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Molecularly Imprinted Polymers for Detection of Herbicides – A Review

M. A. Ansari [a*], R.K. Prajapati[b]
[a]*Department of Chemistry, Bipin Bihari College, Jhansi (UP),India.*
[b]*Department of Chemistry, D.J. College, Baraut. Baghpat (UP), India.*

ABSTRACT
Contamination of environment due to indiscriminate use of herbicides poses severe risks soil, water and air as well as severe risk to human health. So need of easy, rapid and of low cost detection triggered the researcher to find out new technology. Molecularly imprinted polymers (MIPs), the synthetic materials are very useful in these circumstances. It offers several advantages to the environmental scientist, chemist, pharmaceutical, and agro food industry for analysis, sensoring, extraction, or preconcentration of analytes. Since last two decade new types of imprinted polymeric materials with molecular recognition sites for herbicides have been prepared using the molecular imprinting approach. In this review paper, the recognition and transport properties of molecularly imprinted polymer (MIP) membranes prepared for herbicides in particular are summarized and analyzed. It has been found with micro porous and macro porous MIP membranes that they exhibit largely different transport phenomenon with same receptor. The nature of selectivity of microporous MIP membranes and their different methods of preparation is discussed. The high specificity and stability of MIPs make them as promising alternatives to enzymes, antibodies, and other natural receptors usually used in affinity chromatography and sensor technology. In general, these investigations open a way to the design of supramolecular devices that could perform highly selective functions such as recognition, transformation, transfer, regulation and allow signal and information processing. The herbicides are used as pesticides, insecticides and chemical war agents. The high toxicity of herbicides neurotoxins and their large use in modern agriculture practices has increased public concerns. Here imprinting and detection of herbicide have been discussed.

Keywords: Herbicides, Molecularly Imprinted polymers, affinity chromatography, Bio membrane, supramolecular devices, Sensor**.**

INTRODUCTION

MIPs are specialty synthetic materials with selectivity for a specific target species afforded by imprinted binding sites with complementary size, shape and electronic properties of the target. This provides MIPs with the capability to exclusively bind and extract the target species from a complex solution matrix, such as a biological fluid, wastewater or reaction mixture of a chemical synthesis.[1]

It can be easily observed from literature that MIPs have been applied in a different field of technologies including immunoassays,[2] catalysis, [3,4] affinity chromatography,[5,6] sensory

devices, [7,8,9] and SPE. [10,11] MIPs in immunoassays have a distinct advantage over natural antibodies because of their easy preparation, minimum cost and reusability.[12] The binding sites of MIPs are also capable of providing catalytic activity by aligning reacting groups during synthesis, and these approaches have led to enantiomeric excesses of 36% for synthesis of compounds such as L-Threonine. [3] In addition, MIPs with selectivity for the transition state of a chemical reaction can provide increased rates for reactions, such as hydrolysis of carboxylic esters.[4] The application of MIPs as enantioselective stationary phases for affinity chromatography has provided for isolation of biologically active compounds, such as (S)-ibuprofen [6] and yohimbine [7] from their enantiomers. For the detection of TNT vapours twenty four MIPs have been prepared., [7] atrazine contamination in groundwater,[8] and halo acetic acids in drinking water.[9] Currently, the area with greatest interest by the wider scientific community is the application of MIPs as selective sorbents for SPE. Recent studies have demonstrated the lower limits of detection achievable by using a MIP sorbent for extraction of β-blockers from wastewater, compared to the most commonly used polymeric materials, [10] and higher capacity for the retention of mycotoxin from cereal extracts compared to a standard immunoaffinity cartridge. [12]
Usually, herbicides are present in food, soil and water at low concentration (ng/g) levels, dispersed in highly different intermediates, complex and structure, with an elevated degree of sample-to-sample variability. Thus, their rapid detection and monitoring is urgent need to provide no public health risk. Application of MIPs in detection of herbicides has been utilised in Luminescence recognition of different organophosphorus pesticides by the luminescent Eu(III)–pyridine-2,6-dicarboxylic acid probe.[13] A Surface molecular imprinting technique based on spherical molecular imprinted monolayer (SMIM) was prepared with preadsorbed templates of parathion-methyl from 3-mercaptopropionic acid self-assembled on core-shell Fe_3O_4 at Au nanoparticles (NPs).[14] Simultaneous separation and determination of eight organophosphorous pesticide residues in vegetables through molecularly imprinted solid-phase extraction coupled to gas chromatography was synthesized using O,O-dimethyl thiophosphoryl chloride as the template.[15] A novel composite of vinyl group functionalized multiwalled carbon nanotubes (MWCNTs) molecularly imprinted polymer (MIP) was synthesized and applied as a molecular recognition element to construct an electrochemical sensor for parathion-methyl.[16] A novel sensor for the determination of parathion-methyl based on couple grafting of functional molecular imprinted polymers (MIPs) was fabricated which is developed by anchoring the MIP layer on surfaces of silica particles embedded Cd Se quantum dots by surface imprinting technology.[17,18] A new electrochemical modified electrode for the detection of parathion was constructed based on molecularly imprinted polymer of self-assembled o-aminothiophenol onto gold electrode. Cyclic voltammetry was employed in the process of electropolymerization and electrochemical measurements. [19] A sensitive sensor for the detection of parathion based on molecularly imprinted polymer was constructed. The sensor exhibited good selectivity and sensitivity to parathion. [20-28] MIP for the detection of Isoproturon and 2,4-D have been synthesised and electrochemical sensor was fabricated. [29-31]
A new synthetic methodology called as imprinting polymerization which involves formation of a template-monomer complex, followed by its polymerization in the presence of cross-linking agents for preparing specific receptor sites in cross linked polymers was introduced by Wulff and Sarhan.[32] The geometry of the self-assembled template-monomer complex is captured during polymerization in the growing polymer matrix. When templates is removed a cavities is created possessing a shape and an arrangement of functional groups corresponding to that of the template.

