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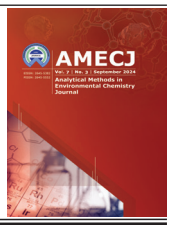

Analysis of pesticides in food: A review of applications on molecularly imprinted polymer nanoparticles by chromatographic methods

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ABSTRACT

Insecticides may build up in food and the environment, where even in deficient quantities, they can have a negative impact on ecosystems and human health. As a result, it's critical to establish a sensitive and trustworthy system for monitoring pesticides to ensure the safety of food and human health. On the other hand, chemical residues from controlling outbreaks in neighboring crop fields may degrade the quality of the food. Additionally, pesticides in the food matrix may signal environmental pollution. It is necessary to utilize extremely sensitive and selective procedures since many pesticides can be found simultaneously and because the amounts of these chemicals in food are often relatively low. Molecularly imprinted polymer nanoparticles (MIPs) were used as a sample preparation technique, and liquid or gas chromatography coupled to mass spectrometry (LC/GC-MS) was reported as the most important analytical technique. In this review, I present and discuss recent studies on the determination of pesticides in food matrices, with a particular emphasis on the use of molecularly imprinted polymer nanoparticles (MIP) for sample preparation and separation of pesticides in food matrices, followed by chromatographic analytical methods for detection such as Ultra-high performance liquid chromatography-MS/MS (UHPLC-MS/MS). Additionally, future perspectives and trends are also provided.

1. Introduction

The usage of pesticides has dramatically grown during the last few decades [1-3]. While using these materials aids in agriculture, many of them are found outside of the intended species, potentially contaminating food, water, and soil. Numerous pesticides, some of which have been linked to cancer, may cause dye functions in the brain and reproductive systems, even at low concentrations [1, 2, 4]. Therefore, the threats to food safety posed by the usage of these substances are a continual source of worry for people worldwide [5, 6]. Since World War II, there has been a rise in the use of pesticides in agriculture to enhance the global food supply. A wide range of pesticides from various organizations has developed considerably since then. The substances and their metabolites are found in all parts of the environment, including the air, water, and soil, as well as in crops, vegetables, and fruits. As a result, the use of pesticides and additional environmental harm caused by industrial emissions during pesticide manufacture [7]. Pesticides are among the most dangerous compounds that can be discovered in the environment. Due to their toxicity,

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accumulation, and extensive natural persistence, they can contaminate fruits, vegetables, and waterways [8]. Their ability to cause cancer, birth defects, neurotoxicity, and neurobehavioral issues makes their presence in water considered a potential threat to both human health and ecosystems [9]. Hazardous pesticide residue levels must be controlled to protect public health and prevent pesticides from entering the environment, waterways, and food chains [10]. However, it is challenging to determine the exact quantities of pesticides in the environment and food due to their considerable regional fluctuation. Furthermore, government data regarding food contamination by pesticides is lacking in several countries. [11]. One of the most commonly utilized types of pesticides is organophosphorus insecticides. This class of pesticides affects both humans and animals. Esterases' toxicological effects are linked to their irreversible inactivation. [12]. Neonicotinoids are systemic insecticides that permeate all parts of the treated plants, including their pollen, nectar, guttation fluids, and the food those plants produce. They were developed to take the role of pesticides like organophosphate and carbamate [13]. These chemicals find essential applications in horticulture, wood conservation, vector control for pets and livestock, urban and residential pest control, and pest control for hundreds of crops in agriculture [14]. They are very efficient against difficult-to-observe sucking, boring, or feeding insects [15]. Unlike most other pesticides, neonicotinoids cannot be eliminated by washing food before consumption [16]. Neonicotinoids are less harmful to birds, animals, and insects than organophosphate and carbamate insecticides. Additionally, insects can be harmed by some breakdown products [17, 18]. Determining pesticide residues in complex samples (biological, dietary, environmental, etc.) requires careful sample preparation before instrumental analysis. Solid-phase extraction (SPE) [19, 20], liquid-liquid extraction (LLE) [21], and QuEChERS (rapid, easy, cheap, effective, robust, and safe) [22] are the most widely used methods for extracting pesticides. Magnetic dispersive solid-phase extraction (MDSPE), one of the SPE methods, has benefits over other methods. The sorbents may be quickly and easily separated using an external magnet rather than centrifugation and filtering. This allows for a fast and easy extraction procedure. Recently, some magnetic nanoparticles from various matrices, including Fe_3O_4 [22-25], $ZnFe_2O_4$ [26], $NiFe_2O_4$ [27], and GO [28], have been created for the MDSPE of organophosphates and neonicotinoids as shown in Table 1. Magnetic mixed metal hydroxide (MMH), in addition to the materials listed above, is currently regarded as an appealing magnetic material due to its ease and speed of manufacture, structural stability, and favorable magnetic characteristics [29]. Since MDSPE's extraction effectiveness depends on the sorbent material's affinity for the target analyte, adding certain functional groups to the materials might increase selectivity. Various techniques, including high-performance liquid chromatography (HPLC) [30, 31], gas chromatography-mass spectrometry (GC-MS/MS) [32, 33], and liquid chromatography-tandem mass spectrometry (LC-MS/MS) [34-36] have been used in the past to analyze pesticides. The most popular of these techniques is LC-MS/MS. To maintain their high sensitivity, routine analyses of pesticides in environmental waters need to be quicker, cheaper, and have a lower detection limit than what is now practiced. Scanner electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, vibrating sample magnetometer (VSM), and X-ray diffraction (XRD) were used to characterize the resulting magnetic MIPs [37]. MIPs are synthetic polymeric substances with recognition sites created intentionally and can selectively rebind a target molecule [38, 39]. MIPs are promising candidates for applications in various fields, such as diagnosis/drug delivery, sensors, catalysts, chromatographic-based separation, and sample pretreatment/preparation [40-42]. This is due to their benefits, such as simple preparation, good stability, low cost, high selectivity, sensitivity, chemical inertness, solubility in water and most organic solvents, and physical robustness. Conventional strategies for MIP production require large amounts of organic or toxic solvents. They also

require significant amounts of time and energy. To overcome these challenges, molecular imprinting technologies (MITs) based on green chemistry principles have been applied to develop novel MIPs[43]. Creating a MIP is based on the cross-linking agent and a functional monomer being chemically polymerized together in the presence of a template molecule (Fig. 1). An imprinted polymer is produced after the imprinted molecule has been eliminated. This polymer's structure and the functional groups' position on the monomer units produce high-affinity sites for the template molecule. The polymerization occurred between the functional monomer and templates (pesticides) via hydrogen-bonding interaction between the nitro, amino, or cyano groups in templates and the O–H groups in the functional monomer. Thus, it is simple to extract and clean pesticide residues from the determined matrices. MIPs have been proven to help develop sensors specific to desired analytes of interest and in enantiomeric separations, catalysis, solid-phase extraction, drug delivery, and chromatography [44-46]. Recently, Arabi et al. (39) offered 14 criteria for green MITs that might be remembered using the word "GREENIFICATION" as a mnemonic device. These guidelines include producing the least amount of trash possible, employing environmentally friendly, renewable chemicals, creating quicker imprinting times, and extending the usage of solvent-free imprinting techniques. Using dummy-template or multi-template molecules, bio-based monomers, ionic liquids, deep eutectic solvents, pure aqueous porogen, and ultrasound- or microwave-assisted reactions are other examples of green techniques [40, 41, 47, 48]. Bagheri et al. created fake MIPs for the MSPE of acrylamide in food samples utilizing propanamide and chitosan as dummy templates and bio-based functional monomers, respectively. The polymerization was accomplished at room temperature without using organic solvents [49]. This new MIP's quick equilibrium kinetics and high adsorption capacity decreased the analysis time and increased the aqueous applicability.

In this context, this review aims to present and discuss the studies published between 2017 and 2023 dealing with pesticide determination in the food matrix. Particular focus was given to MIPs sample preparation methods and separation/detection application of the developed methods worldwide.

2. Molecular Imprinting Technology (MIT)

Molecular imprinting technology (MIT) has created considerable interest in various applications, including chromatographic separation, catalysis, biosensors, and synthetic antibodies. Molecular imprinting is a well-established and straightforward method for creating molecularly imprinted polymers (MIPs) [48] as a result of the demand for fast, reliable, and cost-effective analytical procedures to ensure food protection, molecularly imprinted polymers (MIPs) as attractive materials have garnered considerable attention. They can be designed specifically to bind template target molecules with high selectivity. MIPs are synthesized by concurrently polymerizing functional monomers and cross-linkers in the presence of template target molecules. Following the removal of template target molecules, recognition cavities in the highly cross-linked polymer matrix are developed complementary in shape, size, and spatial arrangement to the template molecules [50]. MIPs have significantly advanced food analysis due to their unique properties. MIP is a frequently used

