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# Recent advances in mitigation methods for herbicide residues in the soil

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**ABSTRACT**

In modern agriculture, with more emphasis on high input systems and the widespread application of herbicides has indubitably improved the crop production but has also resulted in inadvertent harm to the ecosystem. The increased awareness towards the adverse effects of herbicide residues on human health and environment resulted in a significant shift towards the mitigation strategies of herbicide residues in the soil as well as in the plants. Several approaches have been found to be utilized for mitigation of herbicide residues in the soil. The hazards from herbicide residues in the soil can be reduced by using low dosage chemicals, tillage operations, crop rotation, using proper nozzle and spraying technique and by using granular, foam, gel and encapsulated materials. Site specific application using variable rate applicator, enhancement of herbicide degradation through bio-stimulation, use of non-phytotoxic oil, adjuvants, surfactants, adsorbents, protectants, antidotes, safeners, biochar, *etc*. are various other effective ways for mitigation of herbicide residues in the soil. Biochar as an amendment to agricultural soils has been found to increase the bioavailable water, builds soil organic matter, enhances nutrient cycling, lowers bulk density, and can provide shelter for beneficial soil microorganisms. Biochar prevents the mobilization of herbicide residues in soil due to its sorption property and hence helps the crop to escape toxicity. Carbon based nano-absorbents such as carbon nanotubes (CNTs) represents a new class of nanomaterial and has been shown to have good potential in removal of various types of herbicide residues in the soil. Graphene is another carbon nanomaterial that has tremendous potential in water purification as well as in various fields due to its unique physical and chemical properties. Nanocrystalline metal oxides such as ferric oxides, manganese oxides, aluminium oxides, titanium oxides, magnesium oxides and cerium oxides are highly effective adsorbents for a broad range of herbicides. These nanocrystalline metal oxides do not only adsorb but also actually annihilate many chemical hazards by converting them to much safer by-products. The amalgamation of bio-augmentation and bio-stimulation along with organic matter addition might be a promising technology for biodegradation of herbicides in soil.

## INTRODUCTION

In the modern agriculture, herbicide usage becomes inexorable to obtain large harvests and minimize the yield losses due to weeds. The availability of herbicides as a cheaper option and a rally in farm good prices has led to a sharp increase in herbicide demand within the farming community (Mukherjee 2011). Usage of herbicides occupy 44% of the total agrochemicals globally and 15% in India (Sondhia 2014). The astute use of herbicides provides selective and economical weed control; however, recurrent and non-judicial use may lead to soil residues, phytotoxicity and adverse consequence on subsequent crops, non-targets organisms and environment eventually leading to human peril (Janaki *et al.* 2015). The continuous use of herbicides leads to the problem of soil persistency that causes far reaching environmental consequences. The longer persistence of herbicide in soil poses a hazard to subsequent land use, which is undesirable. The increased awareness towards the adverse effects of herbicide residues on human health and environment caused a significant shift towards the adoption of mitigation strategies of herbicide residues in soil as well as in plants.

Several approaches have been utilized for mitigation of herbicide residues in the soil. The hazards from herbicide residues in the soil can be reduced by using low dosage chemicals. Residue levels exceeding the maximum residue limit (MRL), due to unnecessary high application rates or short pre-harvest intervals (PHIs) are contrary to the concept of good agricultural practices (GAP) and necessitating use of mitigation measures. Tillage operations, soil decontamination, crop rotation, site specific application using variable rate applicator, enhancement of herbicide degradation through bio-stimulation, use of non-phytotoxic oil, adjuvants, surfactants, adsorbents, protectants, antidotes, safeners, biochars, *etc*. are various effective ways for mitigation of herbicide residues in the soil. Biochar as an amendment to agricultural soils has been found to increase the bioavailable water, builds soil organic matter, enhances nutrient cycling, lowers bulk density, and can provide shelter for beneficial soil microorganisms. Carbon based nano-absorbents such as carbon nanotubes (CNTs), graphene, nanocrystalline metal oxides represents a new class of material and have shown good potential in removal of various types of herbicide residues in the soil (Firozjaee *et al.* 2018). The amalgamation of bio-augmentation and bio-stimulation along with organic matter addition are also promising technology for biodegradation of herbicides in soil. Despite these traditional means of herbicide residue mitigation methods, there appears need of more modern cost effective, farmer's friendly and modern approaches of soil residue mitigation strategies. Here, in this review, we discussed the different approaches and methods used for the mitigation of herbicidal residues in the soil.

