



Development, validation, comparison, and implementation of a highly efficient and effective method using magnetic solid-phase extraction with hydrophilic-lipophilic-balanced materials for LC-MS/MS analysis of pesticides in seawater

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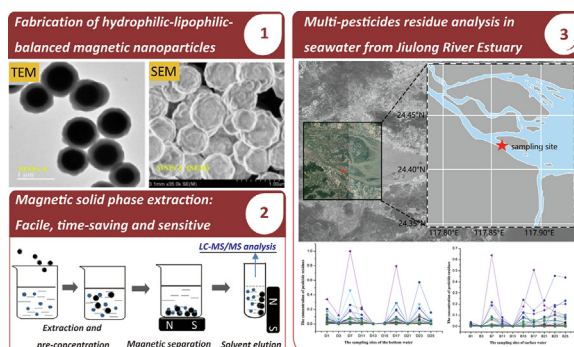
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HIGHLIGHTS

- Fabrication of hydrophilic-lipophilic-balanced magnetic nanoparticles were explored.
- A facile and time-saving multi-pesticides residue analytical method in seawater was developed.
- It affords significant improvements on operation convenience and detection sensitivity.
- Systematic method validation and comparison displayed its prospect in environmental analysis.
- Parts of pesticides were detected in trace level in seawater from Jiulong River Estuary.

GRAPHICAL ABSTRACT



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ABSTRACT

To achieve multi-pesticides residue analysis in seawater, hydrophilic-lipophilic-balanced magnetic particles were designed and fabricated by swelling polymerization of divinyl benzene (DVB) and N-vinyl pyrrolidone (NVP) on the surface of Fe₃O₄@SiO₂ magnetic particles. The ratio of DVB to NVP was adjusted to achieve a proper balance in hydrophilicity and lipophilicity. The obtained magnetic particles were systematically characterized by TEM, SEM, FT-IR and vibrating sample magnetization. Based on the optimized magnetic nanoparticles, a sensitive magnetic solid-phase extraction method was developed for the simultaneous pre-concentration and determination of 96-pesticide residues from large-volume

Abbreviations: DVB, Divinyl benzene; NVP, N-vinyl pyrrolidone; LC-MS/MS, liquid chromatography-tandem mass spectrometry; MSPE, Magnetic solid-phase extraction; SPE, solid-phase extraction; MNPs, Fe₃O₄@SiO₂@DVB-NVP; HPLC, High performance liquid chromatography; MPS, 3-trimethoxysilyl propyl methacrylate; FE-SEM, field-emission scanning electron microscopy; TEM, Transmission electron microscopy; ESI, electro-spray ionization; MRM, multiple reaction monitoring; LOQ, limit of quantification; MRL, maximum residue limit.

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seawater samples prior to being detected by liquid chromatography-tandem mass spectrometry. Recoveries of pesticides in spiked seawater samples (0.001, 0.01, 0.1, 1.0 $\mu\text{g L}^{-1}$) ranged from 62% to 112% with RSDs less than 21%. The method limits of detection of 96 pesticides ranged from 0.13 to 0.42 ng L^{-1} , the method limits of quantification of 96 pesticides ranged from 1.0 to 10 ng L^{-1} . The method was successfully applied to pesticide residue analysis in water samples from Jiulong River Estuary of China, demonstrating the prospects of this technique as a potential method for the rapid determination of trace levels of multi-pesticide residues in seawater.

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1. Introduction

Pesticides are widely used to control agricultural pests and prevent the spread of diseases, and likely represent the largest amount of anthropogenic substances released to the environment (Moreno-González et al., 2013; Wang H et al., 2018). A wide variety of pesticides can reach the marine environment through direct routes such as rivers contributions and atmospheric deposition, and thus the marine environment is regarded as the ultimate “sink” of pesticides in many cases (Moro et al., 2018; Matsushita et al., 2018). Pesticide residues pose potential risks to ecosystems and human health due to their bioaccumulation and low rates of biodegradation. A large number of studies have focused on the effects of pesticide pollution in terrestrial environments (Köck-Schulmeyer et al., 2019); however, the risk assessment of pesticide residues in coastal marine ecosystems is still relatively insufficient (Liu C et al., 2017; Fan et al., 2017; Maldaner and Jardim, 2012; Yu et al., 2012). The concentrations of pesticides that normally exist in seawater are extremely low which were found in $\mu\text{g L}^{-1}$ or ng L^{-1} levels (Maldaner and Jardim, 2012). As detection technologies are not sensitive enough to detect trace pesticide residues, a pre-concentration step is necessary. Nevertheless, the existing pre-treatment methods are limited by the enrichment factor, which results in trace levels of pesticides that cannot be detected in the marine environment. Overall, the analysis of trace pesticide residues in seawater poses a considerable number of challenges for the analyst. Therefore, developing a fast, convenient and highly sensitive analytical methodology to analyze trace pesticide residues has become important for assessing pesticide pollution in seawater.

Up to now, various types of pretreatment techniques for the extraction and concentration of trace levels of organic pollutants based on materials have been developed, such as solid phase extraction (SPE), magnetic solid phase extraction (MSPE), solid phase microextraction (SPME), dispersive solid phase extraction (d-SPE), dispersive micro solid phase extraction (d-m-SPE), micro-solid phase extraction (m-SPE), and stir bar sorptive extraction (SBSE) (Azzouz et al., 2018; Kailasa and Wu, 2015; Rai et al., 2018). MSPE method, which is a new solid-phase extraction (SPE) procedure based on the use of magnetic sorbents, has attracted increasing interest worldwide. Owing to their nanoscale particle size, large surface area and short diffusion pathway, magnetic sorbents have a large extraction capacity and high extraction efficiencies. Additionally, the magnetic sorbents can be quickly isolated from a matrix solution via an external magnetic field, which makes separation easier and faster. Compared with traditional SPE, MSPE results in enhanced extraction efficiencies and avoids time consuming and labor intensive extraction steps, which are especially important for large sample sets (Ma et al., 2016; Luo et al., 2014; Wang P et al., 2018).

In MSPE method, the sorbent plays a key role in obtaining higher enrichment efficiencies of analytes. A series of magnetic particles have been prepared for the extraction of pesticides.

Ferroferric oxide (Fe_3O_4) particles are the most widely used owing to their low price, low toxicity, and ease of synthesis and modification (Liu Z et al., 2017; Yuan et al., 2018). However, Fe_3O_4 particles are relatively unstable and easily oxidized. Surface modification of magnetic Fe_3O_4 by suitable inorganic or organic functional groups can prevent its oxidation and improve its durability and sorption properties. Several types of materials have been used to modify and functionalize Fe_3O_4 particles (Jiang et al., 2016; Lu et al., 2018), including ionic liquids (Liu C et al., 2017; Liu F et al., 2018), C18 (Maddah and Shamsi, 2012; Zhang et al., 2011), graphene (Li et al., 2016; Seidi et al., 2018), graphene oxide (Han et al., 2012; Liu et al., 2013), and various polymers (Shah et al., 2018; Yang et al., 2016). Fe_3O_4 particles modified with octadecylsilane were synthesized and used to extract trace amounts of diazinon and fenitrothion from environmental water (Maddah and Shamsi, 2012), while multifunctional attapulgite/ Fe_3O_4 /polyaniline composites were synthesized for magnetic dispersive solid phase extraction of benzoylurea insecticides in environmental water sample (Yang et al., 2016). Although magnetic adsorbents have been reported to be effective for the analysis of pesticides, most of them still face great challenges in practical applications. In particular, they are too specific to a certain analyte, so previous work used MSPE to establish methods for analyzing a limited range of pesticides. However, the diversity of pesticide residues at trace levels in the environment (e.g. seawater) makes these methods limited for detailed studies. Thus, there is an urgent need to develop a broad-spectrum hydrophilic-lipophilic balanced magnetic adsorbent, which can be used to establish a highly sensitive and efficient pretreatment method for the simultaneous determination of polar and non-polar pesticide residues in seawater samples. A hydrophilic-lipophilic balanced adsorbent can be achieved by modifying magnetic Fe_3O_4 with suitable hydrophilic and lipophilic monomers. The divinylbenzene (DVB) monomer has a strong lipophilicity, while the N-vinylpyrrolidone (NVP) monomer has a strong hydrophilicity (He et al., 2014; Yao et al., 2019). If NVP and DVB are added simultaneously to the surface of Fe_3O_4 particles, an ideal magnetic sorbent with high adsorption ability of both hydrophobic and hydrophilic substances could be achieved.

