MEDDOCS
International

IMPORTANCE & APPLICATIONS OF NANOTECHNOLOGY

A Review on Nanoparticles Based Biosensors for Pesticide Detection in Water

Tarini Vohra*[1]*; Hardik Grover*[1]*; Shagun Saxena*[1]*; Devendra Kumar Verma*[2]*; Rashmi Rameshwari*[1]**

[1]Department of Biotechnology, Manav Rachna International Institute of Research and Studies, Faridabad-121001, Haryana, India.

[2]Department of Chemistry, Sri Venkateswara College, University of Delhi (South Campus), Delhi-110021, India.

Corresponding Author: Rashmi Rameshwari

Department of Biotechnology, Manav Rachna International Institute of Research and Studies, Faridabad-121001, Haryana, India

Tel: 9810039850; Email: rashmi.fet@mriu.edu.in

eBook: Importance & Applications of Nanotechnology

Publisher: MedDocs Publishers LLC

Online edition: http://meddocsonline.org/

Keywords: Pesticides; Nanotechnology; Nanoparticles.

Abstract

Pesticides are chemical compounds that are employed to eliminate, repel, or control certain forms of plant or animal life that are deemed as pests. Usage of pesticides enhances the crop yield, but they are potentially hazardous to humans, animals, and the environment. Toxicity of pesticides including insecticides, fungicides can result in diseases such as nausea, dizziness, vomiting, abdominal muscle cramps, muscle twitching, tremors, weakness or loss of coordination; making their detection the need of the hour. Conventional techniques including mass spectrometry and gas chromatography suffer from limitations such as operational complexities, requirement of sophisticated instruments and issues related to portability. High sensitivity and stability of nanomaterials based biosensors makes them suitable candidates for on-site detection of pesticides. This report reviews different biosensors that have been employed for detection of pesticides, laying down their specific limitations. It also discusses the need to develop alternate nanoparticle based sensors with high specificity, sensitivity and capability of on-site analysis.

Introduction

The combat mode of pesticides has not only proven fatal to pests but their harmful elements are gradually decimating the health of all living beings including humans through the fundamental intakes. The term pesticide includes a diverse range of compounds such as insecticides, fungicides, rodenticides, herbicides, molluscicides, nematicides and plant growth regulators [1]. The origination of synthetic insecticides-organophosphates (OP) in 1960s, carbamates in 1970s and pyrethroids in 1980s along with the initiation of use of herbicides and fungicides in the 1970s-1980s era has contributed immensely to pest control and agricultural output but has simultaneously created havoc in the life of other living organisms including humans. The amount of risk associated with a pesticide depends on the amount of exposure and the toxicity of the ingredients. Pesticides cause acute exposure effects such as dyspnea, pulmonary edema, and eye and skin irritation. Chronic exposure effects include carcinogenesis, mutagenesis, pre- and postnatal damage and reproductive system damage [1]. Organochlorine compounds (OC compounds) can damage tissues of essentially every life form on this planet, such as the fish that live in water bodies and the birds that feed on these aquatic life forms. Ideally a pesticide must be fatal to the target pests, but not to non-target species, including humans. However, the increasing usage of pesticides to increase crop yield has persistently affected human health, thus surfacing the controversy on the use of pesticides.

Prompt, on site and accurate analysis of pesticides is important due to their increasing use to improve crop yield and their consequent health effects. Sophisticated techniques such as gas chromatography [2-4], liquid chromatography-mass spectrometry [5] have been used for analysis. However, these techniques are laborious, require sophisticated instruments and trained personnel for operation. Moreover, they lack the capability of onsite/in-situ application and multiple sample analysis. Biosensing of pesticides using enzymatic, catalytic or immunological sensors [6,7] has helped in overcoming the limitations of conventional techniques opening a new arena in pesticide detection.

Whole cell biosensors based on various amperometric [6], conductometric [8] and potentiometric [9] detection techniques have also been employed for pesticide detection. However, low specificity and narrow detection range of biosensors has led to research on novel detection methods based on nanoparticles. Over a period of time, we have observed increasing synergy between nanotechnology and biosensors which has been utilized owing to their ability in recognizing threat agents in real time as also performing detection with high sensitivity and selectivity. Nanoparticles based on silver, gold, titanium and other materials (like CdS-decorated graphene nanocomposite and TiO_2 decorated graphene) have been used for detection of several small molecules including pesticides [10]. Nanoparticle based sensors have been used for detection of wide variety of pesticides including organophosphate pesticides like malathion [11] and rhodamine [12] herbicides like simazine [13] and insecticides like monocrotrophos [14], paraoxon [15], methyl parathion [16], phoxim and carbofuran [17] in water, food and soil. However, cost of production, facileness of sensor fabrication techniques and the dependability for trace level detection of pesticides are some concerns of nanoparticles based sensors. Hence, research efforts have been directed towards designing efficient biosensors based on nanomaterials that display high sensitivity and stability.

Gold nanoparticles (AuNP) absorb and scatter light strongly at their Surface Plasmon Resonance (SPR) wavelength region and this property of AuNPs makes them one of the most valuable optical probes for applications that involve sensing. The intense absorption or scattering of AuNPs at the visible light region makes them easily discernible by the naked eye or detectable by affordable instruments. This localized SPR property of the nanoparticles enables identification of pesticides at very low concentrations and conserves the sensor activity up to a large extent with a great storage shelf life. This report focuses on different biosensors available for pesticide detection, their limitations and explores the possible use of gold nanoparticles, aptamers, Molecularly Imprinted Polymers (MIPs), and Artificial Neural Networks (ANNs) based biosensors for cheaper, sensitive and in-situ detection of pesticides in water.

