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Review Article

A COMPREHENSIVE REVIEW ON ROLE OF NANOTECHNOLOGY IN THE SOIL POLLUTANTS REMEDIATION

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Abstract

The degradation and pollution of soil remain a significant environmental problem and its recovery is a worldwide concern. Global soil degradation has a serious adverse impact on food security, agricultural production, and human well-being; therefore, it requires immediate attention. This global problem is further exacerbated by the poisoning of soil with heavy metals, pesticides and persistent organic contaminants. The bioaccumulation of these pollutants in the soil increases the danger of food chain contamination. The need to produce more food and prevent further soil erosion severely hamper agricultural productivity. The revitalization of the contaminated soil resources could be feasible using nano-based soil remediation. Applications based on nanotechnology are inexpensive, easy to apply, and suggest more efficient treatment and remediation. The aims of this review to examine the potential of nano-based rehabilitation of soil polluted with pesticides, heavy metals and their residues as well as with persistent organic contaminants and to investigate how this technology can improve bioremediation and phytoremediation.

Keywords: Nanotechnology, Soil, Pesticides, Heavy metals, Bioremediation, Phytoremediation

1. INTRODUCTION

The most essential element of the terrestrial ecosystem and a significant life-supporting system is soil. Soil coordinates important planetary processes to ensure the survival of life on the planet in addition to providing an essential media for plant growth and food supply (Qian et al. 2020). These include the water cycle, biogeochemical cycles, detoxification of pollutants, control of biogenic gases, ecosystem recovery, and preservation of biodiversity (Bakshi and Abhilash 2020). The terms "soil" and "land" are frequently used interchangeably in the context of reference even though many anthropogenic and natural activities have a similar impact on both targets. Soil is a significant component of the land but the soil is more important than land (Guerra et al. 2018). Maintaining soil health is essential for protecting agricultural and food production as well as the stability of the earth's systems and environmental processes. The process of nano remediation for the remediation of soil pollutants is typically on-site without the use of techniques like soil transportation. As a result, Nano remediation is a financially viable way to restore the environment (Ibrahim et al. 2016).

In the present context, soil contamination and degradation pose a significant threat to food security and agricultural productivity. Numerous factors, including overgrazing, deforestation, soil erosion, urbanization and a loss in soil fertility cause soil degradation (Kristanti et al. 2021). In addition, organic pollutants, chemical pollution from heavy

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metals, pesticides, and polycyclic aromatic hydrocarbons are contributed to soil degradation. Pesticides and fertilizers are used excessively and they accumulate in the soil because a huge portion of them (90 percent) is lost to the air where they eventually find their way into the land (Waqas et al. 2020). Additionally, chemical pollutants such as heavy metals generated by companies harm the land far from the industrial plant as well as in its immediate proximity.

Soil pollution is thought to pose serious environmental dangers that threaten the entire ecosystem. It is estimated that 30% of the land is either deteriorated or poisoned as a result of human activities, with the degradation level growing over time. Pesticides, POPs and heavy metals have damaged and poisoned soil resources and future agricultural production on these resources is no longer possible (Usman et al. 2020). Heavy metals, POPs, and pesticides exhibit biomagnification and bioaccumulation properties of the soil and contaminated soil is not only inappropriate for the production of food but also offers significant concerns of food chain contamination. Thus, crop products cultivated on these contaminated soils have detrimental effects on human health (Rabbani et al. 2016). As a result, the majority of these polluted and contaminated areas are abandoned because they are unfit for crop production, which significantly reduces agricultural output. The farmland that is used for agricultural purposes is decreasing with each passing year due to soil contamination and pollution (Zhang et al. 2019). As a result, we must simultaneously produce sufficient food supply for the rising human population on a planet with a finite amount of land, and also prevent the further contamination of the land. Consequently, prevention is essential along with cleanup and restoration of this contaminated soil. This restored land can subsequently be used to meet the world's current needs for food and biofuels after remediation (Tahir et al. 2020).

2 Applications of nanotechnology in the soil remediation

A unique technology which is developing quickly and expanding its wide applications across all dimensions is nanotechnology. Creating, analyzing, and modifying material at an atomic, molecular, micromolecular and macromolecular level to produce materials with distinct characteristics from the source material is the scope of nanotechnology (Qian et al. 2020). The resulting particles are referred to as nanoparticles (NPs) (Linley and Thomson 2021). Numerous sectors including agriculture, pharmaceuticals, medical diagnostics, food production, nano-based encapsulating of pesticides, medicine delivery in humans, genetic material delivery in plants, and treatment of cancer have applications of nanotechnology. Besides this, it has the most expected applications for the soil and water clean-up. These include the remediation of groundwater, treatment of wastewater, and the recovery of polluted soil (Mobasser and Firoozi 2016).

The growing usage and deployment of nano-based technologies and devices for environmental clean-up is the consequence of a pressing need for a technology that is quicker in providing results without adding any further load to a clean-up process (Alazaiza et al. 2021). The nanoparticles are mostly used to remediate soil polluted by contaminants which have a mostly non-biodegradable nature.

Numerous applications of nanotechnology are used for the remediation of soil, including (i) nano-based substances for the transformation of the heavy metals into less hazardous forms, (ii) nanomaterial for POPs and pesticides deterioration, (iii) nano-based sensing systems for pesticides detection in the soil, and (iv) nano-based phytoremediation of contaminated soil (Elizabath et al. 2019).

