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**REVIEW ARTICLE**

# Organic sensing element approach in electrochemical sensor for automated and accurate pesticides detection

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## ABSTRACT

The primary component for human health is food quality and its safety. The world has crossed 8 billion population highlighting major demand to fulfil high consumption food requirement. To overcome food security issue, inorganic farming trend is booming. In the process of boosting agriculture and allied products, unethical practices of using pesticides achieve heights. Protection of plants is necessary from weeds and pests. Thus, in order, to minimize the curb of unwanted growth of weeds and pest attack, pesticides act as an agent for protection and helping for immense production of crops. Therefore, swift and precise detection of harmful pesticides in agriculture products is required in urgent demand. In this review, the distinct organic material-based sensor such as colorimetric sensing, fluorescent sensors, gas chromatography-mass spectrometry, and liquid chromatography, with the organic compounds as sensing elements to monitor pesticides level in distinct samples due to their specificity, reusability, stability, high sensitivity, and selectivity. Apart from it, this study provides a comprehensive overview of the recent major advancement in organic sensing elements in electrochemical sensor pesticides detection based on molecularly imprinted, multimodal sensor polydopamine and conductive polymer at low-cost production.

***Keywords:*** Pesticides; Sensing Elements; Electrochemical Sensor; Pesticide Detection; Sensitivity

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## 1. Introduction

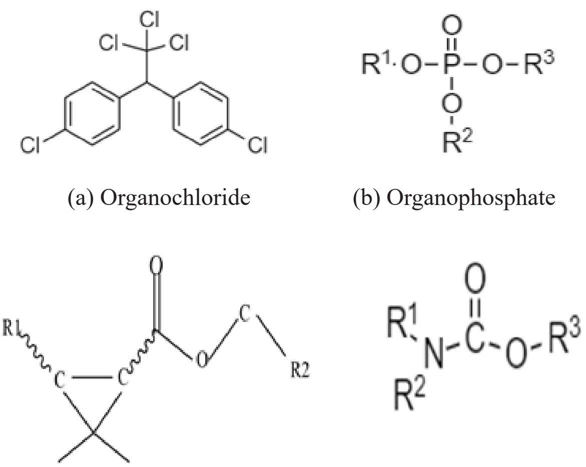
Humans have invested tremendous efforts into agriculture expansion and productivity due to the rising population to ensure security from food risk and shortage. Thus, practicing pesticides has become an effective strategy[1]. Pesticides are used in agriculture, industry and medicine in toxic compound form causing health hazards, environmental damage, and ecological disruption[2]. Toxic pesticides and toxic chemicals are used to control the prevention and elimination of weeds and pests from agriculture and to enhance productivity[3]. Generally, antimicrobial pesticides are used to destroy or inhibit the harmful microorganism. However, after inhibiting and killing pesticides pre-harvesting, still, the residue of fertilizers and pesticides to control weeds remains in agriculture and allied products. The application of pesticides such as 2-chloro-4-ethylamino-6-isopropylamino-1,3,5, triazine (Atrazine) and N-(phosphonomethyl) glycine (Glyphosate) is booming worldwide to a broader extent. Therefore, checking the level of pesticides in post-harvesting, brings the role of sensor-based pesticide detection in post-harvested agricultural products. Several techniques have been developed to sense pesticides such as high-performance liquid chromatography, gas chromatography and capillary. But, the complicated sample preparation for these techniques is not sustainable because of its limitation, non-portability, complex machinery, and expertise requirement[4]. Pesticides detection sensors for pest management have been reviewed from various perspectives in the past. Previous papers deal with mainly conventional methods such as chromatography, colorimetric, and fluorescent sensor. Colorimetric sensors require an indicator is a substance that undergoes a color change when it interacts with the pesticide. The indicator must be selective for the specific pesticide to be detected. The color of the indicator is then observed and compared to a calibration curve or reference standards to determine the concentration of the pesticide in the sample. The colorimetric sensor detects tioconazole, and phosalone by using nano-plasmonic sensor array using gold and silver nanoparticles, which are of high cost. Moreover, they may not be as sensitive as other detection methods, and they may not be selected for all pesticides[5].

