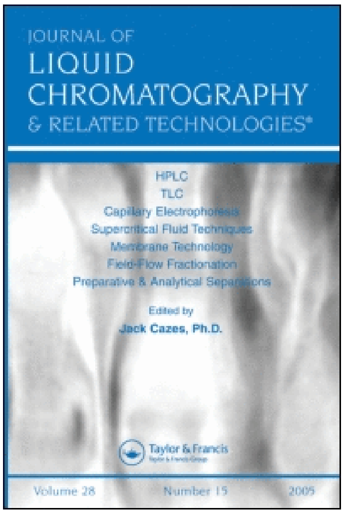

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Development and Application of Molecularly Imprinted Polymer as Solid Phase Extraction of Imidacloprid in Environmental Samples

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Abstract: A molecularly imprinted polymer (MIP) has been prepared by a thermal polymerisation method using methacrylic acid as the functional monomer, ethylene glycol dimethacrylate as cross-linking agent, acetonitrile as porogenic solvent, and imidacloprid as imprinted molecule (template). The experiments of MIPs-packed cartridge binding imidacloprid were done to assess the affinity of the MIPs, which were synthesized according to the different ratio of monomer to template, with imidacloprid. After optimization of MISPE protocol (acetonitrile: water = 1:4 (v/v) as washing solvent and methanol as elution solvent), the MISPE method was used for enrichment and clean up of water and soil samples. The recoveries of imidacloprid from spiked water and soil samples were not less than 87.7% and 89.2%. It confirmed that the MIP as specific SPE sorbents for cleanup and enrichment of the imidacloprid in real samples was feasible.

Keywords: Imidacloprid, Molecularly imprinted polymer, Solid phase extraction, Sorbents

INTRODUCTION

Imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N* -nitroimidazolidin-2-ylideneamine] (Figure 1) is a neonicotinoid insecticide with an extraordinary

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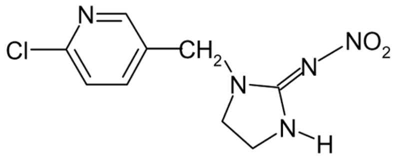


Figure 1. The structure of imidacloprid.

activity at very low applications rates, low toxicity, good systemic properties, and a lasting action.[1] Imidacloprid acts as an agonist of acetylcholine by binding to the postsynaptic nicotinic receptors in the insect central nervous system and its introduction represents a milestone in insecticide research.[2] The high root systemicity of imidacloprid was expected to solve problems arising from the direct contact between honeybees and the active compound, which has been shown to be highly toxic for bees.[3] However, Imidacloprid air dispersion, caused by pneumatic seed drills during sowing, results in contamination of bees and other sucking insects.[4,5] Thus, it is imperative to develop a reliable analytical method for quantifying imidacloprid at very low concentrations.

The most frequently reported method is based on liquid chromatography (LC) with a UV[6,7] or diode array detector (DAD);[8,9] other authors have used LC with a fluorimetric detector[10] and[11] or electrospray ionisation mass spectrometry (ESI-MS).[12] Solid phase extraction (SPE) is routinely used for cleanup and preconcentration in the analysis of biological and environmental samples. SPE has the advantages of simplicity, speed, and less consumption of organic solvents. However, generic sorbents usually lack selectivity, and are easily subjected to interference by non-target substances with similar characteristics.[13,14]

However, molecularly imprinted polymers (MIPs) are synthetic, polymeric materials designed to express high affinity and selectivity towards a single compound or a group of compounds related structurally to the template. Nowadays their use in solid phase extraction, so called molecularly imprinted solid phase extraction (MISPE), is by far the most advanced technical application of MIPs. Due to the inherent selectivity provided by MIPs, past years have seen a growing interest in this area and it has been developed extensively for solid phase extraction in the areas of environmental and pharmaceutical analysis, including compounds from biological matrices and environmental samples.[15–20]

In this paper, we first developed an original MIP against imidacloprid and report upon the application of polymer as solid phase extraction sorbent. The specific aim of the present work was to evaluate the molecular recognition properties of MIP in their application as SPE sorbents for the selective extraction of imidacloprid. In addition, the extraction of water and soil samples containing imidacloprid was investigated using the polymer.