**Management of herbicide residues in soil**

An ideal soil applied herbicide should persist long enough to give an acceptable period of weed control but not so long that soil residues after crop harvest limit the nature of subsequent crops (Wagh 2017). Despite the presence of several cultural and mechanical management practices, management of herbicide residues in the soil remains a challenging task. Management techniques, which can help and are in use to minimise the residue hazards in soil are discussed briefly in this review.

**Use of optimum dose of herbicide**

Expected hazards from herbicide residues can be minimized by the application of herbicide in their lowest effective dose by which the desired weed control is achieved. Application of herbicides in bands will also reduce the total amount of herbicide to be applied. This can be practiced in line-sown crops or crops raised along ridges, such as cotton, sugarcane, sorghum, maize, *etc.* Application of atrazine at the rate of 2.0 kg/ha exhibited more than 90% atrazine degradation on 90$^{th}$ day in the sugarcane grown soil, whereas, the same was achieved in 180 days when the atrazine application rate was 5.0 kg/ha (Shanmugasundram *et al.* 2005). Increase in residue and persistence of herbicides in soil with increase in quantity of application have also been reported for various herbicides (Sondhia 2013, Janaki *et al.* 2015).

**Application of farmyard manure**

Adsorption of the herbicide molecules in the colloidal fractions of farmyard manure makes (FYM) them unavailable for crops and weed. It is also a well-known effective way to mitigate the residual toxicity of herbicides. FYM enhances the microbial activity, which in turn degrades the herbicide at a faster rate. Reduction in atrazine residue has been observed on application of FYM application (12.5 t/ha) followed by application of compost (12.5 t/ha) and phosphoric acid (50 ppm) (Meena *et al.* 2007). Decrease in residual toxicity of atrazine in soybean on application of farmyard manure at 12.5 t/ha or compost 12.5 t/ha or charcoal 5.0 kg/ha along the seed line has also been reported (Chinnusamy *et al.* 2008).

**Ploughing/cultivating the land**

Tillage operations help in bringing deep present herbicide residues to the soil surface, which would aid in decontamination by volatilization (Janaki *et al.* 2015, Sondhia *et al.* 2015). Use of disc plough or inter-cultivators reduces the herbicide toxicity, as the applied herbicide is mixed to a large volume of soil and gets diluted. In case of deep ploughing, the herbicide layer is inverted and buried in deeper layers and thereby the residual toxicity got reduced. The comparative study on the effect of conventional tillage and no-tillage exhibited faster herbicide degradation on the surface layers in conventional tillage (Gaston and Locke 2000). Study on atrazine behavior in soil exhibited faster herbicide degradation in deeper soils than surface layers (Hang *et al.* 2010).

**Crop rotation**

Crop rotation is among another herbicide residue management practices that spreads the planting and herbicide application season, reducing the risk of encountering widespread herbicide runoff during a single runoff event. Ragi–cotton–sorghum is the common example of crop rotation under irrigated field conditions. Fluchloralin 0.9 kg or butachlor 0.75

kg/ha + hand weeding at 35 DAT for ragi + sunflower (border crop), pendimethalin 1.0 kg/ha + hand weeding on 35 DAS for cotton intercropped with onion and two manual weeding at 15 and 35 DAS for sorghum inter cropped with cowpea is the recommended weed control practice (Wagh 2017). Rape seed and sugar beet being sensitive to imidazolinones (imazamox + imazethapyr) must be avoided in rotation as a succeeding crop when the previous crop was applied with these herbicides, however, maize, winter wheat and barley can be used for crop rotation (Suzer and Byuk 2010). Maize and millets can be used for crop rotation in the soils containing triazine residues, whereas crops like, methi, turnip, berseem and gobhi-sarson can be grown in the soil having sulfosulfuron residue (Singh and Walia 2005).

