Research Article

Recent Advances in Biosensors for Pesticide Residue Detection

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Abstract

Continuous overexploitation of pesticides is now becoming a grave problem in the ecosystem because of its persistent nature, acute and chronic toxicity and hazardous health dysfunction potential. Therefore, accurate detection of residues and its analysis is the need of the hour. Most of the conventional, time-consuming multiresidue detection methods require large amount of solvents, not eco-friendly and also required skilled personnel. So, the recent trends shifted towards use of biosensors in pesticide residue detection. Based on the previous literatures, optical, electrochemical and piezoelectric sensors have been reported and the present review classifies the biosensors according to the immobilized recognition elements like enzymes, cells, antibodies and, more rarely, DNA. Tailor designed biomolecules particularly aptasensors and molecularly imprinted polymers are recently considered for detecting novel and more complex pesticide molecules from various matrices. Besides, artificial neural networks, electronic nose etc have been also used for several multiresidue detection. Therefore, the present review consists of the description of the recent trends and advancements in biosensors as well as it the incorporation of highly sensitive nanotechnology for mediating highly efficient detection of pesticide residues from different environmental matrices.

Keywords: Nanotechnology, Biosensors, Aptasensors, Optical, Electrochemical

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Introduction

Agriculture has been glorified with intensified production since the era of green revolution, and this has been possible due to overuse of fertilizers, pesticides and various other modern approaches. Amongst these, injudicious usage of pesticides for controlling insects, bacteria, weeds, nematodes, rodents and other pests has created presence of toxic pesticide residues. Moreover, the persistency enhances its longevity and sometimes it enters into the soil, plant and even the human food chain, thereby causing severe health issues. Carcinogenicity and cytotoxic nature catalyses these ill effects. Therefore, detection of these toxic residues and subsequent elimination of these ill-fated substances from the environment is the need of an hour. Several chromatographic and spectroscopic methods have been used till date particularly for their sensitivity, efficacy and reliability etc. But all of these methods were time consuming and laborious, therefore require skilled personnel and also efficient training. Thereafter, an era of multiresidue analysis came where in a huge number of pesticides can be detected in one go. But use of large amount of organic solvents, toxic reaction residues etc were creating some nuisance. So, a concern regarding the eco-friendly technique for residue detection came forwards and such a technique was discovered named biosensors. A biosensor can be defined as a self-contained tool which assimilates a halted biological component (e.g. DNA probe, enzyme, antibody) that can further distinguish the analyte (including antigen, enzyme substrate, complementary DNA,) & an element of transduction used to alter the (bio)chemical signal consequentially obtained from the analyte and bioreceptor interaction. Depending on the ability to signal transduction, these biosensors can be differentiated into piezoelectric, optical, electrochemical, mechanochemical etc. Transducers which work on the basis of electrochemical signalling, have been extensively adapted in biosensors for determination of pesticides, especially owing to their greater sensitivity [1-3]. In addition, cost-effectiveness, modest design and trivial sizes, enthusiasts them to be used as an excellent candidates towards the advancement of portable biosensors. Therefore, the current review presents the advances in the biosensors for detecting residues of pesticides from various matrices and also exclusive use of some recognition elements which made this technique a portable and successful one.

Types of Biosensors

Enzyme Based Biosensors

Catalytic Biosensors

Organophosphate Hydrolase: OPH, being a well recognized combination of metals and enzyme, which was primarily obtained from *Pseudomonas diminuta*. It can hydrolyze a huge quantity OP(organophosphate) pesticides [4], and most importantly, the obtained products alter the solution pH. An optical biosensor based on this concept was prepared by Simonian et al. [5] by utilizing gold(Au) nanoparticles altered with oversensitive sulfo-N-hydroxy succinimide to which a covalent bond was formed via the lysine residues by this OPH. This detection ability of this biosensor was entirely based on the relationship difference between the fluorescence with the distance change amidst nanogold nanoparticle and fluorophore. The exclusion of experimental work from the measurement of pH was a very significant advantage of this biosensor, which further made the assay much sophisticated and easier [5].

Glutathione-S-Transferase(GST): A fibre-optic biosensor was tried to be developed using GST for detecting atrazine [6]. Main function was the ability of the enzyme to get immobilized through cross-linking on a film that was buttressed on an inside glass disk by means of an transitional binder sol-gel hybrid layer. GST promoted further the nucleophile reaction of GSH on atrazine, thereby releasing H+. Therefore, this change in pH was measured optically by colour variations of bromcresol green, which was added in the sol-gel layer.

Laccase: Polyphenol oxidase or laccase, being a member of Cu-containing enzymatic group, can be able to catalyse oxidation of a wide spectrum of organic compounds, particularly in aerobic conditions. Based on the concept, a biosensor was developed for detecting an carbamate pesticide, methomyl by Zapp et al. [7]. Besides, Oliveira et al. [8] focused on the numeral carbamate insecticides which were detected with laccase from *Trametes versicolor*. Here, the enzyme laccase was unswervingly incorporated on Prussian blue functionalized carbon adhesives drugged with graphene [8]. A laccase-based biosensor was also advanced for providing a decent performance on monitoring formethanate from factual samples, including mango and grapes.

Heme Containing Enzymes: Several heme containing enzymes have been utilized also for detecting some environmental pollutants including pesticides. A heme enzyme House fly cytochrome P4506A1 was restricted in DDAB(dioctadecyl dimethyl ammonium bromide) film. This kind of mimicking was utilized as a biosensor thorugh attaching the enzyme to a planar edge of pyrolytic graphite electrode and thereby using it for amperometric determination of two OCP(organochlorine pesticide)s, including heptachlor and aldrin. The outcomes, obtained inveterate that the epoxidation was the foremost alleyway for oxidation of the selected pesticides by the cytochrome P4506A1, and due to this, the biosensor formed is inclined to to the recognition of aldrin and heptachlor [9]. A wide number of methods were reported regarding peroxide inhibition pathway. In the evaluation of Oliveira et al. [10], peroxidase obtained from atemoya fruit was glued to montmorrilonite clay at the exterior of a carbon paste electrode altered with CNT(carbon nanotubes).