EXPERIMENTAL

Chemicals and Materials

Imidacloprid (>99%) was obtained from Dr Ehrenstorfer Ltd (Augsburg, Germany). Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) were purchased from Fluka (Steinheim, USA). 2,2′-Azobis (2-isobutyronitrile) (AIBN), as the initiator, was from the China National Medicines Corporation Ltd. (Shanghai, China). Methanol of HPLC grade was from Fisher Scientific Co. (USA). Other chemical reagents including chloroform and acetonitrile were of analytical grade. Double distilled water and MilliQ water were prepared in our laboratory.

A stock solution of imidacloprid was prepared in methanol at a final concentration of 300 μg mL^{-1}. Quantification of samples was carried out using calibration curves of imidacloprid at concentrations in the range of 0.30–10.0 mg L^{-1}. Each determination was performed in triplicate.

Preparation of the MIPs

For preparation of the MIPs, the template was dissolved in a 3.5 mL acetonitrile in a 50 mL glass tube. Then a corresponding volume of MAA was added and incubated for 1 h (Table 1). The cross-linker, EGDMA, and the initiator AIBN were then added. After sonication for 10 min and purging with oxygen free nitrogen for 5 min, the tube was sealed and polymerization took place at 68°C for 24 h in a water bath. The resulting bulk polymers were ground mechanically and wet sieved by alcohol through a sieve. The template was subsequently

Table 1. Composition of polymerization mixtures for molecularly imprinted polymers and non-imprinted polymers

Code	Template (mmol)	Monomer (mmol)	Crosslinker (mmol)	Initiator (mg)	Template / Monomer
2-MIP	0.5	1	10	10	1:2
2-NIP	0	1	10	10	1:2
4-MIP	0.5	2	10	10	1:4
4-NIP	0	2	10	10	1:4
8-MIP	0.5	4	10	10	1:8
8-NIP	0	4	10	10	1:8

removed by continuous extraction with acetone in a Soxhlet apparatus for 12 h, until no imidacloprid could be detected by HPLC analysis. Then the polymers were washed with methanol for 30 min and dried at 60°C to reach a constant weight. The non-imprinted polymers (NIPs) were prepared and treated using the same methods as for MIPs, except that there was no template present during polymerization.

Preparation for MISPE Cartridges

One hundred milligrams of dried imprinted and non-imprinted polymer microspheres were suspended in 3–4 mL of methanol, packed into the SPE cartridges of 3.0 mL (Supelco, USA), with two glass wool frits at each end. The cartridges were washed with 5 mL methanol and preconditioned with 5 mL water before water sample loading.

Sample Extraction

Tap water samples, directly take from the laboratory, and soil samples, collected from Minhang campus of Shanghai Jiao Tong University, were shown to be free of imidacloprid contamination by HPLC. The samples were processed as described by S. Baskaran et al.,[21] with some minor modifications.

Triplicate tap water samples (10 mL) containing three spike levels of imidacloprid (5, 50, and 100 $\mathrm{ng \cdot mL^{-1}}$) were aspirated through the preconditioned MIP columns (flow rate 0.2 $\mathrm{mL \cdot min^{-1}}$). Then 1 mL of acetonitrile/water (1:4, v/v) was used to wash off the interferences. For the elution step, 4.0 mL methanol was used. The eluted fraction were concentrated by a nitrogen stream and fixed to 1 mL with methanol.

