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Accelerated Solvent Extraction and Matrix Solid Phase Dispersion Using Molecularly Imprinted Polymer for The Analysis of Monocrotophos in Soil

FENGXIA LIANG*†, XIAOLAN ZHU†, JUN YANG† and QINGDE SU†
Anhui Provincial Center for Disease Control and Prevention
Hefei, Anhui, 230061, P.R. China
E-mail: lfx@ahcdc.com.cn

A rapid, simple and highly selective accelerated solvent extraction (ASE) and matrix solid phase dispersion (MSPD) using molecularly imprinted polymer method has been developed for the determination of monocrotophos in soil. The soil sample is dispersed with molecularly imprinted polymer and loaded into the extraction cell. After two accelerated solvent extraction steps, some impurities including some OPPs were washed when CH_2Cl_2 was used as the solvent in the first extraction step while monocrotophos was eluted separately by 10 % CH_3OH-CH_2Cl_2 in the second extraction step. The molecularly imprinted polymer as dispersing agent showed good performance for selectively discriminating monocrotophos from other impurities. Monocrotophos could be selectively extracted from soil and quantitive recovery of monocrotophos was 99.3 % at fortification level of 1 μg/g.

Key Words: Accelerated solvent extraction, Matrix solid phase dispersion, Molecularly imprinted polymer, Monocrotophos.

INTRODUCTION

Monocrotophos is one of the most widely used pesticides in agriculture. The extensive use of monocrotophos to improve agriculture productivity has resulted in its wide distribution in the environment such as soil and water. monocrotophos inhibits acetylcholinesterase not only in insects but can also affect the nervous system of humans[1]. Therefore, it is necessary to monitor its residues in soil.

The OPPs are usually determined by GC or HPLC[2-4]. The methodology used to extract OPPs generally includes mechanical surging extraction (MSE) and sonication extraction (SE)[5,6]. Unfortunately, these sample preparation techniques demand long extraction time and large volumes of solvents.

†Department of Chemistry, University Science & Technology of China, Hefei, Anhui, 230026, P.R. China.

The accelerated solvent extraction, basing on the use of solvents to extract organic pollutants at elevated pressure and temperature, is a relatively new extraction technique and has been employed in the U.S. Environmental Protection Agency (EPA) method 3545 for the analysis of organic compounds in solid compounds[7]. MSPD is an extraction-cleanup technique and the combination of ASE with MSPD has been applied to the determination of polychlorinated biphenyls in samples and sulfonamide residues in raw meat and infant foods[8,9]. In MSPD, C_{18}, silica and florisil are the sorbents commonly used and the analytes are retained by these sorbents basing upon non-specific interactions. monocrotophos is extremely water soluble and can't be separated from the polar impurities employing these sorbents. Therefore, developing high selective sorbents is very important.

Molecularly imprinted polymers (MIP) have high selectivity toward a particular analyte and have been used as SPE sorbents for the cleanup and preconcentration of target analytes[10-14]. MIP are fabricated by synthesizing highly cross-linked polymers in the presence of a template molecular and removal of the template molecular produces a polymer with recognition sites suitable for specific rebinding of the template molecular. The use of MIP as solid phase extraction sorbent for the determination of monocrotophos has been reported[15,16].

In this paper, a rapid accelerated solvent extraction and matrix solid phase dispersion using MIP method (ASE-MIP-MSPD) are developed. The synthesis and performance of a molecularly imprinted polymer as matrix solid phase dispersion sorbent for the selective extraction of monocrotophos from soil samples were carried out. The elution conditions were optimized and results showed that monocrotophos could be separated from the impurities. Finally, the combination of ASE with MIP-MSPD has also been compared with ASE and matrix solid phase dispersion using MIP (MIP-MSPD) method.

