Chapter 19
Recent Developments in Nanotechnological Interventions for Pesticide Remediation

Rictika Das and Debajit Thakur

Contents

19.1 Introduction 554
19.2 Background of Nanotechnology 554
19.3 Nanobiotechnology 555
19.4 Nanomaterials 556
19.4.1 Nanoparticles in Pesticide Remediation 556
19.4.2 Green Synthesis of Nanoparticles 556
19.5 Mechanism Behind Nanomaterial-Based for Pesticide Sensing and Remediation 559
19.5.1 Homogeneous Chemistry 559
19.5.2 Heterogeneous Chemistry 559
19.6 Various Types of Nanoparticles for Pesticide Sensing, Remediation, and Elimination 560
19.6.1 Metal Nanoparticles 560
19.6.2 Bimetallic Nanoparticles 563
19.6.3 Metal Oxide Nanoparticles 564
19.7 Nanocomposites 567
19.8 Nanobiocomposites 568
19.9 Nanotubes 568
19.9.1 Carbon Nanotubes 569
19.9.2 Halloysite Nanotubes (HNTs) 570
19.10 Nanobioremediation 570
19.11 Biosensors for the Detection of Pesticides 571
19.11.1 Nanoparticle-Based Biosensors 571
19.11.2 Nanoparticle-Based Optical Biosensors 573
19.11.3 Nanotube-Based Electrochemical Biosensors 573

R. Das
Microbial Biotechnology Laboratory, Life Sciences Division, Institute of Advanced Study in Science and Technology (IASST), Paschim Boragaon Garchuk, Guwahati, Assam, India

Department of Molecular Biology and Biotechnology, Cotton University, Guwahati, Assam, India

D. Thakur (✉)
Microbial Biotechnology Laboratory, Life Sciences Division, Institute of Advanced Study in Science and Technology (IASST), Paschim Boragaon Garchuk, Guwahati, Assam, India

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19.12 Future Perspectives........ 573
19.13 Concluding Remarks........ 574
References........ 575

19.1 Introduction

In modern agriculture, pesticides are considered as an inescapable part for suppressing various flora and fauna pests in addition to prompt progression in urbanization and heavy industrialization that has ultimately urged to meet the demand for increase in agriculture yield to fulfill the needs of steady growth of population rate. Use of agrochemicals such as insecticides, herbicides, and fungicides kills the undesirable organisms (pests) along with some beneficial organisms existing in the ecosystem and also degrades the soil quality to a larger extent (Bhattacharyya et al. 2016). Moreover, pesticides tend to persist in the habitat for longer period causing serious issues like accumulation of undesirable residues, leading toxicity into the earth's stratum surface and also raising issues over food security using by the animals as well as the public. Worldwide, environmental protection and safety of public health has been considered as a pivotal issue and need to be addressed before time. Earlier classical methods have been used for removal of toxic wastes by chemical oxidation, adsorption, and biological oxidation, but these methods are time-consuming, with least cost effective. The emergence of nanotechnology in environmental sector has attained a great deal of interest and thus will be helpful for overall remediation through the application of nanoparticles (Prasad and Aranda 2018; Shash et al. 2019; Thangadurai et al. 2020; Saglam et al. 2021). The use of desired nanomaterials in environmental remediation with large surface-to-volume ratios act as sterling adsorbents, catalysts, and sensors thus in course increases the reactivity. Hence, there was utmost necessary for less time constraint as well as cost-effective method to remediate contaminated soil and groundwater at the hazardous sites and also breakdown to less hazardous products into the surroundings.

19.2 Background of Nanotechnology

During the period of 1980s, nanotechnology has come to the fore and gained popularity both in scientific and public domain having dimension sized ranging from 1 to 100 nm, where its unique phenomena enable novel applications. It basically deals with the use of nanomaterials in various scientific fields of biology, medicine, chemistry, physics, material science, engineering, etc. Currently the increasing efforts of using nanotechnology in the environmental sectors have improved the overall effectiveness of classical based remediation methods through the application of nanoparticles. With the constant development in technological tools, the implementation of nanotechnology in the field of detection of pollutants through techniques like

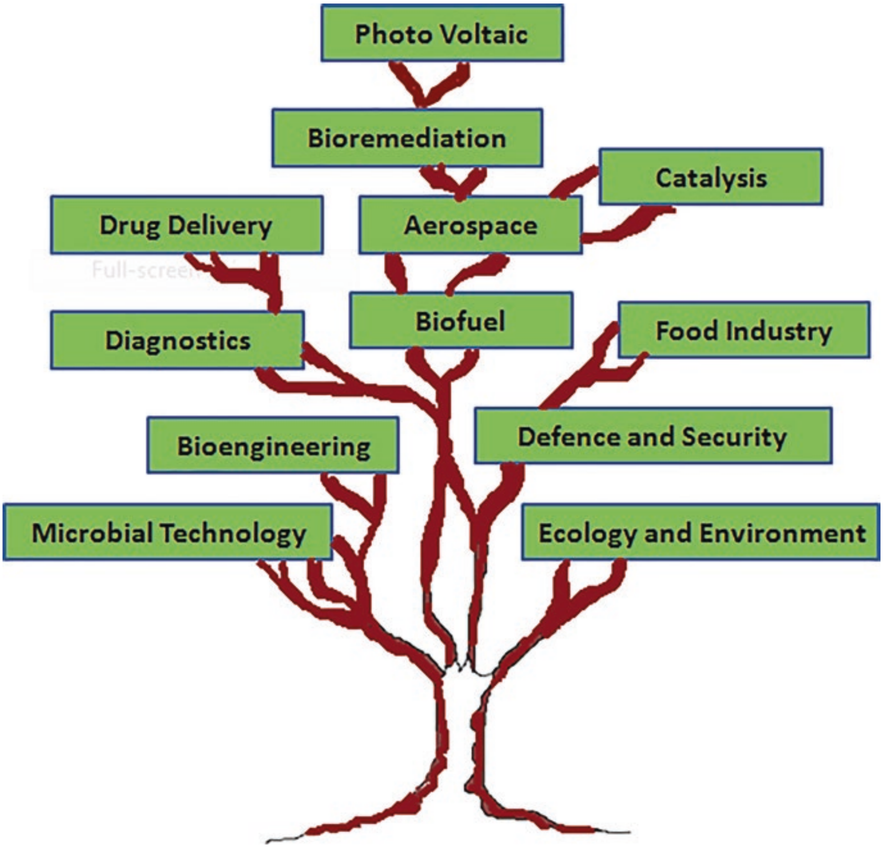

Fig. 19.1 Various branches of nanotechnology

surface-enhanced Raman scattering and electrochemical or optical detection is the need of the hour (Fulekar 2010; Tanwar et al. 2021) (Fig. 19.1).

