Chapter 11
Role of Metal Nanomaterials in Bioremediation of Pesticides

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Abstract Due to increased global demand in agriculture, pesticides are broadly used in agricultural field for controlling pests that infest crops. The overall use of pesticides in the world has reached approximately 2 million tons. The World Health Organization classified itself as very dangerous and highly hazardous. Use of more chemical pesticides in agriculture causes more pollution and also leads to biomagnifications in different trophic level of organisms that affect biodiversity. Several technologies are being used for controlling pollution, among them nano-biotechnology is an alternative technology for remediation of pollution. Bioremediation method utilizes microbes to dispose of pollutants. Carbon nanomaterials, metal nanoparticles, magnetic nanoparticles, and quantum dots are examples of nanomaterials used for water exceptional monitoring, including those used to detect trace contamination and pathogens. Nanosized elemental or zero-valent metallic nanoparticles, i.e., of iron, silver, gold, copper palladium, and nickel have proven promoting effects towards contaminated sites with different hazardous pesticides. This chapter is an effort to consciousness on the promising application of metal nanomaterial-based technology and its assimilation with diverse essential tactics related to the bioremediation of pesticides.

Keywords Pesticides · Metal nanomaterial · Bioremediation · Agriculture · Pollution

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S. Siddiqui et al. (eds.), *Pesticides Bioremediation*,
https://doi.org/10.1007/978-3-030-97000-0_11

11.1 Introduction

Population growth is making more demand in agriculture manufacturing for both industrial advancement and urbanization which are being important resources of environmental pollution in the course of the twentieth century. Pesticides are being used to manage or control the pest populations below the economic injury level. Pesticides are chemical compounds that are broadly used in agricultural field for controlling pests that infest crops. These are the substance or mixture of substance which differ in their physicochemical properties. Hence, they could be classified on the basis of their properties. Moreover, numerous pesticides based on the demands are categorized into different classes. Presently, the three most popular classifications of common pesticides are entry mode, pesticide-based function, and pesticide-based organism. The overall use of pesticides in the world has reached approximately 2 million tons. The World Health Organization classified itself as very dangerous, highly hazardous, and moderately dangerous in four different classes based on the toxicity of pesticides (Pimentel 2002). Due to developing industries and use of chemical pesticides in agriculture, which causes more pollution and also leads biomagnifications in different trophic level of organisms that affect biodiversity. Several technologies are being used for controlling pollution, among them nanobiotechnology is an excellent approach for the environmental remediation. In the present scenario, many pollutants like hydrocarbons, heavy metals, pesticides, and other toxic substances are being more threat to our surroundings. Among these pollutants, contamination of soils, reduction of soil fertility, air and water are polluted with various dangerous substances. Although many conventional methods, i.e., precipitation, electrocoagulation, and adsorption on various substrates are in use, but a safer and cost-effective and environmentally sustainable approach is highly recommended for environment contaminant remediation (Fomina and Gadd 2014). Microorganisms are popularly used in bioremediation as it is economical method compared to other conventional methods. Bioremediation using microorganisms is greatly dependent on the availability of particular microbial species and combination of favorable environmental conditions (Adams et al. 2015). Bioremediation methods are effective for the treatment of contaminated water and soil due to its ability to degrade contaminates by using natural microbial activities which can be easily controlled by using different strains. Bioremediation includes any method that utilizes plants, microbes and their extracts or enzymes to restore the natural world after it has been contaminated (Rathore et al. 2014; El Amrani et al. 2015).

Nanotechnology has the capacity to offer a sustainable option to the worldwide demanding situations associated with defensive soil, water, and providing air cleaner. Nanoscience allows materials to be engineered and controlled at the molecular and atomic levels. Nanomaterials can be produced with specific functions that enable it to identify a specific contaminant within a mixture. The length of nanomaterial along with their excessive floor-to-quantity ratio results very precise detection

(Das et al. 2015; Asztemborska et al. 2015). Carbon nanomaterials, metal nanoparticles, magnetic nanoparticles, quantum dots are examples of nanomaterials used for water exceptional monitoring, including those used to detect trace contamination and pathogens (Xue et al. 2016, 2017). Zero-valent metallic nanoparticles or nanosized elements, such as of iron, silver, gold, copper palladium, and nickel have proven promoting effects towards contaminated sites with different hazardous pesticides. (Li et al. 2016). Despite the fact that technology has received a lot of studies and awareness, there is still a demand to analyze the trends that have emerged in investigating bioremediation during the last decade; some of the areas of focusing include the comparability of existing data, the appropriate use of existing technique, accessibility of in-depth laboratory investigations, geographical diversity, and a lack of knowledge in the field (Adams et al. 2015).

Bioremediation-related nanotechnology is a technological field that can examine several components to help clean the environment and to support life-growth situations. Due to distinctive characteristics of nanomaterial, it attains immense attention from researchers and scientist in various fields like water remediation, biomedical application, degradation of pesticides residue, etc. To increase the annual production of agricultural crops farmers mostly apply or spray pesticides over agricultural fields to control crops from pests, weeds, and any disease. Excessive use of pesticides degrades the soil profile and nearby water bodies. This may lead to negative influence in the growth pattern of flora and fauna. To avoid the drastic effects of pesticides, residue was majorly done by means of bioremediation. To enhance the potentiality of bioremediation technology, it will combine with nanotechnology for an effective reduction of the toxicological effects of pesticides (Rizwan et al. 2014). This method is known as nano-bioremediation which found to be more sustainable and cost effective in nature (Koul and Taak 2018). The degradation of pesticides residue by means of biological processes combining with nanomaterials provides more surface area for binding, less toxic effect on microorganism, enhances the activity of microorganism during eradication of pesticides contamination and found to be more suitable (Kumari and Singh 2016).

Additionally, some researchers name it on the basis of organism used to remediate the contaminants, such as phyto-nanoremediation (plant based), microbial nanoremediation (microbes based), and animal-based remediation (El-Ramady et al. 2017). It is reported that the working mechanism in between nanoparticles, biota/microbes, and contaminants depends on many factors such as morphology of nanoparticles, chemical behavior of nanomaterials and pollutant, pH value, temperature, media, microbes types, etc., which play a vital role during nano-bioremediation (Tan et al. 2018). Various metal, bimetallic, and metal oxides-based nanoparticles are the major categories which have been used for the removal and detection of hazardous pesticides contaminations in different regions. The existing chapter is an effort to consciousness on the promising application of metal nanomaterial-based technology and its assimilation with diverse essential tactics related to the bioremediation of pesticides.

11.2 Main Classes of Chemical Pesticides Utilized in Agriculture and Their Harmful Effects

The use of various synthetic pesticides has increased greatly and contributes to excessive crop yield growth. Soil, groundwater, and sediments constitute the ultimate sink for these contaminants, which are divided into simpler forms or persistent. According to the Stockholm Convention on Persistent Organic Pollutants, pesticides account for 9 out of 12 persistent organic compounds. For synthetic pest control, more than 1000 insecticides have been promoted. Pesticides incorporate herbicides, insect sprays, bactericides, and fungicides and so forth (Adams et al. 2015). Artificially, pesticides are of an extensive assortment, including chlorinated compounds, sweet-smelling rings, nitrogen and phosphorous-containing mixtures, and others. The degree of chlorination and lipophilicity of chlorophenol increases its toxicity and bioaccumulation capacity, Benzene's subordinates are used in a wide range of pesticides. Since the aromatic ring has a large negative reverberation force, benzene and its derivatives are constantly accumulating mixtures (Igbinosa et al. 2013). Adverse effects on water, air, and soil due to extreme use of chemical pesticides are shown in (Fig. 11.1). Major chemical pesticides classes include organochlorine, organophosphate, synthetic pyrethroids, and carbamates (Xue et al. 2016, 2017).

