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Multi-pesticides residue analysis of grains using modified magnetic nanoparticle adsorbent for facile and efficient cleanup

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ABSTRACT

A facile, rapid sample pretreatment method was developed based on magnetic nanoparticles for multi-pesticides residue analysis of grains. Magnetite (Fe_3O_4) nanoparticles modified with 3-(*N*,*N*-diethylamino)propyltrimethoxysilane (Fe_3O_4-PSA) and commercial C18 were selected as the cleanup adsorbents to remove the target interferences of the matrix, such as fatty acids and non-polar compounds. Rice was used as the representative grain sample for method optimization. The amount of Fe_3O_4-PSA and C18 were systematically investigated for selecting the suitable purification conditions, and the simultaneous determination of 50 pesticides and 8 related metabolites in rice was established by liquid chromatography–tandem mass spectrometry. Under the optimal conditions, the method validation was performed including linearity, sensitivity, matrix effect, recovery and precision, which all satisfy the requirement for pesticides residue analysis. Compared to the conventional QuEChERS method with non-magnetic material as cleanup adsorbent, the present method can save 30% of the pretreatment time, giving the high throughput analysis possible.

1. Introduction

Pesticides are widely used in agricultural crops to prevent diseases and pests, leading to many benefits for the farmers. However, the pesticides residue cannot be ignored. It may be remained in the agro-products, transferred to the processed food, and consequently posing a potential risk to the human health. Rice, wheat, soybean and other grains are the largest consumed foods for billions of people all over the world with the increasing consumption in the recent decades (Pizzutti, de Kok, Hiemstra, Wickert, & Prestes, 2009). Thus, it is important to effectively monitor the pesticides residue in grains for ensuring the food safety and human health. Grains usually contain fatty acids, proteins, dietary fiber, vitamins and other micronutrients essential (González-Curbelo, Herrera-Herrera, Ravelo-Pérez, & Hernández-Borges, 2012; Walorczyk & Drożdżyński, 2012). The pesticides analysis of grains is thus considered to be a difficult task. For these reasons there is a clear need to develop reliable method for the multi-residue analysis in grains.

Until now, many sample preparation techniques have been utilized for extraction and purification of pesticides in grains. The main methodologies were based on solid phase extraction (SPE) (Chen, Shi, Shan, & Hu, 2007; Pareja, Fernández-Alba, Cesio, &

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Heinzen, 2011) and QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) (Malinowska, Jankowski, Sosnowski, & Wiśniewska-Kadżajan, 2015; Min et al., 2012; Nguyen et al., 2008) coupled with gas chromatography (GC), gas chromatography–tandem quadrupole (GC–MS/MS) or liquid chromatography–tandem mass spectrometry (LC–MS/MS). SPE can provide a good purification, but its procedure is usually tedious and labor intensive, limiting the speed of sample pretreatment. QuEChERS method can effectively shorten the procedure, decrease manual labor and the usage of organic reagents (Anastassiades, Lehotay, Štajnbaher, & Schenck, 2003), making it widely used in pesticides analysis for various kinds of samples. It involves extraction and purification procedure with dispersive solid phase materials as cleanup adsorbent. After purification, high-speed centrifugation was needed to separate the dispersive adsorbent and sample solution. This step is easy to operate for a small quantity of samples, but it may become a challenge for large quantity of samples. Therefore, it is a meaningful exploration to find an alternative approach for shortening the pretreatment time and improving the efficiency.

The magnetic materials went into our sights owing to its unique super paramagnetic property (Fan et al., 2012; Liu, Cai, & Feng, 2012; Sun, Liu, Sun, Wang, & Ding, 2012; Wang et al., 2012). If the magnetic materials were used as the dispersive adsorbent in the purification process, the extract would be separated with the dispersive adsorbent within 3 s under the external magnetic field. Compared with the centrifugation process in the traditional QuEChERS method, the magnetic separation is ten times quicker for one batch samples. If simultaneously dealing with two or three batch samples, the magnetic separation will be more efficient duo to leaping over the samples switch step. Besides, it is so simple that everyone can operate in every laboratory. You just need to put the samples on the magnet, and draw the supernatant solution. The large and expensive high-speed centrifuger is replaced by a smart magnet or magnetic frame.

Screening the ideal magnetic adsorbent is also important for developing a facile and efficient method. Ferroferric oxide (Fe_3O_4) is a good magnetic core owing to its surface hydroxyl group. This is attributed to the weak alkaline properties of the transition metal oxide. It can be easily modified and formed a series of meritorious magnetic adsorbent (Ahmadi, Rajabi, Faizi, Rahimi-Nasrabadi, & Maddah, 2014; Wang et al., 2015; Yu et al., 2010). The surface modification endues the novel materials with the advantages of super paramagnetic property and the selective adsorption capacity. Commercial PSA is widely used in the traditional QuEChERS method for removing the polar compounds (Hercegová, Dömötörová, & Matisová, 2007). In our previous research, Fe_3O_4 modified with 3-(*N*,*N*-diethylamino)propyltrimethoxysilane ($C_{10}H_{25}NO_3Si$, CAS No. 41051-80-3) (Fe_3O_4-PSA) was prepared and proved to be useful for removing organic acid in fruit samples (Qi et al., 2015). Therefore, a new attempt was carried out to explore its function on removing the fatty acids in grains.

