ASSESSMENT OF PESTICIDES IN ENVIRONMENTAL SAMPLES USING VOLTAMMETRIC MOLECULAR IMPRINTED BASED SENSORS: A REVIEW

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Keywords: Molecular imprinting polymer (MIP); voltammetric sensors; pesticides; environmental samples

The increased concern about toxic effects of pesticide exposure led to the necessity of its monitoring using rapid, sensitive and selective analytical tools because traditional instrumental techniques are often time-consuming, labor intensive and need tedious prior separation or purification steps. The electrochemical sensors can overcome disadvantages of the traditional techniques, MIP-based sensors offer a high degree of selectivity in binding target analytes in the presence of their interferents make them ideal for determination of pesticides in complex environmental samples. This review provides a general overview of MIP-based sensors in the assessment of pesticides in environmental samples using voltammetry as transduction mechanism.

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Introduction

Pesticides are widely used in agricultural production to decrease losses by pests and to improve yield as well as the quality of the produce.[1] The massive use of pesticide has raised serious concerns not only about potential effects on human health (carcinogenicity, neurotoxicity, genotoxicity, birth defects and fetal death),[2] and animal wealth but also about its impact on the environment and sensitive ecosystems (water, soil and air contamination, toxic effects on non-target organisms).[3,4] In recent years, the increased concerns about dangerous and toxic effects of pesticides has led to the necessity of its monitoring. Due to a large variety of pesticides and required environmental analyzes, the need for low-cost, rapid, sensitive and selective analysis is continuously increasing.

There are various analytical methods such as LC-MS, GC-MS[5]HPLC,[6] GC[7] TLC,[8] CE,[9] spectrophotometry,[10] and fluorimetry,[11] for pesticides assessment in environmental samples. However, traditional instrumental analytical techniques are often time-consuming, labor intensive and need tedious prior separation or purification steps and expensive instrumentation. Electrochemical sensors are well suited for the pesticide analysis in the environment. These offer good sensitivity which allows low LOD, fast response which is useful for flow analysis, portability, simplicity in construction and use, miniaturization and low fabrication cost.[12]

Electrochemical sensors can be divided into three types: potentiometric, voltammetric and conductometric sensors.[13] All voltammetric techniques involve the application of a potential (E) to an electrode and recording the resulting current (I) flowing through the electrochemical cell as a function of the concentration of the analyte. In many cases, the applied potential is varied or the current is monitored over a period of time (t). Thus, all voltammetric techniques are some function of E, I, and t.

There are various types of voltammetric techniques such as (*i*) Cyclic voltammetry (CV) which is based on varying the applied potential at a working electrode in both forward and reverse directions (at same scan rate) while monitoring the current. (*ii*) Normal Pulse Voltammetry (NPV) that uses a series of potential pulses of increasing amplitude and the current is then measured near the end of each pulse. (*iii*) Differential Pulse Voltammetry (DPV) that scans a series of pulses at a fixed potential pulse of small amplitude (10 to 100 mV) and is superimposed on a slowly changing base potential. The current is measured at two points for each pulse, the first point just before the application of the pulse and the second at the end of the pulse. (*iv*) Square wave voltammetry (SWV) that consists of a symmetrical square-wave pulse of amplitude superimposed on a staircase waveform of step height, where the forward pulse of the square wave coincides with the staircase step. The net current is obtained by taking the difference between the forward and reverse currents and is centered on the redox potential. (*v*) Anodic stripping voltammetry (ASV) which is a widely used for trace metal determination and has a practical detection limit in the part-per-trillion range. (*vi*) Cathodic stripping voltammetry (CSV) that is used to determine substances that form insoluble salts with mercurous ions. Adsorptive stripping voltammetry (AdSV) is quite similar to anodic and cathodic stripping methods. The primary difference is that the pre-concentration step of the analyte is achieved by adsorption on the electrode surface or by specific reactions at chemically modified electrodes rather than accumulation by electrolysis.[14]

Voltammetric sensors continue to be the most popular ones among electrochemical sensors due to their simplicity, ease of production and the low cost.