Nanoscale zerovalent iron (nZVI), titanium dioxide, zinc oxide, bimetallic nanoparticles, fullerenes and stabilized nanoparticles are among the Nanoparticles that are most frequently utilized for the soil remediation (Kharat et al. 2017). To convert or detoxify pollutants, reactive nanoparticles are applied to the polluted soil during nano remediation. Nanomaterials are effective absorbents because of their huge surface area and sorption sites. In addition, these advantageous characteristics include a smaller interparticle dispersion distance, and variable pore size (HELAL et al. 2016). These characteristics make them exceptional catalysts which can facilitate chemical catalysis and reduction for the minimization of the relevant pollutants. To clean up soil environments affected by the most notorious contaminants, such as polychlorinated biphenyls, organochlorine pesticides, polycyclic aromatic hydrocarbons, chlorinated organic solvents and heavy metals the nanomaterials are gaining much the interest (Tahir et al. 2019).

3 Role of nanomaterials in the removal of heavy metals from the soil

Heavy metal is any element which has a high atomic mass and density. Arsenic, chromium, cadmium, copper, mercury, copper, lead, manganese, cobalt, selenium, zinc, and nickel are the most significant heavy metals from the perspective of their toxicity (Borji et al. 2020). The other less dangerous, less well-known, but equally significant heavy metals are gold (Au), antimony (Sb), molybdenum (Mo), silver (Ag), tungsten (W), barium (Ba), tin (Sn), thallium (Tl), vanadium (V), and uranium (U) (Nizamuddin et al. 2019). The weathering of soil parent material produces heavy metals, which are naturally occurring parts of an Earth's crust, where their proportion is very low. The anthropogenic or external inputs of several heavy metals in the soil are known as paedogenesis (Palani et al. 2021). These anthropogenic inputs are mostly produced by the industries of dye, paint, textile, paper, metallurgical, metal mining, agricultural fertilizer, and tannery. In addition to these, accumulation of heavy metals in soil also caused by spray particles that are produced during the burning of fossil fuels and are carried vast distances by the air from the source (Yang et al. 2019). In many places of the world, a large number of soil sites have heavy metal contamination for all the reasons listed above and posing serious health concerns to people. The sites that are historically poisoned by extensive usage of heavy metals, whose toxic effects were not known earlier, have deteriorated these soils over time and are unsuited for agricultural use (Ahmad et al. 2018). If these sites are not repaired, this may be continued for decades or centuries. To remediate the soil from the heavy metal contamination and prepare it for agriculture and crop production, numerous technical advancements are being investigated. The usage of nanotechnology for the removal of toxic heavy metals from contaminated soil is one of them because of its exceptional ability to adsorb or immobilize metal ions (Subramaniam et al. 2019). Nanoparticles (NPs) are an excellent adsorbent due to their higher adsorption capacity, which has led to an increasing application of the NPs in the elimination of toxic heavy metals from the contaminated soil.

The most extensively researched nanoparticle in the cleanup of inorganic and organic pollutants from the soil is a nanoscale zerovalent iron (nZVI) (Singh et al. 2021a). They are investigated for the conversion of hexavalent chromium to less harmful trivalent chromium form in soil polluted by the tannery waste (Li et al. 2017). In 120 minutes, they claimed that nanoscale zerovalent iron enhanced hexavalent chromium reduction efficacy from 14.5 percent to 86.8 percent (Songa and Okonkwo 2016). Leachability of nZVI-processed and nZVI-unprocessed soil for zinc or lead remediation in the acidified soil is tested using a column experiment. In comparison to untreated soil, they discovered that leachates from columns containing nanoscale zerovalent iron-treated soil had much-reduced quantities of Lead and Zinc (Liu et al. 2019). To assess the ecotoxicological effects of nZVI treatment on soil organisms, they conducted toxicity studies on the bacterial strain *Vibrio fischeri*, the larvae of a specie *Artemia franciscana*, and the nematode *Caenorhabditis elegans* (Khan et al. 2020). The mortality, reproduction, and bioluminescence endpoints of toxicity were all observed to be reduced in nZVI- processed soils and illustrated in table 1.

In a different investigation, the researchers found that applying nanoscale zerovalent iron to a multi-metal polluted calcareous and acidic soil successfully reduced the accessibility of the metals chromium, arsenic, lead, zinc and cadmium (Lu and Astruc 2018). Arsenic, Lead, and Chromium availability was decreased by more than 82 percent, while zinc availability was decreased by a range of between 31 and 75 percent. Cd showed the lowest reduction which varied from 13 to 42 percent (Gil-Díaz et al. 2017).

They discovered that adding 10% of nanoscale zerovalent iron dramatically decreased the Lead uptake in severely polluted soil. Arsenic immobilization was characterized by the production of adsorption complexes between Fe reaction products from the shell of nZVI and ferric arsenates (Ramezani et al. 2021a). Growing barley on these arsenic-contaminated soils cleaned with nZVI resulted in plants that developed more favourably having no negative effects on nutritional content and absorbing less arsenic. Additionally, no negative effects were seen on the various physicochemical characteristics of the soil (Kaur and Roy 2021).