Pesticides and their health effects

Pesticides are substances which intend to mitigate, destroy, repel, or prevent any type of pest. It includes a variety of compounds including herbicides, insecticides, antimicrobials, and bug repellents. Defoliants, plant growth regulators and nitrogen stabilizers are also pesticides. All pesticides have some risk and the amount of risk depends upon the amount of exposure along with toxicity of ingredients. All categories of pesticide increase crop yield by inhibiting growth of pests or unwanted organism, but at the same time pose a great deal of harm to human health.

Dichlorodiphenyltrichloroethane (i.e., DDT) is the most popular organochlorine pesticide that has raised many environmental and human health issues due to its uncontrollable use [18-20]. In-utero exposure to DDT and DDE both has been confirmed to cause neurodevelopment disorders in children. Health effects, such as endocrine disorders [21,22] effects on foetal developments, hepatic alterations and metabolism of lipids have also been associated with excessive use of these chemicals. Chemicals such as organophosphates majorly found in pesticides leads to acute, long term poisoning of human system and neurotoxicity which all are result of inhalation, ingestion, skin or eye contact, and with regular or daily exposure to OPs. Certain reproductive effects (such as birth effects, hostile uterus, pre-term delivery), psychological effects (nervousness, irritation, insomnia) and the chronic neurotoxic effects (delayed organophosphate induced polyneuropathy, Alzheimer disease, attention deficit/ hyperactivity disorder in children) can potentially be caused due to OPs. Therefore, spotlight on OP turns out to be essential for health protection.

Carbamate also a class of popular chemicals, have the ability to cause cytotoxicity and genotoxicity and to induce necrosis in human immune cells [23] natural killer cells [24,25] and also apoptosis in T lymphocytes [26].

Atrazine is a potential endocrine disrupter and according to research, it interferes and alters the levels of key hormones in rats and cause delayed puberty. Rhodamine causes nasal itch and burn, chest pains, excessive tearing of eyes. Acute exposure to this chemical may even cause transient mucous membrane and skin irritation without evidence.

Conventional strartegies for pesticide detection

The detrimental effects of pesticide residues on human health, led to development of techniques that could sense and detect pesticide in various items that were being consumed by humans including food and water. Conventional techniques used for pesticide detection included liquid/gas chromatography [2-4,27], High Performance Liquid Chromatography (HPLC) and mass spectroscopy [5]. However, these techniques were limited by use of sophisticated instruments, need of a trained personnel for operation, tedious pre-treatments of the sample. Moreover, involvement of large time spans, high cost and unsuitability for multiple sample analysis resulted in exploring biosensors for pesticide detection.

Biosensors offer highly sensitive, specific, cost effective and rapid real-time detection of pesticides. Moreover, the developed biosensors are re-usable and allow in-situ monitoring of the trace amounts of pesticide. Different categories of biosensors including enzymatic, whole cell, immunosensors and DNA based biosensors have been successfully developed for pesticide detection. Different biosensors developed have been summarized in the following sections.

Enzymatic biosensors

Enzymatic biosensors are based on the effect of pesticide on the enzymatic activities in the organism that is affected by it. Effect of pesticides is often observed either by inhibition of enzyme activity and thus the products formed (Inhibition based enzymatic biosensors) or in terms of enzymes acting as catalyst (for eg. release of protons or formation of chromophoric/ electro-active substance) which are present in sufficient quantities to be detected (Catalytic enzymatic biosensors). Various pesticides that have been detected using the two mechanisms of enzymatic biosensors along with the enzyme involved have been listed in **Table 1**.

Table 1: Enzymatic Biosensors.

Principle of operation of biosensor	Enzyme utilized	Pesticides detected	References
Inhibition based biosensors	Cholinesterase	Organophosphates and carbamates	[28]
	Tyrosinase	Carbamates and atrazine	[29]
	Peroxidase	Thiodicarb (a carbamate)	[30]
	Alkaline phosphatase	Organochlorine and paraoxon	[31]
	Acid phosphatase	Thiodicarb (a carbamate)	[32]
Catalytic biosensors	Organophosphorus Hydrolase	Organophosphorus (parathion, paraoxon)	Chen et al., 2010, Lee et al., 2010
	Glutathione-s-transferase	Atrazine	Andreou et al., 2002

However, since there are multiple impurities beyond pesticides that include heavy metals and detergents that also affect the enzyme functioning that's why these sensors can't give the proper qualitative and quantitative measure of the analyte present as in AChE. There is a certain extent up to which the enzyme affects which is not revealed by these biosensors. In case of inhibition based sensors there is limited range.

Whole cell biosensors

Whole cell biosensors require cell as an immobilizing element during the detection process during transduction. The categorization of these biosensors is done on the basis of the type of cell being used which includes microbial and plant cells. Whole cell biosensors are based on various transduction schemes such as amperometric, potentiometric & conductometric. **Table 2** summarizes different whole cell biosensors that have been employed for detection of pesticides. Despite the wide range of applications of whole cell biosensors, the market value of these biosensors is reduced due to nonspecific reactions leading to low selectivity and slow response as the products need to diffusion through cell wall to produce a detectable signal [33].

Immunosensors

Antigen antibody interaction marks the basis of forming an immunosensor. The antibodies are immobilized on a substrate and they interact with the antigen forming a complex. Changes in optical and electrochemical aspects of the complex formed is instrumental in detection process. For an ideal immunosensor, it should possess quality of detecting and quantifying the antibodies in real samples. Several immunosensors developed for pesticide detection based on different transduction methods are listed below in **Table 3**.

