REGULAR ARTICLE



Synthesis of magnetic multiwall carbon nanotubes for enantioseparation of three pesticide residues in fruits and vegetables by chiral liquid chromatography

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Abstract

In this study, magnetic multiwalled carbon nanotubes (MMWCNTs) were synthesized and used as adsorbent for preconcentration of chiral pesticide residues (including epoxiconazole, tebuconazole, and metalaxyl) in lettuce, cabbage, and apple. Several parameters affecting the treatment efficiency were investigated, including extraction solvent and absorption solvent. Under the optimal conditions, all three chiral pesticides showed decent enantiomeric separation (Rs > 1.48). The linearity of each target was good with the correlation coefficient (r^2) being greater than 0.9923. The average recoveries of the three spiked levels were 73.4% to 110.9% with repeatability (RSD_r) less than 7.6%, and the limit of quantification of the method was 0.10 to 0.25 mg·kg⁻¹. The results indicated that MMWCNTs had a good purifying effect, which can be applied as an effective pretreatment tool for the determination of residual chiral pesticides in fruits and vegetables.

KEYWORDS

carbon nanomaterials, chiral resolution, garden stuff, hazard residues, pretreatment

1 | INTRODUCTION

Pesticides are widely applied to control pests of fruits and vegetables, which becomes a main problem in food safety. Since more than 1000 pesticides are currently in use around the world, it is estimated that chiral pesticides in China account for more than 40% of pesticides used at present.^{1,2} Although the physical and chemical properties are identical for the pair of enantiomers, different enantiomers tend to exhibit different bioactivity and toxicity in biosystems.¹ One may represent high biological activity, whereas the other may be inefficient or even toxic to non-target organisms. However, the majority of pesticides commercially available are racemates. Accordingly, it is significant to establish an effective method for extraction

and separation of enantiomers for the detection and control of chiral pesticides.

For the pesticides in fruits and vegetables, it is challenging to develop an effective method to extract and analyze since they occur in complex matrixes at trace levels. A number of methods have been used to deal with complex matrixes such as: solid phase extraction (SPE),³⁻⁵ matrix solid-phase dispersion (MSPD),⁶⁻⁸ quick, easy, cheap, effective, rugged, and safe (QuEChERS) method,^{1,9,10} and ultrasound-assisted solvent extraction.¹¹⁻¹³

The SPE technology is one of the most frequently used approaches for cleanup of pollutants, owing to the advantages such as high enrichment factor and low organic solvent consumption.¹⁴ China has promulgated many standards for testing pesticide residues in fruits

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and vegetable crops, of which the solid-phase extraction technology are used as pretreatment method.¹⁵ However, in SPE procedure, the selection of appropriate sorbent is a significant factor, which affects recovery and enrichment factor. In addition, because of the limit of mass transfer rate, extraction processes of ordinary SPE is time-consuming in some cases.^{16,17}

In recent years, QuEChERS method has gradually become a common method for extracting pesticide residues, which means quick, easy, cheap, effective, rugged, and safe. Although commercialized QuEChERS device is convenient, it is disposable with high cost. Therefore, it is necessary to establish an efficient, convenient, and cheap pretreatment method for the extraction of pesticide residues in complex matrix samples.

Carbon nanotubes have been received research interest among scientists since they were discovered by Iijima in 1911. Their application and synthesis system have been explored and refined since then. Carbon nanotubes can be categorized into single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). Because MWCNTs have large specific surface area, they possess strong adsorption capacity and high enrichment ability for the absorption of pesticide residues, metal compounds, and polycylic aromatic hydrocarbons.¹⁸ Zhao et al extracted pesticide residues in vegetables using MWCNTs as solid-phase extraction sorbent. Their results showed that the analytes were quantitatively extracted with satisfactory recoveries and cleanup effect from those complex matrixes.¹⁹ Hadjmohammadi et al compared the adsorption capacity and enrichment factor of MWCNT with C_{18} as adsorbing material in SPE process. Their results demonstrated that MWCNT had higher extraction efficiency and lower detection limit toward C₁₈ material.²⁰ Although MWCNTs have satisfactory adsorption and clean-up ability, their separation from sample solutions is often difficult and time-consuming.²¹ In order to overcome this flaw, magnetization technology was introduced to avoid redundant separation approach. Magnetic multiwalled carbon nanotubes (MMWCNTs) were then synthesized, which have both magnetic nanoparticles and carbon nanotube structure.¹⁶ A unique advantage of this technology is that the particles can be rapidly isolated from sample solution in an external magnetic field after adsorbing.

