REVIEW

Naked eye sensors for on-site pesticide detection: a review

Khushbu Gumber*

Chandigarh University, Gharuan, Mohali, Punjab, India

Abstract

Contamination by pesticides is known to be one of the major issues that are enormously degrading the quality of food and fodder crops together with increased agricultural, environmental and aquatic pollution. Many analytical and laboratory methods are available for detection of these pesticides in products in order to maintain food security but these methods are not readily accessible to most people including farmers for on-site and on-field detection in the crops. The development of more convenient, fast, and cost-effective methods that can be easily accessed by laymen based on simple paper strips or mobile analyzers etc. are need of the time. This review includes a brief discussion about novel devices which have been introduced in the field for pesticide detection *viz.* easy to use colorimetric and non-colorimetric detection methods based on various electrochemical and optical sensing strategies. These techniques exhibited promising results in field of on-site pesticide detection owing to their easy production, high sensitivity and readily accessible results obtained with these portable devices. This review further describes emerging prospects, deficits and challenges associated with the application of the aforementioned sensing devices.

Keywords: colorimetric, detection, electrochemical, fluorometric, on-site, pesticide, portable, residues

Introduction

The use of pesticides has increased dramatically in the last few decades and has become a common practice in order to avert the spread of endemic plant diseases and to improve productivity required to meet global food needs (Popp *et al.* 2013). However, controversies associated with the contamination of various biotic and abiotic components due to pesticide abuse has become a matter of great concern. Pesticide residues at trace levels lead to major food poisoning and has severe negative effects on the ecosystem, posing a great threat to mankind (Liu *et al.* 2016). The major impact of these contaminants is visible in our water resources leading to undesirable effects on human health and wildlife (Naushad *et al.* 2019; Wabaidur *et al.* 2020; Hara and Singh 2021). For appropriate management, many government policies have already been introduced for regulating maximum residue levels in all foods and agricultural commodities that may help in the judicious

use of pesticides and their minimum leaching into the environment. But to improve the existing monitoring techniques for pesticide detection, new technologies are always in demand (Kim *et al.* 2018).

Traditional techniques utilized for pesticide residue analysis involve various analytical methods such as high performance liquid and gas chromatography, mass and surface enhanced Raman spectrometry or enzyme-linked immune-sorbent assays etc. (Al-Shaalan *et al.* 2019; AlFaris *et al.* 2020a). These methods involve potent trace analysis with outstanding sensitivity and great reproducibility along with good sample separation methods, but they require expensive, large, and time-consuming instruments along with educated and trained personnel for the necessary operations (Tripathy *et al.* 2016; AlFaris *et al.* 2020b).

Presently there is a need to focus on alternative approaches for carrying out on-site pesticide detection

in a quick, subtle, selective, precise and user-friendly manner (Chu *et al.* 2020). It necessitates the development of handy techniques that facilitate simple and easy sample preparation with small samples. Moreover, such devices should be easy to transport and provide complete quantitative and qualitative data analysis based on reactions specific to the pesticides as well as selective signals with long-term stability and high reliability (Umapathi *et al.* 2021). Developing such devices would greatly benefit agriculture management if they would be accessible to the average farmer. This review focuses on recent developments in the area of high-impact pesticide sensors with simple portable strategies that can provide complete coverage of pesticide detection. Along with emerging trends, this review includes a brief discussion on deficits and challenges of the techniques, future prospects to improve the opportunities of commercialization and point-of care detection methodologies.

Different on-site detection strategies

Real-time on-site detection methods provide simple, swift, and low-cost methodologies that are easily carried out by unskilled personnel. The methods involve the use of portable strips, nanoparticles or devices that can show visual, amperometric or potentiometric signals involving simple and handy devices. Figure 1 represents various techniques with their response behavior discussed in this review for on-site pesticide detection.

Most of these methods are based on devices with integrated enzymes, antibodies, cells or DNA as biosensors. In bio-sensors, the properties of pesticides act as inhibitors that destroy the activity of the selected enzyme or other bio-sensing materials such as acetyl choline esterase (AChE), butyrl choline esterase (BChE), phosphatase, ascorbate oxidase etc., which arebeing utilized. In other cases, the biosensor may act as a substrate that plays a significant role in various reactions with the pesticides leading to an induction of signals in the form of visual, amperometric or potentiometric responses. The mechanism involving the interaction of AChE/BChE with the pesticides is shown below in Figure 2.

Various naked eye pesticide detection techniques corresponding to different pesticides are tabulated below in Table 1 followed by their complete description in the given sections.

Paper-based colorimetric detection

Paper and screening card based analytical techniques have been given extensive consideration for detection of pesticides owing to their simplicity, disposability, portability and economic cost. Colorimetric sensing technology further adds to real time analysis with easily observable chemical reaction specific results. These cards help in analyzing color changes which occur due to enzyme inhibition or augmentation of chromogenic reagents present on the membrane surface corresponding to their fast evaporation. Also, the inherent hydrophilic nature and porous surface of the paper further adds to the production of sensors with properties that assist the fluid flow by capillary action without any other application technique.

The enzymes involved in most of these paper-based strategies are acetyl-cholinesterase (AChE) or butyryl-
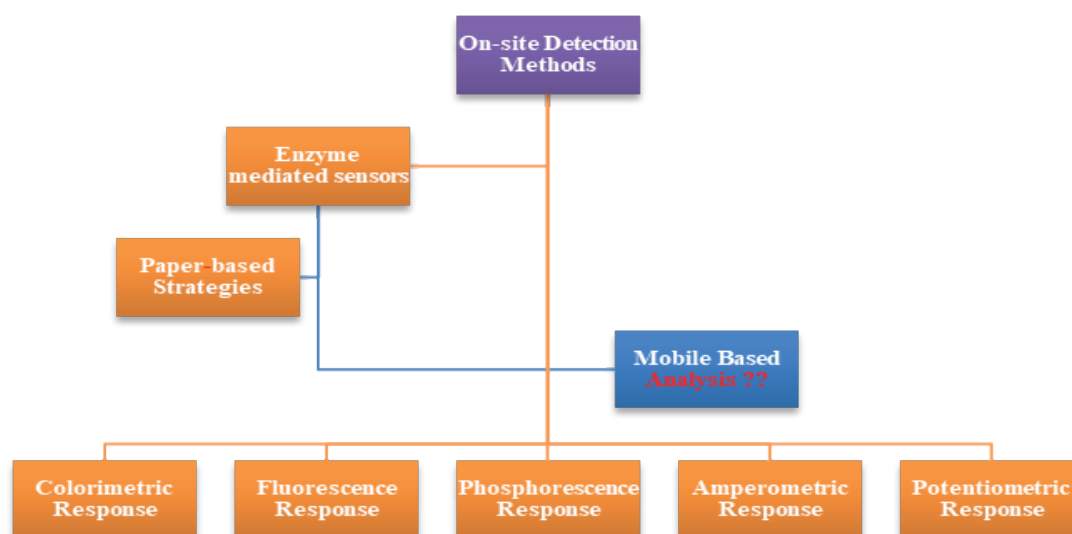

