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# Ultrasonication assisted extraction of chlorpyrifos from honey and brinjal using magnetic molecularly imprinted polymers followed by GLC-ECD analysis

Niranjan Kumar, Neethu Narayanan, Suman Gupta*

*Division of Agricultural Chemicals, ICAR-Indian Agricultural Research Institute, New Delhi 110012, India*

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ABSTRACT

Chlorpyrifos selective magnetic molecularly imprinted polymers (MMIPs) were synthesized by precipitation polymerization using acrylic acid as monomer and ethylene glycol dimethacrylate as cross linker. Properties of prepared polymers were determined using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Vibrating Sample Magnetometer (VSM) techniques. The imprinted polymers showed much higher adsorption capacity towards the analyte ($K_d$ = 12,059.5 mL $g^{-1}$) than the magnetic non-imprinted polymers (MNIPs) ($K_d$ = 962.2 mL $g^{-1}$). Adsorption data fitted well into linearized Freundlich equation ($R^2$ = 0.981) and followed pseudo-second-order kinetic model ($R^2$ = 0.999). Scatchard plot analysis revealed heterogeneous binding sites on MMIPs while it was homogenous on MNIPs. Polymers were highly selective in extracting chlorpyrifos even in the presence of its structural analogue quinalphos (α = 16.2) and triazophos (α = 15.6). Imprinted polymer after regeneration was successfully used three times for rebinding the template without any apparent loss in adsorption capacity. Using prepared polymers, about 86.23–92.04% and 89.42–102.36% of the chlorpyrifos were successfully recovered from fortified market samples of honey and brinjal with relative standard deviation of 1.70–3.93% and 0.17–5.50%, respectively.

## 1. Introduction

Chlorpyrifos is a broad-spectrum organophosphate insecticide, acaricide and nematicide having non- systemic activity. The molecule was introduced by Dow Chemical Company in the year 1965. As per IRAC (Insecticide Resistance Action Committee) MoA (Mode of Action) classification, chlorpyrifos belongs to Group 1B insecticide acting as a nerve poison by inhibiting acetylcholinesterase. It is one of the most commonly used pesticides throughout the world for controlling agricultural as well as non-agricultural pests. In India, it is registered as 10% G, 20% EC, 1.5% DP and 50% EC formulations for controlling pests of paddy, gram, beans, sugarcane, cotton, citrus, brinjal and cabbage, etc. It is also used for controlling termite attack in wood as pre and post construction treatments. As per World Health Organization, chlorpyrifos is reported to be moderately toxic to humans and causes autoimmune disorders in fetus or in children and harm the mental health of generations. It was found to be toxic to shrimps, fish [1] and reportedly alter the physiological behavior and motor function of honey bees [2,3]. As per the studies conducted by researchers in USA, Europe, Brazil and India, around 15% of hive pollen samples and about 20% of honey samples were found to be contaminated with chlorpyrifos residues [4]. In India, chlorpyrifos contamination has been reported in water [5], breast milk [6], tea [7] and fish [8]. Recent studies have revealed that the derivatives of organophosphate pesticides, especially chlorpyrifos, are 100 times more toxic than the parent compounds [9]. On an average, chlorpyrifos toxicity results in around 10,000 human deaths every year [10].

Considering the modern age problems of growing population, pollution and toxic load of pesticides in the environment, one must rely on the recommended use of pesticide in order to achieve self-sufficiency with respect to healthy food, fodder and good health for the present as well as the future generations. Development of analytical approaches allowing the detection of specific analytes with high selectivity and sensitivity constitutes a challenging task and often requires efficient sample pre-treatment techniques due to wide variety of complex sample matrices. Researchers have developed a number of methodologies like microwave-assisted solvent extraction [11], liquid-liquid extraction [12], supercritical fluid extraction [13], modified QuEChERS [14], etc.

* Corresponding author.
*E-mail address:* drsumangupta2002@yahoo.com (S. Gupta).

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for sample processing in order to achieve high sample throughput. Though these methods are able to extract pesticides with lesser amount of solvent and bench space, they lack selectivity and, along with the desired moiety, some interfering pesticides or other co-extractives invariably come in the final analysis extract. This necessitates the development of improved sample preparation techniques capable of cleaning up and enriching the samples for trace level analysis. Molecular imprinting technology is currently being explored to develop polymers with highly specific recognition sites for the analyte of interest. The molecularly imprinted polymers (MIPs) are found to be as effective as natural receptors like enzymes or antibodies [15–17]. Magnetic MIPs possess additional advantage of easy separation from matrix solution by using external magnets. Researchers have used MIPs in the fields of chromatographic separations [18], biomimectic chemical sensors [19–22], process scale purifications [23,24], drug delivery [25,26], solid phase extraction [27–30] and catalysis [31–33].

Scientists worldwide are exploring different surface modification and precipitation methods to enhance selectivity of the MIPs. In recent past, Peng et al., have synthesized photonic-magnetic responsive molecularly imprinted microspheres (PM-MIMs) by seed polymerization and applied to the extraction of 17 β- estradiol from spiked milk powder and drinking water samples. They have reported the recoveries in the range of 97.5–113.0% with < 4.4% relative standard deviations [34]. MMIPs for diazinon were prepared by one-step surface imprinting technique using precipitation polymerization method and efficiently used for extraction of diazinon from spiked tomato, cucumber, apple, and water samples [35]. Bisphenol A selective water-compatible temperature and magnetic dual-responsive MIPs (WC-TMMIPs) were prepared via reversible addition-fragmentation chain transfer precipitation polymerization and employed as adsorbents for magnetic solid-phase extraction (MSPE) with > 85% recovery from seawater samples [36]. Magnetic molecularly imprinted polymer (MMIP) on mesoporous silica ($mSiO_2$)-coated $Fe_3O_4$ nanoparticles was synthesized using surface-imprinting technology for selective adsorption of atrazine. The recoveries of atrazine from spiked river water, lake water, and well water sample using prepared polymer were 87.4, 92.9, and 101.7%, respectively [37]. A multi-templates molecularly imprinted polymer for the rapid and selective detection of alkyl phenol compounds including bisphenol A, 4-tert-octylphenol and 4-nonylphenol has been successfully synthesized via surface imprinting technology [38].

In the present work, a highly selective and specific magnetic molecularly imprinted polymer (MMIP) for chlorpyrifos has been synthesized by precipitation polymerization. The polymeric materials were characterized by FTIR, SEM, TEM, VSM, etc. to know the bond interaction, surface morphology, size and magnetic properties of the MMIPs. Adsorption capacity, kinetics of adsorption and binding selectivity studies were conducted to know its effectiveness after repeated uses. Chlorpyrifos analysis was performed using GLC-ECD (Gas Liquid Chromatography-Electron Capture Detector). Applicability of prepared MMIPs in selective extraction of chlorpyrifos was demonstrated in market samples of honey and brinjal.