MATERIALS AND METHODS

Imprinted polymer membranes- preparation methods.

Molecular imprinting is classified into covalent imprinting (pre-organized approach), non-covalent imprinting (self-assembly approach), and semi covalent imprinting according to the type of interactions between functional monomer building blocks and target molecules in the pre-polymerization mixture and during rebinding.

The non-covalent approach is the most widely used for the preparation of MIPs. In the pre-polymerization mixture, the dissolved target analyte interacts by covalent, noncovalent, or metal coordination interactions with the functional monomer responsible for localizing the chemically active moieties of the target molecules during copolymerization. MIP synthesis involves copolymerisation of the recognition elements, functional monomers, and the matrix forming material, cross-linking monomers, in the presence of an imprint compound, the template, and a porogenic solvent. During the molecular imprinting process highly cross-linked co-polymers are formed around analyte molecules acting as cavity-creating templates. The template molecules are then removed, providing binding sites ideally complementary in size, shape, electronic properties and functionality to the templated analyte. Upon re-introduction of the template preferential rebinding within the cavity should occur. The basic principles [33] of MIP synthesis are presented in Figure 1.

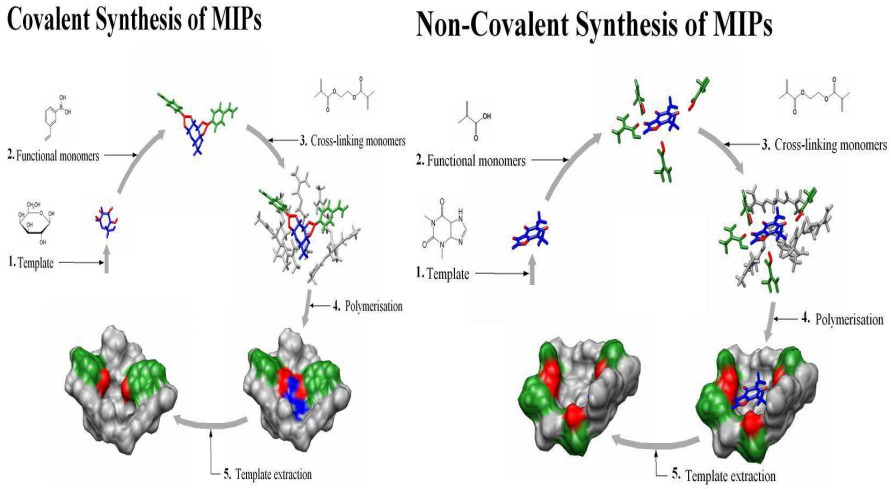

Figure. 1. Schematic illustration of the basic principles involved in the synthesis of a MIP.

Covalent Bonds (pre-organized approach)

In the covalent approach to the synthesis of MIPs, the templates are first reacted with functional monomers to form functional monomers- templates compounds associated by bonds, such as a boronate ester.[34] After synthesis, functional monomers- templates the hybrid compounds are added to a porogenic solvent. The covalent approach to the synthesis of MIPs requires significantly greater effort than the non-covalent approach due to the necessity for synthetic chemistry before polymerisation to link the functional monomers and templates and chemical treatment after polymerisation to extract the template. [35,36] The higher stability of covalent bonds does, however, produce more highly defined binding sites with more uniform target affinities. [37] The current methods for imprinting by covalent bonds involve condensation reactions to form boronate esters, a Schiff's base, a ketal or acetal.[1] However, limited to targets which possess diol, aldehyde, ketone, amine or carboxylic acid functional groups.[36] L-phenylalanine selective MIPs have been synthesised by formation of a Schiff's base between the amine functional group of L-phenylalanine and carbonyl functional group of 5-vinylsalicylaldehyde[38] depected in .(Figure. 2).

D-galactose selective MIPs have been synthesised by formation of a boronate ester between the hydroxyl groups of D-galactose and the boronic acid group of (4-vinylphenyl)boronic acid.[34]

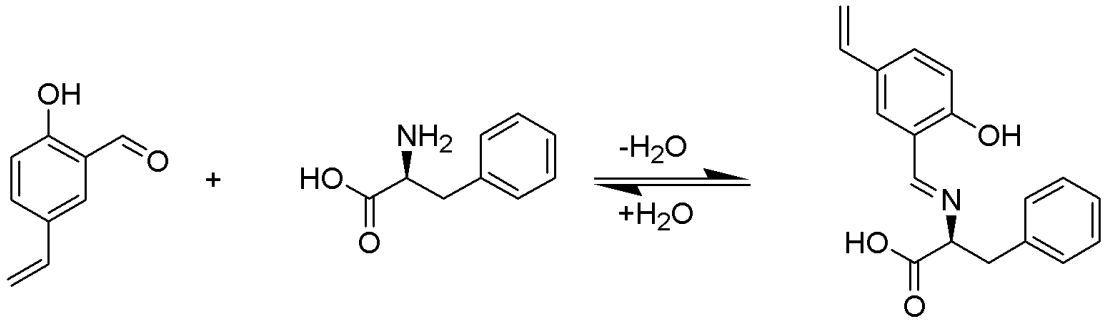

Figure.2. Synthesis of a functional monomer-template hybrid analogue for use in covalent imprinting by using 5-vinylsalicylaldehyde to form a Schiffs base with L-phenylalanine.

