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Analytical Methods

Molecularly imprinted solid phase extraction coupled to high-performance liquid chromatography for determination of trace dichlorvos residues in vegetables

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ABSTRACT

In this paper, we prepared a highly selective imprinted polymer by a room temperature ionic liquid-mediated bulk polymerization technique, using dichlorvos as the template, methacrylic acid as the functional monomers, and trimethylolpropane trimethacrylate as the cross-linker. This functionalized material was characterized by FT-IR, static and kinetic adsorption experiments, and the results showed that this imprinted sorbent exhibited good recognition and selective ability, and offered fast kinetics for the adsorption and desorption of dichlorvos. Using the prepared material as a solid phase extraction sorbent, a novel sample pre-treatment technique that can be coupled to high-performance liquid chromatography (HPLC) had been developed for determination of trace dichlorvos residues in foods. Under the selected experimental condition, the detection limit ($S/N = 3$) of dichlorvos was 94.8 ng L^{-1}, and the peak area precision (RSD) for five replicate detections of 10 μg L^{-1} dichlorvos was 4.41%. The blank samples of cucumber and lettuce spiked with dichlorvos at 0.005 and 0.02 μg g^{-1} levels were determined with recoveries ranging from 82.1% to 94.0%.

1. Introduction

In recent years, organophosphorus pesticides such as dichlorvos (Fig. 1) have been extensively used for crop protection and tree treatment as alternative to high persistent (Yamashita, Yamashita, Tanaka, & Ando, 1997). However, many of these compounds display a high acute toxicity since they can cause protein adduction, are suspected mutagenics and carcinogenics, and are also endocrine disruptor (Kang et al., 2004). As one of the important organophosphorus pesticides, the dermal toxicity of dichlorvos is similar to its oral toxicity and dermal exposure is of particular concern with respect to cancer (El-Behissy, King, Ahmed, & Youssef, 2001). In order to prevent these uncontrolled effects on the human health and provide safe products to consumers, a sensitive method for the separation and determination of dichlorvos is requiring and of great importance.

Many efforts have been devoted to the development of analytical methods for assessing the presence of organophosphorus compounds residues using gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS) (Chen, Su, & Jen, 2002; Lambropoulou & Albanis, 2005; Pang et al., 2006; Xiao, Hu, Yu, Xia, & Jiang, 2006), the electrochemiluminescence, amperometric acetylcholinesterase biosensor and immunoassays methods (Chen, Lin, Cai, Chen, & Wang, 2008; Del Carlo et al., 2006; Vidal, Esteban, Gil, & Castillo, 2001). Among these methods, GC provides high sensitivity and is widely used for the organophosphorus pesticides determination. However, polar pesticides, including non-volatile, thermally labile pesticides such as dichlorvos, cannot be analyzed without a preliminary derivatization step. To overcome this drawback, liquid chromatography-based techniques have been successfully applied for the analysis of a wider range of pesticides (Carabias-Martínez, Rodríguez-Gonzalo, Paniagua-Marcos, & Hernández-Méndez, 2000; Huang, Yang, Baeyens, Yang, & Tao, 2002; Lacorte & Barceló, 1996; Pang et al., 2006). Liquid chromatography (LC) can be used for the analysis of dichlorvos without a preliminary derivatization procedure. However, LC method has insufficient sensitivity for the determination of trace dichlorvos in samples because of the low UV absorbance of dichlorvos. Recently, liquid chromatography–mass spectrometry (LC–MS) and LC/MS/MS have gained increasing popularity for the analysis of polar analytes in biological fluids, particularly for those compounds that are not readily amenable to GC or GC–MS analysis (Inous et al., 2007; Nakazawa et al., 2004). Although these methods offer the more sensitive approaches to the analysis of polar analytes, they require relatively expensive instruments, which are not yet available in all laboratories. Consequently, the development of a convenient and sensitive detection method is of particular