The fluorescent-based pesticides detection technique involves the selection of suitable fluorescent molecules that can selectively bind with the pesticides of interest chosen. When the pesticide of interest present, it binds to the fluorescent molecule on the substrate, causing a change in its fluorescence properties. This change in fluorescence is then detected using a fluorescence spectrometer or a fluorescence microscope. Thus, fluorescent-based sensors have several drawbacks, including the necessity for specialist equipment and the possibility of interference from other ambient toxins[6].

Therefore, this review paper covers various organic sensing materials used in the different electrochemical sensors for pesticides such as molecular imprinted electrochemical sensors, multimodal electrochemical sensors, and polydopamine-based electrochemical sensors due to their specificity and low cost. Rapid and accurate organic sensing element used in electrochemical sensor within time bound gives an edge over colorimetric, fluorescent and other past techniques.

## 2. Categorization of pesticides

Pesticides are categorized based on their origin and structure. It is differentiated into synthetic and biological pesticides. Synthetic pesticides are majorly classified as insecticides, herbicides, fungicides, and nematicides. Moreover, biopesticides are derived from natural sources. Pesticides are grouped into four different families, namely organochloride, organophosphates, carbamates and pyrethroids[3], which have been found in high concentrations in agriproducts (**Figure 1**).



(a) Organochloride (b) Organophosphate

(c) Pyrethroid (d) Carbamates

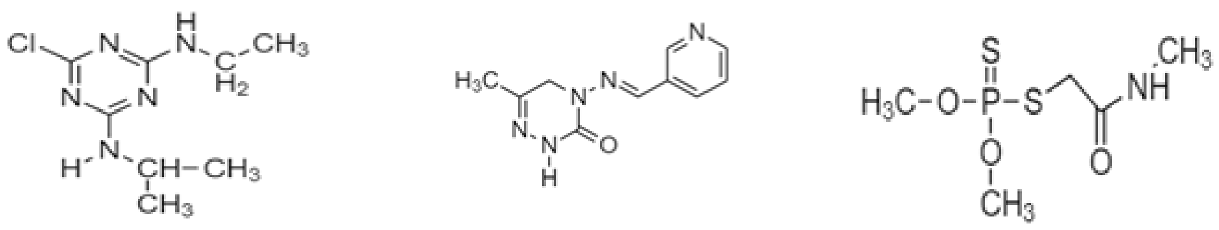
**Figure 1.** Molecular structure of toxic pesticides.

## 3. Pesticides detection sensor

Various sensors have been designed to detect pesticides level in food. Currently pesticide detection has been performed by near-infrared, high-performance liquid chromatography, gas chromatography Raman, ultraviolet-visible, fluorescence spectroscopies, and enzyme-linked immunosorbent assays. These methods are conventional techniques[7]. Chromatography technique shows prominent filtration potential and superior pesticide detection performance but they lack response time and accurate peak extraction problems. The colorimetric sensor detects tioconazole, and phosalone by using nano-plasmonic sensor array using gold and silver nanoparticles. In addition to it, dimethoate, and chlorpyrifos have been detected using platinum nanozyme. Apart from it, surface-enhanced Raman scattering is used as an effective potential technique to identify and detect the presence of analytes such as urea, and fenvalerate by using $SiO_2/TiO_2$ Ag@MIPs. Photoinduced enhanced spectroscopy using $TiO_2$ to detect urea concentration in milk. Fluorescence carbon-based nanomaterials sensors are used to confirm the pesticide bioanalysis[7]. Carbon dots and metal clusters have a low fluorescence quantum yield and poor photostability. Further, organic/polymeric dyes, suffered from complicated preparation conditions, poor water solubility and a significant color loss[8]. However, near infrared, Raman spectroscopy, fluorescence and UV spectra are methods that do not require sample destruction but often their overlapping peaks decrease their specificity. Thus, due to these drawbacks, chromatography and spectroscopy methods are a little difficult to apply for accurate and swift detection. To overcome these challenges, an organic sensing element-based electrochemical sensor to detect toxic pesticides and chemicals rapidly and precisely in agricultural products is crucial and necessary, which is easy to use with specificity and sensitivity. It makes it feasible to analyze numerous analytes. To improve on-site pesticides detection, wearable chemical sensor to detect organophosphorus by ratiometer fluorescence using fluorescent materials BaMOFs, $[H_2N(CH_3)_2][Ba(H_2O)(BTB)]$ (BTB = 1,3,5-benzenetribenzoic acid). Electron transfer mechanism and signal production confirm the pesticide recognitions performed by sensing element[8] (**Figure 2, Table 1**).