19.3 Nanobiotechnology

In biotechnology, the knowledge and techniques of biology are applied to alter the molecular, genetic, and cellular processes to generate products and services that are being used in diverse fields from medicine to agriculture. Thus, nanobiotechnology is considered to be the unique fusion of two most progressive fields: biotechnology and nanotechnology where nanobiotechnology uses (nanoscale) biological starting materials. It has substantial potential for the programmed nano-/microfabrication of structured materials, to build tools for studying biological systems with specificity, better sensitivity, and a higher degree of recognition.

19.4 Nanomaterials

Nanomaterials has great potential in environmental remediation because of their large surface areas compared to their volumes (surface-to-volume ratio), thus acting as superior adsorbents and catalysts than other conventional tools within the range from 1 to 100 nm for efficient removal of hazardous chemicals and biological contaminants from the habitat. They can lead to very sensitive detection of pollutants to remediate the contaminants at a quicker rate with lesser hazardous by-products.

19.4.1 Nanoparticles in Pesticide Remediation

Nanoparticles exhibit a large number of special properties relative to bulk material; because of their specific size > than 100 nm; large surface area with exceptional parameters predominantly leads to a higher rate of detection of contaminants that allows to remediate these contaminants at a faster rate (Sun et al. 2006; Tosco et al. 2014). The utilization of zero-valent metals such as nickel, iron, and palladium has proved to be effective and better results in decontamination of toxic substances. Nanoparticles are synthesized by two approaches: The first approach is top-down synthesis thus involving the breakdown of bulk materials to nanoscale for obtaining nanoparticles, while the second approach is bottom-up synthesis involving the stacking-up of atoms and molecules of the bulk material mainly for the fabrication of nanoparticles. Now-a-days, the use of nanoparticles has been increased significantly by using countless nanoparticles for detecting, degrading, and removing contaminants and turn-up to be the most used in situ approach for remediation purpose (Ding et al. 2008). The major groups of NPs used for detection and degradation of pesticides are metal NPs, bimetallic NPs, and metal oxide NPs that have been frequently studied by the researchers.

19.4.2 Green Synthesis of Nanoparticles

In the past numerous years, nanoparticles synthesized by physicochemical techniques thus increase the accumulation of toxic, hazardous, and non-ecofriendly chemicals into the environment which impart non-lethal impacts on non-target organisms as well as on human population. With advancement of technology, the earnest need in synthesizing eco-friendly nanoparticles using non-toxic precursors having mild reactions and cost-effectiveness with environmental sustainability has help to emerge “green technology” by combining nanotechnology with green chemistry to exploit the potential of biological entities over physicochemical methods. Green synthesis approach provides a fast, easy, and eco-friendly nanoparticle production with environmental sustainability, simple, and reproducible approach with less hazards in the environment.

19.4.2.1 Bacterial Synthesis of Nanoparticles

Prokaryotes are comprised of single cell organisms such as bacteria that are considered as first choice for biosynthesis of nanoparticles due to their simplest structure and easy metabolism. The strong affinity for metals and its metal binding property by bacteria have helped in the synthesis of Au, Ag, Pt, Pd, Ti, nanoparticles, and so forth. The development of resistance mechanism like suppression and enhanced of influx system and efflux system, respectively, extracellular complexation, intracellular chelation, or precipitation and enzyme detoxification of metals (Silver 2003; Prasad et al. 2016) by bacteria after exposure to harsh metals and their metal ions have evolved in the large-scale synthesis of nanoparticles. Bacteria under the genus *Bacillus, Klebsiella, Lactobacillus,* and *Pseudomonas* fall under the category of nanoparticles by applying green technology. For instance, extracellular synthesis of nanoparticles by the member of Enterobacteriaceae (*Klebsiella pneumonia, Escherichia coli*, and *Enterobacter cloacae*) was first reported by Shahverdi et al. (2007). Similarly, silver nanoparticles were first synthesized by *Bacillus thuringiensis*.

19.4.2.2 Phytosynthesis of Nanoparticles

Plants possess the basic biological molecules such as carbohydrates, protein, and enzymes that have the immense potential to reduce metal salts for synthesis of nanoparticles. It is truly a one-step biosynthesis process where different plant extracts are employed due to their cost-effectiveness, easily scalable, safe to handle, less toxicity to overcome the drawbacks possessed by the conventional methods in synthesizing nanoparticles (Gurunathan et al. 2009; Prasad 2014; Srivastava et al. 2021). Biofabrication of nanoparticles by plant-based method can be easily available for large-scale production as compared to nanoparticles synthesized by microbe-based method since the latter rely more on the preservation of microbial culture that might generate toxic moieties which can be responsible for threatening both the environment and human population (Anuradha et al. 2015). Plant extracts are usually prepared from various parts such as extracts from plant leaves, juices of different medicinal plants, etc. are basically involved in mixing of plant extract with that of metal ions in a fixed ratio for synthesizing of nanoparticles. The nanoparticles are characterized by UV, XRD, and FTIR data analysis finally once they are synthesized (Table 19.1).

19.4.2.3 Nanoparticles Synthesized by Fungi and Yeast

Eukaryotic organisms such as fungi and yeast also come under the green synthesis approach of nanoparticles. Fungi has the potential to produce large-scale production of nanoparticles compared to prokaryotes (bacteria) because if the presence of various intracellular enzymes (Chen et al. 2009; Mohanpuria et al. 2008; Aziz et al. 2016, 2019; Prasad 2016, 2017; Prasad et al. 2018; Abdel-Aziz et al. 2018). Apart from monodispersity, fungi also help in the synthesis of well-defined dimensions of nanoparticles. The use of specific enzymes or metabolites; use of isolated

Table 19.1 Biosynthesis of nanoparticles from microbes and plants

Name of NP	Microorganism	References	Plant	References
Silver NPs	*Staphylococcus aureus* *Streptomyces* sp.	Kumar et al. (2011a, b), Alani et al. (2012)	*Sinapis arvensis* *Trigonella foenum-graecum*	Lam et al. (2018), Kavitha et al. (2013)
	Streptomyces naganishii *Brevibacterium casei*	Duran et al. (2011), Tripathi et al. (2015)	*Artemisia nilagirica* *Lantana camara*	Rasheed et al. (2017), Dimitrov (2006)
Gold NPs	*Rhodococcus* sp.	Yadav (2017)	*Abelmoschus esculentus*	Chaturvedi and Verma (2015)
	Klebsiella pneumonia	Balaji et al. (2009)	Angelica, Hypericum, Hamamelis Eucalyptus, Ocimum, Mentha	Subbaiya et al. (2014)
	Rhodopseudomonas capsulate	Park et al. (2011)	*Stevia rebaudiana*	Manivasagan et al. (2016)
	Rhodococcus sp., *Streptomyces* sp., *Streptomyces viridogens*	Ahmad et al. (2003a, b), Balagurunathan et al. (2011)	*Zingiber officinale*	Sinha et al. (2015) Pasca et al. (2014)
Iron NPs	*Shewanella oneidensis*, *Klebsiella oxytoca*	Narayanan and Sakthivel (2011), Binupriya et al. (2010)	Aloe vera, *Eucalyptus tereticornis*	Kumar et al. (2011a, b) Mishra et al. (2015)
	C. globosum	Elcey et al. (2014)	*Rosemarinus officinalis* Green tea	Kumar et al. (2012)
	E. coli, *Plerotus* sp.	Arcon et al. (2012) Kaul et al. (2012)	*Dodonaea viscose*	Kumar et al. (2012) Phumying et al. (2013)
Zinc NPs	*Lactobacillus*	Zhang (2003); Lee et al. (2008)	Aloe vera	Laokul and Maensiri (2009); Phumying et al. (2013)
	Streptomyces sp.	Raliya and Tarafdar (2014); Raliya and Tarafdar (2013)	*Nyctanthes arbor-tristis*	Taranath and Patil (2016)
	Candida albicans	Xu et al. (2005); Mazumdar and Haloi (2011)	*Nyctanthes arbor-tristis*	Jamdagni et al. (2016)