The present work aimed at developing a simple, rapid and efficient method for the multi-pesticides analysis in grains coupled with LC–MS/MS. Selecting of the cleanup adsorbent was systematically discussed using rice as the representative sample. Based on the optimum conditions, the method was validated regarding the linearity, sensitivity, precision and further applied for wheat and soybean samples analysis. The satisfactory results demonstrated its feasibility for multi-pesticides residue analysis in grain samples.

2. Experimental

2.1. Materials

50 pesticides and 8 related metabolites were purchased from the Agro-Environmental Protection Institute, Ministry of Agriculture (Tianjin, China) or Shanghai pesticide research institute (Shanghai, China). High performance liquid chromatography (HPLC) grade acetonitrile and methanol were purchased from Merck (New Jersey, USA). HPLC grade ammonium formate was from Tedia (Fairfield, USA). Sodium chloride, magnesium sulfate were all analytical reagent. C18 (50 μm), PSA (40–60 μm) were purchased from Agela Technologies Co. Ltd. (Tianjin, China). Purified water was obtained with a Millipore Milli-Q apparatus (Massachusetts, USA). Fe_3O_4-PSA was homemade with the particle size in the range of 531–955 nm. The detailed preparation procedure can refer to our previous report (Qi et al., 2015).

2.2. Sample extraction and purification

A 5 g grain sample was weighed into a 50 mL Teflon centrifuge tube, followed by addition of 5 g water and 10 mL acetonitrile for extraction. The mixture was vortexed for 1 min to ensure the solvent interact well with the sample. After adding anhydrous NaCl (1.5 g) and anhydrous $MgSO_4$ (4.0 g) to the above mixture, the sample was shaked vigorously for 1 min and centrifuged at 5000 r min^{-1} for 3 min using Thermo scientific biofuge Primo R centrifuge (Germany).

For the sample purification with magnetic adsorbent, 1 mL of the upper layer acetonitrile extracts was drawn into 2 mL centrifuge tube containing 30 mg Fe_3O_4-PSA, 10 mg C18 and 150 mg anhydrous $MgSO_4$. After shaking for 1 min, the samples were separated under outer magnetic field for 3 s. 0.5 mL of the supernatant was transferred into 2 mL centrifuge tube containing 0.5 mL water. The solution was filtered through 0.22 μm filter for LC–MS/MS analysis.

For comparison, the upper layer acetonitrile extracts were also purified by a traditional QuEChERS method with non-magnetic materials as adsorbent. 1 mL extract was added to 2 mL centrifuge tube containing 50 mg C18 and 50 mg PSA and 150 mg $MgSO_4$. The mixture was then shaken vigorously for 1 min and then centrifuged for 3 min at 7000 r min^{-1}. 0.5 mL of the supernatant was drawn into 2 mL centrifuge tube containing 0.5 mL water. The solution was filtered through 0.22 μm filter for LC-MS/MS analysis.

2.3. LC–MS/MS for determination of multi-pesticides

LC–MS/MS was used for determination of multi-pesticides residue in grain samples. It was performed on ultra high performance liquid chromatography LC-30A (Shimadzu, Kyoto, Japan) and AB 4500 triple-quadrupole mass spectrometer (ABSCIX Pte. Ltd., Massachusetts) with electro-spray ionization source (ESI). The chromatographic separation of the pesticides was performed on Waters BEH C18 (100 mm × 2.1 mm, 1.7 μm) analytical column (Waters Corporation, Massachusetts, USA). The mobile phase consisted of water and methanol (1:9, v/v), both methanol and water contained 5 mmol L^{-1} ammonium formate. The flow rate was kept at 0.25 mL min^{-1}. The sample volume was 2 μL. The column temperature was maintained at 40 °C. The tandem spectrometer was operated in the multiple reaction monitoring (MRM) mode. ESI-MS/MS detection was performed at positive ion mode for most of the pesticides, and negative mode for fluorine and its three metabolites. The MS parameters were as follows: ion spray voltage, 5500 V for positive ion mode and 4500 V for negative mode; temperature, 450 °C; ion source gas were air and collision gas was high purity nitrogen. All the gas was supplied by Peak Nitrogen (Peak Scientific, Scotland, UK). Each compound is determined by two pairs of parent ion and ion pairs. The MRM precursor ion, the product ions and the corresponding collision energy and declustering potential for all the pesticides were listed in Table S1.