**Table 1.** Earlier sensors to detect pesticides

| Sensor detection methods | Sensing materials | Pesticides | References |
|---|---|---|---|
| Gas chromatography | Polypyrrole-coated ZnO nanorods | 1-2,4-DMA (amitraz's final degradation produce) | [9] |
| Liquid chromatography | Zein nanoparticles | Atrazine | [10] |
| Fluorescent spectrophotometry | BaMOFs $[H_2N(CH_3)_2][Ba(H_2O)(BTB)]$ (BTB = 1,3,5-benzenetribenzoic acid) | Organophosphorus<br>Neonicotinoids<br>Carbamates<br>Pymetrozine | [11] |
| Surface-enhanced Raman spectroscopy (SERS) | $SiO_2/TiO_2$ Ag@MIPs | Fenvalerate | [12] |
| Colorimetric | Platinum nanozyme | Dimethoate<br>Chlorpyrifos | [13] |
| Enzyme-linked immunosorbent assay [ELISA] | $SiO_2$@Au | Fenthion | [14] |



(a) Atrazin (b) Pymetrozine (c) Dimethoate

**Figure 2.** Molecular structure of pesticides.

## 4. Electrochemical [EC] pesticide detection sensors

The adoption of electrochemical sensors comparable to other detection methods is due to their adaptability, rapid analysis and less solvent consumption. These sensors are simple to build and portable since they are made up of electrodes that exhibit chemical changes such as charge transfer as an electrical response[15]. It obtains extensive interest, because it improves the electrocatalytic activity, increases the current response and decreases the peak-to-peak separation. Here, metal-based electrodes such as Au electrode modified with the nanomaterials, for example, reduced graphene oxide [rGO][16], and zinc oxide Nanoflower [ZnONFs] are employed for acetylcholinesterase [AChE] immobilization and engineered nanoparticle based on $SnO_2$ for pesticide remediation electrochemical sensing of especially organophosphate [OP] pesticides[17]. The accomplishment of the developed sensor was further assessed for its linearity, reproducibility and stability. To improve the viability of electrochemical sensors for various pesticide detection approaches, numerous types of electrochemical sensors based on various target analytes have been developed. Electrochemical sensors are highly used in monitoring environments, the process control systems in the food industry and biomedical analysis. They have excellent properties of rapid response time and are highly sensitive. Antibodies, peptides and enzymes are used as molecular recognition of elements in the sensor for the electrochemical methods[18] (**Figure 3**).