In this study, MMWCNTs were synthesized by chemical coprecipitation method and chracterized by Fourier transform infrared spectroscopy (FTIR) characterization, magnetization curve, and magnet adsorption phenomenon. The performance of the prepared particles was evaluated by extracting three chiral pesticides in lettuce, cabbage, and apple. An enantioselective highperformance liquid chromatography with ultraviolet detection (HPLC-UV) method was developed for the CHIRALCEL OJ-H separation using column (4.6 mm \times 250 mm, I.D. 5 μ m). To the authors' knowledge, such a method based on MMWCNTs for the extraction of pesticides from fruits and vegetables has never been exploited.

2 | MATERIALS AND METHODS

2.1 | Chemicals and reagents

Carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOHs) were purchased from Chengdu Organic Chemistry Co Ltd, Chinese Academy of Sciences (Chengdu, China). Racemic epoxiconazole, tebuconazole, and metalaxyl (Figure 1) (all 95% purity) were brought from Shandong Weifang Runfeng Chemical Co, Ltd (Shandong, China). The pesticide stock solutions were prepared in *n*-hexane (HPLC grade) at a concentration of 1 mg/mL and kept at 4°C. Ammonium sulfate dodecahydrate ($NH_4Fe(SO_4)_2 \cdot 12H_2O$) and ammonium ferrous sulfate hexahydrate $((NH_4)_2Fe(SO_4)_2 \cdot 6H_2O)$ were offered by Hengxing Chemical Reagent Factory (Tianjin, China). Ammonia, methylene chloride, toluene, methanol, n-hexane, acetonitrile, and isopropanol andacetic acid were of analytical grade and supplied by Yuwang Industrial Co, Ltd (Shandong, China). Hexane and isopropanol of HPLC grade were supplied by Concord Technology Co, Ltd (Tianjin, China).

2.2 | Sample preparation

Lettuces, cabbages, and apples were purchased from local market in Shenyang, and the edible parts were mashed and homogenized. Afterwards, the homogenates were







metalaxyl

tebuconazole

epoxiconazole

FIGURE 1 Structures of three chiral pesticides

then placed respectively in 500 mL round bottom flasks and frozen for 12 hours before being freeze-dried. The resulting dry powders were put into jars for later use.

2.3 | Preparation and characterization of **MMWCNTs**

One gram of MWCNT was suspended into 200 mL of mixed solution containing 1.7 g (NH_4) ₂ Fe (SO_4) 2.6H2O and 2.51 g NH4Fe(SO4) 2.12H 2O. Under the protection of nitrogen, ammonia solution was added dropwise to control the pH of the solution above 11. Afterwards, the mixture was sonicated for 15 min, and then mechanically stirred for 30 min on a temperature controlled water bath at 50°C. After reaction, the obtained MMWCNTs were collected by magnet isolation and rinsed three times with distilled water and absolute ethanol, respectively, and then dried under vacuum at 50°C.

The surface chemistry of MMWCNTs and MWCNTs were studied using FTIR spectrum (Figure 2). Compared with the spectrum of bare MWCNTs, the FTIR spectra of MMWCNTs composites appeared at 584.7 cm^{-1} for Fe–O characteristic band, 3427.7 cm⁻¹ for O–H stretching band, and 1384.3 cm⁻¹ for -CH₃ stretching band, indicating the MMWCNTs were composed of oxidized MWCNT and iron oxide.^{16,22}

Determination of magnetization curve is another potent method to evaluate magnetic property of magnetic materials. Typical magnetization curve of the modified MMWCNTs is shown in Figure 3. Clearly, the curve has no hysteresis, suggesting that the particles are superparamagnetic.²¹ The composite has a saturation magnetization of 38 $emu \cdot g^{-1}$, which validates its good



FIGURE 2 IR spectra characterization of multiwalled carbon nanotubes and magnetic multiwalled carbon nanotubes



FIGURE 3 Hysteresis loop diagram of magnetic multiwalled carbon nanotubes

magnetic property. What is more, the cluster of particles in external magnetic field (Figure 4) reflects its satisfactory magnetic property.