The present work aimed at fabricating an amphiphilic magnetic material $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{DVB-NVP}$ (MNPs) and developing an efficient and effective method for the simultaneous extraction of 96 pesticides from seawater samples. The influence of the relative amount of NVP and DVB monomers were adjusted to obtain the hydrophilic-lipophilic balance of the polymer. The main factors on extraction efficiency including the amount of adsorbent, extraction time, pH, and the type and volume of desorption solvent were tested. Furthermore, pesticide residues in seawater from the Jiulong River Estuary were analyzed to validate this method and reveal the extent and type of pesticide pollution in this area. To the best of our knowledge, this work constitutes the first application of magnetic MNPs as an extraction phase for the pre-concentration of multi-pesticide residues in seawater samples.

2. Experimental

2.1. Materials

96 pesticides were purchased from 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). Formic acid was an analytical grade reagent. Purified water was obtained with a Millipore Milli-Q system (Massachusetts, USA). Ferric trichloride hexahydrate, tetraethylorthosilicate, sodium citrate, sodium dodecyl sulfate, aqueous ammonia, ethylene glycol, 3-trimethoxysilyl propyl methacrylate, anhydrous ethanol, DVB, NVP, and azodiisobutyronitrile were all obtained from J&K Scientific (Shanghai, China).

2.2. Preparation of MNPs particles

Magnetic MNPs particles were successfully prepared by a swelling polymerization method using NVP and DVB modified on the surface of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ microspheres. Fe_3O_4 and $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ particles were prepared in the lab using our previously reported method (Qi et al., 2015; Sun et al., 2018). Fe_3O_4 particles were synthesized by a solvothermal method, and the magnetic $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ particles were fabricated by silica coating the surface of Fe_3O_4 particles. MNPs particles were further synthesized using two discrete steps as below.

First, 3-trimethoxysilyl propyl methacrylate (MPS) was fabricated on the surface of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$. $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ particles (3 g) were dispersed in 400 mL ethanol/ H_2O (v/v, 3:1). 8 mL aqueous ammonia was added to the mixture under nitrogen at room temperature, followed by the addition of solution A (8 mL MPS in 10 mL anhydrous ethanol) with vigorous stirring. The homogeneous mixture was heated to 60 °C, and vigorous stirring continued overnight. And the product was collected by a magnet, being washed with water and ethanol several times, and the washed $\text{Fe}_3\text{O}_4@/\text{MPS}$ product was vacuum dried at 60 °C overnight.

Second, to synthesize MNPs particles, the $\text{Fe}_3\text{O}_4@/\text{MPS}$ particles were functionalized with DVB and NVP. 3 g $\text{Fe}_3\text{O}_4@/\text{MPS}$ was dissolved in 500 mL acetonitrile, and the solution was sonicated for 15 min. 0.1 g azodiisobutyronitrile was added to the solution, followed by the addition of DVB and NVP and being vigorously stirred for 30 min (300 rpm/min) under nitrogen. The homogeneous mixture was heated to 75 °C, and allowed to react for 16 h. The MNPs particles product were magnetically separated, rinsed with acetone and then ethanol several times, and vacuum dried at 60 °C overnight.

2.3. Characterization of magnetic particles

The particle size and structure of MNPs particles were observed by field-emission scanning electron microscopy (FE-SEM). FE-SEM was performed with a Hitachi S-4800 instrument (Hitachi, Tokyo, Japan) at an accelerating voltage of 1.0 kV. Transmission electron microscopy (TEM) images of the particles were obtained by a JEM-1200EX microscope (JEOL, Tokyo, Japan). The vibrating sample magnetization (VSM) curves of the obtained particles were recorded with a LDJ9600 magnetometer (LDJ Electronics, Troy, USA) by changing the magnetic field intensity (H) between +20000 and -20000 Oe at room temperature. FT-IR spectra of the particles were obtained on the samples prepared in pressed

KBr pellets by using a NEXUS 670 FT-IR spectrometer (Nicolet Thermo, Waltham, MA).

2.4. Preconcentration of pesticides with MSPE

Seawater sample with 500 mL was added into a beaker containing 50 mg of magnetic adsorbents that were pre-activated with 1 mL methanol. The sample was sonicated for 15 min to accelerate the extraction process. During this process, the target analytes were adsorbed onto the magnetic adsorbents, which were then collected by a magnet placed in the bottom of the beaker. The supernatant was discarded. Next, ultrasound-assisted desorption of the analytes were performed from the magnetic adsorbent by elution with 3 mL acetonitrile containing 0.1% formic acid. Finally, the solution containing the analytes was evaporated to dryness under a mild stream of nitrogen at 40 °C. The residue was then reconstituted in 1 mL acetonitrile and filtered through a 0.22 μm filter for liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis.

2.5. SPE procedure as a comparison method

The performance of the proposed method was compared with the previously reported SPE methods using HLB cartridges for multi-pesticide residue analysis in seawater (Köck-Schulmeyer, 2019). Oasis HLB (500 mg, 6 mL) cartridges were pre-conditioned with 5 mL of methanol-dichloromethane (v/v, 1:1) and 5 mL of Milli-Q water. Seawater samples (500 mL) were loaded into the cartridges at a flow-rate of approximately 5 mL min⁻¹. The retained pesticides were eluted with 4 mL of methanol-dichloromethane (v/v, 1:1). The resulting solution was evaporated to dryness under a mild stream of nitrogen at 40 °C. Finally, the residue was dissolved in 1 mL acetonitrile and filtered through a 0.22 μm filter for LC-MS/MS analysis.

2.6. LC-MS/MS determination of multi-pesticide residues

LC-MS/MS was used for the determination of pesticides extracted from seawater samples, using an ultra high performance liquid chromatograph Nexera X2 LC-30AD (Shimadzu, Kyoto, Japan) equipped with a Shimadzu 8050 triple-quadrupole mass spectrometer (Shimadzu, Kyoto, Japan) with an electrospray ionization (ESI) source. Chromatographic separation of pesticides was performed on a Waters BEH C18 column (100 mm × 2.1 mm, 1.7 μm , Waters Corporation, Massachusetts, USA). The mobile phases were 5 mmol L⁻¹ ammonium formate in water (mobile phase A) and methanol (mobile phase B), with the following gradient program (with respect to phase B): 20% B (0 min, hold 1 min), 90% B (12 min, hold 2 min) and 20% B (14.2 min, hold 4.8 min). The total analysis time was 19 min. The flow rate was held at 0.3 mL min⁻¹. The sample injection volume was 2 μL . The column temperature was maintained at 35 °C. The ESI-MS/MS was operated in multiple reaction monitoring (MRM) mode. Detection was performed in positive ion mode for most of the pesticides, and negative mode for fipronil and its three metabolites. The MS parameters were as follows: ion spray voltage, 3500 V for positive ion mode and 3000 V for negative mode; temperature, 400 °C; the ion source gas was air and the collision gas was high purity nitrogen. The gases were both supplied by a ATN-1050 N₂ gas generator (Shimadzu, Kyoto, Japan). Each compound was determined by two pairs of parent ions and product ion pairs. The MRM precursor ion, the product ions and the corresponding collision energy and deviation for all the pesticides are listed in the Table S1.