To boost the reactivity and mobility of nanoparticles in the polluted soil, the usage of bimetallic NPs and stabilizers like starch in the manufacture of nano-based materials has been examined. The porous medium's surface chemistry and mobility of TiO2 nanoparticles were reported to be significantly impacted by their encapsulation with carboxymethyl cellulose (Virkutyte et al. 2014). The reduction of Chromium using carboxymethyl cellulose (CMC) with stabilized zerovalent iron nanoparticles was reported (Madhavi et al. 2014). The reduction was boosted further by the addition manure to these nanoparticles. An elevation in hexavalent chromium reducing range of around 60% - 80% was seen with increasing loading concentrations of 0.1 to 0.3 mg/100g for the Nanoparticles. The scientists reported that the reduction capability is enhanced in the presence of functional groups with FYM such as hydroquinones (Singh et al. 2021b). For the conversion of hexavalent chromium to trivalent chromium in soil, these functional groups served as a significant electron donor. Fe-Mn binary oxide nanoparticles stabilized by carboxymethyl cellulose (CMC) are created for the arsenic treatment in contaminated soil (An and Zhao 2012). These Nanoparticles decreased the amount of dissolved arsenic in water by 91% to 96%. Arsenic (III)-containing soil's TCLP leachability was decreased by 94% to 98%, whereas the amount of arsenic (III) left in a soil bed was decreased by 78%. Synthesized nZVI accompanied by biochar were transformed the redeemable Chromium into Fe-Mn oxides (Su et al. 2016). The immobilization effectiveness of Chromium (VI) and overall Chromium was 91.94% and 100% for the 15 days remediate period. Additionally, biochar Nanoparticle-based pollutants remediation was discovered to efficiently raise the organic material contained in the soil, which increased soil fertility and pH and also enhanced plant growth (Sehgal et al. 2018a). The zerovalent iron nanoparticles remediation through iron-copper bimetallic NPs was reported to be highly influenced by temperature and pH (Zhu et al. 2016). At higher doses, nanoscale zerovalent iron/copper showed higher efficacy in reducing Chromium (VI). Cr (VI) exclusion rate has improved as temperature rose with soil Cr (VI) concentration falling around 2 mgL1 over 30 minutes as the temperature rose to 298 K and then to 303 K (Ahmad et al. 2020).

To clean up soil and groundwater contaminated with Cr (VI), iron sulphide nanoparticles (FeS NPs) stabilized with carboxymethyl cellulose (CMC) were successful at immobilizing Cr (VI) through adsorption, reduction, and coprecipitation (Wang et al. 2019). To decrease the mobility of chromium and mercury in polluted soil, the water treatment residual nanoparticle (nWTR) formed in the process of water decontamination process are employed (Moharem et al. 2019). The addition of this nWTR to the polluted soil dramatically increased the metal sorption for both Mercury and Chromium. The Stable complexes Hg (OH)2 and Cr (OH) were produced by both Mercury and Chromium. The iron-based nanoparticles that were created with starch stabilization contained magnetite (Fe3O4), iron sulphide (FeS) and zerovalent iron (ZVI) (An and Zhao 2012). They employed it to immobilize arsenic, and they discovered that as the Iron/Arsenic molar ratio increased, the leachability and bio accessibility of arsenic in polluted soil was reduced. The soils with higher Arsenic and lower Iron concentrations the usage of these Nanoparticles for in-situ arsenic immobility was suggested. The use of artificial Fe (II) phosphate nanoparticles decreased the bioaccessibility and leachability of soil-bounded Cu(II) and Lead(II) (Liu and Zhao 2007). The leachable proportion of Lead in the polluted soil was reduced from 10 to 66 percent (Liu and Zhao 2013). According to the researchers, due to their minor particles size, Nanoparticles exhibited auspicious outcomes for soil remediation in both trials. They also had increased mobility and reactivity in soils. Additionally, it was predicted that these Nanoparticles might be used to clean up other dangerous heavy metals and radioactive isotopes like Copper, Cadmium, Zinc, and Uranium (Kumar et al. 2019b). Additionally, they suggested using these Nanoparticles as nanofertilizers to meet the phosphorus needs of crops and prevent the eutrophication issue that is frequently linked to the usage of conventional fertilizers that contain phosphate. The synthesis of Na-zeolitic nanotuff and examination of their impact on the sorption of Cadmium (Ghrair et al. 2010). They discovered that pH had a significant impact on the sorption of Cadmium and hypothesized that pH and textures may affect the zeolitic nanotuff's ability to immobilize the metal in soil. Regulatory threshold standards of Arsenic, Cadmium, and Lead for soil discharge are 0.01 mg/L and 0.05 mg/L, respectively, and the treatment with nano-Iron/Calcium lowered the concentration of leachate below these threshold values (Mallampati et al. 2013). In multimetal-contaminated (Zinc, Cadmium, and Nickel) noncalcareous and calcareous soils, the immobilization capability of TiO2, Al2O3, and SiO2 NPs is examined (Naderi Peikam and Jalali 2019). In calcareous soils SiO2 Nanoparticles were the most operative in immobilizing the metals, whereas in noncalcareous soil, Al2O3 Nanoparticles exhibited the greatest decrease in mobility for Cadmium and Zinc. This was mostly related to the higher SiO2 surface area and high Al2O3 site density. Furthermore, it has been discovered that soil with a high carbonate calcium content has a high metal immobilization capability because liming soil increases its adsorption potential and lowers the bioavailability of metals (Zhou et al. 2020).