Applicability of immunosensors in limited, as they require cumbersome processes of producing monoclonal antibodies are costly and time consuming. Moreover, immunosensors are also associated with complexities in the form of animal care to generate monoclonal antibodies limiting their application.

DNA Biosensors

DNA biosensors are recognized by the molecule of DNA that is immobilized on the electrode. The changes in redox properties of the DNA form the basis of the sensing abilities of these sensors. Pesticides including atrazine, 2, 4-Dglufosinate ammonium, carbofuran, paraoxon-ethyl and difluorobenzuron have have been detected using DNA biosensors [51]. These biosensors generally lack selectivity and further cost and reusability issues limit them.

Nanoparticles based biosensors for pesticide detection

Use of nanomaterials in sensors allows the use of many new signal transduction technologies in their manufacture. Nanosensors, nanoprobes and other nanosystems are radically transforming the fields of environmental analysis in lieu of their size. The immobilization of nanomaterials onto sensing devices generates novel interfaces that enable the sensitive optical or electro- chemical detection of analytes. Table 4 below lists various nanoparticle-based biosensors that have been designed for detection of pesticides. Within the group of noble metal nanoparticles, gold nanoparticles are mostly used for biosensor application due to their biocompatibility, optical and electronic properties, and relatively simple production and modification . These magnificent properties of gold nanoparticles have made them rising candidates not only for bio-analytics but for various other research fields.

Application domain of nanomaterials based sensing for pesticide residue detection is vast, nevertheless some issues such as availability of the nanomaterials sensitive to common pesticide residues, ease of sensor fabrication techniques and instrumentation, desired reliability and repeatability in trace level detection, cost and issues related to nanomaterial exposure to the surrounding environment need to be considered [52].

Table 2: Whole cell biosensors used for pesticide detection.

Type of biosensor	Recognition microorganism	Pesticide detected	Reference
Microbial biosensors	*E. Coli*	Organophosphates	[34]
	Arthrobacter, Flavobacterium and *Pseudomonas putida*	Organophosphates	[35,36]
Plant tissue and photosynthesis based biosensors	*Chlorella vulgaris* (Plant tissue based)	Alkaline phosphatase linked pesticides	[37,38]
	Dictyosphaeriumchlorelloides, *Scenedesmusintermedius* (Photosynthesis based)	Simazine and herbicides	[39-42]

Table 3: Immunosensors for pesticide detection.

Type of biosensor	Method of transduction	Pesticide detected	Reference
Electrochemical	Amperometric	2,4-Dichlorophenoxy acetic acid	[6]
		Atrazine	[7]
	Conductometric	Atrazine	[8]
	Potentiometric	Terbuthylazine (tba)	[9]
	Electrochemical impedance spectroscopy	Atrazine	[43]
		2,4-Dichlorophenoxy acetic acid	[43]
Optical	Surface plasmon resonace	DTT, Chlorpyrifos and Carbaryl.	[44]
	Fluorescence polarisation	Atrazine	[45]
	Total internal reflection fluorescence (TIRF)	Atrazine, simazine and alachlor	[46]
	Polarisation-modulation infrared reflection-absorption spectroscopy (PM-IRRAS)	Atrazine	[47]
Piezoelectric immunosensors		Clorpyrifos, Triclopyr	[48]
Mechanical Immunosensors		Atrazine	[48,49]
		DDT	[50]
		2,4-Di chlorophenoxy acetic acid	[48]

Table 4: Gold Nanoparticles based biosensors for detection of pesticides.

Type of material	Pesticide detected	Detection limit	Principle of detection	Reference
Gold nanoparticles (AuNP)	Herbicide simazine	0.013 µM	Electrochemical	[13]
	Organophosphate pesticides	35 ppb	Colorimetric	[53]
	Methyl parathion	0.07 ppb	Electrochemical	[54]
	Methyl Paraoxon Carbofuran Phoxim	$2x10^{-11}$M $1x10^{-10}$ M $2x10^{-9}$M	Amperometric	[17]
	Dichlorodiphenyltrichloroethane (DDT)	27 ng/mL	Dipstick immunoassay	[55]
	Paraoxon	12 µg/L	Electrochemical	[15]
	Paraoxon Carbofuran	$1x10^{-4}$ µM $1x10^{-5}$ µM	Amperometric	Sirvent et al., 2001
Gold nanoparticles/ dragon fly arrays	Rhodamine	10^{-8} M	Surface Enhanced Raman Spectroscopy (SERS)	[12]
Fe_3O_4 functionalized grapheme oxide – AuNP	Catechol Hydroquinone	0.8 µM 1.1 µM	Electrochemical	[56]
4-amini-3-mercaptobenzoic acid functionalized AuNP	Cyhalothrin	0.75 µM	Colorimetric	[57]
Au-Na dodecylbenzene sulphonate nanoparticles	Methyl parathion	$8.6x10^{-8}$ mol/L	Electrochemical	[16]
CdTe quantum dots/ AuNPs	Monocrotrophos	1.34 µM	Amperometric	[14]
Aptamers based nanoprobes	Malathion	1.94 pM	Optical	[11]
	Acetamiprid	3.2 nmole/L	Optical and electrochemical	[58]

Various detection mechanisms have been employed in the development of biosensors for the estimation of pesticides up to miniscule levels.

New trends in biosensors

The new trends in the biosensor offer advantage over the conventional types of biosensors. These include:

Aptamers

The nucleic acid sequences that bind to the analyte not necessarily a Nucleic Acid is known as an Aptamer. SELEX (Selection Evolution of Ligands by EXponential enrichment) is the technique used for designing these aptamers specific to a particular analyte.

