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Molecularly imprinted polymers for solid phase extraction of orghanophosphorus pesticides

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ABSTRACT

Molecularly imprinted polymer-solid phase extraction (MIP-SPE) adsorbent was prepared for the analysis of selected organophosphorus pesticides (OPPs) in environmental sample. In this work, the influence of process parameters on the preparation of imprinted polymer is presented. In the procedure of polymerization, molecularly imprinted bulk polymer was prepared using quinalphos and methacrylic acid (MAA) as template molecule and functional monomer, respectively. The influence of the following parameters on recognition properties was investigated namely, types of crosslinker (ethylene glycol dimethacrylate (EGDMA) or divinylbenzene (DVB)) and porogenic solvents (acetonitrile, dichloromethane, toluene, chloroform). Molar ratio of template:functional monomer:cross linker was fixed at 1:4:20. Soxhlet extraction method was conducted to remove the imprint molecule in order to create the recognition sites. A blank/non-imprinted polymer (NIP) was produced simultaneously using identical procedure except in the absence of template molecule.

| Molecularly imprinted polymer | Solid phase extraction | Organophosphorus pesticides |

1. INTRODUCTION

A molecular imprinted polymer (MIP) is a polymer that is formed in the presence of a molecule that is extracted afterwards, thus leaving complementary cavities behind [1]. MIPs are tailor-made materials with high selectivity for target molecules. The selectivity of MIPs arises from the synthetic procedure by varying several factors, such as functional monomer, cross linker, porogenic solvents, and polymerization methods. One of the most exciting applications of MIPs is as sorbent for solid-phase extraction (SPE). In SPE, the sample is passed through a cartridge or a packed column filled with a solid sorbent where the analytes are absorbed and then eluted with an organic solvent. This procedure present several advantages: (i) it is less time consuming than liquid-liquid extraction (LLE) procedure, (ii) it decreases the use of toxic solvents, (iii) the extraction efficiency is not hindered by the formation of emulsions, and (iv) offers the possibility of automation [2,3].

Organophosphorus pesticides are a type of pesticides extensively used as alternatives to highly persistent, bioaccumulated organochlorine compounds for crop protection and tree treatment.

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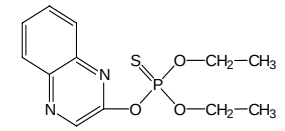
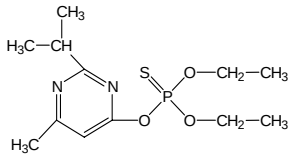
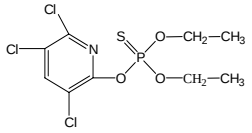


Quinalphos



Diazinon



Chlorpyrifos

Figure 1: Target analytes

Over the past few years, organophosphorus pesticides (OPPs) contamination of drinking water and agricultural products has become a major concern and the application of OPPs is steadily increasing. It is therefore of interest to develop a new MIP-SPE by using quinalphos as a template by non-covalent imprinting method. Target analytes with similar structures, namely quinalphos, diazinon, and chlorpyrifos (Figure 1) were considered in this study. The

process parameters influencing the polymerization, the types of cross linker, and porogen solvents were studied to enhance the selectivity of MIP-SPE towards the analyte. A MIP-SPE method based on the imprinted polymer was also developed to selectively extract target analytes from sample matrix.

2. EXPERIMENTAL

2.1 Preparation of the polymers by "bulk" polymerization

Several MIPs for quinalphos were prepared under different conditions. In the preparation procedure (Figure 2), quinalphos (1 mmol) and methacrylic acid (MAA, 4 mmol) as template and functional monomer, respectively, were dissolved in 6 mL of different porogenic solvents namely acetonitrile (ACN), dichloromethane (DCM), toluene, or chloroform (CHCl3) in a glass polymerization test tube. After oscillating for 15 min, ethylene glycol dimethacrylate (EGDMA, 20 mmol) or divinylbenzene (DVB, 20 mmol) as cross-linker and 2,2′-Azobisisobutyronitrile (AIBN, 50 mg) as initiator were added into the solution. The test tube was placed on ice and deoxygenated with nitrogen for 15 min, then sealed under vacuum. After that, polymerization reaction was carried out at 60°C for 24 h in the thermostat-controlled water bath. The resultant hard bulk polymers were crushed, ground, and sieved through 75 µm sieve. The polymer particles obtained were washed with a mixture of methanol-acetic acid (9:1, v/v) successively in Soxhlet apparatus until template could not be detected by UV spectrophotometry. The extracted particles were then washed with methanol to remove residual acetic acid. Finally, the collected particles were dried at 55°C in oven under vacuum for 12 h. For comparison, blank/non-imprinted polymer (NIP) was prepared and treated in exactly the same way except that the template molecule was absent in the polymerization step.