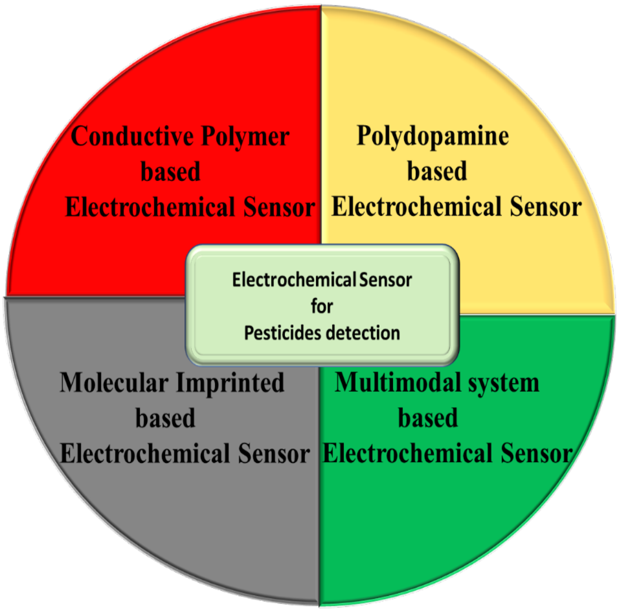



**Figure 3.** Recent various development in electrochemical pesticide detection sensors.

## 4.1 Pesticides detection mechanism of electrochemical sensors

In electrochemical sensors, the electrode surface is coated with a thin film of a material that selectively interacts with the target pesticide. This material is called a recognition element or a sensing layer, and it can be an enzyme, antibody, aptamer, or another biomolecule. When the pesticide interacts with the recognition element, it induces a change in the electrical signal of the sensor, which is measured by a readout device. Because of their excellent sensitivity, selectivity, and low cost, electrochemical sensors are extensively utilized for pesticide detection. The detecting process involves the interaction of the pesticide with the electrode surface, which results in a change in the electrical characteristics of the sensor. The electrochemical (EC) sensor contains three important elements, transduction element, inductive element, signal processing and display system[19]. The transduction element provides a surface for the electro-oxidation process with high selectivity and sensitivity[20]. The interactivity between the sensing electrode with the target analyte generates chemical signals. At the surface of sensing electrodes, the electrochemical redox reaction performs to detect toxic chemicals and pesticides. At the surface of the electrode sensor, pesticides are subjected to electrochemical redox reactions. The induction signal absorbs by transducers and further amplifies the electronic system, which displays the electrical signal as an output. The linear relationship between the chemical signals and the concentration of target pesticides is realized by the quantitative analysis of the amplified electrical signals concerning the magnitude of the target analyte[21] (**Figure 4**).

The sensitivity and selectivity of the electrochemical sensor depend on the properties of the recognition element, the electrode material, and the measurement conditions. Optimization of these parameters is essential for achieving high accuracy and reliability in pesticide detection.

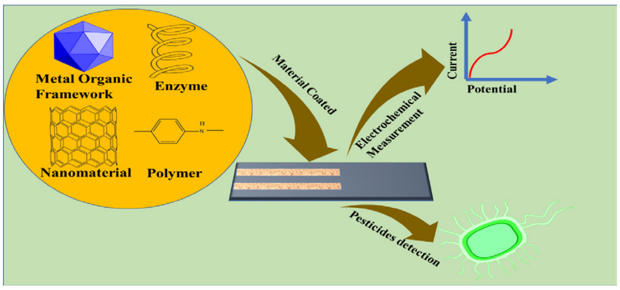



**Figure 4.** The schematic diagram for MOF/nanoparticles/organic/inorganic molecule for working electrode mechanism for pest detection sensor.

## 4.2 Polydopamine-based electrochemical sensor

Polydopamine has a high adsorption capacity to detect pollutants in agriproducts. Therefore, its adhesive property has been utilized to extract pesticides from food. PDA-based sensors are microdevices have good sensitivity, and selectivity of pesticide detection. This technique is mainly based adsorbent or nature of coating used during pesticide analysis, such as using magnetic ferro ferric oxide/p-polydopamine imprinted polymer composite as an adsorbent to detect DDT in food samples. The investigative principle of polydopamine-derived

AChE sensor is depending on the potential of the pesticides to obstruct the AChE enzyme. Thus, AChE sensors are applied to identified pesticides whose mode of action is the inhibition of the AChE enzyme in the target organism[22]. A similar principle electrochemical sensor has been adopted using adsorbent polydopamine-reduced graphene oxide [rGO] gold nanoparticles to identify carbofuran in tomatoes[23]. Further gold nanoparticle coated over polydopamine amine substrate provides an active platform by inducing lipase to detect the target analyte, as depicted in **Figure 5**.