Aldehyde Dehydrogenase: It has the ability to catalyse the translation of aldehydes to (-COOH)carboxylic acids in presence of the NAD+ (nicotinamide adenine dinucleotide) or nicotinamide adenine dinucleotide phosphate (NADP+) as an enzymatic cofactor. Subsequent to the finding that dithiocarbamates can inhibit aldehyde dehydrogenase from baker's yeast, numerous electrochemical enzymatic biosensors have been formed by Noguer et al. [11-12]. Apart from dithiocarbamates, benzimidazole fungicides including benomyl also inhibit AlDH. This benzimidazole can be linked directly to the Parkinson's disease when exposed to human directly. All this emphasize the significance of this fast and sensitive methods for detecting the AIDH inhibiting fungicides.

Inhibition Based Enzymatic Biosensors

Tyrosine Based: Many species of bacteria contains this tyrosinase enzymes (monophenol, o-diphenol: oxygen oxidoreductase). They are basically Cu-containing, dioxygen triggered enzymes, that stimulate the conversion of diphenolic & monophenolic composites as precise substrates to quinones & o-diphenols, respectively. Various electrochemical biosensors have been discovered for detecting pesticides utilizing tyrosine as an element for biorecognition, like for example, one expedient planned with an interpretation to conserve tyrosinase activity after immobilization. This was attained by using abridged pyrroloquinoline quinone (PQQ) covalently attached to Au nanoparticles placed onto a glassy carbon electrode for sensing 2,4-D. Shim et al. [14] occupied bromomethylated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) single-layered membrane pores with cross-linked polyvinyl alcohol (PVA) comprising tyrosinase. The altered membrane was committed to a glassy carbon electrode. Extraordinary sensitivity with approximately 0.1 ppt lod was conveyed for atrazine recognition with amperometric biosensor

dependent upon Tyr/TiO2−NTs (tyrosinase-immobilized vertical growth TiO2 nanotubes). A group of scientists also studied the significance of the procedure of immobilisation and electrode type on the sensitivity of amperometric biosensors for Atz.

Alkaline Phosphatase Based: Being basic in nature, Alkaline phosphatase (ALP) is broadly substrate specific and displays extreme commotion in alkaline pH. It is a metalloenzyme having active centre Zn2+ and Mg2+ ions, thereby generating potential inhibiting capacity for a series of organophosphorus pesticides, heavy metals and inorganic salts. Recently, García Sánchez et al. [15], were utilizing a hybrid sol–gel improved with ALP for developing a biosensor for the preliminary screening of pesticides and heavy metals. The system, developed was capable to sense OCP (tetradifon), carbamates like metham-sodium, and Ops including fenitrothion and some inorganic toxic ions. Based on the hybridization techniques, a chemiluminescent ALPbased biosensor have been constructed for detecting paraoxon [16]. Furthermore, Mazzei and co-workers formatted an ALP mediated electrochemical biosensors for recognizing malathion and 2,4-dichlorophenoxyacetic acid (2,4-D) particularly by using phenyl phosphate, ascorbate-2- phosphate or 3-indoxyl phosphate as enzyme substrates [17]. Also voltammetric method have been implemented with ALP for detecting another OP pesticide, chlorpyriphos. The principe involved in this detection technique was entirely based on the inhibition of AP-algae in presence of chlorpyrifos and also deprived of any matrix interference from acephate, malathion, alkali metals and triazophos.

Peroxide Based: The molecules of peroxidase can get first oxidized through H2O2 and thereafter reduced by phenolic constituents. This procedure includes 2 enzyme intermediates. Phenolic molecules are therefore oxidized to free radicals or quinone products, capable to be electrochemically reduced on the surface of the electrode. A carbamate pesticide namingly thiodicarb was detected by a biosensor based on the principle of peroxidase inhibition [18]. Horsh Reddish Peroxidase was rigidly bonded covalently on Au electrode. When H2O2 is present, p-benzoquinone was formed by oxidation from hydroquinone via peroxidase. On the other method, HRP was restrained by electrostatic attraction to a nano-polymeric poly 2,5-dimethoxyaniline film doped with poly 4-styrenesulfonic acid (PDMA-PSS) at the exterior of an Au electrode [19]. Apart from the glyphosate, peroxidase is likewise subdued by sulphides, heavy metals etc., so an additional all-inclusive tactic considering all probable inhibitors within a tangible sample is necessary while constructing an original peroxidase-based biosensor.

Cholinesterase Based: Pesticidal detection on the basis of enzyme as a sensor is mainly dependant upon the inhibition of ChE (Cholinesterase). The major inhibitors of ChE are the carbamates and organophosphates. Other composites, like nitrate, fluoride, nerve gas, heavy metals, or nicotine, can similarly inhibit ChE. 2 kinds of naturally occurred ChE enzymes have been reported in which acetylcholinesterase (AChE) having hydrolysing tendency towards acetyl esters and BChE (butyrylcholinesterase) which can hydrolyse butyrylcholine. An alternative substrate for ChE enzymes have also been proposed by La Rosa et al. in which they mentioned use of 4-aminophenyl acetate to be as effective as the natural ones [20]. They are also able to oxidize the enzymatic produce 4-aminophenol at +250 mV vs SCE. Nevertheless, 4-APA is not accessible commercially & its usage encompasses a arduous and inefficient synthesis. Moreover, this is also wobbly and entails superior storage environments. ChE gets transformed into ChOD in most of the times. Based on this concept, a biosensor tool have been developed via immobilization of ChOD and AChE onto the gold-platinum bimetallic nanoparticle and was used to detect various pesticide mixtures and nerve agents. The synergism working in between the NPs and enzymes, enhanced surface area, enabled electron transmission process and decreased the applied potential for recognizing H2O2. Other than oxidation of H2O2, ChE inhibition can be trailed with a Clark electrode that is capable to determine the amount of O2 disbursed by the ChOD catalysed response. Peroxidase can also be involved in a bi-enzymatic system to advance into a tri-enzymatic biosensor system. A Quartz Crystal Microbalance (QCM) sensor was used by Karousos et al. which was founded on 3 enzymes for identifying the OPs and Carbamates [21]. Inhibition of AChE was accelerated by pesticides decreased the quantity of QCM-identifiable precipitate formed. This QCM system permitted sensing of dichlorvos and carbaryl at a concentration dejected to 1 ppm. Sources are important in case of optimum activities like AchE obtained from insects are more subtle as compared to other bases together with Bovine, Electric eel or erythrocytes in human and Horse serum etc. An investigation bu Valdes-Ramirez et al. studied the comparison of the utilization of 3 AchEs in the biosensors for recognition of dichlorvos in an apple skin sample [22]. Further, genetic modification has resulted in decrement of AChE in about 4 orders of magnitude from the LOD actually used for AChE obtained from wild type *Drosophila melanogaster* and Electriceel.