3. Results and discussion

3.1. Fabrication of hydrophilic-lipophilic-balanced magnetic particles

Amphiphilic magnetic materials were fabricated via swelling copolymerization of hydrophilic monomer (NVP) and lipophilic monomer (DVB) on the surface of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ magnetic particles. The hydrophilic-lipophilic balance of the polymer is mainly achieved by adjusting the amount of the hydrophilic NVP and hydrophobic DVB monomers. Hence, various magnetic particles were synthesized and the weight ratios of NVP to DVB are displayed in Table 1. The dosage effect of DVB and NVP monomers on the prepared magnetic polymer particles extraction performance was first investigated. As the most important function of magnetic adsorbents is to achieve the simultaneous extraction of a variety of pesticides with different properties, the extraction capacities of the prepared MNPs were compared. The pretreatment process was referred to the above 2.4. The extraction efficiencies of prepared MNPs are shown in Fig. 1. The adsorption ability of the MNPs increased with an increase in the amount of DVB used for modification within a certain range. The MNPs-5 sorbent showed the highest extraction performance for all target pesticides, with mean recoveries of 81% of the pesticides in the range of 70%–100%. The desirable adsorption performance mainly based on the hydrogen bonding interaction between the pesticide and the pyrrolidone functional group of MNPs-5, π - π interaction between the pesticide and the benzene group of MNPs-5, as well as the hydrophobic interaction in water phase system. The adsorption efficiency to pesticides with strong polarity ($\text{LogP} < 1.5$) decreased relatively, their recoveries ranged from 60% to 70%. The recoveries of most pesticides (LogP : 1.5–6.9) were concentrated on the range of 70% to 120%. These differences in adsorption efficiency could be mainly ascribed to the different strength of the interactions between pesticides and adsorbents. The adsorption of polar pesticides is relatively weak, leading to the weaker retention on MNPs and lower recoveries.

The morphology of the synthesized MNPs was assessed by TEM (Fig. 2). It can be clearly seen that MNPs-1 has no clear core-shell structure, and MNPs-2, MNPs-3, MNPs-4, MNPs-6 and MNPs-7 displayed the typical core-shell structure. However, the monomers were not uniformly modified on the surface of the magnetic Fe_3O_4 core. While the surfaces of MNPs-5 were well-defined, the core-shell composite microspheres had a spherical shape, uniform particle size and good dispersion. The DVB-NVP layer had obviously coated surface of the Fe_3O_4 particles. The size and morphology of the obtained MNPs-5 were characterized by SEM. As shown in Fig. 2, the average size was about 760 nm, and the MNPs microspheres were uniform and well-dispersed. The particle size of the obtained MNPs was larger than the reports (Yu et al., 2017; Sung Lee et al., 2015), which could be attributed to the synthesized method. The particle size of Fe_3O_4 could range from 16 to 512 nm under different reaction conditions (Sung Lee et al., 2015). Generally, the particle size is relatively smaller using the coprecipitation method than the solvothermal method. Meanwhile, the surface of the microspheres became relatively rough, which helps to adsorb the target pesticides. In summary, based on the results of adsorption and morphological characterization, MNPs-5 was selected for further experiments.

Superparamagnetism and high saturation magnetization of the magnetic sorbent are necessary for its practical application. The magnetic properties of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$ and MNPs-5 were investigated by a VSM technique at room temperature. As shown in Fig. 3A, the magnetic hysteresis loops of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, and MNPs-5 displayed S-like curves, which passed through the zero

Table 1

The MNP sorbents synthesized with different ratios of DVB and NVP.

Name of the MNP sorbents	Weight ratio of DVB and NVP
MNPs-1	0:12.5
MNPs-2	5.2:8.6
MNPs-3	5.6:8.0
MNPs-4	6.3:7.5
MNPs-5	7.5:6.3
MNPs-6	8.0:5.8
MNPs-7	10.2:3.6

point of magnetization. All the VSM curves had little hysteresis, remanence and coercivity, which indicates their typical superparamagnetic property. The values of saturation magnetization of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$ and MNPs-5 were 70, 57 and 22 emu g^{-1} , respectively, which were higher than those of previously reported magnetic materials (Yao et al., 2019). Although the addition of non-magnetic material led to decreased saturation magnetizations, the obtained MNPs-5 can be isolated from the seawater solution conveniently and quickly by using an external magnet.

The FT-IR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4/\text{SiO}_2$, and MNPs-5 are shown in Fig. 3B. The absorption peak at 3400 cm^{-1} was assigned to the stretching vibration of the hydroxyl group, indicating that a certain amount of hydroxyl groups exist on the surface of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$. The absorption peak at 3400 cm^{-1} disappeared in the FT-IR spectra of MNPs-5; the hydroxyl group on the surface of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ may react with other groups. The absorption peaks at 586, 540 and 588 cm^{-1} are attributed to the characteristic absorption peak of the Fe-O group. In the FT-IR spectra of $\text{Fe}_3\text{O}_4/\text{SiO}_2$, the absorption intensity of the Fe-O group decreased with the addition of silica, and a strong absorption intensity of the Si-O-Si group appeared at 1040 cm^{-1} owing to the silica coating, which indicated that Fe_3O_4 had been successfully coated with SiO_2 (Chen et al., 2018; Zhang et al., 2011). The Fe-O group stretching vibration at 540 cm^{-1} for MNPs-5 was the result of a large shift to a lower wavenumber of about 46 cm^{-1} from the free Fe-O mode of 586 cm^{-1} , which indicated the interaction between Fe-O and the surface groups of the nanoparticles. In the FT-IR spectra of MNPs-5, there was a peak absorption intensity at approximately $1500\text{--}1640 \text{ cm}^{-1}$, which was assigned to the characteristic band of aromatic C=C double bond bending vibrations. The peak at $1250\text{--}1300 \text{ cm}^{-1}$ is attributed to the C-C stretching vibration, and the peak at $1400\text{--}1500 \text{ cm}^{-1}$ was attributed to the C-N stretching vibration of NVP (Chen et al., 2018). These absorption peaks confirmed the successful modification of the DVB and NVP monomers onto the surface of Fe_3O_4 .

3.2. Optimization of the sample pretreatment method

In the MSPE procedure, the extraction and elution processes play an important role in achieving satisfactory recovery of analytes. To obtain higher extraction recoveries, the multi-pesticide residues in seawater were enriched by MNPs-5 with ultrasonic assistance; the main experimental parameters that affect the extraction's recovery were optimized, such as the amount of MNPs-5, ultrasonication time, desorption conditions and the pH of sample. The optimum extraction conditions were established. The distribution of the recoveries for all the pesticides was utilized to evaluate the overall recovery from the sample. In all optimization experiments, the recoveries were investigated using a 500 mL blank seawater sample pre-spiked with the pesticides, each at a target concentration of $0.1 \mu\text{g L}^{-1}$.

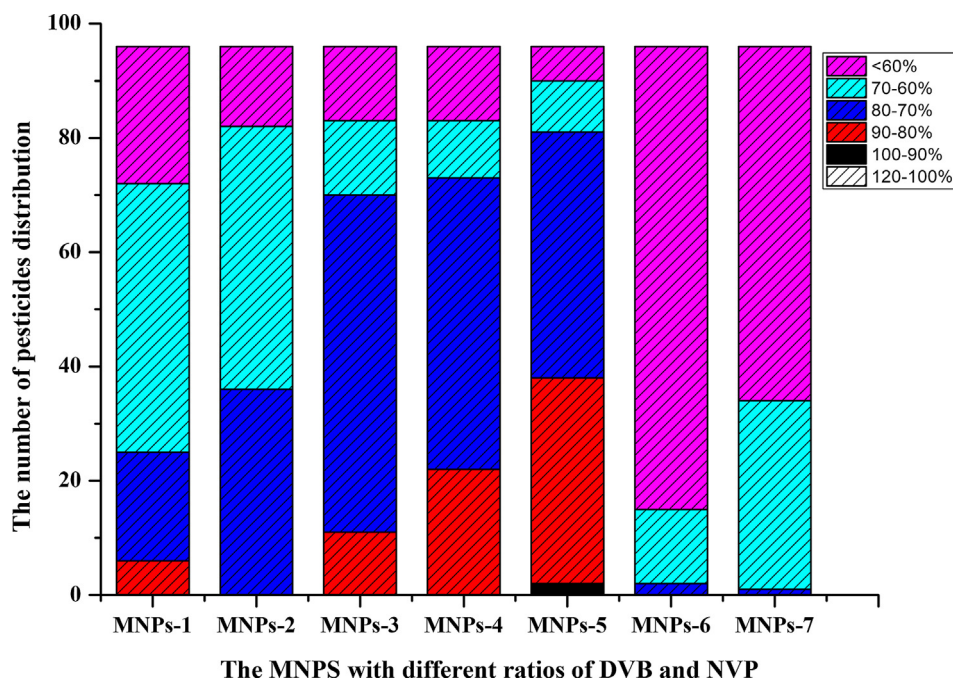


Fig. 1. Recoveries of pesticides under different ratios of DVB and NVP.