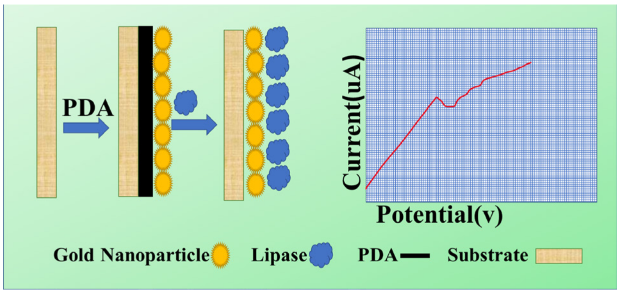



**Figure 5.** Simplified representation for preparation of AuNP/PDA active platform for pesticide selective recognition.

## 4.3 Multimodal system based electrochemical sensors

The progress of multimodal sensors has performed a crucial role in various applications. The multimodal sensor provides collective transducers on a single platform concerning comparing with a single modality sensor. Surface-enhanced Raman spectroscopy and electrochemistry are the two most prominent detective method in multimodal which gives good sensitivity and specificity. A metallic strip composed of palladium (Pd) and gold (Au) with electrodeposition of silver nanoparticles provides a sensing platform to detect chlorfenypyr[24]. Based on this multimodal sensor system sensitive and quickly tracing heavy metal ions such as arsenic (As) in food samples and water, featured with quick response time, highly sensitive and low cost. For this method, especially stripping voltammetry, to detect traces of As(III) in food samples showing tremendous progress. The fundamentals of stripping voltammetry assay are that As(III) is initially pre-concentrated and then reduced into As(0) deposited on the working electrode surface, further the stripping process is executed in an anodic scan mode to re-oxidize As(0) to As(III) with a specific stripping current[25] (**Figure 6**).

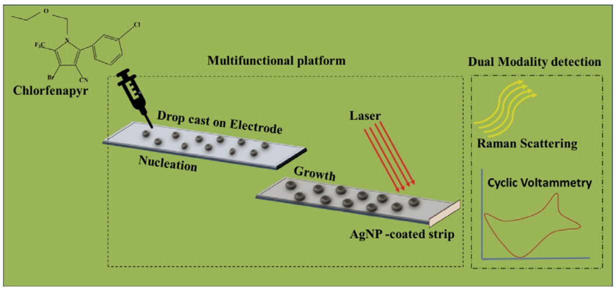



**Figure 6.** Diagrammatic illustration based on binary detection of chlorfenapyr through EC and SERS on test strips coated with AgNP via electrodeposition preparation.

## 4.4 Molecularly imprinted electrochemical sensors

The simulation of a biological system for molecular recognition participates to construct MIPs-based sensor by natural and synthetic compounds. The polymerization of functional monomers helps at the initial stage to format MIPs when imprinted molecules/target molecules are available through covalent or non-covalent bonds. This sensor is used to detect organophosphate. The crucial role of the molecular imprint technique is the high selectivity for the targeted pesticides. Verification of the selectivity of molecularly imprinted, numerous experiments with several interfering substances are performed[26]. Oxime-based electrochemical sensor is used for non-electroactive organophosphates determined by using pralidoxime (PAM). For this 5-({(1E)-[4-(Diethylamino)Phenyl]Methylene}Amino)-1-Naphthol (1) is used as pesticide detection. They have superior chemical and thermal stabilities[27]. Molecularly imprinted technology provides a simplified and economically friendly solution for toxic elimination is complicated. Environment, such as Tong *et al*. described N,N-dimethylacetamide and ceramic carbon electrode-based carbon nanotubes performed exhibit functional monomer for electrochemical sensor detection of cholesterol[28] (**Figure 7**).

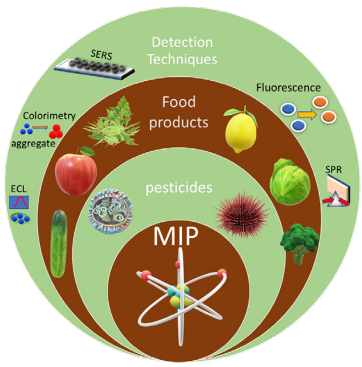



**Figure 7.** Schematic illustrative picture of several MIP -based sensor to detect pesticides.

## 4.5 Conducting polymer-based electrochemical sensors

The conducting polymer is used in pesticides—electrochemical biosensors, including polyaniline, polypyrene, polythiophene etc. Controllable electrochemical properties of conducting polymers such as polyaniline, are competent enough for constructing electrochemical sensor. Enhancing variation in doping level adjusts the electrical properties of polyaniline. Its advantage is a simple fabrication with better conductivity and environment-friendly[6]. In addition, composite materials such as polyaniline transition metal oxide [TMOs], and polyaniline carbon material help to improvise the structural and mechanical properties of polyaniline. Also, raffia-based porous carbon has been synthesized to support polyaniline to detect imidacloprid pesticides[29]. Working on the same principle, conducting polymer-based electrochemical biosensor has been designed with acetylcholinesterase enzyme immobilization to detect acetylthiocholine and pesticides[30] (**Figure 8, Table 2**).