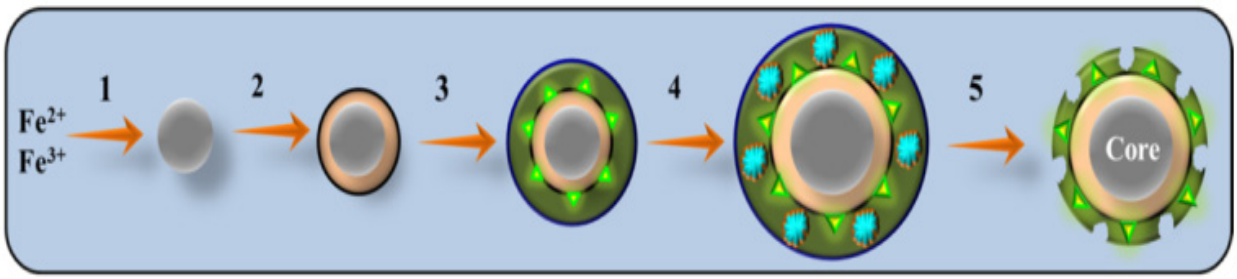

Fig. 1. Magnetic MIP nanoparticles-based extraction method [50]

technique in the field of sample preparation. Because of the complicated interactions between food matrix components and trace levels of target compounds, the output of analytical instruments is highly dependent on the sample treatment method. However, this is a component of analysis development that is commonly disregarded. To support the analysis of food samples, researchers must develop applicable sample preparation methodologies. MIPs have been used to prepare samples as sorbents [40]. Compared to conventional adsorbents such as C18 silica gel, MIPs have many evident advantages, including improved loading capacities, enhanced selectivity, and higher recovery performance during the retention procedure. Numerous studies have repeatedly demonstrated that using MIPs to prepare food samples can result in significant detection limits and recoveries. Until now, the majority of cases have included the use of MIPs in conjunction with traditional sample preparation procedures such as solid-phase microextraction (SPME) and solid-phase extraction (SPE) [51]. Recent improvements in MIPs combined with magnetic bead extraction have greatly improved sample processing and pre-treatment methods, enabling the integration of sample preparation with new analysis equipment such as biosensing/microfluidic platforms [52]. While MIP technology has tremendous potential for food analysis, commercial success has been relatively limited thus far. Only a few commercial examples of MIPs are utilized as sample preparation adsorbents, and no MIP-based biosensors are commercially available. Various challenges have limited the commercialization of MIPs, including incomplete template deletion, insignificant selectivity, and limitations in mass-producing MIPs. Efficient methods for preparing MIPs should be established to allow MIPs to significantly improve properties and accelerate the adoption of MIPs methods in the food sector [53].

3. Molecular Imprinting Methods

3.1. Synthesis of MIPs

MIPs can be created in several ways. The most frequent imprinting is non-covalent imprinting, where interactions between templates and functional monomers in a per-polymerization mixture are established, as illustrated in (Fig. 2) [54]. Non-covalent imprinting technologies include bulk polymerization, precipitation polymerization, core-shell imprinting, mini-emulsion polymerization, and solid-phase imprinting. The imprinting technique selected will depend on the kind of template used, the size and form of the desired MIP, such as (nanoparticles, thin films, etc.), and the planned application of the MIP as well as in the creation of food samples[55]. It is usually produced in bulk before applying the MIPs approach to a solid-phase structure. In contrast, MIP-based biosensors frequently apply thin layers to the sensor's surface. While non-specific binding should be minimized, MIPs with many binding sites and an enormous surface area are ideal for both purposes [54]. Due to its simplicity, bulk polymerization is the most often utilized procedure for creating MIP sorbents for sample extraction. However, the method produces particles with no binding sites and high batch-to-batch variation [44, 56]. The method is also complicated to process, includes many templates, and is vulnerable to template leakage. Due to their improved, well-defined size and surface-area-to-volume ratio, MIP nanoparticles are now being developed with a focus on biosensors, food, and sample preparation [57]. Precipitation polymerization is a practical method for imprinting nanoparticles, established through monomer research. It makes it possible to create pure nanoparticles, has control over particle size, and has high yields [40]. The method uses a cross-linker and diluted monomer solution to dilute the template, producing a high dilution factor. MIP gradually precipitates out of the solution after synthesis. Precipitation polymerization permits the imprinting of biomolecules like proteins in a tiny quantity of surfactant. However, the method is limited to great abundance templates [58]. The creation of MIPs has demonstrated the flexibility of emulsion polymerization. This method emulsifies the template, cross-linkers, and functional monomers in an aqueous phase. The dispersion phase is subsequently stabilized by restricting diffusion through the continuous phase and creating tiny, stabilized homogeneous-sized emulsion droplets.

High yields of monodispersed nanoparticles are produced by the process, although limited binding capacity might result from surfactant residues that prevent the analyte from being recognized upon rebinding [59]. Polymerization utilizing a solid phase effectively imprints minute molecules, endotoxins, and even whole viruses. Before chemical or photo-induced polymerization, the template compound is mixed with the monomers, initiator, and cross-linker and attached to a solid support, frequently glass beads or silica gel with a diameter of up to 1 m [60]. The method provides various significant benefits over existing methods for producing MIP nanoparticles. This concerns how easily the template can be removed, allowing it to be reused for more reactions. The resultant MIPs nanoparticle is also monoclonal, creating just one or two recognition sites per nanoparticle. Also, the technique may be used as an affinity column to distinguish between MIPs with a high affinity and those with a low affinity or those that are not imprinted [61]. Many other linker chemistries may be used to join the template to the support. For instance, MIPs for trypsin were created by covalently bonding the protein to its inhibitor and p-amino benzamidine in a glass bead template, as displayed in (Fig. 3) [62]. Compared to the binding cavity, this caused the MIPs nanoparticles to have a more consistent size and orientation. The huge surface area of the nanoparticles allows for rapid MIP binding kinetics and makes it easier for the analyte to get to the MIP. Moreover, adding a shell layer or changing the surface of nanoparticles might lessen their tendency to aggregate. Besides, the core of the imprinted nanoparticle may be composed of any precursor nanoparticles, including silicon oxide, iron oxide (magnetite), quantum dots, or polymers, which can give MIP nanoparticles extra functionality [63]. Pérez-Moral et al. (2007) devised the surface-initiated live radical polymerization approach to imprinting an MIP with a polymer-based core [64]. Magnetic nanoparticles were formed via iron chloride coprecipitation, resulting in magnetic core nanoparticles. After that, a SiO_2 shell layer was created by salinizing with tetraethyl orthosilicate (TEOS). The MIP layer was then grafted onto the core shell to allow biotin binding [60]. The ease with which these nanoparticles may be removed from food matrixes has boosted interest in using molecularly imprinted magnetic core-shell nanoparticles for effective sample separation. Quantum dots are commonly used as a substrate for molecular imprinting to create fluorescence-based sensors [65]. The core nanoparticles for imprinting are likewise silver and gold nanoparticles. MIPs made of silica and containing silver nanoparticles were developed to use the unique optical properties of silver nanoparticles, known as metal-enhanced fluorescence [66]. A core for imprinting MIPs can also be made of gold nanoparticles because of their unique UV absorbance properties, as shown in (Fig. 4) [67]. Core-shell imprinted polymers that include numerous functional components have shown promise by combining the distinctive qualities of many nanoparticle systems. Han et al. 2014 developed hybrid Fe_3O_4-CdTe quantum dot core-shell imprinted nanoparticles capable of detecting and binding 4-nonylphenol. The scientific community has been attracted to hollow shell imprinting, in which the particle's center is extracted after imprinting [68]. Several research groups have focused on methods for imprinting thin films. They are beneficial in biosensors like electrochemical sensors, where the surfaces may be produced by electro-polymerization. In situ, electro-polymerization is a form of electrode surface imprinting [69]. One notable advantage of this technology is that it allows for fine control of the polymer thickness via different factors, such as current density and applied voltage, resulting in a more uniform coating of the MIP on the electrode surface [70]. The polymer deposition region may also be accurately controlled. Combining an electrochemical transducer with non-conducting imprinted polymers can be accomplished by in situ electro-polymerization of monomers in the presence of aniline or ethylene-dioxy thiophene. On the other hand, electro-spraying or spin coating can immobilize the imprinted polymers on the electrode's surface. Other imprinted polymers, such as nanoparticles, can be linked via carbon electrode paste, ink casting, gels, and membranes [71].

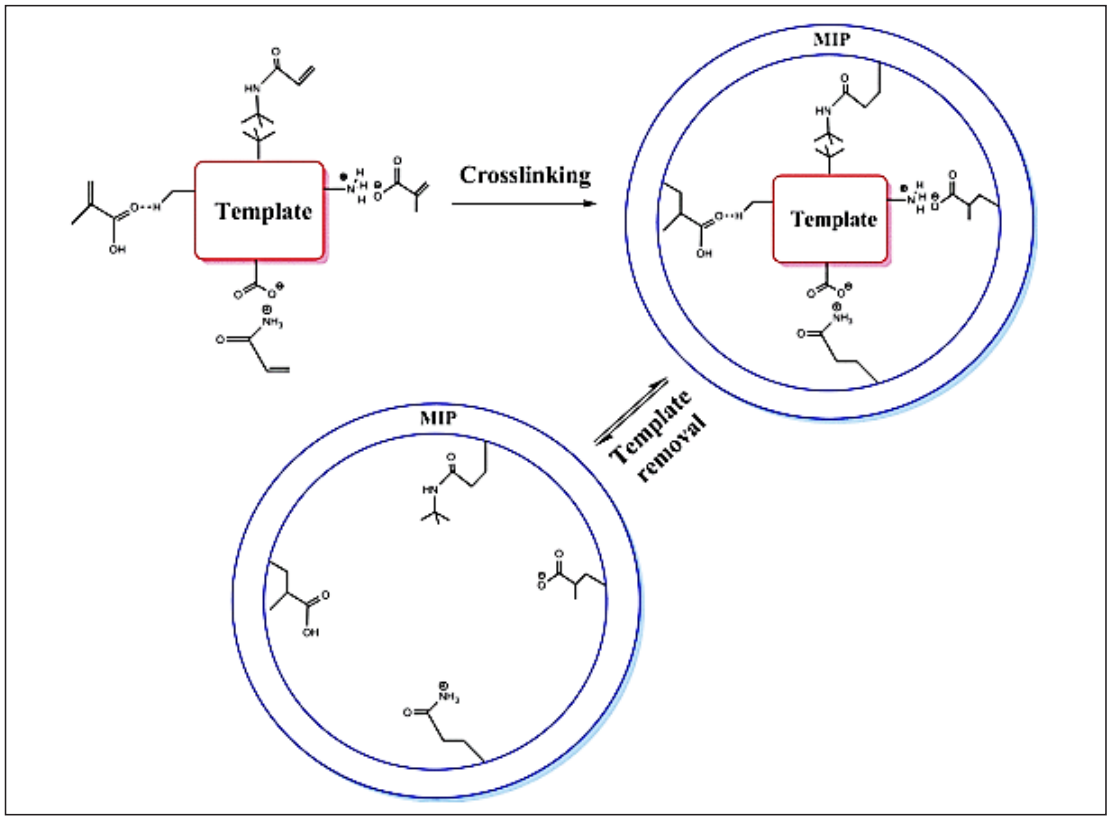

Fig. 2. Synthesis of molecular imprinting polymer nanoparticles [50]