2.2 Adsorption study

Adsorption experiments were carried out to study the rebinding performance of polymers and the adsorption effect for different cross linker and solvent during polymer preparation as follows. The MIP (50 mg) was added into 50 mL conical flask and was mixed with 10 mL of solution containing a known concentration of 10 mg L^{-1} quinalphos in acetonitrile. The mixture was shaken at room temperature for 24 h and centrifuged using a high-speed centrifuge. The supernatant (5 mL) was taken out for the determination of free quinalphos concentration and quantity of quinalphos adsorbed for different types of cross linker and porogen solvent. The free concentration (C_{free}) of quinalphos after the adsorption was recorded by UV spectrometry at 236 nm. The adsorption quantity (*B*) was calculated by subtracting the free concentrations from the initial concentrations.

2.3 Molecularly imprinted polymer solid phase extraction procedure

Dry imprinted and non-imprinted polymer particles (300 mg each) were packed into 3.0 mL empty SPE cartridges with two glass-wool frits at each end. The cartridges were washed with methanol (10 mL) and conditioned with acetonitrile (10 mL) before use. A 10 mL mixture of selected OPPs (5 mg L^{-1}) was loaded onto the MIP-SPE and NIP-SPE cartridges, respectively. After loading, vacuum was applied to the cartridges for 30 min in order to remove the residuals solvent. The cartridges were washed with 10 mL of acetonitrile to eliminate molecules retained by non-specific adsorption to the polymer. Eluting step was then performed using 10 mL of methanol-acetic acid (9:1, v/v) mixture solution. Finally, the elution fractions were dried under the gentle nitrogen stream. The residue was redissolved in 1 mL acetonitrile for HPLC-UV analysis.

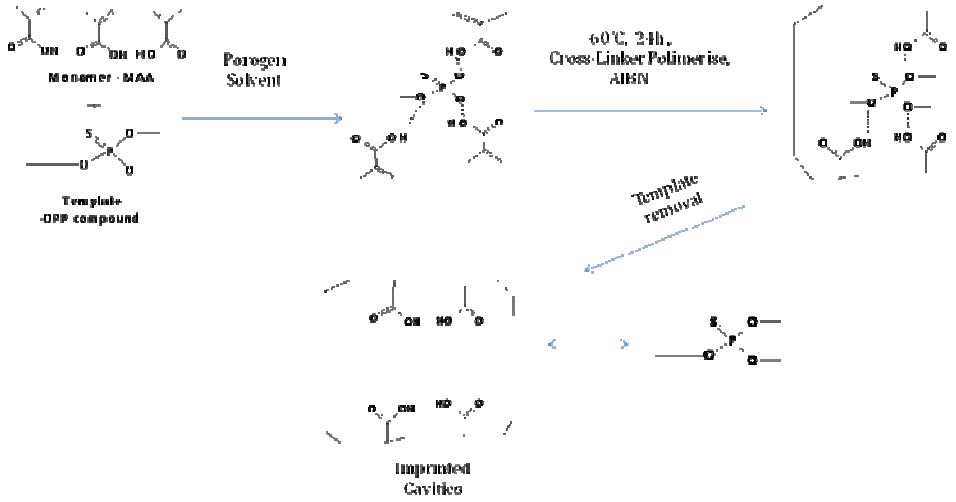


Figure 2: Schematic depiction of the preparation of molecular imprints

3. RESULTS & DISCUSSION

3.1 Polymers synthesis and characterization

Since MIPs have a stronger load capacity and a larger population of micropores by thermal initiation [4], a thermo-polymerization procedure was employed at 60˚C for 24 h. MAA was choosen as functional monomer due to the high specific binding but low non-specific adsorption of the MIPs.

