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Novel Zeolitic Imidazolate Frameworks Based on Magnetic Multiwalled Carbon Nanotubes for Magnetic Solid-Phase Extraction of Organochlorine Pesticides from Agricultural Irrigation Water Samples

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Abstract: Magnetic solid-phase extraction is an effective and convenient sample pretreatment technique that has received considerable interest in recent years. A lot of research indicated that magnetic nanocarbon-material-based composites have good application prospects as adsorbents for magnetic solid-phase extraction of pesticides. Herein, a novel zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes (M-M-ZIF-67) has been prepared as an adsorbent for magnetic solid-phase extraction of nine organochlorine pesticides from agricultural irrigation water samples. The obtained M-M-ZIF-67 material possessed porous surfaces and super-paramagnetism due to the utilization of magnetic multiwalled carbon nanotubes as the magnetic kernel and support. To evaluate the extraction performance of the M-M-ZIF-67, the main parameters that affected the extraction efficiency were researched. Under the optimal conditions, a good linearity for the nine organochlorine pesticides was achieved with the determination coefficients (R^2) higher than 0.9916. The limits of detection (signal/noise = 3:1) were in the range 0.07–1.03 $\mu\text{g L}^{-1}$. The recoveries of all analytes for the method at spiked levels of 10 and 100 $\mu\text{g L}^{-1}$ were 74.9–116.3% and 75.1–112.7%, respectively. The developed M-M-ZIF-67 based magnetic solid-phase extraction method has a potential application prospect for the monitoring of trace level of organochlorine pesticides in environmental water samples.

Keywords: zeolitic imidazolate framework; multi-walled carbon nanotubes; magnetic solid phase extraction; organochlorine pesticides; agricultural irrigation water

1. Introduction

Sample pretreatment is a crucial step in analysis of trace or ultra-trace amounts analytes in complex matrices. Solid-phase extraction (SPE) is a type of widely used pretreatment for effective concentration of analytes in complex matrices before instrumental analysis [1]. A variety of pretreatment methods has been developed based on this technique, including solid-phase microextraction (SPME) [2], micro-SPE (μ -SPE) [3], and stir-bar sorptive extraction (SBSE) [4].

Magnetic solid-phase extraction (MSPE), as a new type of SPE, is a pretreatment method that has received considerable interest in recent years. In this technique, magnetic adsorbents are directly

dispersed into sample solutions, and this dispersive extraction mode can enhance the contact area between adsorbents and analytes [5]. Notably, magnetic adsorbents can be separated from the sample solutions under an external magnetic field without the need of traditional centrifugation or filtration, thereby simplifying the extraction process. Furthermore, magnetic adsorbents can be recycled and reused easily, which is cost effective and environmentally friendly [6]. Therefore, the MSPE technique shows comprehensive advantages of simplicity, time, reagent and labor savings, and excellent extraction efficiency, which meet the principles of green analytical chemistry [7]. The diversity of the materials used in MSPE is the main factor that has led to extensive development of this technique in recent decades [8]. Multiple magnetic sorbents have been synthesized by embedding magnetic cores in different organic or inorganic materials, such as chitosan [9], ionic liquids [10], polymers [11], silica [12], metallic oxides [13], molecularly imprinted polymers [14], and carbon nanomaterials [15,16].

Multiwalled carbon nanotubes (MWCNTs) are formed by seamless rolling up of several layers of graphite sheets. Because of their excellent properties, such as high surface area and inner volume, stability, mechanical strength, ability to establish π - π interactions, and capacity for functionalization, MWCNTs have the possibility of acting as good sorbents [17]. MWCNTs have recently attracted considerable interest as adsorbents in MSPE for extracting different analytes, such as antibiotics [18], estrogens [19], mycotoxins [20], metal ions [21], environmental pollutants [22], and pesticides [23,24]. The use of magnetic MWCNTs combined with other materials has attracted great interest.

Metal-organic frameworks (MOFs) are microporous inorganic-organic crystalline structure materials. They are formed by self-assembly of metal ions (clusters or secondary building units) and organic ligands (linkers) by coordination bonds, and they have a highly ordered and three-dimensional structure [25]. MOFs are promising sorbent materials, and using them for extraction could have the advantages of enhanced selectivity and stability, permeable channels and coordination nanospace, framework flexibility and dynamics, easy tunability, and modification [26]. However, application of MOFs is limited in certain cases owing to the lack of water and thermal stability, for example, MOF-199 and MOF-5 lose their extraction efficiency when they are exposed to moisture for a long time [27].

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs that are composed of tetrahedral transition metal ions (e.g., Zn and Co) and imidazolate-type organic linkers, and they exhibit high water stability in aqueous media [28]. Owing to their features of microporosity, uniform structured cavities, and a high surface area, ZIFs have many applications, such as chemical pollutant removal [29,30], chromatographic separation [31,32], and drug delivery [33]. ZIF-67 is a recently developed ZIF compound that has the formula $\text{Co}(\text{Hmim})_2$ (mim = 2-methylimidazole) with a sodalite-related zeolite type structure [34]. Because of the low coordination of the Co cation, ZIF-67 has three times higher adsorption capacity for dye from aqueous solutions than ZIF-8 [35]. Owing to the hydrogen bonding and π - π electron donor-acceptor interactions between the adsorbent and analytes, Fe_3O_4 -MWCNTs-OH@poly-ZIF67 shows good selective extraction of aromatic acids [36]. This research indicates that magnetic nanocarbon-material-based ZIFs have good application prospects for adsorbing pesticides because of their good adsorptive properties derived from the magnetic carbon nanocomposite.