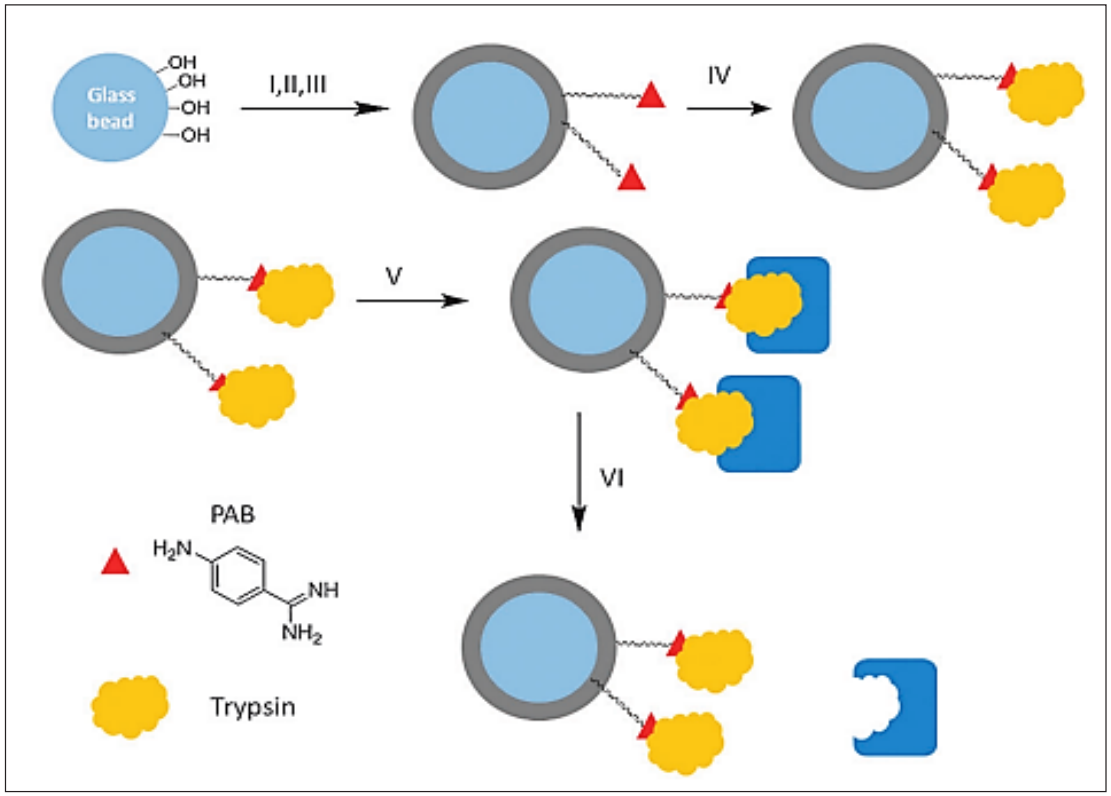

Fig.3. Schematic representation of the solid-phase synthesis of MIP-NPS. I: 3-Aminopropyl)triethoxysilane (APTES); II: glutaraldehyde; III: p-aminobenzamidine (PAB); IV: trypsin; V: pre polymerisation mixture; VI: release of thermoresponsive MIP-NPS (temperature change from 37 ̊C to room temperature) [59].

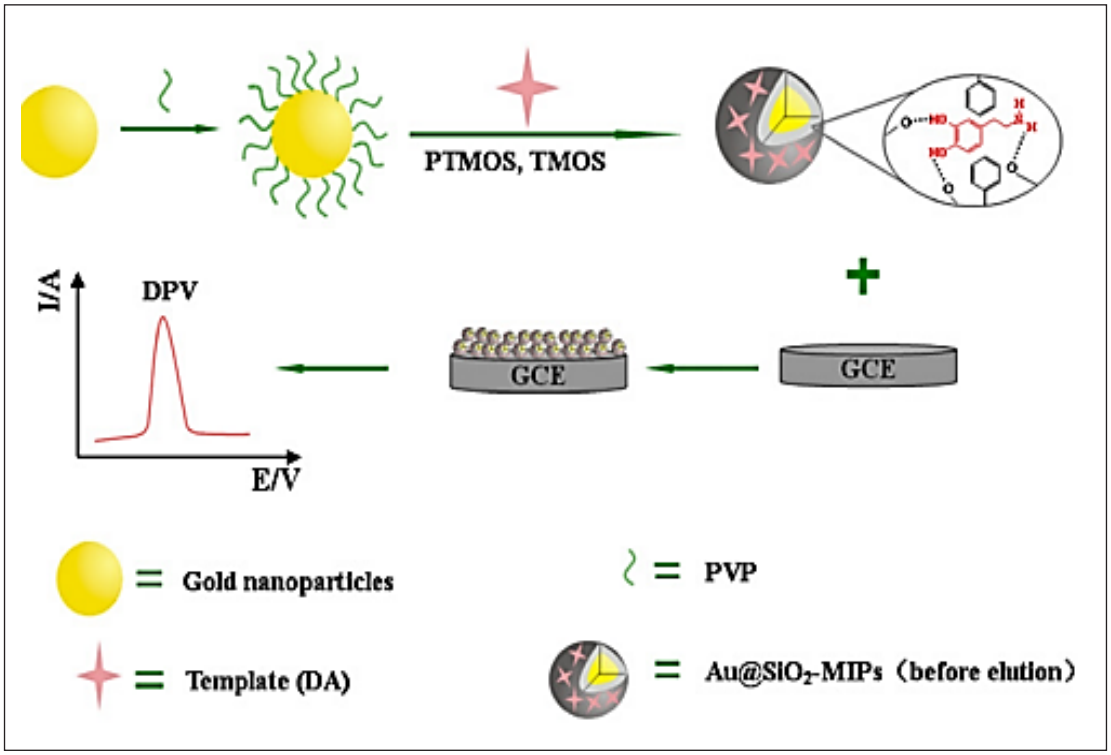

Fig. 4. Preparation procedure of the AuNPs@SiO_2-MIPs [64]

3.2. Design of MIPs

MIP development for new templates is often time-consuming and involves trial and error. Numerous experimental factors must be examined, including the shape and concentration of the monomer, the template, and the cross-linker [72]. When using temperature-responsive monomers or temperature-sensitive templates, it is equally necessary to examine the temperature at which the polymerization was carried out. MIPs have been designed using chemometrics, molecular modeling, combinatorial techniques, and experimental methods [73]. Chemometric-based design approaches have been shown on a variety of templates. It focuses on statistical analysis, allowing MIPs to be generated from the results of experiments. By simulating essential imprinting parameters, molecular modeling has become prominent as a technique for rationally constructing MIPs [74]. For example, a model including Monte Carlo simulations and analytical data was given to establish MIPs rationally [73]. The binding energy was calculated using the Hawtree Flock technique, which led to the selection of methacrylic acid as the monomer and ethylene glycol dimethyl acrylate as the cross-linker for imprinting [75]. Hawari et al. (2013) utilized 3D simulation to assess the binding of several monomers to pinene, a volatile substance emitted by ripening mangos [76]. Using computational chemistry in MIP design can speed up MIP synthesis with fewer reagents. On the other hand, it is still difficult to effectively simulate larger macromolecules. In 2011, researchers used molecular docking, one of the few examples of macromolecule MIP modeling, to simulate macromolecule-monomer interactions [77].

3.3. MIP characterization

The possibility of an MIP is associated with certain cavities that encourage a high level of contact with the intended insecticides. In most works, a non-imprinted polymer (NIP) is synthesized under identical circumstances as the MIP but without the template [78]. This control polymer has no imprint and is investigated in parallel with the MIP characterization. Because the same monomers, porogen, and interactions are used, the nature of the interactions formed between an MIP and a template

is the same as that between an NIP and a template. The difference between the two sorbents is the strength of these interactions. The strength of the interactions is more significant on the MIP than on the NIP if well-defined cavities are formed during the polymerization process because the template can be held by various sites (sum of the interactions) owing to the spatial complementarities between the template and the cavities [79]. The initial assessment of the synthesized MIPs may involve describing the surface of the MIP/NIP by SEM in terms of the form and size of the particles [80]. The porosity of MIP/NIP may also be determined and compared using the BET adsorption technique. The optimal monomer, the template/monomer ratio, and other parameters were chosen using binding assays that include introducing a specified quantity of MIP/NIP in the presence of a known amount of an OPP and then measuring, after a determined period, the amount retained by the MIP and the NIP [81]. In these circumstances, the solvent utilized is extremely near to or identical to the solvent used for polymer synthesis, promoting the same interactions as those generated during the polymerization process to create the imprint. The adsorption isotherm obtained from these binding studies also permits the number of binding sites and their affinity towards the template molecules and, in certain circumstances, structural analogs to be defined to be calculated using different models (Langmuir, Freundlich, Langmuir-Freundlich) [82]. Binding tests were also performed in a pure solvent that was highly comparable to the nature of the sample matrix, such as aqueous buffer, pure water, or acetonitrile, for further study of pesticides in aqueous or acetonitrile vegetable extracts, respectively [83, 84] as presented in Table 2. These binding examines were also conducted in heptane, the solvent used to dilute oil samples [85]. This method provides a more accurate assessment of the retention potential and selectivity that may be expected in actual samples. Similarly, by performing binding examinations on multiple solvents, the solvent with the best selectivity may be chosen to dilute the sample or sample extracts [86]. On the other hand, in the SPE technique [87], the solvent that provides the lowest affinity can be selected as the eluting medium. HPLC measurements were also used to examine how the types of solvents affected the retention characteristics. This technique was employed to assess the solvent that facilitates retention and the selectivity towards various analogs [88].