2.4 **Chromatographic conditions**

Three pesticides (epoxiconazole, tebuconazole, and metalaxyl) were quantified using chiral liquid chromatography with a UV detector. The chromatography column was CHIRALCEL OJ-H column (4.6 mm \times 250 mm, I. D. 5 µm) provided by Daicel Chiral Technologies Co, Ltd (Tokyo, Japan). The chiral separation was carried out under gradient elution condition, and the following gradient conditions were used: n-hexane: isopropanol (95:5, v/v) originally, then a linear gradient to *n*-hexane: isopropanol (80:20, v/v) until 30 min, followed by a linear gradient from *n*-hexane: isopropanol (80:20, v/v) to *n*hexane: isopropanol (95:5, v/v) until 45 min. The flow



FIGURE 4 Actual magnetic phenomenon

2.5 | Pretreatment procedure

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2.5.1 | Extraction procedure

One gram of freeze-dried powder was added into a 50-mL centrifuge tube and extracted with 20-mL dichloromethane by ultrasonic for 30 min. The mixture was then centrifuged at 4000 rpm for 10 min. The supernatant was collected, and the residue was extracted again. The supernatant was combined and evaporated under nitrogen stream at 40°C, then dissolved by 20 mL of *n*-hexane.

2.5.2 | Magnetic clean-up procedure

Eighty milligrams of MMWCNTs were added to the sample extract. The mixture was sonicated for 2 min, and then shaken for 30 min at 40°C water bath heating. After the oscillating, the composites were isolated by a magnet on the outer wall of the centrifuge tube, and the supernatant was discarded. The remained carbon nanotubes were then washed with 2-mL methanol by ultrasonicating for 15 min. The washing operation was repeated for three times. Afterwards, the supernatants were combined, and then evaporated to dryness under nitrogen stream at 40°C. The residue was diluted to 200 μ L with *n*-hexane: isopropanol (95:5, *v*/*v*). Finally, 20 μ L of the sample solution was injected into HPLC.

3 | **RESULTS AND DISCUSSION**

3.1 | Optimization of pretreatment procedure

3.1.1 | Optimization of extraction solvent

The type of extraction solvent might have direct impacts on the recoveries. The selection depends mainly on the structure of the analytes and their solubility. In this experiment, three kinds of solvents with good solubility for the pesticides were selected: dichloromethane, toluene, and methanol. The effects of different extraction solvents on the recovery rate were investigated and the result is shown in Figure 5A. Obviously, the best extraction efficiency was obtained when dichloromethane was used as the extraction solvent. Thus, pesticides in fruit and vegetable samples were extracted with dichloromethane by sonication.

3.1.2 | Optimization of absorption solvent

The type of adsorption solvent also plays a significant role in the extraction efficiency. It is expected that the selected solvents have certain solubility of the pesticides to be tested, so as to facilitate the adsorption of pesticides by MMWCNTs. In this study, acetonitrile, *n*-hexane, and isopropanol were selected as alternative adsorption solvents. The results showed that the highest extraction recovery when *n*-hexane was used (Figure 5B). In addition, the vegetable extracts changed from to colorless



FIGURE 5 Optimization of the pretreatment process: A, extraction solvent; B, absorption solvent; C, amount of MMWCNTs; D, eluent; E, elution time. The text in abscissa is as follows: a dichloromethane, toluene, methanol; b *n*-hexane, acetonitrile, isopropanol; c 20, 40, 60, 80, 100; d CH₂Cl₂, CH₂Cl₂-acetic acid, methanol, methanol-acetic acid; e 5, 10, 15, 20

after adsorption by *n*-hexane. Given the above, pesticides in samples were extracted with *n*-hexane.

3.1.3 | Optimization of the amount of MMWCNTs

The effects of the amount of MWCNTs on the recovery were carefully investigated at a fortification concentration of 10 mg·kg⁻¹ (Figure 5C). As shown in the diagram, the recovery increased as the amount of MMWCNTs ranging from 20 to 80 mg. When the amount increased above 80 mg, the recovery remained constant almost. Therefore, 80 mg of magnetic particles were added in the following experiments considering that the adsorption was greatest when this dosage was used.

3.1.4 | Optimization of the eluent

Different eluent has certain effect on the recovery rate. Four organic solvents including dichloromethane, dichloromethane-acetic acid (95:5, v/v), methanol, and methanol-acetic acid (95:5, v/v) were investigated for their elution capacity. As the results shown in Figure 5D, the acetic acid could improve the recovery of compounds. However, the solution always contained precipitation after being evaporated and dissolved when acetic acid was added, which made it difficult to filtrate through a 0.45-µm micron filter. Take all the factors into account, methanol was chosen as eluent in order to get satisfactory results.

3.1.5 | Optimization of the elution time

Elution time is another influential parameter on the extraction recovery. In general, extraction recovery improves with the elution time increasing. However, on the negative side, the structure of MMWCNTs may be destroyed simultaneously. Therefore, the influence of elution time varying from 5 to 20 min was tested. As shown in Figure 5E, extraction efficiency reached maximum at 15 min. Therefore, 15 min was used to elute in subsequent experiments.