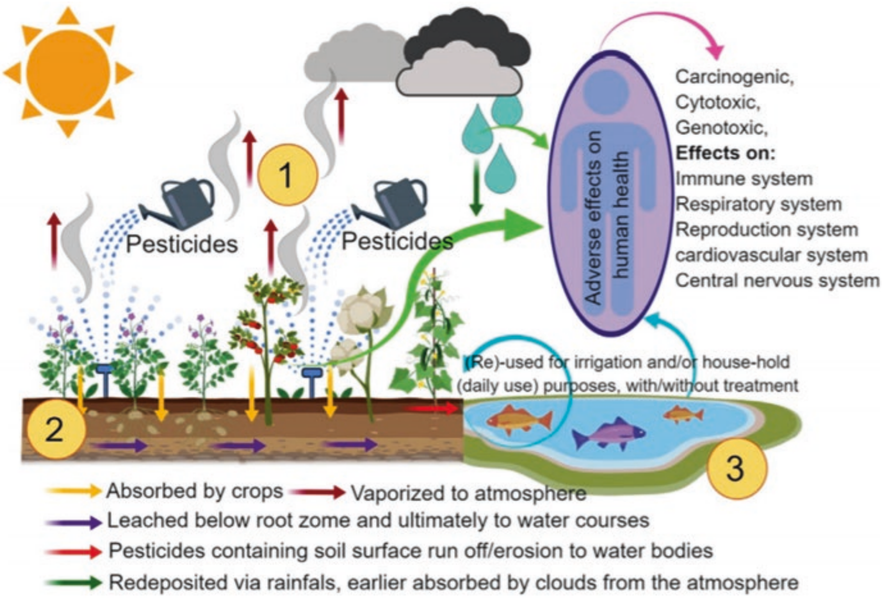

Fig. 11.1 Excessive use of chemical pesticides and adverse effect in modern agriculture; (1) air, (2) soil, and (3) water. (Reproduced with permission from Liu et al. 2019)

11.2.1 Organochlorine Pesticides

The first organic chemicals to be used to control pests and vectors were these. In broad spectrum, they have long-lasting low toxicity effects. They are, however, difficult to degrade in the natural environment due to their chemical stability. Their extensive use polluted the atmosphere and contributed to accumulation in mammals, resulting in poisoning or damage over time. As a result, organochlorine pesticides were outlawed in most cases and were eventually replaced by other pesticides. Organochlorine pesticides include endosulfan, DDT, and lindane, to name a few (Barragán-Huerta et al. 2007).

11.2.2 Organophosphate Pesticides

These toxins are distinguished by their various purpose and capability to control a wide range of pests. They are nerve toxic which used as a stomach toxic, a contact poison, or a fumigant. These biodegradable pesticides are pollutant-free, and slow the development of pest resistance. Organophosphate pesticides include methyl parathion, phosphamidon, and fenitrothion (Das et al. 2015).

11.2.3 Carbamates

These pesticides act in the same way as organophosphate pesticides, disrupting nerve signal transmission and causing the pest to die from poisoning. Carbamates can also be used as stomach poisons, touch poisons, and fumigants. Furthermore, since their molecular structures are largely identical to those of natural organic compounds, they can be degraded naturally with minimal emissions. Carbamate pesticides like propoxur (Tewari et al. 2012).

11.2.4 Synthetic-Pyrethroid Pesticide

These pesticides are combined by imitating the structure of natural pyrethrins. When compared to natural pyrethrins, they are stable and have longer residual effects. Artificial pyrethroid pesticides are more harmful to insects as compared to mammals. Permethrin and allethrin are the example of synthetic-pyrethroid pesticides. The pyrethroids are utilitarian poisons that produce unfriendly impacts in an optional manner as a result of neuronal hyper edginess.

Harmful impacts of carbamate and organophosphate pesticides happen in the sensory system where synthetics disturb the protein that controls acetylcholinesterase, a synapse. World Health Organization (WHO) assesses that 1,000,000 pesticide harming cases happen each year worldwide. Not just this, a drawn-out proficient openness to these pesticides additionally brings about expanded danger of a few ongoing and deadly illnesses like malignancy. Around 100 dynamic fixings in pesticides have been found to cause disease in exploratory creatures or people (Pimentel 2002).

11.3 Pesticide Bioremediation

Advances in research and ingenuity have enabled us to use natural variety's capacity to reduce pollutants, a process known as bioremediation. The guideline of this strategy is to eliminate poisonous toxins from the climate or convert the harmful items to nontoxic items by utilizing microorganisms (Nawaz et al. 2011). This methodology is at present applied to disinfect soil, dregs, surface water, groundwater, and air. Due to comparatively low capital costs, least disruptive techniques, and inherently aesthetic design, this technique has become desirable alternatives to conventional cleanup technologies as compared to traditional physicochemical methods (Rajendran et al. 2003; Wasi et al. 2011a, b).

Pesticide consistency in nature results either of their physical and chemical properties or the absence of life forms capable of degrading them. Certain pesticides may be lost due to volatilization or corruption as a result of light, warmth, or stickiness. On the other hand, degradation caused by living things (biodegradation) may be able to significantly reduce pesticides' persistent presence in the environment. This knowledge could be used to enhance the disposal of the harmful effects of contaminations by using living organisms; this process is known as bioremediation. The organism's ability to clean up pesticides is basically founded on their biodegradation movement. In spite of the fact that bioremediation has been first and foremost accomplished utilizing microorganisms (microbes or growths), different organic entities like plants or green growth can be utilized (Núñez et al. 2020). Elimination of pollutants would be valuable but not always possible; however, it could be confined or immobilized by some organisms. Organisms, for example, can accumulate contaminants and reduce, but do not eliminate, their presence and environmental effect. That strategy, which is indeed employed, should be included in the concept of "bioremediation" (Tyagi et al. 2011). Bioremediators would be called those organisms which can bioremediate, for example, Algicides–Algae, Fungicides–Fungi. The strategy of Bioremediatory organism like Micro bioremediation or Bioremediation for Microorganism Phytoremediation for plants.

A fruitful bioremediation procedure requires a proficient bacterial strain that can degrade the biggest contamination to the least level. The rate of soil biodegradation is dependent on four parameters, i.e., microorganism physiological condition, pesticide or microorganisms availability, survival or proliferation at a contamination site of pesticide degrading microorganisms, and the sustained population. The biodegrading in surface soil is oxygen consuming and fast because soils have an enormous number of vigorous microorganisms and their number typically diminishes (Tewari et al. 2012).

11.3.1 In Situ Bioremediation

This technique is very effective and desirable because of cost effective and creates less disturbance as they remove toxins in the environment instead of exploring and transporting them. The soil depth that can be effectively decontaminated limits in situ treatment. By the circulation of aqueous solutions naturally occurring bacteria stimulate to degrade contaminants, biodegradation adds oxygen and nutrients to polluted soils. The most significant treatments are bioventing, biosparging, and bioaugmentation (Adams et al. 2015).

11.3.2 Ex Situ Bioremediation

Land farming is a simple procedure in which degraded soil is unearthed, spread over a prepared bed, and intermittently ploughed until toxins are corrupted. Composting is a procedure that combines polluted soil with nontoxic organic contaminants such as excrement or rural waste. Biopiles are a hybrid of soil fertilization and agro farming that provide an ideal environment for native oxygen consuming and anaerobic microorganisms (Philp and Atlas 2005). Ex situ treatment of water and soil syphoned up from a polluted tuft is accomplished using slurry reactors or fluid reactors.