## 2. Experimental

### 2.1. Reagents and chemicals

Analytical grade chlorpyrifos, quinalphos and triazophos were obtained from Sigma-Aldrich, Germany. Chlorpyrifos (Tech.) used for preparation of imprinted polymer was supplied by Insecticide India Limited. Acrylic acid, ethylene glycol dimethacrylate (EGDMA) and azobisisobutyronitrile (AIBN) were procured from Sigma-Aldrich, USA. Oleic acid and polyvinylpyrrrolidone (PVP) were purchased from Thomas Baker (Chemicals) Pvt. Ltd., Mumbai, India. $Fe_3O_4$ nanopowder (99.5 ± 5%, 80 nm) and Buffer capsules of pH 4.0, 7.0 and 9.2 were obtained from Nanoshel and Fisher chemicals USA, respectively. Solvents like acetone, dichloromethane (DCM), methanol, hexane etc. were procured from Merck Life Science Private Limited, India. Water with a resistivity of 18.2 MΩ.cm was taken from Milli-Q water system (Millipore, Billerica, MA, USA).

Stock solutions (1000 μg $mL^{-1}$) of chlorpyrifos, quinalphos and triazophos were prepared in 100 mL volumetric flask separately by dissolving 100 mg of each pesticide in acetone and making the volume up to the mark. Working solutions of lower concentrations for analysis were obtained by diluting in hexane. All the samples and standard solutions were stored in refrigerator at 4 °C until used.

### 2.2. GLC-ECD/TSD analysis

Analysis of chlorpyrifos, quinalphos and triazophos was done using Varian CP-3800 GC. The instrument was equipped with CP-Sil 5 CB (15 m × 0.53 mm) column, electron capture detector (ECD) and thermionic specific detector (TSD) (bead current, 3.100 A). Carrier gas was $N_2$ (IOLAR I grade) having the flow rate of 2 mL $min^{-1}$ through column. Sample analysis was done with GLC-ECD except for selectivity studies where GLC-TSD (Thermionic Specific Detector) was used because of the poor response of triazophos in ECD. While operating with ECD, column oven temperature was programmed as 190 °C for 1 min, temperature increased @ 10 °C/min to 240 °C held for 1 min, temperature increased @ 30 °C to 280 °C, held for 10 min with a retention time of 4.88 min for chlorpyrifos (Fig. 1A).The detector and injector port temperatures were maintained at 300 °C and 280 °C, respectively. Samples were injected in split mode (1:20) with an injection volume of 2 μL. During GLC-TSD analysis, column oven temperature was programmed at 160 °C for 1 min, temperature increased @ 20 °C/min to 280 °C and maintained for

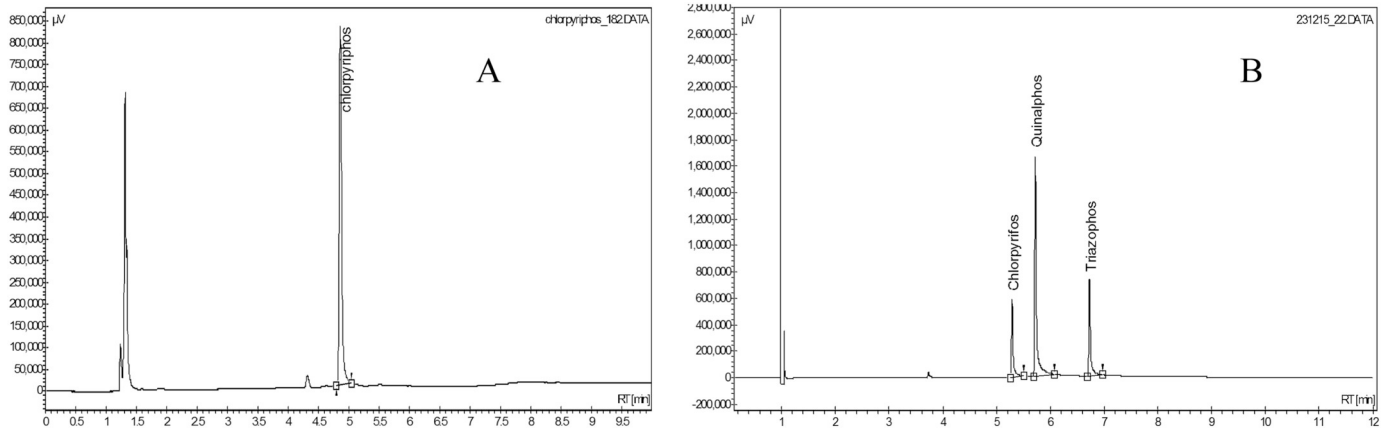


**Fig. 1.** (A) GLC-ECD chromatogram of chlorpyrifos (B) GLC-TSD chromatogram of chlorpyrifos, quinalphos and triazophos.