These aptamers have wide range of detection abilities including metal ions, microbes, proteins and so on. They offer more stability than the antibodies used in the immunosensors as they can be used under extreme conditions they offer modifications without any compromise to their activity [59-63]. Less batch to batch variation while production makes them a good candidate for organophosphate detection [28].

Further, these aptamers are use in various fields of medical diagnosis, bioimaging, drug delivery and therapy, environmental toxicity testing as biomaterials.

Table 5: Aptamers based biosensors for detection of pesticides.

Type of material	Pesticide detected	Detection limit	Principle of detection	Reference
Platinum	Acetamiprid	0.6 X 10^{-11} M	Impedimetric	[64]
	Atrazine	0.4 X 10^{-10} M		
Micro cantilever array sensor	Profenofos	1.3 ng mL^{-1}	optical	[65]
Silver	Malathion	5 X 10^{-7} to 1 X 10^{-5} $mol.L^{-1}$	Surface-enhanced Raman scattering	[66]
Gold	Malathion	1.94 pM	Colorimetric	[11]
Platinum	Acetamiprid	1 pM	Impedimetric	[64]
	Atrazine	10 pM		
GO-CuNPs*	Prophenofos	0.003 nM	Co-electrodeposition	[67]
	Phorate	0.3 nM		
	Isocarbophos	0.03 nM		
	Omethoate	0.3 nM		

*GO-CuNPs: Graphene oxide-copper nanoparticles

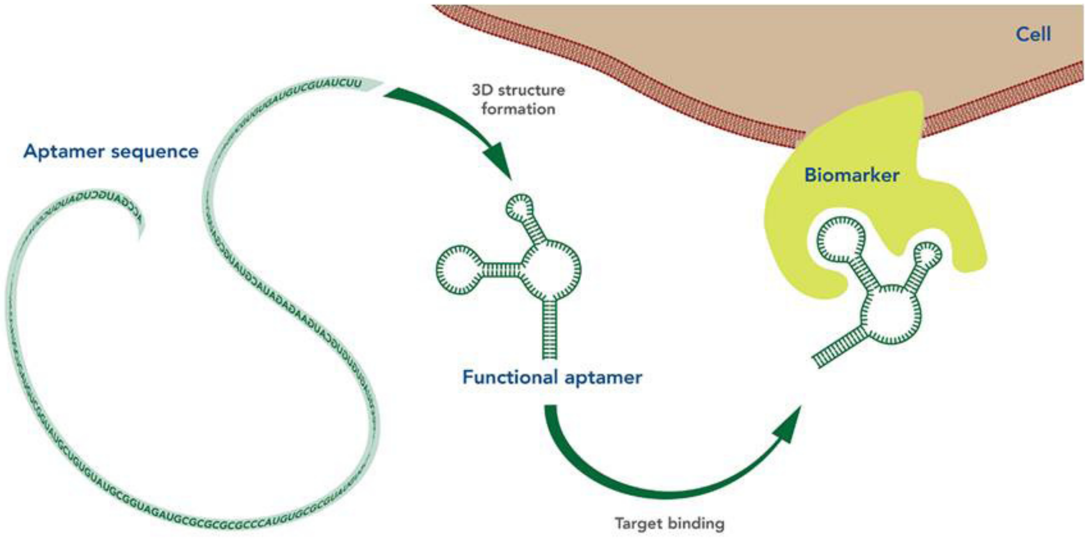

Figure 1: Engineering aptamers to bind specific targets.

Molecularly imprinted polymers (MIPs)

Various polymers are can be moulded into sensors using the molecular imprinting technique as this technique provides recognition site for the desired analyte.

General strategy for making as stated by Mayes and Whitcombe [68] starts with template that interact with monomers using covalent bonding or by self-association. These monomers later on polymerizes around the template and after that the template is washed off and we obtain a synthetic polymer. These polymers can also be used for detection of pesticides.

Table 6: MIP based biosensors for detection of pesticides.

Type of material	Pesticide detected	Detection limit	Principle of detection	Reference
Silica nanoparticles	Pyrethroid (3-phenoxybenzaldehyde)	$0.1\ \mu g\ mL^{-1}$ - $1\ \mu g\ mL^{-1}$	Colorimetric	[69]
SiO_2@QDs@m-MIPs	2,4-dichlorophenoxyaceticacid	2.1 nM	Fluoroscence	[70]
Methacrylic acid based m-MIP	Methyl parathion	1.22×10^{-6} mg L^{-1}	Electrochemical	[71]
Photonic hydrogel film	Imidacloprid	10^{-13} to 10^{-7} g.mL^{-1}	Optical	[72]
AuNPs/ERGO-SPCE*	Cyhexatin	0.20 ng mL−1	Electrochemical	[73]
MIP coated-QDs	Cyphenothran	9.0 nmol L^{-1}	Fluoroscence	[74]
Ag-N@ZnO/CHAC#	Cypermethrin	6.7×10^{-14} M	Electrochemical	[75]
MWCNT-MIP	Lindane	1×10^{-10} M	Potentiometric	[76]
MWCNT-MIP	Dicloran	4.8×10^{-10} mol L^{-1}	Volatmmetric	[77]
Molecularly imprinted film	Methyl parathion	10^{-13} mol L^{-1}	Optical	[78]

* AuNPs/ERGO-SPCE: Gold nanoparticle/electrochemical reduction graphene oxide-modified screen-printed carbon electrode

Ag-N@ZnO/CHAC: Ag and N co-doped zinc oxide ultrasonically supported on activated carbon prepared from coconut husk

