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Binsalom, A., Chianella, I., Campbell, K., & Zourob, M. (2016). Development of Solid-Phase Extraction Using Molecularly Imprinted Polymer for the Analysis of Organophosphorus Pesticides-(Chlorpyrifos) in Aqueous Solution. Journal of Chromatography and Separation Science, 7(6). DOI: 10.4172/2157-7064.1000340

Published in:
Journal of Chromatography and Separation Science

Document Version:
Publisher's PDF, also known as Version of record

Journal of Chromatography
Separation Techniques

Binsalom et al., J Chromatogr Sep Tech 2016, 7:6
DOI: 10.4172/2157-7064.1000340

Research Article Open Access

Development of Solid-Phase Extraction Using Molecularly Imprinted Polymer for the Analysis of Organophosphorus Pesticides-(Chlorpyrifos) in Aqueous Solution

Binsalom A[1], Chianella I[2], Campbell K[1] and Zourob M[3]

[1]Institute for Global Food Security, School of Biological Sciences, Queen's University, UK
[2]Cranfield Health, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK
[3]Department of Chemistry, Alfaisal University, Riyadh, KSA

Abstract

A new and selective sorbent for molecularly imprinted solid-phase extraction (MISPE) was prepared to extract chlorpyrifos (CPF) residue from solutions. The extracted analyte was analyzed by high performance liquid chromotography (HPLC) coupled with photodiode array detection. To synthesize the molecularly imprinted polymers, four different pyrogens (acetonitrile, toluene, dichloromethane and chloroform) were initially studied. CPF was used as the template molecule, methacrylic acid as the functional monomer, ethylene glycol dimethacrylate as the cross-linker. Thermo-polymerization method was used to produce bulk polymers. In order to determine the medium that enhances the best molecular recognition, the adsorption study of CPF to the MIPs was investigated. Both organic solvents and water were utilized as media. The acetonitrile solvent was finally selected as pyrogen for the synthesis of the polymers and water was chosen as the medium for loading the analytes into the polymers. The selectivity of the MISPE method for CPF and other pesticides in aqueous solution was also assessed.

Keywords: Molecularly imprinted polymer; Solid phase extraction; Chlorpyrifos pesticide

Introduction

Sample preparation plays a key role for a fruitful and accurate analysis of pesticide residues in food [1]. The ultimate objective of the sample preparation is to pre-concentrate and purify the desired compounds of a complex matrix. Solid Phase Extraction (SPE) is amongst the most common techniques used to extract, purify and concentrate analytes. This technique relies on the repartition of the analyte between a solid phase (usually a polymeric sorbent such as C18 packed in a tube) and a mobile phase namely the solvent used for loading, washing and finally recovering the analyte. Standard sorbents like C18 do not have the require selectivity and binding capacity. Molecularly imprinted polymers (MIPs), which are synthetic polymeric materials that contain receptor sites able to recognize a target compound or similar structures [2], have shown to be an excellent sorbent for molecularly imprinted solid-phase extraction (MISPE). MISPE usually is used to purify and pre-concentrate a target analyte [3-5]. MIPs are produced by a polymerization process following a self-assembly step between the target analyte and functional monomers. Figure 1 shows the synthetic process; which involves a functional monomer, a cross-linker, an imprinted molecule (template), an organic solvent (or pyrogen) and an initiator.

MIPs are highly cross-linked polymers, with binding sites specific and selective for the target molecule template), which was used during the polymerization. MIPs have several advantages over natural bio-molecules, with stability being the most important. In fact they can be used in harsh conditions, such as high temperature, pressure, extreme pH, and organic solvents [6].