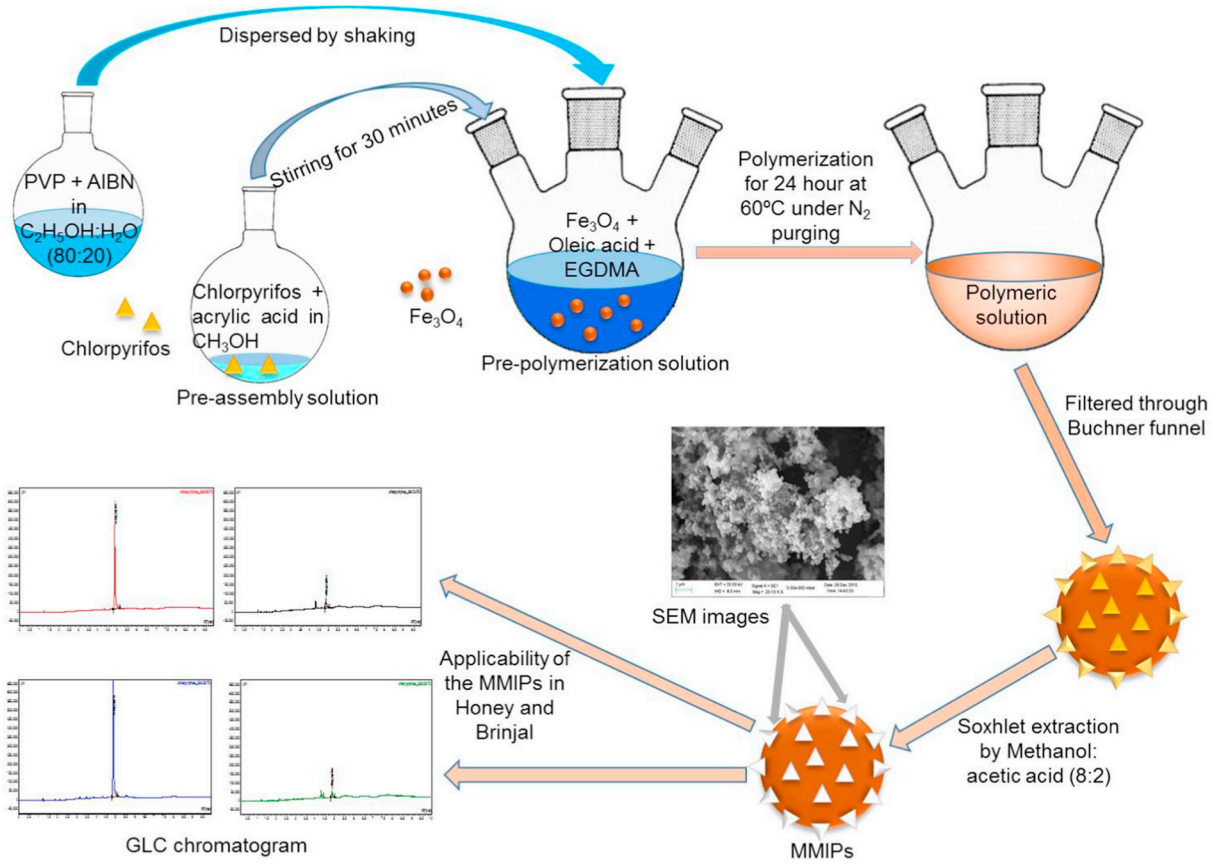


**Fig. 2.** Schematic representation of synthesis and utility of MMIPs in selective extraction of chlorpyrifos from honey and brinjal.

5 min. Retention time for chlorpyrifos, quinalphos and triazophos with the above programming were 5.30, 5.73 and 6.73 min, respectively (Fig. 1B).

### 2.3. MMIPs/MNIPs preparation

Polymers were prepared by precipitation polymerization in 100 mL ethanol:water (80:20) using acrylic acid (4.0 mmol, 288.2 mg) as monomer, EGDMA (20 mmol, 3.9 g) as cross-linker, AIBN (50 mg) as initiator and chlorpyrifos (1.0 mmol, 350.6 mg) as a template molecule. Preassembly solution was prepared by dissolving chlorpyrifos and acrylic acid in 10 mL methanol in a round bottom (RB) flask followed by 30 min of stirring. In a separate three mouth RB flask, magnetic $Fe_3O_4$ nanoparticles (1 g) were thoroughly dispersed in 1 mL of oleic acid for 10 min followed by addition of preassembly solution and EGDMA. The contents were ultrasonicated for 30 min to obtain pre-polymerization solution. Polyvinylpyrrrolidone (PVP, 0.4 g) and AIBN dispersed in 100 mL of ethanol:water (80:20) was added to the pre-polymerization solution. The solution was continuously stirred and purged with nitrogen gas for 15 min. Reaction temperature was slowly increased to 60 °C and kept constant for 24 h. After polymerization, the magnetic molecularly imprinted polymer precipitate was filtered through Buchner funnel and washed thoroughly with water and methanol. Finally the material was washed with methanol: acetic acid (8:2) in Soxhlet till no chlorpyrifos was detected in the washing. MMIPs were dried under vacuum at 60 °C and stored at ambient temperature in glass bottle. MNIPs were prepared and processed in similar way without addition of the template molecule.

### 2.4. Polymeric material characterization

Synthesized MMIPs/MNIPs were characterized by FTIR, SEM,TEM and VSM to know the bonding interaction of monomers, crosslinker, template molecule and magnetic particles, their surface morphology and magnetic properties. FTIR was recorded on Bruker (Alpha) instrument in the range of 4000–400 $cm^{-1}$ using polymer:KBr (1:100, *w*/w) pellets. Surface morphology of the polymers was imaged by CarlZeiss-Evo-MA-10 scanning electron microscope (SEM) at 20 KV/EHT and 10 Pa by coating the polymers with gold and palladium followed by imaging under high vacuum. Polymers size and voids were measured by transmission electron microscopy (TEM, JEOL 100CX-11). Polymer suspension in 1% ethanol was mounted on the grid by staining with 2% uranyl acetate and images were taken after drying the grid. Magnetic properties of the polymer were assessed by vibrating sample magnetometer (VSM) at room temperature using VSM Lake Shore 7410 system at a magnetization of 2.0 T.

### 2.5. Binding studies

To optimize the amount of polymeric material that can absorb maximum amount of chlorpyrifos, different amounts of polymers viz. 5, 10, 20, 50 and 100 mg were dispersed in chlorpyrifos solution (3 mL of 50 μg $mL^{-1}$) prepared in MeOH:Water (1:1) and the tubes were shaken on a horizontal shaker. After 2 h, tubes were centrifuged at 3500 rpm for 5 min. Supernatant (1 mL) was drawn and partitioned with DCM (3 × 20 mL). Residues were reconstituted in hexane for analysis by GC-ECD.