Immunosensors

Immunosensors are specific as compared to the enzymes. We can characterize them by the interactions of highly

selective affinity between immobilized antigens (Ag) or antibodies (Ab) on the surface of transducer, in addition to their explicit analytes, Ab or Ag respectively.

Optical Immunosensors

Fluorescent labels are to be incorporated over the immunospecies to construct immunosensors. Nevertheless, luminous organic dyes do suffer due to a photo-bleaching situation. FLIS, a FL-dependent immunosensor, is one of the premium examples of the fluorescent immunosensors. It particularly assimilates the greater perceptibility of FL recognition along with the optimum choosiness & distinguishing ability of Ag/Ab immunoassays. For the last some of the decades, FL proteins and organic dyes were considered to be the most commonly utilized FL probes for developing FL based immunosensor platforms. Moreover, as the advancement in technology progresses, nanotechnology with its broad spectrum and diverse materials came into existence including metal NPs, semiconductor nanocrystals, carbon materials, UCNPs (up-conversion nanoparticles), and occasionally occurring earth materials have appeared as the auspicious labels for evolving FLIS [23]. As a original means of producing FL labels, semiconductor quantum dots showed outstanding FL features, including high illumination and significant quantum yields, size-tuneable emission, comprehensive spectrum of excitation, huge coefficient of absorption. So, by formulating mAb (Quantum Dots-anti-benzothiostrobin monoclonal antibody) probes, Wu et al. [24] projected a CdSe/ZnS (core/shell) QDs-based FL lateral flow test strip (FLFTS), grounded on the concept of mAb, for the perceptive, pictorial, and quantifiable recognition of benzothiostrobin in different strawberry samples. Besides, Zhou et al. [25] produced the FL immunoassay probes consisting of polymer dots (PDs)-Ab through linking phosmet-Ab with PDs. This method utilized the PDMS piece of sheet for the in-situ pictorial and quasi quantifiable detection and analysis of phosmet on PDMS. A new FLIS platform has been constructed by Li et al. [26] in which they utilized the Au nanoclusters -attached Co oxyhydroxide (CoOOH) to form a nanocomposite. The present method acquired benefit of the accessible ALP-activated substrate hydrolysis, along with ascorbic acid-mediated breakdown of nanoflakes of CoOOH, particularly for the sensual quantification of imidacloprid (IMD). Besides its returns including quickness and modest operation, a FPIA (FL polarization immunoassay) have been constructed for identifying imidacloprid, carbaryl, triazophos along with tetraconazole and thiabendazole in grains of wheat as well as in the agricultural harvests. This further provides significant outlook for pesticide recognition from wide variety of matrices.

Due to a wide number of profits, including ease of development, faster analysis, visual detection, cost effictiveness, along with the dismissal of exclusive and erudite devices, CMIS(Colorimetric) assays have lately fascinated substantial consideration for using in various sensing applications [27]. The present technique represents immunochromatographic test strips (ITSs) for detecting pesticides depending on changes in color before and after the reaction deprived of the help of any sophisticated instruments. Gold nanoparticles were synthesized utilizing *Serratia nematodiphila* by Malarkodi et al. [28] for the constructing a CM dipstick by diffidently layering AuNPs over the strips of nitrocellulose membrane for the visual identification of Organophosphate pesticides in various vegetable and fruit samples. Herein, change from red to colorless indicated the in-situ presence of OPPs. When compared to singular signal-dependent approach in CM ITSs, the double signals or readouts might upsurge exactness and variety. A new immunochromatographic biosensor has been developed by Ouyang et al. [29] in which they created luminol-reduced AuNPs (LRAuNPs) as a CM/CL dual-signal probe for concurrent detection of fenpropathrin and methyl parathion. Due to accumulation of LRAuNPs, a red colour is developed. This has been recently utilized for developing a quanti/qualitative ITS for the colorimetric identification of residues of pesticide indicating fenvalerate as a prototypical analyte. Further, a rapid and perceptive lateral flow immunochromatographic (FIC) assay through Zou et al. [30] combining original FL material and UCNP labelled with a widely-specific mAb for detecting multi-residue of 3 OPPs. Furthermore a typical study by Cheng et al. [31] helped in the construction of an augmented 2D Pt–Ni(OH)2 NSs 2-way CMIS podium with a smart mobile phone-based signal for the concurrent recognition of acetochlor and fenpropathrin on 2 test lines.

RAIR(Reflection-absorption IR) spectroscopy amalgamated to modulated polarization was anticipated as a fresh ocular signal transduction method. Of late, PM-IRRAS was utilized to construct immunosensors consenting the identification of environmentally concerning contaminants. Pradier and co-workers first implemented the principle to detect Atz with the help of an indirect competitive format [32]. Firstly, sensor chips have been covered with ovalbumine-atrazine byproducts. The exteriors were quantified by PM-IRRAS and the unified part of the peptide bands was quantified. Thereafter, several stages of traditional ELISA test have been completed. Consecutive attachment of anti-Atz antibody and 2ndary anti-rabbit IgG antibody gave rise to an alteration in the properties of the IR absorption spectra of the immobilized organic components at the surface of the sensor. Atrazine recognition was entirely dependent upon the amide bands (I and II) analysis. Whenever the amount of unrestricted pesticide augmented, the amide band’s intensity got reduced.