Organophosphate (OP) is a major class of pesticides and has a number of applications in agriculture, public health and home use. Chlorpyrifos (CPF) is used as an insecticide to control insects in the field, indoor and outdoor. MIPs have been already successfully developed for organophosphorus pesticides. For example, MIPs were synthesized by bulk polymerization for the chromatographic determination of OP pesticides, using disulfoton as a template [7]. Liu and his colleagues produced MIP microspheres (MIPMs) via emulsifier-free polymerization method for CPF [8]. Also, MIP utilizing quinalphos as a template was developed and applied as SPE sorbent for sample enrichment of organophosphorus pesticides including diazinon and CPF [9]. Besides, CPF was used to synthesize magnetic MIP (MMIPs) by surface imprinted polymerization [10].

This work reports the synthesis of different MIPs synthesized using various pyrogens: acetonitrile (ACN), dichloromethane (DCM), chloroform ($CHCl_3$) and toluene (TOL). The four different MIPs were all prepared in bulk format by thermal polymerization using CPF as template, methacrylic acid (MAA) as monomer and ethylene glycol dimethacrylate (EGDMA) as cross linker. Among all the pyrogens tested for preparation of MIPs, ACN has shown to produce the best MIP for extraction of CPF. The resulting polymer has the potential to be applied as MISPE for selective extraction for CPF pesticide from aqueous solutions.

Materials and Methods

Materials

Chlorpyrifos (CPF), chlorpropham (CIPC), propham (IPC), 3-chloroanaline (3-CA), 3,5,6-trichloropyridinol (TCP), methacrylic acid (MAA), 2,2′-azobisisobutyronitrile (AIBN), ethylene glycol dimethacrylate (EGDMA), and silicon oil were purchased from

***Corresponding author:** Binsalom A, Institute for Global Food Security, School of Biological Sciences, Queen's University, UK, Tel: +4402890976514; E-mail: abinsalom01@qub.ac.uk

Received November 01, 2016; **Accepted** November 08, 2016; **Published** November 14, 2016

Citation: Binsalom A, Chianella I, Campbell K, Zourob M (2016) Development of Solid-Phase Extraction Using Molecularly Imprinted Polymer for the Analysis of Organophosphorus Pesticides-(Chlorpyrifos) in Aqueous Solution. J Chromatogr Sep Tech 7: 340. doi: 10.4172/2157-7064.1000340

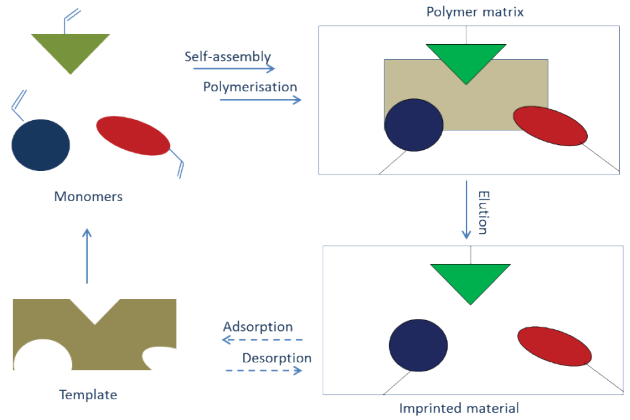


Figure 1: Synthesis of molecularly imprinted polymers (MIPs).

Sigma Aldrich (UK). Acetonitrile (ACN), methanol (MeOH), toluene, dichloromethane (DCM), acetic acid, mortar and pestle with 199 mL capacity were purchased from Fisher Scientific (Dorset, UK). The 75 and 125 µm mesh size sieves used were from Retsch. All chemicals and solvents were HPLC-analytical grade and used as received.

HPLC chromatography method

The quantification of the target analyte was conducted in a isocratic mode using an HPLC (Agilent Technology, 1200 series) equipped with UV/Vis detector and coupled with a Gemini C18 (150 × 4.6 mm, 5 µm) column (Phenomenex, UK). A sample volume of 20 µl was injected using a mobile phase consisting of 85% MeOH and 15% H_2O, adapted from [11] the mobile phase flow-rate was set at 1 ml/ min. Chromatograms were recorded for 10 minutes at the wavelength of 240 nm. A calibration curve for the target analyte was performed for every quantification experiment using standards over a concentration range of 10 to 500 ng/ml.