Time required for maximum binding of chlorpyrifos on MMIPs was

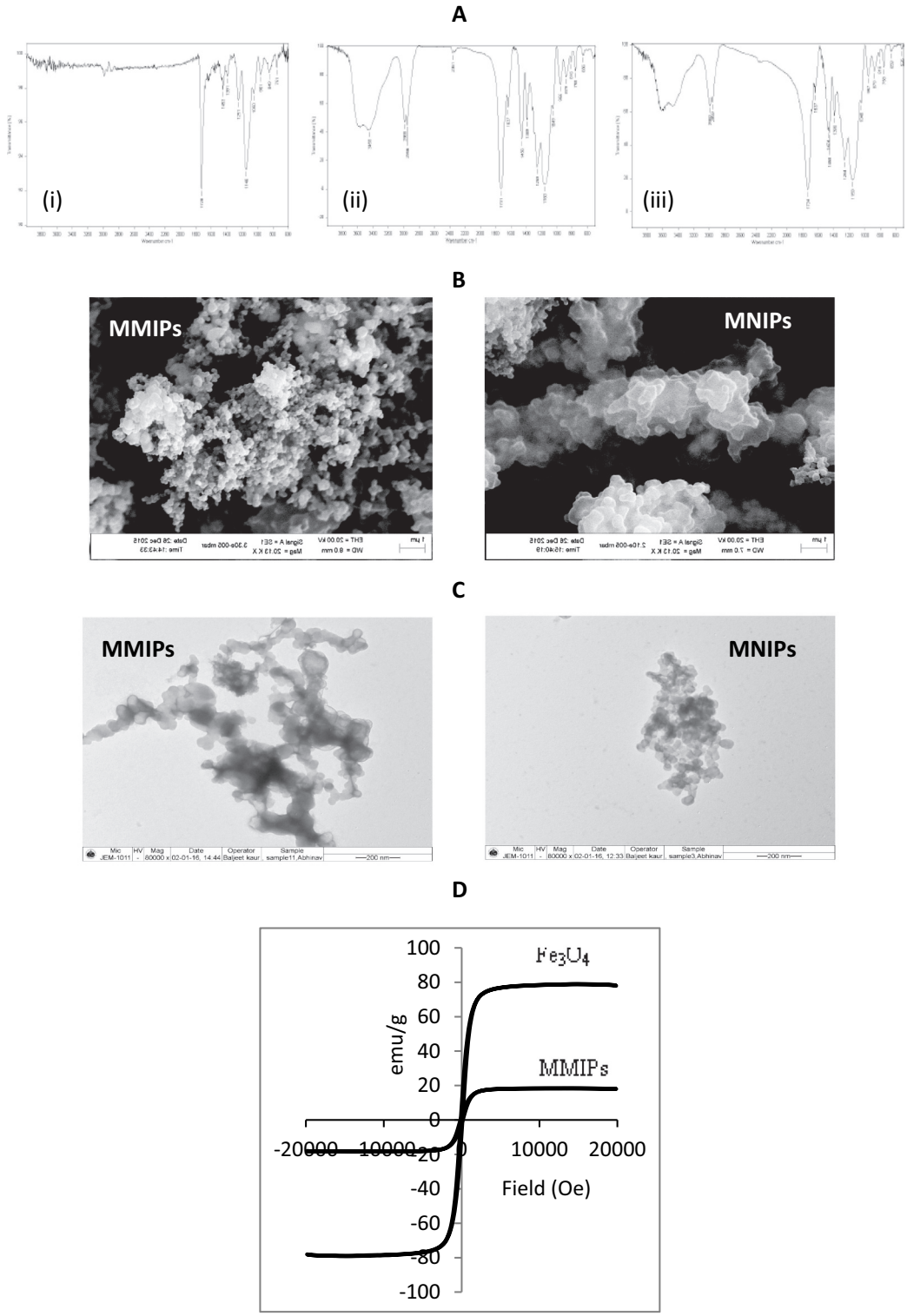


**Fig. 3.** (A) FTIR spectra: (i) MMIPs before washing, (ii) MMIPs after washing, and (iii) MNIPs, (B) SEM images, (C) TEM images of MMIPs/MNIPs and (D) Hysteresis loops of $Fe_3O_4$ and MMIPs.

evaluated by conducting the adsorption kinetics experiment. Optimized amount of polymers in the above experiment (20 mg) were dispersed in 3 mL of 50 μg $mL^{-1}$ chlorpyrifos solutions in test tube and kept on a horizontal shaker. Sample was drawn periodically to determine the equilibration time.

Binding isotherm was obtained by conducting the sorption experiment with different concentrations viz. 1, 5, 10, 20, 50 and 100 μg $mL^{-1}$ of the chlorpyrifos solution (3 mL). Polymers (20 mg)

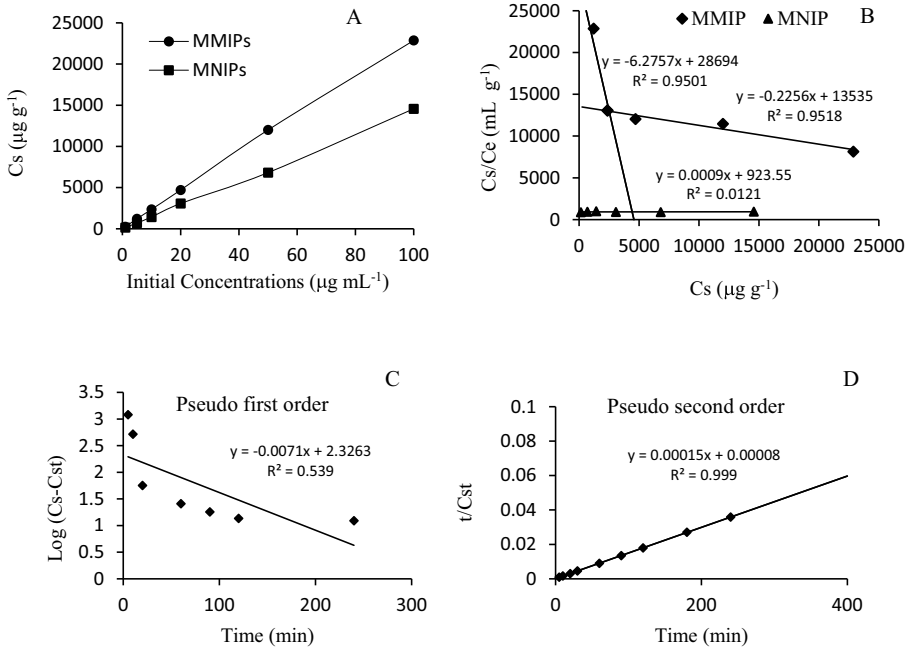


**Fig. 4.** (A) Adsorption isotherms, (B) Scatchard plot analysis, (C) Pseudo first order kinetics, and (D) Pseudo second order kinetics of chlorpyrifos binding on MMIPs and MNIPs.

were added and test tubes were kept on a horizontal shaker. After equilibrium was achieved, the supernatants were drawn and processed.

Binding selectivity of the polymers was evaluated by conducting the sorption experiment in the presence of chlorpyrifos structural analogue quinalphos and triazophos. 20 mg of polymers were taken in test tube and 3 mL of 50 μg $mL^{-1}$ mixture solution of chlorpyrifos, quinalphos and triazophos was added to each test tube. Supernatants were processed after 2 h of shaking and analyzed by GC-TSD.

Effect of solution pH on binding of the polymers was studied by dispersing 20 mg of sorbent in 3 mL of 50 μg $mL^{-1}$ chlorpyrifos solution prepared in different pH buffers (4.0, 7.0 and 9.2). Test tubes were shaken for 2 h on horizontal shaker and then supernatants were processed and analyzed by GC.

All experiments were conducted in triplicate. The amount sorbed on the polymeric material was obtained by subtracting the amount analyzed by GC in supernatant from the total amount added in the test tube.