proteins instead of fungi culture has shown promising results in nanoparticle production. There are many reports regarding the ability of fungi to produce metal and metal oxides nanoparticles. The fungus *Verticillium* sp. is reported to reduce $AuCl_4$ ions and synthesis of Au nanoparticles on both the outer surface and the inner fungal cells with negligible reduction in the solution (Mukherjee et al. 2001; Shankar et al. 2004). *Fusarium oxysporum* have turn up for the extracellular synthesis of highly stable Au and Ag nanoparticles within the dimension range of 2–50 nm (Mukherjee et al. 2002; Ahmad et al. 2003a, b). The fungus *Aspergillus flavus* employed for the synthesizing of Ag nanoparticles wherein two proteins of 32 and 35 kDa are involved in the synthesizing process as well as gaining stability of synthesized Ag nanoparticles. Yeast (single-celled microorganisms) is also engaged in the synthesis of metallic nanoparticles (Ag and Au) by *Saccharomyces cerevisiae* regarded as more advantageous as compared to bacteria.

19.5 Mechanism Behind Nanomaterial-Based for Pesticide Sensing and Remediation

Pesticide detection, degradation, and finally removal from the environment basically involve two different type of chemistry: (a) homogeneous and (b) heterogeneous (Bond 1997). Thus, it is regarded as the fundamental method behind the chemistries for nanomaterials-based pesticide detection and removal, especially from water bodies.

19.5.1 Homogeneous Chemistry

This method first involves the nanoparticles diffused in water sample in presence of pesticide. The diffused nanoparticles then helps in the degradation or detection of pesticides present in water. The usage of most of the surface area, presented by the nanoparticles, is the fringe benefit of using this method. However, these nanoparticles are difficult to be removed from the water system, once they get diffused into it and might release toxic effects into the water system which can be a major concern of this method.

19.5.2 Heterogeneous Chemistry

This method involves the immobilized nanoparticles used on varied support materials before their use for detection of pesticides and remediation. Then these support materials are diffused into the water samples in presence of pesticide. The presence

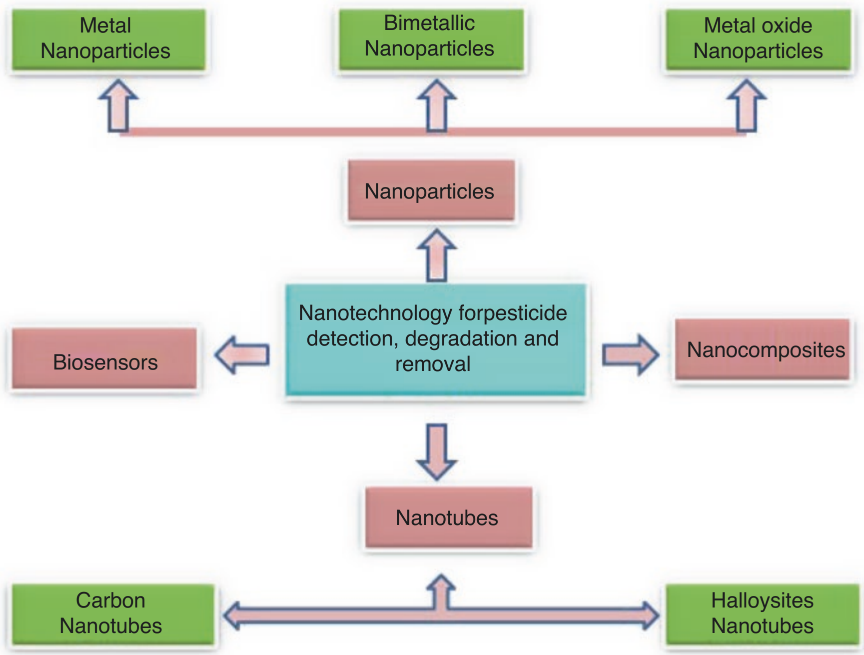

Fig. 19.2 Classification of nanotechnology-based approaches for pesticide sensing and detection

of immobilized nanoparticles into the support material helps in the detection and degradation of pesticides in the water system. The boon for heterogenous chemistry is the reuse of support systems for different water samples while detecting and degrading pesticides. The clump formation of nanoparticles is prevented through immobilization on solid supports are thus regarded as another benefit of using this method (Figs. 19.2 and 19.3).

19.6 Various Types of Nanoparticles for Pesticide Sensing, Remediation, and Elimination

19.6.1 Metal Nanoparticles

The NPs under the category of noble metals, namely, gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) along with the transition metal nanoparticles like iron (Fe), copper (Cu), and zinc (Zn) have found limitless applications in environmental remediation. The incomparable surface chemistry of these NPs allows the redox reaction that takes place at the exterior of the nanoparticle thus playing a significant part in the decomposition of toxic pesticides to small-scale size and less hazardous pollutants (Street et al. 2014).

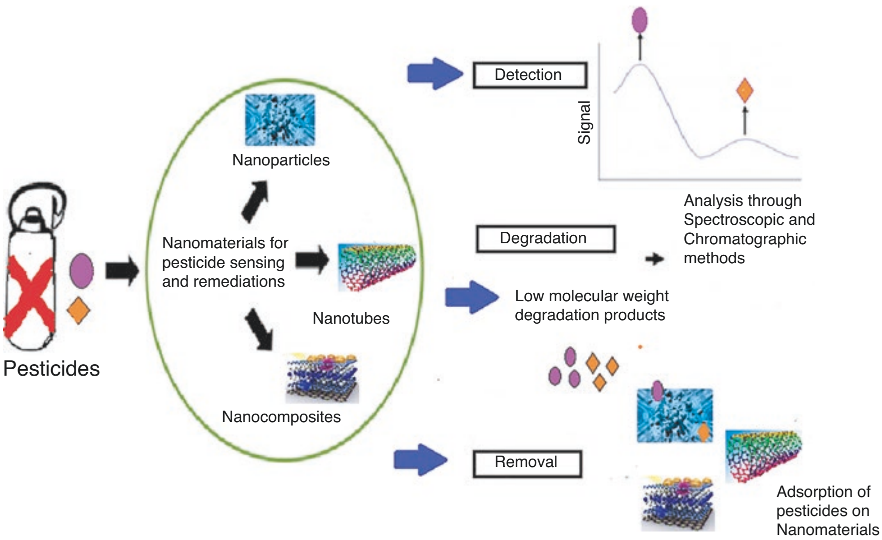

Fig. 19.3 Graphical representation of pesticide sensing, degradation, and elimination using nanomaterials