Polymer preparation

All CPF-MIPs were prepared under the same conditions except for the pyrogen. The synthetic compositions are represented in Table 1. The polymerization was achieved with the ratio (1:4:20) for template, MAA and EGDMA respectively as follow: CPF (0.5 mmol), MAA (2 mmol) as functional monomer, EGDMA (10 mmol) as a cross-linker. These were dissolved in 3.017 mL of different pyrogens namely ACN, DCM, $CHCl_3$ and TOL in a 15 mL glass vial. After mixing, the initiator AIBN (30 mg) was added into the solution, which was purged with nitrogen for 5-7 min, and then polymerization was performed at 65°C for 24 h in a thermostat-controlled oil bath. Then the resulting monoliths were ground and sieved using 75-125 µm sieves. After that, MIPs were washed with a mixture of MeOH-acetic acid (9:1, v/v) in a Soxhlet extractor for 24 h to remove any trapped template molecule and were dried at 55°C in an HPLC oven (Shimadzu CTO-10AC). For each MIP, a corresponding non-molecularly imprinted polymer (NIP) was prepared and handled in the same way but without the presence of the template at the polymerization step.

After the synthesis, portions of the polymers (30 mg of both MIPs and NIPs) were packed into empty 1 mL SPE columns (polypropylene, from Sigma) and these were fitted into a solid phase extraction manifold with 12 positions (Supelco) connected to a pump (KNF Laboport® mini-pump) for the vacuum.

MIPs	T	FM	XL	Molar ratio*	Solvent	Polymerisation condition
MIP1	CPF	MAA	EDGMA	1:4:20	ACN	Thermal 65°C
MIP2	CPF	MAA	EDGMA	1:4:20	$CHCL_3$	Thermal 65°C
MIP3	CPF	MAA	EDGMA	1:4:20	DCM	Thermal 65°C
MIP4	CPF	MAA	EDGMA	1:4:20	TOL	Thermal 65°C

*Molar ratio: Template (T); Functional monomer (FM); Crosslinking monomer (XL).

Table 1: Different pyrogens were used to develop the MIPs and NIPs.

Affinity assessment of MIP by SPE

First, an attempt was made to assess whether the same organic solvents used as pyrogens could be utilized as media for loading the target analyte into the MIPs. For these experiments, solutions of CPF (1 mL of 100 ng/mL), prepared in the four different organic solvents, were loaded into the MISPE and NISPE tubes. The filtrates were collected and injected into the HPLC to quantify the residual amount of CPF.

To assess the affinity of the polymers in aqueous solutions, after conditioning MISPE tubes with MeOH (3 mL) and water (3 mL), CPF (30 mL of 500 ng/mL prepared in water) was loaded into all MISPE tubes. These were then washed with several different amounts and mixtures of ACN-water and MeOH-water followed by elution with MeOH-acetic acid (90:10, v/v). The filtrates of all the steps were collected and injected into the HPLC CPF quantification. Based On the results of the washing step optimization, the final SPE protocol was as follow: loading 30 mL of CPF sample (500 ng/mL prepared in water) into MISPE and NISPEs, followed by washing with 5 mL of methanol-water (50:50 v:v) and elution with 5 mLs MeOH-acetic acid (90:10; v/v). All filtrates were collected for HPLC analysis.

Polymer binding capacity

After packing SPE tubes with the CPF-MIP (30 mg), the binding capacity was determined by continuously loading a CPF standard solution prepared in water into the MISPE tubes. After conditioning the tube with MeOH (3 mL) and water (3 mL), 1 L of 500 ng/mL of CPF solution prepared in water was loaded on the tubes, a total amount of CPF (500 µg). MeOH-water (50:50, v/v) (5 mL) and MeOH-acetic acid (90:10, v/v) (5 mL) were used for washing and elution steps. All filtrates in the loading, washing and elution steps were collected for HPLC analysis. The binding capacity of the MISPE reported as µg of CPF bound / g polymer was calculated with the following formula: binding capacity=[(500-X)/0.03 g], where 500 (µg) is the total loaded amount of CPF, X (µg) is the amount of CPF-residue-found in the filtrates, and 0.03 (g) is the polymer mass of a MISPE. The value was then extrapolated for 1 g of MIP.