### 2.6. Regeneration of MMIPs/MNIPs

To dislodge chlorpyrifos bound on the MMIPs (as per section 2.5, 20 mg MMIPs in 3 mL of 50 μg $mL^{-1}$), following three methods were tried:

Method-1: Soxhlet extraction using methanol: acetic acid (8:2) as solvent for 12 h. Washings were evaporated, partitioned with DCM and reconstituted in hexane for analysis by GC.

Method-2: Dipping in 5 mL of acetone: acetic acid (8:2, v/v) followed by ultrasonication for 1 min. MMIPs were collected by using an external magnet. Again the washed MMIPs were dispersed in 5 mL of acetone: acetic acid (8:2, v/v) followed by ultrasonication for 1 min and polymers were separated using external magnet. MMIPs were washed one more time. Combined supernatants obtained from the three washings were evaporated, processed and reconstituted in hexane for analysis by GC.

Method-3: In this method, washing was done as per Method-2 but the solvent system used was methanol: acetic acid (8:2, v/v) instead of acetone: acetic acid (8:2, v/v).

Considering the ease and efficiency of extraction, Method-3 was selected for further use in the study for regeneration of MMIPs.

### 2.7. Reusability of the MMIPs

MMIPs (20 mg) were dispersed in 3 mL of 50 μg $mL^{-1}$ chlorpyrifos solution and shaken for 2 h on horizontal shaker. MMIPs were extracted from the solution using an external magnet. Bound chlorpyrifos on MMIPs was washed out using Method-3 (as described in Section 2.6) and the polymers were dried. The regenerated MMIPs were again dispersed in 3 mL of 50 μg $mL^{-1}$ chlorpyrifos solution and subjected to sorption. After 2 h, MMIPs were recovered and washed again as per Method-3. This adsorption desorption cycle was done two more times. The washing obtained from the first use and the three successive reuses were processed separately and analyzed by GC.

### 2.8. Method validation

Chlorpyrifos standard solution of different concentrations were injected into GLC-ECD under earlier optimized instrumental conditions and a calibration curve for chlorpyrifos was generated by plotting the concentration of the analyte versus peak area obtained in ECD detector. For recovery studies untreated control samples of brinjal were procured from the farm unit of Division of Vegetable Science, ICAR-IARI, New Delhi and honey samples were obtained from Project Coordinator, All India Coordinated Research Project on Honey bees and Pollinators, ICAR-IARI, New Delhi, India.

Honey sample (2 g) was fortified at 5 μg $g^{-1}$ level using 50 μg $mL^{-1}$ chlorpyrifos solution. Viscous sample was diluted to 10 mL using distilled water and mixed with MMIPs (50 mg) and anhydrous $MgSO_4$ (150 mg). The test tubes were shaken for 15 min. Magnetic polymers

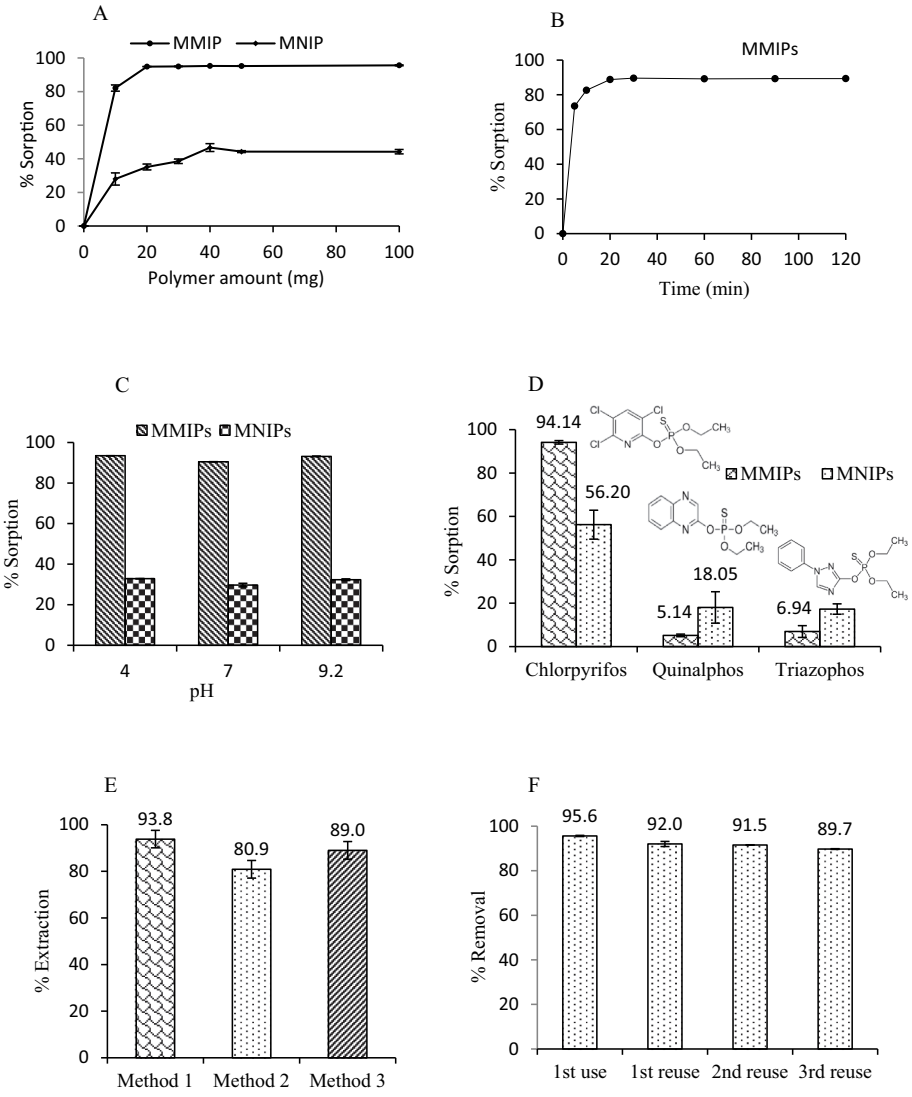


**Fig. 5.** Sorption of chlorpyrifos with respect to (A) polymer amount (B) equilibration time (C) solution pH (D) structural analogues; (E) washing method optimization (F) reusabilility.

from the solution were separated using an external magnet and washed as per earlier optimized Method-3 to extract bound chlorpyrifos on the MMIPs. Remaining solution in the test tube was partitioned with dichloromethane to extract unbound chlorpyrifos. Samples were analyzed on GC-ECD to determine actual sorption percentage of chlorpyrifos on the MMIPs from fortified honey sample.

