A concise overview on pesticide detection and degradation strategies

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ABSTRACT

Pesticides are a gift to agriculture for its flourish of crop production. For production of heavy grown crops, growing multiple crops in a season or enriching the soils for better productivity, pesticides are a mandate in modern world to meet the food requirement. However, controversy arises on the fact of overuse and the underlying problems associated with it. The problems include environmental contamination, public health compromise, disturbance in the ecological niches, long-term persistence in soil and water bodies, etc. Pesticide residues present in the foods or crops may get circulated by bioamplification through the food chains. Therefore, it is imperative to detect the pesticides present in the environment and decontaminate the same by degradation to maintain the safety of environment. This review outlines the recent strategies of various pesticide detection techniques and discusses the overview of degradation strategies worked on for removal of pesticides from the environment.

1. Introduction

Pesticides started playing a pervasive role in modern agriculture evolution as early as 1950. The last century have observed a surge in pesticide utilization in benefit of modern agricultural practices, promoting improved crop production by managing the insects and diseases, which potentially caused harm to the crops [1]. Escalation of human population has wiped away several hectares of cultivable lands and made it necessary for escalating the food production, which in turn lead to further surge in pesticide utilization. This is the point which raised the question about public health and environment safety and soon it emerged as a matter of concern. The pesticides not only degrade surface soil quality but also affect biodiversity. Pesticides covered soil organic matter is less mobile and is difficult for degradation. Pesticides can enter the food chain by bioamplification and hence disturbs the tropic levels. Pesticides may also percolate into the ground water table. Level of ground water, topographical outline and agriculture practices affect the pollution rate [2]. Fatal dose of intoxication may also lead to cancers and death of individuals [3]. There is often non-specific pesticide interference, which can lead to loss of biodiversity [4]. Another aspect of negative impact of pesticide is air pollution, which is comparatively less noted [2]. The weather conditions like humidity and temperature decide the degree of evaporation of pesticides. Some are short existing, whereas some are quite persistent in nature. These contaminants may intrude the environment by water cycle or may simply remain as air particulate matter. The risk associated with pesticides to human mostly depends on the extent of exposure [5]. Based on that, pesticides may leave short-term effects like skin itching, eye irritation, dizziness, etc., or may lead to fatal long-term effects like cancer, breathing difficulties, ulcers, blood-related issues, neurological disabilities or even infertility [6]. In connection to these, ‘cancer village’ terms became quite popular. Cancer villages are those villages, which are having high cancer morbidity rate than normal standard due to their unintentional occupational threat in exposure to harmful pesticide pollutants [7].

The utilized pesticide residues or treated residual compounds are sometimes toxic too. The residues are mostly transformed products of the ‘Parent’ pesticides compounds, which are recalcitrant in nature for several decades [8]. Pesticides may follow several pathways after their release into the environment, which may include transformation/degradation, sorption-desorption, volatilisation or is taken up by plants [9]. These may also get carried to the water bodies or may get leached into ground water table leading to contamination [10].

Thus, besides restricting the pesticide utilization, it is requisite to develop strategies to detect and quantify these necessary harmful compounds as well as lessen the toxic intensity or to remove the residual pesticide from the soil. This review portrays a cumulative report of recent researches and updates on various pesticide detection and degradation techniques. This discusses various approaches of quantification and detoxification.
of pesticide traces in the environment. It also gives a brief account of the detailed principles, detection efficiency, advantages and disadvantages of the advanced technologies used. The comprehensive compilation and multi-directional coverage of detection as well as degradation methods can support a quick overview of the current strategies blooming in this field.

2. Overview of pesticides in the environment

Pesticides are often toxic chemicals, mixtures of chemicals or bio-agents, which are purposely incorporated in the environment to curb the attack of pests, rodents and control plant diseases of microbial origin. Pesticides are available in several forms like powder, spray, granules, dust or cakes. However, agrochemical-based pesticides are the most widely used variety among all and its inadequate use is a major point of concern.

Classification of pesticides are quite complex. Pesticides can be a collective term which may include classes like insecticides, fungicides [11], rodenticides, fumigants and insect repellents. All these groups broadly differ in their physical and chemical properties as well as mode of their activity [12]. Besides this, it can also be classified into broader categories of organic and inorganic classes. Depending on functional group present in the parent structure of pesticides, it can be categorized as organophosphorous, organochlorine, carbamates, triazines and phenoxy sub-classes. Although different pesticides have exclusively different action course, however, pesticides belonging to similar classes manifests similar activity, intoxication intensity, recalcitrance duration and responds to similar removal treatments [13]. Table 1 below lists the broad outline of pesticides classification.

