Chapter 10
Use Nanotools for Weed Control and Exploration of Weed Plants in Nanotechnology

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Abstract During the last decades, agriculture sector faces many difficulties due to worldwide loss by pests estimated by 30% from food production. Within this, weed caused about 13% loss, besides the ill effects of synthetic herbicides on human and the environmental health. The present chapter reviews the use of nanotools in weed management, in which many trials are being conducted to facilitate this technology for future weed management, by minimizing the costs and the environmental effects of the use of chemical herbicides. Nanoherbicides provide a good opportunity for farmers to control annual, perennial, and parasitic weeds by blending with the soil or sprayed on weed plants without the use of excessive amounts chemicals to leaving any toxic residues and environmental problems. Nanoformulations are being used in weed control, especially polymer formulation (control release or nanocapsulation) or nano-emulsions for natural product extracts, essential oils, and active ingredient (AI) of synthetic herbicides. Conventional application of herbicide is causing serious hazard for human health through water pollution. The use of nanoparticle for degradation of polluting herbicides from water sources' aspect is also covered in this chapter. Biological synthesis is an efficient method for nanoparticles and has been used in various applications. Many researchers are focusing on using weed to find an environment-friendly technique for producing well-characterized nanoparticles which has been reviewed in this chapter.

Keywords Nanotechnology · Nanoherbicides · Nanoformulation · Weed management · Photodegradation · Biological synthesis

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10.1 Introduction

Weeds are uncultivated plants that grow associated with crops in agricultural lands and other places. They are not desirable because they cause various economic and environmental losses. It reduces the crop productivity, causes loss of groundwater by consumption and evaporation, acts as obstacle in the flow of water canals and as barrier for navigation in the airports and railways, and reduces the quality of land, especially the presence of perennial species. In general, weeds are difficult to eradicate and control for many reasons. Seeds are produced in large numbers that are not comparable to crops. They have more than one means of propagation and have a long period of dormancy to ensure the length of survival. Many of which are like the crop plants that are associated with them, especially in the early stages of development, which saves them from disposal, and ends their life period quickly and before the maturity of crops. The worldwide plant disease caused 13%, insect 14%, and weed 13% loss in food production and accounted 2000 billion $ economic loss per year (Pimentel 2009). The weed control methods can be divided into three large sections, including mechanical, biological, and chemical control. The widespread use of herbicides causes environmental pollution and many problems. Some are like the high cost of synthetic herbicides, concern for the environmental damage, the public concern for food safety, the unacceptability of many herbicides chemical groups, the lack of new herbicide with new modes of action, the reduction in the number of registered herbicides, and the rapid evolution of herbicide resistant weeds.

In recent two decades, many advanced technologies are being introduced in the field of weed control to make the process easier and more efficient. Among the latest technological advancements, nanotechnology occupies a central position. It has many applications in all stages of production, processing, storing, packaging, and transport of agricultural products. The reduced use of herbicides and pesticides with increased efficiency, controlled release, and targeted delivery will lead to precision farming. Preliminary studies show the potential of nanomaterials in improving seed germination and growth, plant protection, pathogen detection, and pesticide/herbicide residue detection (Khot et al. 2012). This chapter reviews the use of nanotools that has proved highly successful in control of different types of weeds and in many sites and weed communities. Recent research producing crystals in the nano-size range has provided evidence of improved efficacy of agrochemicals (Crooks et al. 2003). Worldwide consumption of herbicides represents 47.5% of the 2 million tons of pesticide consumed each year. However, the heavy use of herbicides has given rise to serious environmental and public health problems. It is therefore important to develop new herbicide formulations that are highly effective, that are safer (for the worker and for the environment), and that involve a low cost/production ratio. In this sense, controlled release formulations of herbicides have become necessary in recent years, since they often increase herbicide efficacy at reduced doses (Sopeña Vázquez et al. 2009). The present chapter also reviews in detail the components of various types of herbicide formulations, with an emphasis on controlled release formulations and micro-encapsulation. These kinds of release systems could reduce the herbicide resistance potential, maintain the activity of the active ingredient, and prolong their release over a longer period (Manjunatha et al. 2016).

Nanoherbicides represent an efficient means specially in the early weed control and are being developed to address the problems in perennial weed management and exhausting weed seed bank. Research in nanotools has led to the emergence of unconventional forms of herbicides that have their unique characteristics than those used for decades. Along with the new area of research is emerging where worthless weeds are being used to synthesize different nanoparticles for various applications. Also, to address the issue of herbicides polluting the water and soil has encouraged many studies on the use of nanoparticles for degradation of herbicides. Despite all these scientific attempts, nanotechnology in the field of weed control, herbicide degradation and biosynthesis of nanomaterial face many futuristic difficulties. This chapter reviews the current status of nanotechnology in weed management and its related aspects.

10.2 Types of Different Weeds

The life cycle of broadleaf annual weeds gets completed by one winter or summer season. The seeds of these weeds germinate in the fall, their vegetative growth occurs in the winter, and their fruit growth gets completed before entering summer. The few examples of major broadleaf annual weeds are *Medicago polymorpha*, *Melilotus indicus*, *Anagallis arvensis*, *Beta vulgaris*, *Brassica kaber*, *Capsella bursa-pastoris*, *Chenopodium* sp., *Malva parviflora*, *Rumex dentatus*, *Urtica urens*, *Sonchus oleraceus*, *Euphorbia* sp., *Coronopus* sp., *Emex spinosus*, *Vicia sativa*, *Cichorium endivia*, *Senecio glaucus*, *Calendula arvensis*, *and Lathyrus hirsutus*.