Organochlorine pesticides (OCPs) are ubiquitous in the environment due to their extensive application and persistent organic pollutants characteristics, which pose great risks to human health and ecosystems [37]. On account of their bioaccumulation, degradation resistance and carcinogenesis, tetratogenesis, and mutagenesis to human, 15 OCPs, including hexachlorocyclohexane (HCHs) and dichlorodiphenyltrichloroethane (DDTs), were banned with the issue of the Stockholm Convention in 2004. However, the current study showed that the concentration level of OCPs in aqueous environment around Beijing were ranged from 9.81 to 32.1 ng L^{-1} (average $15.1 \pm 7.78 \text{ ng L}^{-1}$) [38]. Therefore, it is necessary to develop sensitive and accuracy analytical methods for continuous monitoring trace level of the OCPs in water samples.

Inspired by the abovementioned studies, a novel magnetic Co-based ZIF composite was synthesized by organic-inorganic coordination. The obtained M-M-ZIF-67 composite possessed porous surfaces and super-paramagnetism due to the utilization of Fe_3O_4 -MWCNTs as the magnetic

kernel and support. In addition, due to the large surface area and excellent adsorption capacity of MWCNTs, the prepared hybrid material could be good adsorbent for MSPE of OCPs. In the end, an M-M-ZIF-67 based MSPE method was established and applied for the extraction of OCPs from agricultural irrigation water samples prior to gas chromatography–tandem triple quadrupole mass spectrometry (GC–MS/MS).

2. Materials and Methods

2.1. Reagents and Materials

The standard liquid pesticides α -HCH (CAS number: 319-84-6), β -HCH (CAS number: 319-85-7), γ -HCH (CAS number: 58-89-9), δ -HCH (CAS number: 319-86-8), p,p'-DDD (CAS number: 72-54-8), o,p-DDE (CAS number: 3424-82-6), p,p'-DDE (CAS number: 72-55-9), o,p-DDT (CAS number: 789-02-6), and p,p'-DDT (CAS number: 50-29-3) were obtained from the Agro-Environmental Protection Institute, Ministry of Agriculture (Tianjin, China) at concentrations of 1000 mg L⁻¹. A standard mixture containing 20 mg L⁻¹ of each of the nine OCPs was prepared in methanol and stored at -20 °C in the dark. High-performance liquid chromatography grade acetonitrile, methanol, and n-hexane were purchased from Sigma-Aldrich (St. Louis, MO, USA). Anhydrous sodium sulfate was supplied by Agilent (CA, California, USA). The MWCNTs (8–15 nm inner diameter (id), 10–30 μ m long, 95% purity), analytical grade ferric chloride hexahydrate (FeCl₃•6H₂O), ferrous chloride tetrahydrate (FeCl₂•4H₂O), 2-methylimidazole, cobalt nitrate hexahydrate (Co(NO₃)₂•6H₂O), and ammonium hydroxide (mass fraction 28%) were provided by Aladdin Co. (Shanghai, China). Ethanol and all of the other reagents were of analytical grade and acquired from the Beijing Chemical Reagents Co. (Beijing, China).

2.2. Preparation of Fe₃O₄-MWCNTs-ZIF-67

2.2.1. Synthesis of Fe₃O₄-MWCNTs

The Fe₃O₄-MWCNTs were prepared according to the authors' previously reported method with slight modification [39]. In brief, MWCNT powder (0.2 g) was suspended in ultrapure water (240 mL) by sonication for 1 h and then transferred to a three-necked flask. After a solution of FeCl₃•6H₂O (1.8 g) and FeCl₂•4H₂O (0.8 g) dissolved in ultrapure water (25 mL) was added to the flask, the mixture was vigorously stirred with a mechanical stirrer (THZ-82A, Youlian instrument research institute, Jintan, China) under protection of N₂ at 150 rpm and 80 °C conditions for 30 min. Ammonium hydroxide (28%, 10 mL) was then added and the mixture was vigorously stirred for another 30 min. After cooling to room temperature, the sediments were collected by magnetic separation and washed three times with ethanol and ultrapure water to eliminate unreacted chemicals. The obtained Fe₃O₄-MWCNT nanoparticles were dried in a vacuum oven at 60 °C for 24 h.

2.2.2. Synthesis of ZIF-67 and M-M-ZIF-67

The ZIF-67 material was fabricated following a reported method [40]. The preparation procedure for M-M-ZIF-67 was as follows. First, the Fe₃O₄-MWCNTs were dispersed in ultrapure water (20 mL) and mixed with 3 mL of an aqueous solution of Co(NO₃)₂•6H₂O (0.45 g) with consistent stirring for 30 min under 150 rpm condition. An aqueous solution of 2-methylimidazole (20 mL, 0.45 g) was then added to the solution and the solution was stirred for 6 h. All of these synthetic processes were performed at room temperature. Finally, the M-M-ZIF-67 product was obtained by magnetic separation and washed three times with ethanol and ultrapure water. The synthesized material was dried in a vacuum oven at 60 °C for 24 h.