Different pesticides have different levels of persistence in nature. Soil adsorption coefficient and half-life of the pesticides determines whether it will be non-persistent, moderately persistent or long-term persistent. Pesticides with less soil adsorption coefficient adhere less with the soil organic particles and tends to leach. However, if the half-life is less, the toxic tendency can be considered minimal as it will probably degrade and mineralize within less time span. Thereby, remains in the environment for a very short time and has least capacity to become a biohazard. Table 2 lists few commonly used pesticides stating their half-life and soil adsorption coefficient. According to Kerley et al., less than 30 days of half-life can be denoted as non-persistent and greater than 100 days can be categorized to be highly persistent [16].

Table 1. Classification of pesticides.

| SI No. | Category | Classes/Families of Pesticides |
|--------|----------|--------------------------------|
| I.     | Mode of action [14] | (I) Insecticides | (I) Fungicides | (I) Herbicides |
| (1)   | Pyrethroids | Thiocarbamates | (1) Triazines |
| (2)   | Organophosphate | Dithiocarbamate | (2) Acetanilides |
| (3)   | Carbamate | Tiabendazoles | (3) Chlorophenoxy |
| (4)   | Organochlorine | Triazoles | (4) Glyphosate |
| (5)   | Manganese compounds | Dinitrophenols | (5) Bipyridylium |

| (6)   | Rodenticides | Dicrboximides | (7) Cupric salts |
| (7)   | Rodenticides | (8) Thiocarbamates |
| (8)   | Rodenticides | (I) Fumigants | (I) Insect repellents |
| (9)   | Rodenticides | Diethyltoluamide |

| (I)   | Inorganic | (I) Organic | Basic carbon structure associated with oxygen/fluoride/phosphorous/chloride/sulphur |
| (I)   | Inorganic | Combined mixture of elements like copper, sulphur, heavy metals like arsenic, cyanide, mercury |

| III.  | Functional group [15] | (I) Organo-phosphate | (I) Organo-chlorine | (I) Carbamates |
| (1)   | Chlorpyrifos | Chlor dane | (1) Aldicarb |
| (2)   | Parathion | Lindane | (2) Carbofuran |
| (3)   | Malathion | Dieldrin | (3) Carbaryl |
| (4)   | Glyphosate | β-Endosulfan | (4) Ethionocarb |
| (5)   | Triazophos | Endrin | (5) Fenobucar |
|       |           |             | (6) Oxamyl |
|       |           |             | (7) Methylothyl |

| (I)   | Triazines | (I) Phenoxy | (I) Mecoprop |
| (1)   | Atrazine | (1) Dichlorprop | (2) Propazine |
| (2)   | Propazine | (3) Simazine |
| (3)   | Simazine | (4) Prometon |
| (4)   | Prometon | (5) Terbutazon |
| (5)   | Terbutazon | (6) Secbumeton |

| (I)   | Phenoxy | (I) 2,4-dichlorophenoxyacetic acid (2,4-D) |
| (I)   | Phenoxy | (I) 4-chloro-2,6-dimethylphenoxycetic acid (MCPA) |

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3. Detection of pesticides

Pesticides are necessary in development of agriculture. But there are certain limits that have been assigned for its usage by the authorized bodies. Beyond that limit, it is a threat to the nature and environmental components. The remediation process is at its bloom on this issue. However, it is equally necessary to detect the residual pesticide for proper detoxification of the targeted area. Some pesticides like atrazine, triazines are poorly absorbed by the soil due to their chemical structure and remains persistent leading to hazards [18].

The traditional methods for pesticide determination generally follow the techniques like chromatography coupled with mass spectroscopy (MS), simple gas chromatography (GC) or high performance liquid chromatography (HPLC) [19]. Although all these processes produce elaborate and nearly accurate result, however, conventional existing procedures of pesticide detection are often impractical in the field usage. Additionally, the constraint is also unavoidable as complex pre-treatments and cost-inducing instruments are required for the analysis including expertise for handling of the same [20].

Currently, nanoparticle-mediated pesticide detection is a recent approach that is gaining stature. The nanoparticles have a wide spectrum of flexibility in stability, compatibility and sensitivity, which are easily modifiable. Nanoparticle-based pesticide detection is mostly annexed with electrochemical, antibody or enzyme immobilized sensors [21] or grooved with fluorophores for fluorescence, chemiluminescence or surface-enhanced Raman spectroscopy based analysis. Modified silica nanoparticle (SNIP) is mentioned to be used as a mode of ‘direct detection’ of pesticide [22]. Some of the recent advanced detection methods have been discussed in subsequent sections.