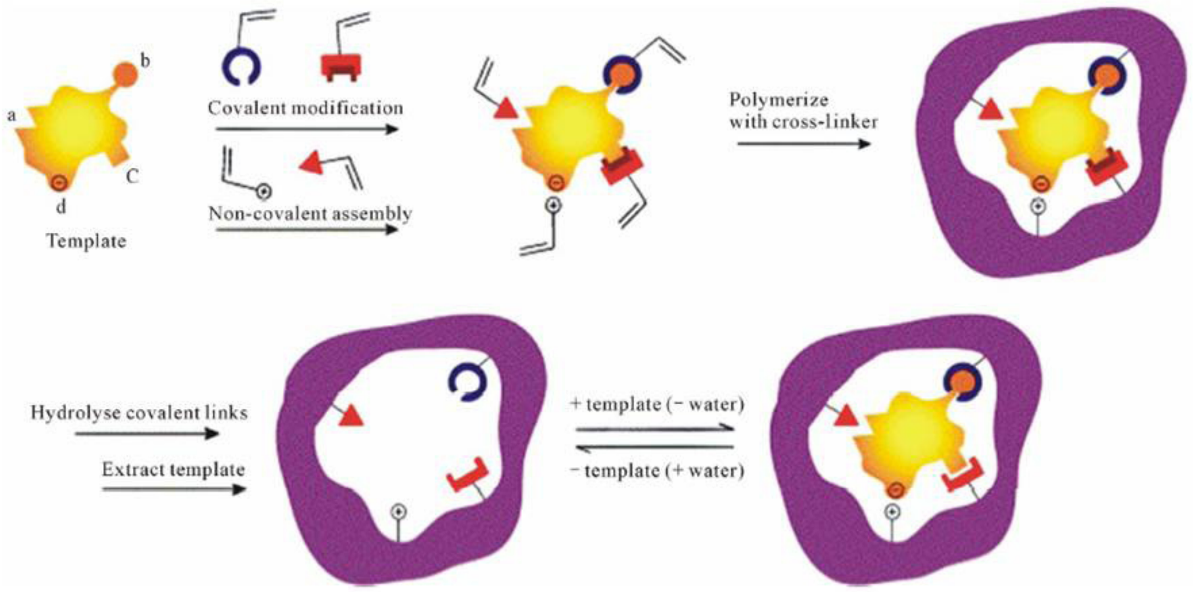

Figure 2: Schematic representation of the molecular imprinting [68].

Artificial neural networks

In order to simultaneously identify and differentiate among a multiple number of pesticides especially in the case of Ace inhibitors, ANNs can be instrumental and promising. In this an array of sensors is linked with an ANN.

This ANNs is a procedural data processing unit based on the enzymatic response pattern that depends on the concentration of each inhibitor in the sample [79].

Conclusions

Pesticides, although, successful in eliminating unwanted pests and other insects from the soil, have proven to be a menace for water bodies, soil quality, plant and human health. Hence, the need to develop adequate analytical techniques for their detection is indispensable. The conventional methods of analysis such as gas chromatography and mass spectrometry seem unsuitable because of their operational complexities, issues in portability, inability to perform multiple sample analysis, time consuming nature and need for tedious pre-treatment of the samples to be analysed. These limitations led to the emergence of alternate analytical techniques including development of biosensors such as enzymatic, catalytic, immune-sensing and whole cell biosensors based on various amperometric, conductometric and potentiometric detection techniques.

Biosensors based on nanomaterials, aptamers, Molecularly Imprinted Polymers (MIPs) and Artificial Neural Network (ANN) offer robust, stable, sensitive and specific detection of pesticides along with their ability for in-situ analysis. With controllable structure and interface interaction properties, nanomaterials such as gold nanoparticles and carbon nanotubes exhibit unconventional and novel chemical and physical features that are vital for widespread future sensor applications. Gold nanoparticles based biosensors are potent candidates for screening pesticide residues and are becoming increasingly pertinent in environmental as well as food analysis because of their sensitivity, specificity, rapidity, simplicity, and cost-effectiveness.

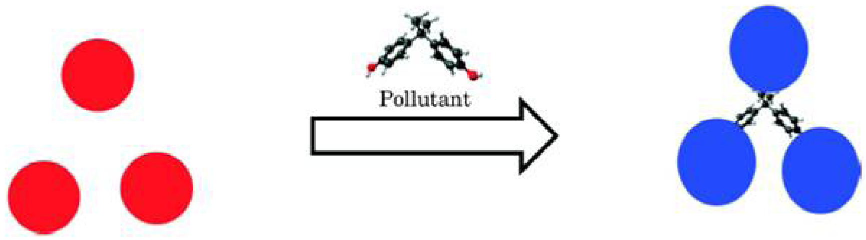

Figure 3: Detection of pesticides based on gold nanoparticles.