Various methods used for ex situ and in situ bioremediation are shown in (Fig. 11.2). Most bioremediation technologies are intended to remove pollutants after they have been produced or released into the environment. Studies of the microbial population, activities, and enzymes in the soil can provide a mirror image of the soil's functional status. Bioaugmentation (adding an organism or enzyme to a contaminant) and biostimulation are two examples (Tyagi et al. 2011).

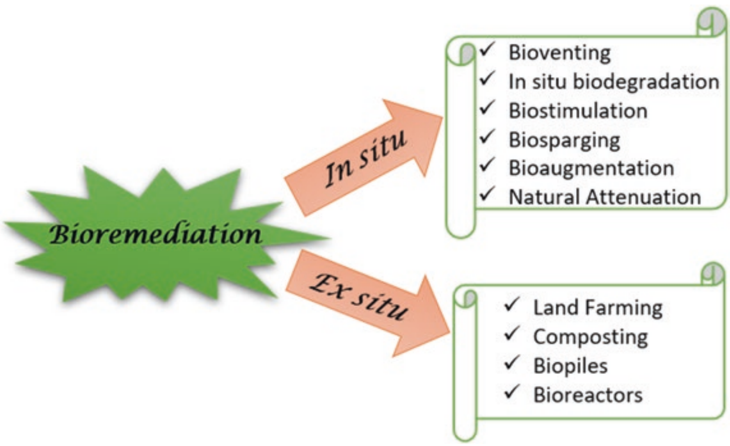

Fig. 11.2 Various bioremediation approaches for pesticides

11.4 Nano-Based Approaches for Pesticide Bioremediation

A series of technologies have been studied to identify systemic procedures to remove harmful pesticides from environmental matrices, including nanotechnology-based bioremediation. Understanding the interplay between the pollutant, nanomaterials (NMs), and microorganism is crucial because negative and positive impacts can occur. For instance, some nanomaterials are microorganism stimulants, whereas others are toxic. Therefore, it is crucial to select properly. For complete and effective pesticide bioremediation, detection, degradation, and removal of pesticide are three most important parameters. In physical and chemical processes, nanotechnology has remarkable advantages. Nanotechnology has a potential impact in above mentioned three categories: detection, degradation, and removal (Fig. 11.3).

Applications of various metal nanoparticles can effectively remove many hazardous substances from the environment in a shorter duration (Kalyani et al. 2021). Nowadays various nanomaterials are popularly used for bioremediation (Fig. 11.4). Metal nanomaterials are largely utilized for the detection of pesticides along with its elimination and degradation . These nanomaterials have been broadly categorized into the nanotubes, nanoparticles, and nanocomposites. Various forms of nanoparticles such as metal nanoparticles, bimetal nanoparticles, and nanoparticles metal oxide have been used in the detection and degradation of pesticide and are shown in (Fig. 11.4).

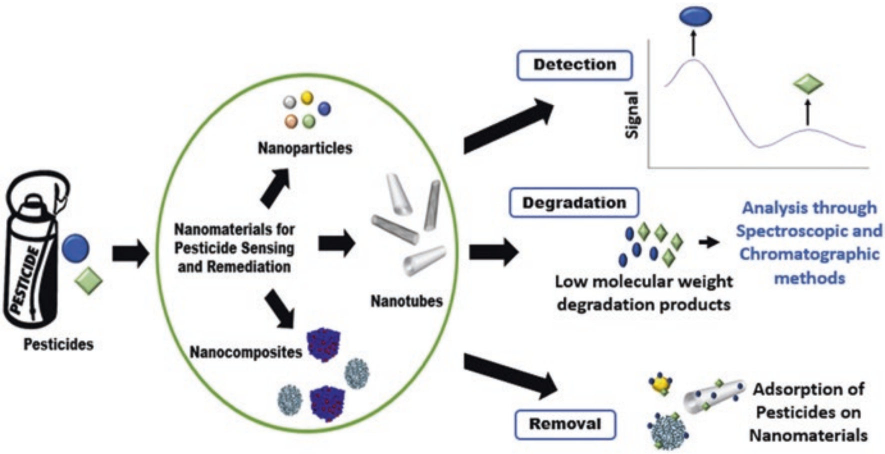

Fig. 11.3 A diagram depicting the use of nanomaterials for pesticide detection, degradation, and removal. (Reproduced with permission from Rawtani et al. 2018)

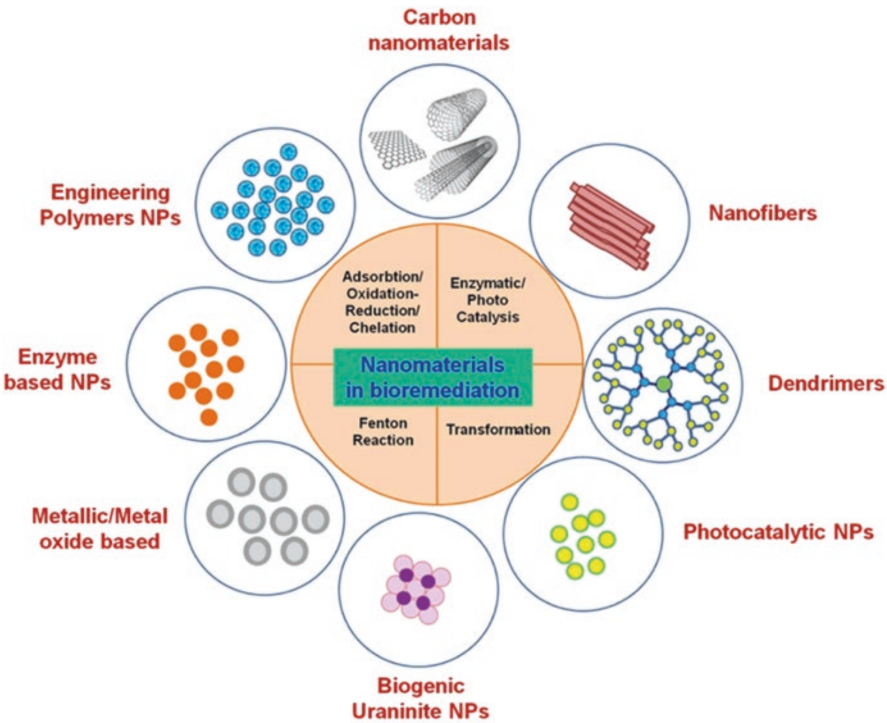

Fig. 11.4 Various types of nanomaterials used in bioremediation technique. (Reproduced with permission from Singh et al. 2020)

11.5 Role of Different Metal Nanomaterials in Detection of Pesticide Levels

Detection of pesticide levels before and after remediation is very important factor for deciding need and efficiency of any remediation technique. Pesticide identification is of great concern because of their toxicity, extensive use, and proclivity for bioaccumulation. Commercial pesticides already include over 800 active ingredients in over 100 separate substance groups. Carbamates, triazines, organophosphorus (OP), and neonicotinoids are the most common groups, and they have been the focus of nano-enabled pesticide detection till date (Kalyani et al. 2021). High insecticide level is a common source of pesticides (fungicides, herbicides, insecticides) in industry and agriculture. Not only is the trace content being measured, but also the section of high efficiency and low environmental pesticides present in food safety attractive (Das et al. 2015). Today's methods of detection are difficult and costly, limiting their uses. Applications of enzymes immobilized on various carriers such as mesoporous magnetic nanoparticles, nanoparticles, metal oxide and metal nanoparticles, and many other forms of nanomaterials are emerging in order to simplify the detection procedure. Experimentally successful in pesticide detection, the new biosensor based on the electrochemical method (Du et al. 2008) was demonstrated. Silicon nanoparticles (SiNPs), also used in biosensor fields, are widely used nanomaterials (Kalyani et al. 2021). Many of them are sensitive and can be used as a sensor care point in different sensors based on different physical principles and with rapid progress in instruments (Xu et al. 2016).