In case of brinjal, 10 g of homogenized sample was taken in a test tube and fortified to the level of 5 $\mu g\,g^{-1}$ by addition of 1 mL of 50 $\mu g\,mL^{-1}$ chlorpyrifos solution in the test tube. Then 1 g of NaCl, 4 g of $MgSO_4$ and 10 mL of ethyl acetate was added in tube followed by vortexing for 2 min. After vortexing thoroughly, tube was centrifuged for 5 min at 3500 rpm and the upper layer of ethyl acetate (2 mL) was pipetted out in microcentrifuge tube. MMIPs (50 mg) and $MgSO_4$ (150 mg) were added to the tube, followed by vortexing for 2 min. MMIPs were separated from the tube using an external magnet. The bound chlorpyrifos on the MMIPs were washed out as per Method-3. The chlorpyrifos remaining in the solution was extracted with dichloromethane. Final residues were dissolved in hexane and analyzed to know the actual sorption percentage of chlorpyrifos on MMIPs from the fortified brinjal sample.

## 3. Results and discussion

### 3.1. Synthesis and characterization of MMIPs

Imprinted polymers for chlorpyrifos were synthesized by precipitation polymerization via non-covalent imprinting method. Schematic representation of the synthesis process has been shown in Fig. 2. Polymerization took place under nitrogen purging at 60 °C for 24 h. Non-covalent imprinting approach enables easy removal of template from the polymeric cavity due to weak interactions like hydrogen bonding between acrylic acid monomer and the chlorpyrifos.

Fig. 3A (i-iii) shows the FTIR spectra of imprinted and non imprinted polymers. Characteristic peaks at ~1730 $cm^{-1}$, 1150 $cm^{-1}$, 2960 $cm^{-1}$ and 1450 $cm^{-1}$ were attributed to carbonyl stretching, C—O stretching, C—H stretching and C—H bending vibrations suggesting incorporation of cross-linker in the polymeric matrix. A characteristic peak of Fe—O appeared at 526 $cm^{-1}$ indicates inclusion of magnetic

particles in the matrix. Broad peak around 3600–3400 $cm^{-1}$ may be assigned to –OH stretching vibration in acrylic acid. Due to same chemical composition there was no significant difference observed in the FT-IR spectra of non-imprinted polymers and imprinted polymer (after washing). FT-IR spectra of imprinted polymers (before washing) shows reduced intensity peaks. Reduction in the intensity of –OH stretching vibration at3600–3400 $cm^{-1}$ could be due to the disruption in the hydrogen bonding among acrylic acid molecules due to interaction of chlorpyrifos with the monomer [39,40]. SEM images of MMIPs suggest spherical, porous and rough surfaces of polymeric particles as compared to the flat, compact and smooth surfaces of MNIPs (Fig. 3B). These porous surfaces of the MMIPs with specific cavity enable high binding affinity for chlorpyrifos than for the MNIPs. TEM images of MMIPs appear more irregular due to presence of the imprint as compared to the smoother, uniform appearance of MNIPs spheres (Fig. 3C). Dark spots in the images are due to incorporation of magnetic nanoparticles in polymeric matrix.

For determining magnetic properties of polymeric materials, magnetic saturation hysteresis curves were obtained for MMIPs and $Fe_3O_4$ using vibrating sample magnetometer (VSM) (Fig. 3D). Magnetic hysteresis loops of MMIPs and $Fe_3O_4$ were found to be symmetrical about the origin. The MMIPs responded well to the external magnetic field. The saturation magnetization of $Fe_3O_4$ and MMIPs were 78.0 emu $g^{-1}$ and 18.2 emu $g^{-1}$, respectively. Reduction in magnetization of MMIPs as compared to $Fe_3O_4$ magnetite indicates the formation of polymeric layer on the magnetite [41].

### 3.2. Adsorption isotherms

Adsorption capacities of MMIPs/MNIPs were evaluated in different concentrations of chlorpyrifos solution by conducting static adsorption experiment (Fig. 4A). It can be interpreted that the amount of chlorpyrifos adsorbed on MMIPs and MNIPs goes on increasing as the concentration increases. The amount of sorption is much higher in case of MMIPs than that of MNIPs, thus showing the presence of chlorpyrifos imprints or cavities on MMIPs. The binding properties of MMIPs were determined by Scatchard plot analysis (Fig. 4B) which is based on the following equation:

$$C_s/C_e = (C_{max} - C_s)/K_{dc}.$$

where $C_e$ is the equilibrium concentration of chlorpyrifos in the solution, $C_s$ is the amount of chlorpyrifos bound to the MMIPs at equilibrium, $C_{max}$ is the apparent maximum binding amount and $K_{dc}$ is the dissociation constant. It can be seen that MMIPs show two types of adsorption curves. The left part of the curve suggests higher binding affinity in the concentration range 1–10 μg $mL^{-1}$. The $K_{dc}$ and $C_{max}$ calculated from the intercept and slope of the regression equation Cs/Ce = −6.2757 × + 28,694 were found to be 0.159 μg $mL^{-1}$ and 4562.3 μg $g^{-1}$ of dry polymer, respectively. The right part of the curve shows lower binding affinity in the concentration range of 10–100 μg $mL^{-1}$ with $K_{dc}$ and $C_{max}$ values of 4.43 μg $mL^{-1}$ and 60,000.6 μg $g^{-1}$ of dry polymer calculated from regression equation Cs/Ce = −0.2256 × + 13,535, respectively. The two straight lines in Scatchard plot of MMIPs are indicative of the presence of heterogeneous binding sites in comparison to single line curve observed for MNIP. Zhu et al. (2002) have also reported that MMIPs prepared with non-covalent imprinting possess heterogeneous distribution of binding sites [42].

Pseudo first and second order kinetic models were employed to the sorption data (Fig. 4C & D). The pseudo-second order kinetic model gave high values of correlation coefficients ($R^2$ = 0.999) as compared to the pseudo first order kinetics ($R^2$ = 0.539). Cs value of 6725.6 calculated from the pseudo-second order kinetic model also correlated well with the Cs Exp value of 6714.6.The adsorption data fitted better in Freundlich isotherm ($R^2$ = 0.981) as compared to Langmuir isotherm ($R^2$ = 0.738). Adsorption of chlorpyrifos on MMIP was favorable with intensity factor 'n' = 1.23.

### 3.3. MMIPs amount

Sorption experiment with varying amounts of polymer was conducted to evaluate optimum binding of chlorpyrifos on MMIPs. From Fig. 5A, it can be illustrated that sorption increases with the increase in polymer amount. A sorption maximum was reached with 20 mg of MMIPs. Further increase in the polymer amount did not lead to any appreciable increase in sorption. Although, MNIPs also showed increased sorption with increasing polymer amount, the extent of sorption was much lower as compared to MMIPs.