The application of MIP in sensor development has continued to flourish. This is reflected by the rapid and enormous growth in the number of published papers concerning MIP-based electrochemical sensors. One of the main reasons for this is the high degree of selectivity in binding target analytes in the presence of their interferents making them ideal for determination of pollutants in complex environmental samples.

Molecular imprinting technology (MIT) is a versatile and promising technique based on the template-assisted synthesis with specific memory toward the template. This technology depends on the formation of a complex between an analyte (template) and a functional monomer in the presence of a cross-linking agent After polymerization process, the template is removed from the formed three-dimensional polymer network leaving specific recognition cavities complementary in shape, size and chemical functionality to the template molecule. Usually, intermolecular interactions like hydrogen bonds, dipole–dipole and ionic interactions between the template molecule and functional groups present in the polymer matrix drive the molecular recognition phenomena. Thus, the resultant polymer recognizes and binds selectively the template molecules.[15]

The review provides a general overview of MIPs field discussing first methods of MIP preparation and then dealing with applications of MIP-based sensors in the assessment of environmental samples using voltammetry as transduction mechanism.

Synthesis of molecularly imprinted beads

The imprinting approach can be classified into two wide branches based on the matrix material used for template incorporation. These two main approaches are discriminated by the use of organic and inorganic matrices.[16]

Organic Matrix

Organic polymers used as the imprinting matrix are further divided into covalent and non-covalent ones based on of the type of the binding between template and polymer matrix.

Covalent approach

The template binds to the matrix by covalent bonds, and the molecular recognition is achieved by formation and cleavage of these bonds.[17] An advantage of this approach is the creation of a strong and specific affinity towards the template. However, this strong binding is sometimes considered as a disadvantage because of the difficulty in template removal. For this reason, this approach is considered more suitable for catalytic[18] and separation purposes[19] than for sensing applications.[20]

Non-covalent approach

The other approach is non-covalent binding between template and monomer in the organic matrix. The main interactions include van der Waals forces, hydrogen bonding, ionic interactions, π-π interactions and hydrophobic forces.[21] The most successful and widely used combination is methacrylic acid (MAA) as a functional monomer and ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent. MAA is the most popular functional monomer because it can form hydrogen bonds with a wide variety of functional groups on a template.[22] Most commonly, polymerization is initiated either by adding free radical initiator (AIBN, 2,2-azo-bis-isobutyronitrile, or benzoyl peroxide, BPO) or induced photochemically at low temperatures or thermochemically at temperatures higher than 60 °C.[23]

The previous two approaches have advantages and disadvantages. In covalent approach, strong binding results in highly selective imprinting sites However, it suffers from a major drawback which is low reversibility and slow rate of template removal. In the non-covalent approach, specificity of binding sites strongly depends on the amount of functional monomer The affinity the template increases by increasing the amount of functional monomer On the other hand, excess functional monomer molecules in the matrix create a larger number of non-specific binding sites, thus lowering the selectivity of the imprinted polymer . Because of these problems active search is conducted to find alternative imprinting approaches[24] or modify the classical ones.

Inorganic matrix

Organic MIPs suffer from certain drawbacks arising from their physicochemical properties such as rigidity, stability, penetrability and aging. A specific example to this is the swelling of the organic polymer when it is immersed in the solution.[25,26] Moreover, a small amount of the template usually remains in the imprinted polymer in spite of the careful extraction step . In addition to that, the leakage of the template, when solvents are exchanged, may produce a false response in sensor applications. Fortunately, inorganic materials posses the ability to overcome such disadvantages of the organic MIPs.