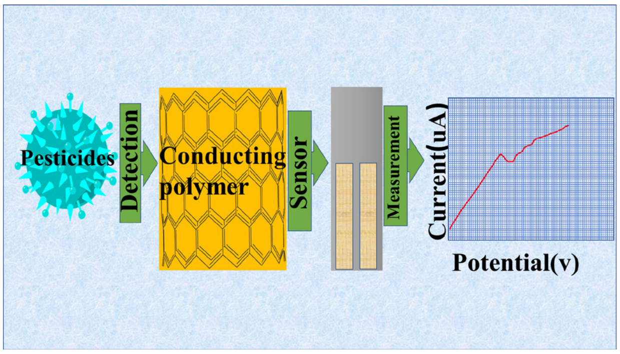



**Figure 8.** Conducting polymer/noble metal nanoparticle nanocomposite-based electrochemical sensor.

## 4.6 Nanozyme-based electrochemical sensors

Existing nanozyme research in the analytical field has primarily relied on the colorimetric strategy for identifying organophosphate pesticides. But, because most nanozymes are of black, brown and yellow color which generate interference in realistic samples, and limit the nanozyme-based colorimetric systems. To succeed over this challenge, an electrochemical strategy in nanozyme-based sensor is introduced[31]. For the quick detection of methyl-paraoxon, distinct on-site analysis approaches based on the suppression of bio enzyme activity, such as acetylcholinesterase, have been used. Nanozymes have been widely used in the development of quick detection methods due to their great stability, strong catalytic activity, and ease of synthesis[32]. A new electrochemical technique based on cerium oxide ($CeO_2$) acts as a nanozyme for the detection of Methyl-paraoxon. $CeO_2$ has organophosphorus hydrolase mimicking activity, which can catalyze the breakdown of Methyl-paraoxon (MP) to produce para-nitrophenol[33]. Moreover, nanomaterials derived from carbon have been demonstrated to mimic natural enzymes. Such nanozyme show considerable impact on the degradation and detection due of the pesticides to their great stability under harsh temperatures[34]. Based on manganese dioxide and tris(2,2'-bipyridine) ruthenium, an inorganic recognizer-based homogeneous electrochemiluminescence (ECL) sensor for the highly sensitive and believable assessment of OPs has been developed. Manganese dioxide nanoflakes-$[Ru(bpy)_3]^{2+}$ nanocomposites (MnNFs-Ru) are created through electrostatic contact and the confinement of $[Ru(bpy)_3]^{2+}$ in MnNFs-Ru results in a weak ECL signal. It's interesting to note that MnNFs-Ru can detect thiols because the analyte initiates the reduction of MnNFs into $Mn^{2+}$ and the release of $[Ru(bpy)_3]^{2+}$ from MnNFs-Ru into solution[35].

Moreover, colorimetric nanozyme sensor arrays for aromatic pesticide detection using graphene doped with heteroatoms are designed. When various pesticides are adsorbed on graphene, the active sites of nanozymes may be variably veiled, which in turn reduced their peroxidase-mimicking activity. Five pesticides (fluoroxypyr-meptyl, lactofen, fomesafen, bensulfuron-methyl, and diafenthiuron) with concentrations ranging from 5 to 500 uM are successfully differentiated by the sensor arrays using this technique[36].

The primary response of nanozyme-based OPs sensors was the peroxidase-like activity, which involved unstable and poisonous $H_2O_2$. By growing PtPdNPs in situ inside the extremely thin two-dimensional (2D) graphitic carbon nitride ($g\text{-}C_3N_4$) nanosheet, a hybrid oxidase-like 2D fluorescent nanozyme ($PtPdNPs@g\text{-}C_3N_4$) was produced. The oxidation of o-phenylenediamine (OPD) into 2,3-diaminophenothiazine was hindered by the removal of $O_2$• from the dissolved $O_2$ catalyzed by PtPdNPs@g-oxidase-like $C_3N_4$'s activity when acetylcholinesterase (AChE) hydrolyzed acetylthiocholine (ATCh) to (DAP)[37].