4. Sample Preparation

Sample preparation is crucial in the process of conducting a chemical analysis. The best sample preparation methodology should be easy to use, effective, selective, affordable, and work with a variety of instrumental procedures [89]. Analyzing the sample directly in a chromatographic system is impossible because environmental samples have a very complex composition and include analytes at low concentrations. Isolation, concentration, and analyte purification (clean-up) are required steps in sample preparation. The selection of the sample preparation technique is influenced by the analyte's physicochemical characteristics (such as its acid-base properties, stability, volatility, and solubility in water and organic solvents), the sample's nature (such as its aggregate state, purity, fat, and oil content), and the analytical technique used to analyze the sample [52].

4.1. Sample Preparation in Pesticides Analysis

Pesticide residue analysis in foods entails sample preparation and instrumental determination. At the same time, analytical instruments continue to advance rapidly in technologies [90]. Typically, interferences from food matrices affect their detection limits, detector noise, and final quantification [91]. Thus, sample preparation is the bottleneck for performing an efficient and reliable study of trace pesticide residues. The sample preparation procedure is designed to separate trace amounts of analytes from various complex matrices while minimizing interferences from the food matrix. Sample collection/homogenization, extraction, and clean-up are common sample treatment steps. The separation and clean-up steps

are critical for successfully analyzing pesticide residues [90]. Liquid-liquid extraction (LLE) is possibly the oldest and most widely used of all sample preparation techniques. Before LLE, solid samples are mechanically ground, mixed, agitated, chopped, crushed, macerated, minced, pressed, or pulverized to produce fine and homogeneous particles. Repeated extractions with an immiscible organic solvent are performed on homogenized solid or liquid samples. Before the final analysis of extraction solvents and analytes, the extracts are centrifuged, concentrated, and purified using the similarity concept. Due to its simplicity, robustness, and performance, liquid-liquid extraction (LLE) is a well-established process for routine sample preparation [92]. Supercritical-fluid extraction (SFE) is a relatively new technology that utilizes supercritical fluids to extract target analytes from solid samples rapidly. Supercritical fluids can permeate the solid matrix and dissolve analytes because their physicochemical properties vary from liquid and gas phases. Thus, supercritical fluids may be used instead of organic solvents when preparing samples for pesticide residue analysis. Organic solvent modifiers are used to increase the polarity of extraction solvents to eliminate pesticide residues that are moderately polar or polar [93]. Since its introduction in the mid-1970s, solid-phase extraction (SPE) has been the most commonly used sample treatment process for insecticide residue analysis in food [51]. Before usage, the extract is passed through the cartridge and adsorbed on the solid phase components. It is then conditioned and activated with water and an organic solvent. After pre-washing with organic solvents, the interferences are removed while the analytes remain on the sorbents. Following this cleaning step, the target components can be eluted with additional organic solvents to yield extracts [19]. Due to the fact that SPE requires small solvent volumes, simple experimental procedures, quick sample processing, and standard experimental equipment, it has been widely accepted as a viable alternative to LLE for sample treatment methods, particularly for cleaning and enriching organic compounds water samples. SPE is typically conducted by selectively retaining target components on sorbent packed in a disposable extraction mini-column. Numerous sorbents have been created to clean/pre-concentrate pesticide residues in foods to ensure adequate analyte absorption [94]. A solid-phase micro-extraction (SPME) approach is another alternative to traditional sample preparation methods. Modern insecticide residue analysis patterns necessitate simplifying sample preparation and reducing operation time and organic solvent. Solid-phase micro-extraction (SPME) was initially introduced as an SPE invention that is widely commercialized nowadays. SPME, like SPE, depends on the equilibrium of the analyte partition between the stationary phase and the sample [52]. This means that the analytes are absorbed in the solid phase and then desorbed utilizing either the thermal energy generated by the GC injection port or the solvent elution of the HPLC mobile phase during the subsequent chromatographic determination. SPME is a sample preparation method incorporating sampling, extraction, concentration, and injection into a single step [95, 96]. SPME is a beneficial alternative analytical approach to many conventional procedures because it significantly reduces and complicates organic solvents. While SPME is capable of quickly obtaining equilibrium adsorption, it is affected significantly by matrix contaminants. Typically, the impacting variables of SPME have been optimized. In comparison to SPE, SPME is an automated, one-step, straightforward, and solvent-free extraction method. The primary advantages of SPME are its superior analytical efficiency and ease of use [97]. Additionally, it is free of the plugging and channeling issues associated with solid-phase extraction. However, SPME remains laborious, as achieving equilibrium between the fiber and the sample solution takes a long time and requires numerous strict extraction conditions. Additionally, the fibers used in SPME are expensive and sensitive [98]. A method known as liquid phase micro-extraction (LPME)) has been created for miniaturized liquid phase

extraction [99]. During the LPME, the target components are moved from an aqueous phase (also called donor phase) to several microliters of a water-insoluble solvent (also called extractant or acceptor) [100]. Based on the sample treatment method, the LPME of pesticides in foods may be classified into three basic categories: dispersive liquid-liquid micro-extraction (DLLME), hollow-fiber LPME (HF-LPME), and single-drop micro-extraction (SDME). Compared to standard sample preparation methods for pesticide analysis in food samples, the LPME approach removes the SPE phase, eliminates the clean-up step, simplifies the sample treatment process, minimizes solvent usage, and lowers the analysis cost [20]. The target molecules are frequently extracted and concentrated in a bit of injection solution to improve the sensitivity of the analysis. This uses a significant amount of organic solvent and necessitates lengthy laboratory methods and expensive equipment. In 1976, Watanabe and colleagues developed micelle-mediated extraction (MME) and cloud point extraction (CPE) to improve the extraction methods [101]. When non-ionic surfactants are concentrated above their critical micelle concentration, micelles develop, and they become cloudy at their cloud-point temperature, which is often higher than their critical temperature. The cloudy solution is then extracted into an aqueous and a surfactant-rich phase, the latter containing only small amounts of analytes. Due to the viscosity of the concentration analytes for chromatographic injection, they may be dissolved in a minimal volume of mobile phase or organic solvent. Since different surfactants have different extraction efficiencies, the surfactants must be optimized for adequate analyte extraction [101]. CPE has a range of benefits over other extraction methods. It is simple to use, requires only a small amount of non-volatile surfactant, and is relatively non-flammable. Furthermore, CPE combines extraction and enhancement into a single step. As a result, CPE was developed as a feasible alternative to separation technologies. However, certain surfactants in CPE can interfere with the HPLC-UV to determine the analyte [102]. QuEChERS, a more modern and now widely used sample treatment method, was established in 2003 [103]. This approach is based on microscale extraction with ACN, water absorption and liquid-liquid partitioning with MgSO4 and NaCl, and d-SPE clean-up with a primary-secondary amine (PSA) sorbent. Mixing the separation and clean-up procedures into a single step significantly decreases the quantity of mixing, solvent transfers, evaporation/condensation, filtration, and solvent exchanges necessary for chromatographic analysis. QuEChERS is an acronym that stands for quick, easy, cheap, effective, rugged, and safe [22]. Compared to conventional LLE, the advantages of QuEChERS include a more straightforward and faster process and less organic solvent use. Since the QuEChERS approach considerably facilitates the separation and clean-up steps during the sample treatment procedure and generates quantitative results, it has a promising future in analyzing insecticide residues in foods [104]. It was done using molecularly imprinted polymers (MIPs), which are made by co-polymerizing a monomer and a cross-linker with a template analyte. The template is removed, followed by the polymer containing complementary recognition sites. There are recognition sites in the polymer that are structurally, chemically, and physically compatible with the template molecules [105]. Due to their ability to bind preferentially to the template (target component) and comparable structures, MIPs exhibit excellent molecular recognition and a high affinity for template molecules [53]. MIPs can, therefore, be utilized as adsorbents to identify and enrich pesticide residues in foods specifically. For instance, molecularly imprinted polymers were created when suspension polymerizing methacrylic acid polymers with ethylene dimethacrylate in the presence of a carbaryl template and its metabolite. These polymers were then packed into a pre-column to make it possible to isolate analytes from complex matrices without the need for extensive sample preparation and cleanup [106]. The sample preparation techniques previously outlined apply to studying different pesticide residues, and MIPs are

made to analyze analogous chemicals. Pesticide residues in food samples have been successfully examined using MIPs [38]. As a result, MIPs need to be low-cost, easy to prepare, have a higher population of homogeneous binding sites, produce clean extracts with high selectivity, and have excellent physicochemical stability in various solvents and laboratory conditions [107].

4.2. Application of MIPs in Food Sample Preparation

The dynamic impacts of food matrixes and the low concentration of target components make sample preparation a substantial bottleneck in the analytical procedure. The processes for sample treatment have recently seen advancements in their selectivity. MIPs have been used as adsorbents during sample treatment and are frequently advised. The ability of MIPs to concentrate analytes and selectively extract the target ingredient from bulk samples is their key competitive advantage. They provide more sensitive and focused detection by overcoming the non-specific affinity of traditional adsorbents such as C18-bonded silica gel [108]. Additionally, MIPs provide the following benefits: high sample load efficiency, ideal physical resilience, high stability, and strong resistance to high temperatures, as well as being simple to prepare, inert to organic solvents, as well as acidic and basic solutions, and affordable. MIPs are mostly used with popular sample treatment techniques like SPE and SPME. Recent advancements in magnetic MIP nanoparticle technology have made it possible to employ MIPs in conjunction with magnetic bead extraction, greatly simplifying sample-handling operations as shown in (Fig. 5) [109, 110].

