancers, birth defects and hormone imbalances to human body [2]. The alarming increase in triazine herbicides usage is a major concern throughout the world. The European Union (EU) legislation has recommended the maximum residue limits (MRLs) for triazine herbicide residues in agricultural products as $0.05\ \text{mg kg}^{-1}$, while the Environmental Protection Agency (EPA) of America specified the tolerance limit for triazine herbicides in most food products as $0.25\ \text{mg kg}^{-1}$ [3,4].

During sample preparation, analytes were extracted and separated from complex matrix to improve the selectivity and sensitivity of the following analysis. Many sample preparation procedures, such as solid phase extraction (SPE) [5], solid-phase microextraction (SPME) [6], dispersive liquid-liquid microextraction (DLLME) [7], liquid-liquid extraction (LLE) [8,9] and matrix solid phase dispersion (MSPD) [10,11] are regularly employed for the extraction of triazine herbicide residues in food samples. However, most of these traditional sample preparation methods are time-consuming or require expensive apparatuses and

large quantities of organic solvents, which make the experimental cost inappropriate.

In recent years, magnetic solid-phase extraction (MSPE) has been proved to be a simple, highly efficient, low-cost and environment-friendly approach for the extraction of target analytes from complex matrix [12–15]. In MSPE, magnetic materials, which can be separated by an external magnet from the matrix easily, are used as adsorbents for the extraction of targeted analytes. Currently, various magnetic nanoparticles (MNPs) [16–19] have been synthesized and used successfully as magnetic adsorbents in MSPE. Large surface area to volume ratio, efficient adsorption capacity and fine separability are the main advantages of these nanoparticles for their successful application.

Fe_3O_4 nanoparticles (Fe_3O_4 NPs) coated with various compounds containing modified functional groups are typical MNPs employed in MSPE. Common compounds used for coating Fe_3O_4 nanoparticles to prepare MNPs include C18 [20,21], nanoporous carbon [22], carbon nanotubes [23], graphene [24–26], graphene oxide (GO) [27,28], polymeric ionic liquids [29], silica-based materials [30,31] and metal-organic frameworks (MOFs) [32]. MOFs are highly ordered crystalline materials prepared by the self-assembly of metal ions with organic linkers via coordination bonds. In analytical processes, MOFs have been successfully used as sorbents and chromatographic stationary phases for extraction and separation of target analytes from complex matrix [33]. In a previous study, Chen et al. [34] synthesized $\text{Fe}_3\text{O}_4@\text{MIL-100}$ core-shell magnetic microspheres for extracting polychlorinated biphenyls

* Corresponding author.

E-mail address: songdq@jlu.edu.cn (D. Song).