4 Nanotechnology for the remediation of persistent organic pollutant and pesticides

The General Conference in 2004 on the Persistent Organic Pollutants resulted in a complete prohibition of these pollutants due to the contamination of soil by persistent organic pollutants (POPs) and pesticides through the anthropogenic sources (Fei et al. 2022). Then, the removal of these contaminants from the polluted soil through nano remediation has been a top priority on a global scale. Eight of the "dirty twelve" POP chemicals, which have been prohibited, are insecticides (Karthigadevi et al. 2021). Pharmaceuticals and industrial solvents or chemicals are among the other POPs. Due to the biomagnification and bioaccumulation characteristics of POPs and many pesticides, there is a significant risk of food supply chain contamination, especially for individuals on the food web (Bakshi and Abhilash 2020). In addition, Persistent Organic Pollutants are lipophilic and they can build up in the tissue of humans and animals, having both acute and chronic consequences. Numerous pesticides have lately banned but the risks they represent can remain even after years of ceasing to be used (Mukhtar et al. 2021). Their persistent nature means that they take many years to break down, leaving behind residues that continue to contaminate the land where they were once used either directly or indirectly. Additionally, POPs can travel the world via evaporation and deposition, where they can be deposited in locations far from their source and pollute it (Ganie et al. 2021). Therefore, to rejuvenate the agricultural land use and the production of bioenergy, remediation of these pollutants becomes crucial. For their potential function in the breakdown of pesticides and POPs, nanoparticles are also the subject of extensive research (Negrete-Bolagay et al. 2021). Photocatalysis is the process involved in the breakdown of pesticide contaminants. In this procedure, chemical pollutants such as pesticides and POPs are reacted and NPs work as a catalyst in the occurrence of light. These nano photocatalysts transform these pollutants into less complex and dangerous molecules like Carbon dioxide, Nitrogen gas, and Water (Corcimaru et al. 2019). Zinc oxide (ZnO) and titanium dioxide (TiO2) are currently regarded as effective photocatalysts at the nanoscale. Three organochlorine insecticides, including dicofol, cypermethrin, and hexachlorobenzene, are examined for their photocatalytic destruction by nano-TiO2 (Yu et al. 2007). By absorbing peroxide or hydroxyl radicals and facilitating electron transport, TiO_2 permitted photolytic destruction of these insecticides on their surface. Nano-TiO_2 incapacitated with rhenium has been shown to photocatalytically degrade carbamate and organophosphorus insecticides detected in the soil and tissues of tomato plants at the rate of 15% to 30% (Rui et al. 2010). The same nanomaterial may degrade carbofuran at the rate of 55%, which is 30% faster than biological decomposition. Additionally, it was discovered that the photocatalytic activity of (modified) TiO2 nanomaterial can shorten pesticide half-lives without compromising efficacy. Metolachlor a popular herbicide, is catalytically ozoned using multi-walled carbon nanotubes (MWCNTs) as catalysts (Restivo et al. 2012). For increasing MTLC mineralization and reducing its toxicity, a carbon catalyst was used. Furthermore, it was thought that using carbon nanofibers grown on a structured support could help metolachlor fully mineralization, otherwise this chemical has the potential to produce a number of hazardous by-products such aromatic compounds and organic acids (Boregowda et al. 2021). The effects of nZVI on the breakdown of DDT in a polluted soil that has been sharped with the chemical as well as in previously contaminated soil was investigated (El-Temsah et al. 2016). The breakdown rate was found to be 50% in soil that had been spiked, but it was only 24% in soil that had been poisoned over a longer time. In another study, they examined how nZVI affected soil organisms such as collembolan and ostracods (Boregowda et al. 2021). It is examined whether zerovalent iron at the nanoscale (nZVI) can be used to clean up organochlorine-contaminated environments (Tilston et al. 2013). After adding nZVI, they observed changes in the composition of the soil bacterial population and a decrease in the activity of chloroaromatic mineralizing microorganisms. To be used as catalytic agent for malathion photodegradation, the semiconductor nanoparticles are created using various metal core-shell nanocomposites, like Titanium dioxide, Au/TiO2, Zinc oxide, and Au/ZnO. (Fouad and Mohamed 2011). Malathion was broken down more quickly in a time-dependent order due to the usage of nanocomposite materials with a semiconductor and metal core combination. In a study, the impact of nano-titanium dioxide on the photo electrocatalytic breakdown of the phenanthrene was examined (Gu et al. 2012). The 1/2 life of the phenanthrene was lowered from 46 to 31 hours, as the Titanium dioxide was loaded between 0 to 4 weight percent, Titanium dioxide significantly accelerated soil surface deterioration whereas compost, illuminance, and hydrogen peroxide concentration further accelerated the deterioration (Table 2). For in-situ PCB-contaminated soil clean-up, the utilization of nZVI and Pd/Fe bimetallic nanoparticles is being researched (Chen et al. 2014). According to their findings, Pd/Fe bimetallic nanoparticles degrade the hydrodechlorinated 2,2,4,4,5, 5-hexachlorobiphenyl more quickly and completely than nZVI. Additionally, it was deduced that soil characteristics like sand and clay concentration encouraged Pd's catalytic activity, enhancing the rate of PCBs degradation (Chen et al. 2021). The organic matter of soil slowed down the hydrodechlorination but a lesser clay concentration and a high sand concentration encouraged increased PCB exclusion efficacy. Pentachlorophenol (PCP)-contaminated clayed soil was cleaned up using CMC-stabilized nano Pd/Fe (Yuan et al. 2012). By using the electrokinetic transport mechanism displayed by nano- Palladium/Iron the PCP in polluted soil was de-chlorinated to phenol. Same as, the electrokinetic transport kinetics of the xanthan gum-stabilized nano-Palladium/Iron are studied for the clean-up of soil contaminated with PCBs (Fan et al. 2013). The solubility and rate of PCB breakdown in the soil were both accelerated by the surfactants. An integrated nanobiotechnological strategy involving the use of FeS nanoparticles and microbial degradation is used to study the catalytic dechlorination of the organochlorine insecticide lindane (Paknikar et al. 2005). It was discovered that within 8 hours the stabilized nanoparticles degraded 5mg L1 of lindane with 94 percent effectiveness. After undergoing a further microbiological treatment, the stabilizing polymer, together with the leftover lindane and its partially degraded intermediates, were entirely destroyed in 1 h. Thus, in a period of 9 hours, the authors were totally able to eliminate 5mg L1 of lindane. In order to degrade pentachlorophenol biological encapsulated nanoparticles agent are coated on the nZVI that contains Pd nanoparticles to create the bimetallic iron (BioCAT slurry) bio composite (Dien et al. 2013). This bimetal-Fe was reported in the sandy soil to decompose 90 percent of pentachlorophenol after 21 days of treatment (Tahir and Sehgal 2018).