11.5.1 Nanosensor

The development of nanosensors in contaminant environments is growing rapidly and nanomaterials and identification agents are continually united in latest and innovative ways. Latest developments in sensor design have been designed to address the limitations of sensors of first generation like unspecific binding, nano parts aggregation, variation in particle size, and stabilization of nanoparticles. There remain issues of test sensitivity and selectivity in multifaceted environmental matrices, but rising numbers of reports indicate the stability and selectivity of their sensors using representative matrices. Robust sensors are a must when individuals are deployed (Kaushal and Wani 2017).

Main focus of researchers is to improve the specificity, sensitivity, and selectivity, of environmental monitoring sensors, either by focusing on the contaminant-recognition factor binding or by revamping the transduction and electronic interface to the sensing layer. Nano-based technique is helping to solve these problems in many ways. First, the nanoparticles' capacity to be immobilized with a broad variety of chemical and biological ligands aids in the sensor's specificity. Several researchers have documented coating nanoparticles with variety of ligands such as enzymes, DNA, proteins, and many more (Nune et al. 2009). The interaction of these ligands with the analyte is highly precise. Finally, the ability to make nanoparticles out of various metals improves conductivity and thus sensitivity. To detect organic contaminants, scientists have proposed employing porous silicon semiconductor nanostructures (Stefano et al. 2005). Photoluminescence is produced in porous silicone and in the presence of inorganic or organic molecules, this luminescence is quenched. This technology allows the detection of very low pesticide concentrations such as 1 ppm (Stefano et al. 2005). Nanosensors and nanoscale coatings are on the verge of marketing to replace more resistant and thicker polymer coating, nanosensors for the decommissioning of aquatic toxins, nanoscale biopolymers that improve the recycling and decontamination of heavy metals and nanosized metals that break down toxic organic matter at room temperature (Homaeigohar 2020). Furthermore, nanotechnology-based methods are less expensive and more efficient.

11.6 Green Synthesis of Metal Nanomaterial for Pesticide Bioremediation

Metal nanoparticles prepared by green synthesis methods are excellent for bioremediation of pesticide as it already has capping of biological material utilized for bioremediation. Microorganisms have potential to reduce the metal ions to form nanomaterials. Extracellular enzymes secreted by microorganism have tendency to synthesize pure nanoparticles (Kalishwaralal et al. 2010; Durán et al. 2011; Kumar et al. 2011; Alani et al. 2012; Tripathi et al. 2015). These metal nanomaterials are very effective in accelerating conventional bioremediation in which only microbes or plants are used. Figure 11.5 showing a schematic representation of the green synthesis process for the preparation of metal nanoparticles.

Specifically bacterial species have unique property of metal binding which makes them valuable for synthesizing metal nanoparticles having potential for bioremediation. Due to characteristics of having high volume of protein, fungi generally used when large amount of nanomaterials is needed to be synthesized. Comparatively for the synthesis of nanomaterials microbial method is slower than techniques using plants extract (Saravanan and Nanda 2010; Mishra et al. 2011). *Zingiber officinale*, *Abelmoschus esculentus*, *Eucalyptus*, *Mentha*, *Angelica*, *hypericum*, etc. were used for synthesizing the gold nanoparticles (Mishra et al. 2010; Pasca et al. 2014; Subbaiya et al. 2014; Suman et al. 2014; Sinha et al. 2015). For the extraction of iron nanomaterial through green synthesis by phytoextract species

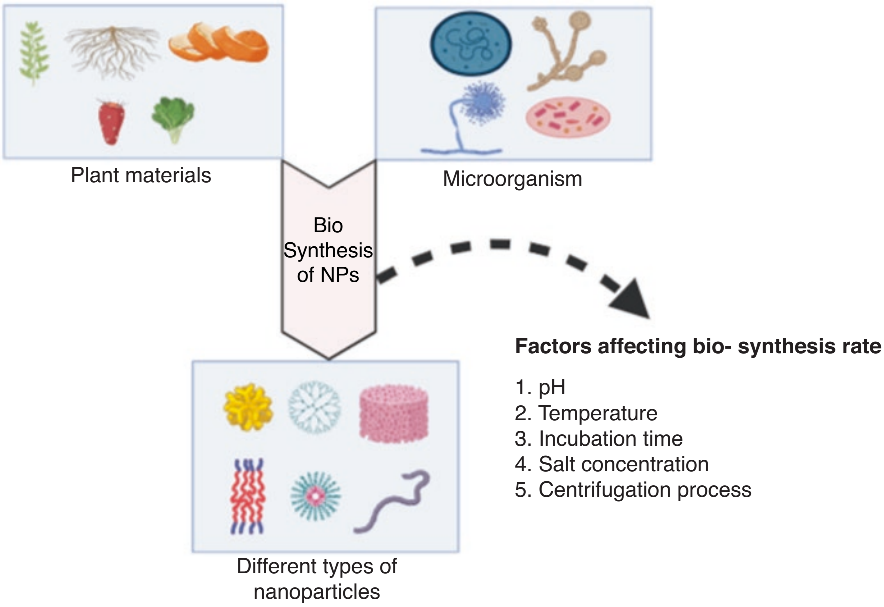

Fig. 11.5 Green synthesis process for the preparation of metal nanoparticles

of *Dodonaea viscose*, *Aloe vera*, *green tea*, *Rosmarinus officinalis*, etc. (Kumar et al. 2012; Phumying et al. 2013; Mahdavi et al. 2013; Pattanayak and Nayak 2013; Latha and Gowri 2014). Table 11.1 represents different plant species and microbes used for extracting various nanoparticles.

11.7 Metal Nanomaterials in Bioremediation of Pesticides

Metal Nps like gold, silver, iron, palladium, and platinum are highly used in different environmental concerns. Nanoparticles have unique chemistry and morphology which makes them suitable candidate to be used in pesticides removal through nano-bioremediation. The reaction that occurs over the surface of the nanomaterials plays a vital role in degrading pesticides and converts the hazardous material to simpler or less toxic compounds (Street et al. 2014). Nowadays, nanotechnological enabled approach is popularly used to remove the pesticides from contaminated soil or water. Researchers investigated the combination of metal nanoparticles with microbial cells for the degradation of pesticides (Wang and Tseng 2009). Figure 11.6 shows different type of metal nanomaterials used for nano-bioremediation of pesticides.

11.7.1 Metal Nanoparticles

11.7.1.1 Iron Nanoparticles

Nanoscale iron particles and their derivatives provide a number of remediation technologies with more alternatives. Commonly iron found under two valence states in nature, one is water soluble, i.e., ferrous iron Fe(II) and another is ferric iron Fe(III) which is water soluble below pH 3.5 and become insoluble above this pH. Under neutral to alkaline pH, it become stable with oxygen rich environment and precipitate as yellow/orange compound. Due to its retained magnetic properties, iron nanoparticles possess increased binding site during the removal of pollutant (Andrew et al. 2008). Researchers observed the potential of magnetic iron nanoparticles (MNPs) using laccase enzyme to degrade the chlorpyrifos an organophosphate pesticide. For this magnetic iron nanoparticles are developed by using co-precipitation method and nanoparticles size was about in between 10 and 15 nm. Results revealed that magnetic iron nanoparticle immobilized with laccase enzyme effectively degraded about 99% pesticides over 12 h at 60 °C and 7.0 pH. It has been also reported that 2,4-bis (1,1 dimethylethyl) phenol is the by-product obtained after the degradation process (Das et al. 2017).