Surface Plasmon Resonance is defined as the resonating vacillation of migrating electrons happening at the boundary between the positive and negative diffusivity material illuminated with bright incident light, like for example, a dielectric media and a metal, whereas the subsequent quantum is called as surface plasmon. For the last few years, immunosensors based on SPR have drawn fascination for detecting and analyzing a broad spectrum of food, biomedical, and ecological analytes [33]. Online monitoring of pesticides in actual water samples have been recently progressed via a commercial SPR (SENSIA). Conjugates formed with pesticides and BSA have been restrained via SAM(Self-assembled monolayer) over an Au electrode to get a recyclable sensory surface. The similar surface was reused for more than about 200 times in various assays, without any deterioration in reproducibility. Competitive identification of 2,4-D was initiated by Miura and co-workers with the help of a SPR-based immunosensor [34]. Herein, a 2,4-D-ovalbumine complex was restrained over the gold sensory chip surface for the purpose of competing with unrestricted 2,4-D, for specific attachment of it onto the monoclonal anti2,4-D. Intensification via avidin-biotin connections was designated to improve the sensory perceptibility. Further, Li et al. [35] constructed a gold/magnetite nanocomposite-based SPR immunosensor for detecting methyl 2-benzimidazole carbamate (MBC or Carbendazim). Of late, Yılmaz et al. [36] recognized an affinity immunosensor depending on SPR, thereby increasing the detection of Atz using a polymerizable system of aspartic acid as the recognition element.

Apart from the above, Raman spectroscopy can be used because it has high potential to achieve molecular "fingerprint recognition" for a broad spectrum of analytes particularly used for recognizing their amount via the continuous vibrations of the molecules. The dramatically developed approach has now become a sensible and powerful tool to detect various analytes starting from low molecular weight pollutants to the high molecular weight proteins [37]. A sensor based on Raman spectroscopy necessarily relied upon the electro-chemical interactions in between the laser of the spectrophotometer, the sample containing the analyte and also a selective and specific substrate to significantly increase the readouts for more sensitive identification of the targeted analytes. Amidst the accessible SERS sensor substrates, gold nanoparticles are the foremost and can be broadly utilized due to their high efficiency. In this regard, Li et al. [38] developed an Ab conjugated AuNPs as the SERS substrate and labelled FL tags over the surface of AuNPs working as the Raman reporters on lines of the test strip to construct a SERS-dependent ICA immunosensor for detecting 2 pyrethroid pesticides, including esfenvalerate and cypermethrin. In spite of being proved as a promising detection system for quick analysis of pesticide residues, the present research is till date in ts early phase, and therefore some tough tasks remained, particularly the ability to recognize several kinds of pesticides.

The Chemiluminescence method has also attracted attention for fabricating various optical probes and sensors in different scientific fields particularly due to its [39] greater intrinsic advantages. A researchers group premeditated a very perceptual Chemiluminescent enzyme immunoassay (CLEIA) approach for competent identification of residues of pesticide triazophos in about 1500 actual agrarian products. Fu's group constructed an immunoassay involving CL strategy that is dependent upon a bienzyme competitive immunoreaction by means of using a bispecific mAb as exclusive recognition element, along with ALP and horseradish peroxidase (HRP) with diverse CL dynamic features as the CL probes, for highly-sensitive recognition of imidacloprid and methyl parathion in multifaceted ginseng and American ginseng [40]. The recent advancement concerning the utilization of CLIS for detecting pesticide residues has grasped a much advanced level owing to initiation of usage of various new generation nanomaterials, like gold nanoparticles, Quantum Dots and magnetic substances, encouraging important revolutions and innovative outlook into the CLIS development [41]. Ouyang et al. [42] took the advantages of MnO_2 nanofilms, Au nanoparticles and g-C3N4/BiFeO3 NCs, and therefore consecutively established 3 CL dual-readout immunochromatographic assay (ICA) platforms for the identification of miscellaneous pesticide residues.

Further, electrochemiluminescence (ECL) method has been utilized now a days. In case of detection of thiacloprid insecticide from vegetable samples, Shan et al. [43] constructed an ECL immunosensor. Immense hard work have been dedicated for evolving new ECL immunosensors, for example, the on/off type signal,& the label free sequence. Additionally, performance of the ECL was enhanced by the application of new generation NPs, like multi-walled CNTs (Carbon nano tubes), C-dots, graphene NSs, whereas novel ECL components, modes of immobilization, molecular recognition foundations, and probing signal improved methods have been discovered for expansion of their implementation in various arenas [44]. Futuristic plan and programmes should be focussed entirely on the novel ECL based immunosensors, hybrids of ECL and rest other ECL based techniques [45] for proper amendment of the quality control and safety assessment of water, food, TCMs, soil, and other matrices.

Piezoelectric Immunosensors

Piezoelectric immunosensors are devices based on materials such as quartz crystals with Ab or Ag immobilized on their surface. The PZ immunosensor can detect the binding events that occur on the surface of the PZ material, and has attracted considerable research interest as an alternative to the conventional immunoassay tools for the detection

of a broad range of analytes, offering excellent benefits, such as real-time output, high sensitivity, simplicity of use, and cost-efficiency. A QCM immunosensor, a mass sensitive device, was developed for the analysis of carbaryl, and 3,5,6-trichloro-2-pyridinol (TCP), the main metabolite of the insecticide chlorpyrifos and of the herbicide triclopyr [46]. The biosensor was based on the immobilization of hapten conjugates onto the gold electrode via SAM. Recently, Piezoelectric immunosensors based on high fundamental frequency quartz crystal microbalance (HFF-QCM) have been developed for the detection of carbaryl and DDT in honey. Biorecognition was based on competitive immunoassays in the conjugate-coated format, using monoclonal antibodies as specific immunoreagents [47].