3.1. Electrochemical detection of pesticides

The conventional methods of field sampling or chromatographic detection procedures undoubtedly provide explicit results [23]; however, outcome may confront dispute in cases of sources like water bodies which is dynamic.

Electrochemical sensing determines the target by measuring charge, current or potential, which occurs as an interaction between the targeted analyte and the sensing electrode. The three basic components of electrochemical sensing device are working electrode, counter electrode and reference electrode. The detection sensors can be based on direct-detection for electroactive analytes, enzymatic detection, immunosensors or microbial (biological) sensors depending on the suitability. Qiu et al. have detected organophosphate pesticide (OP) using the same method by targeting p-nitrophenol group using TiO₂-amino acid conjugate. The range of detection was approximately 0.2 μM [24]. Gold, copper, carbon and mercury electrode have been successfully used to detect glyphosate. In general, electrochemical techniques, bulk volume of samples and complex instrumentation contributed to the unsuitability for using the application in field samples. Development of screen printed electrodes (SPE) helped to overcome these limitations. Made of plastic or ceramic plates and imprinted with gold, silver, carbon or graphite ink, these SPEs are more advanced in terms of analytical value [25]. Current upgradeation is being scratched on immobilized enzyme or antibody with affinity towards particular pesticides [26], selection of suitable electrode of different nanomaterials [27]. Special emphasis is also focused on a specialized process called Molecular Imprinted Polymer (MIP), which creates a negative embossing on electrode surface enhancing the selectivity and specificity towards particular pesticide for

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Table 2. Persistence and leaching ability of some common pesticides.

| Pesticide   | Pesticide family | Pesticide genera | Half-life (Days) | Soil adsorption coefficient (µg/g) | Persistence* | Leaching ability | Reference |
|-------------|------------------|------------------|-----------------|-----------------------------------|--------------|-----------------|-----------|
| Picloram    | Pyridine         | Herbicide        | 90              | 16                                | MP           | High            | [16,17]   |
| 2,4-Dichlorophenoxyacetic acid | Phenoxyacetic acid | Herbicide        | 10              | 20                                | NP           | High            |          |
| Carbofuran  | Carbamate        | Insecticide      | 50              | 22                                | NP           | High            |          |
| Aldicarb    | Carbamate        | Insecticide      | 30              | 30                                | NP           | High            |          |
| Atrazine    | Triazine         | Herbicide        | 60              | 100                               | HP           | Low             |          |
| Prometon    | Triazine         | Herbicide        | 500             | 150                               | HP           | Low             |          |
| Carbaryl    | Carbamate        | Insecticide      | 10              | 300                               | NP           | Low             |          |
| Tebufos     | Organophosphate  | Insecticide      | 5               | 500                               | NP           | Low             |          |
| Malathion   | Organophosphate  | Insecticide      | 1               | 1800                              | NP           | Low             |          |
| Chlorpyrifos| Organophosphate  | Insecticide      | 30              | 6070                              | NP           | Low             |          |
| Parquat     | Pyridine         | Herbicide        | 1000            | 1000                              | HP           | Low             |          |
| Glyphosate  | Organophosphate  | Herbicide        | 47              | 24,000                            | MP           | Low             |          |
| Fluzifop-p-butyli | Phenoxy | Herbicide        | 15              | 5700                              | NP           | Low             |          |

* NP: Non-persistent, HP: Highly-persistent, MP: Moderately persistent
more perfect detection [28]. MIP is also used using to detect glyphosate using graphite electrode with gold nanoparticle imprinting.

Electrochemical sensors generally uses the change in current, electric potential or the resistance (electrical impedance) to detect the pesticides and the sensors are named accordingly. Electrochemical detection can be carried out by different voltammetric techniques like cyclic voltammetry, differential pulse voltammetry, square wave voltammetry, by amperometry or by electrochemical impedance spectroscopy [25,29]. The sample preparation for this technique is simple. Generally pesticide-spiked samples are applied on biosensors to detect the signals. Drechsal et al. designed an auto-dip biosensor to detect chlorpyrifos pesticide in food samples [30]. Food sample like apple were cut fresh, homogenized with buffer and spiked with the selected pesticide. The signal was estimated by the current peaks. Some electrochemical detection techniques are listed in Table 3, which are drawn from different literature review.