Table 11.1 Different biotic components used in green synthesis of nanoparticles

Sources used for extracting metal nanoparticles		Nanoparticles synthesized	Morphology: Size (nm)	Morphology: Structure	References
Bacterial strains	*Pseudomonas rhodesiae*	AgNP	20–100	Spherical	Hossain et al. (2019a, b)
	Bacillus siamensis		25–50		Ibrahim et al. (2019)
	Bacillus cereus		18–39		Ahmed et al. (2020)
	Pseudomonas poae		20–45		Ibrahim et al. (2020)
	Bacillus sp.		7–21		Gopinath and Velusamy (2013)
	Serratia sp.		10–20		Mishra et al. (2014)
	Pseudomonas sp., *and Achromobacter* sp.		20–50		Kaur et al. (2018)
	Aeromonas hydrophila	ZnO	57–72	Crystalline	Jayaseelan et al. (2012)
	Streptomyces spp.	CuO	78–80	Spherical	Hassan et al. (2019)
	Streptomyces capillispiralis	Cu	4–59		Hassan et al. (2018)
Plants	*Citrus limon*	ZnO and TiO_2	20–200	Polymorphic	Hossain et al. (2019a, b)
	Phyllanthus emblica	Ag	20–93	Spherical	Masum et al. (2019)
	Rosmarinus officinalis	MgO	<20	Flower	Abdallah et al. (2019)
	Matricaria chamomilla	MgO and MnO_2	9–112	Disc shaped	Ogunyemi et al. (2019a, b)
	Matricaria chamomilla	ZnO	50–190	Crystalline	Ogunyemi et al. (2019a, b)
	Lycopersicon esculentum		66–133		Ogunyemi et al. (2019a, b)
	Piper nigrum	Ag	9–30		Paulkumar et al. (2014)
	Artemisia absinthium		5–100	Spherical	Ali et al. (2015)
	Abelmoschus esculentus	Au	45–75		Jayaseelan et al. (2013)
	Syzygium aromaticum	Cu	15		Rajesh et al. (2018)

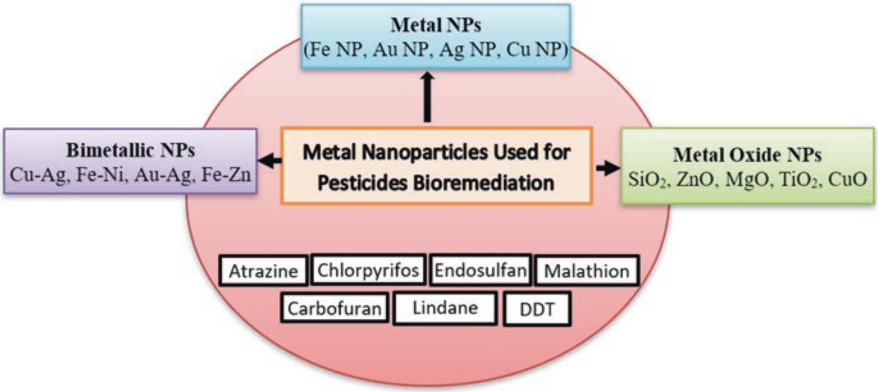

Fig. 11.6 Different types of metal nanomaterials used for nano-bioremediation of pesticides

Some study showed that iron nanoparticles are also used as catalyst for the removal of environment pollutant. Researchers evaluated the prospective of the iron nanoparticles synthesized using extract of *Euphorbia cochinchinensis* leaves for the degradation of 2,4-dichlorophenol pesticides. It was determined that the removal efficiency gets improved by 52% when iron-based nanoparticle was used as catalyst in the presence of hydrogen peroxide (H_2O_2) (Guo et al. 2017).

Zero-Valent Iron (ZVI)

Presently zero-valent iron (ZVI) is widely utilized for the management of pollutants due to its ease of use, effective pollutant degradation, low waste production, and secondary pollutants (Joo and Cheng 2006; Thompson et al. 2010). ZVI are classified into two types of ZVI (nZVI) nanoscale and iron reactive nanoscale (RNIP). nZVI particulates are 100–200 nm in diameter and consist of iron (Fe) with zero valence, whereas 50/50 wt% of RNIP particles consist of Fe and Fe_3O_4 (Yunus et al. 2012). Research has demonstrated that numerous pesticides are susceptible to ZVI degradation.

Many scientists used zero-valent iron nanoparticles for the elimination of lindane in which benzene, chlorobenzene, and dichlorobenzene are the by-product obtained (San Román et al. 2013). Zero-valent iron nanoparticles were utilized for the removal of nitrogen heteroatom compounds such as atrazine, olinate, picloram, chlorpyrifos, diazinon, and diuron (Joo and Cheng 2006; Kim et al. 2007; Jiang et al. 2018) to a limited extent. As the major reduction products, nitroaromatic pesticides with zero-valent iron were rapidly reduced to the corresponding amines. Only very small concentrations of intermediate products were found in certain reactions. Furthermore, analysis indicated a significant lower aromatic dechlorination than a reduction in nitrogen (Keum and Li 2004).

11.7.1.2 Gold Nanoparticles

Gold nanoparticles (AuNPs) due to different states of agglomeration show variation in color according to their size which makes it ideal for used in detecting various contamination level in the environment (Tsai et al. 2005). Due to ability of developing different coloration, the AuNPs were used in dipstick immunoassay for the detection of DDT (Dichlorodiphenyltrichloroethane). In this study, AuNPs were conjugated with anti-DDT antibodies to check its potentiality for decreasing the DDT concentration in the sample. The result was analyzed calorimetrically and intensity of the developed red color (due to AuNPs) was observed. Results demonstrated that the intensity of the developed color was increased with decrease in DDT concentration and reported with maximum intensity in absence of zero DDT concentration. Overall results showed that this kind of techniques may be used for rapid on-site testing to detect toxicity level of the pesticides (Lisa et al. 2009). Other researchers also used same techniques for detecting the organophosphorus pesticides (kitazine) in various samples like tomato, cucumber, grapes, etc. Here the detection of targeted pesticides was done on the basis of purple color development over the strips which were further confirmed by using ELISA (Enzyme Linked Immunoassay). Results showed that grape juice has highest color intensity during detection of pesticides (kitazine) (Malarkodi et al. 2017). Abd El-Aziz et al. (2018) prepared AuNPs with henna (*Lawsonia inermis*) extract. In this study also the degradation of DDT was monitored by evaluating the initial concentration taken, i.e., 10 or 20 mg/L. Result showed that after 72 h maximum degradation was found in the sample with starting concentration of 20 mg/L, i.e., 77% than 10 mg/L, i.e., 64%. The GC/MS spectra also confirm the presence of DDT by-product during degradation, i.e., (DDE), dichlorodiphenyldichloroethane (DDD), dichlorodiphenylmethane (DDM), and dichlorophenylethane (DCE). Researchers concluded that AuNPs have high potential for the cleanup of environmental toxic elements.