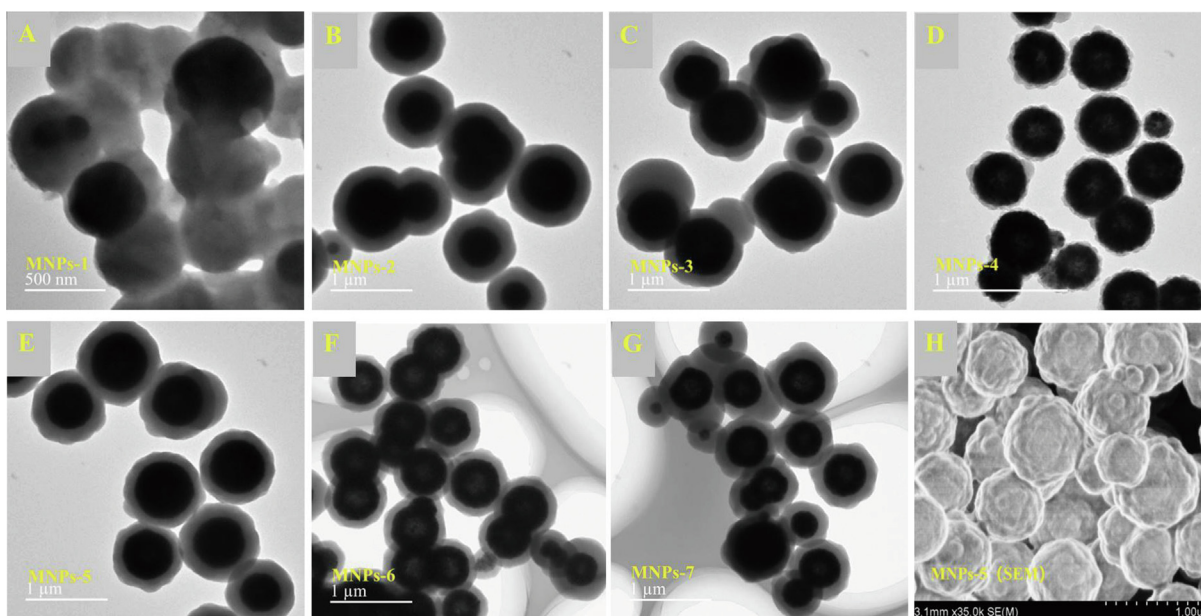


Fig. 2. TEM images of MNPs-1 (A), MNPs-2 (B), MNPs-3 (C), MNPs-4 (D), MNPs-5 (E), MNPs-6 (F) MNPs-7 (G) and FE-SEM image of MNPs-5 (H).

3.2.1. Influence of the amount of MNPs-5 on pesticides recoveries

The amount of magnetic adsorbent plays an important role in achieving satisfactory recoveries of the target analytes. A compromise needs to be made between the amount of adsorbent and extraction efficiency. Briefly, 500 mL seawater pre-spiked samples were added into a beaker containing different amounts of pre-activated MNPs-5. The mixture was then extracted ultrasonically for 10 min. 5 mL of acetonitrile was utilized for eluting the target analytes. In order to evaluate the effect of the adsorbent amount on the extraction of pesticide residues, 30, 50, 70, 90, 100, 120 and 150 mg of MNPs-5 were directly utilized to enrich the analytes. As shown in Fig. 4A, pesticide recoveries varied with the amount of MNPs-5. The dosage of adsorbents is proportional to

the adsorption rate within a certain range; the larger the dosage of magnetic adsorbents, the more active sites on the surfaces of the adsorbents (Liu et al., 2018). When the amount of adsorbent was 30 mg, the recoveries of 20% of the pesticides were in the range of 70%–120%; the recoveries of more than 78% of the pesticides were lower than 60%. As the amount of adsorbent was increased to 50 mg, the recoveries of the pesticides were maximized in the range of 70%–120% with mean value of 84.4%. When the amount of adsorbent increased to more than 50 mg, the pesticide recoveries began to decrease, implying that the volume of desorption solvent became the limiting factor. Ultimately, 50 mg is the optimum amount of MNPs-5 to ensure the good recovery of each compound, thus it was used in the further experiments.

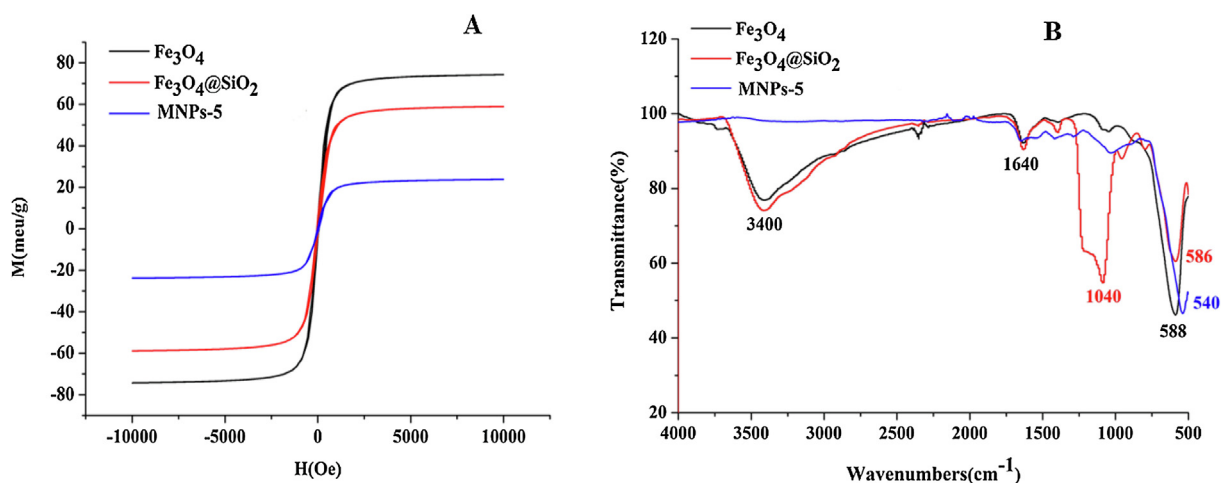


Fig. 3. FT-IR spectra (A) and VSM curves (B) of Fe₃O₄, Fe₃O₄@SiO₂, and MNPs-5.