2.3. MSPE Procedure

The workflow of MSPE using M-M-ZIF-67 is shown in Figure 1. First, M-M-ZIF-67 (6 mg) was placed in a 10 mL centrifuge tube containing 5.0 mL of the aqueous standard solution or sample solution and shaken for 20 min for extraction. With aggregation of the adsorbent in the tube, the supernatant was discarded with the aid of an external ferrite magnet. Acetonitrile (2 mL) was then added into the tube, and ultrasonic elution of the analytes from the magnetic materials was performed for 5 min. After the M-M-ZIF-67 composite was collected, the supernatant desorption solution was transferred to another centrifuge tube. The same desorption procedures were performed one more time. Finally, the combined desorbed elution was evaporated to dryness under a gentle stream of nitrogen at 40 °C. The residue was redissolved in 0.5 mL acetone, and 1 μ L of it was injected into the GC-MS/MS for analysis.

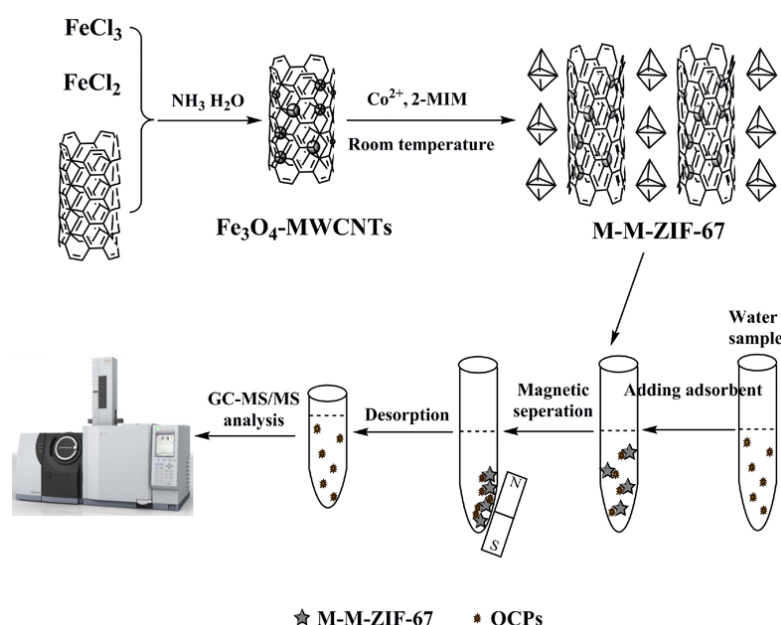


Figure 1. Schematic illustration of the synthetic route to prepare zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes and the magnetic solid-phase extraction steps for organochlorine pesticides analysis.

2.4. Sample Preparation

The river water sample was collected from the Liangshui River, Beijing, China. The tap water sample was obtained from the tap in the laboratory; and the underground water sample was obtained from Langfang City, Hebei Province, China. All of the samples were filtered through a 0.45 μm polytetrafluoroethylene membrane filter and stored at 4 °C in amber dark glass bottles.

2.5. Apparatus and Gas Chromatography–Tandem Triple Quadrupole Mass Spectrometry Conditions

The surface morphologies and particle sizes of the as-synthesized nanoparticles were observed by scanning electron microscopy (SEM, JSM-6300, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-200CX, JEOL, Tokyo, Japan). The powder X-ray diffraction (XRD) patterns of the as-synthesized nanoparticles were obtained with an X-ray powder diffractometer (D8 Advance, Bruker, Karlsruhe, Germany). The Fourier-transform infrared (FT-IR) spectra of the as-synthesized nanoparticles were obtained with an FT-IR-8400 spectrometer (Shimadzu, Kyoto, Japan). A vibrating sample magnetometer (VSM, Lake Shore 7410, Columbus, OH, USA) was used to investigate the magnetic properties of all of the synthetic materials.

Gas chromatography–tandem triple quadrupole mass spectrometry (GC–MS/MS) analysis was performed with a Shimadzu GC-2010 plus gas chromatograph coupled with an AOC-20s autosampler, a Shimadzu TQ8040 triple-quadrupole MS. The pesticides were separated on an Rtx-5MS capillary column purchased from RESTEK (Bellefonte, PA, USA) (0.25 mm (id) × 30 m, 0.25 μm film thickness). Helium gas was used as the carrier gas at a constant flow rate of 1 mL min^{−1}. The column temperature was programmed as follows: the initial temperature of 40 °C was maintained for 4 min, the temperature was increased to 125 °C at 25 °C min^{−1}, the temperature was ramped to 300 °C at 10 °C min^{−1}, and the temperature was maintained at 300 °C for 6 min. The total run time was 30.9 min. The injector temperature was 250 °C, and the injection volume was 1.0 μL in splitless mode. The specific multiple reaction monitoring (MRM) transitions for all the nine OCPs and the other parameters are given in Table 1.

Table 1. Acquisition and chromatographic parameters of the nine organochlorine pesticides.