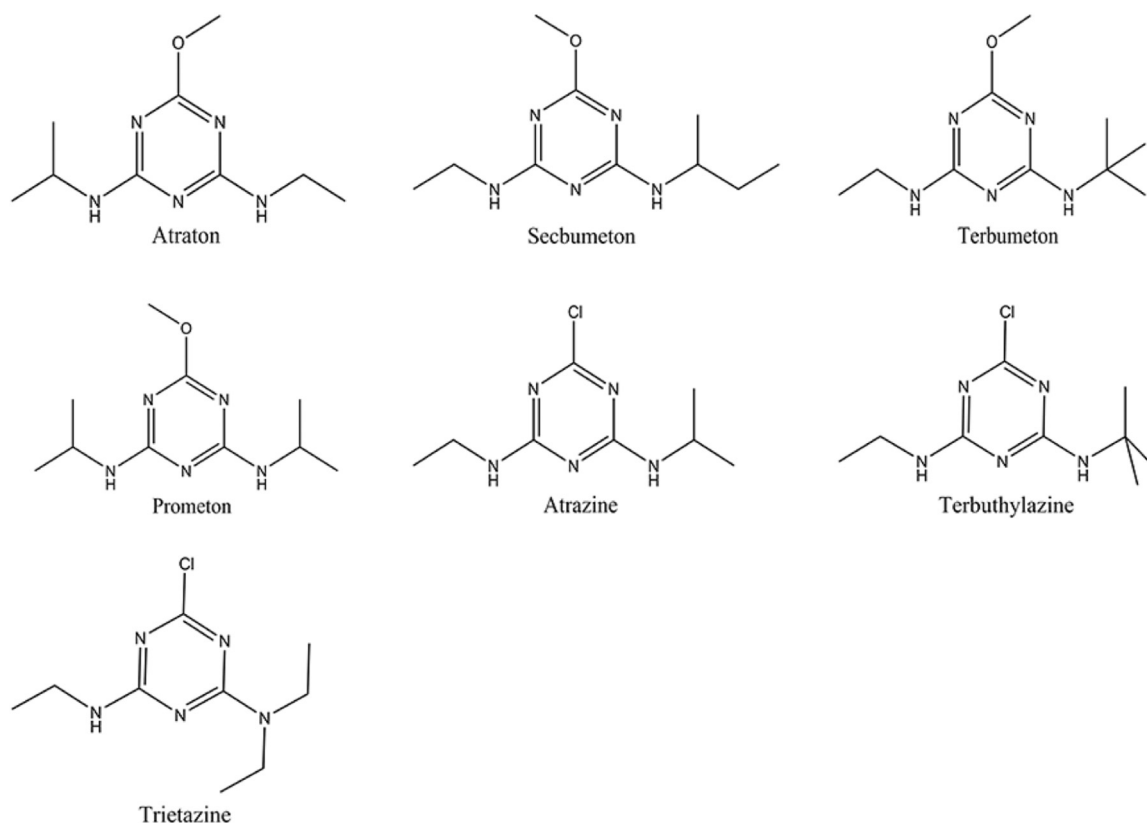


Fig. 1. Chemical structures of seven triazine herbicides.

from environmental water samples. Also, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}(\text{Cr})$ was proved as an effective sorbent for the extraction of pyrazole/pyrrole pesticides in water samples [35].

In this work, graphene oxide (GO), MIL-101(Cr) and magnetic mesoporous silica are combined and employed as a magnetic adsorbent for MSPE of triazine herbicides in rice. The properties of the composite MSPE adsorbents were characterized, and several important extraction parameters, including amount of MIL-101(Cr), type and volume of extraction solvent, extraction time, volume of desorption solvent and desorption time were investigated in detailed manner to achieve high MSPE efficiency.

2. Experimental

2.1. Reagents and materials

Analytical standards, including terbutylazine, secbumeton, terbumeton, atraton, atrazine, prometon and trietazine were purchased from Aladdin Industrial Corporation (Shanghai, China). The chemical structures of these triazine herbicides are shown in Fig. 1. Stock solution of each triazine herbicide was prepared in HPLC-grade acetonitrile at the concentration of $500 \mu\text{g mL}^{-1}$ and stored at 4°C . Mixed and single working standard solutions were prepared by diluting the stock solutions with HPLC-grade acetonitrile.

Iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonium hydroxide and 1,4-benzene dicarboxylic acid (H_2BDC , $\geq 98.5\%$) were supplied by Guangfu Fine Chemical Research Institute (Tianjin, China). Dimethylformamide (DMF), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), and *n*-hydroxy succinimide (NHS) were purchased from Aladdin reagent (Shanghai, China). Triton X-100, 3-aminopropyltriethoxysilane

(APTES), and tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich (St. Louis, USA). $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($> 99.0\%$) was purchased from XLong chemical Co., Ltd. (Guangdong, China). Hydrofluoric acid (HF , $\geq 40\%$) was purchased from Aladdin Industrial Corporation (Shanghai, China). Pure water was prepared by a Milli-Q water purification system (Millipore Co., USA). All other chemicals used in this study were of analytical-reagent grade and were purchased from Beijing Chemical Factory (Beijing, China).

2.2. Instruments

Liquid chromatographic analyses were performed by a LC-20ADXR liquid chromatograph (Shimadzu, Japan) with two LC-20AD pumps, a SIL-20A automated sample injector, a CTO-20A column oven and a SPD-20A UV-Vis detector. An eclipse XDB-C18 column ($150 \text{ mm} \times 4.6 \text{ mm}$, with $3.5 \mu\text{m}$ particle size, Agilent Technologies Inc., USA) was carried out for the separation of triazine herbicides. A transmission electron microscope (TEM, Hitachi H-800, Japan) operating at 200 kV and a scanning electron microscope (SEM, Hitachi SU-8020, Japan) were employed for the observation and characterization of the morphology of magnetic nanocomposites. A magnetic property measurement system (SQUID-VSM, Quantum Design, USA) was utilized to study the magnetic properties of the synthesized adsorbent.

2.3. Sample preparation

Rice samples (samples 1–3) were purchased from local markets and powdered with a crusher. The powdered samples were sealed and stored in a freezer at 4°C , and then used for the subsequent experiments. Spiked samples were prepared by adding appropriate volume of mixed working solutions to blank samples, followed by homogenization

Download English Version:

<https://daneshyari.com/en/article/7677407>

Download Persian Version:

<https://daneshyari.com/article/7677407>

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