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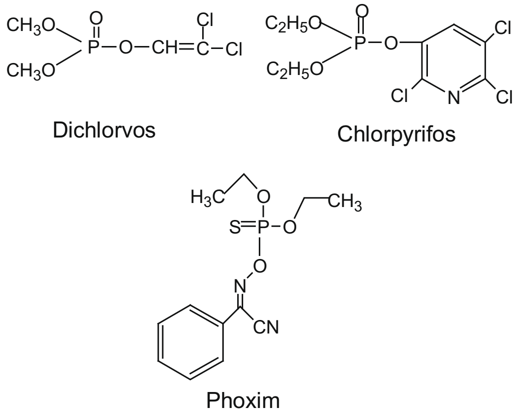

Fig. 1. Chemical structures of dichlorvos, chlorpyrifos and phoxim.

significance and urgently required. Usually, dichlorvos is present in complex samples at low concentrations, an effective extraction and preconcentration step prior to detection is required.

Many sample preparation procedures for the isolation of organophosphates from water, human serum, vegetables and egg samples have been published (Carabias-Martínez et al., 2000; Chen et al., 2002; Lacorte & Barceló, 1996; Lambropoulou & Albanis, 2005; Xiao et al., 2006). Among these, solid phase extraction (SPE) is recognized as the most common sample pre-treatment technique to enhance the concentration of the target analyte in the analysis of biological and environmental samples. SPE coupled with high-performance liquid chromatography (HPLC) offers a potentially advantageous method for determination of the trace organic compound, and this method not only possesses the advantages of SPE, but also possesses the advantages of HPLC (Fang, He, & Wang, 2006). Bonded silica is popularly used as the commercial solid phase in SPE as it is efficient at concentrating a variety of pollutants but it unfortunately shows a lack of selectivity. The development of selective sorbent material for SPE is crucial.

Molecularly imprinted polymers (MIP) are tailor-made functional materials that can exhibit high selectivity, physiochemical stability and applicability in harsh chemical media, and thus have been given much attention in many fields, such as chiral separation, chemical sensors and biomimetic immunoassay (Vivek & Hunagxian, 2004; Wulff, 1995). Their use as sorbent material for SPE is potentially one of the most exciting applications of MIP (Wang et al., 2007; Francesco et al., 2005; Christina & Hans, 2006; Fang, Tan, & Yan, 2004) because it would provide a simple and effective pre-treatment method for complex samples. The traditional preparing methodology for MIP is organic-polymer-based system, which may shrink or swell when exposed to different mobile phases, and the various degrees of swelling in different solvents may considerably change the morphology of the polymer network and the relative positions of the functional groups that are essential for molecular recognition (Yu & Mosbach, 2000).

Room temperature ionic liquids (RTILs) are interesting solvents with unique characteristics. The low vapor pressure of RTILs could assist in reducing the problem of MIP bed shrinkage and can also act as pore template in the polymerization reaction (Yoo, Choi, & Dionysiou, 2004; Liu et al., 2005). RTILs have been shown to accelerate the synthesis process, improve the selectivity and adsorption of *trans*-asconitic acid imprinted organic polymers (Booker, Bowyer, Holdsworth, & McCluskey, 2006; Wang, Zhu, Yan, Gao, & Zheng, 2006).

The objective of this work is to synthesize a novel imprinted functional material by a molecular imprinting technique using a room temperature ionic liquid-mediated template to overcome the drawbacks previously described and to use this material as a SPE sorbent for the selective separation and quantitative determination of dichlorvos at low concentration level in vegetable samples coupled with HPLC. The factors affecting the preconcentration and separation of the analytes are discussed in detail and the applicability of this method was evaluated.

2. Experimental

2.1. Samples

The cucumber and lettuce samples were purchased randomly from the Carrefour supermarket in Tianjin, China.