References

1. Aktar W, Sengupta D, Chowdhury A. Impact of pesticides use in agriculture: Their benefits and hazards. Interdisciplinary toxicology. 2008.
2. Leoni O, Iori R, Palmieri S. Immobilization of myrosinase on membrane for determining the glucosinolate content of cruciferous material. Journal of Agricultural and Food Chemistry. 1991; 39: 2322-2326.
3. Sherma J. Pesticides, Anal. Chem. 1993; 65: R40-R54.
4. Sherma J. Pesticides, Anal. Chem. 1995; 67: R10-R20.
5. Hall GL, Mourer CR, Shibamoto T, Fitzell D. Development and validation of an analytical method for naled and dichlorvos in air. Journal of Agricultural and Food Chemistry. 1997; 45: 145-148.
6. Kröger S, Setford SJ, Turner AP. Immunosensor for 2, 4-dichlorophenoxyacetic acid in aqueous/organic solvent soil extracts. Analytical chemistry. 1998; 70: 5047-5053.
7. Grennan K, Strachan G, Porter AJ, Killard AJ, Smyth MR. Atrazine analysis using an amperometric immunosensor based on single-chain antibody fragments and regeneration-free multi-calibrant measurement. Analytica Chimica Acta. 2003; 500: 287-298.
8. Valera E, Muñiz D, Rodríguez Á. Fabrication of flexible interdigitated μ-electrodes (FIDμEs) for the development of a conductimetric immunosensor for atrazine detection based on antibodies labelled with gold nanoparticles. Microelectronic Engineering. 2010; 87: 167-173.
9. Mosiello L, Laconi C, Del Gallo M, Ercole C and Lepidi A. "Development of A Monoclonal Antibody Based Potentiometric Biosensor for Terbuthylazine Detection," Sensors And Actuators B. 2003; 95: 315- 320.
10. Wang M, Gu X, Zhang G, Zhang D, Zhu D. Continuous colorimetric assay for acetylcholinesterase and inhibitor screening with gold nanoparticles. Langmuir. 2009; 25: 2504-2507.
11. Bala R, Dhingra S, Kumar M, Bansal K, Mittal S, et al. Detection of organophosphorus pesticide–malathion in environmental samples using peptide and aptamer based nanoprobes. Chemical Engineering Journal. 2017; 311: 111-116.
12. Wei Y, Zhu YY, Wang ML. A facile surface-enhanced Raman spectroscopy detection of pesticide residues with Au nanoparticles/dragonfly wing arrays. Optik. 2016; 127: 10735-10739.
13. Zhang J, Wang C, Niu Y, Li S, Luo R. Electrochemical sensor based on molecularly imprinted composite membrane of poly (o-aminothiophenol) with gold nanoparticles for sensitive determination of herbicide simazine in environmental samples. Sensors and Actuators B: Chemical. 2017; 249: 747-755.
14. Du D, Chen S, Song D, Li H, Chen X. Development of acetylcholinesterase biosensor based on CdTe quantum dots/gold nanoparticles modified chitosan microspheres interface. Biosensors and Bioelectronics. 2008; 24: 475-479.
15. Hu SQ, Xie JW, Xu QH, Rong KT, Shen GL, et al. A label-free electrochemical immunosensor based on gold nanoparticles for detection of paraoxon. Talanta. 2003; 61: 769-777.
16. Li C, Wang Z, Zhan G. Electrochemical investigation of methyl parathion at gold–sodium dodecylbenzene sulfonate nanoparticles modified glassy carbon electrode. Colloids and Surfaces B: Biointerfaces. 2010.
17. Yin H, Ai S, Xu J, Shi W, Zhu L. Amperometric biosensor based on immobilized acetylcholinesterase on gold nanoparticles and silk fibroin modified platinum electrode for detection of methyl paraoxon, carbofuran and phoxim. Journal of Electroanalytical Chemistry. 2009; 637: 21-27.
18. Alewu B, Nosiri C. Pesticides and human health. In: Stoytcheva M, editor. , editor. Pesticides in the Modern World – Effects of Pesticides Exposure. InTech. 2011: 231-50.
19. Turusov V, Rakitsky V, Tomatis L. Dichlorodiphenyltrichloroethane (DDT): Ubiquity, persistence, and risks. Environmental health perspectives. 2002; 110: 125-128.
20. van den Berg H. Global status of DDT and its alternatives for use in vector control to prevent disease. Environmental health perspectives. 2009; 117: 1656-1663.
21. Mnif W, Hassine AI, Bouaziz A, Bartegi A, Thomas O, et al. Effect of endocrine disruptor pesticides: A review. International journal of environmental research and public health. 2011; 8: 2265-2303.
22. Lemaire G, Terouanne B, Mauvais P, Michel S, Rahmani R. Effect of organochlorine pesticides on human androgen receptor activation in vitro. Toxicology and applied pharmacology. 2004; 196: 235-246.
23. Li Q, Kobayashi M, Kawada T. Ziram induces apoptosis and necrosis in human immune cells. Archives of toxicology. 2011; 85: 355-361.
24. Li Q, Kobayashi M, Kawada T. Mechanism and Ziram-Induced Apoptosis in Human Natural Killer Cells. International journal of immunopathology and pharmacology. 2012; 25: 883-891.
25. Li Q, Kobayashi M, Kawada T. Carbamate pesticide-induced apoptosis and necrosis in human natural killer cells. Journal of biological regulators and homeostatic agents. 2014; 28: 23-32.
26. Li Q, Kobayashi M, Kawada T. Carbamate pesticide-induced apoptosis in human T lymphocytes. International journal of environmental research and public health. 2015; 12: 3633-3645.
27. Lacorte S, Barcelo D. Rapid degradation of fenitrothion in estuarine waters. Environmental science & technology. 1994; 28: 1159-1163.
28. Ionescu RE, Gondran C, Bouffier L, Jaffrezic-Renault N, Martelet C, et al. Label-free impedimetric immunosensor for sensitive detection of atrazine. Electrochimica Acta. 2010; 55: 6228-6232.

29. De Albuquerque UP, De Medeiros PM, De Almeida AL, Monteiro JM, Neto EM, et al. Medicinal plants of the caatinga (semi-arid) vegetation of NE Brazil: A quantitative approach. Journal of ethnopharmacology. 2007; 114: 325-354.

30. Moccelini SK, Vieira IC, de Lima F, Lucca BG, Barbosa AM, et al. Determination of thiodicarb using a biosensor based on alfalfa sprout peroxidase immobilized in self-assembled monolayers. Talanta. 2010; 82: 164-170.