Soil materials (5 g) spiked with different concentrations of imidacloprid (20, 100, and 500 ng/g dry soil) were extracted with 10 mL of acetonitrile-water (80:20, v/v). The suspension was stirred and equilibrated for 2 h using a shaker. Following centrifugation (20 min, 1000 rpm), the aqueous solutions were filtered through filter paper and the operation of shaking and filtration was repeated. The combined extract was transferred to a 100 mL round bottomed flask and concentrated using a rotary evaporator. The residue was redissolved in 0.5 mL of acetonitrile for MISPE cleanup, then for HPLC analysis. Three replicates at each fortification level were extracted and analyzed by HPLC.

High Performance Liquid Chromatography (HPLC) Condition

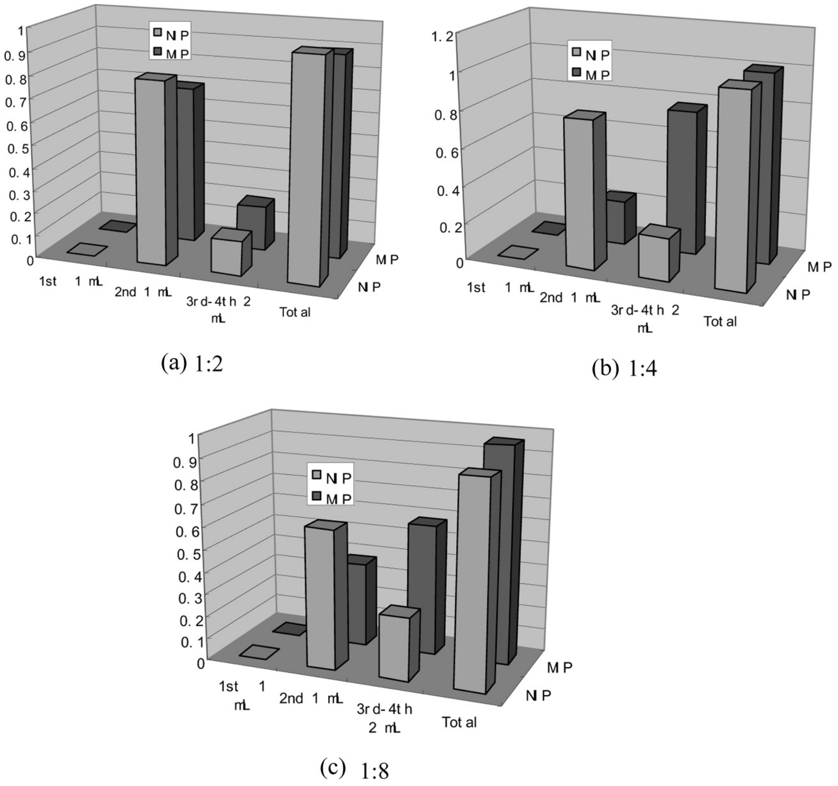
Samples were filtered through 0.45 μm filters before analyses by HPLC-DAD. The mobile phase was methanol with 0.8 $\mathrm{mL \cdot min^{-1}}$ flow rate. The column oven was kept at 30°C. The volume of the injection was 20 μL. The external standard method was adopted. Imidacloprid, $300 \cdot \mu g\,mL^{-1}$, was diluted with methanol. Serial dilutions in methanol were made to produce solutions with final concentrations in the range of 0.30–$10\,mg \cdot L^{-1}$. Concentrations of imidacloprid were determined and the peak areas of the standards were recorded. The slope and intercept of the calibration graph were obtained by linear regression of peak area versus concentration: $y = ax + b$, where a is the slope, b is the intercept, x is the concentration, and y is the peak area. The parameters obtained by the selected chromatographic conditions for imidacloprid calibration corresponded to: $y = 247915\ x + 24610$, $R^2 = 0.9949$. The accuracy and precision of the analytical method were 99.5% and 99.1%, respectively. The minimum detectable amount of imidacloprid was 3.2×10^{-9}g.