19.6.1.1 Gold Nanoparticles

From ancient times, gold has been regarded as a precious metal, and among the nanoparticles, gold is leading and has revolutionized the daily life. The AuNPs are familiar to have some properties like exhibiting various colors with change in size. The color change of AuNPs at different stages of agglomeration provides them to be a suitable visible material for analyte (Tsai et al. 2005). The sensitivity and specificity of AuNPs can be increased by their surface modification toward different pesticides. Sensors conjugated with AuNPs also help in the detection of organophosphates and organochlorines in the environment. The detection of DDT (organochlorine), by using AuNPs, is basically a colorimetric assay, where anti-DDT antibodies conjugate with AuNPs in the presence of DDT with various concentrations. The tested sample along with DDT blocks the anti-DDT antibodies followed by reduction of color intensity which is inversely proportional to the amount of DDT present in the tested sample.

19.6.1.2 Silver Nanoparticles

The AgNPs possess some specific properties of shape and size that enables their use in different fiber composites, biosensors and as antimicrobial properties (Rawtani et al. 2013; Prasad and Swamy 2013; Joshi et al. 2018). The optical properties of AgNPs with different sizes help in the sensing of pesticides. The surface modification of AgNPs similarly to AuNPs thus helps in increasing the sensitivity and specificity for the pesticides detection. Generally, dipterex an organophosphate insecticide found to be contaminated in aquatic bodies is detected by using AgNPs capped with citrate. When immobilized acetylcholinesterase enzyme is present along with citrate-capped AgNPs, it forms pink color due to the occurrence of thiocholine from acetylthiocholine in the presence of the enzyme acetylcholinesterase. But, no occurrence of thiocholine or pink color development takes place when the organophosphate dipterex is present since it inhibits the acetylcholinesterase enzyme (Lia et al. 2014). Due to the presence of acetylcholinesterase enzyme, it allows the formation of thiocholine on the substrate. This enzymatic action helps in the conversion of yellow color solution of RB-AgNPs to grey color. At the same time, the fluorescence of rhodamine B dye was also unquenched. Whereas, due to the presence of pesticides, no color formation or fluorescence occurs in the tested sample (Luo et al. 2017). Thus, this method of detection of pesticides is based on both colorimetric as well as fluorescence assay.Similarly, a herbicide known as paraquat has also been detected by using citrate-capped AgNPs. It also helps in the detection of carbaryl, an insecticide present in the vegetables, fruits, and river water with the help of modified rhodamine B dye. Various pesticides such as paraoxon and thiram (fungicide) are detected by using AgNPs as active substrates in surface-enhanced Raman spectroscopy (SERS). The emission of Raman signals from the target pesticide that gets deposited on the nanostructure surface (in this case AgNP) is increased by using SERS, thereby helping to detect very low limits of pesticides in the tested sample (Wang et al. 2014; Tanwar et al. 2021).

19.6.1.3 Iron Nanoparticles

The importance of iron is well understood in environmental remediation due to its contaminant portability, adsorption property, and mainly breakdown of iron into two valence states, i.e., ferrous iron Fe(II) (water soluble) and ferric iron (III) (water insoluble). The rusting of iron is well known in presence of oxygen helps in the formation of iron oxide. Thus both iron and iron oxide nanoparticles are considered as convenient nanoparticles for environmental remediation. For instance, the degradation of the pesticide 2,4-dichlorophenol is being degraded by biosynthesizing FeNPs by means of adsorption. The split of the benzene ring on 2,4-dichlorophenol during the degradation process emerge in the formation of acetone and acetic acid as the starting products which are then detected on GC-MS (Guo et al. 2017).

The utilization of zero-valent iron nanoparticles (ZV-FeNPs) is considered as a useful technique for remediation of organochlorine as well as micropollutant from the environment. It has been reported that lindane, an organochlorine, has been degraded by using ZV-FeNPs. It was found that the organochlorine was degraded to a large extent by the particles post polymer stabilization thus raising the exposure period of the pesticide. Lindane degradation mainly involves dichloroelimination and dehydrohalogenation, and during this degradation phase benzene, chlorobenzene, and dichlorobenzene are regarded as the main products (San Roman et al. 2013) (Table 19.2).

Table 19.2 Nanomaterials used for detection of pesticides

Nanomaterial	Type of nanomaterial	Modification	Pesticide	Matrix	Detection limit	References
Metal nanoparticle	AuNPs	Conjugation with anti-DDT antibodies	DDT	Grapes, Cauliflower	27 ng/mL 0.65–	Lisa et al. (2009)
		Conjugation with IgG antibody	Kitazine	Tomato, Cucumber	2.44 mL/mL	Malarkodi et al. (2017)
	AgNPs	Capping with citrate	Dipterex	Water	0.18 ng/mL	Lia et al. (2014)
		Conjugation with Rhodamine B	Carbaryl	Tomato, Apple, River water	0.023 ng/L	Luo et al. (2017)
Metal oxide nanoparticle	SiO_2NPs	Immobilization of AChE and AuNPs	Paraoxon	Spiked pesticide solutions	500 nM	Luckham and Brennan (2010)
		Conjugation with anti-FNT and anti-CLT antibodies	FNT and CLT	Spiked pesticide solutions	0.25 ng/mL	Wang et al. (2013)
Nanotube	Carbon nanotubes	Coating with silica and immobilization of phthalocyanine ruthenium	FNT	Orange juice	0.45 mg/mL	Canevari et al. (2016)
		Immobilization of AgNPs	Dimethoate	Orange and lake water	0.01 mg/mL	Hsu et al. (2017)
	Halloysite nanotubes	Immobilization of TiO_2NPs	Parathion	Strawberry, celery, apple		Saraji et al. (2016)

AuNPs gold nanoparticles, *AgNPs* silver nanoparticles, *DDT* dichlorodiphenyl trichloroethane, *SiO_2* NPs silica nanoparticles, *AChE* acetylcholinesterase, *FNT* Feni-trothion, *CLT* chlorpyrifos methyl, *TiO_2NPs* titanium oxide nanoparticles

19.6.2 Bimetallic Nanoparticles

These nanoparticles consist of some interesting characteristics of combination of two metal nanoparticles in the interior of a single nanoparticle (Zaleska-Medynska et al. 2016). The utilization of bimetallic nanoparticles (BNPs) in the field of pesticides removal and degradation takes place by means of reduction by using Fe/Ni NPs (Liu et al. 2014). The degradation of the organophosphate, profenofos, takes place by using Fe/Ni BNPs as a catalyst. Here, nanoscale zero-valent iron (nZVI) particles act as a reducing factor for the pesticide degradation wherein Ni safeguards the surface of nZVI particles from corrosion. Various studies have found the utilization of Fe/NiNPs, having nZVI particles for dechlorination of the herbicide sulfentrazone (Nascimento et al. 2016). In addition to this, the degradation of 4-chlorophenol takes place where superoxide radicals provide an effective mechanism for its degradation via bimetallic system having nZVI/Ni particles (Shen et al. 2017). Recently, chlorpyrifos, an organophosphate, where degradation is being carried out by green synthesized of Ag/CuBNPs where BNPs act as nano-catalyst that provides an environmental friendly route for water purification from pesticide contamination (Rosbero and Camacho 2017) (Table 19.3).