EXPERIMENTAL

Monocrotophos, fenitrothion, phoxim, parathion and fenthion were purchased from Beijing Bai-Ling-Wei Chem-Tech. Methacrylic acid (MAA) and ethylene glycoldimethacrylate (EGDMA) were from Aldrich and cleaned to remove the inhibitor prior to polymerization. Azobisisobutyronitrile (AIBN) was from Factory of Special Reagent of Nankai University. All other chemicals were of analytical grade and solvents HPLC quality. Ultrapure water used for sample preparation was obtained from a Milli-R04 purification system (Millipore, Germany).

The soil was collected from dry land of Yongan county (Fujian, China) and ground to a fine powder before use.

Preparation of MIP: The procedure of molecularly imprinted polymer (MIP) preparation was performed using a method based on that of Zhu[16], which involved dissolving the monocrotophos template (2mmol), methacrylic acid (8 mmol) in 11.2 mL of dichloromethane in a glass tube. Then the EGDMA cross-linker (40 mmol) and the AIBN initiator (80 mg) were added to the mixture, degassed by nitrogen for 10 min. After sealed under vacuum, the tube was immersed into a shaker bath at 58 ºC for 24 h. The monolith polymer was crushed with a pestle and mortar and then the 75-150 μm size fraction was isolated by sieving. The collected fractions were washed with 10 % acetic acid methanol solution in a soxhlet extraction apparatus to remove the MCP. After that, the particles were washed with methanol to eliminate the acetic acid and dried to constant weight under vacuum at 70 ºC.

ASE-MIP-MSPD: The extraction was performed on a dionex ASE 200 (Dionex Corp., Sunnyvale, CA, USA) system. Aliquots of soil sample (2 g) were ground with CH_2Cl_2 (1 mL) and MIP (500 mg) in an agate mortar with a pestle to obtain a homogenous mixture of sample. Then the mixture was placed into the stainless-steel extraction cell with 1 g of anhydrous sodium sulfate at the bottom. The extraction was carried out under the following conditions: pre-heating period (5 min), static extraction time (10 min) solvent flush volume (10 %) of the extraction cell volume; number of extraction cycles, 1; purge, 60 s using pressurized nitrogen (150 psi); the volume of the resulting extract was about 15 mL. The cell was eluted with solvent of CH_2Cl_2 and then followed by the elution solvent of 10 % CH_3OH-CH_2Cl_2. The two fractions were collected respectively, evaporated to dryness by a rotary evaporator and then dissolved in 1.0 mL mobile phase before HPLC analysis.

ASE: The sample of soil (2 g) and anhydrous sodium sulfate (1 g) were mixed and loaded into the extraction cell. The extraction condition was the same as the ASE-MIP-MSPD. The cell was eluted with solvent 10 % CH_3OH-CH_2Cl_2 under the above extraction condition. The fraction was collected, evaporated to dryness by a rotary evaporator and redissolved in 1.0 mL mobile phase before injection.

MIP-MSPD: A 2.0 g amount of soil sample, 1 mL CH_2Cl_2 and 500 mg MIP was ground in a glass mortar to obtain a homogenous mixture. The mixture was placed in a glass column with 1 g anhydrous sodium sulfate at the bottom. The column was washed consecutively with 30 mL of CH_2Cl_2 and 30 mL of 10 % CH_3OH-CH_2Cl_2. The fractions were collected, concentrated to dryness and dissolved in 1.0 mL mobile phase respectively.

High performance liquid chromatography: An Agilent 1100 series high performance liquid chromatography, equipped with a 1312A binary gradient pump, a 1313A thermostatted auto sampler, a G1316A column

oven, a G13156A diode array detector and a G1319A Chemstation, was used. The analytes were separated on an Agilent XDB-C_{18} column (250 mm × 4.6 mm I.D., particle size 5 μm). The mobile phase, operated at 1 mL/min, consisted of an isocratic mixture of methanol/water (7:3, v/v). The system operated at 25 ºC and 220 nm was selected as the detection wavelength.