11.7.1.3 Silver Nanoparticles

Silver nanoparticles (AgNPs) showed versatile and fascinating properties among various metallic nanoparticles that involve in the bioremediation of the pesticides. The working efficiency of the AgNPs generally depends on the properties like surface properties, morphology, particles distribution, shape, composition, caping, etc. (Carlson et al. 2008). Various plant and microorganisms such as *Artemisia nilagirica*, *Sinapis arvensis*, *Nerium oleander*, *Trigonella foenum-graecum*, *Lantana camara*, *Pithophora oedogonia* were utilized to synthesize silver NPs (Kavitha et al. 2013; Vijayakumar et al. 2013; Rasheed et al. 2017; Lam et al. 2018). Some researchers used citrate for capping AgNPs for the prompt detection of dipterex, type of an organophosphorus pesticides found in different waste sample. Pink color masses were observed over citrate-capped AgNPs immobilized with acetylcholinesterase due to formation of thiocholine from acetylthiocholine through the enzymatic action of acetylcholinesterase. Study revealed that if the samples contain some concentration of pesticides, then the enzymatic based action of acetylcholine esterase was suppressed due to which thiocholine was not formed. Results confirmed that due to the presence of dipterex in the samples, there is no any color variation observed, which confirmed the presence of pesticides contamination in the water sample (Lia et al. 2014; Luo et al. 2017).

Siangproh et al. (2017) prepared a simple, rapid, economical detecting tool for detecting the concentration of herbicides contamination in canal water and groundwater samples. In this study AgNPs are coated with citrate to form colorimetry probe. Silica gel was used to adsorbed pesticides contamination. The presence of contamination was detected by color change mechanism from yellowish green to pale yellow. Other studies also showed that AgNPs were also used in combination with SERS (Surface Enhanced Raman Scattering) technique which helps in detecting the pesticides contamination at a very low level, this type of combined techniques is used to detect paraoxon and thiram type of pesticides (Wang et al. 2014). Same method was done in which cellulose nanofibers coated with AgNPs in combination with SERS used to detect thiabendazole in the samples (Liou et al. 2017).

11.7.2 Metal Oxide Nanomaterials

Crystalline metal oxides nanoparticles such as ferric oxide (Fe_2O_3), manganese oxides (MnO_2), aluminum oxide (Al_2O_3), titanium oxide (TiO_2), magnesium oxides (MgO), and ceric oxides (CeO_2) are very efficacious adsorbents used for the wide range of pesticides. Due to versatile properties of metal oxides nanoparticles such as fast kinetics due to nano size, high adsorption rate, less intraparticle diffusion distance, etc. (Cheng 2013; Bardajee and Hooshyar 2013; Tavakkoli and Yazdanbakhsh 2013; Dehaghi et al. 2014), nanocrystalline metal oxides also have tendency to abrade the hazardous pesticides contamination into the less toxic compounds (Fryxell and Cao 2012).

11.7.2.1 Titanium Oxide Nanoparticles

Titanium oxide (TiO_2) nanoparticles are used for the removal of different types of pesticides found in the various samples. TiO_2 was used as photocatalyst for the removal of monocrotophos and chlorpyrifos pesticides from the water sample. During degradation process of the pesticides, various parameters such as pesticides concentration, pH of the examined solution, photocatalysts, etc. are also observed. Results showed that on increasing the illumination time, the photodegradation activity of TiO_2 also enhanced (Amalraj and Pius 2015; Selvakumar et al. 2018). Liu et al. (2015) prepared mesoporous TiO_2 NPs for the extraction of some organochlorine pesticides such as *trans* and *cis* chlordane, hexachlorobenzene (HCB), *p*,*p*-DDT, *o*,*p*-DDT, and mirex in the water samples. Prepared mesoporous TiO_2 NPs were used to prepare solid phase microextraction fiber and it was analyzed that prepared fiber shows greater efficiency in comparison to commercial based fibers towards the degradation of pesticides. Doping method is also with different metal ions (iron and silica) in combination with TiO_2 NPs for analyzing the degradation potentiality for carbendazim, type of fungicide. Due to adopting doping method, the photocatalytic behavior was boosted very high and removed about 98% of the fungicides under solar light (Kaur et al. 2016). Same technique of doping was used to prepare Cobal doped TiO_2 NPs used as photocatalyst to enhance the reaction rate of degradation for dichlorophenols in visible light (Hoseini et al. 2017). Schematic illustration of pesticide degradation mechanism of TiO_2 is shown in (Fig. 11.7).

Photocatalytic oxidation is a process that is eco sustainable for removing a broad variety of chemical toxins. It is a pre-treatment method which is appropriate to improve biodegradability of harmful and non-biodegradable contaminants. The treatment of the recalcitrant organic compounds can also be done using photocatalysis as a polishing step (Lasa and Rosales 2009). During photocatalysis, solid surfaces are photo-excited by radiation either near solar light or UV. Mobile electrons are therefore generated and positive surface charges. These electrons excited sites are essential steps for accelerating the oxidation and reduction reactions to degradation of pollutants (Reddy et al. 2013; Coronado et al. 2013). The advancement of nanotechnology has altered the reactivity and the detection limit of semiconductor photocatalysts. Based on this principle, photocatalytic degradation has treated a wide range of pesticides. The semi-manufacturing materials are different, such as ZnO, TiO_2, Fe_2O_3, CdS, and WO_3. Among all of these chemical stability, low toxicity, low cost, and high abundance of raw materials are main features that have made titanium dioxide most used. Many scientists reported photodecomposition of pesticides with TiO_2. The photodegradation of organochlorine pesticides on TiO_2 coated films exposed to airborne UV irradiation was investigated. Yu et al. (2007) investigated the photocatalytic activity of TiO_2 coated film for the degradation of organochlorine pesticides in air when exposed to UV irradiation. In a short period, all pesticides can be degraded. Under high power UV lamp, the degradation

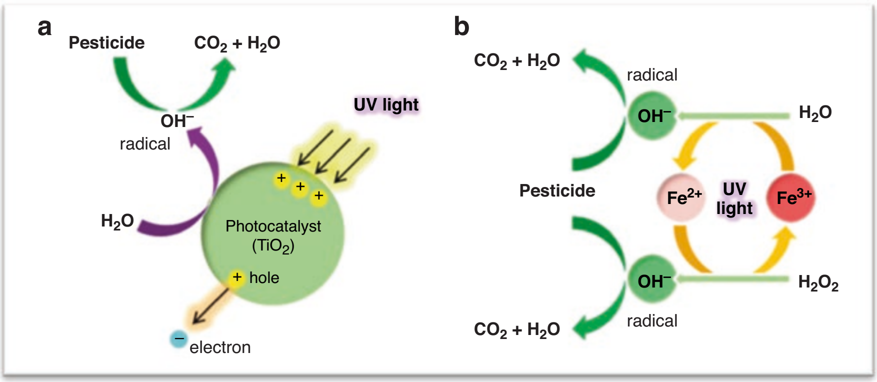

Fig. 11.7 Schematic illustration of pesticide degradation by TiO_2 (**a**) photocatalytic oxidation and (**b**) photo-Fenton degradation. (Reproduced with permission from Aragay et al. 2012)