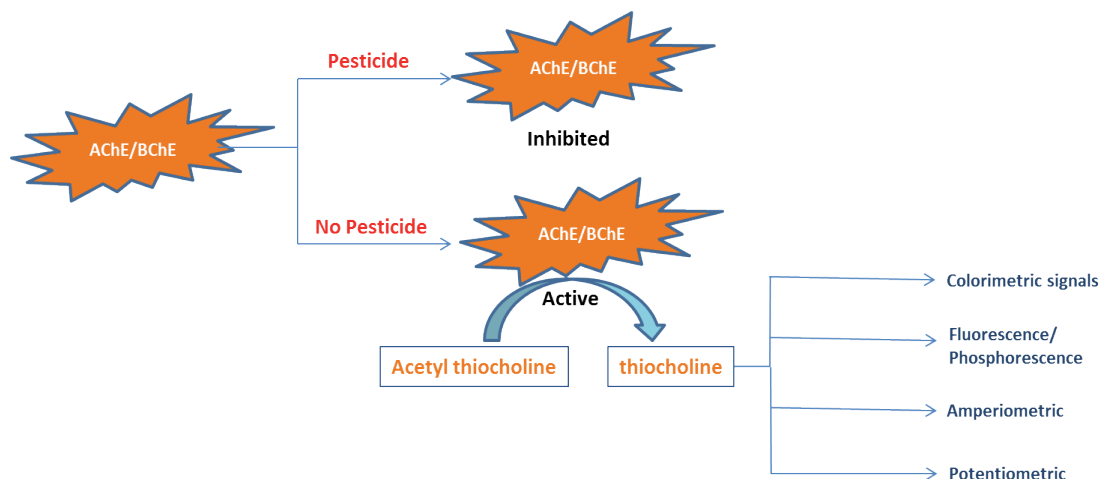**Fig. 1.** Different on-site detection techniques

Fig. 2. Mechanism of interaction of acetyl choline esterase (AChE)/butyrl choline esterase (BChE) with the pesticides

Table 1. Different pesticide detection methods

Detection method	Important components	Pesticides detected	References
Paper-based colorimetric detection	AchE inhibition	omethoate (LOD: 1 mg · ml^{-1})	Guo *et al.* (2013)
	AChE and indoxyl acetate interactions	chlorpyrifos (LOD: 8.6 µg · ml^{-1})	Wu *et al.* (2017b); Kim *et al.* (2018)
	AchE inhibition	phoxim, acephate, malathion, omethoate, carbofuran and aldicarb (LOD: 0.04–0.1 mg · ml^{-1})	Sun *et al.* (2017)
	AChE and 5,5'-dithiobis(2-nitrobenzoic) acid (DTNB) interaction on chitosan gel immobilized over a paper strip with cross-linked glutaraldehyde	malathion, methomyl and profenofos (6.16 × 10^{-4} – 0.27 mM)	Kavruk *et al.* (2013); Badawy and El-Aswad (2014)
	nanoceria; choline oxidase (ChOX) and AChE interaction	methyl paraoxon and chlorpyrifos-oxon (LOD: 18 and 5.3 ng · ml^{-1})	Nouanthavong *et al.* (2016)
	AuNPs-coated cellulose paper for AChE inhibition	organophosphates (LOD: 35 ppb)	Wu *et al.* (2017a)
	AChE and indoxyl acetate interactions	carbamate, organochlorine, organophosphate, fungicide and herbicide (LOD: 1–10, 1–50, 250–500, 1–50 and 1 ppb, respectively)	Dasriya *et al.* (2021)
	γ-MnOOH nanowires producing Mn^{2+} by thiocholine produced by AChE interaction with acetylthiocholine iodide	organophosphorus (LOD: 0.007 mU · ml^{-1})	Huang *et al.* (2019)
	Meisenheimer complex	dicloran, methyl parathion, pendimethalin, PCNB and trifluralin (LOD: 0.67–10 µM)	Kovida *et al.* (2020)
	smartphone detection by copper ions decorated NaYF$_4$:Yb/Tm paper strips	thiram (LOD: 0.1 µM)	Mei *et al.* (2016)
Paper-based fluorescence detection	AChE inhibition with fluorescent tetraphenylethylene (TPE)	organophosphates (LOD: 0.5 ng · ml^{-1}).	Chang *et al.* (2016)
	scopoletin (SC) and amplex red (AR) fluorescent indicators over MnO$_2$ nanosheets	organophosphates	Yao *et al.* (2019)
Enzyme mediated electrochemical detection (potentiometric)	carbon nanotube – polyvinylchloride composite for the determination of butyrylcholine (BCh)	ethion and its bi-products (LOD: 0 to 330 ng · ml^{-1})	Khaled *et al.* (2014)
	carbon nanotube – polyvinylchloride composite for determining AChE inhibition	methomyl, chlorpyrifos and prothiofos (LOD: 0.25 ng · ml^{-1} – 37.5 µg · ml^{-1})	Khaled *et al.* (2015)

Table 1. Different pesticide detection methods – *continuation*

Detection method	Important components	Pesticides detected	References
Enzyme mediated electrochemical detection (amperometric)	tin oxide nanoparticles with chitosan, and multi-walled carbon nanotubes AChE	chlorpyrifos (LOD: 100 ng · l^{-1})	Guo *et al.* (2015)
	body fluid and microcontroller sensors based on AChE inhibition		Jain *et al.* (2019)
Enzyme mediated nanoparticle based technique	Cu (I)-catalyzed AChE–ATCh with terminal azide and alkyne-functionalized AuNPs	paraoxon (LOD: 106–104 g · l^{-1})	Fu *et al.* (2013)
	citrate-coated AuNPs	methamidophos (LOD: 0.02–1.42 μg · ml^{-1})	Li *et al.* (2011)
Metal nanoparticles based assay strategies	gold nanoparticles-silk fibroin	chlorpyrifos (LOD: 10 ppb)	Mane *et al.* (2020)
	silver (Ag), gold (Au) and bimetallic silver-gold (Ag-Au)	ethion, parathion, malathion, and fenthion (LOD: 9, 11, 18, and 44 ppm, respectively)	Dissanayake *et al.* (2019)
	glutathione-capped gold nanoclusters	thiram (LOD: 0.05 μg · mL^{-1})	Zhao *et al.* (2019)
	adenosine triphosphate (ATP) and Rhodamine B-modified gold nanoparticles (RB-AuNPs)	ethoprophos (LOD: 37.0 nM)	Li *et al.* (2018)
	Rhodamine B-Ag@Au nanoprobes	organophosphates (LOD: 16.3 nM)	Lin *et al.* (2021)
Quantum dots mediated assay strategies	CdTe quantum dots with silica nanoparticles	thiram (LOD: 59 nM)	Chu *et al.* (2020)
	Mn-doped ZnS quantum dots	thiram (LOD: 25 nM)	Zhang *et al.* (2017)
	L-tyrosine methyl ester functionalized carbon dots	methyl parathion (LOD: 4.8 × 10^{-11} M)	Hou *et al.* (2015)
	gold nanoparticles on ratiometric fluorescent quantum dots	acetamiprid (LOD: 16.8 mg · l^{-1})	Yan *et al.* (2014)
Other novel developments	"lab-on-a-glove" device with carboxy methyl cellulose aerogel with fluorescent Eu-metal organic frameworks	organophosphates (LOD: 50 nM)	Xu *et al.* (2018)
	optical fiber sensor	methyl parathion (LOD: 0.24 nM)	Arjmand *et al.* (2017)
	SERS substrate cellulose p-toluene sulfonates	thiram (LOD: 50 ng · g^{-1})	Chen *et al.* (2018)
	aptamers	organophosphates (LOD: 0.01 nM)	Bala *et al.* (2016)
	DNA aptamer	tebuconazole (LOD: 10 nM)	Truong *et al.* (2021)
	palladium-gold nanorods	malathion (LOD: 60 ng · ml^{-1})	Singh *et al.* (2017)

cholinesterase (BChE). These enzymes prevent the catalysis of its substrates *viz.* acetylthiocholine, butyrylthiocholine, or prevent the conversion of ACh into choline, thiocholine and acetic acid. It therefore terminates the signaling and neuronal transmission across the synapses leading to deactivation of ACh and its spreading through the receptors. This method is more pronounced for organophosphates that act as an inhibitor of AChE enzyme making this an excellent indicator of the contamination of the class of pesticide (Guo *et al.* 2013; Kaur *et al.* 2020).