Sol-gel approach

Instead of organic monomer inorganic precursors are used to form siloxane based polymers via a sol-gel imprinting process that incorporate template molecules. Water and low molecular weight alkoxides are the most commonly used sol-gel precursors. Generally, a catalyst is needed to accelerate the polymerization process which is based on hydrolysis followed by condensation step. The hydrolysis step can be promoted by acid catalysis while the condensation step can be accelerated by basic catalysis.[27] Careful control of the sol-gel reaction parameters allows obtaining various imprinting forms (powders, thin films, monoliths, etc.). The sol-gel process provides a convenient method for the production of organically modified surface by incorporating alkoxysilane monomers that contain desirable functional groups in the starting polymerization mixture.[28,29]

Liquid phase deposition approach (LPD)

The LPD is an aqueous method for the preparation of metal oxide thin films from metal fluoro complexes $(MF_n)^{(m-n)}$ (where *m* is the cation charge and *n* is the number of fluoro ligands) whose hydrolysis in water is modulated by the addition of boric acid (H_3BO_3) or aluminum metal.[30,31] This process is assumed to proceed according to the following reactions:

$$[MF_n]^{(m-n)}(aq) + m/2H_2O \rightarrow MO_{m\backslash 2}(s) + nF^-(aq) + mH^+(aq) \quad (1)$$

$$H_3BO_3(aq) + 4HF(aq) \rightarrow BF_4^-(aq) + H_3O^+(aq) + 2H_2O \quad (2)$$

H_3BO_3 is used to promote the reaction (1), by shifting the equilibrium of equation (2) to the right.[32] As a result, very stable BF_4^- anion is produced and the metal oxide thin film is then formed on the substrate. The advantage of LPD method lies in its simplicity, low cost and uniform film fabrication. For molecular imprinting, mainly TiO_2 films have been prepared from ammonium hexafluoro titanate (IV) ($[NH_4]_2TiF_6$) and boric acid in solution.[33,34] The ligand exchange hydrolysis of $[TiF_6]^{2-}$ has been proposed in the equilibrium reaction (3).[35]

$$[TiF_6]^{2-}(aq) + xH_2O \rightarrow [TiF_{6-x}(OH)_x]^{2-}(aq) + xHF(aq) \quad (3)$$

Polymerization options[16]

Free-radical polymerization

Vinyl based monomers and crosslinkers are commonly used in this type of polymerization. The process involves three steps; initiation to activate the monomers, propagation to grow the active chain, and termination of the active chain to form the final polymer chain. The external initiator is usually added to activate the polymerization process either by thermal or radiation process. The reactor is usually sealed under inert gas to avoid termination or radical species.

Condensation polymerization

Reactive chemical functional groups of monomers react with each other to form new bonds. By-products such as water or hydrogen chloride may be produced from these reactions.

Electro-polymerization

In an electrochemical polymerization, the monomer is oxidized at the surface of an electrode, by an anodic potential (oxidation) that is applied to it. This process is carried out in an appropriate solvent containing the desired anionic doping electrolyte. The solvent and electrolyte should be stable at the oxidation potential of the monomer and able to provide an ionically conductive medium. Upon the initial oxidation, the radical cation of the monomer is formed then it reacts with other monomers forming oligomeric products. The anode can be fabricated of a variety of materials including platinum, gold, glassy carbon, and tin or indium-tin oxide coated glass.

Electro-polymerization can be considered the most attractive procedure. This is because thickness, viscoelastic properties, porosity, and morphology of the resulting film can be easily controlled by selecting the suitable experimental conditions (e.g., the amount of charge transferred, solution pH, and the nature of the solvent, the supporting electrolyte, the functional monomer, and the cross-linking monomer).[36]

Configuration of matrix[37]

Bulk

The synthesis is performed using one pot method, where all the ingredients are mixed together. The MIP obtained is in the form of a block, having the shape of the reaction chamber. The bulk MIPs usually need further sample pre-processing by grinding and sieving to obtain micrometer-sized particles. A major disadvantage of this process is that the particles of MIP obtained are of irregular shape and size. Practically, the binding sites are distributed throughout the ground particles and a large number of them remain in the core of the matrix. Some of the imprinting sites may lost as a result of the grinding process thereby the final yield of the MIP is expected to be low.

