分类号：　　　　　　　　　　　　　　　　　　　　　　　　　　　　密级：否

華中農業大學

HUAZHONG AGRICULTURAL UNIVERSITY

博 士 学 位 论 文

Ph D DISSERTATION

新型磁性纳米复合材料的合成及其在唑类农药 残留分析和去除中的应用

SYNTHESIS OF NOVEL MAGNETIC NANOCOMPOSITES AND THEIR APPLICATION IN ANALYSIS AND REMOVAL OF AZOLE PESTICIDE RESIDUES

研 究 生:

CANDIDATE: **IBRAHIM ABDELHAI ABDELMAGEED SENOSY**

学　号：

STUDENT NO.: **2017301060023**

专　业: 农药学

MAJOR: **PESTICIDE SCIENCE**

导　师: 李建洪 教授

SUPERVISOR: **PROFESSOR LI JIANHONG**

中国 武汉

WUHAN，CHINA

二〇二二年六月

June，2022

Abstract

Pesticides are widely used in the prevention and control of diseases, insects, and weeds in the process of agricultural production, and play an important role in improving the quality of agricultural products. Among these, azole pesticides have been widely used in the protection of plants against fungal pathogens. However, a large number of reports have confirmed that the residues of azole pesticides can persist in various agricultural products and the water environment after application, which may seriously affect the health of humans, animals, and the stability of the ecosystem. Therefore, in order to handle and quickly analyze the residues of azole pesticides in complex samples, it has become increasingly important to design and develop new methods for the quantitative detection and removal of azole pesticides based on highly efficient adsorbents. New methods for accurate quantitative detection and removal of pesticide residues are becoming increasingly important. In this study, new methods for the detection and removal of four azole pesticide residues (epoxiconazole, flusilazole, tebuconazole, and triadimefon) in different complex samples matrices were established using novel magnetic nanocomposites as adsorbents. The main results are as follows.

1. Magnetic metal-organic framework (Fe)/PEI-nanocomposite namely Fe_3O_4@MIL-100 (Fe)/PEI was successfully prepared for construction of a modified MSPE method of azole pesticides in complex vegetable and fruit samples. The morphological structures of the synthesized materials were investigated using FE-SEM, TEM, FT-IR, XRD, VSM, and TGA. The results illustrated that Fe_3O_4@MIL-100 (Fe)/PEI showed a nearly spherical and coated layer of the polymer with maintaining core-shell structure. Fe_3O_4, MIL-100 (Fe), and PEI were successfully introduced, and the crystal structure of Fe_3O_4 remained intact during the preparation of Fe_3O_4@MIL-100 (Fe)/PEI. The saturation magnetization of Fe_3O_4@MIL-100 (Fe)/PEI was 23.4 $emu \cdot g^{-1}$, which can be rapidly collected by an external magnet. From TGA characterization, different thermal degradation behaviors between Fe_3O_4@MIL-100 (Fe) and Fe_3O_4@MIL-100 (Fe)/PEI indicated successful loading of PEI on MIL-100 (Fe). Through a series of optimization of proposed methods, the optimal pretreatment parameters were obtained. Under the optimum conditions, the obtained linearity of this method was ranged from 5 to 1200 $\mu L \cdot L^{-1}$ with correlation coefficients (R^2) ≥0.9908. The limits of detection (LODs) were ranged from 0.21 to 3.04 $\mu g \cdot kg^{-1}$, and limits of quantitation (LOQs) were ranged from 0.71 to 10.14 $\mu g \cdot kg^{-1}$. The adsorbent could be regenerated multiple times and maintained the extraction recovery rate of

higher than 85 % after 5 cycles. Finally, the proposed material has been successfully applied to analysis in several fruit and vegetable samples (apple, orange, tomato, cabbage, and cucumber), and the recoveries of the four azole pesticides were in the range of 73.9-109.4 % with RSD in the range from 0.5 to 6.2 %. Taken together, this work provides a novel method for the preparation of polymer-based metal-organic frameworks composites, and the synthesized Fe_3O_4@MIL-100 (Fe)/PEI was proved to be an efficient adsorbent for enrichment and extraction of pesticides from complex vegetable and fruit samples.

2. Improved magnetic solid-phase extraction was successfully established based on magnetic β-cyclodextrin polymer for the analysis of residual azole pesticides in complex medicinal plant samples. The synthesized material was confirmed by its morphology and structure through a series of characterization. The characterization results revealed that the outer shell of Fe_3O_4@TFN-CDPs had been coated with a network of the polymer and formed a core-shell structure, and the crystal structure of Fe_3O_4 remained intact during the preparation process. From VSM characterization, Fe_3O_4@TFN-CDPs particles were shown to have a saturation magnetization of 27.54 $emu \cdot g^{-1}$. The main influencing parameters were evaluated and optimized. Under the optimum conditions, good linearity ranged from 6 to 1000 $\mu g \cdot Kg^{-1}$ for all analytes could be achieved (correlation coefficients ≥0.9910); LODs and LOQs of target pesticides were ranged from 0.011 to 0.106 $\mu g \cdot Kg^{-1}$ and from 0.036 to 0.354 $\mu g \cdot Kg^{-1}$, respectively. Besides, after five times regeneration, Fe_3O_4@TFN-CDPs particles were proved to be an economic adsorbent and had good reusability. Finally, the developed method has been successfully applied to the determination of pesticides in six medicinal plant samples (basil, spearmint, parsley, chamomile, dill, and coriander), the achieved recoveries fluctuated from 60.1 to 102.3 %. Altogether, this method based on Fe_3O_4@TFN-CDPs nanocomposites provided a new idea for the analysis of trace pesticides in complex medicinal plant samples.