Table 1: Various types of nanomaterials for the removal of heavy metals

Nanomaterial	Target pollutants	References
Al_2O_3, TiO_2 NPs, SiO_2,	Zinc, Nickle, Cadmium	(Kumar et al. 2022)
Starch-stabilized Fe_3O_4, FeS, nZVI	Arsenic	(Latif et al. 2020)
Water treatment residuals NPs (nWTR)	Chromium, Mercery	(Kumari et al. 2019)
Na-zeolitic nanotuff	Cadmium	(Bakshi and Abhilash 2020)
Nano-Fe/Ca/CaO	Arsenic, Lead, Cadmium,	(Qian et al. 2020)
CMC-stabilized (nFMBO) nanoparticles	Arsenic ((III))	(Xie et al. 2015)
Ca (II) phosphate Nanoparticles	Lead (II)	(Zhang et al. 2013)
Fe (II) phosphate	Lead (II)	(Baghayeri et al. 2018)
CMC-stabilized FeS Nanoparticles	Chromium (VI)	(Zhao et al. 2019)
Bimetallic nZVI/Cu	Chromium (VI)	(Qu et al. 2020)
Biochar supported nZVI	Chromium (VI)	(Liu et al. 2020)
CMC-stabilized nZVI	Chromium (VI)	(Yu et al. 2020)
CMC-nZVI	Chromium (VI	(Bian et al. 2021)
nZVI	Arsenic, Chromium, Lead, Cadmium, Zinc	(Li et al. 2014)

Table 2: Persistent organic pollutant (POP) and pesticides degradation using nanomaterials

Nanomaterial	Target pesticides	References
FeS Nanoparticles	Lindane	(Zhao et al. 2020)
Bimetallic Fe	Pentachlorophenol	(Rawtani et al. 2018)
Xanthan gum stabilized nano-Pd/Fe	Polychlorinated biphenyls	(Nasrollahzadeh et al. 2021)
CMC stabilized nano-Pd/Fe	Pentachlorophenol	(Islam et al. 2022)
Rhenium-doped nano-TiO_2	Carbofuran	(Rathna et al. 2018)
Anatase TiO_2	Phenanthrene	(Tian et al. 2014)
TiO_2-coated film	Organochlorine pesticides	(Taghizade Firozjaee et al. 2018)
TiO_2, ZnO, Au/ZnO and Au/ TiO_2,	PCBs and organochlorine pesticides	(Rani and Shanker 2020)
nZVI	DDT	(Ulucan-Altuntas and Debik 2020)
MWCNTs	Metolachlor	(Kumar et al. 2019)

5. Biosensing sensors based on nanotechnology for detecting pesticide residues

Research on NPs is still in its early stages, it has been predicted that they will offer enormous potential for environmental cleanup and agriculture. Nanomaterials and biosensors have a wide range of uses in the detection and monitoring of pesticides, hazardous materials, contaminants in the form of germs, bacteria that generate smells, and other microbes, as well as other harmful materials, both in the field and in manufacturing facilities (Rawtani et al. 2018). By providing a variety of services, including the detection of pesticide residue, Nano sensors can considerably subsidize to increase in soil productivity and health. In addition, nanosensors are presently employed in the food processing industries to detect poisons, chemicals, and microbes in food, aiding in the reduction of foodborne sickness (Maghsoudi et al. 2021). Groundwater and soil have been highly poisoned in many locations due to the widespread use of persistent pesticides for pest control and increased agricultural output around the world, posing numerous health risks to non-target species. The use of pesticides has also caused pests to become resistant to the chemicals, as well as killed off their natural predators, making pest management even more challenging (Pandit et al. 2016). The Food and Drug Administration (FDA) has identified 1045 compounds as pesticide residues. Pesticide residues in soil, waterways, and agricultural products can be accurately and quickly detected using nanosensors (Singh et al. 2020). As a result, they have received a lot of attention as a quick and efficient field monitoring tool in comparison to the traditional methods of detecting pesticide residues, like gas chromatography (GC), liquid chromatography, mass spectroscopy, and high-performance liquid chromatography (HPLC), which are highly efficient and discriminatory for pesticides, but they are time-consuming, costly, sophisticated, and unsuitable for field analysis (Zhang et al. 2017). Nanosensing methods can be categorized into three primary categories based on their sensing mechanisms. These include organophosphorus hydrolase, immunoassays, and the suppression of cholinesterases. Acetylcholinesterase (AChE)-based electro-chemical sensors make up the majority of the sensors being developed for the detection of pesticide residues, particularly for pesticides like organophosphate and carbamate (Narenderan et al. 2020). Both of these pesticides are particularly toxic to acetylcholinesterase (AChE), which is a key enzyme in the human central nervous system and is used frequently in many nations. The inhibition of acetylcholinesterase activity has been employed more frequently to create human biological markers for the early identification of toxicity arising from exposure to these insecticides because it is a specific molecular target of organophosphate and carbamate pesticides (Mustafa and Andreescu 2020). Pesticides that block these enzymes can be identified in a before-and-after incubation method by evaluating the kinetic performance of the beginning rate of a reaction which catalyzed by the AChE.