Monoliths

This format can be prepared by grafting of MIPs layer on a performed particle, utilizing a surface bond radical initiator.[38,39] In this method, azo–initiators or specifically known as iniferters are first immobilized on the surface of the performed particles. An iniferter is an initiator for free radical polymerization.

Membranes

MIPs can be fabricated on thin film layers or membranes by three approaches, sandwiching or in situ cross-linking method, phase inversion -method or composite blending method.

Applications of voltammetric MIP-based sensors in pesticides analysis

The application of molecularly imprinted polymers (MIPs) has attracted much attention as reflected by innumerable references in the literature. A survey of literature in last ten years (2006-2015) about applications of voltammetric MIP-based sensors in pesticides analysis was summarized in the following table.[40-87]

Table 1. Properties of voltammetric MIP-based sensors used in pesticides analysis

Pesticide	Monomer/crosslinker /initiator	Porogen	Conditions of MIP preparation	Extraction conditions	Transduction method	Solution for analyte binding	Linear concentration range	LOD
4-Aminophenol	MAA/TRIM/AIBN/ hemin[40]	Dimethylsulfoxide, acetonitrile	Heating at 60 ºC for 9 h	Methanol: acetic acid (9: 1, v/v)	Ampero-metry	0.05 M TRIS buffer (pH 7.0) contg. 100 µM H_2O_2.	9.8-79.4 µM	3 µM
Acephate	*o*-Phenylenediamine[41]	Phosphate buffer (pH 5)	Potentiody-namic −0.2 - 1.0 V vs Ag/AgCl	Methanol, acetic acid (9:1, v/v)	DPV	0.1 M phosphate buffer (pH 5) contg. 5 M $K_3[Fe(CN)_6]$, 0.2 M KCl	5×10^{-7} - 1×10^{-4} M	1.3×10^{-7} M
	4-(Dimethoxyphospho-rothioylamino)buta-noic acid/3-amino-propyltriethoxysilane/ tetraethoxysilane[42]	Tetrahydrofuran	Potentiody-namic −0.4 - +0.8 V vs SCE	Methanol, acetic acid (9:1, v/v)	DPV	$K_3Fe(CN)_6$/ $K_4Fe(CN)_6$	1×10^{-4}- 1×10^{-10} M	6.81×10^{-11} M
Atrazine	Acetic acid/ thio-phene/3,4-ethylene-dioxythiophene[43]	Dichloromethane	Potentiosta-tic at 1.45 V vs. Pt	Methanol: acetic acid (0.7: 0.3, v/v)	CV	0.1 M $Bu_4NO_3SCF_3$ in CH_2Cl_2	10^{-9}-$1.5\text{x}10^{-2}$ M	10^{-7} M
	o-Phenylenediamine[44]	0.1 M Phosphate buffer (pH 7.4)	Potentiody-namic 0–0.8 V vs SCE	Methanol, acetic acid (9:1, v/v)	DPV	$K_3[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$, 0.1 M KCl	5×10^{-9}- 1.4×10^{-7} M	1×10^{-9} M