Pesticides	Retention Time (min)	MRM1 ^a (<i>m/z</i>)	CE1 ^b (eV)	MRM2 (<i>m/z</i>)	CE2 (eV)
α-HCH ^c	15.32	218.90 > 182.90	8	218.90 > 144.90	20
β-HCH	15.87	218.90 > 182.90	8	218.90 > 144.90	20
γ-HCH	16.01	218.90 > 182.90	8	218.90 > 144.90	20
δ-HCH	16.59	218.90 > 182.90	10	218.90 > 144.90	20
o,p'-DDE ^d	19.47	246.00 > 176.00	30	246.00 > 211.00	22
p,p'-DDE	20.09	246.00 > 176.00	30	246.00 > 211.00	22
p,p'-DDD ^e	20.90	235.00 > 165.00	24	235.00 > 199.00	14
o,p'-DDT ^f	20.95	235.00 > 165.00	24	235.00 > 199.00	16
p,p'-DDT	21.61	235.00 > 165.00	24	235.00 > 199.00	16

^a MRM means multiple reaction monitoring transitions; ^b CE means collision energy; ^c HCH means hexachlorocyclohexane; ^d DDE means 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene; ^e DDD means [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene]; ^f DDT means 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethylene.

2.6. Quality Control and Quality Assurance

Quality control and quality assurance (QA/QC) experiments, including a blank sample test, recovery test, repeatability test, and limits of detection (LOD) experiment were performed to evaluate the feasibility of the method. In addition, 5 L ultrapure water served as the water sample for the blank test, while the water samples for the recovery test and repeatability test were made by spiking 50 μL 20 mg L^{−1} working solution into 100 mL ultrapure water. The LOD experiment was undertaken following the USA Environmental Protection Agency method.

3. Results

3.1. Characterization of M-M-ZIF-67

The micro-morphologies of the Fe₃O₄–MWCNTs and M-M-ZIF-67 were observed by SEM and TEM. As shown in Figure 2A, the Fe₃O₄ nanoparticles are attached to the MWCNT surface. The SEM image of M-M-ZIF-67 in Figure 2B shows that the composite has a rough surface, indicating that the material has good potential as an adsorbent [27].

VSM was performed to investigate the magnetic behavior of the magnetic materials, and the results are shown in Figure 3A. The magnetic hysteresis loops show that both the remanence and coercivity values of the three types of magnetic materials are zero, which indicates that they have typical supermagnetic properties and could be separated using an external magnet. The saturation magnetization values of Fe₃O₄, Fe₃O₄–MWCNTs, and M-M-ZIF-67 are 66.8, 59.6, and 53.1 emu g^{−1}, respectively. As shown in the insert of Figure 3A, well-dispersed M-M-ZIF-67 particles exist in the absence of an external magnet, and they are rapidly attracted to the walls of the vial in a short time (about 20 s) with application of a magnet. The powder XRD patterns of Fe₃O₄, Fe₃O₄–MWCNTs, and M-M-ZIF-67 are shown in Figure 3B. The diffraction patterns of M-M-ZIF-67 are in very close

agreement with the materials of Fe_3O_4 and Fe_3O_4 -MWCNTs. This indicates that Fe_3O_4 is well retained in the Fe_3O_4 -MWCNTs and M-M-ZIF-67. The FT-IR spectra are shown in Figure 3C. For M-M-ZIF-67, the adsorption band at 577 cm^{-1} corresponds to the stretching vibrations of Fe-O, and the band at 1566 cm^{-1} corresponds to in-plane bending of CH_2 of the MWCNTs. This suggests that M-M-ZIF-67 is composed of Fe_3O_4 and MWCNTs. The bands in the region 673 to 1454 cm^{-1} are attributed to complete ring stretching or bending vibration of 2-methylimidazole, and the main adsorption bands are preserved in the spectrum of the composite, which indicates that ZIF-67 is successfully synthesized on the surface of M-M-ZIF-67.

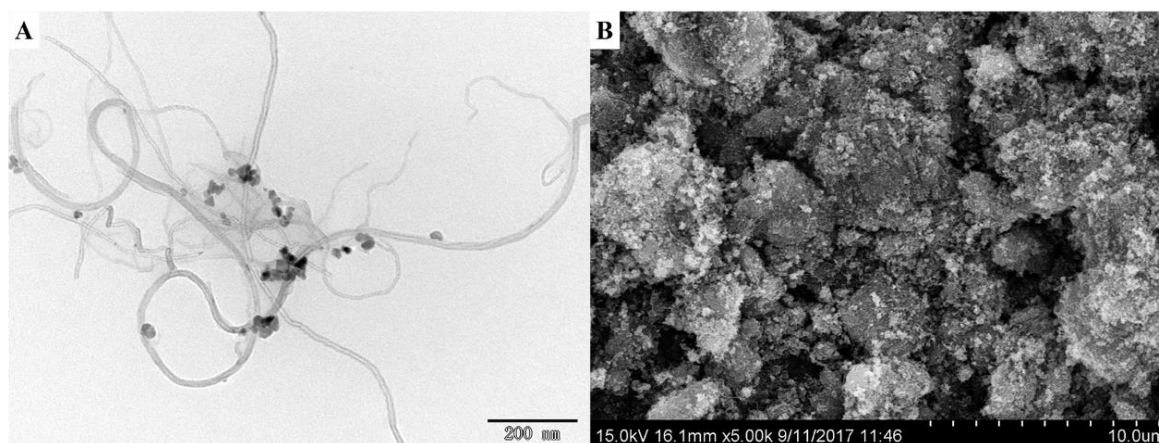


Figure 2. (A) transmission electron microscopy image of magnetic multiwalled carbon nanotubes and (B) scanning electron microscopy image of zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes.