The responses of these devices to pollutant exposure are sensitive, simple to measure, and dose-dependent in nature (Kaur et al. 2021). However, one major obstacle to the creation of sensitive and reliable AChE and OPH-based biosensors is the unstable property of the enzymes. However, it has been demonstrated that due to the special characteristics of nanoparticles, they can serve as substrates for the immobilization of enzymes, keeping them stable and active (Krishna et al. 2018). Numerous studies are currently being conducted to successfully utilize the ability of acetylcholinesterase to immobilize and stabilize it with different nanoparticles to obtain maximum enzyme activity, consistency, and specificity of the biosensing systems that rely on the tracking of organophosphates (Chawla et al. 2018). The silicon-made nanocomplex, which consists of silicon nanowires coated with gold nanoparticles, has been reported (Su et al. 2008). Dichlorvos, an organophosphate insecticide detected by the sensor down to a concentration of 8 ng/L was greatly improved by the nanocomplex's strong electrical conductivity and good compatibility with the enzymes. Same as, the recognition of the carbaryl is reported using a Raman scattering sensor comprised of Silver nanoparticles-coated silicon nanowires (Wang et al. 2010). They discovered that the present substrate has a remarkably high sensitivity for the detection of carbaryl. The sensor offered excellent repeatability and was very sensitive and stable for detecting the carbaryl. A biosensor relying on inactivating acetylcholinesterase on 3-Acarboxyphenylboronic/reduced graphene oxide-Au nanocomposite electrode material has been applied for the detection of pesticides carbamate and organophosphorus (Liu et al. 2011). Effective immobilization was made possible by the significant activity of the interaction between the glycosyl of acetylcholinesterase and the 3-carboxyphenylboronic acid group. Due to the strong electron transport capabilities of gold Nanoparticles, the biosensor displayed good sensitivity. Additionally, by encouraging the electron transfer reaction, reduced graphene oxide improved the electrochemical responsiveness (Kim et al. 2018). For the detection of carbamate in cabbage, broccoli and apples a sensor based on the immobilization of cholinesterase in the core-shell improved glass electrode of multi-walled carbon nanotube and polyaniline has been created (Cesarino et al. 2012). The detection limits of the MWCNT/PANI/AChE-based biosensor were 0.95mol/L for methomyl and 1.4mol/L for carbaryl. Dichlorvos, a hazardous organophosphate which is monitored with a sensor made of Nafion nanocomposite Nafion nanocomposites and graphene oxide (Wu et al. 2013). The sensor had a broad operating scope between 1 to 20 g/mL and 5 to 100 ng/mL. A biosensor that detects methyl parathion by immobilizing AChE on modified glassy carbon electrodes made from multi-walled nanotubes. This procedure coupled AChE inhibition with electrochemical reductions of Ellman reagent (Anand and Panigrahi 2021). The detection point for methyl parathion was a suppression of AChE activity followed by a change in the electrochemical reduction sensitivity of DTNB. For the recognition of organophosphate paraoxon, organophosphate hydrolase is conjugated with Au nanoparticles treated with a luminous enzymes inhibitor decoy (Simonian et al. 2005). The normalized ratio of fluorescence intensities was evaluated after adding various paraoxon amounts to an OPH-nanoparticle-conjugate-decoy combination. The equimolar concentrations of OPH-gold Nanoparticles and decoys give the maximum sensitivity of paraoxon (Table 3). There are few challenges that must be resolved for the successful applications of nanomaterial-based recognition of the pesticide residues (Sinha et al. 2017). These include (1) the accessibility of nanomaterials to pesticides residue which are left behind, (2) the simplicity of nanosensors fabrication methods and instrumentation, (3) detect the presence of small concentrations with the require repeatability and reliability, (4) cost of manufacturing, and (5) environment issues related to nanomaterial disclosure to environments (Martinazzo et al. 2020). Manufacturing intelligent nanomaterials and nano pesticides, which would serve as both sources of pesticide and analytical sensors for detection, is another concept that is currently growing (Sehgal et al. 2018). This might completely do away with the requirement for biosensors to detect pesticide residue in soil (Antonacci et al. 2018). Additionally, a nanomaterial that can both serve as an effective delivery system for substances like pesticides and fertilizers and can also detect nutrient deficiencies in soil via an indication mechanism like a change in color is greatly desired. Farmers might use it as a sophisticated alarm system to choose the amount, rate, and frequency of pesticide application (Umapathi et al. 2021).

Table 3: Pesticide residue detection using nano-enabled sensors

Nanomaterial	Targeted analyte	References
Organophosphate hydrolase conjugated Au Nanoparticles	Paraoxon	(Liu et al. 2013)
MWCNT chitosan nanocomposite	Methyl parathion	(Rotariu et al. 2016)
Er-GRO-Nafion nanocomposites	Dichlorvos	(Mishra et al. 2021)
PANI/ MWCNT /AChE	Methomyl and Carbaryl	(Arduini et al. 2016)
AChE/RGO-Gold nanocomposites	Carbamate and Organophosphate	(Boregowda et al. 2021)
Ag Nanoparticle-coated Si nanowire	Dichlorvos	(Bapat et al. 2016)