Non-Covalent Bonds.

In the non-covalent approach complexation is achieved by mixing template, functional monomer, and cross-linker in a porogenic solvent matrix, where the functional monomers form clusters with the templates associated by interactions, such as hydrogen bonding. [35]

Non-covalent bonds are weaker than covalent bonds with typical interaction energies of 1 – 20 kcal mol-1 as compared to a typical covalent bond of approximately 100 kcal mol-1. [39] Consequently, non-covalent bonds are transient and typically result in the synthesis of binding sites with lower selectivities.[37] The non-covalent approach is, however, much simpler as it does not require synthetic chemistry to link functional monomers and templates and is suitable for targets with a wider variety of functionalities, including hydrogen bond donors, hydrogen bond acceptors, ionic functional groups and aromatic functional groups.[36]

The types of non-covalent bonds involved in the synthesis of MIPs include ion pair interactions, dipole interactions, hydrogen bonds, London dispersion (dispersion) interactions and π-π stacking interactions. The strength of this attraction is dependent on the magnitude of the charges and distance between charges. The strongest non-covalent bonds are ion pair interactions between positively and negatively charged functional groups which is shown in Table 1. Dipole interactions between partially charged functional groups are weaker due to the lower charge density. A hydrogen bond is, however, a special type of dipole interaction. The small size of hydrogen allows a closer approach than a typical dipole interaction and results in an exceptionally strong attractive force.

Table 1. Types and estimated bond energies of non-covalent interactions

Bond type	Bond energy [8,9,10] [kJ/mol]	Relative strength
Hydrogen bond	20[8] 4-60[9] 2-5[10]	weak/medium
Hydrophobic effects	1-3[8]	weak
Ion-ion (1/r)	250[8] 100-350[9]	strong
Dipole-ion ($1/r^2$)	15[8]	weak
Dipole-dipole ($1/r^3$)	2[8] 5-50[9]	weak/medium
π-π stacking	0-50[9]	weak/medium
Dispersion (London) ($1/r^6$) (attractive van der Waals)	2[8] <5[9]	weak
Cation-π	5-80[9]	medium

These interactions are favored in weakly polar aprotic solvents such as acetonitrile. In contrast, more polar protic solvents support interactions such as metal-ion coordination of the template molecule. Comparatively weak electrostatic interaction such as stacking may occur between aromatic rings in polar solvent such as water and methanol. Hydrophobic interactions are only facilitated in highly polar solvents or solvent mixtures such as water/methanol. Successful imprinting by the non-covalent approach is dependent on the stability of functional monomer interactions with the template during polymerisation. [40] These interaction can be easily seen in case of typical multifunctional templates, such as homovanillic acid, are capable of forming relatively stable interactions by acting as both a hydrogen bond donor and a hydrogen bond acceptor in interactions with a typical functional monomers, such as methacrylic acid (MAA), [35] lower functionality templates, such as 2,4-dichlorophenoxyacetic acid (2,4-D), have been successfully imprinted by the combination of highly stable ion pair interactions and relatively weak π-π stacking interactions with 4-vinylpyridine.[41]

MIP membrane preparation by dry phase inversion.

Phase inversion technique has also been applied to prepare MIP. Yoshikawa et al. have used polystyrene resin with peptide recognition to prepare MIP by dry phase inversion technique. In this technique solidification of polymer is used instead of an in situ polymerisation. [42-45] The permeability was much higher for the MIP as compared with the blank membrane.

MIP membrane preparation by wet phase inversion.

Kobayashi et al. have used functional acrylate copolymer for wet phase inversion method to prepare MIP. These membranes had an asymmetric structure with pores in the separation layer of about 20-50 nm average. When temperature of the casting solution and the precipitation bath is decreased then both the efficiency of complex formation as well as the template selectivity of the membrane increases. [46-49]

MIP membrane preparation by surface imprinting.

The first MIP preparation by surface modification was carried out by H.Y. Wang, T. Kobayashi and etal. [50] But it has certain disadvantages e.g. the use of a special polymer for membrane formation, the very long reaction times for MIP functionalization (24 h), and the strongly asymmetric pore morphology with large macro voids and very low permeability which is poorly suited for an affinity membrane.

Role of the binding sites in molecular recognition.