The first reported method in the field included a new, innovative, swift, and subtle paper-based card that showed changes in color intensities corresponding to the inhibition of AChE by pesticides. The designed strips were utilized for real-time pesticide residue analysis in the juice of grapes, oranges, and apples. The

results indicated that 1 mg · ml^{-1} of omethoate produced a visible change in comparison to the negative control that contained no omethoate. Also, in orange and apple juices, 1 mg · ml^{-1} of omethoate resulted in only a slight color difference, indicating that the color of the orange and apple juices had a negligible influence on the color development results. The limit of detection (LOD) value, i.e., the minimum pesticide concentration that can be easily distinguished from the control sample in a test device, for omethoate pesticides in the presented method appeared to be 1 mg · ml^{-1} which is significantly lower than the standard limit of detection. Therefore, the described method can be considered to be a strong contestant for quick, on-site, and group-specific screening of carbamate and organophosphate pesticide residues in food. The only drawback of the method is that it cannot be used for the analysis of

colored test materials since the color sometimes affects and alters the actual results (Guo *et al.* 2013).

Kim *et al.* (2018) employed this strategy by layering plates that produce colorimetric quantification due to interaction between acetyl cholinesterase (AChE) and indoxyl acetate (a chromogenic agent). The results were based on the fact that the color of the chromogenic agent was inhibited by the test pesticide chlorpyrifos present in the test solution (Wu *et al.* 2017b). The method can sensitively detect the pesticide to the limit of 8.60 ppm within 5 min. Trehalose was used as a stabilizing agent for improving the shelf life of the test kit.

In another study, a double-film screening card with the same enzyme produced a blue-green compound that showed proportional reduction in color intensity to the amount of pesticide in its test window within 15 min. Polyester and glass fiber were used as optimum materials for holding the enzyme and chromogenic agent, respectively. Overall the card displayed acceptable reproducibility and great sensitivity with a limit of detection between 0.04 and 0.1 mg $\cdot$ ml^{-1} for various test pesticides *viz.* phoxim, acephate, malathion, omethoate, carbofuran and aldicarb in real food samples (Sun *et al.* 2017).

Badawy and El-Aswad (2014) analyzed a set of organophosphates and carbamates with a range of detection between 6.16×10^{-4} and 0.27 mM. Chitosan gel immobilized over a paper strip with cross-linked glutaraldehyde, AChE and 5,5'-dithiobis(2-nitrobenzoic) acid (DTNB) was utilized for the assay. Acetylthiocholine iodide acted as an external reagent. The test pesticide, introduced in a sensing zone by dipping in the solution, was incubated to initiate hydrolysis of the test material, producing a yellow color change. The reduction in the intensity of yellow colorrelates to the levels of the inhibitors (methomyl and profenofos). Sugar and protein stabilizer were utilized to improve the shelf life of a biosensor for detection of malathion (2.5 ppm) (Kavruk *et al.* 2013).

A nanoceria coated paper device was used as a colorimetric detection platform with choline oxidase (ChOX) and AChE that catalyzes the formation of H_2O_2. Incubation with pesticides leads to inhibition of AChE activity with less H_2O_2 that decreases the intensity of yellow coloration. The limit of detection for methyl paraoxon and chlorpyrifos-oxon appeared to be 18 and 5.3 ng $\cdot$ ml^{-1}, respectively. The results were confirmed with LC-MS/MS (Nouanthavong *et al.* 2016).

Highly sensitive AuNPs-coated cellulose paper-based dipsticks were prepared for analysis of organophosphorus (OPs) compounds in an observable range of 35 ppb. The AuNPs in the form of Au^{3+}-cetyltrimethyl ammonium bromide (Au^{3+}-CTAB) undergoes dissolution with enzymatic hydrolysis of AChE for colorimetric detection of organophosphorus pesticides. In the absence of OPs, thiocholine reduces the Au^{3+} and

guards the nanoparticles from dissolution by the Au^{3+}-CTAB interactions. On the other hand, the activity of AChE is inhibited in the presence of OPs leading to a very small amount or no thiocholine to consume the Au^{3+} that solubilizes the AuNPs and reduces both the size and concentration of the AuNPs, thus leading to an evident color change from red-to-light pink or colorless (Wu *et al.* 2017a).

Dasriya *et al.* (2021) reported another paper strip-based sensor that worked on the phenomenon of AChE inhibition for on-field pesticide residue analysis in milk, cereal-based food, and fruit juices. The method was validated with GC-MS/MS for detection of different pesticides *viz.* carbamate, organochlorine, organophosphate, fungicide and herbicide with detection limits of 1–10, 1–50, 250–500, 1–50, and 1 ppb, respectively. Among 125 milk samples on the market, 33 samples were found to be positive by this paper strip sensor. Also, six cereal flour and four juice samples were found to show observable positive results. The results were further validated on the basis of GC-MS/MS that confirmed the presence of different pesticides at trace and above MRL levels.

γ-MnOOH nanowires (NWs) act as another novel base material for a facile colorimetric paper sensor with 3,3',5,5'-tetramethylbenzidine (TMB) for quick and subtle screening of different organophosphorus molecules. The mechanism of action is based on the simple breakdown of the oxidase-like γ-MnOOH NWs into invalid Mn^{2+} ions by selective reaction of thiocholine (TCh) produced by AChE and acetylthiocholine iodide (ATCh), activating a remarkable loss of activity of MnOOH nanozymes towards TMB oxidation. The system has low limits of detection (LODs) for AChE activity (0.007 mU $\cdot$ ml^{-1}). The portable system of AChE-nanozyme sensing system exhibited a pronounced selectivity and anti-interfering tendency that produces noteworthy and sustainable results in real-time analysis of serum and vegetable samples (Huang *et al.* 2019).

Another fast and expedient method for on-site identification of dangerous nitro-containing poly-aromatic molecules using paper-based sensors was proposed by Kovida *et al.* (2020). The novel sensing approach was employed for real-time study of five extensively used pesticides (dicloran, methyl parathion, pendimethalin, PCNB and trifluralin) by intensely colored Meisenheimer complex formation among polynitro aromatic compounds (pesticides) and tetrabutylammonium hydroxide (TBAOH) in the presence of different ionic liquids. The detection limit of the reported method was found to be in the range of 0.67–10 μM.

Mei *et al.* (2016) reported an integration of smartphone and paper-based sensors for quantitative and rapid analysis of thiram fungicide. It involves the utilization of 3D printingcomprised of an auxiliary reusable

device that helps in digitally imaging the luminescence variations on test paper by a smartphone. The copper ions decorated $NaYF_4$:Yb/Tm upconversion nanoparticles were fixed onto filter paper to form test paper, and the blue luminescence on it would be quenched after additions of thiram by luminescence resonance energy transfer mechanism. These variations were monitored by the camera of a smartphone and the blue channel intensities of obtained colored images were calculated to quantify the amount of thiram through a self-written Android program installed on the smartphone, offering a reliable and accurate detection to the limit of 0.1 μM.

Paper-based fluorescence detection

Fluorescence is one of the most widely used methodologies for the detection of pesticides. It involves the use of various fluorescence based sensors including enzymes, metal nanoparticles, dyes, semiconducting materials, etc., that show visible changes in interactions with pesticides and thus, it is well utilized for pesticide residue analysis on-field (Fauzi *et al.* 2021). Different techniques are reported in this section.