### 3.4. Sorption equilibrium time

Time required for maximum adsorption of chlorpyrifos on MMIPs was determined by conducting the static binding experiment for different durations of sorption. Fig. 5B shows that most of the added chlorpyrifos was adsorbed within 30 min. Fast attainment of sorption equilibrium could be due to the large number of chlorpyrifos imprinted sorption sites on the MMIPs.

### 3.5. pH sensitive adsorption on MMIPs

Sorption experiments were conducted to estimate the effectiveness of MMIPs in extracting chlorpyrifos from different pH solutions. From Fig. 5C, it can be seen that the solution pH has almost no effect on the sorption efficiency of MMIPs/MNIPs. At pH 4.0, 7.0 and 9.2, the MMIPs showed the sorption percentage of 93.46, 90.49 and 93.15 respectively. Other researchers have also concluded that binding ability of MIPs remain unaffected in acidic or basic solution thus making it a superior recognition element [43,44].

### 3.6. Binding specificity

Competitive binding of chlorpyrifos on the MMIPs/MNIPs were evaluated by conducting the sorption experiment in the presence of its structural analogue quinalphos and triazophos (Fig. 5D). It was found that the synthesized MMIPs were highly selective and specific in extracting chlorpyrifos. The static distribution coefficient ($K_d$ = Cs/Ce), separation factor ($\alpha = K_{d\ chlorpyrifos}/K_{d\ analogue}$) and relative separation factor ($\beta = \alpha 1/\alpha 2$) presented in Table 1 were calculated as per our previous publication [45].

High value of static distribution coefficient (12,059.5 mL $g^{-1}$) observed for chlorpyrifos reflects high adsorption capacity of imprinted polymer for chlorpyrifos as compared to quinalphos (744.0 mL $g^{-1}$) and triazophos (770.8 mL $g^{-1}$). High separation factor values of MMIPs (16.2 and 15.6) compared to MNIPs (5.8 and 6.1) are indicative of very high selectivity of MMIPs towards chlorpyrifos in comparison to its

**Table 1**
Selectivity parameters of MMIPs and MNIPs of chlorpyrifos.

| | MMIP | | MNIP | | |
|---|---|---|---|---|---|
| Compounds | $K_{d1}$ (mL $g^{-1}$) | α1 | $K_{d2}$ (mL $g^{-1}$) | α2 | β |
| Chlorpyrifos | 12,059.5 | – | 962.2 | – | – |
| Quinalphos | 744.0 | 16.2 | 165.3 | 5.8 | 2.8 |
| Triazophos | 770.8 | 15.6 | 156.7 | 6.1 | 2.5 |

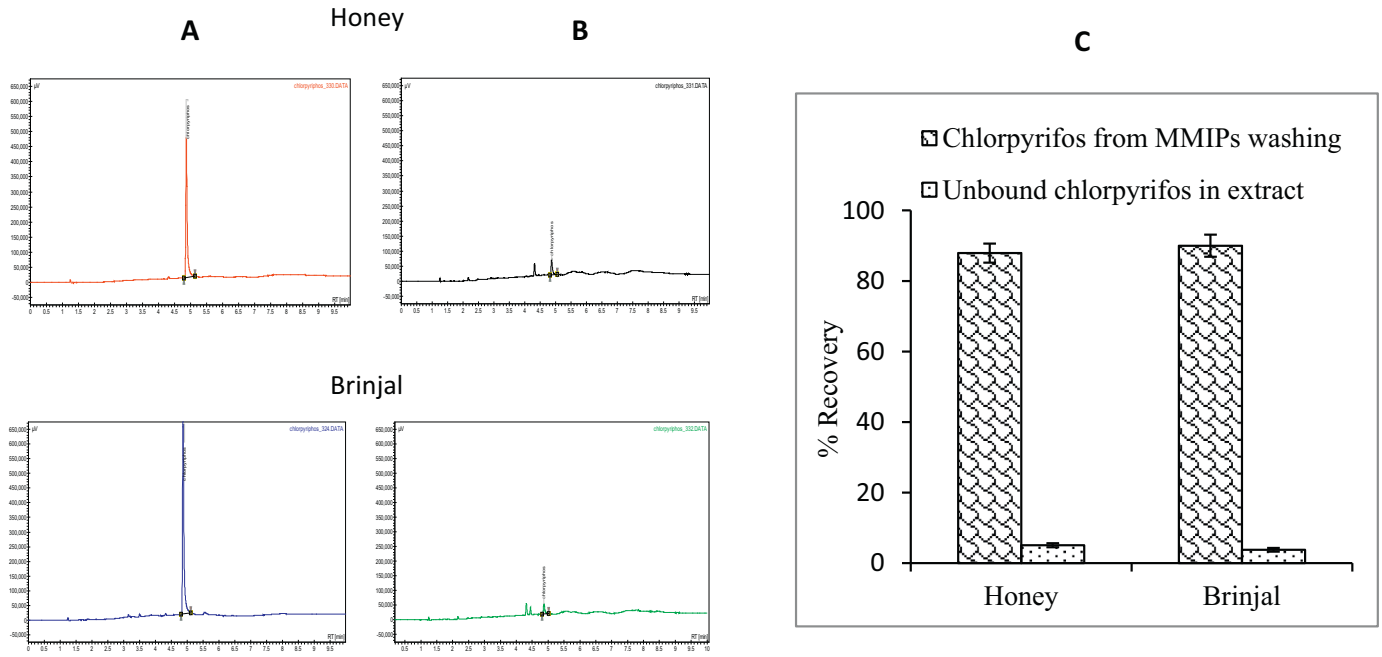


**Fig. 6.** GLC chromatograms of (A) MMIP washings and (B) residual chlorpyrifos in honey and brinjal extract (C) Extraction efficiency of MMIPs.

structurally similar analogues quinalphos and triazophos. Relative separation factor values further showed the presence of chlorpyrifos selective imprints in MMIPs.

### 3.7. Washing method optimization

Bound chlorpyrifos on imprinted polymer was dislodged using three methods (Fig. 5E). Soxhlet extraction with methanol: acetic acid (8:2, v/v) for 12 h (Method-1) gave the maximum removal percentage (93.8%) followed by sonication with methanol: acetic acid (8:2, v/v) (89.0%) (Method-3) while the least removal was achieved by sonication with acetone: acetic acid (8:2, v/v) (80.9%) (Method-2). Since Soxhlet extraction was time consuming as compared to the other methods, Method-3, i.e. sonication with methanol: acetic acid (8:2, v/v) was selected for template removal. It took 10–15 min to extract chlorpyrifos from the cavities of MMIPs and the removal percentage was at par with the Soxhlet extraction.