In supramolecular host/guest chemistry a guest molecule fits the internal cavity of a correspondingly designed host structure. Bond fixation, coordination (self-assembly involving coordination chemistry), and molecular recognition are three important factors in this process. In the recognition step, spatial (shape/size) and chemical (functional groups) complementarily play a crucial role. Similarly, molecularly imprinted polymers provide biomimetic receptor sites, which may recognize and selectively rebind the templated analyte. Evidently, the performance of MIPs will depend on the quality of the binding pockets and binding sites. Hence, two effects need to be balanced: (i) if the binding constant is too high, the guest molecule will block the binding site and will prevent further use of the biomimetic polymer; (ii) if the binding constant is too low, the MIP will show limited selective recognition. These simple initial considerations already lead to a very important conclusion: without knowledge on and deliberate control over intermolecular forces involved in non-covalent molecular imprinting, no reliable predictions on structure and properties of the formed prepolymerization complexes and, consequently, on the recognition properties of the resulting MIP can be made. Evidence for shape selectivity in MIPs synthesized via non-covalent interactions has been found using molecular probes of different sizes. [51] In the self-assembly

approach, the cross-linker may be a third component influencing the properties of the formed prepolymerization complexes. The binding constants of different possible complex configurations ultimately determine their ability to 'survive' the polymerization process, which results in the formation of binding pockets or binding sites. In consequence, it is expected that polymers with a heterogeneous binding site distribution will be formed with affinity distributions ranging from binding sites with high affinity for the template, to non-specific binding to the cross-linked polymer matrix, including multi-site recognition (multimers). [52] Results on studies related to the nature of recognition in MIPs are widely contradictive and range from indications towards recognition taking place in cavities and not by interaction with residual template molecules, to recognition due to residual template interaction. [53, 54]

Porogen

The solvent i.e. *Porogen* plays a crucial role during the process of molecular imprinting. Besides influencing the polymer morphology, the solvent properties govern the types and the strength of non-covalent interactions available for the self-assembly processes. By the same argument, in depth understanding of these processes enables control of the recognition efficiency of the resulting MIP by appropriate selection of the solvent matrix and tuning of its dielectric properties. In general, optimum recognition during the application of MIPs occurs in the same solvent used as porogen during the polymerization. Nevertheless, MIPs prepared in aprotic solvents have also demonstrated recognition in entirely aqueous solutions. [55, 56]

Evaluation of Molecularly Imprinted Polymer.

After synthesis, the efficacy of a MIP is typically evaluated by a rebinding assay in which the binding of the target to the MIP is analysed. The common methods for a conducting rebinding assay are by chromatographic means or batch rebinding.

The binding of a target to the MIP can occur by specific interactions within the imprinted binding sites and by non-specific interactions with the cross linking monomer and randomly distributed functional monomer. A higher degree of specific binding is desirable and leads to higher selectivity.

To evaluate binding due to non-specific interactions, a non-imprinted polymer [NIP] is prepared in an identical manner as the MIP, excepting for addition of the template. Accordingly, the NIP does not have imprinted binding sites and target binding occurs by non-specific interactions only. As the NIP has the same composition as the MIP, non-specific binding by the NIP is assumed to be equal to non-specific binding by the MIP. This is a crude approximation as non-specific binding by the MIP and NIP are unlikely to be equal.

Evaluation of MIP by chromatography method involves elution from the MIP and NIP column and binding is evaluated by calculation of the retention factor (k) using Equation (1). [57]

$$k = (t_r - t_m)/t_m \quad (1)$$

In Equation 1 t_r is the retention time of the target (or structurally related compound) and t_m is the retention time of a non-retained solute. A higher retention factor equals higher affinity of the target for the MIP or NIP.

In batch rebinding assay a quantity of the MIP and NIP are added to solutions containing a measured amount of the target (C_i). The polymers and rebinding solution are then mixed for a period of typically 24 hours to allow binding to equilibrate. The amount of target remaining in solution (C_f) is then measured and the amount of target bound to the MIP (Tb_{MIP}) and NIP (Tb_{NIP}) is calculated by Equation (2). [58]

$$Tb_{MIP \text{ or } NIP} = C_i - C_f \quad (2)$$

Selectivity of the MIP can then be evaluated by the imprinting factor (IF) calculated using Equation (3)

$$IF = Tb_{MIP} / Tb_{NIP} \quad (3)$$

An IF of 1.0 means that the amount of target bound to the MIP was equal to the amount of target bound to the NIP. This is highly suggestive that rebinding of the target with the MIP occurred by non-specific interactions only and the MIP lacked selectivity. An IF of greater than 1.0 indicates that a larger amount of target was bound to the MIP than the NIP, and this is attributed to interactions with the imprinted binding sites. Accordingly, a higher IF demonstrates a greater number of imprinted binding sites and is evidence of a more successful synthetic procedure. A more thorough evaluation, however, involves calculation of the target affinity for the binding sites.

Thermodynamics of Imprinting.

Successful imprinting of a template by the non-covalent approach is dependent on stability of the functional monomer- template clusters in the pre-polymerisation mixture. (interaction energies is 1-20 kcal mol^{-1} as compared to a typical covalent bond of approximately 100 kcal mol-1).[31] Consequently, non-covalent interactions are regarded as transient with the functional monomer-template clusters in a dynamic equilibrium with their component parts.[36]

The equilibrium constant for cluster association is a factor of the change in Gibbs free energy in accordance with Equation (4)

$$\Delta G_{assc} = --RT \ln K \quad (4)$$

In Equation (4) ΔG_{assc} is the Gibbs free energy of association of the functional monomer-template cluster; R is the gas constant, *T* is the temperature (K) and is the equilibrium constant.

In consideration of the thermodynamics of the MIP pre-polymerisation mixture and the status of the functional monomer-template cluster, the equilibrium constant requires a negative and the more negative the larger the equilibrium constant and, consequently, the greater the predicted stability of the cluster. ΔG_{assc} itself is a factor of the relative contributions from the enthalpy and entropy of association in accordance with Equation (5).

$$\Delta G_{assc} = \Delta H - T\Delta S \quad (5)$$

ΔH is the change in enthalpy that occurs as a result of the pre-polymerisation cluster formation, *T* is the temperature (K) and ΔS is the change in entropy during association.