3.2 | Method validation

The developed method was validated under optimum conditions based on linearity, limits of quantification (LOQs), trueness, precision, and retention time referring to SANTE 11813/2017.

The linearity was established at five concentration levels in the range of 0.5 to 20 $mg{\cdot}kg^{-1}$ for all of the

WILEY ⁵ pesticides. The correlation coefficients (r^2) for all pesticides enantiomers ranged from 0.9923 to 0.9998, which meant good linearities of the method (Table 1). The LOQ was selected as the lowest spike level for which trueness was in the range of 70% to 120% and reproducibility below 20%. LOQ was set at 0.25 mg·kg⁻¹ for metalaxyl and tebuconazo, and 0.10 mg·kg⁻¹ for epoxiconazole. In this study, the weight of matrix is calculated on the basis of freeze-dried powder. As the weight of fruits and vegetables reducing substantially in the freeze-drying process, it meant that LOQs might be higher than that of the methods extracting directly. All of the three pesticides

Trueness was calculated on five replicates and ranged from 73.4% to 110.9% with the repeatability (RSD_r) varying from 1.3% to 7.6%. The within-laboratory reproducibility (RSD_{wR}) was measured over 3 days. As shown in Table 2, all precision values fulfilled the analytical requirements regulated in the SANTE 11813/2017. It suggests that as a novel adsorbent material, MMWCNTs have adequate capability to adsorb analytes thoroughly, which can be used as an effective pretreatment tool for the determination of contaminants in complex matrix.

attained satisfactory resolution (Figure 6).

The retention time of the analyte in the spiked sample was compared with that of the calibration standard. The deviations are shown in Table 3. The deviations were thought to be acceptable within ± 0.1 min according to SANTE 11813/2017.

3.3 | Comparison among MMWCNTs and other absorbents

In order to further demonstrate the superiority of the method, the sorption capacity on MMWCNTs were compared with MWCNTs in this study. It can be seen in Figure 7, the recovery of metalaxyl was higher when MMWCNTs were used as absorbents, whereas that of tebuconazole and epoxiconazole were slightly lower. This phenomenon might be due to two reasons: on the one

TABLE 1 Specificity, sensitivity, and linearity of the proposed method

| Compounds | t_R (min) | LOQ (mg·kg ⁻¹) | Linearity (mg·kg ⁻¹) | r ² |
|------------------|-------------|-------------------------------|-------------------------------------|----------------|
| Metalaxyl E1 | 18.841 | 0.25 | 0.5-20 | 0.9996 |
| Metalaxyl E2 | 24.130 | 0.25 | 0.5-20 | 0.9998 |
| Tebuconazole E1 | 21.449 | 0.25 | 0.5-20 | 0.9998 |
| Tebuconazole E2 | 31.309 | 0.25 | 0.5-20 | 0.9995 |
| Epoxiconazole E1 | 26.479 | 0.10 | 0.5-20 | 0.9923 |
| Epoxiconazole E2 | 33.059 | 0.10 | 0.5-20 | 0.9992 |



FIGURE 6 Enantioseparation chromatograms of three chiral pesticides: A, Metalaxyl, B, Tebuconazole, C, Epoxiconazole

hand, the specific surface area (SSA) of MWCNT was larger than that of the same weight of MMWCNT on which were iron oxides covering.²³ On the other hand, in the process of the experiment, different adsorbents were weighed in the same quality, while the volume of MWCNTs was almost twice than that of the MMWCNTs. That is to say, the attachment of iron oxide leads to substantial extra weight. Despite these, a significant advantage of being conveniently isolated from solution made MMWCNT a promising adsorbent to remove pollutant from matrix.

Some other common pretreatment methods such as SPE, MSPD, and QuEChERS method are the methods that developed in recent years. Their theories are identical to that of MMWCNT. In general, the amount of their adsorbent ranges from a few hundred milligrams to several grams, whereas the amount of MWCNT adsorbent^{16,17} is generally not more than 100 mg. It reflects the high uptake capacity of the latter. In addition, MMWCNTs can be regenerated in comparison with many other methods. Experiments showed that after repeatedly adsorption–desorption experiments, the recovery of MMWCNT can still achieve satisfactory results.^{8,23-25} To sum up, MMWCNT can greatly reduce scientific research cost.