### 3.8. Reusability of MMIPs

Sorption efficiency of MMIPs regenerated as per section 3.7 was tested by conducting sorption experiments three times with the intermittent regeneration of MMIPs. The polymers were found effective in removing 95.6, 92.0, 91.5 and 89.7% of the sorbed chlorpyrifos in first use and successive reuse respectively (Fig. 5F). Results revealed that the material can be regenerated and reused, at least three times, for removing chlorpyrifos from the matrix without any appreciable loss in the sorption efficiency. Results also suggest that the imprints or the sorption cavities on the MMIPs are mechanically strong and are not disturbed by acid washing and ultra-sonication.

### 3.9. Method validation

The calibration curve of chlorpyrifos was found to be linear from 0.01 to 5 μg $mL^{-1}$ with $R^2$ value of 0.967 and instrument detection limit of 0.01 μg $mL^{-1}$. Recovery results revealed that MMIPs were able to extract 87.9% and 90.0% of added chlorpyrifos from fortified honey and brinjal samples with relative standard deviation of 5.35% and 6.0%, respectively. GLC chromatograms of the MMIPs washing and the honey and brinjal extract after MMIP treatment are presented in Fig. 6A and B. A small peak of chlorpyrifos in the honey and brinjal extract is due to unbound residual chlorpyrifos in the extract (Fig. 6C).

The results of chlorpyrifos analysis using synthesized MMIPs were also compared with the findings of recently published literature (Table 2). It can be seen that the analysis of chlorpyrifos using different detection techniques in tomato [46], honey [47,48], sweet corn, soil [49], water [50], coffee extract [51], Chinese cabbage and tomato [52] gives sensitivity and precision comparable with our results. The separation factor values of the prepared MMIPs are much higher than that reported by Chen et al., 2017 [52] indicating formation of better imprints for chlorpyrifos on MMIPs. Comparison of our results with the earlier reported results show that the synthesized MMIPs possess very high selectivity and enrichment ability in extracting chlorpyrifos from complex environmental matrices.

### 3.10. Applicability in real samples

Optimized methodology was used to check the applicability of the method for extraction of chlorpyrifos from market samples of honey and brinjal collected from three different locations of Delhi. As market samples of honey and brinjal were found to contain very less residues ($< 0.05$ μg $g^{-1}$), they were fortified at 5 μg $g^{-1}$ level and processed as per earlier optimized method. Recovery results are presented in Table 3. Recovery of chlorpyrifos from the fortified market samples of honey and brinjal samples were found to be 86.23–92.04% (RSD 1.70–3.93%) and 89.42–102.36% (RSD 0.17–5.50%), respectively, which further validate the method accuracy.

In this work, we are able to get highly selective MMIPs as adsorbent with additional advantage of separation using an external magnet. Extraction of chlorpyrifos from food matrices hardly took 15 min with no need of further cleanup for analysis.

**Table 2**
Comparison of the proposed method with the findings of reported literatures for analysis of chlorpyrifos.

| Sample | Sample preparation | Detection | LOD | Recovery (%) | Precision (RSD, %) | References |
|---|---|---|---|---|---|---|
| Tomato | QuEChERS | LC–MS/MS | 0.8 μg $kg^{-1}$ | 93.7 | 10.4 | Golge and Kabak [46] |
| Honey | USAEME, ultrasoundassisted emulsification microextraction | GC–MS | 0.03 ng $g^{-1}$ | 91 ± 2 | 4 | Mousavi et al. [47] |
| Honey | 2:2:1methanol:water:formic acid as the extraction reagent | ND-EESI-MS | 1.64 ng $mL^{-1}$ | 82.02 | 4.02 | Luo et al. [48] |
| Sweet corn, Soil | 20 g samples wereextracted with 80 mL ethylacetate for 25 min in an ultrasonic bath | GC-NPD | 0.0125 μg $mL^{-1}$ | 85–104 (Sweet corn)<br>94–106 (Soil) | 2.06–6.74 (Sweet corn)<br>6.01–17.0 (Soil) | Wang et al. [49] |
| Water | Dispersive liquid–liquid microextraction using tetrachloroethylene and methanol | GC–MS | 0.01 μg $L^{-1}$ | 91 | 3.2 | Tankiewicz and Biziuk [50] |
| Coffee extract | Acetonitrile based extraction and d-SPE sorbents cleanup | LC-ESI-MS/MS | 10 μg $kg^{-1}$ | 80 | 20 | Reichert et al. [51] |
| Chinese cabbage, Tomato | Extraction using MMIP followed by elution with methanol/acetic acid (97:3, *v/v*) for 10 min. | GC–MS | 30 ng $L^{-1}$ | 89.60 (Chinese cabbage)<br>94.83 (Tomato) | 2.7 (Chinese cabbage)<br>2.4 (Tomato) | Chen et al. [52] |
| Honey, Brinjal | Ultrasonicated extraction using MMIPs in methanol: acetic acid (8:2) for 15 min. | GLC-ECD/TSD | 0.01 μg $mL^{-1}$ | 87.9 (Honey)<br>90.0 (Brinjal) | 5.35(Honey)<br>6.0 (Brinjal) | Our study |

**Table 3**
Applicability of MMIPs in market samples of honey and brinjal.

| Sample | Found (μg $g^{-1}$) | Spiked (μg $g^{-1}$) | Recovered (μg $g^{-1}$) | Recovery % | RSD % |
|---|---|---|---|---|---|
| **Honey** | | | | | |
| Brand 1 | 0.040 | 5.00 | 4.38 | 86.85 | 3.93 |
| Brand 2 | 0.046 | 5.00 | 4.64 | 92.04 | 3.68 |
| Brand 3 | 0.048 | 5.00 | 4.35 | 86.23 | 1.70 |
| **Brinjal** | | | | | |
| Market 1 | 0.036 | 5.00 | 4.50 | 89.42 | 0.17 |
| Market 2 | 0.025 | 5.00 | 5.14 | 102.36 | 1.26 |
| Market 3 | 0.047 | 5.00 | 4.79 | 94.97 | 5.50 |

## 4. Conclusions

A simple and rapid method has been developed to extract chlorpyrifos from honey and brinjal using magnetic molecularly imprinted polymers. The prepared polymers showed the features of high sorption capacity, faster attainment of sorption equilibrium, easy separation and specific removal of chlorpyrifos from honey and brinjal. Use of the synthesized MMIPs can be extended for extracting chlorpyrifos from other complex environmental and food matrices.

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## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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