Chang *et al.* (2016) reported a paper strip-based fluorescence detection technique that utilized similar enzyme activity, emission induced by aggregation of the fluorescent molecule tetraphenylethylene (TPE) followed by an addition reaction with maleimide, for on-site naked-eye detection of organophosphorus molecules to the detection limit of 0.5 ng · ml⁻¹. The activity involved ATCh hydrolysis with AChE that further prompted maleimide ring destruction and activation of the fluorescence performance of TPE. The validation of the method was further made on diluted human serum samples.

Another ratiometric fluorescence biosensor is composed of scopoletin (SC) and amplex red (AR) where both of them showed contrasting reactions to MnO_2 nanosheets (NS) having peroxidase-like activity. They involved reduction in the fluorescence of SC and augmentation of the fluorescence of AR. In the absence of the test pesticide, acetylcholinesterase hydrolyzed acetylcholine chloride into choline and acetate. Choline led the decomposition of MnO_2 NS to manganese ions (Mn^{2+}), increasing signal of SC and decreasing signal of AR whereas, the presence of OPs, inhibited the activity of AChE and hindered the decomposition of MnO_2 NS leading to the opposite fluorescence activity for both SC and AR (Yao *et al.* 2019).

Enzyme mediated electrochemical detection

Electrochemical bio-sensing involves numerous advantages of electro-active materials *viz.* easy production, low cost, high sensitivity, portability, low power

requirements, and suitability for *in situ* analysis of the samples. This method in the field of pesticide detection mainly involves the production of electro-active species that on interaction with a target analyte produces visible results. Further, based on the general electrochemical phenomenon, it is divided into two main categories *viz.* potentiometric and amperometric detection.

Enzyme mediated potentiometric detection

One time use of potentiometric sensors was first reported with an aim of sensitive detection of ethion and its bi-products in a range of 0 to 330 ng · ml⁻¹. A multi-walled carbon nanotube – polyvinylchloride composite with ionophore α-cyclodextrin was utilized for the determination of butyrylcholine (BCh). A linear change in electrode potential was observed corresponding to the concentration of BChE in a range of 0.04 to 0.4 U. It was observed that with inhibition by dioxon and monooxon, the degradation products of ethion were more than the parent pesticide and the system emerged as being auspicious for determination of various environmental pollutants in a natural environment (Khaled *et al.* 2014).

Another portable potentiometric biosensor was investigated for carbamate and OPs *viz.* methomyl, chlorpyrifos and prothiofos. This method involves the relative inhibition activity of pesticide against AChE in a range of 0.25 ng · ml⁻¹ to 37.5 μg · ml⁻¹. The method was validated with average recoveries in a range of 96.22 to106.02% and its applicability was verified by estimating the pesticide components in commercial formulations and agriculture waste water samples without pre-treatment. The portable sensors are considered to be promising, simple screening devices for monitoring in the field by unskilled users (Khaled *et al.* 2015).

Enzyme mediated amperometric detection

Another cheap, and flexible method having a wide scope of use is an enzyme-based microcontroller portable electronic detection circuit for bio-monitoring of pesticides in the field. It includes Tin oxide nanoparticles with chitosan, and a multi-walled carbon nanotube based acetylcholinesterase (AChE) sensor that involves the enzyme mediated amperometric detection system for rapid on-site detection of pesticides (chlorpyrifos) in real time fruits and vegetable samples. The system consists of an automatic data processing system with display and data storage options. It is considered to be a good option for pesticide residue detection to the limit of 100 ng · l⁻¹ (Guo *et al.* 2015).

In another study, a test strip with a body fluid is implanted in a detection circuit and a microcontroller senses the presence of a pesticide, and the AChE value is displayed on a LCD screen (Jain *et al.* 2019).

Enzyme mediated nanoparticle based technique

A Cu (I)-catalyzed click chemistry-based reaction is an extremely subtle colorimetric detection method for organophosphate pesticides (OPs). The method involved the amplification of signals by utilizing the AChE–ATCh along with terminal azide and alkyne-functionalized AuNPs as colorimetric probes. The indirect modulation of click chemistry-induced AuNPs aggregation by the AChE–ATCh system was demonstrated with Paraoxon as the test moiety in the concentration range from 106 to 104 g · l^{-1} (Fu *et al.* 2013). Citrate-coated AuNPs as a colorimetric probe, based on the same principle, showing a color change from claret-red to purple or even gray due to decreased plasmon absorption is another reported method in the field. Methamidophos in the range of 0.02–1.42 μg · ml^{-1} was utilized as a test analyte with a detection limit of 1.40 ng · ml^{-1}. The proposed assay method exhibited good reproducibility and precision, providing a rapid and simple process for the analysis of various organophosphorus pesticides (Li *et al.* 2011).

Other metal nanoparticle based assay strategies

Gold nanoparticle-silk fibroin dispersion was utilized for label-free colorimetric detection of chlorpyrifos. The silk fibroin solution was extracted from *Bombyx mori* silk by a three-step process *viz.* degumming, dissolving and dialysis. The AuNPs were prepared *in situ* using fibroin solution as a reducing as well as a capping agent. The resultant SF-AuNPs dispersion exhibited rapid and excellent colorimetric pesticide sensing responses even at 10 ppb concentration with positive results under additional parameters *viz.* pH, ionic concentration and interference from other pesticide samples. The method was validated with different real-time analysis of tap water, soil and agricultural products. The proposed system is a simple and effective method that can also be employed by an untrained rural population (Mane *et al.* 2020).

Plasmonic nanoparticles *viz.* silver (Ag), gold (Au) and bimetallic silver-gold (Ag-Au) were utilized to detect and differentiate between four thion based OPs (ethion, parathion, malathion, and fenthion) with the naked eye in real time samples. The interaction of the pesticides with the plasmonic NPs leads to wavelength shifts of the localized surface plasmon resonance (LSPR) accompanied by color change. The wavelength shifts were specific to the structure of a pesticide and its concentration whereas no such interactions were observed for oxon pesticides. The limits of detection (LOD) of AgNPs w.r.t. ethion, fenthion, malathion, and parathion were found to be 9, 11, 18, and 44 ppm,

respectively. The LODs of AuNPs with ethion, fenthion, malathion, parathion were 58, 53, 139, and 3203 ppm, respectively. Ag-Au NPs showed values of 228, 231, 1189, and 1835 ppm for ethion, fenthion, malathion, and parathion, respectively (Dissanayake *et al.* 2019).

Zhao *et al.* (2019) reported a fluorometric method for on-site detection of thiram via the aggregation-induced emission enhancement (AIEE) of glutathione-capped gold nanoclusters (GSH-AuNCs). Dissociated Ag$^+$ ions can effectively enhance the fluorescent emission intensity of GSH-AuNCs at 570 nm owing to the AIEE phenomenon. The presence of thiram leads to a weak fluorescence signal due to the strong coordinative interaction between Ag$^+$ and thiram. By monitoring the signal change, the thiram residues were quantitatively analyzed with the detection limit of 0.05 μg · ml^{-1}. A home-made electronic-eye (E-eye) system, includinga test-strip and a smartphone, act as a portable platform to recognize and quantitatively analyze thiram in 10 min on the basis of captured fluorescence signals from a test strip with an immobilized probe by direct photographing.

Another simple and dual modal (colorimetric and fluorescent) sensor for organophosphates with high sensitivity and selectivity using adenosine triphosphate (ATP) and rhodamine B-modified gold nanoparticles (RB-AuNPs) was developed. The method was utilized for ethoprophos with quantitative determination in the range of 4.0–15.0 μM. The limit of detection for ethoprophos was as low as 7.0 nM (Li *et al.* 2018).