Chlorpyrifos	4-Aminothiophe-nol/AuNPs[45]	0.05 M Phosphate buffer (pH = 6.86), 0.1 M KCl	Potentiody-namic, -0.2 to +0.6 V vs. Ag/AgCl	0.5 M HCl	CV	0.05 M phos-phate buffer (pH = 6.86) contg. 0.1 M KCl	0.5-10 µM	0.3 µM
Cyanazine	AA/EGDMA/AIBN[46]	Toluene	Heating at 60 °C for 16 h	MeOH/ace-tic acid (9:1, v/v) (Soxhlet extraction)	DPV	0.1 M HCl (pH 2.7)	5–1000 nM	3.2 nM
Carbaryl	p-Aminothiophenol/ tetrabutylammonium perchlorate[47]	Ethanol	Potentiody-namic, -0.2 −1.4 V vs SCE	20 % EtOH, 0.2 M HCl	DPV	5mM $K_3Fe(CN)_6$/ $K_4Fe(CN)_6$, 0.2 M KCl	0.03 µM – 6 µM	8 nM
Dimethoate	*o*-Phenylenediami-ne/Au NPs[48]	Acetate buffer (pH = 5.2)	Potentiody-namic 0 to 0.8 V vs. SCE	Ethanol	Ampero-metry	Water	1-1000 ng mL^{-1}, 1-50 µg mL^{-1}	0.5 ng mL^{-1}
2,4-Dichlorophe-noxyacetic acid	Pyrrole[49]	0.05 M Phosphate buffer (pH = 6.86), 0.1 M KCl	Potentiody-namic, -1.3 to +1.0 V vs. Ag/AgCl	Overoxi-dation at 1.3 V vs. Ag/AgCl in 0.2 M Na_2HPO_4	CV	0. 05 M phosphate buffer (pH = 6.86), 0.1 M KCl	1-10 µM	0.83 µM
	Pyrrole[50]	15 mM Cetyltri-methylammonium bromide	Chemical oxidation	Ethanol: acetic acid (99: 1, v,v)	Ampero-metry	50 mM phosphate buffer (pH = 6.8)	0.1-8 µM	100 nM
2,4-Dichlorophe-noxybutyric acid	(Co(III) tetrakis(o-aminophenyl)por-phyrin[51]	0.1 M Bu_4NPF_6, acetonitrile	Potentiody-namic -0.1 to +1.0 V vs. Pt	MeCN, MeOH	Ampero-metry	0.1 M Bu_4NPF_6 in MeCN	200 µM-2 mM	40 µM
4,6-Dinitro-*o*-cresol	*o*-Phenylenediami-ne/aniline[52]	0.2 M Sulfuric acid: methanol (1:1, v/v)	Potentiody-namic -0.1 to +1.0 V vs. Ag/AgCl	Water: methanol (6: 4, v/v)	SWV	0.04 M Britton–Robin-son buffer (pH 3) contg. 10 % MeOH	0.8 µM-0.1 mM	0.2 µM
O,O-dimethyl-(2,4-dichlorophe-noxyacetoxyl)-(3-nitrobenzyl)meth-anephosphonate	p-tert-Butylcalix[6]-arene/TiO_2[53]	-	Condensa-tion	Dichloro-methane	DPV	0.1 M phosphate buffer (pH = 5.5)	0.1-50 µM	0.04 µM
Diuron	MAA/ TRIM/AIBN[54]	Acetonitrile	Heating at 60 °C for 24 h	Methanol, acetic acid (9:1, v/v)	SWV	Water, ethanol (20:1, v/v)	5.2×10^{8} - 1.25×10^{6} M	9×10^{9} M
Fenitrothion	Ni(II)-phthalocya-nine[55]	0.01 M Sodium hydroxide	Potentiody-namic -0.1 to +0.6 V vs. Ag/AgCl	0.1 M NH_4Cl/NH_4OH (pH 9.5)	SWV	1 M NaCl	3 µM-0.1 mM	0.8 µM
Hexazinone	AA, 2-vinylpyridi-ne/MAA/EGDMA/ AIBN[56]	Dichloromethane	Heating at 60 °C for 24 h	Methanol, acetic acid (9:1, v/v)	DPAdCSV	Hydrochloric acid (pH 2.5)	1.9×10^{-11}- 1.1×10^{-10}M	2.6×10^{-12}M
Imidacloprid	o-Phenylenediamine[57]	Acetate buffer (pH 5.2)	Potentiody-namic −0.2 - 0.8V vs SCE	0.5 M HCl	CV	0.1 M phosphate buffer (pH 7)	7.5×10^{-7} - 7×10^{-5} M	4×10^{-7} M