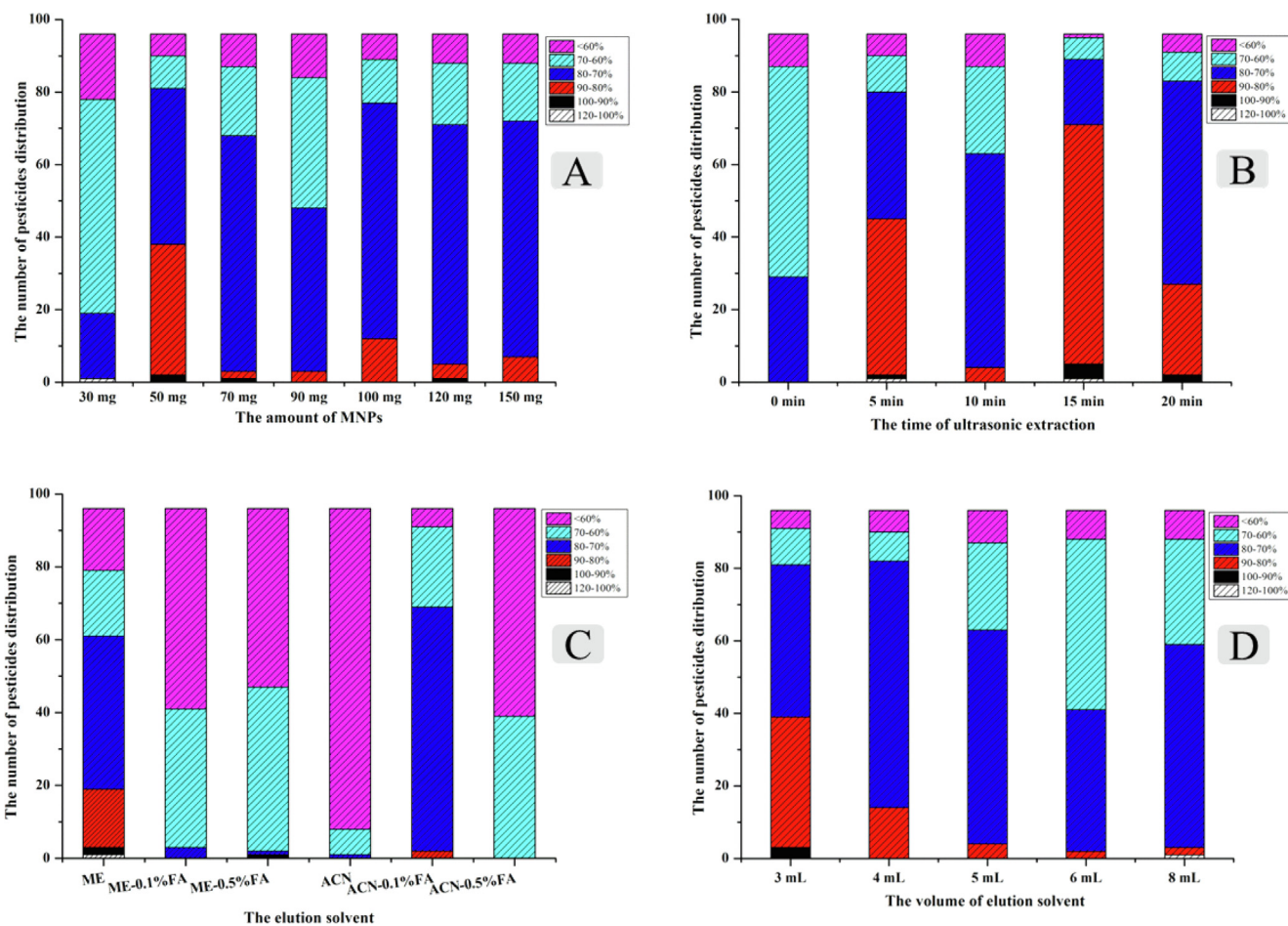


Fig. 4. Influences of adsorbent amount (A), ultrasonic extraction time (B), type of desorption solvent (ME – methanol; FA – formic acid; ACN – acetonitrile) (C) and volume of desorption solvent (D) on extraction efficiency of pesticides using MSPE.

3.2.2. Ultrasonic extraction time

The ultrasonic extraction method provides excellent contact between adsorbents and pesticides. Recent studies have shown that ultrasonic extraction is an effective technique in sample pre-treatment for pesticides analysis (Pan et al., 2008; Rezić et al., 2005). Therefore, The MNPs sorbents were dispersed in the seawater solution by ultrasonic treatment to get a homogeneous

suspension. Adsorption equilibrium was approached in a short time because of the small mass transfer distance and the high adsorption ability of the MNPs sorbents (Zhang et al., 2011). The effect of ultrasonic time on extraction efficiency was investigated in the range of 5–20 min, while the treatment without ultrasonic assistant was also performed as a comparison test using the extraction time of 20 min. The influence of different ultrasonication times

on extraction efficiency is shown in Fig. 4B. The ultrasonic time at 0 min represents the comparison test. It was proved that the ultrasonic treatment could improve the extraction efficiency. Without ultrasonic treatment, the recoveries for only 30% of the pesticides were in the range of 70%–120%, even though the extraction time was 20 min. Under the assistant of ultrasonication, the recoveries of the analytes were enhanced with an increase in extraction time. When the extraction time was 15 min, the recoveries of all analytes were in the range of 60%–100%, except for 3-hydroxy-carbofuran. Furthermore, the recoveries of 93% of the analytes ranged from 70% to 120%. Therefore, 15 min was selected as the optimum ultrasonic time for adsorption.

3.2.3. Elution solvent and volume

Selecting a suitable solvent for desorption of analytes is another important factor that should be considered. Desorption of the analytes from the magnetic adsorbents was studied by using different organic solvents. The volume of desorption solution was also optimized. In this study, six desorption solvents, including pure methanol, methanol containing 0.1% or 0.5% formic acid (v/v), pure acetonitrile, and acetonitrile containing 0.1% or 0.5% formic acid (v/v) were investigated. The influence of elution solvents on the recoveries of pesticides are shown in Fig. 4C. Acetonitrile showed better elution capability than methanol, and the addition of 0.1% formic acid further improved elution capacity. Thus, acetonitrile with 0.1% formic acid was selected as the elution solvent for the further experiments.

In addition, the volume of desorption solvent is also a key factor to obtain reliable and reproducible analytical results. The effect of different volumes of acetonitrile-0.1% formic acid (3, 4, 5, 6 and 8 mL) on the recoveries of target analytes was further investigated. As shown in Fig. 4D, it was found that there was no significant difference between 3 mL and 4 mL of acetonitrile-0.1% formic acid, which both resulted in recoveries of 84% of the target compounds ranging from 70.0% to 120%. Increasing the volume of the desorption solution did not improve the elution efficiency, but prolonged the following evaporation time. Therefore, 3 mL of acetonitrile-0.1% formic acid was selected as the elution solvent.

3.2.4. Effect of sample pH

The pH of the sample solution plays an important role in the adsorption of pesticides by affecting both the form of the pesticides and the charge of the MNP sorbent for the ionic sorbents; it is thus important to adjust the pH value of the extraction solvent to ensure analytes have a particular molecular state. The pH of the seawater sample used in this study was 7.86. The effect of pH on the extraction of target analytes was investigated over the range of 3.0–9.0, as shown in Fig. S1. The pH of the sample did not affect the extraction efficiency. Over the examined pH range of 3.0 to 9.0, there was no significant effect on the extraction efficiencies of the target pesticides; the recoveries of approximately 90% were in the range of 70%–120%. Therefore, there is no need to adjust the pH of seawater samples when using this method.

3.3. Method performance validation

The developed method was validated by evaluating its linearity, sensitivity, precision and matrix effects. For linearity, both solvent and matrix-matched calibration curves were constructed by plotting pesticide peak area versus concentration. The concentration of the analytes was set at 0.5, 2, 5, 10, 25, 50, 100 and 250 $\mu\text{g L}^{-1}$. As demonstrated in Table 2, the pesticides displayed good linearity between 0.5 and 250 $\mu\text{g L}^{-1}$ except for isocarbofos, diniconazole, ronnel, chlorbenzuron and tolclofos methyl. The correlation coefficients of the 96 pesticides ranged from 0.9830 to 0.9999. As demonstrated in Table S2, the method LOD was taken

both the response of each compound in instrument (three times signal to noise as LOD) and the enrichment factor (five hundred times) during sample pretreatment into consideration. Hence, the method LODs can achieve 0.13 to 0.42 ng L^{-1} for all the target compounds. The limit of quantification (LOQ) of the method was determined as the lowest spiked level that meets the accuracy and precision requirements in the European Commission guidance document SANTE/11813/2017. In the present work, the pesticides were enriched by 500 times during sample pretreatment; the lowest spiked concentration was 0.001 $\mu\text{g L}^{-1}$, and the recoveries of all the pesticides were in the range of 63%–117%, except for isocarbofos, diniconazole, ronnel, chlorbenzuron and tolclofos methyl. Therefore, LOQs were at 0.001 $\mu\text{g L}^{-1}$ for most of the pesticides, while the LOQs of isocarbofos, diniconazole, ronnel, chlorbenzuron and tolclofos methyl were at 0.01 $\mu\text{g L}^{-1}$. Additionally, related regulations on the maximum residue limit (MRL) of the pesticides were consulted and the MRLs of all the pesticides are not lower than 0.001 $\mu\text{g L}^{-1}$, indicating that this method can meet monitoring requirements in seawater.