In another study, Lin *et al.* (2021) reported the fluorescent composite Rhodamine B-Ag@Au nanoprobe for the visual and semi-quantitative assay of organophosphorus pesticide (OP) residues via a "light up" sensing phenomenon for the detection of organophosphate residues. The fluorescent nanoprobes show a sensitive response to the pesticide residues in the range of 0.001–0.4 μM with a limit of detection of 7.89 nM. Moreover, combined with the smartphone color recognizer application (APP), the ratio of fluorescence intensity response is recorded on the green channel (G)/red channel (R), which isemployed for visual quantitative determination of OPs with an LOD of 16.3 nM. This proposed light up fluorescent sensor is also applied to OP residue identification in real water and agricultural samples with highly promising performance. The method reported here provides a convenient pathway for rapid and visual detection of pesticide residues utilizing organic composite nanomaterials (Lin *et al.* 2021).

Quantum dots mediated assay strategies

Quantum dots are another evolving lead that have a significant role in field sensing due to their exclusive electronic properties. A portable, easy to use mini-

device was engineered by integrating a paper strip and a smartphone sensing platform that involves a UV lamp and dark cavity with 3D-printing technology. The visual quantitative detection of pesticide was made with fluorescence on-off-on responses with a single dual emissive ratiometric paper strip. The paper strip was comprised of red-emitting CdTe quantum dots (rQDs) entrenched into the silica nanoparticles (SiO_2 NPs) as an internal reference, while blue-emitting carbon dots (bCDs) as a signal indicator that is covalently bonded to the outer surface of SiO_2 NPs. The results are based on the fact that the blue fluorescence is quenched by gold nanoparticles (AuNPs) whereas this signal is recovered in the presence of pesticide. The color channel values of the generated images were determined by a color recognizer application installed in the smartphone, with a sensitive detection limit (LOD) of 59 nM. The method was validated on the basis of dithiocarbamate fungicide, thiram that shows strong affinity for the surface of metal due to sulfur-gold interaction (Chu *et al.* 2020).

Another selective and on-site detection method involved the utilization of phosphorescent Mn-doped ZnS quantum dots ($ZnS : Mn^{2+}$ QDs). The system involved the strong interaction between thiram and Ag^+ ions that leads to the inhibition ofphosphorescence signals due to theformation of an Ag-thiram complex. The phosphorescence of as-prepared $ZnS : Mn^{2+}$ QDs appeared at 590 nm. The method provides instant and visual detection to the limit of 25 nM with doped QDs (Zhang *et al.* 2017).

L-tyrosine methyl ester functionalized carbon dots (Tyr-CDs) prepared by simple hydrothermal reaction using citric acid as a carbon resource and L-tyrosine methyl ester as a modification reagent was used as another fluorescent sensor for methyl parathion. The carbon dots showed strong photoluminescence with a quantum yield of 3.8%. Tyrosinase can catalyze the oxidation of tyrosine methyl ester on the surface of carbon dots to corresponding quinone products, which can quench the fluorescence of carbon dots. In the presence of organophosphorus pesticides there is decreased enzyme activity leading to a decrease in the fluorescence quenching rate. Experimental results showed that the enzyme inhibition rate is proportional to the logarithm of the methyl parathion concentration in the range 1.0×10^{-10} to 1.0×10^{-4} M with a detection limit of 4.8×10^{-11} M. The method was validated by analyzingreal samples of cabbage, milk and fruit juice, etc. (Hou *et al.* 2015).

In another study, visual detection of acetamiprid based on the inner-filter effect (IFE) of gold nanoparticles (AuNPs) on ratiometric fluorescent quantum dots (RFQDs) was reported. The RFQDs based dual-emission nanosensor was produced by assembling green emissive QDs on the surface of red emissive QDs-doped silica microspheres. The photoluminescence (PL) intensity of RFQDs could be quenched by AuNPs based on IFE. Acetamiprid can adsorb on the surface of AuNPs due to its cyano group that has good affinity with gold. This leads to an aggregation of AuNPs accompanied by color change from red to blue. Under optimized conditions, the PL intensity of the RFQDs/AuNPs system was proportional to the concentration of AC in the range of 0.025–5.0 mg $\cdot$ ml^{-1}, with a detection limit of 16.8 mg $\cdot$ l^{-1} (Yan *et al.* 2014).

Other new developments

A convenient and reliable fluorescence based wearable glove sensor was reported for non-invasive monitoring of OP molecules as a significant development. This novel "lab-on-a-glove" based device involves a flexible carboxy methyl cellulose (CMC) aerogel as a good host material and fluorescent centers *viz.* Eu-metal organic frameworks (MOFs) as a working center for fluorescence and nanosized carbon dots as a reference fluorescence center. This real-time detecting system showed a rapid response (30 s) owing to the porosity of the CMC aerogel and MOFs structure with naked-eye results (red to blue transition) that increases with an increasing concentration of OPs. The system was found to be highly sensitive with LOD = 50 nM (Xu *et al.* 2018).

Another portable, sensitive, simple optical fiber sensor based on modal interference was developed for label free determination of OPs pesticides by Arjmand *et al.* (2017). They established a sensor displaying excellent sensitivity higher than 2100 RIU^{-1} to bulk refractive index. The method is based on the same reaction between enzyme acetyl cholinesterase and methyl parathion. The LOD for methyl parathion was found to be 0.24 nM. The sensor showed a broad range, quick response and adequate reproducibility (Arjmand *et al.* 2017).

A novel in-situ extraction and fabrication of SERS substrate to perform selective and reliable on-site determination of thiram residue in soil, fruits and vegetables was reported by Chen and coworkers. The thiram residue on complex surfaces facilely diffuse into the solvent and specifically bind to AuNPs, affording the SERS substrate through the embedding of the thiram-trapped AuNPs into the cellulose p-toluene sulfonates (CTSA) film. SERS signals of the specifically prepared CTSA could be used as an internal standard to calibrate the absolute signal of thiram, which can avoid the fluctuation of SERS intensities caused by uneven and irregular morphology of SERS substrate. The recognized method showed strong anti-interference ability along with good linear response from 0.1 to 12 μg $\cdot$ g^{-1} and LOD of 50 ng $\cdot$ g^{-1}, which is quite significantly less than the previously reported techniques. The recovery

of thiram in paddy soils ranges from 91.76 to 112.3 %, indicating that the established IE-SERS method is reliable and applicable for the detection of thiram residue in real soil samples. Furthermore, the measurement of the residual thiram on strawberry and cucumber surfaces also gave reproducible results indicating that the method has great potential for *in situ* ultrasensitive detection of thiram on irregular fruits and vegetables (Chen *et al.* 2018).

An aptamer based highly sensitive and rapid method was employed for the detection of the widely used and exceedingly toxic OP pesticide, phorate. An aptamer acted as the recognition element as well as a stabilizing agent for AuNPs that act as an optical sensor. In the presence of the target pesticide, the aptamer acquires a rigid conformation resulting in the aggregation of the gold nanoparticles. An observable color change from red to blue takes place in the concentration range of 0.01 nM to 1.3 μm with the limit of detection as low as 0.01 nM. The proposed method is highly selective for phorate in the presence of other interfering substances and, thus, can be applied to real samples for rapid and efficient screening (Bala *et al.* 2016).