3. Increasing dispersibility of ZIF-8 in water through loading on magnetic graphene oxide was successfully synthesized and applied in MSPE technology for the analysis of residual azole pesticides in complex aqueous samples. In this work, GO powder was interacted with the Fe_3O_4@APTES particles to form Fe_3O_4@APTES-GO. Then, the resulting mixture was modified with ZIF-8 nanoparticles to form the Fe_3O_4@APTES-GO@ZIF-8 nanocomposite. The results indicated that magnetic graphene nano-sheet was covered by the ZIF-8 crystals with the hexagonal shape and size ranging diameter of ZIF-8 from 60 to 90 nm. The main functional

groups of ZIF-8 and GO were successfully introduced, and the crystal structure of Fe_3O_4 remained intact during the preparation process. The saturation magnetization of Fe_3O_4@APTES-GO/ZIF-8 is 29.32 emu·g^{-1}, and an adsorption-desorption isotherm shape indicated a typical type-IV mesoporous material with the surface area and pore volume of 913.13 $m^2 \cdot g^{-1}$ and 0.66 $cm^3 \cdot g^{-1}$, respectively. Besides, the main parameters which could affect the experiment results were optimized. Under the optimum condition, the obtained linearity was ranged from 1 to 1000 μg·L^{-1} for all analytes, with correlation coefficients (R^2) ≥0.9914. Limits of detection (LODs) and limits of qualification (LOQs) of four azole pesticides were ranged from 0.014 to 0.109 μg·L^{-1} and from 0.047 to 0.365 μg·L^{-1}, respectively. The obtained results showed that the adsorbent could be reused five times without significant loss of extraction recoveries, which could reduce the cost and save time. Based on comparison with outcomes from reported studies, Fe_3O_4@APTES-GO/ZIF-8-MSPE could provide high performance and achieve satisfactory results for the analysis of trace azole pesticides in complicated matrices.

4. A novel Fe_3O_4@MIL-100 (Fe)/β-CD was successfully synthesized and applied in water purification of the removal residual azole pesticides. The characterization of Fe_3O_4@MIL-100 (Fe)/β-CD revealed that β-CD had been successfully tethered to the shell of Fe_3O_4@MIL-100(Fe) via tetrafluoroterephthalonitrile as a cross-linker with the elementary composition of carbon, oxygen, nitrogen, fluorine, and iron. Characteristic peaks of Fe_3O_4, MIL-100(Fe), and β-CD polymer were also observed using FTIR spectro-photometer, and the magnetic nanocomposite had a crystalline structure of the face-centered cubic lattice of Fe_3O_4. The saturation magnetization value of Fe_3O_4@MIL-100 (Fe)/β-CD was 9.40 emu·g^{-1}, and the composite exhibited the type II adsorption isotherms indicative of mesoporosity with the surface area and average pores size of Fe_3O_4@MIL-100 (Fe)/β-CD of 2.60 $m^2 \cdot g^{-1}$ and 1.70 nm, respectively. Isotherm adsorption study showed the Langmuir isotherm was more suitable than Freundlich and Temkin to describe the adsorption behaviors of Fe_3O_4@MIL-100(Fe)/β-CD, and maximum adsorption capacities were ranged from 64.52 to 102.10 mg·g^{-1}. The kinetic models had shown that the pseudo-second-order model was fitted better than the pseudo-second-order and Weber-Morris order, indicating the chemical process was the judgment process when adsorbing azole pesticides. The adsorption capacity of the adsorbent to the target azole pesticides has no significant change at different concentrations of humic acid, which indicated the selective adsorption ability of the adsorbent to the target analytes. Moreover, the adsorbent indicated

excellent stability after the regeneration of the adsorbent was explored through 5 successive cycles. The adsorption mechanism includes host-guest interaction, hydrogen bonds, and π-π interactions. Finally, the proposed material had been successfully applied to the removal of four pesticides in actual environmental water samples. Compared with other reported materials, Fe_3O_4@MIL-100(Fe)/β-CD displayed outstanding adsorption capacity, short adsorption equilibrium time, and could offer a new platform for the removal of trace pesticides in complex aqueous samples.

Keywords: Azole pesticides; Magnetic nanocomposite; Pesticide residues analysis; Pesticide residues removal; Metal-organic framework