In an imprinted polymer, the cross linker employed ensures a high degree of cross-linking (excess 80%) for achieving specificity. The functions of the cross-linker are to stabilize the imprinting binding sites, control morphology and influence the mechanical stability of the polymer matrix [5]. Two cross-linkers, EDMA and DVB were investigated to determine their influence on the adsorption properties of MIPs. Based on UV absorbance, the results showed that the absorption of EDMA on template molecule was much higher than that for DVB cross linker (Figure 3). This is due to the molecular chains of MIPs linked by EDMA are more feasible while the polymers containing DVB are considerably rigid but sometimes they do not facilite the rebinding molecule with MIPs.

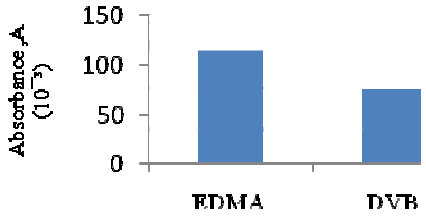


Figure 3: Effect of different cross-linkers on the absorbance towards molecule template by rebinding experiment.

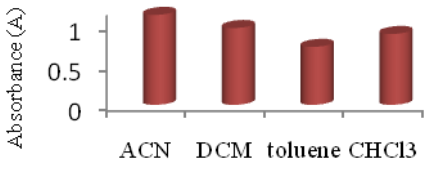


Figure 4: Effect of various porogen solvents on absorbance towards molecule template by rebinding experiment.

Table 1: Porosities of polymers determined by BET analysis

Sample	MIP	NIP
BET surface area (m^2g^{-1})	6.753	1.007
Pore volume (cm^3g^{-1})	9.461	1.355
Pore size (Å)	5.604	4.879

Since the specific surface area, pore volume, and pore size of polymer strongly influence the efficiency of adsorption, the nitrogen adsorption analysis of Brunauer-Emmett-Teller (BET) was used to evaluate these parameters. The results are shown in Table 1. It was clearly evident that the MIP has larger BET size and pore volume than the NIP due to the existence of imprinting effect in polymer.

3.2 MIP-SPE analysis

Figure 5 shows a HPLC-UV chromatogram of the separation of target pesticides in tap water sample (spiked with 5 mg L^{-1} OPPs). Peak areas of the analytes obtained from the MIP-SPE and NIP-SPE analyses are summarized in Table 2. The results showed that the MIP-SPE is a potential sorbents for selective enrichment, separation, and detection of OPPs from sample matrix.

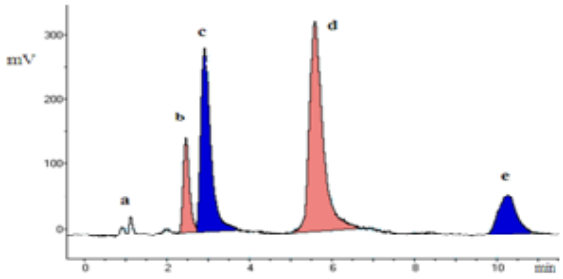


Figure 5: HPLC-UV separation of organophosphorus pesticides. Peak identification: (a) acetonitrile, (b) diazinon, (c) hexaconazole (internal standard), (d) quinalphos, (e) chlorpyrifos.

Table 2: Peak area of OPPs

Sample	Peak area (mV)		
	Diazinon	Quinalphos	Chlorpyrifos
MIP	1434.23	6953.10	1984.05
NIP	1102.75	5730.53	1657.79

4. CONCLUSION

This study demonstrated that quinalphos imprinted polymer for the separation and preconcentration of quinalphos was successfully synthesized by bulk thermal polymerization at a temperature of 60˚C by non-covalent approach using MAA, EDMA, and acetonitrile as functional monomer, cross linker, and porogen solvent, respectively. Optimal imprinting parameters for enhanced recognition properties towards quinalphos were obtained, which were very important for the successful preparation of the MIPs. The synthesized polymer showed good selectivity and high adsorption capacity. The results showed that MIP-SPE has great potential to be used as an alternative adsorbent for selective enrichment and separation and detection of OPPs from sample matrix prior to HPLC-UV.

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