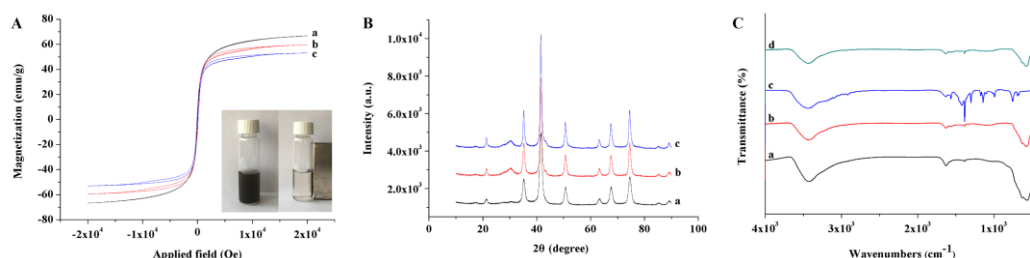


Figure 3. (A) magnetic hysteresis loops for (a) Fe_3O_4 ; (b) magnetic multiwalled carbon nanotubes; and (c) zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes. The insert shows magnetic separation and dispersion of zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes; (B) X-ray diffraction patterns of (a) Fe_3O_4 ; (b) magnetic multiwalled carbon nanotubes; and (c) zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes; (C) Fourier-transform infrared spectra of (a) Fe_3O_4 ; (b) magnetic multiwalled carbon nanotubes; (c) zeolitic imidazolate framework-67; and (d) zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes.

3.2. Optimization of the MSPE Parameters

The MSPE parameters affect extraction of the OCPs and the desorption performance. The amount of M-M-ZIF-67, extraction time, type of desorption solvent, desorption time, and frequency of desorption were investigated by single-factor experiments following a step by step procedure at a spiked level of $50\text{ }\mu\text{g L}^{-1}$.

3.2.1. Optimization of the Extraction Process

The present study aims to achieve satisfactory extraction performance for analytes in water samples. The effect of the amount of M-M-ZIF-67 on extraction was investigated using different amounts of the sorbent ranging from 2 to 10 mg. The experimental results (Figure 4A) show that the extraction recoveries of the OCPs rapidly increase when the amount of M-M-ZIF-67 is increased from 2 to 6 mg, and the recoveries then slightly decrease when the amount of sorbent is increased from 6 to 10 mg. Based on these results, 6 mg of M-M-ZIF-67 was chosen for the following experiments.

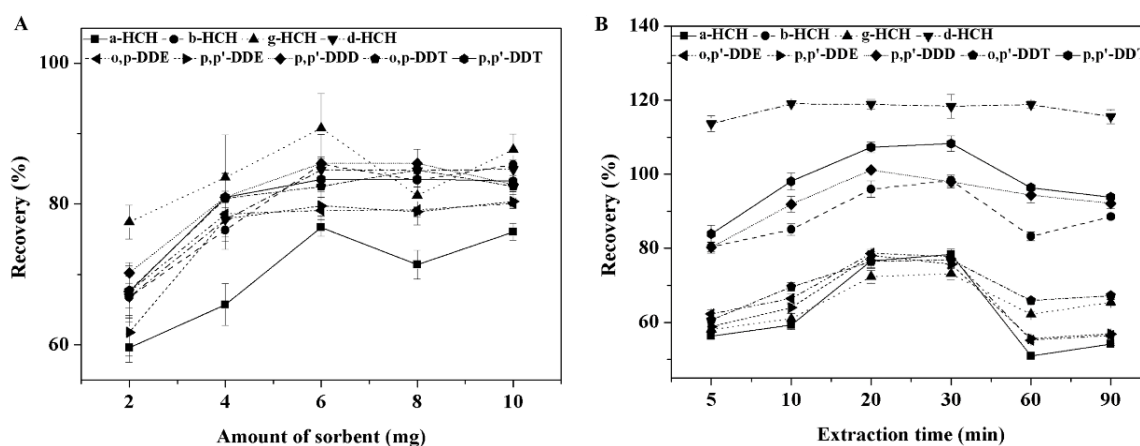


Figure 4. Optimization of the extraction process for $50 \mu\text{g L}^{-1}$ organochlorine pesticides using zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes: (A) amount of sorbent and (B) extraction time. Desorption conditions: 2 mL of acetonitrile; ultrasonication time, 5 min; and ultrasonication performed one more time. The error bars show the standard deviation of the mean ($n = 3$).

The extraction time is an important factor for MSPE because it influences the adsorption equilibrium of the analytes between the sample solution and adsorbent. Therefore, the extraction time was varied in the range 5–90 min to investigate its influence on the extraction efficiency. As shown in Figure 4B, the recoveries of the target OCPs increase with increasing extraction time from 5 to 20 min, and they then remain almost constant until 30 min. The extraction recoveries for most of the analytes then decrease with a further increase of the extraction time. This is probably because of desorption of the analytes from the adsorbent, especially when the adsorption equilibrium is reached. Thus, 20 min was chosen as the extraction time for the following experiments.

3.2.2. Optimization of the Desorption Process

The desorption solvent is crucial and it can significantly affect the MSPE efficiency. Three different solvents were investigated as desorption solvents to investigate their effect on the extraction efficiency: acetonitrile, acetone, and n-hexane. Figure 5A shows that the extraction recoveries of the target analytes eluted by acetonitrile are better than those with the other solvents. Therefore, acetonitrile was used as the desorption solvent for the following experiments.