Truong *et al.* (2021) reported another simple and sensitive method for quick detection of pesticides exploiting a pesticide-specific DNA aptamer as the bioreceptor of an optical biosensor. DNA aptamers were adsorbed on the nanoparticle's surface, to detach it from the nanoparticles when interacting with the pesticide. This leads to pesticide-induced aggregation and a change of the absorption spectrum of metallic nanoparticles upon high-salt concentrations, which can be monitored with an unaided eye or absorbance measurement. Using tebuconazole as a model analyte for detection of pesticide, the designed aptasensor exhibited highly sensitive and selective results with a limit of detection of ~10nM. The recovery range of tebuconazole in spiked rice samples was found to be 89.90–110.86%.

Singh *et al.* (2016) reported another colorimetric assay method involving palladium-gold nanorod as a nanozyme for malathion detection. The peroxidase potential of the nanozyme on colorimetric substrates was investigated and the effect of selected organophosphates on their enzyme mimetic activity was explored. Palladium-gold nanozyme showed excellent peroxidase mimetic activity with o-phenylenediamine in the presence of hydrogen peroxide. The nanozyme activity was found to be quenched with increasing concentrations of malathion. The method has a low limit of detection (60 ng · ml^{-1}) with no cross-reaction with other analogous organophosphates or metal salts. The method was further validated on tap water samples spiked with different concentrations of malathion with recovery between 80–106%.

Challenges and deficits

Pesticide residue in food and fodder crops has emerged as an important environmental issue that is affecting the quality of life. The commonly used method for detection of pesticides involves uin of conventional chromatographic techniques. Although these are well eveloped techniques that can identify even the lowest concentrations their expensive operation by skilled personnel makes them difficult to be utilized at a basic level (Kumar *et al.* 2015; Bala *et al.* 2017). Also, on-site detection and monitoring of environmental components and pollutants are important since sample concentrations vary during the day and with time. Therefore, the time of collection and transportation to the lab leads to huge variations in the actual results. Thus, there is a real need for technology that allows on-site detection of variable environmental samples under different environmental conditions.

Recent developments in different on-site detection methods with various portable devices has made it a bit easier to analyze pesticide residues of different environmental samples in the field. However, these techniques are lagging at many points. Colorimetric analysis has the drawback of involving natural color of the test materials, which leads to poor discriminating colorimetric effects (Guo *et al.* 2013). To overcome this challenge various chemical absorbents such as activated charcoal, sodium sulphate or primary secondary amines, are already in use. They help to remove interfering pigments and soluble solids, which eventually helps to improve the selectivity and sensitivity of these assays. However, the discussed methods are not frequently used for on-site detection and more importantly they are only utilized in lab based sophisticated studies since these steps complicate simple on-site detection by the layman (Purushottam *et al.* 2014). Fluorescence analysis requires specific probes and the technique is not conducive for all the molecules.

It was observed that most of the on-site detection techniques are simple and involve portable devices designed specifically for biosensing technology based on the inhibition of AChE that primiarily deals with the detection of organophosphate and carbamate pesticides (Hossain *et al.* 2009; Oujji *et al.* 2012; Kavruk *et al.* 2013). As a result, more strategies for sensing of new molecules of different categories that are more widely used for crop protection must be given consideration. Also, the colorimetric techniques based on the aggregation of nanoparticles offers a tactical and an efficient means to carry out point-of-care observation of pesticide residues in agriculture and food products. However, these methods of on-site analysis are not very efficient and they do not provide

good quantitative results. Also, these strategies are both temperature and pH-dependent. The poor sensitivity and reproducibility of these on-site test methods are also the main reasons that these methods are less functional on a larger scale. To overcome these issues, several techniques integrating the surface-modified and surface functionalized NPs are now being utilized. Modification of these NPs with different ligands also augments the optical properties, binding interactions, and surface plasmon resonance behavior of these on-site detection methods (Singh *et al.* 2020). Efforts in the field are still required to develop the methods for more widely used pesticides on a larger scale.

Future prospects and conclusions

In this literature survey, various methods of on-site pesticide residue detection in different food, agriculture and environmental samples are discussed. Pesticides are commonly being utilized for improved agriculture production in both developed and developing countries. However, the detrimental effects of pesticide residues on human health and the environment need significantly improved monitoring techniques for stringent action to remove the high levels of pesticides in food products. Similarly, good agricultural practices must be increased and farmers must be motivated to follow them in order to minimize the use of chemical pesticides. To further check the level of pesticide residues in samples, the techniques for on-site pesticide detection must be increased and brought to the field at a faster pace.

Nanotechnology is dominating every aspect of modern science. Nano sensors are emerging as significant detection systems for huge numbers of adulterants and contaminants in various food systems. More research is needed that focuses focused on developing sensitive nanosensors for detecting pesticides at ground level, so that the use of sophisticated instruments can be omitted. Nanoparticles for pesticide residue detection provide highly promising and cost-effective on-site detection methods but these reported methods are facingchallenges associated with selectivity, sensitivity, and reproducibility. Also, the applicability of these methods is not widespread and they do not cover a wide range of pesticides, especially new molecules that are commonly being used for crop protection. So, there is a need to increase the scope of the novel methods for more widely used newer ranges of pesticides. More attention must be given to the nanoparticle-based colorimetric probes due to their good stability and extraordinary capability. These probes can be integrated with smartphone based portable devices in order to obtain a measurable digital signal. Zhang *et al.* (2022) reported that enzyme-free and rapid visual quantitative detection for pesticide residues with portable smartphones were utilized for the analysis of glyphosate in real samples for on-site visual detection. These kinds of strategies can be further improvised to produce novel techniques in the field. The other emerging technology in the field for sensitive and promising on-site pesticide detection is integration of nanoparticles into small nano-based chips that leads to a novel concept of "labonchip". These techniques provide a new generation of portable analytical devices for real-time on-site detection.

Future work must focus on the development of on-field methods of pesticide residue removal after the analysis of pesticide residues with these developing sensors from various food and fodder crops. Here also nanotechnology could possibly help to eliminate pesticides fromvarious food matrices. However, inadequate information is available in the field and thus more scientific work is required. More efforts should be made to develop different nano-based techniques for the removal of pesticides from both liquid and solid food matrices at ground level before bringing them to market for sale and consumption. These techniques must be able to precisely target and remove the residues of pesticides from food matrices without harming its natural properties and nutritional value.

References

AlFaris N.A., ALTamimi J.Z., ALOthman Z.A., Al Qahtani S.F., Wabaidur S.M., Ghfar A.A., Aldayel T.S. 2020a. Analysis of aflatoxins in foods retailed in Saudi Arabia using immunoaffinity column cleanup and high-performance liquid chromatography-fluorescence detection. Journal of King Saud University - Science 32 (2): 1437–1443. DOI: https://doi.org/10.1016/j.jksus.2019.11.039

AlFaris N.A., ALTamimi J.Z., ALOthman Z.A., Wabaidur S.M., Ghafar A.A., Aldayel T.S. 2020b. Development of a sensitive liquid-liquid extraction and ultra-performance liquid chromatography-tandem mass spectrometry method for the analysis of carbaryl residues in fresh vegetables sold in Riyadh. Journal of King Saud University – Science 32 (4): 2414–2418. DOI: https://doi.org/10.1016/j.jksus.2020.03.030

Al-Shaalan N.H., Al-Othman Z.A., Al-Wahaibi L.H., Alabdulmonem H. 2019. High performance removal and simulation studies of diuron pesticide in water on MWCNTs. Journal of Molecular Liquids 289: 111039. DOI: https://doi.org/10.1016/j.molliq.2019.111039

Arjmand M., Saghafifar H., Alijanianzadeh M., Soltanolkotabi M. 2017. A sensitive tapered-fiber optical biosensor for the label-free detection of organophosphate pesticides. Sensors and Actuators B: Chemical 249: 523–532. DOI: http://dx.doi.org/10.1016/j.snb.2017.04.121