RESULTS AND DISCUSSION

Selectivity of MIP in ASE-MIP-MSPD: To evaluate the selectivity of molecularly imprinted polymer as sorbent for MCP, fortified samples were prepared by adding 0.2 mL of standard solution (10 μg/mL of each of five OPPs) to 2.0 g soil. Then the spiked sample was extracted using ASE-MIP-MSPD method and the results were shown in Fig. 1a-c. As shown in Fig. 1, almost no monocrotophos was washed in the first step. We can easily conclude that MIP has particular selectivity towards the template monocrotophos and monocrotophos was specifically bond on the MIP. After the grinding procedure, monocrotophos and some impurities would absorb on the MIP. It is reported that the optimum recognition is frequently observed using the same solvent that was employed during polymerization[17]. The interferences that nonspecifically bond on the MIP would be eluted out by the CH_2Cl_2 solvent, which is the synthesis solvent of this MIP. The structures of the five OPPs were shown in Fig. 2. There is amino group in the structures of MCP, which is capable of forming hydrogen bonds with monomer methacrylic acid[18]. Accordingly, monocrotophos could hydrogen bonds with MIP in the imprinting sites. On the contrary, there is no such group that could form hydrogen bond with MIP in the other four OPPs and they were completely removed in the first step. The binding affinity was also influenced by the solvents, for the hydrogen bonding capability of polar solvents such as methanol would compete with the binding sites for the template. For the swelling properties of solvents for the MIP[19], We choose 10 % CH_3OH-CH_2Cl_2 as elution solvents. we can see that the template monocrotophos could be eluted by 10 % CH_3OH-CH_2Cl_2 in the second step and recovery of monocrotophos was 99.3 %.

Comparison of ASE-MIP-MSPD with ASE: The ASE-MIP-MSPD was compared with ASE. As shown in Fig.1d and Table-1, a large amount of impurities which would interfere with the determination of monocrotophos and other OPPs were simultaneously extracted by 10 % CH_3OH-CH_2Cl_2 using ASE method. On the contrary, in the ASE-MIP-MSPD method, the impurities that interfered the determination of monocrotophos were removed by CH_2Cl_2 in the first step; accordingly, monocrotophos could be quantatively determined in the second extraction step.

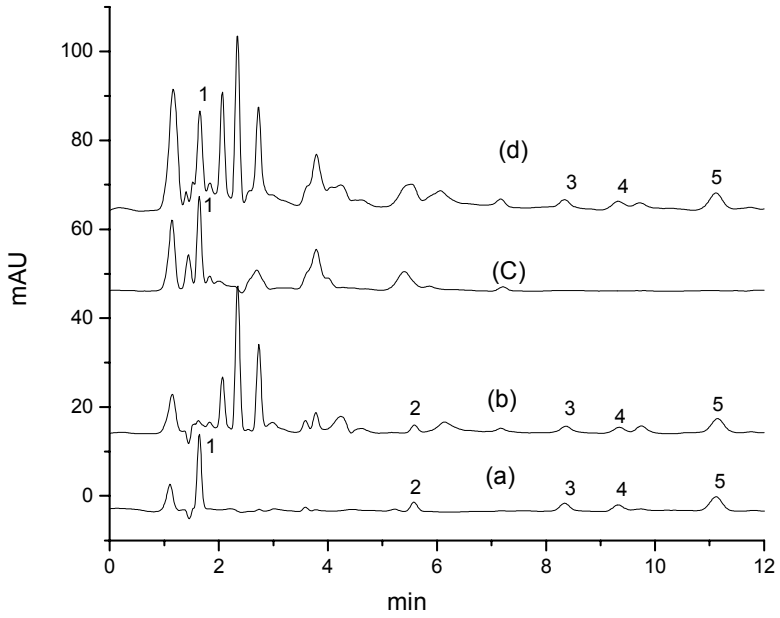

Fig. 1. Chromatograms obtained by ASE-MIP-MSPD and ASE (a) standard solution; (b) soil samles using ASE-MIP-MSPD, CH_2Cl_2 fractions; (c) soil sample using ASE-MIP-MSPD, 10 % CH_3OH-CH_2Cl_2 fraction; (d) soil sample using ASE, 10 % CH_3OH-CH_2Cl_2 fraction
(1) MCP, (2) fenitrothion, (3) parathion, (4) fenthion, (5) phoxim