However, the electrochemical sensors have some flaws like high maintenance and operating cost. Sometimes low electroactivity analytes like glyphosate may produce poor output [40]. Moreover, sample pretreatment in few cases, interference from co-existing compounds or pollutants in the targeted field sample often alters the desired result. Inspite of these drawbacks, electrochemical is one of the widely detection technique for pesticide even in field samples. It is efficiently fast, reliable, accurate and selective enough with minimal sample preparation compared to tedious traditional chromatographic techniques [41]. Currently, improvisations with molecular imprinted electrodes, incorporation of nanotechnology are subjected to broader interest, which can be expected to overcome the flaws in terms of electrode fabrication, sample stability and continuous assessment of field samples.

3.2. Enzyme conjugated nanoparticle based detection

Pesticides are developed for controlling pests by intending the inhibition of the functional enzymes present in the organism. The enzymes mostly include acetylcholinesterase, alkaline or acid phosphatases, organophosphate hydrolase, butyrylcholinesterase, tyrosinase, aldehyde dehydrogenases, etc [41]. Thus, sensors are developed utilizing these enzymes. The enzyme-conjugated detectors mostly work by either inhibition mechanism or catalytic mechanism [42]. Inhibition mechanism can be used for pesticide quantification on basis of the inhibited enzyme activity in presence or absence of the targeted analyte. However, the catalytic approach of enzyme-conjugated sensors uses the analyte directly as substrate. The result is interpreted on the fact that the extent of interaction is directly proportional to the concentration of pesticide in the sample [43]. Figure 1 demonstrates the basic concept of enzyme conjugated nanoparticle-based pesticide detection.

Enzymatic sensors have promising potential in pesticide detection. However, fabrication of the micro-reactors is necessary for up-gradation of analytical efficiency. Enzyme immobilization plays a crucial part in this process. A summarized account of various enzyme immobilization processes is discussed in Table 4.

Table 3. List of some successful electrochemical detection of pesticide.

| Pesticide   | Technique                        | Electrode                  | Buffer/Medium                                  | Sample/Matrix   | Detection limit | Reference |
|-------------|----------------------------------|----------------------------|-----------------------------------------------|-----------------|----------------|-----------|
| Lindane     | Differential pulse voltammetry   | CuO-MnO<sub>2</sub>         | TBAB solution (0.05 M) 60:40 methanol/water containing 0.05 M TBAB | Tap water Lindane lotion | 4.80 nM | [27]     |
|             | Cyclic voltammetry, Differential pulse voltammetry | Cellulose-acetate/Glassy carbon electrode (CA/GCE) | | | 37 µM | [31]     |
|             | Square wave voltammetry          | 6.6/MWCNT/ZnO, GCE/ Nylon | 60:40 methanol/water containing 0.05 M TBAB | Tap water | 3.20 nM | [32]     |
| Glysophsate | Amperometry                      | Hg/Pt                      | 0.10 M TBAB in DMSO | Sewage sludge Spiked corn sample | 0.59 nM | [34]     |
|             | Amperometry                      | horseradish peroxidase/poly (2,5-dimethoxyaniline)-poly(4-styrene sulfonylic acid)/Au | PBS | | | |
|             | Amperometry                      | Gold(Au)                   | 0.10 M NaOH | River water | 1.89 µM | [35]     |
|             | Amperometry                      | Gold Screen Printed Electrode | Tap water | Ground water | 2.0 µM | [36]     |
|             | Coulometry                       | Copper (Cu)                | 0.03 M PBS/Methanol | Tomato extract | 0.59 µM | [37]     |
|             | Differential pulse voltammetry   | Electro-aggregated silver carbonate modified-Pt | 0.1 M Na<sub>2</sub>CO<sub>3</sub> | | 40.0 µM | [38]     |
| (LSV)       | Linear sweep voltammetry (LSV)   | Molecularly imprinted polymer/gold nanoparticles-pencil graphite electrode | 10.0 mM Ferricyanide/ Ferroxyanide [Fe(CN)<sub>6</sub>]<sup>3-</sup>/4- | Tap water sample | 4.73 nM | [39]     |
Table 4. List of some enzyme immobilization systems.

| Enzymatic microsystem | Matrix         | Carriera | Advantages                                      | Reference |
|-----------------------|----------------|----------|------------------------------------------------|-----------|
| Capillary             | Monolithic capillary | Gold NP | Increased stability, availability, activity of enzyme | [85]       |
| Open tubular capillary| Magnetic NP     | Gold NP  | High efficiency, easily modificable, bio-compatible | [46]       |
|                      | Carbon NP       | Graphene oxide | Automation, high efficiency, re-usability | [48]       |