Badawy M.E., El-Aswad A.F. 2014. Bioactive paper sensor based on the acetylcholinesterase for the rapid detection of organophosphate and carbamate pesticides. International

Journal of Analytical Chemistry 2014: 536823. DOI: https://doi.org/10.1155/2014/536823

Bala R., Dhingra S., Kumar M., Bansal K., Mittal S., Sharma R.K., Wangoo N. 2017. Detection of organophosphorus pesticide–malathion in environmental samples using peptide and aptamer based nanoprobes. Chemical Engineering Journal 311: 111–116. DOI: https://doi.org/10.1016/j.cej.2016.11.070

Bala R., Sharma R.K., Wangoo N. 2016. Development of gold nanoparticles-based aptasensor for the colorimetric detection of organophosphorus pesticide phorate. Analytical Bioanalytical Chemistry 408: 333–338. DOI: https://doi.org/10.1007/s00216-015-9085-4

Chang J., Li H., Hou T., Li F. 2016. Paper-based fluorescent sensor for rapid naked-eye detection of acetylcholinesterase activity and organophosphorus pesticides with high sensitivity and selectivity. Biosensors & Bioelectronics 86: 971–977. DOI: doi:10.1016/j.bios.2016.07.022

Chen M., Luo W., Liu Q., Hao N., Zhu Y., Liu M., Wang L., Yang H., Chen X. 2018. Simultaneous in-situ extraction and fabrication of SERS substrate for reliable detection of thiram residue. Analytical Chemistry 22: 13647–13654. DOI: https://doi.org/10.1021/acs.analchem.8b03940

Chu S., Wang H., Ling X., Yu S., Yang L., Jiang C. 2020. Portable smartphone platform using ratiometric fluorescent paper strip for visual quantitative sensing. ACS Applied Materials & Interfaces 12: 12962–12971. DOI: https://doi.org/10.1021/acsami.9b20458

Dasriya V., Joshi R., Ranveer S. 2021. Rapid detection of pesticide in milk, cereal and cereal based food and fruit juices using paper strip-based sensor. Science Reports 11: 18855. DOI: https://doi.org/10.1038/s41598-021-96999-w

Dissanayake N.M., Arachchilage J.S., Samuels T.A., Obare S.O. 2019. Highly sensitive plasmonic metal nanoparticle-based sensors for the detection of organophosphorus pesticides. Talanta 200: 218–227. DOI: https://doi.org/10.1016/j.talanta.2019.03.042

Fauzi N.I.M., Fen Y.W., Omar N.A.S., Hashim H.S. 2021. Recent advances on detection of insecticides using optical sensors. Sensors 21: 3856. DOI: https://doi.org/10.3390/s21113856

Fu G., Chen W., Yue X., Jiang X. 2013. Highly sensitive colorimetric detection of organophosphate pesticides using copper catalyzed click chemistry. Talanta 103: 110–115. DOI: 10.1016/j.talanta.2012.10.016

Guo X., Zhang X., Cai Q., Shen T., Zhu S. 2013. Developing a novel sensitive visual screening card for rapid detection of pesticide residues in food. Food Control 30 (1): 15–23. DOI: https://doi.org/10.1016/j.foodcont.2012.07.015

Guo Y., Sun X., Liu X., Sun X., Zhao G., Chen D., Wang X. 2015. A miniaturized portable instrument for rapid determination pesticides residues in vegetables and fruits. IEEE Sensors Journal 15: 4046–4052. DOI: 10.1109/JSEN.2015.2410532

Hara T.O., Singh B. 2021. Electrochemical biosensors for detection of pesticides and heavy metal toxicants in water: recent trends and progress. ACS EST Water 1 (3): 462–478. DOI: https://doi.org/10.1021/acsestwater.0c00125

Hossain S.M., Luckham R.E., McFadden M.J., Brennan J.D. 2009. Reagentless bidirectional lateral flow bioactive paper sensors for detection of pesticides in beverage and food samples. Analytical Chemistry 81 (21): 9055–9064. DOI: https://doi.org/10.1021/ac901714h

Hou J., Dong J., Zhu H., Teng X., Ai S., Mang M. 2015. A simple and sensitive fluorescent sensor for methyl parathion based on l-tyrosine methyl ester functionalized carbon dots. Biosensors & Bioelectronics 68: 20–26. DOI: https://doi.org/10.1016/j.bios.2014.12.037

Huang L., Sun D.W., Pu H., Wei Q., Luo L., Wang J. 2019. A colorimetric paper sensor based on the domino reaction of acetylcholinesterase and degradable γ-MnOOH nanozyme for sensitive detection of organophosphorus pesticides. Sensors and Actuators B: Chemical 290 (1): 573–580. DOI: https://doi.org/10.1016/j.snb.2019.04.020

Jain D., Kaur B.P., Pasricha R. 2019. Design of microcontroller based cost effective portable detection circuit for pesticide recognition. International Journal of Innovative Technology and Exploring Engineering 9: 2228–2232. DOI: 10.35940/ijitee.A4793.119119

Kaur J., Singh P.K. 2020. Enzyme-based optical biosensors for organophosphate class of pesticide detection. Physical Chemistry Chemical Physics Journal 22 (27): 15105–15119. DOI: https://doi.org/10.1039/D0CP01647K

Kavruk M., Ozalp V.C., Oktem H.A. 2013. Portable bioactive paper-based sensor for quantification of pesticides. Journal of Analytical Methods in Chemistry 2013: 932946. DOI: https://doi.org/10.1155/2013/932946

Khaled E., Kame M.S., Hassan H.N.A., Abdel-Gawad H., Aboul-Enein H.Y. 2014. Performance of a portable biosensor for the analysis of ethion residues. Talanta 119: 467–472. DOI: 10.1016/j.talanta.2013.11.001

Khaled E., Kamel M.S., Hassan H.N.A., Malhat F.M., Abdel-Gawad H. 2015. Rapid detection of Methomyl and organophosphorous pesticides with portable potentiometric biosensor. Transactions of the Association for Computational Linguistics 5: 117–126. DOI: https://doi.org/10.1080/22297928.2015.1090332

Kim H.J., Kim Y., Park S.J., Kwon C., Noh H. 2018. Development of colorimetric paper sensor for pesticide detection using competitive-inhibiting reaction. Biochip Journal 12: 326–331. DOI: https://doi.org/10.1007/s13206-018-2404-z

Kovida, Sharma V., Koner A.L. 2020. Rapid on-site and naked-eye detection of common nitro pesticides with ionic liquids. The Analyst 145: 4335–4340. DOI: https://doi.org/10.1039/d0an00452a

Kumar D.N., Rajeshwari A., Alex S.A., Sahu M., Raichur A.M., Chandrasekaran N., Mukherjee A. 2015. Developing acetylcholinesterase-based inhibition assay by modulated synthesis of silver nanoparticles: Applications for sensing of organophosphorus pesticides. RSC Advances 5 (76): 61998–62006.