31. Ayyagari MS, Kamtekar S, Pande R, Marx KA, Kumar J, et al. Biosensors for pesticide detection based on alkaline phosphatase-catalyzed chemiluminescence. Materials Science and Engineering: C. 1995; 2: 191-196.

32. Mazzei F, Botrè F, Botrè C. Acid phosphatase/glucose oxidase-based biosensors for the determination of pesticides. Analytica Chimica Acta. 1996; 336: 67-75.

33. Kaur N, Prabhakar N. Current scenario in organophosphates detection using electrochemical biosensors. TrAC Trends in Analytical Chemistry. 2017; 92: 62-85.

34. D’souza SF. Microbial biosensors. Biosensors and Bioelectronics. 2001; 16: 337-353.

35. Mulchandani P, Chen W, Mulchandani A, Wang J, Chen L. Amperometric microbial biosensor for direct determination of organophosphate pesticides using recombinant microorganism with surface expressed organophosphorus hydrolase. Biosensors and Bioelectronics. 2001; 16: 433-437.

36. Mulchandani A, Mulchandani P, Chauhan S, Kaneva I, Chen W. A potentiometric microbial biosensor for direct determination of organophosphate nerve agents. Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis. 1998; 10: 733-737.

37. Chouteau C, Dzyadevych S, Chovelon JM, Durrieu C. Development of novel conductometric biosensors based on immobilised whole cell Chlorella vulgaris microalgae. Biosensors and Bioelectronics. 2004; 19: 1089-1096.

38. Chouteau C, Dzyadevych S, Durrieu C, Chovelon JM. A bi-enzymatic whole cell conductometric biosensor for heavy metal ions and pesticides detection in water samples. Biosensors and Bioelectronics. 2005; 21: 273-281.

39. Nguyen-Ngoc H, Tran-Minh C. Fluorescent biosensor using whole cells in an inorganic translucent matrix. Analytica Chimica Acta. 2007; 583: 161-165.

40. Guedri H, Durrieu C. A self-assembled monolayers based conductometric algal whole cell biosensor for water monitoring. Microchimica Acta. 2008; 163: 179-184.

41. Védrine C, Leclerc JC, Durrieu C, Tran-Minh C. Optical whole-cell biosensor using Chlorella vulgaris designed for monitoring herbicides. Biosensors and Bioelectronics. 2003; 18: 457-463.

42. Ventrella A, Catucci L, Agostiano A. Herbicides affect fluorescence and electron transfer activity of spinach chloroplasts, thylakoid membranes and isolated Photosystem II. Bioelectrochemistry. 2010; 9: 43-49.

43. Navrátilová I, Skládal P. The immunosensors for measurement of 2, 4-dichlorophenoxyacetic acid based on electrochemical impedance spectroscopy. Bioelectrochemistry. 2004; 62: 11-18.

44. Ramón-Azcón J, Valera E, Rodríguez Á, Barranco A, Alfaro B, et al. An impedimetric immunosensor based on interdigitated microelectrodes (IDμE) for the determination of atrazine residues in food samples. Biosensors and Bioelectronics. 2008; 23: 1367-1373.

45. Cummins CM, Koivunen ME, Stephanian A, Gee SJ, Hammock BD, et al. Application of europium (III) chelate-dyed nanoparticle labels in a competitive atrazine fluoroimmunoassay on an ITO waveguide. Biosensors and Bioelectronics. 2006; 21: 1077-185.

46. Mallat E, Barcelo D, Barzen C, Gauglitz G, Abuknesha R. “Immunosensors For Pesticide Determination In Natural Waters,” Trends In Analytical Chemistry. 2001; 20: 124-132.

47. Salmain M, Fischer-Durand N, Pradier CM. Infrared optical immunosensor: Application to the measurement of the herbicide atrazine. Analytical Biochemistry. 2008; 373: 61-70.

48. Kaur J, Singh KV, Schmid AH, Varshney GC, Suri CR, et al. Atomic force spectroscopy-based study of antibody pesticide interactions for characterization of immunosensor surface. Biosensors and Bioelectronics. 2004; 20: 284-293.

49. Suri CR, Kaur J, Gandhi S, Shekhawat GS. Label-free ultra-sensitive detection of atrazine based on nanomechanics. Nanotechnology. 2008; 19: 235502.

50. Alvarez M, Calle A, Tamayo J, Lechuga LM, Abad A, et al. Development of nanomechanical biosensors for detection of the pesticide DDT. Biosensors and Bioelectronics. 2003; 18: 649-653.

51. Nowicka AM, Kowalczyk A, Stojek Z, Hepel M. Nanogravimetric and voltammetric DNA-hybridization biosensors for studies of DNA damage by common toxicants and pollutants. Biophysical chemistry. 2010; 146: 42-53.

52. Viswanathan S and Manisankar P. 2015.

53. Wu S, Li D, Wang J, Zhao Y, Dong S, et al. Gold nanoparticles dissolution based colorimetric method for highly sensitive detection of organophosphate pesticides. Sensors and Actuators B: Chemical. 2017; 238: 427-433.

54. Liu G, Guo W, Yin Z. Covalent fabrication of methyl parathion hydrolase on gold nanoparticles modified carbon substrates for designing a methyl parathion biosensor. Biosensors and Bioelectronics. 2013.

55. Lisa M, Chouhan RS, Vinayaka AC, Manonmani HK, Thakur MS. Gold nanoparticles based dipstick immunoassay for the rapid detection of dichlorodiphenyltrichloroethane: An organochlorine pesticide. Biosensors and Bioelectronics. 2009; 25: 224-227.