rate was greatly increased. Another dicofol degradation photocatalytic study of TiO_2 UV-light-irradiation nanoparticles showed that dicofol could react with dicofol to produce chloride ions and lower chlorine-containing toxic compounds and could be completely damaged by active hydroxy radicals. By optimizing particle shape and dimension, maximizing reactive facets, reducing e^-/h^+ recombination through noble metal doping, and surface treatment to develop adsorption capacity, the photoactivity of nano-TiO_2 may be improved (Fujishima et al. 2008). The prepared catalysts are nanosized particles and anatase type according to the consequences. The catalysts had a redshift in the adsorption edge and showed greater absorption in the visible light field. In comparison to nonmetal doped titania, metal doping tends to be more effective in moving the absorbance spectrum to a visible area. Under UV and solar light illumination, the degradation behavior of Th-doped photocatalytic TiO_2 was investigated. These findings suggest that Th-doped photocatalytic TiO_2 with altered electronic properties is an adequate photocatalyst for oryzalin degradation in contaminated water when exposed to sunlight. Under UV irradiation, however, these modifications display only small variations in photocatalytic rates. First-order kinetics govern all photodegradation reactions. Many other photocatalysts such as WO_3, ZnO, etc. have been utilized to degrade pesticides in addition to titania (Mohagheghian et al. 2015). Eight pesticides were degraded to pilot plant size by the use of tandem $ZnO/Na_2S_2O_8$, as a photo-sensitive/poisoning sensitive and parabolic collector compound in natural sunlight (Navarro et al. 2009), in leaching water having pesticides and other solubilized chemicals as they penetrate through the ground. The results revealed that ZnO as a photosensitizer is a successful solution when using solar photocatalysis.

11.7.2.2 Zinc Oxide Nanoparticles

Nanoparticles of zinc oxide (ZnO) exhibit distinctive chemical and physical behavior. Due to surface modification, it shows enhanced sensing and catalytic behavior to effectively remove different contaminants present in the soil and water. Sharma et al. (2016) studied the degradation rate of methyl parathion and parathion, types of organophosphorus pesticides by the comparative effect of direct photolysis and by UV-ZnO nanocrystal. Recorded results showed that photocatalytic crystals were found to be more effective in degrading the pesticides.

Kaur et al. (2017) evaluated the effect of surface functionalization on ZnO nanoparticles for adsorbing the pesticides from the aqueous solution. ZnO nanoparticles were modified by 1-butyl-3-methylimidazolium tetrafluoroborate (BMTF-IL), CTAB functionalized and bare ZnO nanoparticles. It was observed that 1-butyl-3-methylimidazolium tetrafluoroborate modified ZnO showed high adsorption (148.3 mg/g) followed by CTAB functionalized (90 mg/g) and bare ZnO nanoparticles (76 mg/g). Dehaghi et al. (2014) prepared chitosan/ZnO-based composite beads to analyze its potential towards removal of permethrin, vastly used neurotoxic pesticides in agricultural fields. Adsorption method was adopted to detect the change in initial concentration of the targeted pesticides. It was observed that only 0.5 g of bio-nanocomposite used up at pH 7 and normal room temperature which showed about 99% removal rate of pesticides from the sample. After three cleaning cycles it showed 56% regeneration capacity proved to be a new potential candidate for the removal of pesticides. Salam and Das (2015) developed a bionano hybrid system using *Candida* VITJzN04 and nanosized ZnO for lindane degradation. They studied the lindane degradation efficacy of *Candida* VITJzN04 along with ZnO nanoparticle and found more effective degradation of lindane by hybrid compared to native yeast alone. The lindane was completely removed within 3 days from the sample.

11.7.2.3 Silica Oxide Nanoparticles

For bioremediation of pesticides, use of microbes and enzymes as biotic component is more powerful as they are very much effective under normal atmospheric conditions. After immobilizing microbes and/or enzymes on some inert supports such as metal nanomaterials, they can be used repeatedly. Silica nanoparticles possess desirable properties to be used as support to immobilize different enzymes. Microbes expressing recombinant proteins and various enzymes such as carboxyesterases, organophosphate hydrolases, laccases, etc. have been successfully immobilized on silica nanomaterials for bioremediation of pesticides. Figure 11.8 depicts use of silica nanomaterials as immobilization matrices for enzymes and whole cell to enhance bioremediation. Basically, chemical and biological methods are adopted to synthesize spherical silica nanoparticles (SiO_2) which are porous in nature (Rao et al. 2005). The porous behavior of the SiO_2 nanoparticles majorly depends upon

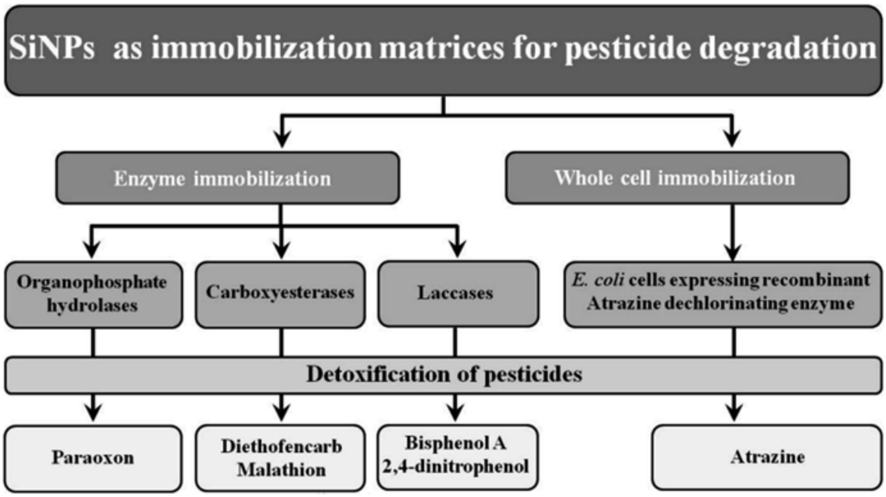

Fig. 11.8 Use of SiNPs as immobilization matrices for enzymes or recombinant whole cells for pesticide degradation. (Reproduced with permission from Bapat et al. 2016)

the surface functionality. The rage of porosity in SiO_2 particle ranges from microporous, mesoporous, and hollow porous (Bapat et al. 2016). Due to nanostructure and highly porous behavior, these nanoparticles are highly used for the remediation of various pollutant (Khung and Narducci 2015).

Boubbou et al. (2012) immobilized organophosphate hydrolases (OPH) derived from *Flavibacterium* species. They studied degradation of organophosphate pesticide paraoxon by using this immobilized enzyme and found excellent highest hydrolysis rate of paraoxon with immobilized enzyme on mesoporous silica with 6 nm diameter (Boubbou et al. 2012). Lerma-García et al. (2013) observed the enhance effect of SiO_2 nanoparticle modified by *N*-methylimidazole to detect the sulfonylurea in the water sample. It was observed that due to change in surface chemistry the rate of degradation was increased up to the mark. Other scientist also modified the surface of SiO_2 nanoparticles with polar and non-polar compound to check the efficiency towards removal of organophosphate pesticides (Ibrahim et al. 2013). In some studies mesoporous silica nano particles were used for the immobilization of enzymes such as organophosphorus hydrolase (OPH) to check the hydrolysis rate of paraoxon (diethyl-4-nitrophenyl phosphate). Results showed that OPH with silica nanoparticle shows higher tendency to hydrolyze the paraoxon comparative to the plain one (Boubbou et al. 2012). Wang et al. (2013) prepared silica colloidal crystals beads depend on photonic suspension array for the detection of chlorpyrifos-methyl and fenitrothion. During detecting the pesticides residual concentration, the binding capacity and the stability of the surface increased due to nanostructured silica particles. The prepared suspension array able to detect the pesticides in the ranges of 0.40–735.37 ng/mL and 0.25–1024 ng/mL, respectively. Observed results showed that this technique proved to be possible detecting tool for the pesticides residual present in the samples.