19.6.3 Metal Oxide Nanoparticles

This type of nanoparticle due to their superconducting nature is widely used for environmental remediation. These superconducting properties of metal oxide NPs come up with an effective and specific photocatalysis activity that has been applied in diverse research work for sensing and remediation of pesticides. Various types of metal oxide NPs are involved for pesticides sensing, degradation, and removal from diverse sources. These nanoparticles (NPs) are mainly silicon oxide (SiO_2), zinc oxide (ZnO), titanium oxide (TiO_2), and iron oxide (Fe_2O_3orFe_3O_4) have been taken into account.

19.6.3.1 Titanium Oxide Nanoparticles

TiO_2NPs have proved to be a promising candidate for metal oxide NPs due to their exceptional features, like photocatalysis, cost-effective, non-toxicity, and stability in connection with chemicals. They possess huge surface area for photocatalytic activity, thus increasing their consumption for pollutant remediation from the surrounding. It was reported that a study was carried out at Dindigul district in Tamil Nadu, where TiO_2NPs have been applied for chlorpyrifos and monocrotophos degradation present in pond and deep well water. The degradation of these pesticides was triggered by irradiation of the photocatalyst in presence of UV light. It was found that with increase in glow time, there was an increase in the photodegradation efficiency (Amalraj and Pius 2015).

Mesoporous TiO_2NPs is regarded as the most widely used mesoporous material due to their large surface area and intrinsic property. This NP was first synthesized by Antonelli and Ying using modified sol-gel method (Antonelli and Ying 1995). These NPs are used for the microextraction of six organochlorine pesticides, namely, hexachlororbenzene (HCB), *trans*-chlordane, *cis*-chlordane, o,p-DDT, p,p-DDT, and mirex. Fabrication of solid-phase microextraction fiber by using TiO_2NPs helps in the removal of these pesticides. TiO_2NPs helps in the degradation of carbendazim, a widely used fungicide, by doping with Fe and Si ions. Thus by doping, the photocatalytic activity of NPs has been increased resulting to a larger extent of degradation (98%) of the fungicide in presence of UV light (Kaur et al. 2016).

Table 19.3 Nanomaterials used for degradation of pesticides

Nanomaterial	Type of nanomaterial	Modification	Pesticide	Matrix	Mechanism of degradation	Degradation efficiency (%)	Reference
Metal nanoparticle	FeNPs	Immobilization with laccase	Chlorpyrifos	Spiked pesticide solution	Enzyme-based catalysis	99	Das et al. (2017)
		Coating with carboxymethyl cellulose	Lindane	Water	Dichloroelimination and dehydrohalogenation	95	San Roman et al. (2013)
Bimetallic nanoparticle	Fe/NiNPs	e	Profenofos	Spiked pesticide solution	Catalytic reduction	94.5	Mansouriieh et al. (2019)
		e	Sulfentrazone	Spiked pesticide solution	Dechlorination	100	Nascimento et al. (2016)
	Ag/CuNPs	e	Chlorpyrifos	Water	Catalytic reduction	e	Rosbero and Camacho (2017)
Metal oxide nanoparticle	TiO_2NPs	e	Chlorpyrifos and Monocrotophos	Pond and bore well water	Photocatalysis	>95	Amalraj and Pius (2015)
		Doping with Fe and Si ions	Carbendazim	Spiked pesticide solution	Photocatalysis	98	Kaur et al. (2016)
	ZnONPs	e	Methylparathion and parathion	Water	Photocatalysis	93	Sharma et al. (2016)
Nanocomposite	Graphene oxide and AG NPs	e	Chlorpyrifos, Endosulfan and DDE	Water	Catalytic dehalogenation	95	Koushik et al. (2016)

FeNPs iron nanoparticles, *Fe/Ni* NPs iron/nickel nanoparticles, *Ag/Cu* NPs silver/copper nanoparticles, *TiO_2NPs* titanium oxide nanoparticles, *ZnO NPs* zinc oxide nanoparticles, *AgNPs* silver nanoparticles, *DDE* dichlorodiphenyl- dichloroethylene, *Fe_3O_4 NPs* ferric oxide nanoparticles

19.6.3.2 Zinc Oxide Nanoparticles

ZnO NPs possess both distinctive chemico-physical nature, due to their specific size and high density at the edge of the surface. The surface functionalization of ZnO NPs increases their detection and catalytic properties and thereby engaged in pesticide remediation from varied samples. ZnO NPs act as nano-photocatalyst that helps in the degradation of methyl parathion and parathion present in water samples. These pesticides were basically degraded after irradiation of the photocatalyst with the UV light. It showed around 93% degradation of the target pesticides when carried out under optimum condition (Sharma et al. 2016).

ZnO NPs helped in the removal of permethrin, a broadly used neurotoxic pesticide in agriculture field that was removed from nearby water samples. This NP along with chitosan helps in bead formation for the effective removal of the pesticide. Highest removal efficiency was found to be 99% of the pesticide at neutral pH. The beads formation has proved to be a convenient one for water purification with 56% recovery after three cycles (Dehaghi et al. 2014).

19.6.3.3 Iron Oxide Nanoparticles

These nanoparticles mainly consist of maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) particles having wide applications in pesticides remediation from varied samples. The basic concept of nanoparticles is the increase in the surface area to volume ratio remarkably thus the immobilization of iron oxide nanoparticles in different matrices helps in the sensing and degradation of the target pesticides. This perspective of involvement of iron oxide NPs for pesticide remediation thus increased by controlling the size, shape and surface properties of these NPs with both efficiency and specificity. Thus it plays an important role in the detection of various kinds of agro-inputs used in different sources. Glyphosate, a broad-spectrum systemic herbicide, is being removed from water system by using iron oxide NPs, entrapped in mesoporous silica where the immobilization increases greatly the surface area and the porous nature of the magnetic adsorbent (Fiorilli et al. 2017). The systemic fungicide, fenarimol, is being removed of post immobilization in palygorskite, a type of clay mineral by using iron oxide (Fe_2O_3) NPs thereby increasing the holding capacity of palygorskite for removal of the fungicide fenarimol. This method showed 70% adsorption rate for fenarimol, thus suggesting the broader use of iron oxide NPs for sustained removal of fungicide (Ouali et al. 2015).