Matrix effect is evaluated by calculating the ratio of the slope of the matrix-matched calibration curve to the slope of the solvent standard calibration curve (Gosetti et al., 2010). If the slope ratio value is 1, there is no matrix effect; if the ratio value is lower than 1, it represents signal suppression; if the ratio value is higher than 1, it means signal enhancement. As displayed in Table 2, the slope ratio ranged from 0.8 to 1.2 except for chiordimeform (0.7) and ethofenprox (1.6), demonstrating 98% of the studied pesticides showed no obvious matrix effect. Therefore, the standard calibration curve can be used to calculate the pesticide concentrations.

The pesticides were spiked into seawater samples at concentrations of 0.001, 0.01, 0.1 and 1.0 $\mu\text{g L}^{-1}$. The recoveries and the corresponding RSDs are displayed in Table 2. The recoveries of most of the pesticides ranged from 63% to 117% with RSDs lower than 21%. Isocarbofos, diniconazole, ronnel, chlorbenzuron and tolclofos methyl cannot be detected after pre-treatment at spiked concentration of 0.001 $\mu\text{g L}^{-1}$. However, when the spiked concentrations were set at 0.01, 0.1 and 1 $\mu\text{g L}^{-1}$, these recoveries ranged from 70% to 100%. Thus, the developed method is efficient and feasible when the concentrations of the pesticide residue are higher than the corresponding LOQs.

3.4. Method comparison with SPE method

To evaluate the performance of the proposed MSPE method, traditional SPE method was utilized as a comparison method based on HLB cartridges for multi-pesticide residue analysis in seawater (Köck-Schulmeyer et al., 2019). The presented MSPE method is superior to HLB-SPE in terms of the recoveries, adsorbent amounts, solvent consumption and operation efficiency (Table 3). Recovery studies were carried out by spiking seawater samples with each pesticide at a concentration of 0.1 $\mu\text{g L}^{-1}$. As listed in Table 3, the recoveries of pesticides by SPE method ranged from 48% to 89%, while MSPE resulted in recoveries in the range of 63%–90%. Regarding the amount of extraction adsorbent, MNPs possess high surface areas and unique magnetic properties. Hence, 50 mg of adsorbent was enough for sample pretreatment in MSPE, while 500 mg of adsorbent was necessary for the Waters Oasis HLB SPE method to deal with 500 mL sample. Concerning organic solvent use and time consuming, MSPE offers significant advantages over SPE, being more environmentally friendly, economical, and rapid. MSPE uses only 5 mL of organic solvent, compared to the 10 mL used for SPE. Additionally, the MSPE method directly adds adsorbent into the sample solution, and collection of sorbent is easily carried out by an external magnetic field, the whole process requires 106 min. On the contrary, SPE method requires at least 440 min for one sample, which spends 4.15 times longer than

Table 2
The method validation of matrix effect, LOQs and the recoveries of the analytes in spiked seawater samples with different concentration levels (0.001, 0.01, 0.1, 1.0 $\mu\text{g L}^{-1}$).

Analytes	LogP	Matrix effects	LOQ ng L^{-1}	Recoveries (RSD), %			
				0.001 $\mu\text{g L}^{-1}$	0.01 $\mu\text{g L}^{-1}$	0.1 $\mu\text{g L}^{-1}$	1.0 $\mu\text{g L}^{-1}$
<i>Organophosphorus</i>							
Dimethoate	0.75	0.9	1.0	64 (15)	63 (11)	69 (4)	69 (3)
Phosphamidon	0.79	0.9	1.0	65 (15)	80 (10)	79 (8)	80 (2)
Azamethiphos	1.05	1.0	1.0	83 (13)	75 (9)	81 (5)	79 (3)
Fosthiazate	1.68	0.9	1.0	81 (14)	75 (4)	84 (5)	81 (2)
Methidathion	2.57	0.9	1.0	77 (1)	77 (2)	81 (1)	82 (7)
Isocarbophos	2.70	1.0	10	/	100 (18)	90 (6)	78 (13)
Malathion	2.75	0.9	1.0	101 (1)	99 (4)	86 (2)	80 (2)
Ethoprophos	2.99	1.0	1.0	80 (4)	69 (13)	79 (4)	67 (12)
Pyridaphenthion	3.20	1.1	1.0	85 (10)	76 (6)	84 (1)	80 (6)
Phoxim	3.38	1.0	1.0	84 (11)	73 (14)	78 (2)	71 (4)
Tetrachlorvinphos	3.53	0.9	1.0	107 (5)	86 (8)	83 (2)	80 (1)
Triazophos	3.55	1.0	1.0	91 (2)	77 (10)	82 (1)	74 (2)
Phenthoate	3.69	1.0	1.0	75 (2)	79 (8)	83 (1)	76 (2)
Pyrazophos	3.80	1.0	1.0	84 (20)	77 (10)	81 (1)	78 (6)
Phosalone	4.01	1.0	1.0	69 (3)	68 (14)	82 (1)	78 (1)
Tolclofos methyl	4.56	0.9	10	/	90 (13)	72 (15)	84 (4)
Fenthion	4.84	1.0	1.0	75 (13)	76 (9)	78 (3)	73 (1)
Pyrimithate	4.85	1.0	1.0	83 (6)	72 (9)	75 (4)	67 (5)
Pirimiphos methyl	4.85	1.0	1.0	74 (9)	78 (10)	77 (4)	73 (1)
Ronnel	4.88	1.1	10	/	73 (11)	79 (7)	74 (1)
Temephos	4.95	1.0	1.0	78 (20)	72 (16)	71 (1)	62 (5)
Dichlofenthion	5.14	1.0	1.0	84 (3)	78 (15)	76 (2)	63 (13)
Sulprofos	5.48	1.1	1.0	92 (15)	71 (7)	69 (0)	66 (3)
Paraoxon methyl	/	0.9	1.0	83 (8)	78 (21)	80 (4)	72 (6)
<i>Carbamates</i>							
Bendiocarb	1.70	1.0	1.0	78 (5)	63 (11)	80 (1)	70 (1)
Pirimicarb	1.70	0.9	1.0	66 (19)	73 (9)	78 (9)	82 (1)
Carbofuran	1.80	1.0	1.0	83 (6)	74 (5)	81 (1)	80 (1)
3-hydroxy-carbofuran	/	1.0	1.0	63 (17)	62 (9)	67 (5)	65 (7)
Carbaryl	2.36	1.0	1.0	82 (7)	75 (3)	84 (3)	80 (7)
Benthiavdicarb-isopropyl	2.56	0.9	1.0	71 (5)	74 (17)	87 (2)	77 (0)
<i>Triazoles</i>							
Tricyclazole	1.40	1.0	1.0	68 (16)	69 (5)	66 (8)	70 (1)
Flutriafol	2.30	0.9	1.0	100 (9)	76 (9)	83 (5)	78 (3)
Azaconazole	2.36	1.0	1.0	82 (3)	73 (12)	82 (2)	79 (4)
Myclobutanil	2.89	1.0	1.0	71 (13)	71 (7)	82 (2)	76 (2)
Cyproconazole	3.09	1.0	1.0	77 (8)	75 (8)	83 (1)	77 (6)
Etaconazole	3.10	1.0	1.0	72 (15)	75 (9)	82 (3)	77 (4)
Pacllobutrazol	3.11	1.1	1.0	76 (2)	76 (5)	83 (2)	80 (5)
Triazolone	3.18	0.9	1.0	63 (17)	73 (6)	84 (3)	83 (3)
Triadimenol	3.18	0.9	1.0	78 (9)	73 (1)	83 (4)	82 (6)
Simeconazole	3.20	1.0	1.0	83 (9)	75 (10)	83 (3)	78 (1)
Bromuconazole	3.24	1.2	1.0	103 (4)	73 (9)	92 (3)	83 (9)
Tetraconazole	3.56	0.9	1.0	73 (5)	75 (11)	83 (3)	78 (3)
Tebuconazole	3.70	1.0	1.0	108 (6)	76 (10)	85 (3)	77 (4)
Penconazole	3.72	1.0	1.0	91 (12)	86 (8)	82 (1)	78 (7)
Propiconazole	3.72	1.0	1.0	91 (4)	74 (9)	80 (0)	79 (5)
Flusilazole	3.87	1.0	1.0	89 (1)	74 (8)	84 (3)	77 (4)
Bitertanol	4.10	0.9	1.0	78 (8)	76 (8)	84 (1)	78 (3)
Diniconazole	4.30	0.9	10	/	77 (10)	67 (10)	72 (4)
Ipconazole	4.30	1.1	1.0	72 (13)	79 (18)	75 (5)	73 (13)
<i>Neonicotinoids</i>							
Imidacloprid	0.57	1.0	1.0	65 (18)	70 (6)	64 (5)	71 (13)
Acetamiprid	0.80	1.0	1.0	73 (16)	78 (11)	73 (7)	74 (7)
<i>Organochlorine</i>							
Isazofos	3.10	1.0	1.0	96 (3)	74 (7)	83 (2)	80 (3)
Prometryne	3.34	1.0	1.0	80 (5)	75 (6)	80 (3)	77 (4)
Dicofol	4.30	0.9	1.0	87 (7)	76 (13)	75 (3)	79 (10)
Piperonyl butoxide	4.89	1.0	1.0	88 (4)	72 (11)	86 (2)	90 (3)
Spirodiclofen	5.83	0.9	1.0	105 (7)	76 (19)	71 (3)	70 (9)
Pyridaben	6.37	1.0	1.0	91 (17)	75 (11)	72 (1)	63 (4)
Phorate sulfone	/	1.0	1.0	79 (21)	75 (7)	86 (2)	81 (6)
Fenamiphos sulfoxide	/	1.0	1.0	74 (17)	76 (13)	80 (8)	75 (11)
<i>Other pesticides</i>							
Oxadixyl	0.65	1.0	1.0	90 (10)	78 (3)	80 (5)	86 (4)
Forchlorfenuron	3.30	0.9	1.0	94 (1)	74 (5)	81 (1)	76 (1)
Hexazinone	1.17	1.0	1.0	81 (15)	73 (9)	79 (5)	81 (2)
Chloridimeform	2.89	0.7	1.0	64 (4)	73 (6)	82 (10)	76 (2)
Chlortoluron	/	1.2	1.0	84 (2)	74 (5)	87 (1)	87 (4)
Mefenoxam	1.71	0.9	1.0	76 (16)	76 (7)	83 (3)	78 (4)
Metalaxyl	1.75	1.0	1.0	81 (8)	76 (6)	83 (2)	79 (4)
Carbendazim	1.48	1.0	1.0	101 (14)	88 (13)	62 (7)	65 (2)