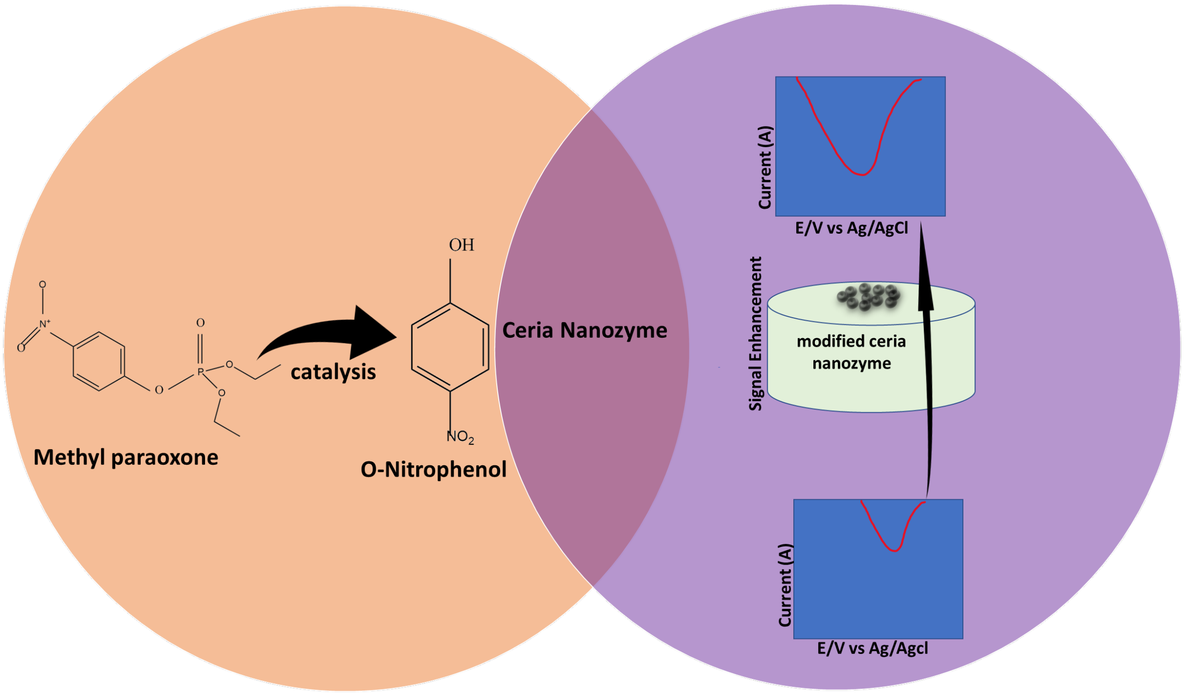



**Figure 9.** Schematically depiction of the electrochemical approach for detecting methyl-paraoxons via bifunctional $CeO_2$ nanozyme.

## 4.7 Electrochemical fabrication of AAO SERS sensors

Raman spectroscopy has the potential to generate finger-print spectra of a number of compounds by detecting, which makes it an excellent characterization tool for the detection of a wide range of analytes through an inelastic scattering of photons[38]. Thus, nanoporous anodic aluminium oxide (AAO) based SERS substrate has gained the potential to sense pesticides signature in Raman spectroscopy. A layer of plasmonic materials, often gold or silver, is sputtered or evaporated onto the AAO substrate to create the SERS-AAO-based substrates. By changing the arrangement of AAO pores and the parameters, these plasmonic NPs (such as silver/gold) can have different sizes and inter-particle distances. The SERS-AAO sensor is ideal for a specific sensing application due to the metal deposition's characteristics (such as time length)[39]. By tuning the pore size shape and etching, different target analyte of pesticides such as organophosphorus, can be detected via Raman spectroscopy which generates the signature of pesticides molecule[40].