Isocarbophos	o-Phenylenediamine, gallic acid/ m-aminobenzoic acid[58]	0.02 M Phosphate buffer (pH 4) , 0.2 M KCl	Potentiodynamic −0.4 - 0.8V vs SCE	Distilled water	CV	2 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1)	7.5×10^{-8} - 5×10^{-5} M 5×10^{-5}- 1×10^{-4} M	2.01×10^{-8} M
Metolcarb	2-Amiothiophenol[59]	0.1 M Hydrochloric acid, ethanol	Potentiostatic at-0.6 V vs. SCE, potentiodynamic -0.2 to +1.4 V	Potentiostaticaly at 0.6 V for 600 s in 1 M HCl	Chronoamperometry	0.001 M $K_3[Fe(CN)_6]$ containing 0.001 M KNO_3	0.5-3.5 µM	13.4 nM
Metamitron	*o*-Phenylenediamine/aniline[60]	0.1 M Sulfuric acid	Potentiodynamic -0.1 to +1.35 V vs. Ag/AgCl	1 M NH_4Cl/ NH_4OH (pH 10)	SWV	0.04 M Britton–Robinson buffer (pH = 1.8)	1 µM–0.1 mM	0.27 µM
Methyl parathion	Tetraethylorthosilicate and vinyltriethoxysilane61	Ethanol, 0.2 M KCl	Potentiostaticat -1.80 V	Ethanol	SWV	phosphate buffer (pH 5.9)	10^{-8}-10^{-5} M	8.9x 10^{-9} M
	3-Mercaptopropionic acid/Fe_3O_4/Au NPs/ polyethylenediamine[62]	Ethanol	-	CV for 50 segments (25 cycles)	DPV	phosphate buffer (pH 5.5)	$2x10^{-7}$-$1x10^{-4}$ M	$1x10^{-7}$ M
	Quercetin/ resorcinol/ $KClO_4$[63]	0.2 M Acetic acid buffer (pH 5.8)	Potentiodynamic −0.2-0.9V vs Ag/AgCl	Ethanol acidic solution (pH 5.2)	CV	5×10^{-3} M $K_3[Fe(CN)_6]$, 0.1 M $NaClO_4$	7×10^{-8} M-1×10^{-6} M	3.4×10^{-10} M
	Phenol[64]	0.13 M Phosphate buffer (pH 8)	Potentiodynamic 0.3-1.2V vs Ag/AgCl	0.1 M Sulfuric acid	CV	5 M $K_3[Fe(CN)_6]$ contg. 0.1 M KCl	0.1 - 10 µg mL^{-1}	0.01 µg mL^{-1}.
	AA/ EGDMA/AIBN[65]	Chloroform	Heating at 60 °C	Ethanol	DPV	0.2 M Phosphate buffer (pH 7)	5×10^{-9} - 1×10^{-5} M	2×10^{-9} M
	AA/ EGDMA/AIBN[66]	Dimethyl formamide	Heating at 60 °C	Methanol, acetic acid (9:1, v/v)	DPV	0.1 M Phosphate buffer (pH 5)	2×10^{-7} - 1×10^{-5} M	6.7×10^{-8}M