Table 5 lists some of the successful works using this technique. The enzymes are often immobilized with different polymeric matrices by covalent bonding encapsulation, entrapment or by adsorption [51]. As discussed earlier, nanoparticles are greatly modifiable. So enzyme substrates are coupled on nanoparticles to give stability for developing the sensor. In the presence of pesticide, the enzymes execute catalytic activity to generate hydrogen ion, which modulate the conductivity of the medium [22,52]. This strategy can correspond with the detection and quantification of the pesticide aided with different electrodes to facilitate the process. The conventional electrodes are not very appropriate for field utility. However, recent technology of screen-printed electrodes (SPE) expedites the detection method as well as aids to the field utility due to easy handling [25].

In recent studies, microchip-based enzymatic sensors improvised with nanoparticles have opened a wide scope in sensor development[125]. These newly developed sensors are exclusively beneficial in terms of fast and accurate result, portability, field application and automation.

3.3. Fluorescence-driven pesticide detection

Fluorescence-driven detection of pesticide is an optical approach in identifying the presence of pesticide and has gained wide acceptance. Inert biosensors are designed for this purpose, where pesticide detection is determined by virtue of enhancement or quenching of fluorescence upon a specific pesticide interaction [22]. The mode of action is shown in Figure 2.

A good number of recent works have been reported on fluorescence-driven detection of pesticide. Enzyme-based sensors have been used to detect and study the interactions of different organophosphate pesticides. Esterase 2 from *Alicyclobacillus acidocaldarius* was used for the same. Additionally, fluorescence-based polarity-sensitive probe was also consolidated to study

Table 5. List of some enzyme conjugated nanoparticle-mediated pesticide detection.

| Method                             | Type(s) of nanoparticle used | System                                      | Targeted pesticide                      | Detection rate           | Reference |
|------------------------------------|------------------------------|---------------------------------------------|------------------------------------------|--------------------------|-----------|
| Enzyme conjugated nanoparticle      | SiO2(2) nanosheet-Nafion nanocomposites | Acetylcholinesterase (AChE) biosensor | Chlorpyrifos, Methyl parathion, Carbofuran | 1.0 × 10⁻¹² – 1 × 10⁻¹⁰ M | [53]      |
|                                     | Gold nanoparticle (AuNP)     | Acetylcholinesterase (AChE) immobilized sensor | Monocrotophos                           | 0.001–1.0 µg/ml         | [54]      |
|                                    | Carboxylic silica nanosheet–platinum nanoparticle | Acetylcholinesterase (AChE): SiO2 paper substrate | Methyl parathion and carbaryl | 1.0 × 10⁻¹² – 1 × 10⁻⁸ M | [66]      |
| Gold nanoparticle                   |                              | Acetylcholinesterase (AChE): Pt-doped | Paraoxon                                 | 500 nM – 1 mM           | [55]      |
interactions [56]. Wang et al. studied on a mixture of carbamate pesticides using 3D-fluorescence spectroscopy based on Genetic Algorithm optimized Back Propagation network model (GA-BP) [13], indole-based biosensor for organophosphate detection [57], alkaline-phosphatase triggered enzyme-based fluorescence detection method of organophosphorus pesticides [58] are some of the recent works can be stated as examples of successful application of this technique.

3.4. Surface-enhanced Raman Spectroscopic analysis for pesticide detection

A recent mode developed for pesticide detection is Surface-Enhanced Raman Spectroscopic (SERS) method. SERS method is technically the amalgamation of nanotechnology and Raman spectroscopy [59]. The detection method works on the basis of enhancement in the Raman signals. This is achieved by chemisorption of target pesticide on nano-metal substrate. When struck by laser light, the electronic state of the complex changes to new absorption frequency, thereby resonating with the frequency of laser excitation (surface plasmon), and there is a shift in Raman signal [60]. The basic function mechanism is depicted in Figure 3.

Surface-Enhanced Raman Spectroscopic analysis is a non-invasive detection tool and advantageous in terms of no unnecessary time consumption, in-situ sample preparation, field applicability, simple reagents usage and high sensitivity [59]. Interference from other pesticides or complexes present in samples [61], presence of similar compound like target analyte [62], operating with a Raman instrument with disparate configuration of laser intensity, spectral properties, wavelength may lead to disputed result [63]. Moreover, non-specific binding occurring due to non-target adsorption on SERS substrate surface generates false signals, background disturbance and reduced tagging-specificity [64]. Amalgamating or functionalizing target molecule with aptamers, MIPs, antibodies facilitate the specificity and generates accuracy in analysis [62].