Annual narrow-leaved weeds germinate in the spring, and their vegetative growth occurs in the summer and matures before entering the winter. The narrow-leaved winter weeds include *Avena* spp., *Phalaris* sp., *Lolium temulentum*, *and Polypogon monspeliensis*, while the narrow-leaved annual summer weeds include *Echinochloa crus-galli*, *Digitaria sanguinalis*, *Echinochloa colonum*, *Eleusine indica*, *Dactyloctenium aegyptium*, *Cenchrus ciliaris*, *Brachiaria eruciformis*, *Setaria viridis*, *and Cyperus difformis*. The important risks of annual weeds are clearly shown in its huge seed production, and the fight against these weeds requires a huge effort by farmer. The use of nanotechnology for weed control can help the farmers for efficient control of the weed.

Perennial weeds are those weeds that stay in the soil more than 3 years. Generally, they are difficult to control, as they reproduce by more than one way like they may multiply with seed or rhizomes or tubules or tubers or creeping roots. There are two major classes of perennial weeds. One is narrow-leaved weeds, including: *Imperata cylindrica*, *Cyperus* spp., *Cynodon dactylon*, *Phragmites* spp., *Alhagi* spp., *and Cyperus* spp. The second type is perennial broad-leaved weed that includes *Convolvulus arvensis*, *Arundo donax,* and *Conyza discoroidis*. Perennial weeds represent a direct threat to the optimal production of crops.

Parasitic weeds depend on the host crop to obtain food, through the roots or stem of the host plant. The examples are Cuscuta sp., *Orobanche crenata*, *Orobanche* aegyptiaca, *Orobanche minor,* and so on.

10.3 Nanoherbicides

Nanoherbicides are being developed to address the problems of all kind of weeds (Manjunatha et al. 2016), as nanotechnology can be used to improve the performance of many existing herbicides or to formulate an alternatives tool that is a quick, efficient, and economical means and exceeds the original product. Nanoherbicides as a "smart delivery system" provides an eco-friendly approach through reducing herbicide inputs, as well as providing control over where and when an active ingredient is released (Pérez-de-Luque and Rubiales 2009). But the manufacturing of nanometric herbicides is in its primary stages and is expected to make significant progress for increasing efficiency against weeds and reducing the quantities of herbicides used to reduce the effects on the environment. Some of the formulation and tools to achieve these objectives are discussed here in details.

10.3.1 Use of Polymer Nanoparticles

Pesticide formulation that increases the use efficiency and reduces environmental pollution is the need of present time. Due to their potential in changing the pesticide release profile, the polymeric nanoparticles have gained focus in the recent days. Encapsulation of herbicide in polymeric nanoparticles is being explored to achieve the environmental safety (Kumar et al. 2015b). In one study, the chitosan was used to encapsulate silver nanoparticles and paraquat herbicide. This nanoformulation was evaluated for controlled release and improved herbicidal activity against *Eichhornia crassipes*. Encapsulation efficacy was found to be 89.0%; controlled release study showed 90.0% of release of AI occurred at 24 h, and the distinct improved herbicidal activity was observed against *Eichhornia crassipes* by the formation of necrotic lesions in all the tested concentration of nanoformulation. Non-target effect study on the various soil parameters revealed that nanoformulation did not affect the soil macro- and micronutrients, soil enzyme, and soil microflora. Seedling emergence and plant growth parameters of the tested plant were not affected in the nanoformulation treatment (Namasivayam and Aruna 2014).

In another study, the researcher has reported the method for synthesis of poly (lactic-*co*-glycolic-acid) (PLGA) nanoformulation loaded with atrazine (Schnoor et al. 2018). An average size of nanoformulation was about 110 ± 10 nm before the lyophilization, and studies with potato plants had shown that 50% encapsulated herbicide was released in 72 h. The formulation resulted in reduced growth of potato plant and proved that PLGA nanoherbicides can be used as an alternative method for inhibiting weed growth (Schnoor et al. 2018). In one study, poly (l-lactide-*co*-glycolide)–poly(ethylene glycol)–poly(l-lactide-*co*-glycolide) (PLGA–PEG–PLGA) terpolymer with PEG (16%) was used as a biodegradable carrier for the controlled release of metazachlor and pendimethalin (Rychter et al. 2019). The addition of PEG helped in uniform progress of degradation, and thus a relatively constant release of herbicides was achieved. PEG–PLGA was also used for developing the delivery system for metolachlor (Tong et al. 2017). As the resultant formulation did not contain any organic solvent or surfactant, it reduced the chances of pollution. The water solubility of this hydrophobic weedicide was also enhanced. The bioassay and other analytical studies have revealed that the nanoformulation had increased the absorption in plants, but reduced cytotoxicity in preosteoblast cell line (Tong et al. 2017).

Nanocapsules of poly(ε-caprolactone) with three triazine herbicides (ametryn, atrazine, and simazine) had shown better stability and were less genotoxic than the free herbicides (Grillo et al. 2012). Similar results were obtained when the herbicidal activity of atrazine that was encapsulated in poly(ε-caprolactone) was evaluated using mustard (*Brassica juncea*). The results have shown that nanocapsules with 1/10th dose of atrazine dosage tenfold was similarly effective as compared to the commercial formulation (Oliveira et al. 2015). In another study with atrazine, poly(epsilon-caprolactone) nanoparticles were evaluated for its herbicidal activity and genotoxicity (Pereira et al. 2014). The nanoformulation was stable up to 3 months and was specific to target. The experiments confirmed the reduced mobility of herbicide in soil and lesser genotoxicity.