### Use of activated carbon

Activated carbon has a high adsorptive capacity because of its tremendous surface area which vary from 600–1200 $m^2$/g. Incorporation of 50 kg/ha of activated charcoal is found to inactivate chlorsulfuron when applied at 1.25 and 2.50 kg/ha and did not affect the yield of maize when compared to untreated control. A study conducted on charcoal application at 5.0 kg/ha along the seed line have shown reduced residual toxicity of atrazine in the soybean crop (Wagh 2017).

### Light irrigation after application

Continuous moist soils often result in a more rapid degradation of herbicides due to creation of favorable conditions for microbial activity. However, controlled irrigations enhance all modes of deactivation, heavy irrigations leach herbicides out of the root zone of the crop. Leaching of the herbicides by frequent irrigation is possible especially in case of water-soluble herbicides. In this case, the herbicides are leached down to lower layers *i.e.,* beyond the reach of the crop roots. Studies have shown that dissipation of metolachlor and formation of soil bound residues are favoured in saturated soils (Rice *et al.* 2002). Lovell *et al.* (2002) reported faster isoxaflutole degradation in soil maintained at -100 or -1500 kPa as compared to that in air-dry soil.

## Modern approaches for mitigation of soil herbicide residue

### Biostimulation

Biostimulation involves the modification of the environment to stimulate existing bacteria capable of bioremediation. This can be done by addition of various forms of limiting nutrients and electron acceptors, such as phosphorus, nitrogen, oxygen, or carbon (Scow and Hicks 2005). Biostimulation can be perceived by addition of adequate amounts of water, nutrients and oxygen into the soil, in order to enhance the activity of indigenous microbial degraders (Couto *et al.* 2010) or to promote cometabolism (Lorenzo 2008). Biostimulation requires modification of a contaminated soil to provide a natural microbial population with a favorable environment that will allow them to destroy the target contaminant. Biostimulation is mostly preferred due to its stimulation and growth of natural microbes, which are already used to the subsurface environment.

The concept of biostimulation is to boost the inherent degradation potential of a polluted matrix through the accumulation of amendments, nutrients, or other limiting factors and has been used for a wide variety of xenobiotics (**Table 1**). Even though the diversity of natural microbial populations apparently displays the potential for contaminant remediation at polluted sites, factors such as lack of electron acceptors or donors, low nitrogen or phosphorus

**Table 1. Use of various amendments for the enhanced degradation of herbicides**

| Amendment | Target herbicide | Reference |
|---|---|---|
| Animal manure and sewage sludge | Atrazine and alachlor | Guo *et al.* (1991) |
| Activated sludge | Atrazine and simazine | Leoni *et al.* (1992) |
| Sewage sludge and corn meal | Alachlor and trifluralin | Dzantor *et al.* (1993) |
| Maize straw | Methabenzthiazuron | Printz *et al.* (1995) |
| Dairy manure | Atrazine | Gan *et al.* (1996) |
| Cornmeal, rye grass, and poultry litter | Cyanazine and fluometuron | Wagner and Zablotowicz (1997) |
| Plant residues, ground seed, or commercial meal | Alachlor, metolachlor, atrazine and trifluralin | Felsot and Dzantor (1997) |
| Cellulose, straw, and compost | Atrazine | Abdelhafid *et al.* (2000) |
| Compost, corn stalks, corn fermentation by-product, peat, manure, and sawdust | Atrazine, trifluralin, and metolachlor | Moorman *et al.* (2001) |
| Raw olive cake | Chlorsulfuron, prosulfuron, and bensulfuron | Delgado-Moreno and Peña (2007) |
| Biogas slurry, mushroom spent compost, and farm yard manure | Atrazine | Kadian *et al.* (2008) |
| Rice straw, farm yard manure, saw dust, and charcoal | Atrazine | Mukherjee (2009) |