Selectivity test

To investigate the MIP selectivity in water, analytical standards of analogues of CPF and other pesticides and herbicides (CIPC, IPC, 3-CA and TCP), whose chemical structures are shown in Figure 2, were tested. For the experiments, after conditioning the MISPE and NISPE tubes with MeOH (3 mL) and water (3 mL), aqueous solutions of CPF, CIPC, IPC, 3-CA and TCP (30 mL of 500 ng/mL) were loaded into MISPEs. This was followed by washing with 5 mL MeOH-water (50:50) and recovery with 5 mL of MeOH and acetic acid (9:1; v/v). The filtrates of all the steps were collected and injected into the HPLC for quantification of CPF and the other tested compounds. The experiments were performed in triplicate.

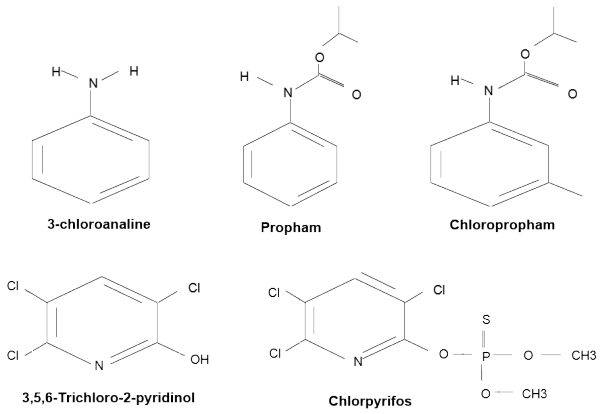


Figure 2: Structures of compounds used in the selectivity test.

Results and Discussion

Polymer preparation

The creation of polymeric binding cavities that capable to recognize a target analyte can be achieved via non-covalent interactions (e.g., hydrogen bonds, electrostatic and ionic interactions) or by covalent and semi-covalent interactions [12]. Regardless of the method, the configuration and alignment of functional groups in the polymeric network are crucial for a specific and selective recognition. In this work, the non-covalent method was preferred over the others, because of its wide applicability and flexibility. Molecularly imprinted polymers can be prepared in many formats (e.g., bulk, films, microparticles and nanoparticles), with the bulk format being the most straightforward, simple and suitable to produce an SPE sorbent. Therefore, bulk polymerization with the optimum ratio of 1:4:20 of template, monomer and cross-linker respectively was selected for this work. The molar ratio for reagents has been proven to produce good monomer-template interactions in the polymeric network of bulk polymers [13]. MAA was chosen here as it is a widely used functional monomer which can behave both as a hydrogen bond donor and acceptor if it is used with a suitable pyrogen [14]. The proposed interaction between MAA and CPF takes place via the oxygen atoms presents in the structure of both compounds [15,16]. EGDMA was used as the cross-linking agent to strengthen the imprinted binding sites and provide mechanical stability to the polymer matrix. In this method, a high proportion of cross-linking agent was used to give the polymeric network specificity and rigidity as well as strengthen the binding site [17].

In this work polymerization was performed by a thermal method to produce polymers with a microporous structure, which maximize surface area and the number of binding sites and consequently to achieve materials with high binding capacity [18,19].