19.6.3.4 Silica Oxide Nanoparticles

These are also known as silicon dioxide nanoparticles or nano-silica particles. They have some special characteristics of adsorbent; spherical, porous nature; as well as the increase in surface area which allow the extraction efficiency of varied pesticides from different sources. Sulfonylurea found in water samples are removed by using silica oxide NPs post functionalization with N-methylimidazole. The process of functionalization helps in the enhancement of adsorption of polar pesticide on the surface of silica oxide NPs. Different types of organophosphates, namely, chlorpyrifos, methidathion, dicrotophos diazinon, mathamidophos, and malathion, have been extracted by using silica oxide NPs after co-functionalization with polar cyanopropyltriethoxysilane (CNPrTEOS) and non-polar methyltrimethoxysilane (MTMOS) and are finally analyzed by using HPLC or GC-MS (Ibrahim et al. 2013). Further, silica oxide NPs have been used by using various methods such as electrochemical, optical, and surface-enhanced Raman spectroscopy (SERS) for pesticides detection (Bapat et al. 2016). The enzyme acetylcholinesterase (AChE) binds with the silica oxide NPs that have been used for the detection of the pesticide paraoxon by using a colorimetric assay particularly known as "dipstick" assay. The detection of the pesticide at very low limits is thus increased by entrapment of AuNPs in silica oxide NPs along with the enzyme (Luckham and Brennan 2010). Similarly paraoxon can also be degraded by using enzymes such as organophosphate hydrolase and carboxyesterase that have been immobilized on mesoporous SiO2 NPs (Boubbou et al. 2012). Chlorpyrifos methyl (CLT) and fenitrothion (FNT) are detected by using antibody-tagged silica oxide NPs where monoclonal antibodies (anti-FNT and anti-CLT) isolated from mouse was found to link covalently with the silica oxide NPs for detection of pesticides (Wang et al. 2013). For detection of pesticides, SiO_2 NPs have been utilized with the help of optical, electrochemical, SERS, or fluorescence methods (Bapat et al. 2016); AChE immobilized SiO_2NPs used for detection of the paraoxon. Again, AuNPs entrapped in SiO_2 NPs along with the enzyme to increase the detection of the pesticide at very low levels (Luckham and Brennan 2010). Moreover, antibody-tagged SiO_2 NPs have been used for detecting fenitrothion (FNT) and chlorpyrifos methyl (CLT) where monoclonal antibodies from mouse (anti-FNT and anti-CLT) were covalently linked with the NPs for the pesticide detection (Wang et al. 2013). Recently, these type of procedures are regarded as a promising approach where silica oxide NPs are involved for degradation of broad range of pesticides using biotic system due to cost-effectiveness and eco-friendly nature which have attracted the attention among the researchers.

19.7 Nanocomposites

A nanocomposite falls under a broad range of materials that consist of a multiphase solid material that incorporates nanosized particles (i.e., metals, semiconductors) into a matrix having at least one dimension in the regime of nanoscopic size. Recently, several nanocomposite materials that include nanoparticles of metals, metal oxides, carbon nanotubes, plant-based nanocomposites, etc. with specific properties have played a major role for environmental remediation of pesticides more effectively from contaminated sites. Generally, nanocomposites express great surface area to large surface and volume ratio compared to normal adsorbents (Kamigaito 1991). Nowadays, graphene oxide (GO) and reduced grapheme oxide (rGO) has been widely used for the production of nanocomposites by using various metal and metal oxide NPs for pollutants remediation. Nanocomposite with Fe_3O_4 NPs has been developed by using rGO for elimination of triazine (broad-spectrum herbicide). The presence of electrostatic interlinkage between nanocomposite and analyte is thus capable of pesticide removal with high adsorption (Boruah et al. 2016). Apart from this, rGO along with AgNPs are also used for the degradation of organophosphates and organochlorine pesticides. This involves a two-step mechanism where AgNP induce removal of halogen from pesticide followed on adsorption of the degradation product of the target pesticide (Koushik et al. 2016). Nanocomposites are also used to prepare montmorillonite clay (a very soft phyllosilicate group of minerals) by using hexadimethrine, a cationic polymer, to increase the efficiency of transduction for removal of a commonly used herbicide, 2-methyl-4-chlorophenoxy acetic acid (MCPA) (Gamiz et al. 2015). Thus, the utilization of nanocomposites works as a boon when it is combined with different materials, which signifies the improvement for the detection and degradation of various pesticides.

19.8 Nanobiocomposites

These are the noble class of composite materials which have great potential where nanofillers are used in biopolymer matrix of the nanocomposite system. Nowadays, bio-based products have shown promising results due to their sustainability in the environment. Biopolymer possesses hydrophilic nature that makes them efficient adsorbents for pollutant remediation from aquatic system. Recently, chitosan-based nanobiocomposite have grabbed more attention among the researchers due to their phenomenal characteristics of biodegradable and biocompatible. The intercalation process helped in the synthesis of Ag/chitosan nanobiocomposite where both chitosan and silver nitrate solution are mix together and followed by microwave irradiation (Saifuddin et al. 2011). Microwave irradiation is a method that uses "one-pot" synthesizing of metal NPs by using metal salts and solutions of polymer surfactants. When it is exposed to this method, silver nitrate reduction takes place for the formation of Ag NPs. Finally, synthesis of Ag/chitosan nanobiocomposite is obtained for the removal of atrazine (herbicide) from drinking water.

19.9 Nanotubes

A nanomaterial with long and hollow cylindrical shaped with length varying from nm to mm is usually defined as a nanotube. The diameter of this tube-form nanotubes ranges in nanometers of (~1–100 nm). Nanotubes functions as good adsorbents due to its different parameters such as big surface area, surface modification with high aspect ratio. Thus these parameters have enabled the use of nanotubes for detection and degradation of pesticides from the contaminated sites. Based on the above based criteria, nanotubes are classified into carbon nanotubes (CNTs) and halloysite nanotubes (HNTs) that have attracted considerable attention among the researchers because of their unique properties and big surface area.