availability, or a lack of stimulation of the metabolic pathways responsible for degradation can inhibit or delay the remediation process. In these cases, accumulation of exogenous nutrients can enhance the degradation of the toxic materials (Kadian *et al.* 2008).

The biostimulation of herbicide degradation in the soil was conceptualized by "land farming techniques," which involves dilution of contaminated soil with uncontaminated soil leading to stimulation of the biodegradation due to the increased activity of soil dehydrogenases (Felsot and Dzantor 1997). Biostimulation requires modification of a contaminated soil to provide a natural microbial population with a favourable environment that will allow them to destroy the target contaminant. Biostimulation is mostly preferred due to its stimulation and growth of natural microbes which are already used to the subsurface environment. The lack of adequate organic matter in the soil generally lead to low microbial population and hence lower decomposition of herbicides (Felsot and Dzantor 1990) leaving the herbicides recalcitrant in the soil for years without degradation.

The addition of organic matter, bioprocessed materials or compost naturally initiates the microbial activity in the soil and could be utilized to treat contaminated soils (Buyuksonmez *et al.* 1999). Fresh bioprocessed materials serve as rich nutrient source and provide an optimum condition for flourishing the microbial growth (Kadian *et al.* 2008). Additions of inorganic nutrients have been reported to facilitate the breakdown of atrazine in the soil (Hance 1973). The addition of inorganic salts like ammonium nitrate, potassium nitrate, and ammonium phosphate have been found to significantly decrease the half-life of herbicides in the soil. Inorganic nitrogen starvation has also found to be more effective in promoting degradation of atrazine and other heterocyclic compounds (Sims 2006). This can potentially be accomplished by supplying excess carbon to make nitrogen limiting.

**Bioaugmentation**

Bioaugmentation is the process of introduction of specific microorganisms aiming to accelerate the biodegradation of target compound or serving as donors of the catabolic genes. Usually this goes in pair with the biostimulation (Kanissery and Sims 2011). If appropriate biodegrading microorganisms are not present in the soil, or if microbial populations have been reduced because of contaminant toxicity, specific microorganisms can be added as "introduced organisms" to enhance the existing populations. Microorganisms help in degradation of the herbicide compounds in the soil by utilizing them as a supply of nutrients and energy. Hence, increasing the population of herbicide degrading, pure culture bacteria by artificial means may be helpful in enhancement of herbicides in the soil. Mixture of pure cultures of microbial population have been found to be effective in enhanced metabolism of atrazine (Mandelbaum *et al.* 1993) with the repeated transfer of the mixed cultures even at the elevated concentrations. *Rhizopus oryzea* is a potential fungal isolate and can be used for the bioremediation of alachlor from soil and the half-life values in sterile and non-sterile soil incubated with *Rhizopus oryzea* were found to be 7.2 and 8.6 days, respectively (Jaya *et al.* 2014).