The desorption time is another important factor that influences the efficiency of the MSPE process. To investigate the influence of the desorption time on the MSPE efficiency, experiments were performed with ultrasonic desorption times of 2, 5, 10, and 15 min. As shown in Figure 5B, the extraction recoveries of the analytes are satisfactory when the sample solution is ultrasonicated for 5 and 10 min. Considering the efficiency, an ultrasonic desorption time of 5 min was chosen for the subsequent experiments.

To investigate the effect of the frequency of desorption, ultrasonic desorption of the nine OCPs was performed one to four times using 2 mL of the desorption solvent and a desorption time of 5 min.

The results are shown in Figure 5C. The optimum recoveries are obtained when the analytes are eluted two times. Thus, the frequency of desorption was set to two for the following experiments.

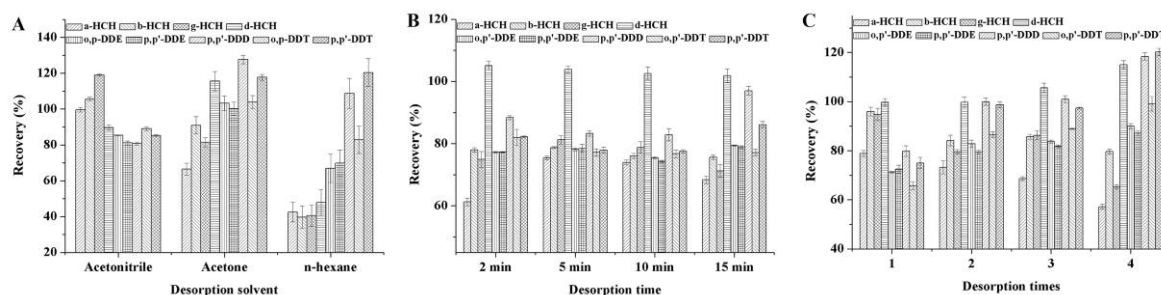


Figure 5. Optimization of the desorption process for $50 \mu\text{g L}^{-1}$ organochlorine pesticides using zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes: (A) desorption solvent; (B) desorption time; and (C) frequency of desorption. Extraction conditions: sample volume, 5 mL; amount of sorbent, 6 mg; and extraction time, 20 min. The error bars show the standard deviation of the mean ($n = 3$).

3.3. Method Characterization

A series of experiments was performed under the optimized conditions (Table 2) and the analytical characteristics, such as the linear ranges (LRs), LOD, and relative standard deviations (RSDs), were determined to validate the developed method. Working solutions containing the target analytes at concentrations of 1, 2, 5, 10, 20, 50, 100, and 200 $\mu\text{g L}^{-1}$ were prepared to construct the working curves. Good linearities for the nine OCPs were achieved with determination coefficients (R^2) ranging from 0.9916 to 0.9989. The LOD for all of the analytes were calculated at signal/noise (S/N) ratios of 3. The LODs range from 0.07 to 1.03 $\mu\text{g L}^{-1}$. The repeatability of the method was evaluated by performing six replicate analyses of spiked samples with 10 $\mu\text{g L}^{-1}$ of each of the OCPs, and the RSDs are in the range 1.0–8.5%. All of these results indicate that the proposed method has high sensitivity and good repeatability.

Table 2. Analytical parameters of zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes as an adsorbent for magnetic solid-phase extraction of nine organochlorine pesticides in an ultrapure water sample.

OCPs	Linear Range ($\mu\text{g L}^{-1}$)	Determination Coefficients	LOD ^a ($\mu\text{g L}^{-1}$)	RSD ^b (%) ($n = 6$)
α -HCH	2–200	0.9953	0.12	8.5
β -HCH	1–200	0.9946	0.13	1.0
γ -HCH	1–200	0.9919	0.15	6.2
δ -HCH	1–200	0.9947	0.07	4.0
o,p'-DDE	1–200	0.9951	0.17	1.5
p,p'-DDE	1–200	0.9989	0.45	1.3
p,p'-DDD	2–200	0.9934	0.41	3.1
o,p'-DDT	2–200	0.9932	0.74	3.9
p,p'-DDT	2–200	0.9916	1.03	3.1

^a LOD means limit of determination; ^b RSDs means relative standard deviations, and were determined by performing six replicate analyses of the spiked samples with 10 $\mu\text{g L}^{-1}$ of each of the organochlorine pesticides.

3.4. Comparison

To investigate the extraction performance of the prepared materials, 4 mg of Fe_3O_4 -MWCNTs and 6 mg of M-M-ZIF-67, which was synthesized based on the same amount of the former material, were applied to extraction of the nine OCPs using the proposed method. The results are shown in Figure 6 based on three replicate analyses ($n = 3$). The peak areas of all of the analytes for M-M-ZIF-67

are 2.7–3.0 times higher than those for Fe₃O₄–MWCNTs, indicating that ZIF-67 plays a greater role in the extraction process.