Mechanical Immunosensors

Microcantilever sensors base upon a response as a result of either variation of surface stress or mass loading. We can detect the interaction between an immobilized ligand and an analyte causing a surface stress alteration of the cantilever by detecting the alterations in the deflection of cantilever. Few microcantilever immunosensors have been developed to detect pesticides like 2,4-D, DDT, and atrazine [48]. A group of scientists are credited for the development of a cantilever-based immunosensor which is ultrasensitive to detect atrazine. Recently, a competitive immunosensor has been developed which is based on cantilever. It was developed to detect 2,6 dichlorobenzamide (BAM). This is the most widely reported pesticide residue in European groundwater [49]. We get a number of advantages from these microcanlitever sensors like easy manufacture of multielement sensor arrays, reduced size, reliability, high precision, and label-free detection.

Electrochemical Immunosensors

This type of immunosensors combine the superior choosiness of Abs with the noteworthy sensitivity of EC recognition. This has turned to be an effective substitute for the cost-effective, reliable, rapid, and simple detection of diverse targets categories, counting proteins, cytokine, mycotoxins, and pesticides in commodity, environmental, clinical, TCM, and food samples. Among these, potentiometric immunosensors recognize the effectiveness consequencing from the particular binding of Ag or Ab to its partner which is immobilized. For terbuthylazine (TBA) which is a herbicide used in a great extent in agriculture is an example of potentiometric biosensor [50]. Concentration-dependent currents produced by reduction or the oxidation of redox species on the surface of electrode can be measured by amperometric immunosensors. To analyze 2,4-D scientists have developed a simple amperometric immunosensor [51].

Conductimetric immunosensors are capable of analyzing the alterations in the current generated by the applied voltage on the electrode surface because of the interaction of Ab and Ag. This is reflected in impedimetric response also. This method was used by Valera and co-workers to detect atrazine [52].

A number of impedimetric immunosensors are reported till date for the purpose of detecting pesticides. Impedance spectroscopy permits a label-free recognition with several budding pros, like shorter analysis times, faster assays, lower assay cost, ease of detection, and higher signal-to noise ratio. In order to detect atrazine, an impedimetric immunosensor was prepared by immobilizing anti-atrazine antibody modified with histidine-tag onto a polypyrrole (PPy) film N-substituted by nitrilotriacetic acid (NTA) electrogenerated on an electrode of gold [53]. Cao et al. [54] developed an EC immunosensor based on IDAMs for the sensitive, specific and rapid detection of CPF. On this platform, the CPF mAb was orientedly immobilized onto the surface of the gold microelectrode via protein A, which could specifically capture CPF, causing a distinct change in impedance on the IDAMs surface compared with a control sample. Mehta et al. [55] fabricated a screen-printed EC immunosensor based on a label-free functionalized graphene quantum dot (GQD) for the detection of parathion. During the process, the screen printed carbon electrode (SPCE) was electrochemically modified with GQDs and 2-aminobenzyl amine, followed by incubation with anti-parathion Abs to allow the realization of a selective sensor system for parathion. Sun et al. [56] synthesized CNTs@f-Fe3O4 via the coprecipitation of Fe3þ and Fe2þ onto polydopamine (PDA)-modified CNTs (CNTs@PDA) with the aid of ethylene glycol (EG). Then, a highly sensitive EC immunosensor for CPF was developed using a biocompatible quinone-rich PDA nanosphere modified glass carbon electrode as the sensor platform and multi-HRP-flake-like-Fe3O4-coated CNT Ab2 NCs (multi-HRPCNTs@f-Fe3O4-Ab2) as the signal label. Further, Supraja et al. [57] used electrospun manganese oxide nanofibers to develop a label-free ultrasensitive EC nano-immunosensor due to its semiconducting nature and considerable ability to transfer electrons at the electrode/electrolyte interface of Mn2O3, as well as the low bandgap Mn2O3 nanofibers synthesized using the electrospinning method. Recently, Perez-Fernandez et al. [58] took advantage of the AuNP biofunctionalization ability and immobilized the self-obtained specific mAb on the AuNP-SPCE to develop a direct competitive immunosensor for the EC determination of IMD. Although the EC immunosensor has been significantly improved and display exciting possibilities for applications in pesticide detection, various challenges remain, such as the creation of recognition elements with more specific binding capability like genetic engineering Abs and aptamers, the improvement of sensing materials and

miniaturization, point-of-care testing, as well as the development of portable, wearable, and implantable sensing devices.

DNA Biosensors

The biosensors with DNA as recognition element can show superior binding of corresponding single-stranded nucleic acid sequences. These generally depend on the holding of a ss DNA probe on the top surface so that it can be able to distinguish its complementary DNA strand sequence through hybridization. A group of researchers developed an electrochemical DNA biosensor for studying damage of DNA which usually was the resultant injury due to different pesticides, like 2,4-D, carbofuran, glufosinate ammonium, paraoxon-ethyl, atrazine, and difluorobenzuron [59]. A DNA probe was selected and therefore biotinylated and then restrained over the surface of a streptavidin-modified electrode. The present probe was mongrelized with biotinylated complementary DNA target analyte. Labelling of Streptavidin using ferrocene was further involved to the mongrelized biotinylated DNA. This ferrocene's proximity, being too close to the surface of electrode generated a current signal. When the pesticides are present in a sample, it results into opening of the DNA strand and therefore a decrement in the oxidation current of ferrocene was detected in voltammetric tests. Atrazine and Paraoxon-ethyl instigated the reckless and utmost impairment of DNA. Recently, a thiol-hitched DNA seizure probe, that consequently be complementary to the selected aptamer sequence, was restrained on AuNPs/polyaniline complex film-modified electrodes (AuNPs/PANI/GSPE) and used for the removal of Profenofos containing solution [60].