**Use of biochar**

Adsorption using commercially available activated charcoal can reduce organic pollutants in soils (Rhodes *et al.* 2008) but is an expensive means due to the use of non-renewable and relatively expensive starting material, such as coal. This resulted in increased interest in using biochar as a soil amendment to sequester carbon to mitigate the herbicide residues in the soil. However, the insinuations of adding biochar to the agricultural soil for the environmental fate of pesticides remain unclear. Experimental evidences reveal that application of biochar as an amendment to agricultural soils increases bioavailable water, builds soil organic matter, enhances nutrient cycling, lowers bulk density, and can provide refugia for beneficial soil microorganisms, such us bacteria and mycorrhizal fungi (Atkinson *et al.* 2010). Application of biochar temporarily immobilizes the herbicide residues in the soil and allows the crop to escape from toxicity. The source of material used for biochar production also affects the sorption of herbicide residues in the soil. Cabrera and Spokas (2011) demonstrated that biochar additions, even in small quantity, increased diuron sorption. Thus, the presence of carbonaceous material, even in small amounts, can dominate sorption of organic compounds in the soils (Cornelissen *et al.* 2005). Soils amended with 1% and 2% biochar showed enhanced sorption, slower desorption, and reduced biodegradation of isoproturon (Sopeña *et al.* 2012).

**Nanotechnological interventions**

Nowadays, the entry of residues in the food chain has raised serious concerns related to health issues. Nanotechnology offers many potential benefits to improve existing environmental technologies using new materials with effective performance that resulting to less consumption of energy and materials. Due to its beneficial effects, researchers and industrial communities also gained much interest in nanotechnology**.** Nanotechnology intervention utilizes the structures and devices with a size range from 1 nm (molecular scale) to about 100 nm (Riu *et al.* 2006). A number of nanotechnological interventions such as carbon-based nanotubes (CNT's), graphene, nanocrystalline metal oxides *etc.* are becoming popular in terms of herbicide residue mitigation (Iavicoli *et al.* 2017).

### Carbon nanotubes (CNTs)

Carbon nanotubes represent a novel class of nanomaterials. They are generally composed of graphite carbons arranged in one or several concentric tubules. CNT's may be single walled nanotubes (SWNTs) as well as multi-walled nanotubes (MWNTs) and possess one dimensional structure, thermal stability and unique chemical properties (Firozjaee *et al.* 2018) and have shown tremendous potential in removal of several types of herbicides. The adsorption capacity of herbicides by CNTs is mainly determined by the pore structure and the existence of a broad spectrum of surface functional groups that can be achieved by chemical or thermal modifications to improve the optimal performance for a particular purpose (Yunus *et al.* 2012). The adsorption of organic chemicals on CNTs may involve several mechanisms, such as hydrophobic interactions, covalent bonding, $\pi-\pi$ interactions, hydrogen bonding and electrostatic interactions. Organic molecules containing double bonds or benzene rings such as polycyclic aromatic hydrocarbons (PAHs) and polar aromatic compounds adsorb on CNT through $\pi-\pi$ interaction (Smith and Rodrigues 2015). Adsorption process may also involve hydrogen bonding between functional groups such as –carboxyl, hydroxyl, amino group and organic molecules (Yang *et al*. 2008). Electrostatic attraction is one of the adsorption mechanisms that causes the adsorption of some organic chemicals such as antibiotics and dyes at suitable pH on the functionalized- CNTs. Functional groups increases the hydrophilicity of the CNTs surfaces and make them suitable for sorption of relatively low molecular weight and polar compounds. Multiwalled nanotubules have been investigated for the adsorption of diuron and dichlobenil (Chen *et al.* 2011) and the results indicated an increased absorption of diuron and dichlobenil with an increase in surface area and total pore volume of MWNTs.

The values of adsorbed amount and surface coverage of diuron were larger than those of dichlobenil, while the surface area, molecular volume, and water solubility of dichlobenil were smaller. The adsorption of atrazine by surfactant-dispersed SWNTs and MWNTs demonstrated that surfactant treatment inhibited atrazine adsorption (Shi *et al.* 2010). The hydrophilic fraction of the surfactant micelles faces in water cause the modified-CNTs to become more hydrophilic, which reduced the adsorption of atrazine significantly. Oxidation treatment on MWCNTs increases the surface area and pore volume of the tubes and subsequently and increase in diuron adsorption in spontaneous and exothermic manner (Deng *et al.* 2012). SWCNTs have been reported to have a higher adsorption capacity for 4-chloro-2-methylphenoxyacetic acid (MCPA), a phenoxy acid herbicide (De Martino *et al.* 2012).