4.2.1.MIP-based SPE

SPE based on MIP is the method most frequently used to prepare food samples because of its simplicity, speed, minimal solvent consumption, and capacity to clean unique analytes. In the standard MIP-SPE technique, the imprinted bulk polymer is packed in a cartridge, separation well plate (for high throughput analysis), or column. MIPs in different forms, such as nanoparticles and

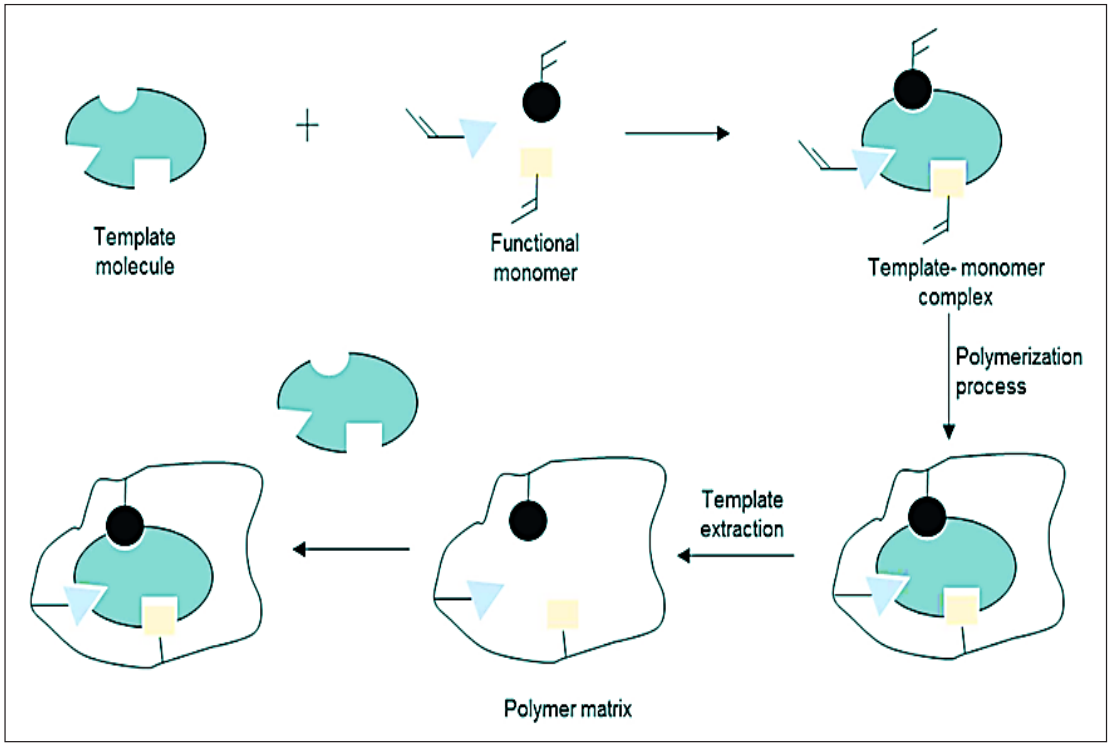

Fig. 5. Schematic diagram of the imprinting process [101].

thin films, have lately been employed as adsorbents in SPE [111]. The "natural phase" mode for food samples dissolved in a low polarity solvent and the "reverse phase" mode for aqueous food samples have been considered two distinct approaches to extract analytes utilizing MIPs. Target components interact with the adsorbent matrix in a shape-specific method to cause the adsorption of the target components onto an MIP adsorbent to occur in the "natural phase" mode. While interfering molecules pass through the separation column with excellent selectivity with ease, increased mobile phase intensity results in analyte elution [112]. In contrast, the target molecules in aqueous samples are then adsorbed onto the MIP adsorbent through hydrophobic interactions when the "reverse phase" mode is employed. Interfering elements can be removed from the target molecule after solvent cleaning. The analyte can be eluted once the column has been sufficiently cleaned with a solvent. The washing solvent can remove non-specific binding without affecting the MIP alone's selective interactions with the target components in food samples [113]. It may be possible to eliminate cleaning with washing solutions in some circumstances, such as when the elution step is highly selective for the target component and does not elute non-specifically bound compounds. This is especially advised for aqueous samples since using a non-polar solvent during the cleaning process might have an adverse effect on miscibility [110]. In previous studies, MIP-SPE was used to remove food samples' antibiotics, insecticides, and mycotoxins [114, 115]. In addition to MIPs created via bulk polymerization, nano-based core-shell type molecularly imprinted sorbents have been used for food analysis. As an example, Wang et al. (2014) used hollow core-shell spheres that were molecularly imprinted to extract estradiol from milk samples [116].

4.2.2.MIP-Based SPME

SPME is a sample treatment method that uses a syringe with a stainless steel microtubing needle and fused silica fiber tips coated with an organic adsorbent [117]. This coated silica fiber may travel forward and backward with the syringe plunger. Several benefits of SPME's distinctive design include the lack of organic solvents, accelerated sample processing, automation ease, and cheap cost [118, 119]. However, SPME shares the same problem as traditional SPE: a lack of selectivity. SPME has demonstrated better sensitivity and selectivity by applying an adsorbent MIP coating to the fiber tips. One of the most intriguing concepts to emerge in recent years is the fusion of MIP and sol-gel technology to create MIP extraction methods compatible with water [120]. In a sol-gel coating of MIP, Wang et al. (2013) utilized polyethylene glycol as the functional monomer and diazinon as the template. The researchers showed that diazinon and its analogs could be determined selectively in green pepper, cabbage, lettuce, cucumber, and eggplant samples. The extraction capacity was significantly higher than that of industrial fibers and unimprinted polymers, owing to the very porous surface, selective adsorption, heat stability, and superior chemical resistance [120]. Recently, Zhao et al. (2015) proved how temperature-sensitive MIPs may be connected to SPME, as displayed in (Fig. 6) [121]. With HPLC connected to SPME coated with MIP, they successfully extracted and tested ofloxacin from milk. Unique molecularly imprinted SPME fibers with the capacity to renew their selective binding sites through progressive polymeric network disintegration were also found with temperature-sensitive MIPs [122]. When using this reusable MIP fiber, the separation of triazole fungicides such as tebuconazole, metconazole, and triadimenol from grape juice samples was highly exact and accurate [123].

4.2.3.Magnetic MIP Nanoparticles-based Extraction

Another sample treatment approach based on magnetic MIP nanoparticles has recently drawn much interest. Since magnetic MIPs generally include a magnetic core and a MIP layer on the shell, they have magnetic susceptibility and good selectivity for target molecules, as shown in (Fig 1)

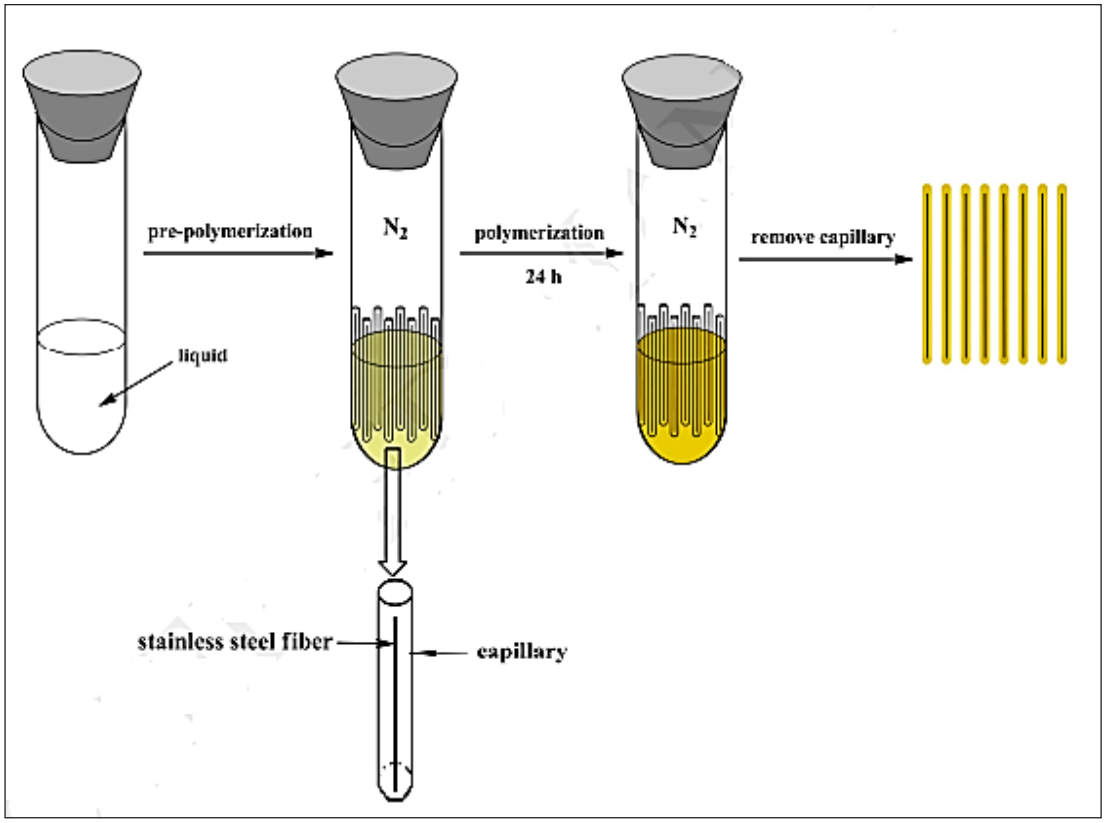

Fig. 6. Synthesized of MIP as SPME coating on the modified SSF in a capillary [112].