3.4 | Real sample analysis

The newly developed method was applied to analyze vegetables and apple samples obtained from local market in Shenyang (China). The results showed that there were no samples found to be contaminated with target pesticides.

| TABLE 2 | Accuracy an | d precision | of the | proposed | method |
|---------|-------------|-------------|--------|----------|--------|
|---------|-------------|-------------|--------|----------|--------|

| | | | | | Intraday | | | · |
|------------------|------------------------|-------------|----------------------|-------------|----------------------|-------------|----------------------|------------------|
| | Spiked | Day 1 | | Day 2 | | Day 3 | | Interday RSDp |
| Compounds | (mg·kg ⁻¹) | Average (%) | RSD _r (%) | Average (%) | RSD _r (%) | Average (%) | RSD _r (%) | (%) |
| Metalaxyl E1 | 8 | 74.7 | 1.7 | 74.2 | 1.8 | 73.0 | 3.0 | 1.2 |
| | 10 | 73.4 | 4.1 | 79.7 | 1.5 | 75.2 | 4.5 | 4.3 |
| | 12 | 76.3 | 1.7 | 74.7 | 2.2 | 76.7 | 1.3 | 1.5 |
| Metalaxyl E2 | 8 | 94.7 | 3.9 | 91.1 | 3.5 | 102.5 | 2.0 | 6.1 |
| | 10 | 93.8 | 2.1 | 95.2 | 2.3 | 93.4 | 2.2 | 1.1 |
| | 12 | 94.4 | 2.7 | 92.1 | 2.1 | 103.5 | 4.4 | 3.6 |
| Tebuconazole E1 | 8 | 104.5 | 2.2 | 99.2 | 2.5 | 94.0 | 1.7 | 2.8 |
| | 10 | 103.3 | 4.7 | 102.3 | 1.8 | 86.7 | 4.7 | 5.2 |
| | 12 | 90.5 | 4.2 | 99.6 | 1.4 | 90.7 | 1.7 | 7.2 |
| Tebuconazole E2 | 8 | 88.5 | 4.1 | 92.6 | 3.7 | 89.9 | 3.9 | 2.4 |
| | 10 | 93.8 | 3.9 | 94.2 | 4.3 | 99.8 | 2.1 | 3.5 |
| | 12 | 96.2 | 1.9 | 94.7 | 2.4 | 104.1 | 2.7 | 5.2 |
| Epoxiconazole E1 | 8 | 101.8 | 2.2 | 99.9 | 1.3 | 102.2 | 3.0 | 1.3 |
| | 10 | 108.2 | 6.3 | 110.9 | 5.8 | 109.9 | 6.0 | 1.3 |
| | 12 | 100.5 | 2.9 | 96.2 | 3.9 | 98.2 | 3.3 | 2.3 |
| Epoxiconazole E2 | 8 | 90.8 | 2.4 | 89.7 | 2.3 | 87.8 | 2.8 | 1.8 |
| | 10 | 94.8 | 1.4 | 91.7 | 2.9 | 91.8 | 1.6 | 2.0 |
| | 12 | 97.0 | 7.6 | 95.2 | 2.0 | 92.4 | 4.1 | 2.5 |

TABLE 3 Deviation of retention time of the proposed method

| Compounds | Retention Time of Extract (min) | Retention Time of Calibration (min) | Deviation |
|------------------|------------------------------------|--|-----------|
| Metalaxyl E1 | 18.841 | 18.802 | 0.039 |
| Metalaxyl E2 | 24.130 | 24.161 | -0.031 |
| Tebuconazole E1 | 21.449 | 21.423 | 0.026 |
| Tebuconazole E2 | 31.309 | 31.348 | -0.039 |
| Epoxiconazole E1 | 26.479 | 26.389 | 0.090 |
| Epoxiconazole E2 | 33.059 | 32.974 | 0.085 |



FIGURE 7 Comparison of absorbability between magnetic multiwalled carbon nanotubes and multiwalled carbon nanotubes (M: Metalaxyl, T: Tebuconazole, and E: Epoxiconazole)

4 | CONCLUSION

In the current investigation, MMWCNTs were synthesized and characterized by FTIR and magnetization curve. The performance of MMWCNTs was evaluated by adsorption of three chiral pesticides in lettuce, cabbage, and apple. The results showed that the three chiral pesticides were enantioseparated under the HPLC-UV condition. Recoveries of pesticide residues in samples were in the range of 73.4% to 110.9% with RSDr less than 7.6% (n = 5). The LOQs of the target pesticide residues obtained by this method were in the range of 0.10 to 0.25 mg·kg⁻¹. It demonstrates that MMWCNTs have the advantages of high extraction efficiency, convenient operation, low cost, and short time consuming as a new type of material. Based on these superiorities, this research

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provides a novel method to extract pesticides in fruits and vegetables. What is more, this study combined this with chiral liquid chromatography, providing a method basis for further research on chiral pesticides in foods.

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