The strength of the assembly between a template and a functional monomer is governed by the physical and chemical characteristics of the solvent. The solvent can impart an effective imprinting particularly in a non-covalent method. In addition, it can also change the polymer morphology and porosity, which subsequently affects the interactions during the rebinding experiments. Therefore, initially, four different pyrogenic solvents were used to synthesize the polymers and then to identify an appropriate pyrogen which could generate a good imprinting for CPF. As a result, aprotic and non-polar pyrogens solvents such as ACN, DCM, $CHCl_3$, and toluene were selected for this study [20]. Such solvents were preferred due to their capability to promote non-covalent interactions without interfering with the radical polymerization. MIPs and NIPs were therefore successfully synthesized using the four pyrogens.

MIP affinty assessment

The basis of molecular recognition is to preserve the interactions established between a template and MAA in the pre-polymerization mixture. It has been indicated that CPF binds MAA via hydrogen bonds. Thus, the four different pyrogenic solvents used in this work were selected to maximize such interactions and impart affinity and selectivity to the resulting MIPs. Therefore, MIPs and NIPs prepared with the four pyrogens were packed in empty SPE tubes and screened for their affinity towards CPF. Initially, the organic solvents; ACN, DCM, $CHCl_3$ and TOL, used for the synthesis, were investigated as solvent for loading CPF (100 ng/ml) into the tubes. In fact, it has been stated that employing the same solvent as a pyrogen for the polymerization and as media for analyte rebinding is beneficial as there can be a memory effect during rebinding [21]. The results indicated none of the MIPs and NIPs showed sufficient affinity and binding capacity for the target analyte in any of the organic solvents tested (data not shown). One reason for these results might be that the highly hydrophobic CPF preferred to establish interactions with the aprotic and low polar organic solvents rather than with the more hydrophilic polymer matrix containing MAA groups [22]. Therefore, the MIP affinity study was repeated using water as a loading solvent.

Changing the loading solvent to water alters the chemistry of interactions between CPF and the MIPs, which in such environment is mainly due to nonspecific hydrophobic interactions and in part to electrostatics interactions [23]. Thus a high absorption (specific and nonspecific) of CPF to the polymers was expected. In this conditions, the washing step following the analyte loading becomes the crucial step capable to evidence the selectivity of the MIPs by disrupting the weakest nonspecific interactions [24]. Even though none of the MIPs synthesized here demonstrated sufficient affinity for CPF in organic solvents, the MIP prepared in ACN was the only one consistently showing better binding than the corresponding NIP in all the testing conditions. Therefore, the washing step was firstly optimised using ACN-MIP and ACN-NIP, polymers that prepared in ACN, a standard solution of CPF (30 mL of 500 ng/ml in water) was loaded and totally bound to the MIPs and N, then different mixtures of methanol or acetonitrile and water (5 mL) were tested as washing. The amount of CPF in the filtrates was quantified by HPLC and the results are reported in Figure 3. Clearly, all mixtures containing ACN at 10, 20 and 50% in

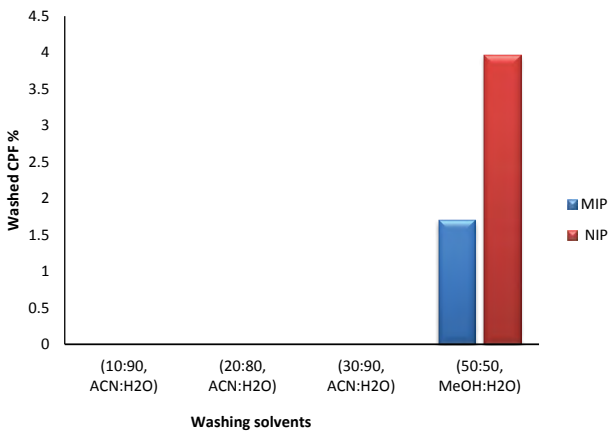


Figure 3: SPF washed by different mixtures (5 ml). MISPE and NISPE prepared in ACN were loaded with 30 ml of CPF (500 ng/mL).