Microbial Biosensors

Electrochemical Microbial Biosensors

For the purpose of developing a microbial biosensor, various kinds of microorganisms have to be restrained on to a transducer with the help of a broad spectrum of physical (e.g. entrapment) and chemical including cross linking techniques. These also can be able to metabolise different varieties of chemical compounds. Utilization of whole cells as a source of intracellular enzymes can help in circumventing expensive methods and protocols of purification of enzymes. Cell permeabilization technique has been implemented to mitigate the only problem related to diffusion of specific substrate and produces via cell membranes ensuing a sluggish retort.

Potentiometric Detection

Predictable potentiometric bacteriological sensors have been technologically advanced with the usage of ion-selective electrodes (e.g, ammonium) or gas-sensing electrodes (pCO2) covered with restrained microorganism layer. Similar biosensor was developed for detecting paraoxon directly and the mechanism was grounded to the restraining of recombinant E. *Coli* on the glass pH electrode. Further, opd gene was engineered in bacteria for encoding the OPH enzyme. The amount of unconfined H+ from the OPH hydrolysate was directly associated to the quantity of hydrolysed paraoxon. A cholinesterase potentiometric biosensor founded upon a glossy C12 electrode improved with modifiable polyaniline was constructed and evaluated for detecting Ops and carbamate insecticides [61]. Moreover, portable potentiometric biosensor has been assessed for rapid in field detection of AchE inhibitory pesticides including methomyl, prothiofos and chlorpyrifos [62].

Amperometric Detection

For the purpose of determining the BOD of any water sample, amperometric microbial sensors have been extensively constructed. This helps in measuring decomposable bio-organic contaminants in water. Biological substrates, existing in contaminated water samples, goes via the dialysis film and are integrated by the restrained microorganisms, thereby growing the microbial exhalation rate. So, minimally dissolved O2 passes via the gas-penetrable Teflon-lined films which are to be sensed by Clark oxygen electrode [63]. A bunch of various strains of microorganisms were utilized as biosensing component like *Bacillus subtilis, Arxula adeninivorans, Serratia marcescens* or yeast. An ampermetric sensor has been formed by Mulchandani et al. for detecting the Ops with p-nitrophenyl constituent (methyl parathion, paraoxon, parathion, and EPN(ethyl pnitrophenol thiobenzenephosphonate), fenitrothion) [64]. Hydrolysable ability of OPH helps the formation p-nitrophenol from OP compound. Therefore this released product was besmirched by some microorganisms, like *Pseudomonas putida* JS444. This dilapidation caused electroactive composites, amperometrically recognized.

Optical Microbial Biosensors

A few numbers of optical sensors immbolize3d with microbes have been developed till date, which can be able to detect different pollutants including heavy metals and phenols. Amongst them, entire cells of *Flavobacterium* sp. was restrained over a glass fibre filter paper. Thereafter due to the activity of enzyme OPH of *Flavobacterium* sp., methyl parathion got hydrolysed into p-nitrophenol that can further be determined at 410 nm.

Photosynthesis and Plant tissue-based Biosensors

Plant Tissue Based Biosensors

Being an alternative to enzymatic sensors, plant tissues can be used because of its long lifetime, greater steadiness and commotion ensuing preservation of the enzyme in its normal settings. Furthermore, greater reproducibility, dodging of monotonous and overtime extraction and purification phases, presence of the mandatory co-factor in the tissues makes the process more sensible and hustle-free. Based on this concept, biosensors with restrained Chlorella vulgaris microalgae was developed [65] and were reported to be able to inhibit enzymes positioned on the peripheral membrane, like ALP(alkaline phosphatases) & esterases, particularly by pesticides and heavy metals.

Photosynthesis based Biosensors

Various kinds of constituents related to photosynthesis were utilized as an element of recognition for developing the biosensors including entire cells (seaweed microalgae), thylakoids or chloroplasts, and PS II(photosystem II). PS II can further catalyse light-encouraged migration of e- from water to Pq(plastoquinone) resulting in evolution of oxygen. Several groups of heavy metals and herbicides can effectively inhibit the activity of PS II. Besides, on the basis of fluorescence tempted by Chl a has been utilized for developing optical photosynthesis-based biosensors. These toxic heavy metals and herbicides tend to stop the flow of photosynthetic electron through hindering the PSII-quinone binding position resulting in an upsurge in emission of the chlorophyll fluorescence. Believing on this code, herbicide biosensors were developed depending on the extent of the algal chl fluorescence at 682 nm (under 469 nm excitation light) [66]. Furthermore, entrapment of 3 microalgae species (*Scenedesmus intermedius, Dictyosphaerium chlorelloides*, and *Scenedesmus* sp.) was done within a silica medium and the surge in the expanse of fluorescence signal of chlorophyll was considered for quantification of simazine [67].

Recent Trends

Artificial Neural Networks/Electronic Nose

A bunch of detection methods have been implemented against various pesticides including that enzyme based, microbial based, immunology based, ELISA etc but their major limitation is exertion in critical identification between diverse inhibitors. To resolve this problematic behaviour, an array of sensors can be attached with an ANN(Artificial Neural Network) particularly to surely recognize the inhibitors existing in the sample. It is nothing but a methodical processing of data stimulated by functioning of the nervous system, especially in animals. ANN cartels the retort of diverse enzymes to develop an unique pattern which can directly relate to the concentration of the inhibitor along with the percent inhibition detected. Various intellectual biosensors have been constructed for analysing the pesticide mixtures depending on the AChE inhibition principle and chemometric data investigation with ANNs. An ANN model was constructed by Marty's group to quantify prototypically the collective retort of 2 pesticides (chlorfenvinfos and chlorpyrifos oxon) by means of using sensors integrating with drosophila mutant AChE & wild-type electric eel AChE, connected or not with PTE [68]. The developed methodologies may be applicable for real water sample pesticide analysis.