19.9.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are believed to be promising material as building blocks that have better efficiency as compared to traditional adsorbents (e.g., activated carbon) due to the presence of mesoporous structure and high surface area consisting of different functional groups like phenol, carboxyl, and hydroxyl. They have higher efficiency in adsorbing large number of organic compounds and thus the process of adsorption takes place between the electrostatic attraction and formation of chemical bonds with an outer diameter ranging from 4 to 30 nm. The structure of CNTs depicts with hollow, ordered, graphene-based nanomaterial and bonded with sp^2 hybridization and acts as an exceptionally strong interaction. Some ideal properties of CNTs like thermal conductivity, high tensile strength, less weight, and high aspect ratio have not only limited their applications to electrical, electronics, sensors, and thermal devices but also attracted the researchers in the field of environmental nanotechnology (E-nanotechnology) for removal of recalcitrant from various contaminated sites. They are classified into two types:

(i) *Single-Walled CNTs (SWCNTs)*
Nanotubes with single sheet of grapheme shell is rotated up, to form a tube-form structure are known as single-walled CNTs (SWCNTs). It was first reported in the year 1993 (Iijima et al. 1993). The diameter of SWCNTs ranges less than 1 nanometer.

(ii) *Multi-walled CNTs (MWCNTs)*
Nanotubes with multi-walled sheets of grapheme shell consisting of concentric SWCNTs having an outer diameter and inner diameter of (50–80) nm and (5–15) nm, respectively, and spacings between the adjacent layers is of 3.4 $\mathring{A}$. In the recent years, adsorption is considered as the most efficient and feasible technology for pollutants removal by transferring the required pollutant from water phase to solid phase (adsorbent) to collect the removal. It was found that MWCNTs are utilized as good nano-adsorbents to eliminate pesticide residues through solid phase extraction technique from tea and later on analyzed by using GC-MS/MS. The spiked pesticide residues in the tea samples are being removed and detected in GC-MS/MS and hence proved to be a skilled technique for pesticides removal.

Fenitrothion, an organophosphate insecticide, is being used in fruits, vegetables, rice, cereals, stored grains, etc. where the insecticide is determined by electrochemical detection with phthalocyanine ruthenium (RuPc); RuPc is being used as the catalyst for the redox reaction by using silica-coated MWCNT. The method behind the detection of dimethoate, an organophosphate insecticide to kill insects and mites with oxidized MWCNTs capped with AgNPs, catalyzes the oxidation of ample red (AR)-hydrogen peroxide system into resorufin, a crystalline dye. So, in the presence of dimethoate, this oxidation reaction is inhibited (Hsu et al. 2017).

19.9.2 Halloysite Nanotubes (HNTs)

HNTs are naturally viable clay nanomaterial having different morphologies, such as tube-form, spheroidal with elongated tubes, the last being the most common among all the three. They exhibit large surface area with both positively and negatively charged from inner and outer surface respectively thus providing greater adsorption properties (Rawtani and Agrawal 2012). This adsorption capacity of HNT plays a major role in detection and degradation of toxic organic compounds from the environment. Due to their increase biocompatibility and lower cytotoxicity, HNT plays a major part in recent applications such as tumor cell isolation, as scaffolds for tissue engineering, novel drug, and gene delivery. Apart from all these, most importantly, the non-toxic effects exhibited by HNTs have been regarded as a boon into the environmental remediation by the replacement of toxic and expensive carbon nanotubes.

19.10 Nanobioremediation

Nowadays, bio-based sustainable remediation has gained a lot of attention due to its low risks by minimizing the subsidiary impacts of waste generation, consumption of natural resource, etc. But it was observed that bioremediation techniques are time-consuming and might have negative impact on the existing microorganisms if present at higher concentration. Basically, a single technology may not be sufficient for removal of recalcitrant from the polluted site that might be expensive and may not be efficient, high specificity, non-hazardous, and viable. This led to the combination of multiple technologies along with their applications for a single as well as effective remediation technology with less cost effective, high specificity, and better efficiency. Therefore, a promising integration of nanotechnology and biotechnology could overcome this limitation and emerged a more strong and sustainable remediation method known as nanobioremediation. It basically uses the applications of physico-chemical (fast, but expensive) and biological methods (cheap, but relatively slow) for biodegradation of soil and water contaminants to a low risk level and less toxic environment. It was found that nanoparticles used by plants, fungi, and microbes could enhance the microbial activity by removal of pollutants such as both organic and inorganic toxins and heavy metals from the surrounding (Singh and Walker 2006).

19.11 Biosensors for the Detection of Pesticides

Biosensor was first introduced by Cammann in the year 1977. Earlier pesticide residues are being determined in soil and water by using some sophisticated instruments like high-performance liquid chromatography and mass spectroscopy, liquid/gas chromatography. Since these approaches are regarded as highly efficient but at the same time require hardcore sample preparation, along with some highly qualified technicians for analyzing the samples. Therefore, great efforts are devoted for replacement of conventional methods with better sensitivity screening, low cost, and stability for detecting low levels of pesticides. Researchers have carried out rigorous efforts for the development of efficient, cost-effective, eco-friendly nanomaterial-based biosensors, which can detect the presence as well as concentration of organic compounds when present in limited or low amounts. A biosensor basically comprises of three parts: a component that recognizes the analyte and produces a signal, a signal transducer, and a reader device (Fig. 19.4).

19.11.1 Nanoparticle-Based Biosensors

19.11.1.1 Enzyme Biosensors

Here, enzymes are being used as identification component for detection of hazardous substances from both stratum and beneath of earth's surface with high accuracy and precision, high specificity and sensitivity, robustness, and safety. Through enzyme biosensor, information is not obtained regarding a particular pesticide; rather they provide detection of broad categories of pesticides. Since acetylcholinesterase is mostly inhibited by organophosphorous pesticides, hence it is regarded as the basis for enzyme biosensor. Acetylcholinesterase (AChE), butyrylcholinesterase (BChE), or urease is being used as biological receptors where they act as catalytic activity reducers for inhibition of enzyme-based biosensors for detecting pesticides is regarded as the basic mechanism behind the enzyme biosensor. In these reactions, several methods like amperometric, conductometric, and optical are employed for choline detection, the main reaction end-product. Hence, researchers have developed AChE-based biosensors where acetylcholine (ACh) is converted by

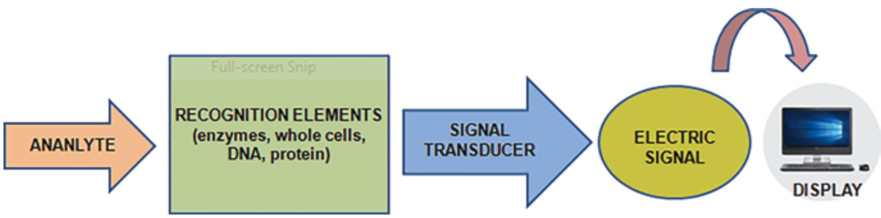

Fig. 19.4 Various parts of a biosensor

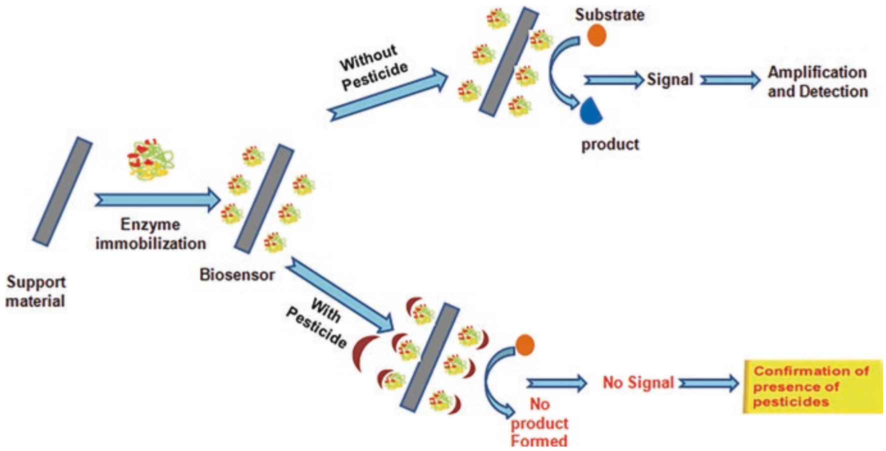

Fig. 19.5 Graphical representation of the mechanism behind pesticide detection using enzyme-based biosensor