water were not capable to disrupt the nonspecific binding in either the MIP or NIP. This could be explained by the fact that ACN was the solvent used to synthesise the polymers and therefore it promotes interactions between the polymers and template. In addition, ACN is slightly more polar than MeOH (polarity index for 5.8 for ACN and 5.1 for MeOH) [25] and therefore less capable to wash out a non-polar compound such as CPF. Conversely, MeOH seemed to be capable to disrupt some of the weak interactions between polymers and CPF to achieve an acceptable washing. Therefore, the mixture MeOH: water (50%: 50%), was then able to disrupt in part the non-specific interactions and remove a greater amount of CPF from the NIP than the MIP. The mixture used for the subsequent step, the elution consisting in 5 mL MeOH containing 10% acetic acid, was adapted from a comparable study [27] and was capable of eluting CPF from both polymers [data not shown].

After this optimisation, the washing experiments were repeated using all the MIPs and NIPs synthesized with the different four pyrogens. Once again there was no detection of CPF in the filtrates at the loading steps, demonstrating that all polymers (MIPs and NIPs) were capable of retaining the analyte completely. This could be attributed to the nature of aqueous solutions, which promote binding between analyte and polymer through hydrophobic and electrostatic interactions.

The optimized washing solution (5 mL of MeOH/water) (50:50%) was then used to wash the cartridges. The percentage of CPF found in the filtrates at the washing step for all the MIPs and NIPs is shown in Figure 4. It can be seen that with the exception of DCM-MIP, a higher amount of CPF was removed from the NIPs than the MIPs. This indicates that the MIPs have a higher affinity for CPF when compared to the corresponding NIPs [26]. Among all the MIPs, ACN-MIP showed the greatest difference with the smallest standard deviations, which makes it the most promising material for an effective MISPE. The large standard deviations shown in Figure 4 were due to the fact that CPF concentrations were close to the LOD of the HPLC measurements.

Following the washing step, all the MISPE cartridges were eluted with 5 mL of the elution mixture, methanol-acetic acid (9:1 v:v). The results, summarized in Figure 5, illustrate that CPF recovered from ACN-MIP, CL-MIP and DCM-MIP was higher than that eluted from their corresponding NIPs. However only the difference between ACN-MIP and ACN-NIP is high enough to be considered significant. In fact, for the other polymers the differences fall inside the standard deviations of the measurements, thus they are not significant. This includes TOL-MIP and NIP, where TOL-NIP seemed to release a higher (but not significant) amount of CPF. One common result for all the polymers is that CPF was not fully recovered with the 5 mL of elution mixture, even considering the amount lost at the washing step. A subsequent 5 mL of elution mixture was passed through the cartridges, but the amount of CPF released was below the LOD of the HPLC measurement and therefore it was not quantifiable. Nevertheless, the MIP prepared with ACN, in addition to possessing the best affinity (greatest differences between MIP and NIP) also showed the highest amount of CPF recovered at the elution step (around 75%), demonstrating to be the best performing MIP. The CPF recovered was also pre-concentrated 6 times, as 30 mL were used to load CPF into the cartridges and 5 mL of elution mixture was used to recover it.

Although other studies in literature have reported the use of DCM, toluene and chloroform as pyrogens for producing MIPs for other pesticides [27,28], this finding agrees with several studies, where MIPs were produced for organophosphate pesticide similar to CPF using ACN as a pyrogen [29].

Breakthrough volume and mass capacity

The binding capacity of the best performing MIP, ACN-MIP, was assessed by a breakthrough experiment where the breakthrough volume, which is the volume of the loading solution at which total analytes adsorption can no longer be attained due to the saturation of polymer binding sites, was determined [30]. In this study, for the experiment, even though a large volume of CPF solution (1 L of 500 ng/mL of CPF prepared in water) was loaded into the MIP cartridges (30 mg of MIP), traces of CPF in the filtrate were still not observed. Therefore, the binding capacity for the MIP was calculated to be higher than 16.7 mg/g polymer.