Figure 2. Fluorophoric detection of pesticides.

Figure 3. Diagrammatic representation of SERS based pesticide detection.
Often some analytes like organophosphate pesticides show a very weak SERS spectrum due to their hydrophobic structure and have a very less affinity towards SERS substrates [65]. This leads to feeble SERS signal. There are recent upgradations developed to detect these types of complex samples or compounds with low SERS substrate affinity. The quality of SERS substrates used may enhance the signal to a desired level. Metal nanoparticles of gold, silver and copper are considered as very good SERS substrate as they are easy to synthesize, stable and efficient in generating SERS signal. The shape, size and morphology of these nanostructures determine the extent of enhancement for the signal produced [66]. Nanostructures with sharp morphological features serves as better substrate compared to the smooth featured nanostructures. The signal production is better when analyte and the substrate are at the maximum proximity. To obtain this, functionalization of the metal surface or metallic organic frameworks (Hybrid crystalline substance) is done, which brings the target analyte closer and generates enhanced SERS signal [67]. Sometimes, trace or weakly-affined samples are pre-prepared by extracting and evaporating to gain high concentration, thus obtaining a prominent SERS signal [65]. Table 6 enlists some successful SERS enhanced strategies for pesticide detection.

Interaction study of chlorpyrifos and thiamethoxam using gold nano-finger [74], 2,4-dichlorophenoxyacetic acid (2,4-D), pyrethroid and thiamethoxam were detected on food surface using mesoporous silica supported gold nanoparticles by Xu et al. [75], cypermethrin and esfenvalerate were detected by Xiali et al. using this technique effectively [66] are some of the recent works reported.

Table 6. List of some enhanced SERS-based pesticide detection.

| Enhancement strategy | Target pesticide | SERS substrate | Detection limit | Reference |
|----------------------|------------------|----------------|-----------------|-----------|
| SERS substrate upgrade | 2,4-D | Silver(Ag) NP, Gold(Au) NP | 61.9 nM [68] |          |
|                      | DDT | Silver(Ag) NP | - [69] |          |
| SERS substrate-Analyte proximity | Aldrin | Silver(Ag) NP | 13.7 nM [71] |          |
|                      | Dieldrin | Silver(Ag) NP, Gold(Au) NP | 0.82 µM [72] |          |
|                      | Endosulfan | Silver(Ag) NP, Gold(Au) NP | 0.41 µM [72] |          |
| Sample processing | Chlordane | Gold(Au) NP | 1 ppm [73] |          |

Different detection technologies that have been discussed so far have specific purpose, benefit and drawbacks. These are being constantly upgraded and studied to achieve more precise detection. Some common advantages and disadvantages for the detection techniques are compiled in Table 7.

4. Degradation strategies of pesticide elimination

Degradation of pesticides is a very complex interaction between different systems including soil and pesticide melding, physical factors, biological factors and types of pesticides. The extent of interlinking and sorption rate between the soil particle and pesticide decides their persistent nature depending on the characteristic feature of pesticide. The mode of action varies from different groups of pesticides and even within same group with similar structures. Degradation is highly influenced by soil type, pH, organic carbon content in soil and bioactivity of microbial community [78]. There are several techniques developed to degrade and efface the pesticide contaminant from environment, which are discussed in the following sections.

4.1. Physical degradation

The two important factors that contribute mostly in physical degradation of pesticide process is light and temperature. The basic physical process includes photolysis. Photolytic degradation is critical for organic compounds. Low freezing temperatures are used sometimes to aid in pesticide degradation [79]. Thermal desorption at low temperatures of 300 F to 1000 F is an efficient technique in physical degradation. This works by volatilizing the pesticides with further treatment of contaminated gas stream extruded in a separate burner to immobilize the targeted pollutants. However, the system is quite costly and requires advanced facilities. Another common process of physical degradation is incineration. Incineration completely destroys the organic contaminants by two phase heating instead of deactivating the contaminants [80].