RESULTS AND DISCUSSION

MIP Synthesis

A molecularly imprinted polymer, a kind tailor made material, with high selectively for a target molecule were arisen from the synthetic procedure followed to prepare the MIP, in which a template molecule is linked by covalent bonds or non-covalent forces, to suitable monomer(s) containing functional groups. This link is responsible for the subsequent specific binding sites in order to binding with the target compound(s). In non-covalent imprinting the interactions between functional monomer and template during polymerization are the same as those between polymer and template in the rebinding step. These are based on non-covalent forces such as H-bonding, ion-pairing, and dipole-dipole interactions. This method was first introduced in organic polymers by the group of Mosbach.[22] Up to date, this method is the most widely used to create imprinted polymers against such as 2,4-D, hydroquinidine and steroids for its simplicity.[23–25] Presently, the most common functional monomer employed is methacylic acid adopted by many reporters.

It is well known that different ratios of template to monomer and/or cross-linker could affect the imprinted polymers' rebinding target compound character. In this study, 3 kinds of MIPs and the corresponding NIPs were synthesized at the different ratios of template to monomer (Table 1). The comparison amount of these polymers in the aspect of affinity to the imidacloprid were investigated in the present study. The results showed that the optimum ratio of template to functional monomer for the specific rebinding of imidacloprid was 1:4 (Figure 2), which had the best specific affinity to imidacloprid and highest recovery of 77.3% (evaluated according to the eluted portion of the third 1 mL plus the fourth



(a) 1:2

(b) 1:4

(c) 1:8

Figure 2. Relative recoveries of imidacloprid from fractions collected after MISPE extraction of 0.1 mL 2 μg · mL^{-1} imidacloprid in acetonitrile using MIPs or NIPs. (a) monomer:template = 2:1; (b) monomer: template = 4:1 and (c) monomer : template = 8:1. 1st present for the first 1 mL of elution after loading (water); 2nd present for the second 1 mL of elution after loading (water) and 3rd–4th present for the third 1 mL plus the fourth 1 mL of elution after loading (methanol).

1 mL) and could give the less washed loss of target analyte (about 23.7%, evaluated according to the eluted portion of the second 1 mL). To the next two kinds of MIPs, the most loss of imidacloprid at the second 1 mL elution portion gives the reason for low recovery of imidacloprid (56.8% for the ratio of 1:8 and 19.4% for the ratio of 1:2). As far as the 3 kinds of NIPs are concerned, they were all given very low recoveries of imidacloprid for their low affinity to the imidacloprid (15.1 ~ 28%). For the polymers with a 1:2 ratio of template to functional monomers, an excess of the template with respect to the functional monomer yielded insufficient specific sites on the surface of polymers. The adsorption recovery and specificity of those at 1:4 was higher than those at 1:8, indicating that lower ratio of template to functional monomers may

not have sufficient specific complexation in pre-polymerization. So these MIPs made by a 1:5 ratio of template to functional monomer were selected for further experiments.

The Effect of Extraction of Percolated Volumes

Sample loading is one of the important steps in MISPE with the main purpose of quantitatively and selectively adsorbing the analyte. In this step, the selection of the sample medium is crucial, because it directly affects the recognition ability of the MIP. In general, if the sample is percolated through the MIP in a low polarity solvent, a selective loading step can be achieved in which only the target analyte is selectively retained on the MIP while the sample matrix is non-retained.[26] The selection of loading solvent is also dependent on the kind of template/monomer interactions during polymerization and on the porogen used.[27] Therefore, many studies have used pre-MISPE transfer of the analyte to an organic solvent by liquid-liquid or solid-liqid extraction prior to the selective MIP extraction.[28–30]