4-nitrophenol	Carbazole[67]	Boron trifluoride diethyl etherate	Potentiodynamic range 0-1.4 V vs SCE	-	CV	Acetate buffer (pH 4.6)	8×10^{-7}- 2×10^{-5} M	0.062 M
	MAA/EGDMA/ AIBN[68]	Dimethyl formamide	Heating at 65 ºC for 24 h	Methanol, acetic acid (4:1, v/v)	DPV	Phosphate buffer (pH 7)	0.01 µM - 100 µM 200 µM - 1000 µM	5 nM
	MAA/EDMA/AIBN[76]	Chloroform	Heating at 60 ºC for 24 h	Methanol (Soxhlet extraction)	DPV	Acetate buffer (pH 4.5)	8×10^{-9}- 5×10^{-6} M	3×10^{-9} M
	1-Dodecanethiol/p-toluenethiol[77]	Dimethyl formamide	Potentiodynamic 0.6 - −0.7 V vs Ag/AgCl	0.1 M Phosphate buffer (pH 6)	DPV	0.1 M Phosphate buffer (pH 6)	2.5×10^{-8} M–1×10^{-6} M 1×10^{-6} M–3×10^{-4} M	2×10^{-8} M
Parathion	p-tert-Butylcalix[6]-arene/TiO_2[69]	-	Condensation	Ethanol	DPV	0.1 M Phosphate buffer (pH = 5)	50 nM-10 µM	10 nM
	MAA/EDMA/AIBN[70]	Chloroform	Heating at 60 ºC for 24 h	Methanol (Soxhlet extraction)	SWV	0.07 M Hydrochloric acid	$1.7\ x10^{-9}$-$9x10^{-7}$ M	$5x10^{-10}$ M
	Polyethylenediamine/ SiO_2/EGDMA[71]	-	Thermal polymerization for 8 h-	0.1 M HCl	LSV	0.1 M Phosphate buffer, (pH = 6.5)	0.015-15 mg kg^{-1}	0.003 mg kg^{-1}
	Chitosan[72]	Hydrochloric acid (pH< 6)	Potentiostatic at -1.1 V vs. SCE	Potentiostaticaly at +0.6 V for 5 min 3 times, 0.01 M KCl	DPV	0.1 M KCl	10^{-7}-8×10^{-5} M	10^{-7} M
	MAA/ EGDMA/ AIBN[73]	$CHCl_3$ (for micro-sized MIP), MeCN (for nano-sized MIP)	Heating at 60 and 65 °C for 24 and 12 h for micro- and macrosized MIP, resp.	Methanol	SWV	0.07 M Hydrochloric acid solution containing 12 % (v/v) of ethanol	0.05 - 150 nM	0.02 nM
	$(NH_4)_2TiF_6/H_3BO_3$/p-tert-butylcalix[4]arene[74]	Ethanol	Self-assembling	Ethanol	DPV	0.1 M Phosphate buffer (pH 5)	5×10^{-8} - 1×10^{-5} M	1×10^{-8} M
	Carmine[75]	0.1 M Phosphate buffer (pH 6)	Potentiodynamic 1-2 V vs SCE		CV and LSV	0.1 M Phosphate buffer (pH 6)	5×10^{-8} - 1×10^{-5} M	1×10^{-8} M.