2.2. Chemicals

The analytical standard dichlorvos, chlorpyrifos and phoxim were obtained from the Institute for the Control of Agrochemicals of Ministry of Agriculture (Beijing, China) with purities of 99%. Methacrylic acid (MAA) and trimethylolpropane trimethacrylate (TRIM) were obtained from Sigma–Aldrich (USA). 2,2-Azobisisobutyronitrile (AIBN), toluene, acetonitrile and ethanol were supplied by Tianjin Chemical Reagent Factory (Tianjin, China). MAA and AIBN were purified before using. 1-Butyl-3-methylimidazolium hexafluorophosphate ($BMIM^{+}PF_6^{-}$) was obtained from Henan Lihua Pharmaceutical Co., Ltd. (Henan, China). LC-grade ethanol was purchased from Concord Tech. Co. (Tianjin, China). All other solvents and reagents used in this study were of the highest available purity and at least of analytical grade. Doubly deionized water (DDW, 18 $M\Omega\,cm^{-1}$) obtained from a Water Pro. water system (Labconco Corp., Kansas City, MO) was used throughout the experiments. The Strata Scx C_{18} SPE column (200 mg/3 mL) was obtained from Phenomenex (USA).

2.3. Apparatus and procedures

The high-performance liquid chromatographic system consisted of two LC-10ATVP pumps and a Shimadzu SPD-10AVP ultraviolet detector (Shimadzu, Kyoto, Japan). All separations were achieved on an analytical reversed-phase Thermo C_{18} column (4.6×250 mm, USA) at a mobile flow rate of 0.6 mL min^{-1} under isocratic conditions using a mixture of 0.01% phosphoric acid water solvent (v/v)/methanol (7:93; v/v) as the mobile phase. Class-vp software was used to acquire and process spectral and chromatographic data. The sample size injected was 20 μL and the UV detection wavelength was 215 nm.

FT-IR spectra (4000–400 cm^{-1}) in KBr were recorded using a Vector 22 spectrometer (Bruker). For the determination of the adsorption capacity of the imprinted and non-imprinted polymer, a Cary 50-Bio UV spectrometer (Victoria, Australia) was used.

2.4. Synthesis of the imprinted polymer

The molecularly imprinted polymer was prepared as follows: 0.134 mL of dichlorvos (1.0 mmol) was dissolved in 3.0 mL of acetonitrile and 1.0 mL of toluene, and mixed with 0.170 mL (2.0 mmol) of MAA and 0.6 mL of $BMIM^{+}PF_6^{-}$. The mixture was surged ultrasonically for 60 min and then 3.166 mL (10.0 mmol) of cross-linker TRIM and 0.04 g of initiator AIBN were added. After ultrasonicated for another 30 min, the solution was purged with nitrogen for 10 min. The mixture was, then, sealed and thermally initiated in a water bath at 30 °C for 24 h. After the polymerization ended, the rigid polymer was ground and sieved through a 200 mesh steel sieve. The resulting particles were flushed with methanol to remove the unreacted reagents and template molecules, and

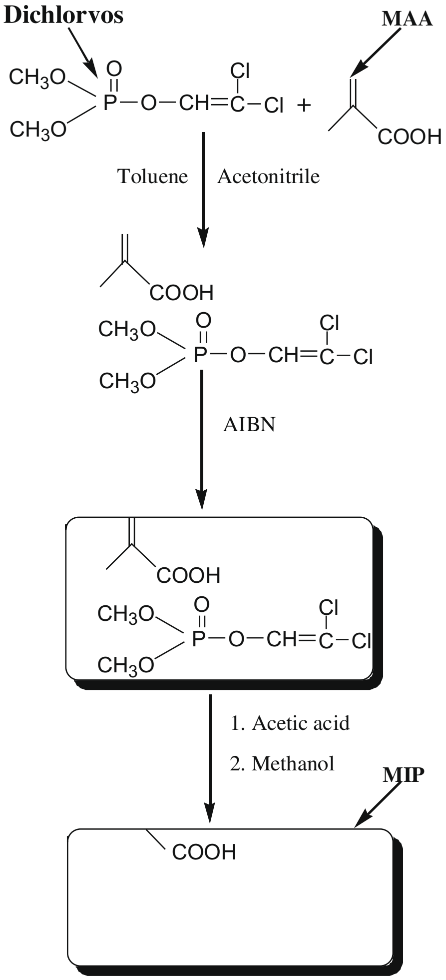

Fig. 2. Schematic representation of the molecularly imprinted polymer used in this study.