The current trend is towards the use of extraction protocols, which are based on direct loading of the aqueous sample. Many studies use a water solvent switch on the column, which removes contaminants by both aqueous and solvent washes prior to selective elution using a solvent containing acid.[31–33] To obtain a polymer able to bind the analyte selectively in aqueous samples, porogens, monomers, and crosslinkers are all researched for the polymer synthesis.[34,35] In this study, it was investigated whether or not the volumes of water sample percolated on the MISPE can give a breakthrough of the target analyte. The loading volume of imidacloprid water solutions ranging from 2.5 to 100 mL was evaluated. The total amount of imidacloprid loading was 0.2 μg in 2.5, 5, 10, 20, 50, and 100 mL water (Figure 3). The results were shown in Figure 3. It can be seen from Figure 3, that the recoveries from the different loading volumes ranged from 71.3–102.4%. The recovery dramatically decreased with the increasing of the sample volume. The results indicated that the imidacloprid would be almost entirely absorbed by MIP, and eluted when the percolated volume is less than 50 mL. Also, there were obvious breakthrough phenomenon when the percolated volumes of samples ranged from 50 to 100 mL.

Solid Phase Extraction Analysis

The purpose of the washing step is to maximize the specific interactions between the analyte and MIP and to simultaneously elute the interfering compounds retained in the polymer matrix. For this purpose, low polarity

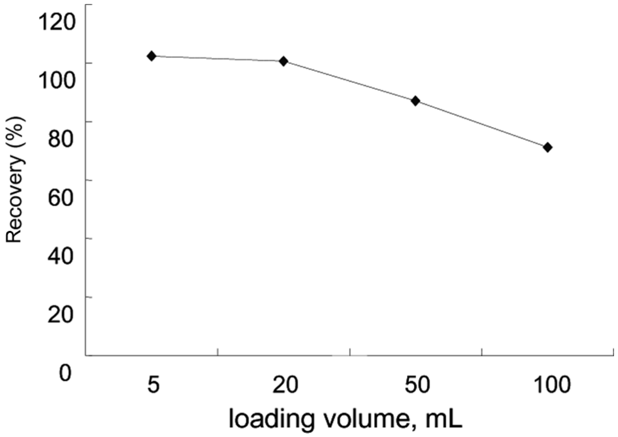


Figure 3. The recoveries of imidacloprid under the condition of different loading volumes.

organic solvents were the most widely used. However, good results have been obtained with acetonitrile and methanol solvents.[36,37] To retain most of the analyte in the polymer, different concentrations of acetonitrile and methanol in water solution were used in the wash step (Figure 4) in our research. The washing solution of MIP was adjusted by optimizing the ratio of acetonitrile in water. With increased acetonitrile in the wash solution, the recoveries of imidacloprid decreased from the MIP. When the acetonitrile concentration is 20% (v/v) the recovery of imidacloprid was only about 80%. The same phenomenon according to the recovery can be observed from Figure 4, when the solution of different concentrations of methanol

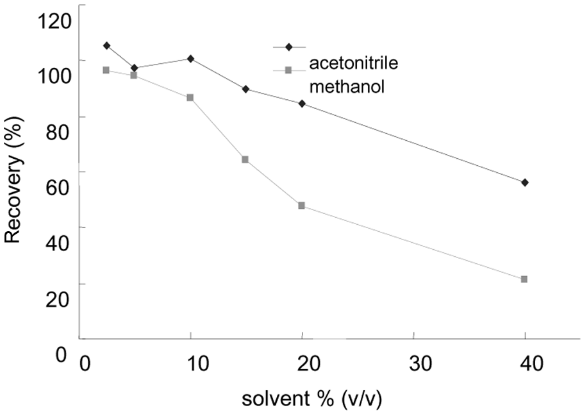


Figure 4. The recoveries of imidacloprid after the different wash solution.

Table 2. Analysis of imidacloprid in spiked water and soil samples on the MISPE cartridges

Sample	Concentration	Recovery (%)	RSD (%)
Water	5 $\mu g{\cdot}L^{-1}$	94.8	5.4
	50 $\mu g{\cdot}L^{-1}$	96.4	3.5
	100 $\mu g{\cdot}L^{-1}$	87.7	4.1
Soil	20 $\mu g{\cdot}kg^{-1}$	89.2	2.7
	100 $\mu g{\cdot}kg^{-1}$	104.3	4.3
	500 $\mu g{\cdot}kg^{-1}$	97.9	7

in water was used as the wash solution. The recoveries from the MIP in the wash condition of methanol water solution were largely decreased compared with those after washing with the wash condition of corresponding acetonitrile concentrations in water. So the 20% acetonitrile water solution (v/v) was adopted as washing solution in the subsequent experiments.