The main contributions to the changes of enthalpy and entropy during the association of small molecules in solution are accounted for by equation (6) which was developed by Williams and Westwell. [59]

$$\Delta G_{assc} = \Delta G_{(t+r)} + \Delta G_r + \Delta G_h + \Sigma \Delta G_p \quad (6)$$

In Equation (6), $\Delta G_{(t+r)}$ refers to the loss of translational and rotational degrees of freedom; ΔG_r refers to the freezing of internal rotations; ΔG_h refers to the hydrophobic effect; $\Sigma\Delta G_p$ and refers to the sum of interacting functional groups.

Kinetics involved in MIP.

In order to understand the kinetics involved in MIP binding events , the kinetics of a binding reaction with host (H) and guest (G) which represents a pair of interacting molecules is given by equation (7).

$$H + G \underset{K_{-1}}{\overset{k_1}{\leftrightarrow}} HG; \qquad K_1 = \frac{k_1}{k_{-1}} \quad (7)$$

Where k_1 is association rate constant and k_{-1} is dissociation rate constant. The temporal progression of the binding reaction is described by

$$\frac{d[HG]}{Dt} = k_1 [H] [G] - k_{-1} [HG] \quad (8)$$

Hence, different types of binding sites will be characterized by different rate constants k_{-1}. Estimates of k_1 are necessary to calculate the time to reach equilibrium. As a comparison, rate constants for antigen-antibody binding are in the range of 10^{4-} to 10^7 $M^{-1}S^{-1}$. Affinity constants for antibodies range from 10^6 to 10^9 $M^{-1.}$ [60]

In general, the amount of high-affinity binding sites in non-covalently prepared MIPs is estimated to be less than or around 1 % of the total number of binding sites. Hence, estimates of multiple host/guest interactions are difficult. However, dissociation constants in MIPs determined by modeling of binding isotherms yield results in the nM to mM ranges.

Thermodynamic and kinetic considerations certainly provide a better understanding of the parameters playing a governing role in obtaining a polymer with optimized recognition properties. The number of parameters with substantial impact on the resulting recognition properties it is evident that there is a tremendous need to analytically characterize each preparation step of molecularly imprinted polymers. Based on sufficient experimental evidence obtained by an array of analytical methods suitable boundary conditions for modeling of molecular imprinting procedures can be established leading to rational design and optimization of MIPs.

Applications of MIPs.

MIPs have been employed in fields where a certain degree of selectivity is required such as assays and sensors, separation, chromatography and catalysis. MIPs offer potential for the removal of pesticides, endocrine-disrupting compounds and heavy metals from waste and drinking water. Application of MIPs in detection of herbicides has been utilised in Luminescence recognition of different organophosphorus pesticides by the luminescent Eu(III)–pyridine-2,6-dicarboxylic acid probe. In this study Luminescence quenching of a novel long lived Eu(III)–pyridine-2,6-dicarboxylic acid probe of 1:2 stoichiometric ratio has been performed in the presence of the organophosphorus pesticides chlorfenvinphos (P1), malathion (P2), azinphos (P3), and paraxon ethyl (P4). The luminescence intensity of Eu(III)–$(PDCA)_2$ probe decreases as the concentration of the pesticide increases [61] as shown in Figure (3). It was observed that the quenching due to P3 and P4 proceeds via both diffusional and static quenching processes. The method was applied to the determination of the OPs in tap, river, mineral, and waste waters. [13]

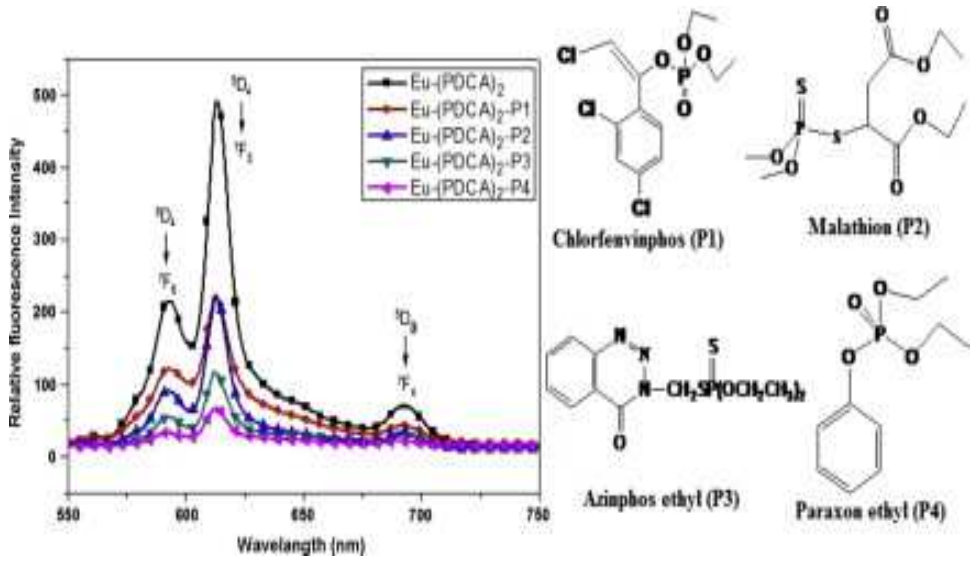

Figure. 3. The luminescence intensity of Eu(III)–$(PDCA)_2$ probe of the organophosphorus pesticides chlorfenvinphos (P1), malathion (P2), azinphos (P3), and paraxon ethyl (P4).