Insecticide residue identification is of premium need, particularly of those residing in the crop foliage, for making decisions on intermittent pest control. A method named electronic-nose or e-nose have been formulated and given a trial for obtaining quick recognitions of types of residues of pesticides at a comparatively low cost. The identification can be proceeded via determination of amount of headspace volatiles unconstrained from inert exteriors in vitro. In an investigation trial, recognition approaches were constructed for an inherently conducting polymer (CP)-type e-nose gas-detecting instrument, the Aromascan A32S, to detect and distinguish amidst 11 insecticides representative of 8 different categories. A vapor library was formed by utilizing analytical vapor profile databases (e-vapor signature designs) from already identified pesticides. This e-nose can be able to efficiently distinguish amid 11 dissimilar residues of insecticides, appropriately recognizing them at rates of occurrences starting from 82% up to 99%. The dispersal of vapor class constituents, depending upon ANN training and study, specified the proportional membership of vapor classes common to the types of insecticides [69].

Nanotechnology

Nanotechnology and sensors have been the most significantly emerging synergists for the purpose of detection of various pesticides over the last few years. The nanomaterials are restrained over the sensory instruments, thereby generating original interfaces which can be capable of ensuing subtle electrochemical or optical recognition of sample analytes. The nanomaterials having electro-catalysing ability, declines the excess potential allied to electroactive composites, curtailing the matrix interferences existing in the sample. In some of the cases, NPs have been utilized as markers to intensify the measured signal.

Nanotube Based Biosensors: CNTs (Carbon nanotubes), both single and multi walled, contain cylindrical nano GO sheets. From the time of their finding, CNTs have been utilized in biomedical engineering, nanoelectronics, bioanalysis and biosensing. A biosensor based on amperometry with a continuous layered assemblage of single-walled CNT-poly diallyldimethylammonium chloride and AChE was constructed for analysing residues of carbaryl [70]. This sensor exhibited upright compassion and steadiness on the way to the pesticide monitoring in water samples. Freshly, depending on the AChE inhibition activity, CNTs have been constructed.

Nano- Optical Biosensors: NPs have too been utilized for constructing effectual ocular biosensors. They are actually semiconductor material, displaying greater fluorescence quantum yields as compared to the traditional organic fluorophores, resulting in greater perceptibility. More recently, an ocular biosensor was generated for detecting monocrotophos using a CdTe probe having fluroscence generating properties [71]. With the usage of +vely charged chitosan molecule, AChE and CdTe were amassed over a quartz matrix by the layering technique. AuNPs showed optical properties and this has further been utilised for developing LSPR (localized SPR) sensor. Based on this, paraoxon was detected through immobilization of AChE over layers of AuNPs using a self-accumulating procedure [72]. When pesticides were present, the activity of AChE was repressed resulting in an alteration in the light diminution. LOD was optimized under an optimal condition was 0.2 ppb. The present sensor reserved 94% of its actual commotion even after 6 inhibition cycles with 500 ppb paraoxon trailed by recrudescence of AChE with 0.5 mM 2-pyriding-adoxime methoiodide.

Nanotechnology based Electrochemical Sensors: Immunosensors: Diuron, a substituted phenyl urea herbicide was screened rapidly by the use of an electrochemical immunosensor [73]. Cost effective deteriorated electrodes fabricated on polystyrene as a substrate were altered with PB(Prussian Blue)-AuNP film. A conductimetric immunosensor was also developed for the identification of atrazine through utilizing nanoparticle labelled antibodies. It was also showed that AuNPs can intensify the signal of conduction and henceforth permit the recognition of Atz by using DC measurements.

Enzyme Biosensors: Nanoparticle based enzymatic biosensors have also been developed recently and it was used for an amperometric identification of trichlorfon by means of using PVP (Polyvinyl pyrrolidine)-capped CdS Quantum Dots [74]. This delivers extremely subtle and steady electrochemical recognition of the enzymatically obtained thiocholine produce. An enzymatic biosensor depending upon colloidal gold nanoparticles altered sol-gel interface was constructed for detecting carbaryl, monocrotophos and methyl parathion [75]. The amassed AuNPs over the sol-gel derived silicate matrix gave a pathway amenable to electron migration and also favoured the hydrolytic enzymatic reaction at the interface, growing the perceptibility of the amperometric retort. At latest, an effectual sensor has been formed for analysing and detecting monocrotophos through combination of the exclusive assets of gold nanoparticles along with that of the QDs. This new combinatorial electrochemical system consisting CdTe QDs-AuNPs was far more effective and sensible as compared to that depending on AuNPs or QDs alone [76].

Aptamers

Gold's group, Robertson's group, and Ellington's group autonomously revealed the expansion of the in vitro assortment method that permitted the detection of precise nucleic acid sequences which bind non-nucleic acid targets having greater affinity and specificity. This approach was known as SELEX (Selection Evolution of Ligands by Exponential enrichment) and the resultant RNA or DNA oligonucleotides are mentioned as aptamers. Aptamers have their own different competitive rewards over antibodies, like their precise and reproducible chemical construction. Moreover, these are more sensible and stable than antibodies. These may be further designated in thrilling circumstances while antibodies are lonely steady under physiological situations. Owing to these major recompences, abundant quantity of aptamer-based biosensors have been formulated for identifying a broad spectrum of target analytes. Of late, an acetamiprid specific DNA aptamer was recognized [77]. Bala et al. [78] used aptamer based

technology for sensing of a harmful OP pesticide, malathion, engaging cationic peptide, aptamer and unaltered AuNPs. Further a scalable and hasty approach was recognized for the detection of four pesticides such as omethoate, isocarbophos, phorate, and profenofos from different samples with a solo aptamer-based capture technique. Herein thiolated aptamer was conjugated onto silver (Ag) dendrites, a nanostructure that can enhance the Raman fingerprint of pesticides, through Ag–thiol bonds.