dried in a vacuum oven at 100 °C for 12 h. Following soxhlet extraction with 300 mL of methanol containing 10% acetic acid for 48 h, the polymer was then washed using 300 mL of methanol for 8.0 h to be free of dichlorvos (Fig. 2), which was verified by analysis of the methanol eluent using HPLC at 215 nm. Finally, the product was dried in a vacuum oven at 80 °C for 12 h to obtain the MIP material.

For comparison, an imprinted polymer was prepared following the same procedure but without the addition of $BMIM^+PF_6^-$ (polymer b), and the non-imprinted polymer, which did not contain the template, was also prepared in parallel with imprinted polymers using the same synthetic protocol.

2.5. Characterization of the MIP

To measure its adsorption capacity, 50 mg of imprinted or non-imprinted polymer was equilibrated with 10 mL of a methanol solution containing dichlorvos at various concentrations. The mixtures were mechanically shaken (200 times/min) for 24 h at room temperature with a horizontal shaker and then separated centrifugally (4000 rpm) for 15 min. The concentration of unextracted dichlorvos in the supernatant was measured by UV spectrometry at 215 nm and the adsorption capacity (Q) was calculated.

The uptake kinetics of dichlorvos by the imprinted polymer was also examined. Fifty milligrams of the polymer was added to 10 mL of 200 mg L^{-1} of dichlorvos methanol solution. The mixture was then mechanically shaken (200 times/min) for 1, 4, 8, 12, 18 and 24 h at room temperature and then separated centrifugally (5000 rpm) for 10 min. The unextracted dichlorvos in the supernatant was measured by UV spectrometry.

The selective property of imprinted and non-imprinted polymer toward the mixture of dichlorvos and the structurally related compounds chlorpyrifos and phoxim at 200 mg L^{-1} was determined. The supernatants were analyzed for the unextracted dichlorvos, chlorpyrifos and phoxim at 215, 290 and 250 nm, respectively. The static distribution coefficient K_D was usually used to evaluate the selectivity of MIP, and the K_D was calculated using the equation $K_D = C_P/C_s$, where C_p and C_s represent the adsorbed and final concentrations respectively.

2.6. Procedures of molecularly imprinted SPE coupled to HPLC (MISPE–HPLC)

To evaluate the applicability of the molecularly imprinted functionalized sorbent for extraction and determination of trace dichlorvos in water, 100 mg amount of imprinted or non-imprinted polymer was packed into an empty SPE column. At the beginning, the molecularly imprinted SPE (MISPE) cartridge was consecutively conditioned with 5 mL of methanol and DDW prior to extraction, followed by loading 50 mL of standard dichlorvos solution at a flow rate of 0.56 mL min^{-1}, so that the dichlorvos was preconcentrated onto the sorbent-packed precolumn while the unwanted water went to waste. When the samples loading was completed, the analytes adsorbed on the SPE microcolumn were eluted using 1.5 mL portions of methanol/water (95:5, v/v) at a flow rate of 2.0 mL min^{-1}. The effluents were collected into a test tube and condensed to dryness under a gentle flow of nitrogen at room temperature and then accurately re-dissolved with 0.5 mL of methanol. After filtered, 20 μL of the filtrate was injected into HPLC for analysis. Finally, the MISPE column was rinsed with 5 mL portions of methanol and DDW for the next sample preconcentration. In this way, a complete cycle of the MISPE preconcentration and HPLC separation and determination of the dichlorvos lasted for 90 min. Chromatograms were recorded and stored on the hard disk of the computer. The peak areas were calculated at 215 nm and used for data evaluation. The same procedure was employed using the C_{18} cartridges for the extraction of the dichlorvos standard solution.