6. Improvement of bioremediation and phytoremediation using nanotechnology

Using plants to remove, deteriorate, or restore environmental components like soil, sediments, and waterways are known as phytoremediation. Plants and the related rhizospheric microbial fauna are both used to clean up these contaminated resources (Vázquez-Núñez et al. 2020). Numerous plant species, including sunflower, tomato, willow, Chinese cabbage, poplar tree, sunbeam, alfalfa and sunbeam have been tested for their ability to phytoremediate polluted soils. Many of these plants have proven to be effective phytoremediators. The same mechanisms that plants and bacteria in nature utilize to break down and store organic and inorganic contaminants are also used in phytoremediation (Kaur and Roy 2021). Phytovolatilization, Phytodegradation, Phytoextraction, Rhizodegradation, and Phytostabilization are some of the different phytoremediation methods utilized for soil pollution. Phytovolatilization is the process through which pollutants are taken up by plants, converted into volatile forms, transported to the leaves, and then exhaled by the plants (Romeh 2022). Pollutants may also be converted into volatile compounds in this process. Utilizing plants to remove and store contaminants in their tissues is known as phytoextraction. Through their enzymatic processes, plants directly degrade organic contaminants as part of a phytodegradation process. Phytostabilization, which arises in a rhizosphere as opposed to the plant, it is the in-situ control of contaminants by plant roots (Mallikarjunaiah et al. 2020). Through root complex formation, adsorption, and precipitation in the rhizosphere, phytostabilization seeks to minimize pollutant mobility and reduce the likelihood that it will infiltrate groundwater or the food chain. Rhizodegradation, also known as phytostimulation, is the process by which bacteria in the rhizosphere of plants break down organic contaminants (Benjamin et al. 2019). The utilization of phytoremediation methods for environmental treatment has long attracted a lot of attention. Benefits of phytoremediation technology have been predicted to include raising organic matter of soil through sequestering carbon, increasing microbs activity, stabilizing soil, and generating biofuel or fiber (Azubuike et al. 2016). However, phytoremediation approaches typically take a long time often years to have beneficial results. Furthermore, its uses are constrained by the climate, soil conditions, and ecotoxicity of pollutants. Due to improved efficacy and cost-effectiveness, the usage of phytoremediation with other technologies, such as nanotechnology and bioremediation has gained traction recently (Prasad and Aranda 2018). Due to its fast act and on-site treatment nanotechnology is increasingly being viewed as an acceptable and practical solution for eliminating environmental toxins. It has been demonstrated that nanoparticles may have an impact on the disposition, conduct, and absorption of contaminants in phytoremediation systems (Khan and Bano 2016). Additionally, due to their predicted increased degradation capability in comparison to the elimination of pollution with a single technology, the combined usage of soil microbes, plants and nanoparticles is currently the subject of substantial research (Song et al. 2019). To purify polluted soil, nanophytoremediation combines the use of phytotechnology and nanotechnology. Carbon-based nanomaterials are the ones that have received the greatest research attention, due to their high surface area, carbon nanotubes have shown excellent adsorption ability for a variety of contaminants, especially hydrophobic organic pollutants (Kumari et al. 2020). The fate and transport of contaminants especially organic pollutants, could be drastically altered by these organic molecules that are loaded with carbon nanoparticles. In cottonwood, nanotubes were observed to improve trichloroethylene absorption. Due to the comparable xylem architecture of the two plant species, similar outcomes were seen in related tests with the shrub plant Redosier dogwood (Bharagava et al. 2020). Three plants, Glycine max (soybean), Solanum Lycopersicon and Cucurbita pepo (zucchini) were found to affect the accumulation and possible toxicity of dichlorodiphenyldichloroethylene a DDT metabolite. All plant species' root and total plant DDE concentrations considerably rose following fullerene exposure, with absorption varying between 30% to 65% (Kumari and Singh 2016). This study made the point that different plant species and their ability to phytoremediate contaminated soil may be affected differently by nanomaterials. These issues were further explored in a different study in which the remediation of DDT, chlordane and its metabolites (DDx) using 4 plants including S. Lycopersicum (tomato), Zea mays (corn), G. max (soybean) and C. pepo (zucchini) was accomplished using Nanowires and C60 (Ramezani et al. 2021). According to the scientists, depending on the species used and the dosage of nanomaterials, pesticide uptake and accumulation ranged from 21 to 80 percent. C60 treatment enhanced chlordane accumulating in tomato and soybean plants to 34.9 percent while entirely suppressing DDx uptake in maize and tomato plants. On the coexistence of DDE and chlordane accumulation in lettuce, the effects of amino-functionalized and nonfunctionalized MWCNT were examined (Hamdi et al. 2015). The presence of various types of Nanotubes had a considerable impact on the availability of pesticides. While amino-functionalized Nanotubes reduced the pesticide concentration in the roots and shoots by only 57 percent and 23 percent, respectively, nonfunctionalized Nanotubes reduced it by 88 and 78 percent, respectively (Tripathi et al. 2022). Pesticide residues' bioavailability significantly decreased as a result of the exposure to Nanotubes, thus reducing the contamination of edible lettuce tissues. After being treated with ZnO and CeO2 Nanoparticles, edible plants including soybean, wheat, alfalfa and corn showed a rise in shoot and root length, indicating the potential role of nanotechnology in greatly increasing phytoremediation effectiveness (Kumar and Bharadvaja 2019). To determine how well nZVI affects the uptake of trinitrotoluene by a plant Panicum maximum from the TNT contaminated soil, a nano phytoremediation analysis is carried out. The study provided evidence that increased TNT accumulation in plant roots was a result of combining nanotechnology with phytotechnology (Nwadinigwe and Ugwu 2018). Particularly at a dosage of 500mg/kg, the uptake of TNT from the soil was more efficient in the presence of nZVI than it was without nZVI. After three days of soil culture studies, it was discovered that Ni/Fe bimetallic nanoparticles reduced the transfer of polybrominated diphenyl ethers and their phytotoxicity to Chinese cabbage in a polluted soil (Patel et al. 2022). It was investigated that the potential impact of FeO nanoparticles on the wheat cultivated in cadmium contaminated soil (Hussain et al. 2019). By boosting plant rate of growth, photosynthesis, antioxidant enzymes, and Iron absorption while lowering Cadmium content in plants, the application of 20 ppm of Synthesized Nanoparticles reduced the negative effects of Cadmium (Prasad et al. 2021). Exogenous treatment of Synthesized Nanoparticles improved the morphological characteristics of wheat such as photosynthetic stains and biomass of roots, shoots, grains and spike shells (Table 4). The study of nZVI stabilized with sodium carboxymethyl cellulose for a remediation of Cr(VI)-contaminated soil found that it considerably improved Chromium immobilization by decreasing Chromium bioaccessibility and leachability (Wang et al. 2014). Chinese cabbage and rape plants growing in the soil, their growth was inhibited by the remediation. The physicochemical characteristics of nZVI were thought to be responsible for the detrimental effects on plants, such as decreased root biomass and germination retardation (Zand et al. 2020). However, when the plants' phytotoxicity test was conducted after a month, then both plants' cultures improved. This suggested that soil quality might be gradually restored through remediation utilizing nZVI. In the meantime, it was examined how wheat seedlings reduced the toxicity of Cadmium(II) and Chromium(VI) in the presence of citrate-coated magnetite Nanoparticles (López-Luna et al. 2016). They discovered that these Nanoparticles promoted the development of wheat seedlings by reducing the heavy metal toxicity. The predicted toxicity was higher than the actual value when magnetite was applied, indicating an interaction antagonistic impact. The Phyto availability attenuation with magnetite Nanoparticles considerably reduced the individual and combined toxicity of Cadmium and Chromium. Investigated was how lead (Pb) bioaccumulation by rice seedlings was affected by four different types of TiO2 nanoparticles in rutile and anatase forms (Cai et al. 2017). They discovered that although Nanoparticles were successful at reducing the bioaccumulation of Lead in rice tissues, but the particles accumulated in the rice roots with the amount of 80%, potentially endangering food safety (Okoh et al. 2020).