Performance of the MIP in Samples

Under the optimal conditions mentioned above, the important parameters of the proposed method, such as recovery and RSD, were studied when the imidacloprid spiked water and soil samples were treated with the MIP cartridge. Normally, blank samples are spiked with known quantities of imidacloprid and recoveries are calculated to check the applicability of the extraction method. In this study, tap water (10 mL) and blank soil (5 g)

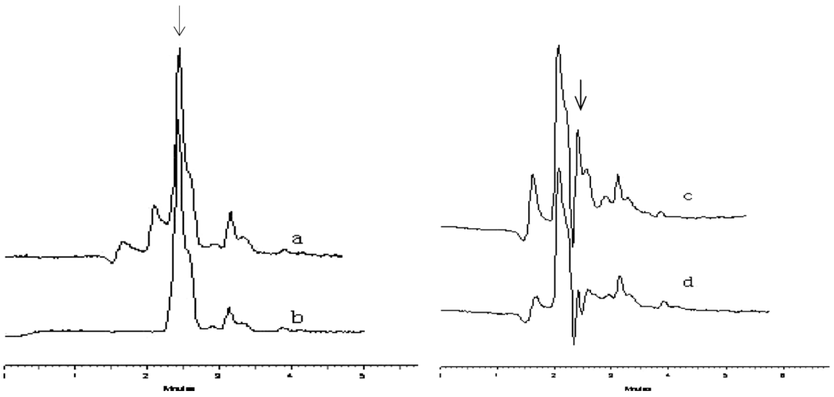


Figure 5. The chromatograms obtained at 287 nm by HPLC with DAD detector. a: extraction from soil sample spiked imidacloprid and treated by MISPE; b: soil standard solution; c: extraction from soil sample spiked imidacloprid without the treatment by MISPE; d: extraction from black soil sample.

spiked with 0.1 mL standard solutions of imidacloprid at three concentration levels (5, 50, 100 ng/mL for water sample and 20, 100, 500 ng/g for soil sample) (Table 2) were used to evaluate the developed method in the aspect of recovery and RSD. The recoveries of spiked water ranged from 87.7% to 94.8% with RSD below 5.4%. For soil samples, the recoveries ranged from 89.2% to 104.3% with RSD below 7.0% (Table 2). Figure 5 showed chromatograms of the black soil sample and imidacloprid spiked soil sample after extraction by the present approach and the imidacloprid standard solution (methanol). There is a little peak near the peak of imidacloprid for the soil sample without treatment by the MIP cartridge. Nevertheless, no peak could be observed at the retention time of imidacloprid after the sample had been treated with the MIP cartridge.

CONCLUSION

A non-covalent polymerization method was used for preparing an imidacloprid molecularly imprinted polymer. The affinity of polymer against imidacloprid with a different ratio of monomer to template was investigated. It was found that the MIP with 4:1 ratio of monomer to template characterized the best recognition with imidacloprid. Furthermore, the MIP particles as adsorbents in SPE were successfully investigated for the enrichment and cleanup of water and soil samples with an optimized procedure. The successful MISPE protocol (acetonitrile:water = 1:4 (v/v) washing and methanol elution) achieved the recovery ranging from 87.7% to 94.8% with RSD below 5.4% for water samples and the recovery ranging from 89.2% to 104.3% with RSD below 7.0% for soil samples. The satisfactory recovery and RSD values indicated that the MIPs obtained have a great potential for utilization as specific SPE sorbents for imidacloprid cleanup and enrichment in practical use.

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