Molecularly Imprinted Polymers

Cell-derived polymers (MIPs) are biomimetic synthetic receptors that have specific spaces for a specific molecule. These are produced by templating at the cellular level by performing polymerization of active monomers and inter connecting them, MIPs are able to detect and bind targeted molecules with more specificity than natural recipients. Their most significant advantages like high stability, long life, and easy preparation have led to the development of various MIPs to be applied in many fields, such as in electrochemical sensing, chromatographic separation, chiral separation, SPE, catalysis. Combining magnetism with MIPs can build a controllable rebinding process and enable magnetic separation to replace the centrifugation and filtration step in a more convenient and economical way. Surface modified molecularly imprinted polymers have added a new page in the history of MIPs by improving their selectivity, adsorption capacity and some other properties. Surface modification can be done in many ways, such as by using acryloyl-βcyclodextrin and acrylamide as monomers for selective recognition of lysozyme in aqueous solution [79], based on silver@gold nanoparticles/ionic liquid modified glassy carbon electrode for determination of ceftizoxime [80], Fe3O4@Au@SiO2 coated MIPs etc. MIP for sulfonylurea herbicides has been synthesized by precipitation polymerization using chlorsulfuron as a template molecule, 2-(diethylamino)ethyl methacrylate (DEAMA) as the functional monomer, and trimethylolpropane trimethacrylate (TRIM) as the cross-linker. A research based on the method for preparing a well-defined molecularly imprinted polymeric system via radiation-induced RAFT polymerization has been published [81] Another research on preparation and adsorption selectivity of deltamethrin molecularly imprinted polymers by two step seed swelling method has been published by Xie et al. [82]. An electrochemical sensor for 2,4-D was developed by electropolymerization of polypyrrole on a glassy carbon electrode in the presence of template 2,4-D molecules. During the electropolymerization step, 2,4-D molecules were embedded in the imprinted polypyrrole by hydrogen bond and electrostatic interacttions. Then, the template molecules were removed from the polymer by overoxidized process at +1.3 V in 0.2 M Na2HPO4 solution for 10 min. Furthermore, Rapid colorimetric detection of cartap residues by AgNP sensors with magnetic molecularly imprinted microspheres as recognition elements has been described by Wu et al. [83].

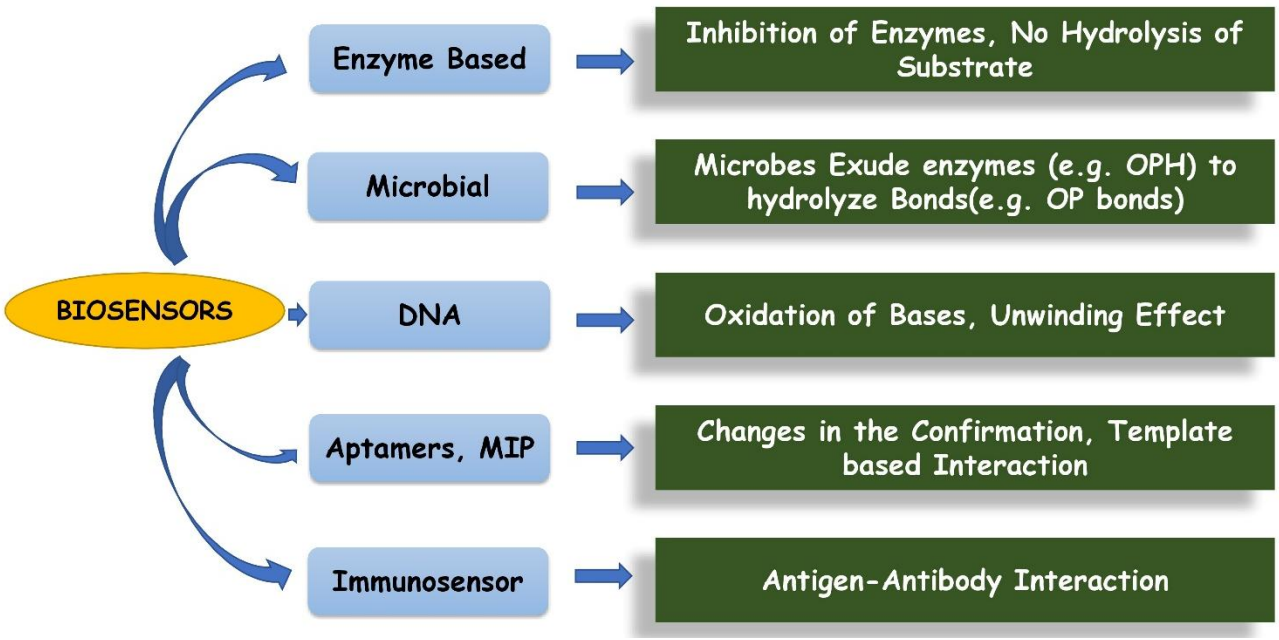

Figure 1 General Biosensors and their Mechanism

Conclusion

Biosensors, being a potential candidate for monitoring pesticides, can analyse efficiently the presence of pesticides from complex matrices with the help of specific recognition elements. Various biological elements are used like

antibodies, enzymes, microbial cells etc. Enzyme based biosensors can detect wide spectrum of pollutants thereby generating toxicity index. Further improvement in inhibitory and catalytic enzymes can generate some specificity towards pesticide recognition. Some genetically engineered microbes can be used to detect pesticides along with some plant parts are recently being used. Immunosensors based on the highly selective and sensitive Ab-Ag reaction, allow the identification of a particular pesticide. Their high specificity can be sometimes a disadvantage. However, recently, aptamer based sensors, MIPs and nanotechnology involving various nanoparticles and nanomaterials have been developed for sensing and identifying pesticide residues. Additional advantages include their compatibility with microfabrication technology and their cost-effectiveness compared to conventional biological receptors. Although there exist limited applications in pesticide residue detection as compared to medicinal applications, the hope is still bright to adapt and improve more advancement in device makings so that pesticide residue detection is no more a tedious job.

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