11.7.2.4 Iron Oxide Nanoparticles

Generally, different oxides of iron were largely exploited in the preparation of nanoparticles with unique features which are further incorporated into different matrices to removal of pollutant from the samples. Iron oxide (Fe_3O_4 and Fe_2O_3) based NPs are vastly applicable to remediate different kinds of contaminants present in various samples. Different matrices are used to immobilize the iron oxides-based NPs for eradicating the pollutants. Quali et al. (2015) used a type of clay mineral, i.e., palygorskite and modified it with the magnetic iron oxide nanoparticle for the removal of fenarimol fungicides. In this study, three composition was used, i.e., sifted palygorskite, purified palygorskite, and palygorskite modified with magnetic iron nanoparticles. The observed adsorption rate for the removal of fungicides was 11%, 50%, and 70% respectively. The clay mineral modified with magnetic iron oxide nanoparticles showed highest removal percentage and also showed 2-week stability.

Iron oxide nanoparticle embedded in mesoporous silica also has tendency to remove glyphosate from the water sample. Modification on the surface of the iron oxide nanoparticles positively increased the porosity and surface area and of the prepared adsorbent (Fiorilli et al. 2017). Fan et al. (2017) proposed quick and simple process to detect the presence of pyrethroid pesticides in various samples of contaminated water. In this method ultrasmall iron nanoparticles in combination with ionic liquid were used to detect pesticides in the water samples. The limit of detection was determined to be between 0.16 and 0.21 g/L.

11.7.3 Bimetallic Nanoparticles

As the term suggests bi means more than one, so it is basically the combination of two distinct metals within a one nanoparticle. These bimetallic nanoparticles have attracted highly due to remarkable properties which can be developing due to combining two metals. The enhanced characteristics of the bimetallic nanomaterial are generally due to the synergistic effects on conjoining (Zaleska-Medynska et al. 2016). Bimetallic nanoparticles consisting of iron and nickel (Fe/Ni) were used for the dechlorination purpose of the sulfentrazone, kind of herbicides. Various factors were also analyzed during the conversion activity such as pH, dosage, initial concentration of herbicides, etc. Recorded results showed that in 30 min about 100% conversion rate was achieved at acidic pH about 4.0 and 1.0 g/L of bimetallic NPs. It was also concluded that the dechlorination rate depends upon the temperature, dosage, and nickel content present in NPs. After dechlorination the formed by-product was less toxic and it was confirmed by mass spectrometry and toxicity assay done over the *Daphnia similis* fish species (Nascimento et al. 2016).

Shen et al. (2017) studied bimetallic nanoparticle consisting of zero-valent iron and nickel for the degradation of 4-chlorophenol. They evaluated the efficiency of the bimetallic nanoparticles towards the removal of 4-chlorophenol in the sample. Observed results confirmed that hydroxyl radicals were the most active class during the degradation process in case of iron nickel bimetallic nanoparticles. Singh et al. (2013) prepared composite of Pd/Fe bimetallic nanoparticles and carboxymethyl cellulose with *Sphingomonas* spp. (strain NM05) as biological component and used for bioremediation of lindane present in soil. They found this integrated technique very effective for bioremediation of lindane. They suggested that this integrated bio-nanocomposite system can also be used for wastewaters. Rosbero and Camacho (2017) prepared bimetallic nanoparticles of silver and copper (Ag/Cu NPs) by green synthesis method using *Carica papaya* leaf extract. The bimetallic NPs have been used as nanocatalyst to degrade chlorpyrifos in waste sample. To synthesize Ag/Cu NPs *Carica papaya* leaf extract was used by adopting co-reduction method. Observed results confirmed that bimetallic NPs have efficient potential to enhance the degradation rate of pesticides contamination from the water samples (Fig. 11.9). Some metal nanomaterials with biotic component and the removal rate of different form of pesticides by these nanomaterials are presented in (Table 11.2).

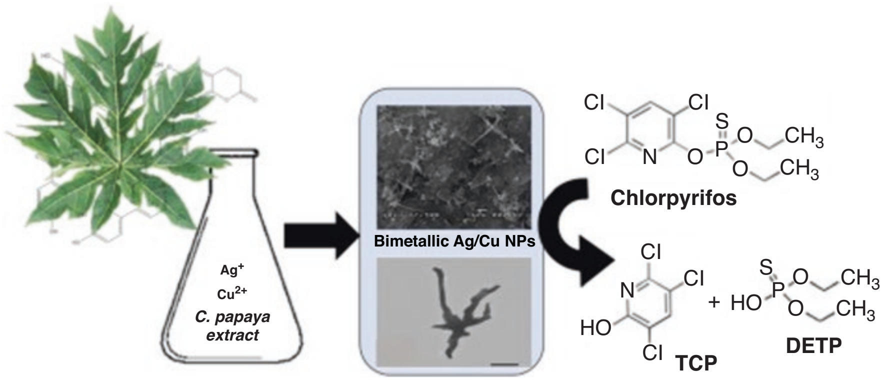

Fig. 11.9 Ag/Cu based bimetallic nanocatalyst degrading chlorpyrifos in contaminated water. (Reproduced with permission from Rosbero and Camacho 2017)

Table 11.2 Removal rate of different pesticides with different metallic nanomaterials with biotic components

S. No.	Type of nanomaterial with biotic components	Pollutant degraded	Removal rate (%)	References
1	Zero-valent iron with *Sphingomonas* sp.	Polybrominated diphenyl ethers	67	Kim et al. (2012)
2	Iron oxide nanoparticles with *Rhodococcus rhodochrous* strain	Chlorophenols	80	Hou et al. (2016)
3	nZVI and nZVI combination with microorganisms	Polychlorinated biphenyls	99	Jing et al. (2018)
4	Bimetallic iron-based NPs and tobacco plants	Hexabromocyclododecane	27	Le et al. (2019)
5	*Arthrobacter globiformis* D47 immobilized nanoparticles	Herbicides	90	Liu et al. (2018)

11.8 Conclusions and Future Prospects

Metal nanoparticles play a very important role to ameliorate conventional bioremediation techniques. Due to excellent architecture and physicochemical properties, different types of metal nanomaterials are used as support material to immobilize active microbes or enzymes. Such types of bionanocatalysts showed enhanced removal of pesticides from contaminated soil and water. Various metallic nanoparticles, bimetallic nanoparticles, metal oxide nanoparticles, and polymer metal nanocomposites are popularly used for bioremediation of pesticides. Many researchers found that rate of degradation of pesticides greatly enhanced when metal nanomaterials were used along with pesticide degrading bacteria. Metal nanomaterials also play a very important role in sensing presence of pesticide residue in environment. Iron, silver, and gold nanoparticles are most common metal nanomaterials which are utilized in bioremediation of pesticides. Due to porous nature of crystalline metal oxides based nanomaterials are very effective adsorbents used for the wide range of pesticides. Also, photocatalytic active metal oxide such as TiO_2 also provides added advantage of photodegradation which results in faster degradation of pesticide. Nowadays, bimetallic nanoparticles have attracted researchers focus for its application in bioremediation because of enhanced characteristics due to the synergistic effects on conjoining two metals in one nanoparticle. In the past decades, many metal nanomaterials and metal nanocomposites have been studied for the bioremediation of pesticide but still it is required to develop some new and greener methods for the preparation of these metal nanomaterials. Green synthesis utilizing pesticide degrading microbe or enzyme provides a single step synthesis for getting bioactive material capped metal nanoparticles.

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