When chitosan and sodium tripolyphosphate (TPP) were used for making the nanoformulation of paraquat, similar results were obtained. To check the herbicidal activity, the maize and mustard plants were used as a model, and the absorption of herbicide in soil was also measured. Along with this, the cyto- and genotoxicity of was evaluated by cell culture viability assays and chromosome aberration test. The encapsulation efficiency was 62.6 ± 0.7% that reduced diffusion rate and ultimately the absorption by soil. Cytotoxicity and genotoxicity studies confirmed the less toxicity of nano-encapsulated herbicide as compared to the control. Herbicidal activity was also preserved, and the encapsulation was shown similar results as shown by pure AI (Grillo et al. 2014). In continuation to this study, the same group evaluated the fate of encapsulated herbicide in the environment. They studied the colloidal stability and toxicity of encapsulated paraquat in aquatic humic substances and found no significant changes in the physical–chemical stability of the nanoparticles. However, these humic substances help in reduction of the ecotoxicity and genotoxicity of nanoparticles containing paraquat. These kinds of studies are required in other formulations also, as it will help in better understanding of interaction between the carrier systems and the ecosystem (Grillo et al. 2015). In one study, when diuron was encapsulated in carboxymethyl chitosan nanoparticles, the herbicidal activity was only for target species (*Echinochloa crus-galli*) and not for non-target species (*Zea mays*) (Yu et al. 2015).

When alginate/chitosan and chitosan/tripolyphosphate nanoparticles was used to encapsulate the imazapic, imazapyr, and paraquat herbicides, the encapsulation had shown better performance in their mode of action, toxicity to other organism (dos Santos Silva et al. 2011; Maruyama et al. 2016). The poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) microspheres were formulated by emulsification/solvent evaporation method with atrazine herbicide, and 25% encapsulation efficiency was achieved. The release kinetics was altered to reduce the environmental loss (Lobo et al. 2011). All these results discussed above along with the other studies (Chi et al. 2017; Guo et al. 2014; Singh et al. 2015a) have shown that polymeric nanoparticles could serve as an herbicide carrier with lower environmental impact, comparable effect, and effective delivery.

10.3.2 Nano-emulsion

Nano-emulsion of herbicides could be another alternative for effective delivery of active ingredients. Nano-emulsion can be defined as a non-equilibrium colloidal system that contains oil(s)/surfactant(s)/water with particle size of diameter typically in the region of 20–200 nm. The nano-emulsion is generally optically translucent and sometimes transparent that is kinetically stable. It is being used in various drug and cosmetic formulations and food industry. Some of nano-emulsion formulations of herbicides are discussed below.

In one study, nano-emulsion formulations were produced from micro-emulsion-based pre-formulations of water-soluble herbicide glyphosate isopropylamine. It was generated with the low-energy emulsification of gentle stirring with 41% glyphosate. The nano-emulsion system had small particle size and lower surface tension and shown better results than the commercial formulation (Jiang et al. 2012). In another study, the nano-emulsion formulations with glyphosate displayed a significantly lower spray deposition on weeds studied as compared to commercial formulation—Roundup®. Still the visible injury rates of weeds treated with the nano-emulsion formulations were statistically equivalent to those relating to Roundup® at 14 days after treatment and were attributed to the enhanced bioactivity of the nano-emulsion formulations (Lim et al. 2013). These initial findings could aid the development of sustainable nano-emulsion systems as a greener alternative to advanced agrochemical formulations.

The essential oils from plants are being widely used in agriculture and food industries for their different role. Some essential oils have herbicidal properties. In past, there are studies carried out to fabricate and apply the nano-emulsion of plant essential oil for weed control. In our past study, we have used the formulation of *Thymus capitatus* L. (wild and cultivated thyme) and *Majorana hortensis* L. (marjoram) oils for control of *Convolvulus arvensis* and *Setaria viridis* (El Azim and Balah 2016). The results of this study have revealed that the prepared emulsion of *M. hortensis* was better as compared to the *T. capitatus*. Nano-E showed inhibitory effect on *C. arvensis* even at 5–7 leaves stage. In another study, the oil/water

(O/W) nano-emulsion NE of (*Satureja hortensis*) essential oil has shown the herbicidal properties. It affected the weed killing by interfering with its germination, growth, and physiological processes. The nano-emulsion was stable after 30 days of storage and indicated that it can be a promising natural herbicide for weed control (Hazrati et al. 2017).

10.3.3 Nano-absorbents

The application of herbicides that are adsorbed on carrier material can reduce the risk of groundwater contamination resulting from rapid leaching. Like other pesticides, this will limit the amount of herbicide immediately available for undesirable losses. Due to the cost and sustainability, the natural materials like clay and organic waste are of special interest as carrier material. Clay is very popular material for designing the slow release formulation of pesticides, as we can modify the surface by the adsorption of organic cations and transforming it from hydrophilic to hydrophobic. This modified clay mineral surface can adsorb organic active ingredients that have low solubility in water. This has been utilized to make slow release formulation of alachlor and metolachlor that showed improved weed control (El-Nahhal et al. 2000; Nir et al. 2000). Atrazine is a common herbicide that is effective for control of broadleaf weeds and is non-biodegradable in nature. Allophanic clays and nanoclay was added to modify the polymeric matrix containing atrazine, and a controlled release formulations (CRFs) were formulated (Cea et al. 2010). The formulation has shown a reduced leaching loss, and more seedling death was observed with nanoclay containing matrix (Cea et al. 2010). In another study, hydroxyapatite (HAp) was used as nano-adsorbent for atrazine. The formulation has efficiently controlled the growth of *Brassica* sp., and the results are attributed to the adsorbing ATZ over the surface of HAp NPs that restricted its premature runoff (Sharma et al. 2019).