56. Erogul S, Bas SZ, Ozmen M, Yildiz S. A new electrochemical sensor based on Fe3O4 functionalized graphene oxide-gold nanoparticle composite film for simultaneous determination of catechol and hydroquinone. Electrochimica Acta. 2015; 186: 302-313.

57. Imene B, Cui Z, Zhang X, Gan B, Yin Y, et al. 4-Amino-3-mercaptobenzoic acid functionalized gold nanoparticles: Synthesis, selective recognition and colorimetric detection of cyhalothrin. Sensors and Actuators B: Chemical. 2014; 199: 161-167.

58. Asma Verdian. “Apta-Nanosensors For Detection And Quantitative Determination Of Acetamiprid-A Pesticide Residue In Food And Environment”. 2017.

59. Sassolas A, Blum LJ, Leca-Bouvier BD. Electrochemical aptasensors. Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis. 2009; 21: 1237-1250.

60. Sassolas A, Blum LJ, Leca-Bouvier BD. Optical detection systems using immobilized aptamers. Biosensors and Bioelectronics. 2011; 26: 3725-3736.

61. Yuan T, Liu ZY, Hu LZ and Xu GB. “Electro-chemical and Electrochemiluminescent Aptasensors,” Chinese Journal of Analytical

Chemistry. 2011; 39; 972-977.

62. Radi AE. Electrochemical aptamer-based biosensors: recent advances and perspectives. International journal of electrochemistry. 2011; 2011.

63. Xu Y, Cheng G, He P, Fang Y. A review: Electrochemical aptasensors with various detection strategies. Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis. 2009; 21: 1251-1259.

64. Madianos L, Tsekenis G, Skotadis E, Patsiouras L, Tsoukalas D. A highly sensitive impedimetric aptasensor for the selective detection of acetamiprid and atrazine based on microwires formed by platinum nanoparticles. Biosensors and Bioelectronics. 2018; 101: 268-274.

65. Li C, Zhang G, Wu S, Zhang Q. Aptamer-based microcantilever-array biosensor for profenofos detection. Analytica chimica acta. 2018; 1020: 116-122.

66. Nie Y, Teng Y, Li P, Liu W, Shi Q, et al. Label-free aptamer-based sensor for specific detection of malathion residues by surface-enhanced Raman scattering. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2018; 191: 271-276.

67. Fu J, An X, Yao Y, Guo Y, Sun X. Electrochemical aptasensor based on one step co-electrodeposition of aptamer and GO-CuNPs nanocomposite for organophosphorus pesticide detection. Sensors and Actuators B: Chemical. 2019; 287: 503-509.

68. Mayes AG, Whitcombe MJ. Synthetic strategies for the generation of molecularly imprinted organic polymers. Advanced drug delivery reviews. 2005; 57: 1742-1778.

69. Ye T, Yin W, Zhu N, Yuan M, Cao H, et al. Colorimetric detection of pyrethroid metabolite by using surface molecularly imprinted polymer. Sensors and Actuators B: Chemical. 2018; 254: 417-423.

70. Jia M, Zhang Z, Li J, Shao H, Chen L, et al. A molecular imprinting fluorescence sensor based on quantum dots and a mesoporous structure for selective and sensitive detection of 2, 4-dichlorophenoxyacetic acid. Sensors and Actuators B: Chemical. 2017; 252: 934-943.

71. Amal HA Hassan, Silio Lima Moura, Fatma HM Ali, Walaa A. Moselhy, Maria del Pilar Taboada Sotomayor, Maria Isabel Pividori, Electrochemical sensing of methyl parathion on magnetic molecularly imprinted polymer, Biosensors and Bioelectronics. 2018; 118: 181-187.

72. Wang X, Mu Z, Liu R, Pu Y, Yin L. Molecular imprinted photonic crystal hydrogels for the rapid and label-free detection of imidacloprid. Food chemistry. 2013; 141: 3947-3953.

73. Zhang C, Zhao F, She Y, Hong S, Cao X, et al. A disposable molecularly imprinted sensor based on Graphe@ AuNPs modified screen-printed electrode for highly selective and sensitive detection of cyhexatin in pear samples. Sensors and Actuators B: Chemical. 2019; 284: 13-22.

74. Xiaohui Ren, Ligang Chen. Quantum dots coated with molecularly imprinted polymer as fluorescence probe for detection of cyphenothrin, Biosensors and Bioelectronics. 2015; 64: 182-188.

75. Li Y, Zhang L, Dang Y, Chen Z, Zhang R, et al. A robust electrochemical sensing of molecularly imprinted polymer prepared by using bifunctional monomer and its application in detection of cypermethrin. Biosensors and Bioelectronics. 2019; 127: 207-214.

76. Anirudhan TS, Alexander S. Design and fabrication of molecularly imprinted polymer-based potentiometric sensor from the surface modified multiwalled carbon nanotube for the determination of lindane (γ-hexachlorocyclohexane), an organochlorine pesticide. Biosensors and Bioelectronics. 2015; 64: 586-593.

77. Shahtaheri SJ, Faridbod F, Khadem M. Highly selective voltammetric sensor based on molecularly imprinted polymer and carbon nanotubes to determine the dicloran pesticide in biological and environmental samples. Procedia technology. 2017; 27: 96-97.

78. Tan Y, Ahmad I, Wei TX. Detection of parathion methyl using a surface plasmon resonance sensor combined with molecularly imprinted films. Chinese Chemical Letters. 2015; 26: 797-800.

79. Audrey Sassolas, Beatriz Prieto-Simón, Jean-Louis. “Biosensors for Pesticide Detection: New Trends Marty American Journal of Analytical Chemistry”. 2012; 3: 210-232.