2.7. Sample preparation

To test the accuracy of the MISPE–HPLC method, the vegetable samples of cucumber and lettuce leaves were spiked with dichlorvos. Prior to spiking the samples were determined to be free of dichlorvos. Briefly, 50.0 g of blank cucumber and lettuce leaves samples were cut into slices and separately weighed into a 100 mL conical flask, and then 0.1 mL of standard solution (2.5 or 10.0 mg L^{-1}) containing 0.25 or 1.0 μg of dichlorvos in methanol was added to each sample, respectively. After incubated for a period of 2.0 h, the spiked samples were ultrasonicated with 3×10 mL of chloroform solution for 30 min. The resulting extractions were collected and filtered for the MISPE procedure.

3. Results and discussion

3.1. Characteristics of imprinted and non-imprinted sorbent by FT-IR spectra

The FT-IR spectra of dichlorvos, imprinted and non-imprinted polymer and the imprinted polymer without extraction (polymer b) are compared in Fig. 3.

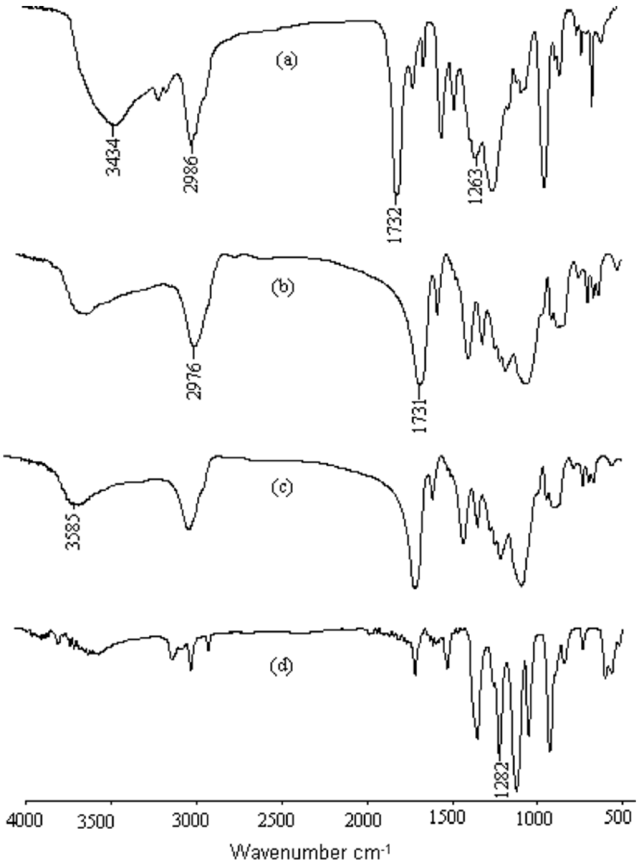

Fig. 3. FT-IR spectras of (a) imprinted polymer without extraction, (b) imprinted polymer, (c) non-imprinted polymer and (d) dichlorvos.

For the imprinted polymer and polymer b, the observed features around 2966 and 2976 cm^{-1} indicated a C–H stretch, and those around 1732 and 1731 cm^{-1} indicated a C=O stretch. For the FT-IR spectra of the non-imprinted polymer and polymer b, the features around 3585 and 3434 cm^{-1} indicated a –OH vibration. This shift can be attributed to the reaction of the –OH group of MAA. For the FT-IR spectra of dichlorvos and polymer b, the features around 1282 and 1263 cm^{-1} indicated the presence of a P=O bond, and the shift in the position of this stretch can be attributed to the hydrophobic interaction between the P=O group of dichlorvos and the –OH group of MAA (Zhu, Cai, Yang, Su, & Gao, 2006). These results demonstrated that dichlorvos had been reacted with MAA and that the polymers have been synthesized.

The FT-IR spectra of the imprinted and non-imprinted polymer after extraction are similar indicating that the template was completely removed from the imprinted polymer. These data also suggested that the $BMIM^+PF_6^-$ used did not interfere with the synthesis and recognition of the imprinted polymer, and was removed from the imprinted polymer after extraction.