The adsorption potential and applicability of surfactant-modified clinoptilolite (SMC) and montmorillonite (SMM) nanoparticles was evaluated with 2,4-D. This slow release formulation has showed the three times higher adsorption potential than the unmodified silicates (Bhardwaj et al. 2015). In one study, the 2,4-D was adsorbed on nanosized husk. The waste husk was considered as better alternative carrier for herbicide due to its easy availability. The optimum ration of nano-rice husk to 2,4-D was 1:0.1, and the mechanism of absorption was accounted to monolayer mode of sorption following chemisorption process. Due to the property of this formulation, it exhibited better herbicidal activity against Brassica plant (Chidambaram 2016).

In one study, the researcher used anionic clay and a commercial cationic organoclay as nanocarriers for imazamox (Imz) herbicide and found that it was adsorbed in interlayer structure. With the similar efficacy, the herbicide concentration in soil column was decreased by 20–35% as compared to commercial formulation (Khatem et al. 2019). The nanotubes of aluminosilicate clay mineral-Halloysite were loaded with botanical herbicide, and loading efficiency of 7.26 wt% eupatorium adenophora spreng (AIEAS) was achieved (Zeng et al. 2019). To slower down the release further, they incorporated this carrier in poly (vinyl alcohol)/starch composites (PVA/ST) film and found the significantly increased service life of bioherbicide.

All the results have indicated that the fabrication of effective nano-adsorbent for slow release of herbicides has great potential to reduce the agricultural runoffs and ensure their effective functioning. The adsorbing efficiency can be varying and mainly depends on method of synthesis and properties of nanocarriers. But the suitability of these nanoformulations in the field condition needs to be confirmed only after its toxicological behavior is studied. This information will help the regulating bodies to regulate its use in agriculture.

10.3.4 Synergistic/Antagonistic Effect of NPs on Herbicides

Some studies have evaluated the interaction effect of nanoparticles on herbicide, and they found both synergetic and antagonistic interaction. The silver nanoparticle (AgNPs) singularly, and in combination with Diclofop-methyl (DM) herbicide was evaluated. The results indicated that AgNPs alone has more impact on the plant growth, as compared to the mixture with herbicide. The antagonistic effect might be because the DM in solution affects the stability of AgNPs and reduced Ag+ release from AgNPs in the mixed solution (Li et al. 2018a). In another study, AgNPs have shown synergistic effect with imazethapyr (IM) (Wen et al. 2016). Combined exposure of AgNPs and herbicide in *Arabidopsis thaliana* had increased the silver concentration in roots. The exposure of AgNPs in plant has increased the accumulation of amino acids and resulting in more Ag+ formation from AgNPs (Wen et al. 2016).

10.4 Use of Nanoparticles for Removal of Herbicides from Soil and Water

Worldwide increasing trends of herbicide consumption and its contamination in soil and water are the major concerns for agricultural community (Hallberg 1986). The methods like photocatalysis and biological methods are being tested for efficient removal of these polluting herbicides from the water and soils. Popular solution to this problem can be the use of an efficient photocatalytic material for their degradation. Till date, several nanoparticles, such as TiO_2, Fe, ZnO, Si, or their composites, have been studied for degradation of organic compounds. Due to the eco friendliness, low cost, and novel properties, the nanocatalysts are gaining popularity. The NPs show properties like band gap in visible region, stability, and reusability. Some of the studies on nanoparticles in removing of herbicides have been discussed in detail below.

10.4.1 TiO_2 and Its Composites

The widely used catalyst TiO_2 is reported to be photochemically stable, non-toxic, and inexpensive. Therefore, the applicability of titania for remediation of pesticides from water was investigated (Daneshvar et al. 2006). In one study, the photocatalytic degradation of paraquat was achieved by TiO_2 nanoparticle that was synthesized by an acid-catalyzed sol–gel method (Marien et al. 2017). The results have shown that the catalytic performance of this composite was dependent on the morphology of particles. Also, it performed better in degradation of paraquat when compared to commercially available P25 nanoparticles. Similar results had been found in case of 2,4-D, when commercial TiO_2 is compared with hydrothermal TiO_2 (Sandeep et al. 2018). The biosynthesized TiO_2 NPs and hollow fibers, chemical synthesized TiO_2 nanotube arrays, and thin films had been used for paraquat degradation (Marien et al. 2016; Phuinthiang and Kajitvichyanukul 2018; Wongcharoen and Panomsuwan 2018; Zahedi et al. 2015), and results had confirmed that morphology of catalyst plays a key role in the photocatalytic activity.

Recently, many efforts are being made to convert the TiO_2 adsorption from UV to the visible light by doping with several transition metals, including platinum ions. The aim of these studies was focused on increasing catalyst degradation process efficiency under the solar spectrum. Efficient photodegradation of azimsulfuron in the presence of TiO_2 nanocrystalline films was achieved by using low-intensity black light tubes emitting in the near-UV. The degradation of the herbicide follows first-order kinetics according to the Langmuir–Hinshelwood model. The presence of platinum at neutral valence state and optimum concentration induced higher photodegradation rates, while silver-modified titania exhibited similar photocatalytic rates with those obtained with pure nanocrystalline TiO_2 films. Finally, the effect of initial pH value was also examined. Acidic or alkaline media were unfavorable for azimsulfuron photodegradation (Pelentridou et al. 2008). In another study with Sn-doped TiO_2 and commercially purchased TiO_2 P25, the photocatalytic degradation of a sulfonylurea herbicide-chlorsulfuron (ChS) was achieved. Comparison between these nanoparticles has indicated that presence of Sn^{4+} in the TiO_2 lattice has beneficial effect on the photocatalytic degradation of chlorsulfuron (Fresno et al. 2005).