A Surface molecular imprinting technique based on spherical molecular imprinted monolayer (SMIM) was prepared with pre adsorbed templates of parathion-methyl from 3-mercaptopropionic acid self-assembled on core-shell Fe_3O_4 at Au nanoparticles (NPs).[14] Simultaneous separation and determination of eight organophosphorous pesticide residues in vegetables through molecularly imprinted solid-phase extraction coupled to gas chromatography was synthesized using O, O-dimethyl thiophosphoryl chloride as the template. [15]
A novel composite of vinyl group functionalized multiwalled carbon nanotubes (MWCNTs) molecularly imprinted polymer (MIP) was synthesized and applied as a molecular recognition element to construct an electrochemical sensor for parathion-methyl. The special molecular recognition properties of parathion-methyl mainly dominated by π–π, p–π interaction and hydrogen bonding formed among functional monomer, template and matrix. A series of electrochemical experiment results proved that the prepared material had good adsorption capacity and fast mass transfer rate to parathion-methyl. The response of the MIPs was linearly proportional to the concentration of parathion-methyl over the range of 2.0×10^{-7} to 1.0×10^{-5} mol L^{-1} with a lower detection limit of 6.7×10^{-8} mol L^{-1}. [16]

A novel sensor for the determination of parathion-methyl based on couple grafting of functional molecular imprinted polymers (MIPs) was fabricated which is developed by anchoring the MIP layer on surfaces of silica particles embedded Cd Se quantum dots by surface imprinting technology.[17,18] A new electrochemical modified electrode for the detection of parathion was constructed based on molecularly imprinted polymer of self-assembled o-aminothiophenol onto gold electrode. Cyclic voltammetry was employed in the process of electropolymerization and electrochemical measurements. Parathion imprinted and nonimprinted polymer films were exposed to a series of closely related compounds and the sensor exhibited good selectivity and sensitivity to parathion. A highly linear response to parathion in the concentration range of 5.0×10^{-7} □ 1.0×10^{-4}mol/L was observed, with a detection limit of 2.0×10^{-7}mol/L estimated at a signal-to-noise ratio of 3.[19] A sensitive sensor for the detection of parathion based on molecularly imprinted polymer was constructed. The sensor exhibited good selectivity and sensitivity to parathion. [20-28]

MIP for the detection of Isoproturon and 2,4-D have been synthesised and electrochemical sensor was fabricated. The MIP membrane prepared for the detection of the Isoproturon and 2,4-D templates in solution in the range of 10^{-3} to 0^{-6}M as shown [62] in Figures (4 and 5)and this sensitivity can even be enhanced by changing the characteristics of the prepared membranes such as contact angle and thickness [29-31]

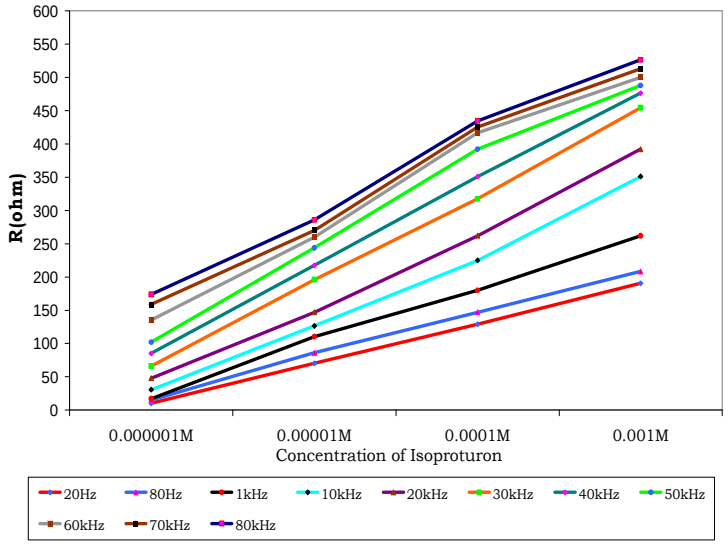

Figure.4. Influence of the current frequency on the sensor response of Isoproturon imprinted polymer membrane.

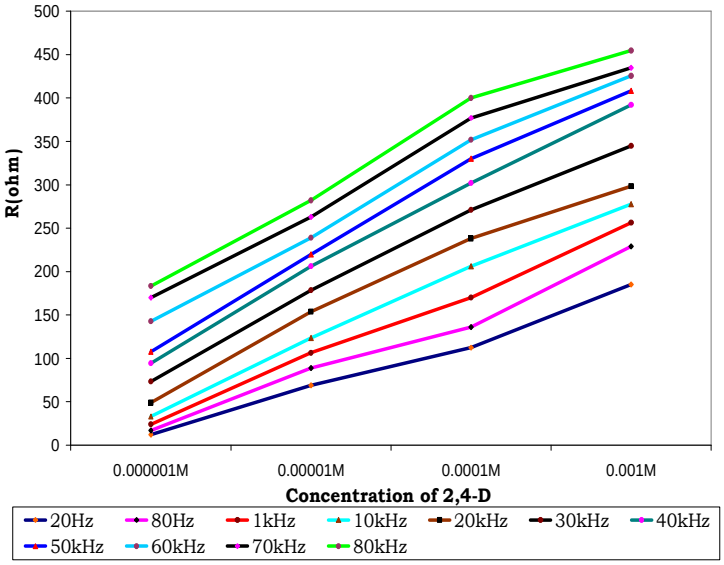

Figure.5. Influence of the current frequency on the sensor response of 2, 4-D imprinted polymer membrane.