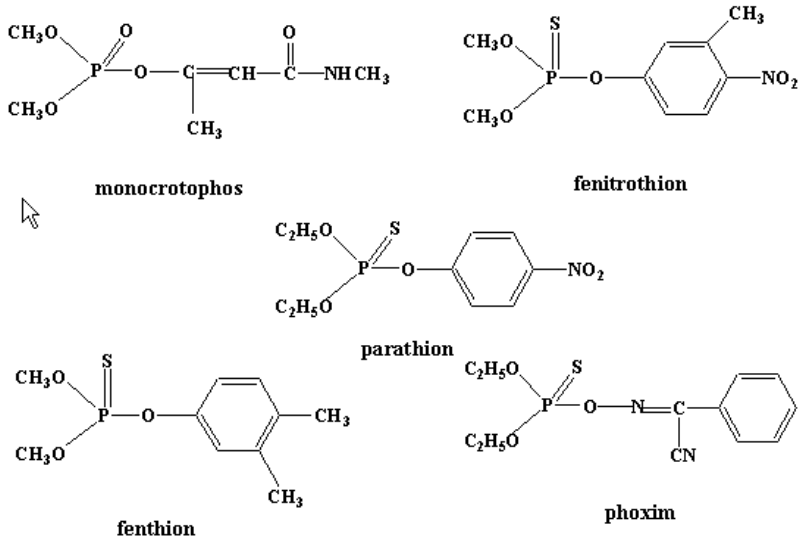

Fig. 2. Chemical structures of monocrotophos, fenitrothion, parathion, fenthionm and phoxim

Comparison of ASE-MIP-MSPD with MIP-MSPD: Three methods were compared and results were shown in Table-1. In MSPD procedure, 30 mL of CH_2Cl_2 were needed to completely remove the four OPPs in the first step and the recoveries of these OPPs were about 90 %. Additionly, another 30 mL of 10 % CH_3OH-CH_2Cl_2 were necessary to elute the monocrotophos from the MSPD column and the recovery of monocrotophos was 94.8 %. The total time needed was as long as 2 h. Compared with MIP-MSPD, the ASE-MIP-MSPD has higher extraction efficiency, shorter extraction time and lower consumption of solvents; moreover, it was more automatized. This may be attributed to the extraction way of accelerated solvent extraction.

TABLE-1
COMPARISON OF THE THREE METHODS

Extraction	ASE-MIP-MSPD (%±SD)		ASE (%±SD)	MIP-MSPD (%±SD)	
	CH_2Cl_2	10 % CH_3OH-CH_2Cl_2	10 % CH_3OH-CH_2Cl_2	CH_2Cl_2	10 % CH_3OH-CH_2Cl_2
MCP	2.8 ± 0.1	99.3 ± 2.0	100.6 ± 2.0	2.5 ± 0.2	94.8 ± 1.8
Fenitrothion	90.8 ± 1.5	0	–	89.5 ± 1.6	0
Parathion	93.1 ± 1.9	0	93.3 ± 1.3	92.7 ± 1.8	0
Fenthion	94.1 ± 1.4	0	95.2 ± 1.2	90.6 ± 1.5	0
Phoxim	98.0 ± 1.0	0	97.6 ± 1.1	94.2 ± 1.3	0
Solvent (mL)	15.00	15.00	15.00	30	30
Time (h)	0.25	0.25	0.25	1	1

Conclusion

In this paper, MIP was prepared and applied successfully in ASE-MIP-MSPD method for the determination of monocrotophos in soil samples. The preparation of this MIP was simple and economical. Moreover, it showed particular affinity and selectivity to monocrotophos and made the preconcentration of trace monocrotophos from complex sample possible. The developed method proved effectively to determine a particular OPP in complex soil sample and the interferences could be eliminated. Hence, the sensitivity and precision for the determination of monocrotophos was improved. Also, the ASE-MIP-MSPD compared very favourablely with ASE and MIP-MSPD.

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