The study was planned to check the feasibility of UV-assisted degradation of commonly used atrazine with TiO_2 nanoparticles doped with trivalent iron. Under the optimal condition, the maximum atrazine removal rate was achieved at pH = 11 in the presence of Fe^{3+}–TiO_2 catalyst (25 mg/L). The results obtained in this study suggested that this catalyst was an appropriate method to reduce atrazine in contaminated water resources up to 99% (Shamsedini et al. 2017). In previous study, sol–gel synthesis method was used to produce N,F-TiO_2 NPs, and this catalyst demonstrated three times more photoreactivity in atrazine degradation as compared to undoped TiO_2 (Samsudin et al. 2015). In another study, boron-doped TiO_2 was four times faster than those pure NPs for degradation of atrazine (Wang et al. 2016b). These doping has helped in effective interparticle electron transfer and resulted in more efficient catalyst.

In one study, the researchers have prepared platinum-modified TiO_2 samples and used them for photocatalytic degradation of 2,4-D and 2,4-DP herbicides (Abdennouri et al. 2015). The results of their study had proved the higher photocatalytic activity of Pt/TiO_2 as compared to bare TiO_2, and the photocatalytic activity increase was positively correlated to presence of the platinum in the catalyst mixture (Abdennouri et al. 2015). In another study, Pt was loaded in nanotube structured TiO_2 on Ti surface in ethylene glycol (Ti/TiO_2NTEG) was used for photo-electrocatalytic degradation of paraquat (Özcan et al. 2018), and the results indicated the better performance due to presence of Pt. Photocatalytic degradation of atrazine was evaluated by TiO_2 NPs that were superficially modified with Au, Ni, Cu NPs (Santacruz-Chávez et al. 2015). Out of these three catalysts, Au/TiO_2 has shown a better catalytic performance in similar reaction condition. It is also found that higher loading of metal ions on TiO_2 resulted in the lower photocatalytic activity, indicating that it needs to be standardized case by case (Yuliati et al. 2016). When Cu NPs incorporated TiO_2 nanotubes for degradation of Simazine—an herbicide used to kill control broad-leaved weeds and annual grasses, it was found that evenly distributed Cu (0.45%) on TiO_2 NTs was optimum to cause approximately 64% degradation in 4 h under UV light. Like other metals, the Cu acted as electron traps and prevented recombination of electron–hole pairs resulting in better photocatalytic activity (Meriam Suhaimy et al. 2016). One report has suggested that OH radical generated during the photocatalysis process by Bi-doped TiO_2 nanotubes anchored on graphene was mainly responsible for degradation of Dinoseb (Alam et al. 2017).

In another study, mesoporous Ga_2O_3–TiO_2 nanocomposites was synthesized with sol–gel method and used for degradation of imazapyr herbicide (Ismail et al. 2018). The experiments confirmed that the 98% of herbicide was degraded within 3 h when treated with 0.1% of catalyst. Another group of researchers used mesoporous In_2O_3–TiO_2 nanocomposites for photodegradation of same herbicide. They found 1.5% increase in photonic efficiency when nanocomposite was compared with TiO_2 (Kadi et al. 2018). Mesoporous titania/zirconia nanopowder was used for photocatalytic degradation of chloridazon (Mbiri et al. 2018). In another study, WO_3/TiO_2 and Fe_2O_3/TiO_2 were better catalysts for degradation of 2,4-D as compared with pure TiO_2 (Macías-Tamez et al. 2017). Mesoporous WO_3–TiO_2 nanocomposites with different WO_3 concentration (0–5 wt%) were used for 100% conversion of imazapyr (Ismail et al. 2016). These results also support earlier findings that addition of metal with TiO_2 shows stronger oxidative capability.

The carbon nanomaterials were also been used in synthesis of composite with TiO_2 for catalytic conversion of herbicides. In one study, the fullerene C60 with tetrahydrofuran and fullerenol nanoparticles was used to surface modification of

TiO_2, and the composite was used for mesotrione degradation under simulated sunlight. The TiO_2 with fullerenol nanoparticles showed the highest photo-activity, and addition of H_2O_2 and $KBrO_3$ as electron acceptors has resulted in better performance for mesotrione degradation (Djordjevic et al. 2018).

To overcome the problem associated with separation/recovery of TiO_2-based photocatalyst, many studies have reported the use of various support materials. The composite of Fe°/TiO_2 on activated charcoal (AC) was evaluated for photocatalytic degradation of 2,4-D. The results have shown that nanocomposite had possibility of recovery and reuse (Baloochi et al. 2018). With the aim to prepare the photocatalytic system with catalyst supported on some membrane, the researchers have used chitosan thin film for immobilization of TiO_2 (Le Cunff et al. 2015). The results of the study indicated that this composite has a potential and can be used in a variety of photoreactor designs. The resultant thin film was tested for photocatalytic treatment of terbuthylazine, and they found that this environmentally friendly material can be useful with negligible loss of TiO_2 activity during degradation reactions. Recently, a magnetic hexagonal mesoporous silica (magnetic HMS) was used to hold N-doped TiO_2, and this catalyst was used to remove three herbicides (trifluralin, 2,4-D, and glyphosate). The magnetic HMS and N-TiO_2 have shown a synergetic effect. Firstly, herbicide molecules were adsorbed on the surface of magnetic HMS and then the photodegradation by N-TiO_2 was achieved (Hosseini and Toosi 2018). Highly porous and permeable silicon carbide (SiC) foam was used with TiO_2 NPs for catalytic degradation of Paraquat (Marien et al. 2018). The SiC has properties like high chemical resistance and outstanding thermal stability. Its macro-porosity provided a huge surface for the immobilization of large amounts of TiO_2 photocatalyst. Natural zeolite–clinoptilolite was impregnated with TiO_2 NPs and used for the degradation of 2,4-D (Mehrabadi and Faghihian 2018). These results have provided possible materials for supported catalysis application.