4.2. Chemical degradation

The reactive components present in pesticides are targeted for chemical degradation. The process may involve simple amendment of pH, which may ease out in detoxification of pH-sensitive components. Some reactive oxygen forms like ozone, peroxide and superoxide also aids in chemical degradation [79]. Chemical degradation process of pesticide exclusion can be quite expensive depending upon the course of treatment. Generally, the contaminated samples are pre-treated and processed chemically to obtain the less toxic intermediate
Table 7. Advantages and disadvantages of common pesticide detection techniques.

| Detection method             | Sample preparation                        | Advantages                                                                 | Disadvantages                                                                 | Reference |
|------------------------------|-------------------------------------------|-----------------------------------------------------------------------------|--------------------------------------------------------------------------------|-----------|
| Electrochemical detection    | Spiked samples                            | • Good sensitivity and selectivity.                                          | • Not suitable for field analysis                                             | [76]      |
| Enzyme conjugated nanosensor | Spiked or direct field samples             | • Better interaction with targeted analyte.                                 | • Development in fabrication is required for increased efficacy              | [77]      |
| Fluorescence driven pesticide detection | Spiked and pre-treated samples with specific buffer or fluorophores | • Fast, efficient, reusable, durable, portable                             | • Multi-enzyme reactor system should be developed to detect complex natural samples or simultaneous multiple pesticides detection | [29]      |
| Surface Enhanced Raman Spectroscopic analysis | Spiked or direct field samples | • Ultra-sensitive detection.                                               | • Weak substrate-analyte interaction, sensitivity decreases                 | [59,90]  |
|                              |                                           | • Portable, field study possible.                                           | • Pesticide quantification is difficult.                                     |           |
|                              |                                           | • High accuracy                                                            | • Multiple pesticides in the same sample may interfere the result           |           |
|                              |                                           | • Least time consuming                                                     |                                                                        |           |

compounds, which are potentially less harmful to environment. In many cases, chemical degradation is collaborated with physical degradation treatments to get the desired results. The following table explains some techniques involved in chemical degradation process of pesticides.

Advanced oxidation process (AOP) is a very common technique, which works by oxidation of almost all type of organic substrate [81]. Hydroxyl radical plays the crucial role in the process. Highly reactive free hydroxyl radical reacts either with molecular oxygen forming peroxy radical and generates a stream of oxidation reaction or pounce the halogen containing aromatic rings of the pesticides to finally mineralize to produce H₂O and CO₂. UV-mediated degradation involves enhancement of AOP reactions in presence of strong and controlled UV light exposure on the pollutants [82]. This is mostly suitable for treating pollutants in aqueous system. High energy UV radiations help to loosen the chemical bonds, thus facilitating the oxidation reaction stream. This process can be UV-peroxide (H₂O₂) or UV-ozone system. Although a very effective technique, still turbidity and UV wavelength might interfere the efficiency. Sometimes reducing agents like zero-valent iron (Fe⁰) are used to reduce the pesticide pollutants. This technique can be employed in soil as well as for aquatic systems. However, efficiency of Fe⁰ decreases with time as the active sites gets blocked due to formation of oxide layer. Successful mineralization was obtained by combination of Fe⁰ with magnetite (Fe₃O₄), aluminium sulfate (Al₂(SO₄)₃) or acetic acid (CH₃COOH) [83,84]. Additionally, some catalysts (semiconductor oxides) like titanium dioxide and zinc oxide are used along with UV, to overcome the drawback of time consumption by the processes stated earlier in this section [85]. Moreover, these metal oxides being inert in nature, cumbers less to the environment safety.

4.3. Nanoparticle-mediated degradation

Nanoparticle-mediated pesticide degradation is a promising technology which will have a great potential in nullifying the toxic effects of recalcitrant compounds from environment [4]. Photocatalysis is the basic backbone of this method. It basically involves high-tech oxidative process in presence of photo energy leading to mineralization of hydrocarbon [86]. This technology involves different photocatalytic reactor systems where the photocatalysts are applied either in suspended or immobilised form [87]. Kanan et al. have discussed about TiO₂ as a photocatalyst, which can be utilized in pure form or doped with some other components and was reported to be an excellent candidate for degradation of a wide spectrum of pesticides [88]. Recent explorations are done on these doping materials, which consist of different nanoparticles. Nanoparticles have raised a great response as it bears special features with large specific surface area, little resistance for diffusion, high capacity of adsorption and rapid adsorption equilibrium [89,90].

Nanoparticles like gold (Au) and silver (Ag) have colossal response for photocatalytic activity [91]. Their optical and electronic properties get modulated to a wide extent by alteration of the size, shape and surface charge [92]. A simplified pictorial representation of the basic nanoparticle-mediated remediation system is shown in Figure 4. According to recent reports, gold
nanoparticles (AuNPs) supported onto TiO2, leads to visible illumination due to photocatalysis as the organic compounds in aqueous environment gets oxidized [93]. Table 8 shows a list of the nanoparticles usage against various pesticides degradation.