### Graphene

Graphene is a carbon nanomaterial that has attracted remarkable attention due to its unique physico- chemical properties and its vital use in water purification. The effective interaction between graphene and pesticides is mediated by polar nature of water (Maliyekkal *et al.* 2012). Graphene has great adsorption capacities for pesticides (ranging from 600 to 2000 mg/g). Graphene has also been used for removal of persistent halocarbon pesticides from water (Sengupta *et al.* 2015). Graphene and related carbon-based nanomaterials can adsorb contaminants with aromatic rings through $\pi-\pi$ interactions (Smith and Rodrigues 2015). Graphene can combine with other materials to improve pesticide adsorption capacity (Zhang *et al.* 2015). Graphene-coated silica (GCS) as a highly efficient sorbent has also been used for removal of residual organophosphorus pesticides from water (Zhang *et al.* 2015).

### Nanocrystalline metal oxides

Nanocrystalline metal oxides are highly effective adsorbents for a broad range of herbicides. Metal oxides such as ferric oxides, manganese oxides, aluminium oxides, titanium oxides, magnesium oxides and cerium oxides are effective and low-cost adsorbents. These metal oxides are used for removal of a broad range of pesticides due to their higher adsorption capacity, faster kinetics, shorter intra-particle diffusion distance and larger number of surface reaction sites (Armaghan and Amini 2012, Moradi Dehaghi *et al.* 2014). Nanocrystalline metal oxides not only adsorb but also degrade the chemical hazards by converting them to much safer by-products under a broad range of temperatures. Their large surface areas and high remedial activities are caused by the size quantization effect. Studies on the removal of organophosphorus pesticides by nano metal oxides revealed that although nano sized metal oxides are effective destructive absorbents for organophosphorus pesticides, production of high-quality fine oxide powders is a relatively difficult task and can be costly.

Herbicide removal using magnetic nanoparticles revealed that the surface modified magnetic core–shell nanoparticles exhibit high adsorption efficiency and high rate of removal of contaminants (Kaur *et al.* 2014). $C_{18}$ fabricated $Fe_3O_4$ core–shell nanoparticle is the most commonly used magnetic nanoparticle for removal of pesticides. They are suitable for extraction of nonpolar and moderately polar compounds due to their suitable separation ability, excellent stability, and convenient operation. $C_{18}$-silane modification of $Fe_3O_4$-$C_{18}$ magnetic particles resulted in hydroxylation as well as adsorption of $C_{18}$ groups on the surface of the magnetite because of adsorption of both hydrophilic and hydrophobic compounds. Organophosphorus pesticides were absorbed by $Fe_3O_4$-C18 by a magnetic field (Shen *et al.* 2007). Nanocrystalline alumina particles have been used for effective adsorption of organophosphate in a short period of time. The faster adsorption may be attributed to high surface area and the concentration of hydroxyl groups on the surface of nanocrystalline alumina. A list of nanocrystalline metal oxides with their adsorption parameters for pesticide removal is summarized in **Table 2**.

**Nanofiltration**

The nanofiltration (NF) membrane is a type of pressure-driven membrane with properties between reverse osmosis and ultrafiltration membranes and is considered the most effective recent technique of membrane filtration. It is a promising technology to remove hazardous organic micro-pollutants, such as pesticides, dyes, and many other synthesized products. Specific nanofiltration membranes of specific pore size can be used for different molecules based on their molecular weight. The adsorption characteristics of organic matter on membrane surfaces are governed by the physical and chemical properties of the membrane, pesticides properties, feed water composition and filtration system operating parameters. The physical and chemical properties of the membrane selected are an important factor for the removal of herbicides. NF70, NF45, UTC-20 and UTC-60 are some nanofiltration membranes used for herbicide/pesticide rejection (Bruggen *et al.* 2001). The major parameters that affect the filtration capacity of membrane are molecular weight cut-off (MWCO), desalting degree, porosity and the membrane material. The molecular weight cut-off (MWCO) of 90% is commonly used by most membrane manufacturers as a measure of the retention properties of NF membranes (Singh 2005). The rejection of uncharged herbicide molecules was positively correlated with membrane porosity parameters.