AChE into acetic acid and choline (Ch) in presence of H_2O. The intensity of this reaction gives information about the detection of pesticides.

$$\text{Acetylcholine} + H_2O \xrightarrow{\text{AChE}} \text{Choline} + \text{Acetic acid}$$

Enzyme-based biosensors customize with different nanoparticles like quantum dots (QDs) and gold nanoparticles (AuNPs) are basically used for organophosphates, organochlorines detection in the environment. For instance, monocrotophos is being able to detect by this type of customized-based enzyme biosensors (Fig. 19.5).

19.11.1.2 Immunosensor

This type of sensor basically provides information regarding a specific pesticide, having high selectivity and sensitivity of antibody-antigen reaction. Conductimetric immunosensor helped in the detection of atrazine, by using antibodies labeled with NPs (Valera et al. 2008). Diuron, a substituted phenyl urea herbicide, was developed by an electrochemical immunosensor for its fast screening (Sharma et al. 2011). Fabrication of polystyrene substrate helps in the removal of low cost electrodes thus by modifying with Prussian Blue (PB)-AuNP film that helped in the enhancement of transfer of electrons in the domain of the gold electrode thereby increasing its sensitivity compared to unmodified gold electrodes.

19.11.2 Nanoparticle-Based Optical Biosensors

The use of nanoparticles has an important role in developing efficient optical biosensors for pesticide detection. Nanoparticles such as semiconductor QDs are frequently used in fluorescent sensing. These QDs or polymer nanoparticles are considered as highly photostable than a conventional fluorophore and thus allow high fluorescence quantum yields and also exhibit high sensitivity. Monocrotophos (organophosphate insecticide) can be detected through optical biosensor by CdTe as fluorescence probe (Sun et al. 2011). Recently, it was found that QDs-based fluorescence assays are able to detect several organophosphates and the activity of AChE (Saa et al. 2010; Chen et al. 2013; Yu et al. 2014; Zheng et al. 2011; Buiculescu et al. 2010; Garai-Ibabe et al. 2014).

19.11.3 Nanotube-Based Electrochemical Biosensors

The interaction between an analyte with an electrode (e.g., platinum, gold, silver, graphite) is usually measured in terms of potential or current for detection of electrochemical wherein various changes like chronoamperometry and chronopotentiometry cyclic voltammetry are observed by using abundant of techniques (Grieshaber et al. 2008). The use of nanoparticles such as modified carbon nanotubes have basically helped in enzyme electrodes, specifically electrochemical biosensor in various fields such as biosensing, biomedical engineering, nanoelectronics, and bioanalysis. Recently electrochemical biosensor has been developed by using CNTs for inhibiting the activity of AChE (Du et al. 2007; Oliveira and Mascaro 2011; Firdoz et al. 2010; Qu et al. 2010). This biosensor has shown promising results in terms of sensitivity and stability regarding pesticides monitoring in aquatic system.

19.12 Future Perspectives

The field of nanotechnology has great perspective in retransforming the previous used conventional techniques with high specificity, cost-effective, small-scale size, low detection limits and high sustainability in environmental remediation. In addition to these, utilization of various nanotechnology-based nanomaterials such as metals and metal oxides helps in increasing the removal of organic pollutants by means of reducing or oxidizing of metals along with functional groupings of chemical groups that can selectively detect the target pesticides from the contaminated sites. The use of nanoparticles such as AuNPs, TiO_2 NPs, ZnO NPs, AgNPs, and SiO_2 NPs together with nanocomposites and nanotubes like CNTs and HNTs helps to detect or sense pesticides when they are present at very negligible level. The surface modifications of these nanoparticles help in the enhancement of both sensitivity and specificity for pesticide detection. For instance, ZnO NPs and nanotubes like CNTs and HNTs have proved to increase the removal efficiency by 99–100%. The practical applications of CNTs or magnetic composites should be explored more in the future. Biosensors are considered as superior candidate for pesticides recognition in complex samples. Enzyme inhibition-based biosensors have shown better results for detection of pesticides. The large-scale use of polymeric adsorbents has shown promising results in adsorption of metals and organic pollutants. Moreover, the capability of reuse and increasing the lifespan of these adsorbents should be investigated further to reduce the cost for pesticide remediation. Further, the understandings of nanotechnological applications in the bioremediation and nano-bio-interactions accelerate the development of nanopesticide. The wide use of the pesticide for the management of tea pest aggravates various concerns such as non-target toxicity to parasitoids and insect predators, development of resistance, and upsetting the ecological balance and heavy load of pesticide residue in tea leaves. Exploiting advantages of nanotechnological interventions and aligning it with green chemistry and environmental sustainability principles hold tremendous potential in combating tea plant pest. Recent report demonstrated alteration of the nonsystemic behavior of the pesticide ferbam on tea leaves by engineered gold nanoparticles (Hou et al. 2015). These finding open up new avenue of research and translational development in nanopesticide for an integral part of Integrated Pest Management (IPM) practices of tea plant.

19.13 Concluding Remarks

Nanoremediation has emerged as a new scope for environmental remediation from the field of nanobiotechnology that has immense potential for diminishing recalcitrants from the habitat to a more greenish environment. The effectiveness of nanoremediation has helped in the overall reduction of xenobiotics that has approximately reach to zero level in in situ nanoremediation due to cost effective, high competency as well as large-scale application compared to ex situ nanoremediation which needs to be workout for better results. The applications of various nanoparticles and biosensors having some specific characteristics of large surface area, high specificity, and small-scale size with quick response have helped to overcome the drawbacks for detection of pesticides at very low levels of detection in the environment over the conventional techniques. However, the toxicity of nanoparticles (carbon nanotubes, metals, and metal oxide NPs) cannot be denied completely because of their lethal effect on the significant proliferation over the microorganisms. Hence, more meticulous research is utmost necessary in this regard so that nanoremediation emerged as a promising tool in the future for contaminant remediation and also for better environmental sustainability.

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