Few researches have examined the function that nanoparticles and microorganisms play in facilitating the bioremediation of contaminated land. Fe3O4 Nanoparticles in combination with soil-based microorganisms were found to have a stronger and more effective potential for degrading the pesticide 2,4-dichlorophenoxyacetic acid in soils (Fang et al. 2012). This combination performed better than the treatment using Nanoparticles or microorganisms alone that used individual technology. The breakdown of Y-HCH in soil was accomplished using a comparable integrated nano biotechnique. Together with a Sphingomonas sp. NM05 microbial strain, they stabilized Pd/Fe0 bimetallic nanoparticles for pesticide breakdown. (Singh et al. 2013). According to the authors, the combination of microbial cells and nanoparticles accelerated the breakdown of y-HCH. Therefore, combining nanotechnology with bioremediation and phytoremediation could have beneficial effects on both plant development and the removal of harmful chemicals from soil (Khan et al. 2018).

Table 4: Utilization of nanomaterials with bacteria and plant species for the pollutant's remediation

Nanomaterials	Species	Targeted pollutants	References
Nickle/Iron bimetallic NPs	Chinese cabbage	Polybrominated diphenyl ether	(Deng et al. 2017)
CMC-Pd/nFe^0	Sphingomonas sp. NM05	γ-HCH	(Banerjee et al. 2022)
Fe$_3$O$_4$ NPs	Soil indigenous microbes	2,4-Dichlorophenoxyacetic acid	(Ganie et al. 2021)
nZVI	Panicum maximum	Trinitrotoluene	(Koç et al. 2022)
MWCNT	Lettuce	DDE and Chlordanes	(Picó et al. 2017)
C$_{60}$ fullerene	Soybean, zucchini, tomato	p, p^0-DDE	(Deng et al. 2017)
MWCNT	Corn, soybean, zucchini, tomato	DDE and Chlordanes	(De La Torre-Roche et al. 2013)
Fullerene	Cottonwood	Trichloroethylene	(Ma and Wang 2018)
TiO$_2$ Nanoparticles	Rice	Lead	(Azimi and Es'haghi 2017)
Citrate-coated magnetite Nanoparticles	Oat, wheat, sorghum	Chromium (VI)	(Han et al. 2020)
CMC stabilized nZVI	Chinese cabbage, Rape	Chromium (VI)	(Usman et al. 2020)
Iron Nanoparticles	Cadmium	Wheat	(Banazadeh and Khaleghi 2016)

7. CONCLUSION AND FUTURE PROSPECTIVE

Although there are many potential applications for nanotechnology and it is seen to be a promising strategy for cleaning up contaminants in soil. The studies of nanotechnology suggesting that using nanoparticles can also cause certain unknown hazards. Since soil is a necessary component for the food production, the nanoparticles travelling down the food chain and affected the humans through the crops produced on Nanoparticles-treated soil, which makes people less motivated to use Nanoparticles for soil remediation. But nanotechnology also has many advantages, so extensive research is needed in this field. Additionally crucial to ensuring the safety of these materials whether in bulk form or in nanoform. In conclusion, nanotechnology is a useful substitute for soil remediation because of its excellent remediation properties. The use of nano remediation has the potential to significantly decrease the expenses and time of large-scale site remediation. Furthermore, nanotechnology is a site-remediation technology which eliminates the post-remediation activities like soil transportation and soil disposal. Full-scale environment investigations with appropriate long-term assessment are required before the use of nanoparticles on a large scale to prevent any potential negative environmental consequences.

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9. CONFLICT OF INTEREST

The authors declare no conflict of interest

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