In experimental condition, Bentazon herbicide has been successfully degraded by ZnO/TiO_2 nanocomposite under the UV light (Gholami et al. 2016). The results indicated that the neutral pH has shown better performance as acidic pH and alkaline pH have induced photocorrosion of ZnO. Removal efficiency of catalyst was more when O_2 was continuously purged along with addition of H_2O_2 into reaction mixture.

10.4.2 Fe and Its Composites

The laterite-based iron nanoparticles synthesized using eucalyptus leaf extracts were used as a catalyst for the degradation ametryn—a herbicide in aqueous medium (Sangami and Manu 2017). The results of study showed that optimum time required for degradation was 135 min with 2.83 mg/L dose if FeNPs and that proved the faster reaction kinetics in the presence of nanocatalysts. Similarly, teak plant extract was used to prepare FeNPs, which was used for oxidation of ametryn, dicamba, and 2,4-D mixture. The total conversion of herbicides was in 135 min when Fe NPs was added at the dose of 25.29 mg/L (Sangami and Manu 2018). In one study, it was postulated that sulfate radicals are the major agent of 2,4-D degradation during the hematite nanoparticle-activated peroxymonosulfate (Jaafarzadeh et al. 2017a).

The sulfentrazone is one of the preemergence and post-emergence weedicide for control of certain broadleaf weeds. In one study, the Fe/Ni nanoparticles were used for its dichlorination. Under the acidic pH (4.0), 1 gm/L of the nanoparticles achieved 100% degradation within 30 min. The conversion of sulfentrazone to lesser toxic substances was achieved by a direct reduction on the catalytic activity sites of nanomaterials and indirect reduction by atomic hydrogen (Nascimento et al. 2016). When Ni was used with core–shell Fe@Fe_2O_3 nanowires (CSFN) for degradation of atrazine, it increased the rate of conversion by six times (Shen et al. 2018). The finding has indicated that reduction of Ni produced active hydrogen (–H) that helped to break recalcitrant *s*-triazine ring, resulting in formation of formic acid and nitrite acid (Shen et al. 2018). Effectiveness of nanozerovalent iron (nano-ZVI) and palladium has been earlier assessed to dechlorinate herbicide atrazine from contaminated water and soil (Satapanajaru et al. 2008), and it was found that Pd has important role in catalytic process and enhanced destruction kinetic rates of atrazine. Composite comprising WO_3 with Fe-based MOF (MIL-53) has also exhibited outstanding photocatalytic efficiency for degradation of 2,4-D (Oladipo 2018). In recent study, α-Fe_2O_3 nanoparticles have been efficiently used for acetochlor degradation under the UV light (Fu et al. 2019).

Glyphosate is a popular choice of herbicide among the farmers due to its non-selective nature and has global presence. In recent study, reusable magnetic bismuth bromide oxide/ferrous oxide (BiOBr/Fe_3O_4) nanocomposites was used (Cao et al. 2019) for glyphosate degradation. It has reported that the degradation was almost double in case of composite when compared to pure BiOBr, and photo-generated holes (h+) were playing a major role in the photodegradation process. In one study, SBA-15 mesoporous silica-based material (Fe–NH_2–SBA-15) containing functionalized Fe NPs was used for removal of glyphosate from wastewaters (Rivoira et al. 2016).

The nano-ZVI when applied with biochar produced from maize was found that adsorption and degradation of 2,4-D were increased. In this study, 2,4-D was completed degraded after 40 h when Fe NPs and biochar were added at the rate of 0.33 and 0.17 g/L in soil medium. The biochar application avoided the aggregation and corrosion of Fe nanoparticles that resulted into better 2,4-D degradation (Ying et al. 2015). The nano-ZVI also found to be effective for degradation of metribuzin (a pre- and post-emergence herbicide) and alachor (K'Owino Isaac et al. 2018; Kabir et al. 2018). The poly(methacrylic-*co*-acrylonitrile) (p(MAc-*co*-AN)) microgels containing cobalt–iron (Co–Fe) bimetallic magnetic nanoparticles have been found to be very effective adsorbents for the removal of paraquat from liquid medium (Ajmal et al. 2015). Ordered mesoporous silicas-SBA-15 and KIT-6 were modified with iron by using the wet impregnation method. This nanostructured catalyst has been found effective degrade atrazine by heterogeneous photo-Fenton process (Benzaquén et al. 2018). Another nanocomposite containing nanoscale zero-valent iron (nZVI) on a clay mineral-attapulgite (ATP) was used to activate peroxymonosulfate (PMS) to generate reactive free radicals during the photocatalysis of for quinclorac (Ding et al. 2019).

In biodegradation, living microorganisms or their products are used to remove the pollutants. In case of herbicides also many potential microorganisms have been isolated for a cost-effective removal of contaminants. Some strains of *Bacillus* spp. can use atrazine as carbon and nitrogen source. Recently, two isolates of *Bacillus* spp. were immobilized on α-Fe_2O_3 magnetic NPs (Khatoon and Rai 2018). The results have shown that biodegradation efficiency was increased due to α-Fe_2O_3 magnetic NPs carrier. Due to immobilization, the physicochemical properties of biodegradation process can be extended, like pH (4.0–9.0), temperature (20–45 °C), initial concentration (50–300 mg L^{-1}), and agitation speed (50–300 rpm).