Table 2 (continued)

Analytes	LogP	Matrix effects	LOQ ng L ⁻¹	Recoveries (RSD), %			
				0.001 µg L ⁻¹	0.01 µg L ⁻¹	0.1 µg L ⁻¹	1.0 µg L ⁻¹
Diphenamid	2.17	1.1	1.0	94 (2)	80 (4)	86 (1)	78 (4)
Azoxystrobin	2.50	0.9	1.0	85 (6)	72 (7)	84 (2)	76 (4)
Clomazone	2.54	0.9	1.0	82 (13)	75 (15)	81 (2)	72 (6)
Dimethomorph	2.68	0.9	1.0	72 (20)	74 (8)	85 (6)	83 (5)
Fluoxastrobin	2.86	1.0	1.0	70 (7)	70 (6)	79 (3)	78 (7)
Chlorantranilprole	2.86	0.8	1.0	85 (10)	76 (8)	82 (4)	79 (1)
Spiroxamine	2.89	1.0	1.0	64 (2)	66 (13)	73 (8)	66 (1)
Alachlor	3.09	1.0	1.0	70 (15)	72 (10)	81 (1)	78 (3)
Flutolanil	3.17	1.0	1.0	89 (4)	74 (6)	86 (1)	79 (4)
Isoprothiolane	3.30	1.0	1.0	78 (3)	77 (6)	83 (1)	76 (3)
Kresoxim-methyl	3.40	1.0	1.0	99 (18)	67 (10)	87 (1)	76 (3)
Prochloraz	3.50	1.1	1.0	111 (4)	87 (7)	81 (3)	75 (5)
Benodanil	3.54	1.0	1.0	81 (7)	80 (7)	80 (1)	84 (5)
Terbutryn	3.66	1.0	1.0	86 (4)	76 (6)	83 (2)	79 (3)
Mepromil	3.66	1.0	1.0	83 (3)	75 (7)	83 (2)	82 (6)
Fenarimol	3.69	1.0	1.0	68 (8)	73 (13)	82 (4)	78 (5)
Methoxyfenozide	3.72	1.0	1.0	86 (18)	78 (15)	82 (2)	81 (5)
Fipronil	3.75	0.9	1.0	83 (17)	88 (18)	86 (5)	76 (2)
Fipronil-sulfone	/	0.9	1.0	90 (4)	79 (6)	77 (3)	73 (1)
Fipronil-sulfide	/	0.9	1.0	81 (4)	78 (6)	84 (2)	79 (1)
Pyraclostrobin	3.99	1.0	1.0	117 (7)	79 (12)	78 (3)	71 (9)
Tebufofenozide	4.25	1.0	1.0	86 (11)	78 (11)	79 (1)	78 (4)
Tebufofenpyrad	4.93	1.0	1.0	86 (7)	74 (11)	76 (4)	74 (2)
Fenpyroximate	5.01	0.9	1.0	78 (4)	79 (17)	71 (1)	65 (2)
Tolfenpyrad	5.61	1.0	1.0	90 (3)	70 (17)	75 (3)	66 (3)
Hexaflumuron	5.68	1.0	1.0	86 (12)	74 (7)	79 (2)	78 (6)
Chlorbenzuron	/	1.1	10	/	81 (20)	80 (13)	70 (14)
Spinosad	/	0.9	1.0	73 (5)	71 (7)	72 (8)	71 (5)
Ethofenprox	6.9	1.6	1.0	98 (12)	65 (12)	64 (3)	63 (0)

Table 3

Comparison of the consumption of solvent and time, and recoveries obtained in the current method and reported methods for the determination of pesticides of one seawater sample.

Comparison program	SPE	MSPE (MNPs-5)
The adsorbent amount (mg)	500	50
Recoveries (%)	48–89	63–90
<i>The consumption of organic solvent (mL)</i>		
Activated solvent	5	1
Eluent solvent	4	3
Redissolved solvent	1	1
Sum	10	5
<i>The consumption of time (min)</i>		
Activated time	10	0.25
Extraction time	120	15
Elution time	10	0.5
The time of blow-dry with nitrogen	300	90
Sum	440	106

the MSPE methodology. It fully exhibited its advantage in improving operational efficiency and providing a new approach for a high-throughput sample pretreatment technique. Furthermore, the outdoor sampling process is necessary and always the first step to perform. The present work can help us rapidly preconcentrate the target analytes from the seawater samples without carrying all the water samples back to the laboratory. This is a significant improvement for researchers to perform lots of outdoor investigation experiments.