3.2. Evaluation of adsorption and selectivity of the imprinted polymer

The isothermal adsorptions of the imprinted and non-imprinted polymer are plotted in Fig. 4. This data showed that the adsorption capacity of molecularly imprinted or non-imprinted polymer toward template molecules increased with dichlorvos initial concentrations increasing. However, the imprinted polymer exhibited a stronger memory function and a higher adsorption capacity for dichlorvos than the non-imprinted polymer. The adsorption capacity of the imprinted polymer (4.58 mg g^{-1}) was more than 1.6-fold that of the non-imprinted polymer (2.87 mg g^{-1}) at a 400 mg L^{-1} concentration of dichlorvos. However the adsorption capacity of polymer b synthesized without the addition of $BMIM^+PF_6^-$ was 4.03 mg g^{-1} at the same concentration.

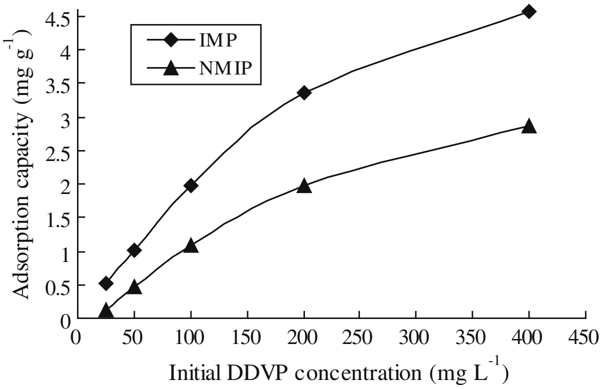

Fig. 4. Adsorption isotherms of the imprinted and non-imprinted polymer.

The Scatchard model was also used for evaluating of the adsorption of imprinted polymer. The equation used for this model is the following (Gong, Yu, Meng, Hu, & He, 2004)

$$Q/C = Q/b + Q_{max}/b.$$

In this equation, C is the initial concentration of the analytes in the solution, Q is the adsorption capacity at adsorption equilibrium, and Q_{max} is the saturated adsorption capacity. From the equation, Q/C versus Q is plotted.

The experimental results indicated that the adsorption isotherms of imprinted polymer toward the template molecule dichlorvos were in good accordance with the linearity and a Scatchard model with an R^2 value of 0.9679 in the experimental conditions. The saturated adsorption capacity (Q_{max}) of the imprinted sorbent toward dichlorvos was 9.20 mg g^{-1} calculated from the linear slope ($-b$). The results from the Scatchard analysis also showed that the imprinted polymer had higher binding association constants and more apparent binding sites than the non-imprinted polymer. This demonstrated that the binding affinity of the imprinted polymer was originated from the specific sites formed by the imprinting process.

The uptake kinetics of dichlorvos by the imprinted polymer was also examined. The results indicated that the imprinted polymer had fast uptake kinetics, 78.2% of binding was obtained within a shaking period of 12 h, and the adsorption equilibrium was almost reached within 18 h. Furthermore, if the concentration of dichlorvos was lower, the time to saturation would become shorter.

Selective recognition property studies of the imprinted polymer and non-imprinted polymer were performed with dichlorvos, chlorpyrifos and phoxim at a concentration of 400 mg L^{-1} (Table 1). Results demonstrated that the adsorption capacity of imprinted polymer toward dichlorvos was higher than the adsorption capacity toward chlorpyrifos and phoxim. However, the adsorption capacities of non-imprinted polymer toward dichlorvos, chlorpyrifos and phoxim were almost the same. The selective properties of imprinted and non-imprinted polymer were also evaluated by determining the static distribution coefficient K_D. The K_D value of the imprinted polymer (0.061) for dichlorvos was 2.4-fold that of the K_D value for chlorpyrifos and 2.8-fold that of the K_D value for phoxim, and it was 1.7-fold that of non-imprinted polymer (0.037). The large K_D value of the imprinted polymer was an indication of its high selectivity for dichlorvos over chlorpyrifos and phoxim. This selectivity might result from the imprinting effect, the difference in the molecular interactions and structures. During the preparation of the imprinted polymer, dichlorvos was

Table 1
Competitive loading of dichlorvos and structurally related compounds chlorpyrifos and phoxim by imprinted and non-imprinted polymer.