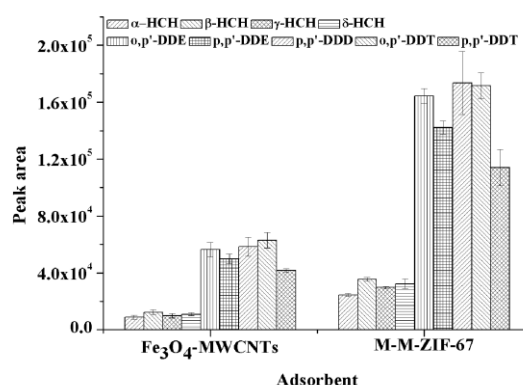


Figure 6. Effect of the sorbent on the adsorption capacities for the nine organochlorine pesticides. Extraction conditions: sample volume, 5 mL; amount of sorbent, 6 mg zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes and 4 mg magnetic multiwalled carbon nanotubes; and extraction time, 20 min. Desorption conditions: 2 mL of acetonitrile; ultrasonication time, 5 min, and ultrasonication performed one more time. The error bars show the standard deviation of the mean ($n = 3$).

The performance of the current method was compared with some recently reported methods used for analysis of OCPs in water. The comparison data (Table 3) show that the proposed method based on the M-M-ZIF-67 adsorbent exhibits good sensitivity (as the LOD), less use of sample and adsorbent. However, the Fe₃O₄–MWCNTs based adsorbent can make the phase separation process easier and faster without additional centrifugation or filtration procedures, and also can avoid the time-consuming column passing operations encountered in SPE. Therefore, the developed M-M-ZIF-67 based magnetic solid-phase extraction method showed agreement in accordance with the principles of green analytical chemistry [41].

Table 3. Comparison of different methods for analysis of organochlorine pesticides.

Method	Sorbent	Sample Amount (mL)	Number of OCPs	Volume of Elution Solvent	Sorbent Amount (mg)	Extraction Time (min)	LOD	RSD (%)	Spiked Level	Ref.
MSPE-GC-MS/MS ^a	BMZIF-derived carbon ^b	10	8	Dichloromethane, 2.00 mL	6	10	0.39–0.70 ng L ⁻¹	5.5–9.1	5–500 ng L ⁻¹	[42]
μ-SPE-GC-MS ^c	ZnO-CF ^d	10	15	Toluene, 0.30 mL	15	30	0.19–1.64 μg L ⁻¹	2.3–10.2	1–50 μg L ⁻¹	[43]
PT-SPE-GC-ECD ^e	GUF-MIR ^f	1	3	Cyclohexane-ethyl acetate (9:1, v/v), 0.60 mL	5	-	0.24–0.66 ng g ⁻¹	3.5–6.7	2.2–220 ng g ⁻¹	[44]
MSPE-GC-ECD	RGO/Fe ₃ O ₄ @Au ^g	10	6	Acetonitrile, 0.25 mL	20	10	0.4–4.1 μg L ⁻¹	1.7–7.3	100 μg L ⁻¹	[45]
MSPE-GC-μECD	Fe ₃ O ₄ @MAA@IBL ^h	20	5	Acetonitrile, 0.20 mL	20	10	1.0–1.9 ng L ⁻¹	6.2–8.3	100 μg L ⁻¹	[46]
d-μSPE ⁱ -GC-MS	rGO-amino-HNT@PT ^j	10	6	Acetonitrile, 0.50 mL	5	5	2–13 ng L ⁻¹	6.1–9.7	5–70 μg L ⁻¹	[47]
μ-SPE-GC-MS	MIL-101 ^k	10	5	Ethyl acetate, 0.20 mL	4	40	2.5–16 ng L ⁻¹	4.2–11.0	10 μg L ⁻¹	[48]
MSPE-GC/ECD	β-CD/MRGO ^l	50	16	acetonitrile-dichloromethane (4:1, v/v), 1.00 mL	15	3	0.5–3.2 ng Kg ⁻¹	3.3–7.8	50 ng kg ⁻¹	[49]
MSPE-GC-MS/MS	M-M-ZIF-67 ^m	5	9	Acetonitrile, 4.00 mL	6	20	0.07–1.03 μg L ⁻¹	1.0–8.5	10 μg L ⁻¹	This work

^a magnetic solid-phase extraction followed by gas chromatography–tandem triple quadrupole mass spectrometry determination; ^b micro solid-phase extraction followed by gas chromatography–mass spectrometry determination; ^c Bimetallic MOF; ^d Zinc oxide nanoparticles incorporated in carbon foam; ^e Miniaturized pipette tip solid-phase extraction followed by gas chromatography combination with electronic capture detector determination; ^f Glyoxal–urea–formaldehyde molecularly imprinted resin; ^g Reduced graphene oxide/Fe₃O₄@gold nanocomposite; ^h Fe₃O₄@mercaptoacetic acid@imine-based ligand; ⁱ dispersive micro solid-phase extraction; ^j Reduced graphene oxide–amino-halloysite nanotubes@polythiophene; ^k metal-organic framework; ^l β-Cyclodextrin/iron oxide-reduced graphene oxide hybrid nanostructure; ^m zeolitic imidazolate framework based on magnetic multiwalled carbon nanotubes.

3.5. Real Sample Analysis

The proposed MSPE method was applied to determination of OCPs in real agricultural irrigation water samples, including tap water, river water, and underground water. The results are summarized in Table 4 and the total ion chromatograms (TICs) of the analytes acquired from the tap water samples are shown in Figure 7. There are no OCPs in the selected water samples and the recovery results indicate that the developed method has good utility for analysis of OCPs in real water samples.

Table 4. Analytical results for determination of organochlorine pesticides in real water samples.