10.4.3 ZnO and Its Composites

Zinc oxide (ZnO) is also a widely used catalyst that shows efficient activity at low cost, so is widely used for pollutant degradation. In recent study, the two herbicide derivatives, metamitron and metribuzin, were exposed to photodegradation process assisted by Ag/ZnO composite (Xu et al. 2017). The Ag nanoparticle was present in every sheet of ZnO microflower, and the composite had shown the enhanced photocatalytic performance. This performance was accounted to the reduction of the recombination probability of electron–hole pairs due the presence of Ag that plays a critical role in photocatalysis. Similar results were obtained when Ag/ZnO powders had been used for degradation of diuron under solar light (Saidani et al. 2018). The results showed that addition of Ag helps to increase the rate of degradation by 14 times as compared to unmodified ZnO. When Ag and/or Au nanoparticles were added to Cu-doped ZnO, the photodegradation of diuron was significantly increased due to the synergistic effect by efficient electron transfer (Saidani et al. 2019). In one study, N-doped ZnO was used for degradation of 2,4-D and picloram under the on visible light. N-doping on ZnO shifted the photo-absorption wavelength range to longer wavelength, making it suitable for visible photocatalytic activity (Macías-Sánchez et al. 2015). Zinc oxide (ZnO) nanotube that was loaded with WO_3 nanoparticles was used for photodegradation of chlorinated phenoxyacetic acid. It has shown better efficiency as shown by other composites because of the improved separation of photo-generated charges (Li et al. 2018b). Biosynthesized ZnO was also tested for paraquat degradation (Munshi et al. 2018).

10.4.4 Other Nanoparticles/Composites

When researchers used combination of oxidants like peroxymonosulfate (PMS) and ozone, along with magnetic copper ferrite nanoparticles as a catalyst ($CuFe_2O_4$) for degradation of 2,4-D, it was found that 20.0 mg/L of 2,4-D could be completely degraded in 40 min. The reaction components were optimized in pH = 6.0, where the concentrations of PMS and ozone were 2.0 mM and 16.0 mg/L, respectively (Jaafarzadeh et al. 2017b). Zinc oxide nanoparticles alone were also used as catalyst for degradation of S-Metolachlor herbicide under the direct sun light (Rao et al. 2016).

A catalyst comprising of silver–tungsten oxide on porous siliceous SBA-15 (Ag-WO_3/SBA-15) support was used for degradation of atrazine in water samples. The photocatalytic degradation under visible light was significantly enhanced due to addition of Ag that resulted in reduction of electron–hole recombination (Gondal et al. 2016). WO_3 was coated on ZnO nanorods (NRs) and used for degradation of 2,4-D under natural sunlight. This catalyst has shown better performance as compared to pure ZnO NRs, and commercial WO_3, and might be due to the altered the optical properties (Lam et al. 2015). For 2,4-D, WO_3 nanorod doped with Pd was also effective photocatalyst, and activity was positively correlated with the quantity of doped Pd (Mkhalid 2016).

A catalyst comprising of Cu NPs on montmorillonite and quarts sand was also tested for atrazine degradation. The degradation of atrazine by montmorillonite and Cu NPs composite was found to be 1.7957 g mg^{-1} min^{-1}, while it was 0.8133 g mg^{-1} min^{-1} when Cu NPs was deposited on sand. The reaction rate was linked to redox-active species of Cu that are spread over the structure of composite (Kalidhasan et al. 2017). Cerium(IV) oxide (CeO_2) nanoparticles play a vital role in photocatalysis because the oxygen vacancies arise from multiple valency. In one study, the graphitic carbon nitride/CeO_2 (g-C_3N_4/CeO_2) composite was utilized for degradation of diuron, and the results indicated the good performance of the catalyst under the visible light. The better performance of this composite was due to the enhanced separation efficiency of photo-induced electron–hole pair by forming heterojunction between ceria and g-C_3N_4 (Kesarla et al. 2018). When two semiconductors—CeO_2 and Sb_2S_3—were used with chitosan/starch support for degradation of Paraquat under the UV light, it was found that hydroxide form present in the composite produced more –OH. Also the heterostructured NPs influenced the band gap of the product resulting in better performance (Hosseini et al. 2018).

Nanostructured bismuth oxide has shown a strong potential for photocatalytic degradation of pollutants in aqueous medium. When different sizes of Bi_2O_3 nanoparticles were used for atrazine degradation, the results suggested that particle size effect is very important factor that needs to be considered while developing a Bi_2O_3-based catalyst system (Sudrajat and Sujaridworakun 2017). A composite of manganese dioxide/graphite (MnO_2/C) was synthesized by high-energy electron beam irradiation. This synthesis method introduced large number of hydroxyl groups on MnO_2 nanosphere surface. These hydroxyl groups increased the adhesion of MnO_2 on graphite by hydrogen bond and were mainly responsible for the catalytic degradation of glyphosate through hydroxyl radicals (Wang et al. 2016a).

Recent years, graphene and graphene-based nanomaterials have gained immense interest as heterogeneous catalysts due to their properties like a larger surface area, high electrical conductivity, and excellent absorptivity. In one study, a composite consisting of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (NZF) nanoparticle and reduced graphene oxide (RGO) was used to degradation of trifluralin (Moitra et al. 2016).

Silica nanoparticles (SiNPs) are among the promising nanomaterials that have applications in the various fields like drug delivery, catalysis, immobilization, and sensing. They possess broad range of compatibility with the biosystems and can be easily synthesized. The application of silica nanoparticles for detection and degradation of herbicides is already highlighted in earlier reviews (Bapat et al. 2016; Nsibande and Forbes 2016). Palladium (Pd) nanoparticles when attached to carpet-like arrays of CNT that were anchored on porous carbon foams found effective in degradation of atrazine (Vijwani et al. 2018). The results indicated that this kind of hybrid structure can be used as potential platform for catalytic degradation. Also the green synthesized gold particles had also been used for highly efficient degradation of quinclorac (Shi et al. 2017).