However, this method of pesticide degradation is relatively new and complex compared to other techniques. Polymeric, inorganic or carbonaceous nanoparticles are widely being researched. Suitability of the same has not been tallied in actual field condition [94]. There are only scarce work existing due to arduous work of delineating and preparation of nanoparticles. Additionally, exhilarating the photocatalytic reaction, often UV light is used, which may lead to detrimental condition to researcher without proper care.

**Figure 4.** General mechanism of nanoparticle-mediated degradation.

| Pesticide | Nanoparticle (NP) used | Reference |
|-----------|------------------------|-----------|
| DDT (1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane) | Ni-Fe | [95] |
| DDT (1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane) | Nano-sized zero valent Fe | [96] |
| Lindane (1, 2, 3, 4, 5, 6-hexachlorocyclohexane, g-HCH) | Zero valent Fe-Fe-Pb | [97] |
| Endosulfan (6, 7, 8, 9, 10-hexachlor-1, 5, 5a, 6, 9, 9a hexahydro-9, 9-methano-2, 3, 4-benzo dioxathiepin-3- oxide) | Ag-TiO2 | [98] |
| Chlorpyrifos | TiO2 | [99] |
| Chlorpyrifos | Fe-ZnO2 | [100] |
| Chlorpyrifos | Chitosan coated magnetic iron NP | [101] |
| Lindane | Fullerene (Carbonaceous engineered nanoparticle) | [102] |
| Aldrin | Chitosan supported iron NP (Chi-EDGE-Fe) | [103] |

4.4. **Microbe-assisted degradation**

Microbial community of a particular area plays major role in maintaining the environment quality [104]. Researchers have explored a wide array of microbes isolated from different sources that were potent enough to degrade toxic pollutants from the soil and water. However, there are both pros and cons for this degradation process. Although it is cost-effective and bears almost negligible side effect on environment apparently [79], it may also produce some more toxic and persistent metabolite in course of degradation. Additionally, the microbes incorporated into the soils often shows less viability in actual environment condition due to several physical parameters [105]. There are several factors affecting the microbe-assisted pesticide degradation.

1. The type of micro-organism employed for the purpose, their metabolic pattern and their extent of adaptation to the tainted condition [106].
2. The chemical skeleton of the targeted pesticide, which includes molecular weight, presence of functional groups, nature of bioavailable residual component (Complex polymer composites or simple compounds) determines the degradation of pesticides by microbes [107].
3. Micro-organisms generally degrade the complex compounds by their enzymatic machinery, the proper functioning of which depends on temperature, pH, nutrient and substrate availability, balanced C: N: P in the locale [108].
Table 9 shows a list of microbe succored pesticide degradation and the extent of their efficiency.

4.5. Enzymatic degradation

Another current approach to break down toxic pesticides in most natural and congenial way is the implication of microbial enzymes in the process. Unlike the technological methods, which often involve a huge cost and mostly inefficient in real-time utility, this microbial enzyme detoxification is way more efficient. This enzymatic degradation was found suitable in both soil and aquatic environment. The schematic representation of the enzymatic action is represented in Figure 5. Additionally, soil fertility enhancement, crop growth and nutrient richness were improved as reported. Some of the recent reports are listed in Table 10.

5. Conclusion

This review covers the recent spectra from the research fields of detection and degradation of pesticides. The various detection techniques with their simple working principles, comparative analyses are summarized. Researchers are focusing on the improvisation and fabrication of sensors for upgradation and accuracy. The detection sensors should be...
upgraded in terms of sensitivity and specificity annexing femto level detection. Advancements can be designed by combining multiple technologies, hence minimizing the limitations behind each technique. Currently, integrative technologies are coming up like combination of smartphone and electrochemical sensors for real-time monitoring. Sufficient literature exists for degradation strategies too. However, detailed metabolic pathways need to be explored for advanced monitoring and detoxification of pesticides from environment. The intermediate degradation products and compound kinetics should be explored more to determine the pathway of elimination of pesticide from the environment. Accurate detection techniques, followed by precise degradation, may help in solving the problems created by unavoidable pesticide usage. Beside all these scientific commodities, a proper legislative control and awareness can lead to the eradication of this pesticide pollution[122123].

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Disclosure statement

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