[124]. Magnetic adsorbents MIP can be dispersed directly in food samples to remove analytes during separation. A magnet is then utilized to separate the nanoparticles and analytes from the solution. The combination of magnetic nanoparticles and MIP technology has proven a highly effective technique for sample pre-treatment and analysis due to the outstanding target compound-adsorbent interaction and the ease with which magnetic nanoparticles may be removed from sample matrices [40]. Magnetic MIP nanoparticle extraction is quickly utilized to concentrate food contaminants such as pesticides, herbicides, antibiotics, endocrine-disrupting compounds, and growth hormones in complex sample matrices such as honey, milk, fruit juices, eggs, and meat products. Magnetic MIPs revealed sample recoveries ranging from 75% to 96% on average for diverse pollutants. The magnetic MIP approach required much less sample preparation time since extraction and clean-up were simplified by isolating the magnetic polymers in the sample matrix [107, 125, 126]. The utilization of new magnetic hollow nanoparticles with an etched core for quick enrichment of triazines and precise identification in food samples has been demonstrated [127]. Furthermore, a magnetic MIP nanoparticle adsorbent was established for the separation of imidacloprid pesticide residues from honey and eggplant samples, with an extraction recovery of 87.1-95.6% and selectivity for imidacloprid significantly higher than that of structurally related analogs acetamiprid and thiamethoxam [126].

5. Quantitative Analysis Methods

Previously, quantitative analysis was carried out using immunoassay techniques such as liquid chromatography (LC) and evaporative light scattering detection (ELSD) in conjunction with chemiluminescent nitrogen detection (CLND). However, techniques such as gas chromatography combined with mass spectrometry, liquid

chromatography, electrochemical detection, ultraviolet (UV), and fluorescence have advanced. These techniques are the most extensively utilized because they are more linear, exact, and sensitive, and they can analyze tiny sample volumes in food matrices at the same time [4]. Only molecules that can absorb UV light are detected by UV rays, and the absorbed energy is proportional to the concentration of the molecules of interest across a wide concentration range. As a result, analogs of the target molecule can absorb the same UV area [128]. Fluorescence and electrochemical detection are more sensitive than UV detection, but their applications are limited since they contain substances with electroactive or fluorescent groups. As a result, extraction of the chemicals will be required, altering the physical-chemical characteristics of the pesticides evaluated and adding time to the process [128]. However, by combining capillary GC with the unparalleled specificity of the MS, GC-MS analyses low-polarity compounds. Despite having low polarity, some of these molecules are too large to analyze without decomposition. Additionally, this technique cannot test many pesticides because they are non-volatile, thermolabile, and polar [128]. In terms of quantitative analysis, several methods mentioned above have limitations. However, with ongoing advancements in the hyphenation of analytical methods, liquid chromatography-tandem mass spectrometry (LC-MS/MS) has emerged as the most successful method for pesticide component analysis. Due to its unparalleled capacity for high throughput analysis, selectivity, and sensitivity, it has been used to classify and quantify novel pesticide targets in food samples and degradation products/metabolites [129]. Various analytical techniques have been employed to separate and identify pesticides in food. It is crucial to utilize analytical methods that offer excellent selectivity and sensitivity due to the low concentration of these chemicals and the incredible complexity of the matrix. The most used methods for analyzing multiple residues of pesticides in bee products are Gas Chromatography-Electron Ionization-Mass Spectrometry (GC-EI-MS) and Liquid Chromatography-Electrospray Ionization-Tandem Mass Spectrometry (LC-ESI-MS/MS) [129]. The features of the targeted pesticides play a significant role in selecting the separation method. While gas chromatography can identify volatile, semi-volatile, and thermally stable compounds, liquid chromatography can identify non-volatile and/or thermally unstable compounds [130]. Table 3 provides an overview of studies on pesticides in food published in the literature between 2017 and 2022, utilizing liquid or gas chromatography to separate these substances.

5.1. Gas chromatography

A potent method for quantitatively identifying low amounts of pollutants in complicated matrices is gas chromatography (GC) with quadruple mass spectrometry detection [6, 131]. It has been widely used to detect pesticides in food. For the examination of the food matrix, GC has been coupled with several detection methods, including (i) MS [132, 133]; (ii) MS/MS [134]; (iii) NPD [135, 136]; (iv) ECD [137, 138]; (v) AED [139]; and (vi) FPD [133, 140]. Mass spectrometry offers structural formation in a multi-residue study and is the most selective pesticide detector. This is because it gives unequivocal confirmation, which is crucial. When specific ions or their transitions are chosen, MS enables the simultaneous detection and identification of co-eluting substances [141, 142]. Mass spectrometry is frequently used to identify several pesticide classes in the food matrix. The most popular mode, selected-ion monitoring (GC-SIM/MS), has increased sensitivity due to its capacity to identify particles. In this method, the analyte's three strongest ions are chosen, one for quantification and the other for confirmation. It is possible to select more than two ions for confirmation; however, doing so can reduce the method's sensitivity. In the full-scan mode, the target analyte is confirmed and quantified using all of the ions generated by the MS. Standard MS libraries, such as the National Institute of Standards and Technology (NIST), which include more than 150,000 mass spectra

of standard organic compounds, can be achieved the reliability of compound identification [143, 144]. Although gas chromatography is frequently mentioned as the most powerful separation tool, it requires a derivatization step for non-volatile and thermally unstable compounds. This adds more handling and response time, which may affect repeatability and recovery rates [131, 145, 146]. The selection of the GC column is a critical step in pesticide analysis. The stationary phase should be chosen based on the polarity of the insecticides. As shown in Table 3, non-polar columns (5% phenyl 95% dimethylpolysiloxane) are the most widely employed for pesticide analysis in honey [134, 147, 148]. However, medium-polar (50% phenyl, 50% dimethylpolysiloxane) and medium to high-polar (50% Cyanopropylphenyl Polysiloxane) columns have also been employed [60, 113]. The number of pesticides to be determined concurrently can also be used to optimize other column characteristics like length, inner diameter, or film thickness. Contrary to LC-MS, GC-MS was formerly the technology most frequently employed to analyze residues in food products [95, 96]. The examination of thermally unstable pesticides used HPLC the most successfully. Today's pesticides are more polar, thermally unstable, or challenging to evaporate, making them more amenable to liquid chromatography analysis [43, 149, 150].

5.2. Liquid chromatography

Pesticides in food have also been extensively analyzed using liquid chromatography (LC), particularly for thermally labile chemicals. Although the most effective and appropriate detector for this type of analysis is mass spectrometry [10, 151, 152]. In addition to this mentioned above, variable wavelength [153], diode array (DAD) [154, 155,156], and spectrofluorimetric [133] have also been utilized as detector types. However, these other types of detectors are often only employed to analyze a small number of pesticides or classes of pesticides. Pesticides at low concentrations in complex matrices can be detected using liquid chromatography-tandem mass spectrometry. This system is crucial for structural information, decreases matrix interference, and increases sensitivity. in which utilizes multiple reactions monitoring (MRM) mode to improve the accuracy of the results [155]. Furthermore, in recent years, the LC-MS/MS technique has been widely employed to identify the presence of target analytes in commercial food and related samples, as shown in Table 2. Using high-resolution Orbitrap mass spectrometry and ultra-high-performance liquid chromatography, Gómez and Pérez [157] created a method that could analyse 350 compounds from three different classes of contaminants (pesticides, biopesticides, and veterinary drugs) in just 14 minutes. Nevertheless, despite all the benefits that the current detection techniques offer, it is still necessary to use an appropriate sample preparation method because matrix effects can negatively affect detection by creating significant noise and altering ionization efficiency, which leads to a reduction in sensitivity [141].

6. Matrix effect

Pesticide residue analysis in food matrices is typically tricky owing to their deficient concentrations and the interference of the complex matrix [158,159]. The matrix effect might result in an increased or reduced analyte signal from extracts obtained in the presence of a matrix compared to extracts obtained without a matrix [135]. Typically, two methodologies are used to investigate the matrix effect. One possibility is to compare the slopes of standards in a solvent to the slopes of matrix-matched standards. The matrix impact (%) is determined using the equation [(slope of standards in matrix-slope of standards in solvent/ slope of standards in solvent) x100]. The matrix impact is considered low when the values are between -20% and +20%, medium when between -50% and -20% or +20% and +50%, and higher when they are lower or higher than +50% [158]. A further method involves comparing the areas of standard solutions prepared within a matrix with those prepared in a solvent multiplied by 100. If the result is 100%, there is no matrix influence;

otherwise, values higher or lower than 100% indicate enrichment or suppression of the ionization by the matrix component [155]. To reduce the impact of the matrix, the authors created analytical curves in the food matrix extract concentration, which increased the analyte concentration and signal. However, it increases matrix effects and causes ion suppression in the ionization source, resulting in poorer signals with higher noise [130]. Therefore, diluting the extracts, which was Blascoetal's method [160], is an alternative approach to reducing the matrix effect. When samples were diluted, recoveries were higher. Studies have revealed that the floral origin of food can impact the matrix effect. Adopting matrix-matched standards is necessary to reduce the quantitative mistakes caused by matrix effects [158].

Table 1. Nano sorbent removes pesticides and other organic compounds from food matrices and biological fluids.