10.5 Preparation of Nanomaterials Using Weeds

To generate develop any material to nanomaterials or create new materials, nanotechnology builds materials beginning with atoms that implemented through chemical, physical, and biological methods are used to produce nanoparticles which are reviewed earlier (Panigrahi et al. 2004). In recent past, the development of efficient green synthesis methods for nanoparticles has become a major focus of many studies. Many researchers have investigated the biological route to find an environment-friendly technique for producing well-characterized nanoparticles (Iravani 2011). The weeds which are available abundantly all over the word can be a very useful source of biotemplate for production of metal and other various nanoparticles. Some of the studies that have used weed for synthesis of nanoparticles are summarized in Table 10.1.

Many studied have used the extract of different tissues of weeds to synthesize particles like silver and gold (Table 10.1). In some studies, ZnO, iron, and palladium NPs had been synthesized. These biologically produced nanoparticles had shown potential application ranging from antimicrobial properties to catalyst for pollution degradation (Table 10.1). These studies provided a base for scaling up NPs synthesis by using freely available weed resources. This will open a possibility for its large-scale utilization for a rapid, non-polluting method of NPs synthesis.

Table 10.1 Green synthesis of different nanoparticles using weed extracts for various application

Nanoparticle	Weeds	Size	Application	References
Silver	Parthenium leaf extract	~50 nm	–	Parashar et al. (2009)
	Ipomoea aquatica, *Enhydra fluctuans* and *Ludwigia adscendens*	100–400 nm	–	Roy and Barik (2010)
	Desmodium triflorum	5–20 nm	Antimicrobial activity	Ahmad et al. (2011)
	Ipomoea carnea	–	Degradation of organic pollutants	Ganaie et al. (2014)
	Cannabis sativa (industrial hemp)	20–40 nm	Antimicrobial activity	Singh et al. (2018)
	Lepidium draba	20–80 nm	Antimicrobial activity	Benakashani et al. (2017)
	Mimosa pudica	10–60 nm	–	Ganaie et al. (2015)
	Lantana camara L.	~33.8 nm	Antibacterial activity	Manjamadha and Muthukumar (2016)
	Euphorbia hirta L.	40–50 nm	–	Elumalai et al. (2010)
	Solidago altissima	–	Plasmonic photocatalyst	Kumar et al. (2016)
	Chenopodium aristatum L.	3–36 nm	Catalytic/ Antibacterial activity	Yuan et al. (2017)
	Chenopodium murale	30–50 nm	Antioxidant and antibacterial activity	Abdel-Aziz et al. (2014)
	Chenopodium album	10–30 nm	–	Dwivedi and Gopal (2010)
	Malva parviflora	19–25 nm	–	Zayed et al. (2012)
	Prosopis juliflora	–	Antimicrobial activity	Raja et al. (2012)
	Lantana camara	–	Antimicrobial activity	Ajitha et al. (2015)
	Lantana camara	75.2 nm	Antioxidant activity	Kumar et al. (2015a)
	Trianthema decandra	36–94 nm	Antimicrobial activity	Geethalakshmi and Sarada (2012)
	Cynodon dactylon	8–10 nm	Antibacterial activity	Sahu et al. (2013)
	Lantana camara	~40 ± 2.8 nm	Antibacterial activity	Singh et al. (2015b)
	Calotropis procera	35 nm	–	Babu and Prabu (2011)
	Aerva lanata	~18.62 nm	Nanocatalysts	Joseph and Mathew (2015)
	Solanum nigrum	~28 nm	Antibacterial activity	Krithiga et al. (2015)

(continued)

Table 10.1 (continued)

Nanoparticle	Weeds	Size	Application	References
Gold	*Cannabis sativa*	12 and 18 nm	Antimicrobial activity	Singh et al. (2018)
	Tinospora cordifolia	16–75 nm	–	Abbasi et al. (2014)
	Mimosa pudica	–	Catalytic and antioxidant properties	Pirathiba et al. (2018)
	Pistia stratiotes L.	2–40 nm	–	Anuradha et al. (2015)
	Antigonon leptopus	–	Degradation of organic pollutants	Ganaie et al. (2016c)
	Chenopodium album	10–30 nm	–	Dwivedi and Gopal (2010)
	Prosopis juliflora	–	–	Raja et al. (2012)
	Trianthema decandra	33.7 nm and 99.3 nm	Antimicrobial activity	Geethalakshmi and Sarada (2012)
	Lantana camara	–	Dye Reduction	Phukan et al. (2018)
	Aerva lanata	~17.97 nm	Nanocatalysts	Joseph and Mathew (2015)
Silver-Gold	*Antigonon leptopus*	10–60 nm	–	Ganaie et al. (2016b)
Iron	*Eichhornia crassipes*, *Lantana camara* and *Mimosa pudica*	40–230 nm	Wastewater remediation	Prabhakar and Samadder (2017)
ZnO	*Parthenium hysterophorus* L.	Spherical and hexagonal particle, sizes 27 ± 5 nm and 84 ± 2 nm, respectively	Antifungal activity	Rajiv et al. (2013)
Palladium	*Antigonon leptopus*	5–70 nm	–	Ganaie et al. (2016a)

10.6 Conclusion

Nanotechnology is developing rapidly in recent years and producing new techniques, new structures, and new materials. This can act as the starting point for exploring nanotools in weed control. Many nanomaterials and nanostructures have biological properties against different types of weeds. In herbicide industry, many nanomaterials can be used in polymeric formulation. These nanoformulation materials' structure and property, and its stability are characterized to test the application with special properties. Designed nanoformulation using cheaper materials and that are more effective is required for reducing the product cost. The safety and environmental consideration for nanomaterials is another issue before its applications to overcome the traditional herbicides difficulties. Finally, we can conclude that nanotools are promising to change the field of weed control, ranging from the efficiency, good delivery systems and lower adverse effects on the environments. These technologies are in the early stage and can be used safely if many considerations taken into account.

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