So from above of studies it is evident that detection of herbicides and pesticides, is easy because these substances are enriched in crops and cattle and also in environmental. Thus, a number of studies have put forward the possibility of using the imprinted materials in, for example, sewage and wastewater analyses. In addition to basic recognition studies and imprinting protocol advancement. Several applications have been developed. Thus, MIPs toward herbicides/pesticides have been used in radio ligand binding assays and in sensor devices. However, now-a days the use in solid-phase extraction, so-called molecularly imprinted solid-phase extraction (MISPE), is by far the most advanced technical application of MIPs. Current sample pre-treatment methods, mostly based on the solid phase extraction technique, are very fast and economical. As economical, rapid and selective clean-up methods (relying on “intelligent” materials) are needed, solid phase extraction and clean-up methods based on molecularly imprinted polymers (molecularly imprinted

solid phase extraction, MISPE) seem to represent natural candidates to circumvent the drawbacks typical of more traditional solid phase extraction techniques. [63-75]

CONCLUSION

Molecularly imprinted polymer membranes demonstrate ligand specificity in detection of herbicides. MIPs have proven to be useful as a tool in agricultural and food technology. Highly selective and robust recognition matrices produced in this way can be employed in various applications when the analysis of diverse pollutants present in environment. MIPs offer potential for the removal of pesticides, and heavy metals from waste and drinking water. MIP polymers can also be used to remove heavy metals, rare metals and radioisotopes with high specificity. They are expected to be effective in extreme environments, such as wastewater from caustic cleaners. Having superiority of molecularly imprinted materials viz. its endurance, high stability, easy to prepare and minimum cost of production, MIP based material will come to the market very early.

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Tables And Figures:

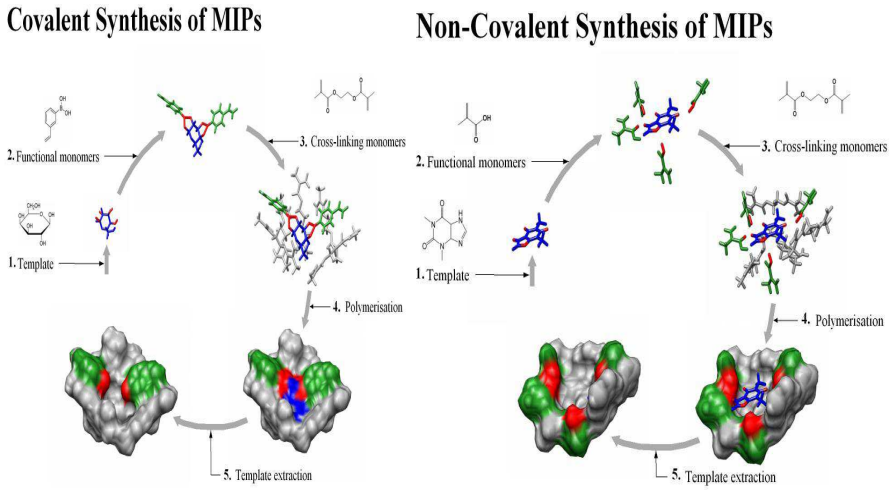

Figure. 1. Schematic illustration of the basic principles involved in the synthesis of a MIP.

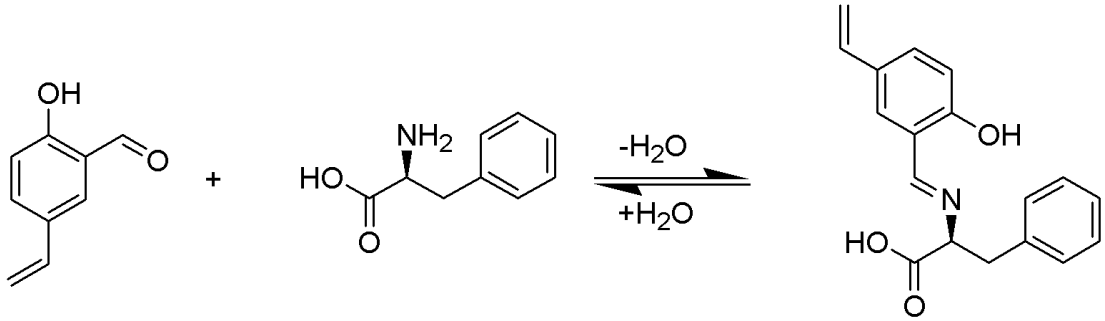

Figure.2. Synthesis of a functional monomer-template hybrid analogue for use in covalent imprinting by using 5-vinylsalicylaldehyde to form a Schiffs base with L-phenylalanine.