Target molecule	*Nano adsorbents	References
Malathion	$ZnFe_2O_4$	[26]
Methamidophos, Malathion, Parathion, and Diazinon	$NiFe_2O_4$	[27]
Diazinon, Fenitrothion, Chlropyrifos, Profenofos	GO	[28]
Diazinon, Malathion, and Chlorpyrifos	Fe_3O_4@SiO_2	[47]
Chlorpyrifos	MOFs & COFs	[54]
Thiamethoxam	Fe_3O_4@MIPs	[57]
Carbendazim	Nano Fe_3O_4 particles	[62]
Dimethoate	MIP-Quantum dots	[64]
Carbofuran	MIP-MWCNT	[69]
Dimethoate	**MIP-CNTs-Fe_3O_4@Au/CPE	[70]
Dimethoate	Activated carbon	[76]
Imidacloprid	CNT	[81]
Carbofuran	MIP-SPR sensor	[83]
Dimethoate	MIP-GO-AuNPs/ MIP-SPR	[94]
Dimethoate	AuNPs-Electrochemical sensor	[98]
Carbofuran	AuNPs-Colorimetric sensor	[102]
Dimethoate	AuNPs-FRET	[114]
Carbofuran	MIP-Electrochemical sensor	[123]
Dimethoate, Imidacloprid, and Methamidophos	MOFs	[129]
Dimethoate and Carbofuran	Fe_3O_4@SiO_2	[134]
Imidacloprid	Activated carbon	[137]

*Nano adsorbents// GO: Graphene Oxide, MOFs: Metal-organic frameworks, COFs: Covalent organic frameworks, MIP-MWCNT: Poly(acrylic acid)-MWCNT nanocomposite, CNT: Carbon nanotube, SPR: Surface plasmon resonance and FRET: Fluorescence resonance energy transfer

**MIP-GO-AuNPs/ MIP-SPR: MIP-GO-AuNPs/Electrochemical microfluidic chip MIP-SPR sensor

Table 2. MIPs are involved in extraction methods, synthesis conditions of MIPs for the determined pesticides, and selected compounds in real samples in previous studies.

Extraction Method	Chemical compounds	Synthesis	Monomer/CL/ Porogen/ Initiator	Matrix	Ref.
MIP-MDSPE	Material A	Precipitation Polymerisation	ATA/EGDMA/Water/APS	Tangerine, Chinese celery, Red grape, Cherry tomato,	[147]
MIP-SPE	Parathion Methyl, Fenamiphos, Diazinon, and Malathion	MIP film on steel blades	MAA/EGDMA/ 1-octanol/DMPA	Water and Apple juice	[47]

MIP-MSPE	Material B	Bulk Polymerisation	MAA/4-VP/EGDMA/ MoH/ AIBN	Cabbages	[35]
MIP-MISPE	Chlorpyrifos	Bulk Polymerisation	GBDA/GDPEA/Water/ IRGACURE 184	Water	[148]
MIP-SPR	Dimethoate and Carbofuran	Photo polymerisation	MATrp monomer /EGDMA/ Ethyl alcohol/AIBN	Water	[143]
MIP-SPE	Butyl benzyl phthalate, Diethyl phthalate, Dibutyl phthalate, and Dimethyl phthalate	Precipitation Polymerisation	MAA/EGDMA/MoH/AIBN	Tea	[140]
MIP-MISPE	Atrazine, Terbuthylazine, Acetochlor and Alachlor	Bulk Polymerisation	MAA/EGDMA/Toluene/ AIBN	Cannabis bud	[141]
MIP-SPE	Carbendazim	Precipitation Polymerisation	MAA/EGDMA/ACN/AIBN	Water, Fruits, and Vegetables	[142]
MIP-SPE	Azamethiphos and Chlorpyrifos	Bulk Polymerisation	MAA/EGDMA/ACN/ACPA	Mineral water and Grape	[143]
MIP-SPE	Material C	Bulk Polymerisation	APTES/PMTOS/Water:EoH/ NH4OH solution	Almond oil	[76]
MIP	Thiamethoxam	Precipitation polymerization	VBA/EGDMA/DMF/AIBN	Grain	[145]
MIP-SPE	Imidacloprid and Acetamiprid	Precipitation Polymerisation	MAA/EGDMA/Toluene/ AIBN	Tea	[146]
MIP	Pyriproxyfen, Deltamethrin and Etofenprox	Precipitation Polymerisation	MAA/EGDMA/Chloroform/ AIBN	Apple juice	[147]
MIP-SPE	Thiamethoxam and Thiacloprid	Bulk Polymerisation	2-VP/EGDMA/DMF/AIBN	Light and dark honey	[23]
MIP-SPE	Nitenpyram and Imidacloprid	Bulk Polymerisation	MAA/EGDMA/DMF/AIBN	Light and dark honey	[24]
MIP-SPE	Imidacloprid	Bulk Polymerisation	AA/EGDMA/MoH/AIBN	Eggplant and Honey	[114]
MIP	Imidacloprid	Bulk Polymerisation	MAA/EGDMA/ACN/AIBN	Chili and Tomato	[148]
MIP	Imidacloprid	Bulk Polymerisation	VBA/EGDMA/DMF/AIBN	Rice	[149]
MIP-SPE	Imidacloprid	Bulk Polymerisation	MAA/EGDMA/Water/AIBN	Apple	[150]
MIP-SPE	Imidacloprid	Bulk Polymerisation	MAA/EGDMA/PVA/AIBN	Water and Apple	[151]
MIP	Chemiluminescence	Bulk Polymerisation	AP/EGDMA/DMF/AIBN	Vegetables	[152]
MIP	Imidacloprid	Precipitation Polymerisation	MAA/EGDMA/MoH/AIBN	Strawberry and Apple	[153]
MIP-SPE	Trichlorfon, Dimethoate, Imidacloprid	Bulk Polymerisation	MAA/EGDMA/ O,O′-dimethyl thiophosphoryl chloride/AIBN	Lettuce and Cucumber	[154]
MIP	Imidacloprid	Emulsion Polymerisation	MAA/EGDMA/ACN/AIBN	Water	[155]
MIP	Material D	Precipitation Polymerisation	MAA/EGDMA/ACN/AIBN	Cauliflower, Radish, Pear	[156]
MIP-SPE	Imidacloprid	Precipitation Polymerisation	MAA/EGDMA/DMF/AIBN	Fruit juice	[157]
MIP	Parathion	Precipitation Polymerisation	AA/EGDMA/DMSO/AIBN	Vegetables	[158]

MIP-SPE	Material E	Precipitation Polymerisation	MAA/EGDMA/MoH/AIBN	Fruit juice	[159]
MIP	Parathion	Precipitation Polymerisation	MA-Bt/EGDMA/1,4-dioxane/AIBN	Water	[57]
MIP	Pyriproxyfen	Precipitation Polymerisation	AA/EGDMA/MoH/AIBN	Strawberry	[160]
MIP-DSPE	Chlorpyriphos	Bulk Polymerisation	MAA/EGDMA/MoH/AIBN	Waters, Soils and Vegetables	[36]
MIP	Tolfenpyrad	Bulk Polymerisation	2-VP/EGDMA/DMF/VTMS	Lettuce	[132]
MIP	Dinotefuran	Precipitation Polymerisation	MAA/EGDMA/MoH/AIBN	Cucumber and Soil	[42]
MIP-SPE	Material F	------	Fe_3O_4@C@UiO-66	Water and juices	[133]
MIP-SPE	Material G	------	MIH@MIL-101(Cr)-NH2-TDES	Honey and Tea	[134]

Materials; MIP: Molecularly imprinted polymer, MISPE: Molecularly imprinted solid-phase extraction, SPE: Solid-phase extraction, MDSPE: Magnetic dispersive solid-phase extraction, CL: Crros-linker, ATA: 3-amino-1,2,4- triazole, EGDMA: Ethylene glycol dimethylacrylate, APS: Ammonium peroxodisulfate, MAA: Methacrylic acid, DMPA: 2,2- dimethoxy-2-phenylacetophenone, 4-VP: 4-vinyl pyridine, AIBN: 2,2-azobis (isobutyronitrile), MoH: Methanol, GBDA: Glyoxalbis diallyl acetal, IRGACURE 184: 1-hydroxycyclohexyl phenyl ketone, VTMS: vinyltrimethoxysilane, MATrp monomer: N-methacryloyl-L-tryptophan methyl ester, SPR: Sensor chip nanofilms, CAN: Acetonitrile, ACPA: 4-cyanovaleric acid, APTES: 3-aminopropyl triethoxysilane, PTMOS: Phenyltriethoxysilane, DMF: N,N-dimethylformamide, VBA: 4-vinylbenzoic acid, AA: Acrylic acid, EoH: Ethanol, 2-VP: 2-vinylpyridine, VBA: P-vinylbenzoic acid, PVA: Polyvinyl alcohol, AP: Acephate, DMSO: Dimethyl sulfoxide, MA-Bt: Methacryloyl benzotriazole, VTMS: Vinyltrimethoxysilane

Material A: Azinphos-methyl, Parathion methyl, Azinphos-ethyl, Fenitrothion, Diazinon, Parathion ethyl, profenofos, and Chlorpyrifos

Material B: Methyl-parathion, Parathion, Paraoxon, Fenitrothion, Quinalphos, Isazophos, Chlorpyrifos-methyl, Chlorpyrifos, Fenthion, Methidathion, Profenofos, and Triazophos

Material C: Dimethoate, Fenthion sulfoxide, Fenthion sulfone, Methidathion, Malathion, Fenitrothion, Diazinon, Pirimiphos-methyl, Fenthion and Chlorpyrifos-ethyl

Material D: Ethoprophos, Parathion-methyl, Malathion, Triazophos, Fenthion, Fenamiphos and 2-methylimidazole

Material E: Chlorpyrifos, Haloxyfop-R-methyl, Oxadiazon, Diniconazole, Clodinafop-propargyl, Fenpropathrin, and Fenoxprop-P-ethyl

Material F: Diniconazole, Epoxiconazole, Hexaconazole, Imazaquin, Metalaxyl, Myclobutanil, Prothioconazole and Triticonazole

Material G: Hexachlorocyclohexane, Dichlorodiphenyl dichloroethylene and Dichlorodiphenyl dichloroethane

Table 3. Methods of separation and detection for pesticide determination in food matrix by gas and liquid chromatography.