Polymer	Adsorption capacity (mg g^{-1})			K_D[a]		
	Dichlorvos	Chlorpyrifos	Phoxim	Dichlorvos	Chlorpyrifos	Phoxim
IMP	4.58	2.01	1.76	0.061	0.026	0.022
NIMP	2.87	2.79	2.53	0.037	0.036	0.033

[a] K_D, static distribution coefficient; $K_D = C_P/C_s$, where C_p and C_s represent the adsorbed and final concentrations.

incorporated into organic polymer networks. After removal of dichlorvos, the imprinted cavities and specific binding sites were formed in a predetermined orientation, whereas the non-imprinted polymer had no such imprinted cavities and specific binding sites.

3.3. Optimization of the MISPE process

To evaluate the applicability of the imprinted sorbent for separation and determination of trace dichlorvos by HPLC, the chemical and flow variables, such as composite and volumes of elution solution, sample acidity and loading flow rate were optimized to achieve good sensitivity and precision of this method.

Different eluent were investigated to identify the influence on desorption of dichlorvos and analogues from the imprinted cartridges. When methanol/water solution (80:20, v/v) was used as the eluent, no dichlorvos signal was observed in the chromatograms, while some dichlorvos could be extracted from the imprinted cartridges by eluting with a methanol/water ratio of 90:10 (v/v). A mixture of methanol/water (95:5, v/v) was selected as the eluent as it allowed the adsorbed dichlorvos to be fully desorbed.

For the selection of the optimum eluent volume, varying volumes (0–2.0 mL) of methanol/water (95:5, v/v) were tested in the MISPE process. The results showed that the chromatographic peak area of dichlorvos increased as the eluent volume increased from 0 to 1.0 mL, increased slightly in the range of 1.0–1.2 mL, and then leveled off in the range of 1.2–2.0 mL. Accordingly, an eluent volume of 1.5 mL was selected to ensure the complete stripping of the adsorbed dichlorvos from the imprinted functionalized packed column.

The effect of loading flow rate on the extraction of 10 μg L^{-1}dichlorvos was studied. It was found that the chromatographic peak area of dichlorvos increased as the sample loading flow rate decreased from 1.67 to 0.56 mL min^{-1} for a loading of 50 mL, but the variation was not obvious, and there was no variation as the sample loading flow rate decreased from 0.56 to 0.39 mL min^{-1}. So based on above results, 0.56 mL min^{-1} of the loading flow rate was chosen as the experiment condition in the following study.

The pH of the sample solution is an important parameter for the effective extraction of analytes in the SPE procedure. Because dichlorvos is stable in acid condition, the influence of sample pH on the extraction of 10 μg L^{-1} of dichlorvos was tested in the pH ranges of 2.3–7.7 at a sample flow rate of 0.56 mL min^{-1} for 90 min. The results showed that dichlorvos could be effectively adsorbed by the imprinted sorbent-packed column in the pH range of 5.0–7.7. Outside of this optimum pH range, the chromatographic peak area decreased, and the maximum chromatographic peak of dichlorvos was achieved in the pH of 6.7. Thus, a pH value of 6.7 was applied for further studies.

3.4. Applicability and merits of the MISPE–HPLC method

The selective adsorptions of dichlorvos by imprinted and non-imprinted sorbent for MISPE–HPLC were tested by passing 50 mL of standard aqueous solution containing 10 μg L^{-1} dichlorvos, chlorpyrifos and phoxim at a sample flow rate of 0.56 mL min^{-1} (Fig. 5). In comparison to chromatogram (b), the chlorpyrifos was obviously appeared in the chromatogram (a) after eluting from the imprinted cartridge (Fig. 5a), however, the peaks of chlorpyrifos and phoxim in chromatogram (a) and (b) were almost the same, which indicated that dichlorvos was selectively extracted onto the imprinted sorbent and the selectivity of the imprinted sorbent for dichlorvos was very high.