The polymer performance cannot be evaluated only by investigating the affinity and capacity; the selectivity to rebind and distinguish the target template from other related compounds is also essential [31]. The MIP binding selectivity towards CPF was evaluated here by testing other pesticide analogues of CPF such as CIPC, IPC, 3-CA and TCP. The same protocol explained above was applied again by loading CPF and the pesticides at a concentration of 500 ng/mL in water (30 mL), followed by the established washing and elution mixtures. The results of the experiments showed that, not surprisingly, all compounds were retained completely at the loading step by the MIP. Conversely the

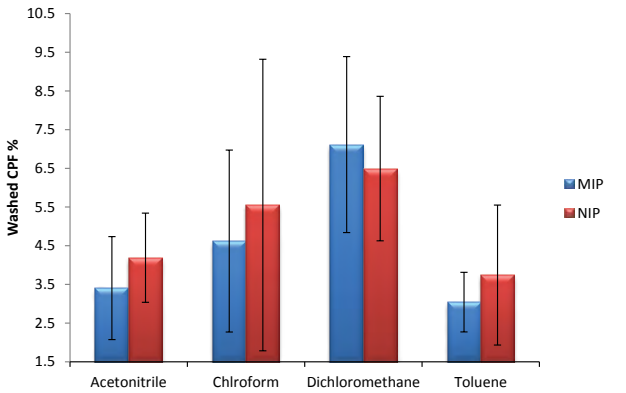


Figure 4: Percentage of CPF washed out from all MIPs and NIPs using 5 mL of a mixture of methanol-water (50:50, v:v) after loading columns with 30 mL containing CPF (500 ng/ml in water). Standard deviations were calculated for experiments repeated in triplicates.

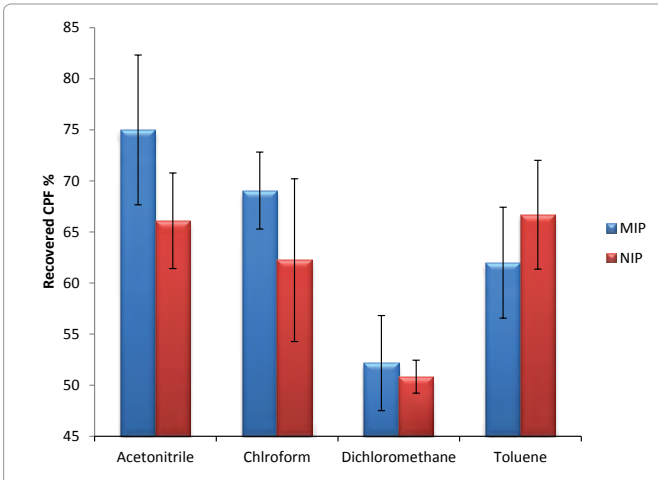
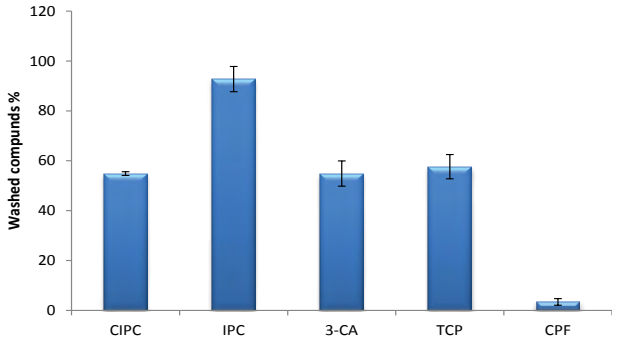


Figure 5: Recovery of CPF from different MIPs and NIPs using 5 ml of methanol-acetic acid (9:1 v:v) after they were dried and reconstituted in 1 mL of ACN. Standard deviations were calculated for experiments repeated in triplicates.



Chloropropham (CIPC); Propham (IPC); 3-chloroaniline (3-CA); 3,5,6-trichloropyridionl (TCP); Chlorpyrifos (CPF)

Figure 6: CPF and other compounds washed off with 5 mL of a mixture of MeOH-water (50:50, v:v). Standard deviations were calculated for experiments repeated in triplicates.