Pesticides	Column	Mobile Phase	Detection	LOD	R (%)	Ref.
Imidacloprid	C18 (50-4.6 mm, 1.8 µm)	ACN: Water	ESI/MS/MS	0.03-0.10 (µg kg^{-1})	102-114	[158]
Azinphos-methyl, Parathion methyl, Azinphos-ethyl, Fenitrothion, Diazinon, Parathion ethyl, Profenofos,	C18-PFP (4.6 mm x 250 mm, 5 mm)	ACN: Water	HPLC-PDA	0.062-0.195 (µg kg^{-1})	81.3-110.0	[147]
Parathion Methyl, Fenamiphos, Diazinon, Malathion, and Chlorpyrifos	C18 (4.6 mm, 1.8 µm)	MoH: Water	ESI/MS/MS	0.002-0.48 (µg kg^{-1})	87.8-115.0	[47]
Dimethoate and Carbofuran	C18 (4.6 mm, 1.8 µm)	Water	LC–MS-TOF	16.92-20.47 (ng L^{-1})	101-104	[149]
Butyl benzyl phthalate, Diethyl phthalate, Dibutyl phthalate, and Dimethyl phthalate	Zorbax Eclipse XDB-C8 column (3.5 µm, 2.1 mm×50 mm)	ACN: Water	LC-ESI-MS	0.23-13.9 (µg kg^{-1})	78-102	[150]

Carbendazim	C18 ODS-3 (5 µm particle size, 4.6 mm × 250 mm, Japan)	ACN: Water	UHPLC-DAD	0.005-0.01 (µg kg^{-1})	84.32-99.14	[152]
Czamethiphos and Chlorpyrifos	A Phenomenex® C18 (250 mm × 4.60 mm, 5 µm)	MoH: Acetic acid	HPLC/UV	0.36-1.5 (µg kg^{-1})	92.3-105.7	[153]
Pesticides A	Accucore PFP (150 x 2.1 mm, 2.6 mm)	MoH: Water	LC-MS/MS	0.1-1.2 (µg kg^{-1})	81-95	[154]
Imidacloprid and Acetamiprid	BEH C18 (1.7 mm, 2.1 mm x 100 mm)	ACN	HPLC-MS-MS	0.5-1.5 (µg kg^{-1})	93.4-95.8	[156]
Pyriproxyfen, Deltamethrin and Etofenprox	C18 (250 mm × 4.60 mm, 5 µm)	EoH: Water	HPLC-UV	0.005-0.001 (µg kg^{-1})	76.18-97.12	[114]
Thiamethoxam and Thiacloprid	UHPLC (100 mm × 2.1 mm, 2.6 µm)	MoH: Water	UHPLC-MS/MS	0.045-0.070 (µg kg^{-1})	95.3-106.5	[23]
Nitenpyram and Imidacloprid	UHPLC (100 mm × 2.1 mm, 2.6 µm particle size)	MoH: Water	UHPLC-MS/MS	0.03-0.09 (µg kg^{-1})	94.3-108	[24]
Imidacloprid	Zorbax Eclipse Plus C-18 (Agilent) (3 x 100 mm, 3.5 µ)	MoH: Water	LC-MS/MS	0.05 (µg kg^{-1})	87.1-96.2	[114]
Imidacloprid	Agilent-C18 (4.6 × 250 mm i.e., 5.0 µm)	EoH: Water	HPLC-UV	0.1 (µg kg^{-1})	75-83.8	[159]
Imidacloprid	A Symmetry® C18 analytical (4.6×250 mm, 5 µm)	ACN: water	HPLC-UV	0.048 (µg kg^{-1})	77.6-96.5	[160]
Imidacloprid	120 EC - C18 (3.0 × 50 mm, particle size 2.7 µm)	MoH: Water	LC/Q-TOF/MS	2.6-3 (µg kg^{-1})	93.7-101.6	[141]
Chemiluminescence	Waters Sunfire™ C18 (4.6 × 150 mm, 5 µm)	MoH: Water	HPLC-MS/MS	0.86 (µg kg^{-1})	88.7-96.8	[142]
Imidacloprid	C18 (250 mm × 4.60 mm, 5 µm)	MoH: Water	LC-MS/MS	0.05-0.1 (µg kg^{-1})	85.47-101.5	[145]
Pesticides B	Agilent-C18 4.6 × 250 mm, 5.0 µm	MoH: Water	HPLC-MS/MS	0.02-0.45 (µg kg^{-1})	82.5-123.0	[146]
Imidacloprid	100 mm × 2.1 mm, 2.6 µm particle size	MoH: Water	UHPLC-MS/MS	0.18-0.62 (ng L^{-1})	92.4	[157]
Pyriproxyfen	Ultra IBD 5-m 250 × 4.6 mm long C18 column	ACN/ water/ MoH	HPLC-DAD	4.93 $x10^{-5}$ (µg kg^{-1})	97.3	[151]
Tolfenpyrad	100 mm × 2.1 mm, 2.6 µm particle size	ACN: Water	LC-MS/MS	1.7 (µg kg^{-1})	90.5-98.8	[132]
Pesticides C	Chiralcel OD-RH (150 mm × 4.6 mm i.d., 5 µm, Daicel, China)	ACN: Water	LC-MS/MS	0.1-0.35 (ng L^{-1})	83.68-95.99	[133]
Pesticides D	GC (30 m × 0.25 mm i.d., 0.25 µm)	-----	GC-MS	1.62-13.9 (ng L^{-1})	81.5-13.4	[35]
Chlorpyrifos	GC (30 m × 0.25 mm i.d., 0.25 µm)	-----	GC-MS	0.05 (µg kg^{-1})	88.0-92.8	[148]

Atrazine, Terbuthylazine, Acetochlor and Alachlor	A Phenomenex ZB5 MSi (30 m with a 5 m guard, 0.25 mm i.d., 0.25 µm)	-----	GC-MS	0.05-0.1 (µg kg^{-1})	76.4-85.0	[111]
Trichlorfon, Dichlorvos, Dimethoate, Imidacloprid, and Methamidophos	RTX-1701 (30.0 m × 0.25 mm × 0.25 µm)	-----	GC-MS	0.14-0.9 (µg kg^{-1})	87.7-92.5	[134]
Pesticides E	GC (30 m × 0.25 mm i.d., 0.25 µm)	-----	GC-MS	0.04-0.06 (ng L^{-1})	81.7-98.5	[139]
Pesticides G	GC (30 m × 0.25 mm i.d., 0.25 µm)	-----	GC-MS	0.07-0.85 (ng L^{-1})	81.7-109.3	[14]

LOD: Limit of detection, MS: Mass spectrometry, MS/MS: Tandem mass spectrometry, ToF: Time of flight, ESI: Electrospray ionization, UV: Ultraviolet detector, HPLC: High-performance liquid chromatography, UHPLC: Ultra high-performance liquid chromatography, DAD: Diode-Array Detection, PDA: Photometric Diode Array, CAN: Acetonitrile, Ethanol: EoH, ethanol: MoH.
Pesticides A: Dimethoate, Fenthion sulfoxide, Fenthion sulfone, Methidathion, Malathion, Fenitrothion, Diazinon, Pirimiphos-methyl, Fenthion, and Chlorpyrifos-ethyl
Pesticides B: Ethoprophos, Parathion-methyl, Malathion, Triazophos, Fenthion, Fenamiphos and 2-methylimidazole
Pesticides C: Diniconazole, Epoxiconazole, Hexaconazole, Imazaquin, Metalaxyl, Myclobutanil, Prothioconazole and Triticonazole
Pesticides D: Methyl-parathion, Parathion, Paraoxon, Fenitrothion, Quinalphos, Isazophos, Chlorpyrifos-methyl, Chlorpyrifos, Fenthion, Methidathion, Profenofos, and Triazophos
Pesticides E: Chlorpyrifos, Haloxyfop-R-methyl, Oxadiazon, Diniconazole, Clodinafop-propargyl, Fenpropathrin,
Pesticides G: Hexachlorocyclohexane, Dichlorodiphenyl dichloroethylene and Dichlorodiphenyl dichloroethane

7. Conclusion

MIPs have been established to meet the demand for easy-to-use, affordable, durable polymers that may take the position of receptors in natural antibodies. Initial attempts to use MIPs were plagued by several issues severely restricting their application. Most notably, binding was delayed in some situations due to extensive diffusion paths. Big analytes were permanently trapped inside the MIP (or, worse, leached from the polymer during the analysis). The usage of MIPs was one of the most significant advances in the sector. They could be used to reduce diffusion paths and the permanent entrapment of template molecules. However, initially, irregularly shaped MIPs had poor reproducibility; binding was poorly understood, and applying the technique to a different analyte was frequently difficult. In recent years, this field has made significant advances to address these challenges. To fine-tune the size and form of MIPs, several approaches, such as bulk polymerization, precipitation polymerization, emulsion polymerization, inverter polymerization, or the incorporation of a solid core, have been used. Furthermore, several polymerization methods have been developed that allow the polymerization endpoint to be controlled. Another intriguing strategy that might be beneficial is to modify the cavity after it has been imprinted. However, care must be taken during the modification to avoid destroying the imprinting effect. With all these improvements, MIPs are more desirable for industrial applications, and MIPs are being used more frequently. In particular, because it acts as an automated reactor for MIPs synthesis, developing the solid-phase imprinting approach revolutionizes the area of MIPs. Template molecules are immobilized on glass beads installed in the reactor for that purpose, enabling reuse. This makes it possible to scale up MIP production and improve repeatability significantly. MIPs are extensively suitable and compatible for integration in a wide range of applications, have high stability, and can be kept for extended periods of time. As a result, rapid advancement and improvement in nanosized MIPs are anticipated. Regarding analytical methods, UHPLC and tandem mass spectrometry are excellent due to regulatory agency regulations that demand even lower limitations. These detectors satisfy these requirements regarding excellent selectivity and sensitivity and precise identification of analytes at very low detection limits. Furthermore, a more significant number of pesticides can be analyzed concurrently. Another significant trend is the advancement of MIPs

approaches. Some studies have described the simultaneous analysis of over a hundred pesticides from various chemical classes. It was made feasible by developing equipment with exceptional selectivity and sensitivity. We are optimistic that the future will improve the MIP approach in food applications.

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