However, Surface-enhanced Raman spectroscopy (SERS)-based rapid identification and quantitative simultaneous analysis for several pesticides in real samples remain challenging due to sample complexity, repeatability, and stability of SERS substrate. To overcome these issues, a SERS-based array test for several pesticides is fabricated using an array of three-dimensional (3D) silica photonic microspheres (SPMs) filled with colloidal silver nanoparticles as the analytical platform, by fixing silver nanoparticles into the gaps created by the self-assembled nanospheres of the 3D SPMs to produce "hot spots", on which the Raman enhanced effect was up to $9.86 \times 10^7$ and the maximum electric field enhancement effect reached to 9.75 times[41].

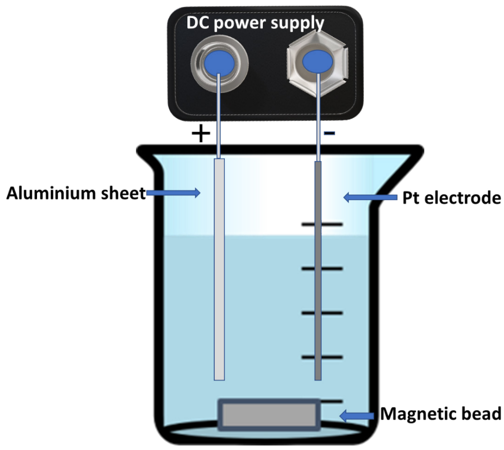



**Figure 10.** Electrochemical setup for aluminium anodic oxidation.

**Table 2.** Distinct organic sensing materials used in electrochemical sensors

| Sensors | Sensing materials | Pesticides | References |
|---|---|---|---|
| Electrochemical sensor | Aptasensor | Isocarbophos | [42] |
| Conducting polymer electrochemical sensor | β-cyclodextrin | Carbendazim | [43] |
| Multimodal-based electrochemical sensor | $MoS_2$ (Ag–$MoS_2$) | Thiabendazole | [44] |
| Molecularly imprinted polymer electrochemical sensor | Fenamiphos sulphoxide | Fenamiphos | [45] |
| Conducting polymer electrochemical sensor | Reduced graphene oxide | Imidacloprid | [46] |
| Molecularly imprinted polymer electrochemical sensor | $SiO_2$/$CsPbBr_3$QD | Phoxim | [47] |

# 5. Future perspective

Besides using synthetic compound-based pesticides such as organochlorine, organophosphate, pyrethroids and carbamates. One goes with using natural organic pesticides such as phosphinothricin, leptospermone, capsaicin, and rotenone-based organic farming. Another recent option is biopesticides which include microbial pesticides, plant-incorporated protectants and biochemical pesticides[48]. These organic compounds are used to inhibit insecticides and pesticides at pre-harvesting to reduce heavy dependence on electrochemical pest detection sensors. These pest detection sensors must be integrated with the image processing software to quantify pesticide residue more effectively. Moreover, the concern regarding rapid accurate pesticide detection has given ample opportunity to develop a novel sensor. To date, the desirable sensing system based on the organic chemicals to detect toxic analytes has a high scope with ultra-low cost and ultra-high sensitivity.

# 6. Conclusion

In conclusion, we demonstrated a workflow of pest detection electrochemical sensors, starting from analysis of the various organic/inorganic compounds acting as a sensing material to detect toxic pesticides. There has been advanced improvement in pesticide's detection and analysis for pest management and control. A distinct sensor-based detection technique has been developed which has reduced sample size and interference and increased sensitivity with sensitiveness and cost effectiveness. The prepared sensor offers a significant linear response and is sensitive towards organophosphate, organochloride, carbofuran, imidacloprid and chlorfenapyr pesticides. Moreover, the sensor array illustrated excellent performance for the identification of target analytes in food products. The prohibition effect of pesticides on AChE activity, the designed method is competent to detect pesticides organophosphate with a low detection limit[49]. However, in near future, the scope and applicability of the current electrochemical pest detection sensor are restricted due to gene mutation in pesticide growth, which obstructs the selectivity and specificity of the sensor. Also, false positive and deviated results are shown because of unacceptable adsorption on the molecularly imprinted surface, often guide to neither selective binding states nor specific[50].

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