**Photocatalysis**

Photocatalysis is an environmentally friendly process used for elimination of a number of organic pollutants and is quite suitable pre-treatment for hazardous and non-biodegradable contaminants to enhance their biodegradability. Photocatalysis can also be used as a polishing step to treat recalcitrant organic compounds (De Lasa and Serrano-Rosales 2009). In a photocatalysis process, photoexcitation of semiconductor solid surfaces happens by irradiation, either by near UV or solar light. As a result, mobile electrons and positive surface charges are generated. These excited sites and electrons accelerate oxidation and reduction of pollutants. Through the development of nanotechnology, semiconductor photocatalysts have been modified in terms of reactivity and selectivity. Based on this principle, a wide range of pesticides has been treated by photocatalytic degradation (**Table 3**).

**Table 2. Nanocrystalline metal oxides commonly used for adsorption of different pesticides**

| Nanocrystalline metal oxides | Modifier | Target pesticide class or pesticide | Reference |
|---|---|---|---|
| $Fe_3O_4$ | Polystyrene | Organochlorine | Cheng 2013 |
| $Fe_3O_4$ | C18 | Organophosphorus | Shen *et al.* 2007 |
| $Fe_3O_4$ | Hexagonal Mesoporous silica (HMS) | DDT | Tian *et al.* 2009 |
| $Al_2O_3$ and MgO | Activated carbon | Diazinon | Behnam *et al.* 2013 |
| $Al_2O_3$ | Cerium Oxide | Dimethyl methyl phosphonate | Mitchell *et al.* 2004 |
| $Al_2O_3$ | — | Diazinon and Fenitrothion | Armaghan and Amini (2012) |
| LFCOs NPs | — | Vitavax | Tavakkoli and Yazdanbakhsh (2013) |
| Zinc oxide | Chitosan | Permethrin | Moradi Dehaghi *et al.* 2014 |

**Table 3. Degradation of pesticides by photocatalysts**

| Photocatalyst | Modifier | Target pesticide | Reference |
|---|---|---|---|
| ZnO | $Na_2S_2O_8$ | Azoxystrobin, kresoxim-methyl, hexaconazole, tebuconazole, triadimenol, and pyrimethanil (fungicides), primicarb (insecticide), and propyzamide (herbicide) | Navarro *et al.* (2009) |
| $TiO_2$ | Ag | Organochlorine pesticides (α-hexachlorobenzene (BHC) and dicofol) | Guo *et al.* (2009) |
| $TiO_2$ | C, N and S | Isoproturon | Police *et al.* (2010) |
| $TiO_2$ | N | Lindane | Senthilnathan and Philip (2010) |
| $TiO_2$ | Au–Pd | Malathion | Yu *et al.* (2010) |
| $TiO_2$ | V, Mo, Th | Chlorpyrifos | Gomathi *et al.* (2011) |
| $TiO_2$ | $CdSO_4$ | Methomyl | Barakat *et al.* (2013) |

## Conclusion

Extensive use of herbicides poses far-reaching consequences and there is an essential need for efficient technologies for mitigation of residues. Integration of the mechanical and cultural management practices with herbicides for managing weeds is the most viable option. The combination of bioaugmentation and biostimulation along with organic matter addition might be a promising technology to accelerate the biodegradation of herbicides in the soil. Present researches have shown significant potential for pesticides removal using the different processes of nanotechnology. Although it needs to be studied further on large-scale application of nanotechnology process to eliminate pesticide and other pollutants associated with the investigation on potential risks of nanomaterials for environmental and human health.

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