Paraoxon	MAA/EGDMA/AIBN[78]	Chloroform	Heating at 65 ºC for 24 h	Methanol (Soxhlet extraction)	SWV	Acetate buffer (pH 5)	3.8×10^{-9}-7.5×10^{-7} M	10^{-9} M
Phoxim	Acrylamide/ ethylene glycol maleic rosinate acrylate/ AIBN[79]	Acetone	Heating at 60 ºC for 5 h	Methanol, acetic acid (7:3, v/v)	DPV	0.05 M Acetate buffer (pH 6)	8×10^{-7} - 1.4×10^{-4} M	2×10^{-8} M
Propazine	MAA/AA/4-vinyl pyridine/ EGDMA/ AIBN[80]	Toluene	Heating at 60 °C	Methanol, acetic acid (9:1, v/v)	DPV	0.1 M Hydrochloric acid (pH 3)	0.01–1 µM 1–55 µM	0.001 µ M
Rotenone	MAA/EDMA/AIBN/ styrene, NaCl/$K_2S_2O_8$/ dibutylphthalate/sodi-um dodecylsulfate /polyvinyl alcohol[81]	Dichloromethane	Heating at 65°C for 20 h	Acetic acid	DPV	Acetate buffer (pH 5.5)	0.2–400 µg L^{-1}	0.1 µg L^{-1}
Trans-resveratrol	AA/EGDMA/AIBN/ γ-methacyloxypropyl trimethoxysilane[82]	Acetonitrile	Heating at 55 °C for 24 h	CV (-0.2-1.2 V (36 cycles)	DPV	Phosphate buffer (pH 7.4)	$2x10^{-6}$-$2x10^{-5}$ M	$8x10^{-7}$ M
Triazophos	o-hydroxyphenol/ NaClO4 (pH 5.5)[83]	0.1 M Phosphate buffer (pH 7)	Potentiody-namic −0.6 - 1.2V vs Ag/AgCl	0.5 M Sulfuric acid	CV	0.1 M Phosphate buffer (pH 7), 0.1 M KCl	2×10^{-7} - 1×10^{-5} M	9.3×10^{-8} M
Triclosan	o-Phenylenediamine[84]	Acetate buffer (pH 5.2)	Potentiody-namic 0–0.8 V vs. SCE	0.1 Sodium hydroxide	Ampero-metry	Acetate buffer (pH 5.2) or 0.01 M $K_4[Fe(CN_6)]$ soln. contg. 1 M KNO_3	$2x10^{-7}$-3.0 $x10^{-6}$ M	$8x10^{-8}$ M
2,4,6-Trichlorophenol	Methacrylamide/ 4-vi-nylpiridine/EGDMA/ AIBN/MWCNTs-COOH in DMF-H_2O[85]	Dimethylsulfoxide	Heating at 65 ºC for 24 h	Methanol with 15 % (v/v) acetic acid	DPV	0.1 M Acetate buffer (pH 5) contg. 10^{-3} M H_2O_2	Above $2.5x10^{-5}$-10^{-4} M	Above $2.5x10^{-5}$ M
Trichlorfon	Tetraethylorthosilicate/ phenyltrimethoxysi-lane/methyltrimeth-oxysilane[86]	Ethanol	Sol–gel technology	Ethanol	CV	2 M $K_3Fe(CN)_6$ contg. 0.05 M KNO_3	1×10^{-8}- 1×10^{-6} g mL^{-1}	2.8×10^{-9} g mL^{-1}
Tolazoline	*o*-Aminothiophenol/ AuNPs[87]	Acetate buffer (pH 5.2)	Potentiody-namic -0.4 to +1.2 V vs. SCE	0.2 M HCl	CV	0.01 M Phosphate buffer (pH 6.8) contg. 0.1 M NaCl and 5 mM $K_3[Fe(CN)_6]$	0.05–5 µg mL^{-1} 5–240 µg mL^{-1}	0.016 µg mL^{-1}

Abbreviations: 2,2′azobisisobutyronitrile(AIBN), Acrylamide (AA), Cyclic voltammetry (CV), Differential pulse adsorptive cathodic stripping voltammetry (DPAdCSV), Differential Pulse Voltammetry (DPV), Ethylene dimethacrylate (EDMA), Ethylene glycol dimethacrylate (EGDMA), Methacrylic acid (MAA), Square wave voltammetry (SWV), Trimethylolpropane tri methacrylate (TRIM)

Conclusion

This review has focused on the molecular recognition of pesticides by synthetic receptors integrated with voltammetric transducers. Over the last 2 decades, great efforts have been done to combine MIP technology with electrochemical transduction. The majority of the sensor systems explored to date have used thermal polymerization including acrylic or vinylic monomers as recognition elements, but other phases (electrochemical polymerization, self- assembled monolayers, Sol-gel systems) have also been tested. Given the advantages of molecularly imprinted materials such as high stability, endurance, and low cost of production, it is plausible that products based on voltammetric sensors will reach the market soon.

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Received: 01.31.2016.
Accepted: 05.04.2016.