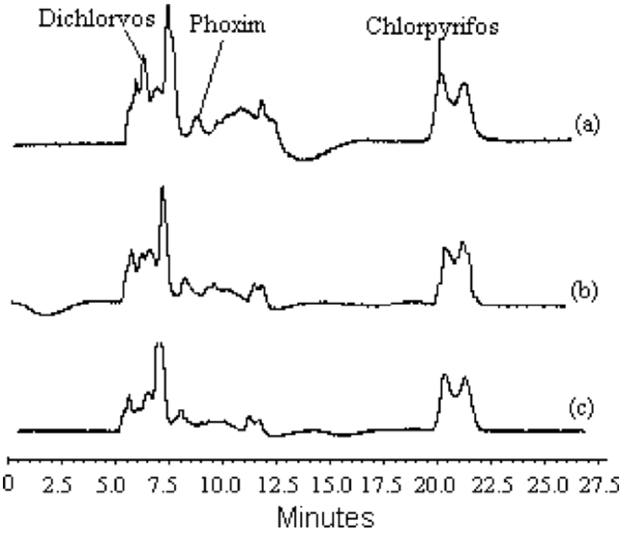

Fig. 5. HPLC chromatograms of the 10 μg L^{-1} of dichlorvos, chlorpyrifos and phoxim standard mixture solution after SPE preconcentration by (a) imprinted sorbent, (b) non-imprinted sorbent and (c) C_{18} sorbent for 50 mL at a flow rate of 0.56 mL min^{-1}.

The selectivity and enrichment of MISPE and C_{18} SPE was compared by passing 50 mL of a standard aqueous solution containing 10 μg L^{-1} of dichlorvos, chlorpyrifos and phoxim mixture at a sample flow rate of 0.56 mL min^{-1}. The results showed that the C_{18} cartridges had good concentration effect but no selectivity for dichlorvos, so the enrichment of dichlorvos, chlorpyrifos and phoxim were almost the same (Fig. 5c). The imprinted cartridge had a higher concentration effect and a better selectivity for dichlorvos than the C_{18} extraction column (Fig. 5a). These results clearly indicated that this imprinted polymer was more suitable as an SPE sorbent for scientific separation and extraction.

The analytical figures of merits for the present of MISPE–HPLC method for determination of dichlorvos were evaluated under optimal experimental conditions. With a sample loading flow rate of 0.56 mL min^{-1}, the detection limit ($S/N = 3$) based on three times the signal-to-noise ratio of the baseline near the analyte peak was 94.8 ng L^{-1}, the RSD for five replicate extractions of 10 μg L^{-1} dichlorvos was 4.41%, and the linear range of the calibration graph was 0.5–500 μg L^{-1}.

To evaluate the accuracy and application of the MISPE–HPLC method, the cucumber and lettuce leave samples spiked with dichlorvos at 0.005 and 0.02 μg g^{-1} were analyzed. For each sample, three measurements were performed. The results were satisfactory with recoveries ranging from 82.1% to 94.0%. It is known that dichlorvos is unstable and easily degraded in samples. Therefore, the recoveries of spiked dichlorvos in cucumber and lettuce leave samples were low. Furthermore, this imprinted extraction column is stable and can be used more than 80 times, enabling it to be used for practical applications.

4. Conclusions

In this study, a novel functional material was prepared by molecular imprinting technique using a room temperature ionic liquid-mediated template that avoided the drawback of traditional preparation methodologies. The prepared material showed improved stability, good selectivity and high adsorption capacity for dichlorvos, and was more suitable as sorbent for SPE than the C_{18}. Thus, a sensitive and fast method for the determination of trace dichlorvos was successfully developed. This method was evaluated for the analysis of cucumber and lettuce samples spiked with low levels of dichlorvos and good recoveries were achieved. The results of this study demonstrated that this MISPE–HPLC method will be a valuable and affordable tool for the monitoring of dichlorvos residues in foods.

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