3.5. Analysis of seawater samples from the Jiulong River Estuary

Estuarine environments are particularly rich and diverse ecosystems at the junction of rivers and oceans. They are also the systems where pollutants entered into the marine environment.

These unique ecosystems are very sensitive to the impacts of organic pollutants. The analytical method developed here was used to monitor the presence of the target pesticides in water samples from the Jiulong River Estuary, located in southeast Fujian, China (24°25'22"N 117°51'34"E). Surface (B1–B25) and bottom water (D1–D25) samples were simultaneously collected, the latter from approximately 5 m depth. The samples were collected during 29–30 November 2018 with sampling times as follows: B1/D1 (12:00), B3/D3 (14:00), B7/D7 (18:00), B11/D11 (22:00), B13/D13 (0:00), B15/D15 (2:00), B17/D17 (4:00), B21/D21 (8:00), B23/D23 (10:00), B25/D25 (12:00). All samples were stored in dark containers at 4 °C until analysis. The concentrations of pesticides in the Jiulong River Estuary are demonstrated in Tables S3 and S4. A variety of pesticides were detected in this area although the residue concentrations are very low. The concentrations of pesticides ranged from ND to 60.4 ng L⁻¹. Among these pesticides, acetamiprid, carbendazim and imidacloprid were detected at a relatively higher level with the highest concentration of acetamiprid at 60.4 ng L⁻¹. The further analysis was performed to distinguish the difference of pesticides residue among different sampling time. Due to the diversity of contaminated pesticides and low concentration level, all the concentrations of pesticides were normalized with the highest detection concentration, 60.4 ng L⁻¹, as a benchmark. The normalized data of pesticides residue in different sampling times is shown in Fig. 5. It can be clearly seen that the concentrations of pesticides at three sampling points B3/D3 (14:00), B17/D17 (4:00), and B23/D23 (10:00), were relatively higher than the rest. The Jiulong river estuary is characterized by intense agricultural and industrial activities. During these three periods, relatively frequent human activity may lead higher levels of pesticide residues, which was involved agricultural activities or untreated sewage discharged from urban areas. The concentrations of pesticides in the bottom water were higher than those at the surface, which may be due to the pesticides being released from the sediment.

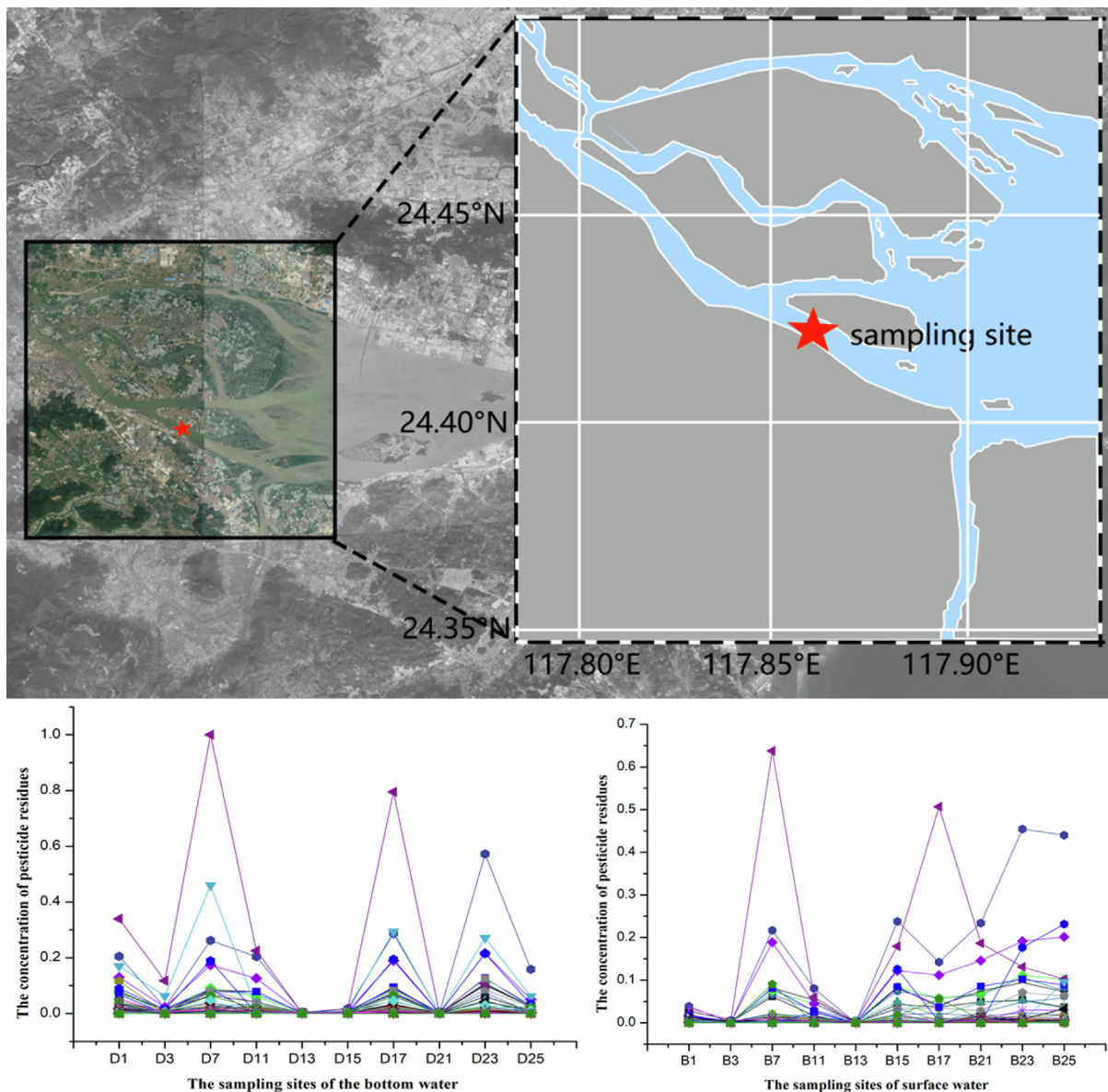


Fig. 5. The distribution of pesticides in different sampling times in the Jiulong River Estuary.

Pesticides at most stations were enriched from the surface water towards the sediments, as pesticides in the sediment are likely transported to the bottom water through re-suspension, resulting in a higher concentration of pesticides in bottom waters (Ogbeide et al., 2018).

4. Conclusions

An amphiphilic magnetic adsorption material was successfully synthesized by swelling polymerization and used as an adsorbent for the simultaneous extraction of 96 pesticides from seawater samples. The hydrophilic-lipophilic balance of the polymer was mainly achieved by adjusting the amount of hydrophilic NVP and hydrophobic DVB monomers. The effect of the dosages of the DVB and NVP monomers on the extraction performance of the prepared magnetic polymer nanoparticles was also investigated. The optimized magnetic polymer nanoparticles possess several merits including magnetic separation, large surface area, low cost,

environmental friendliness, and good extraction performance for both polar and non-polar compounds. Additionally, factors affecting recoveries during multi-pesticide residue analysis were studied. The optimized methods resulted in satisfactory pesticide recoveries from seawater under a range of concentrations. Compared with HLB cartridges, the proposed magnetic material exhibited improved capacity and extraction efficiencies. The MSPE method can minimize the time required for sample pretreatment and uses only a small amount of solvent, making it more environmentally friendly than conventional SPE methods. The new analytical method proposed here has been successfully applied to the analysis of water samples from the Jiulong River Estuary, where the concentration of pesticides was determined to range from ND (or <LOD) to 60.4 ng L^{-1} . The satisfactory recoveries and the low LOQs can fulfill the monitoring requirements for multi-pesticide residue analysis in seawater, and the additional benefits of the MSPE method result in a substantial improvement over previously established SPE methods.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.135221>.

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