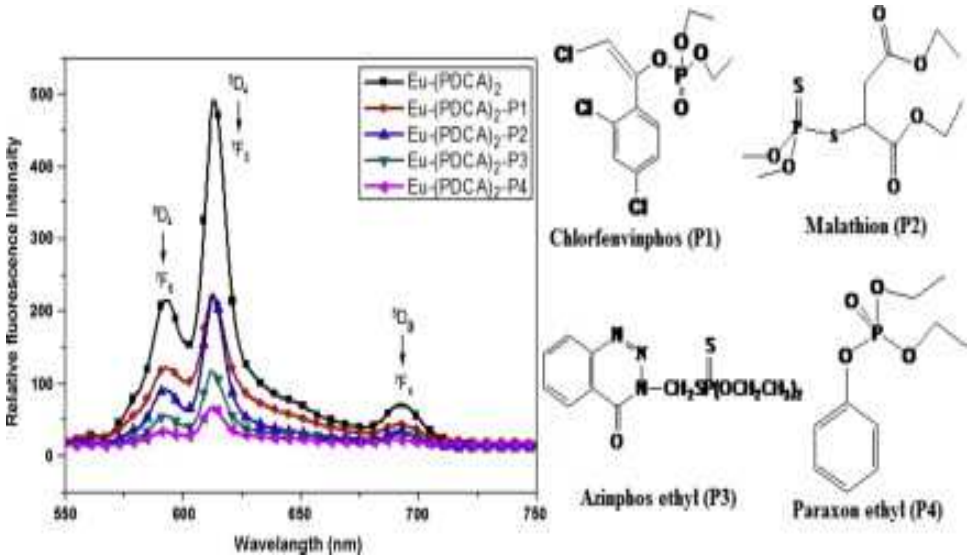

Figure. 3. The luminescence intensity of Eu(III)–$(PDCA)_2$ probe of the organophosphorus pesticides chlorfenvinphos (P1), malathion (P2), azinphos (P3), and paraxon ethyl (P4).

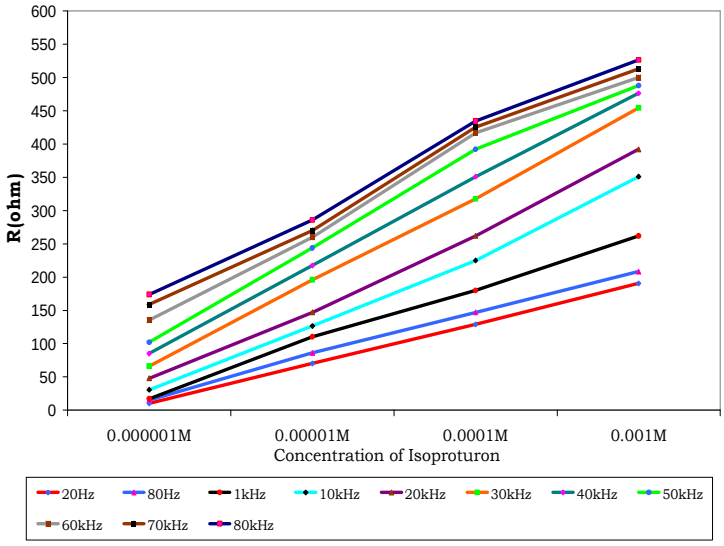

Figure.4. Influence of the current frequency on the sensor response of Isoproturon imprinted polymer membrane.

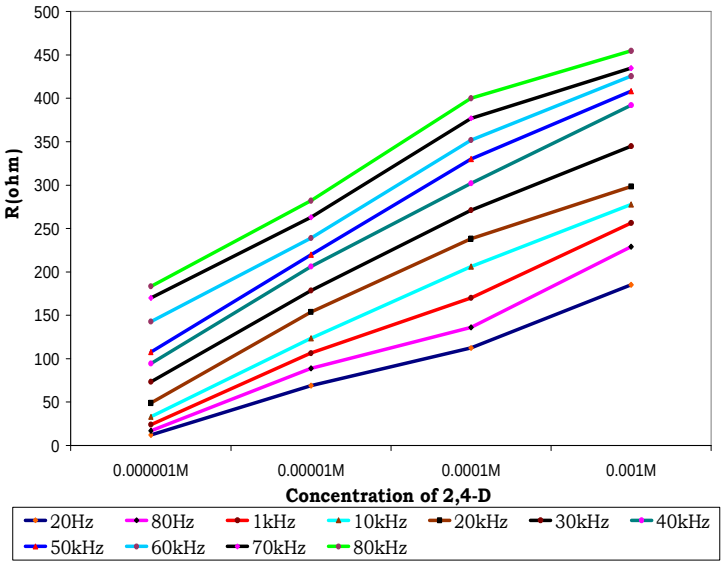

Figure.5. Influence of the current frequency on the sensor response of 2, 4-D imprinted polymer membrane.

Table 1. Types and estimated bond energies of non-covalent interactions

Bond type	Bond energy [8,9,10] [kJ/mol]	Relative strength
Hydrogen bond	20[8] 4-60[9] 2-5[10]	weak/medium
Hydrophobic effects	1-3[8]	weak
Ion-ion (1/r)	250[8] 100-350[9]	strong
Dipole-ion ($1/r^2$)	15[8]	weak
Dipole-dipole ($1/r^3$)	2[8] 5-50[9]	weak/medium
π-π stacking	0-50[9]	weak/medium
Dispersion (London) ($1/r^6$) (attractive van der Waals)	2[8] <5[9]	weak
Cation-π	5-80[9]	medium

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