Matrix	Analyte	Spiked Concentration ($\mu\text{g L}^{-1}$, $n = 3$)				
		0	10		100	
		Found	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Tap water	α -HCH	<LOD	83.4	7.4	84.7	0.7
	β -HCH	<LOD	92.5	9.6	103.7	0.6
	γ -HCH	<LOD	93.3	5.5	91.9	0.4
	δ -HCH	<LOD	94.6	6.6	111.1	1.0
	<i>o,p'</i> -DDE	<LOD	85.4	3.4	99.6	5.3
	<i>p,p'</i> -DDE	<LOD	78.1	1.5	107.5	3.1
	<i>p,p'</i> -DDD	<LOD	76.0	2.5	97.0	2.5
	<i>o,p'</i> -DDT	<LOD	83.1	5.4	89.2	2.1
	<i>p,p'</i> -DDT	<LOD	93.7	2.1	105.7	1.6
River water	α -HCH	<LOD	76.8	5.7	80.5	2.4
	β -HCH	<LOD	91.3	3.1	102.5	0.8
	γ -HCH	<LOD	84.1	8.5	91.2	3.5
	δ -HCH	<LOD	74.9	5.9	112.7	2.6
	<i>o,p'</i> -DDE	<LOD	110.8	4.7	94.3	0.1
	<i>p,p'</i> -DDE	<LOD	102.5	4.8	100.9	1.2
	<i>p,p'</i> -DDD	<LOD	101.9	3.4	92.2	0.7
	<i>o,p'</i> -DDT	<LOD	108.6	4.3	86.9	1.2
	<i>p,p'</i> -DDT	<LOD	110.8	3.5	100.9	0.8
Underground water	α -HCH	<LOD	81.0	8.7	80.3	3.3
	β -HCH	<LOD	83.9	7.8	97.2	2.1
	γ -HCH	<LOD	90.1	7.5	80.4	5.2
	δ -HCH	<LOD	79.5	15.3	112.7	2.0
	<i>o,p'</i> -DDE	<LOD	101.5	8.4	82.9	1.9
	<i>p,p'</i> -DDE	<LOD	95.3	7.6	81.0	1.4
	<i>p,p'</i> -DDD	<LOD	92.8	8.9	75.1	2.2
	<i>o,p'</i> -DDT	<LOD	111.1	6.4	110.3	3.2
	<i>p,p'</i> -DDT	<LOD	116.3	3.7	90.5	2.3

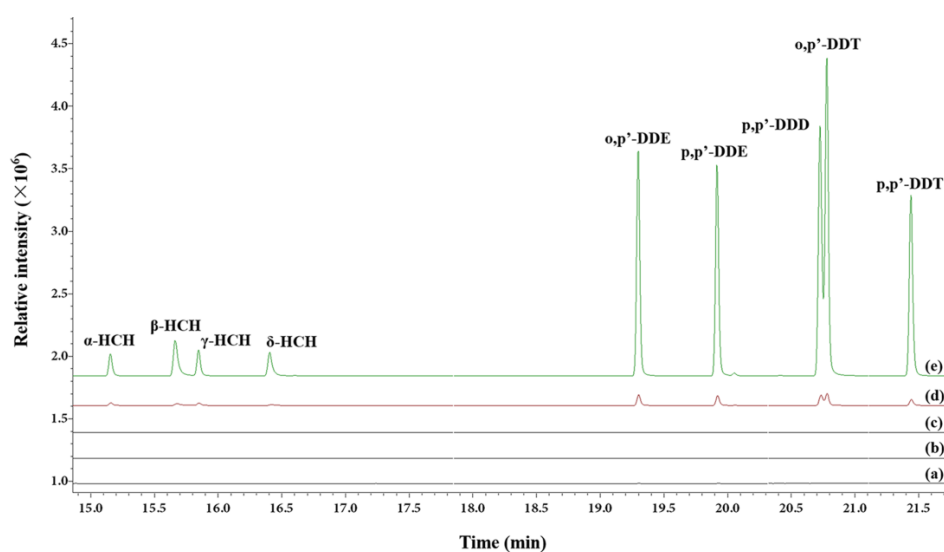


Figure 7. Total ion chromatograms of the nine organochlorine pesticides in water samples obtained by gas chromatography–tandem triple quadrupole mass spectrometry: (a) tap water; (b) river water; (c) underground water; (d) tap water spiked at $10 \mu\text{g L}^{-1}$; and (e) tap water spiked at $100 \mu\text{g L}^{-1}$.

4. Conclusions

Magnetic composites containing Fe₃O₄, MWCNTs, and ZIF-67 have been synthesized. The synthesized materials have porous surfaces and exhibit super-paramagnetism. They were used as sorbents for MSPE to extract nine OCPs from agricultural irrigation water samples. For M-M-ZIF-67, the OCP adsorption capacities are nearly three times higher than those for Fe₃O₄-MWCNTs. The developed method achieves high extraction efficiencies, good linearities, low detection limits, and good accuracies and precision. The results suggest that M-M-ZIF-67 is a simple and effective potential adsorbent for removal of OCPs from environmental water samples.

Author Contributions: X.H. and G.L. conceived and designed the experiments; X.X. and L.L. performed the experiments; X.H. and S.Z. analyzed the data; D.X. and H.L. contributed reagents and materials; X.H. and H.G. wrote the paper. Authorship must be limited to those who have contributed substantially to the work reported.

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