Li H., Guo J., Pinga H., Liu L., Zhang M., Guan F., Sun C., Zhang Q. 2011. Visual detection of organophosphorus pesticides represented by mathamidophos using Au nanoparticles as colorimetric probe. Talanta 87: 93–99. DOI: http://dx.doi.org/10.1016/j.talanta.2011.09.046

Li X., Cui H., Zeng Z. 2018. A simple colorimetric and fluorescent sensor to detect organophosphate pesticides based on adenosine triphosphate modified gold nanoparticles. Sensors 18: 4302. DOI: https://doi.org/10.3390/s18124302

Lin D., Li L., Song X., Xu S., Zhang Q., Hu Z., Yang L., Jiang C. 2021. "Light Up" fluorescence visual sensitive detection of organophosphorus with a smartphone-based platform utilizing a composite rhodamine B-Ag@Au nanoprobe. ACS Sustainable Chemistry & Engineering 9 (43): 14579–14587. DOI: https://doi.org/10.1021/acssuschemeng.1c05544

Liu Y., Li S., Ni Z., Qu M., Zhong D., Ye C. 2016. Pesticides in persimmons, jujubes and soil from China: Residue levels, risk assessment and relationship between fruits and soils. Science of the Total Environment 542: 620–628. DOI: https://doi.org/10.1016/j.scitotenv.2015.10.148

Mane P.C., Shinde M.D., Varma S., Chaudhari B.P., Fatehmulla A., Shahabuddin M., Amalnerkar D.P., Aldhafiri A.M., Chaudhari R.D. 2020. Highly sensitive label-free biointerfacial colorimetric sensor based on silk fibroin-gold nanocomposite for facile detection of chlorpyrifos pesticide. Nature 10: 4198. DOI: https://doi.org/10.1038/s41598-020-61130-y

Mei Q., Jing H., Li Y., Yisibashae W., Chen J., Li B.N., Zhang Y. 2016. Smartphone based visual and quantitative assays on upconversional paper sensor. Biosensors & Bioelectronics 75: 427–432. DOI: https://doi.org/10.1016/j.bios.2015.08.054

Naushad M., Sharma G., Alothmanab Z.A. 2019. Photodegradation of toxic dye using Gum Arabic-crosslinked-poly(acrylamide)/Ni(OH)$_2$/FeOOH nanocomposites hydrogel. Journal of Cleaner Production. 241: 118263. DOI:

https://doi.org/10.1016/j.jclepro.2019.118263

Nouanthavong S., Nacapricha D., Henry C.S., Sameenoi Y. 2016. Pesticide analysis using nanoceria-coated paper-based devices as a detection platform. Analyst 141: 1837–1846. DOI: https://doi.org/10.1039/C5AN02403J

Oujji N.B., Bakas I., Istamboulie G., Ait-Ichou I., Ait-Addi E., Rouillon R., Noguer T. 2012. Acetylcholinesterase immobilized on magnetic beads for pesticides detection: application to olive oil analysis. Sensors 12 (6): 7893–7904. DOI: 10.3390/s120607893

Popp J., Peto K., Nagy J. 2013. Pesticide productivity and food security: A Review. Agronomy for Sustainable Development 33: 243–255. DOI: https://doi.org/10.1007/s13593-012-0105-x

Purushottam T., Sharma V.P., Srivastava L.P., Sarika M. 2014. Determination of organophosphorus pesticide residues in wheat and rice by QuEChERS method. Journal of Environment Research & Development 8 (4):859–866.

Singh R., Kumar N., Mehra R., Kumar H., Singh V.P. 2020. Progress and challenges in the detection of residual pesticides using nanotechnology based colorimetric techniques. Trends in Environmental Analytical Chemistry 26: e00086. DOI: 10.1016/j.teac.2020.e00086

Singh S., Tripathi P., Kumar N., Nara S. 2017. Colorimetric sensing of malathion using palladium-gold bimetallic nanozyme. Biosensors & Bioelectronics 92: 280-286. http://dx.doi.org/10.1016/j.bios.2016.11.011.

Sun Z., Tian L., Guo M., Xu X., Li Q., Weng H. 2017. A double-film screening card for rapid detection of organophosphate and carbamate pesticide residues by one step in vegetables and fruits. Food Control 81: 23–29. DOI: https://doi.org/10.1016/j.foodcont.2017.05.012

Tripathy V., Saha A., Patel D.J., Basak B.B., Shah P.G., Kumar J. 2016. Validation of a QuEChERS-based gas chromatographic method for analysis of pesticide residues in *Cassia angustifolia* (senna). Journal of Environment Science & Health Part B 51: 508–518. DOI: 10.1080/03601234.2016.1170544

Truong P.L., Duyen V.T.C., Toi V.V. 2021. Rapid detection of Tebuconazole based on aptasensor and aggregation of silver nanoparticles. Journal of Nanomaterials 2021, 10 pp. DOI: https://doi.org/10.1155/2021/5532477

Umapathi R., Sonwal S., Lee M.J., Rani G.M., Lee E.S., Jeon T.J., Kang S.M., Oh M.H., Huh Y.S. 2021. Colorimetric based on-site sensing strategies for the rapid detection of pesticides in agricultural foods: New horizons, perspectives, and challenges. Coordination Chemistry Review 446: 214061. DOI: https://doi.org/10.1016/j.ccr.2021.214061

Wabaidur S.M., Khan M.A., Siddiqui M.R., Otero M., Jeon B.H., Alothman Z.A., Hakami A.A.H. 2020. Oxygenated functionalities enriched MWCNTs decorated with silica coated spinel ferrite – A nanocomposite for potentially rapid and efficient de-colorization of aquatic environment. Journal of Molecular Liquids 317: 113916. DOI: https://doi.org/10.1016/j.molliq.2020.113916

Wu S., Li D., Wang J., Zhao Y., Dong S., Wang X. 2017a. Gold nanoparticles dissolution based colorimetric method for highly sensitive detection of organophosphate pesticides. Sensors and actuators B: Chemical 238: 427–433. DOI: https://doi.org/10.1016/j.snb.2016.07.067

Wu Y., Sun Y., Xiao F., Wu Z., Yu R. 2017b. Sensitive inkjet printing paper-based colormetric strips for acetylcholinesterase inhibitors with indoxyl acetate substrate. Talanta 162: 174-179. doi: 10.1016/j.talanta.2016.10.011.

Xu X.Y., Yan B., Lian X. 2018. Wearable glove sensor for non-invasive organophosphorus pesticides detection based on double-signal fluorescence strategy. Nanoscale 10: 13722–13729. DOI: https://doi.org/10.1039/C8NR03352H

Yan X., Li H., Li Y., Su X. 2014. Visual and fluorescent detection of acetamiprid based on the inner filter effect of gold nanoparticles on ratiometric fluorescence quantum dots. Analytica Chimica Acta 852: 189–195. DOI: https://doi.org/10.1016/j.aca.2014.09.008

Yao T., Liua A., Liu Y., Weic M., Wei W., Liua S. 2019. Ratiometric fluorescence sensor for organophosphorus pesticide detection based on opposite responses of two fluorescence reagents to MnO_2 nanosheets. Biosensors & Bioelectronics 145: 111705. DOI: https://doi.org/10.1016/j.bios.2019.111705

Zhang C., Zhang K., Zhao T., Liu B., Wang Z., Zhang Z. 2017. Selective phosphorescence sensing of pesticide based on the inhibition of silver(I) quenched $ZnS:Mn^{2+}$ quantum dots. Sensors and Actuators B: Chemical 252: 1083–1088. DOI: http://dx.doi.org/10.1016/j.snb.2017.06.087

Zhang Q., Zhang Z., Xu S., Da L., Lin D., Jiang C. 2022. Enzyme-free and rapid visual quantitative detection for pesticide residues utilizing portable smartphone integrated paper sensor. Journal of Hazardous Materials 436: 129320. DOI: 10.1016/j.jhazmat.2022.129320

Zhao X., Kong D., Jin R., Li H., Yan X., Liu F., Sun P., Gao Y., Lu G. 2019. On-site monitoring of thiram via aggregation-induced emission enhancement of gold nanoclusters based on electronic-eye platform. Sensors & Actuators: B. Chemical 296: 126641. DOI: https://doi.org/10.1016/j.snb.2019.126641