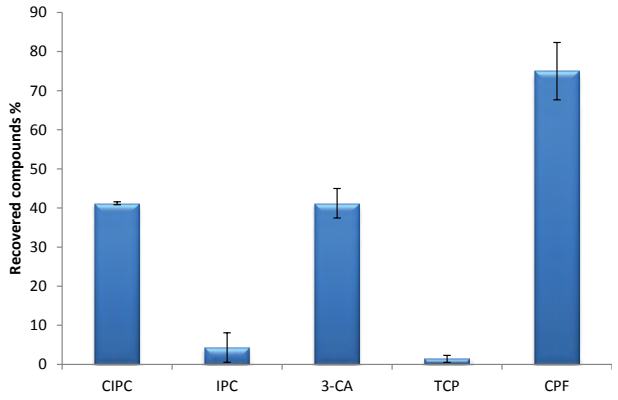


Figure 7: CPF and other compounds recovered after elution with 5 mL of a mixture of methanol-acetic acid (90:10 v:v). Standard deviations were calculated for experiments repeated in triplicates.

amount of CPF and other compounds found in the filtrates after the washing and the elution steps are shown in Figures 6 and 7 respectively. Even though all these compounds were retained by the polymers, about 55-85% of the amount were removed by a 5 mL mixture at the washing step (Figure 6). However, the MIP still selectively retained CPF. The result indicated that the MIP has low affinity for these tested compounds compared to CPF, which possibly contained higher molecular recognition towards its template. In comparison with CPF, the other compounds showed lower affinities for the MIP as larger amounts were removed at the washing step. Significant lower recovery were obtained at the final elution step (Figure 7), the possible explanation for this is that the interaction with these compounds took place mainly via non-specific binding sites available in the polymer. Indeed the MIP can distinguish its target molecule due to the presence of cavities with the right shape, size and specific binding groups suitable to interact with the target molecule [29]. Another explanation for this phenomena could be attributed to the different pKa values for these analytes varying (from 13.3 to - 4.1) as 13.3, 4.55, 3.521, -0.94 and -4.1 [30] for CIPC, TCP, 3-CA, IPC and CPF respectively, which indicate that CPF is the least polar. Nevertheless, the behavior observed does not strictly follow the values of the pKa. In fact, IPC, which is the least polar after CPF, is nearly all lost at the washing step and very little is recovered at the end. Therefore, selectivity could be in part influenced under the applied conditions by the polarity of these analytes [31], but there is definite indication of an imprinting effect.

This result demonstrates that in the tested conditions, ACN-MIP is sufficiently selective for analysis of real samples, which might contain the tested interfering compounds.The main implicit mechanism for the template selectivity of our MIP could be inferred for a shape recognition of the binding sites contained inside the polymeric structure [32].

Conclusion

A MISPE sorbent for the selective binding of CPF was synthesized here by thermo-polymerization. An investigation on how the type of solvent used during polymerization influences the affinity of the polymers was carried out. The MIP prepared with ACN as a pyrogen showed the highest affinity to CPF when tested in water in comparison with MIPs made with other organic solvents. Successful extraction and pre-concentration (6 times) of CPF from water was achieved using ACN MIP. When the MIP selectivity towards CPF was assessed by testing other pesticides, it was found that with the optimized SPE protocol the MIP was capable to selectively recognize CPF. The sorbent developed here is therefore could be a good candidate for extraction CPF from environmental samples.

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Citation: Binsalom A, Chianella I, Campbell K, Zourob M (2016) Development of Solid-Phase Extraction Using Molecularly Imprinted Polymer for the Analysis of Organophosphorus Pesticides-(Chlorpyrifos) in Aqueous Solution. J Chromatogr Sep Tech 7: 340. doi: 10.4172/2157-7064.1000340