



Mechanistic and recent updates in nano-bioremediation for developing green technology to alleviate agricultural contaminants

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Abstract

The rise in environmental pollutant levels in recent years is mostly attributable to anthropogenic activities such as industrial, agricultural and other activities. Additionally, these activities may produce excessive levels of dangerous toxicants such as heavy metals, organic pollutants including pesticide and herbicide chemicals, and sewage discharges from residential and commercial sources. With a focus on environmentally friendly, sustainable technology, new technologies such as combined process of nanotechnology and bioremediation are urgently needed to accelerate the cost-effective remediation process to alleviate toxic contaminants than the conventional remediation methods. Numerous studies have shown that nanoparticles possess special qualities including improved catalysis and adsorption as well as increased reactivity. Currently, microorganisms and their extracts are being used as promising, environmentally friendly catalysts for engineered nanomaterial. In the long term, this combination of both technologies called nano-bioremediation may significantly alter the field of environmental remediation since it is more intelligent, safe, environmentally friendly, economical and green. This review provides an overview of soil and water remediation techniques as well as the use of nano-bioremediation, which is made from various living organisms. Additionally, current developments related to the mechanism, model and kinetic studies for remediation of agricultural contaminants have been discussed.

Keywords Biosynthesis · Environmental contaminants · Nanoparticles · Persistent organic pollutants

Introduction

Agricultural pollution is a global environmental concern that is mainly caused by the function of many farming inputs (such as pesticides and fertilizers) and numerous practices,

such as excessive soil tillage and runoff (El-Ramady et al. 2020). Agricultural pollutants may encompass unsustainable use of agrochemicals resulting in accumulation of heavy metals, halogenated compounds, phenols and organic compounds such as pesticides, insecticides which are one of the most pressing issues confronting agriculture around the world (Singh et al. 2020a). These agro-pollutants are extremely toxic and can have a negative impact on soils, water and air (Khan et al. 2020; Singh et al. 2020a; Ken and Sinha 2020). Organic pollutants primarily consist of phenols, chlorinated phenols, azo dyes, phthalic esters, pesticides, persistent organic pollutants (POPs), and other chemicals. Inorganic pollutants, on the other hand, include heavy metals such as arsenic, nickel, chromium, lead, mercury, and cadmium. These agro-pollutants have been linked to significant negative effects on soil and water pollution, as well as severe toxicity in living creatures (Saxena et al. 2019).

One of the most pressing challenges facing agriculture today is the need to monitor and reduce the use of agrochemicals associated with certain toxic contaminants. It is

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well understood that agrochemical-derived pollutants can have a negative impact on the agro-ecosystem (Mall et al. 2018). Indeed, injudicious use of excessive amount of pesticides may result in volatilization, oxidation and photolysis and only about 0.1 percent of pesticides reach the targeted species (Liang et al. 2017). Toxic pollutants have increased to alarming levels in the environment, deteriorating environmental quality, disrupting ecosystems, and negatively impacting human health (Singh et al. 2020a). As a result, developing innovative techniques capable of eliminating agro-pollutants in trace amounts is critical. Nanotechnological approaches have been rapidly used in every field of science and environmental application owing to their novel characteristics such high surface area and small nano-size in a wide range of application (Hidangmayum and Dwivedi 2021). Several remediation methods have been developed for both *in situ* and *ex situ* applications. However, nano-bioremediation techniques have received much attention in recent times due to their sustainability and minimizing environmental pollutants efficiently (Rajput et al. 2021). Bioremediation, according to the United States Environmental Protection Agency, is a method that transforms harmful compounds into less dangerous or benign ones using naturally existing organisms (Singh et al. 2020b). Bioremediation can primarily be achieved by applying microorganisms to the remediation of pollutants found in water and soil (Saxena et al. 2019; Halecký and Kozliak 2020; Bhojiya et al. 2021). It is worth mentioning that various modern bioremediation approaches, such as the application of biosurfactants, emulsifiers, enzymes, biopesticides, and Genetically Modified Organisms (GMOs), could be used (Halecký and Kozliak 2020). Combining nanotechnology and bioremediation could increase the efficiency, time efficiency and environmental friendliness of remediation, increasing benefits (El-Ramady et al. 2020; Ghani et al. 2022). Nano-bioremediation (NBR) is one of these methods that have attracted the attention of many scientists in recent years due to its unique combination of nanomaterials and bioremediation. NBR is the process of removing environmental pollutants from contaminated areas by utilizing nanoparticles derived from prokaryotes (Gram-negative rods, actinobacteria) and eukaryotes (fungi, algae, and plants) with the aid of nanotechnology. (Mallikarjuna et al. 2011; Rajput et al. 2021). For instance, dechlorination and biodegradation of biphenyls was reported using zinc nanoparticle and the bacterium, *Burkholderia xenovorans* (Le et al. 2015). Also, nanomaterials derived from plants, for example, *Noaea mucronata*, were applied for the bioremediation of heavy metal contaminants from rivers, streams and groundwater (Mohsenzadeh and Rad 2012).

Regarding the benefits of NBR, nanotechnology and bioremediation are integrated for a number of reasons. Since NPs have a large surface area per unit mass, a greater number

of particles can be introduced into the environment, increasing remediation (Kaur et al. 2018). In this way, NBR works to reduce secondary environmental impacts while minimizing pollutant concentrations. Furthermore, nanotechnology and bioremediation are combined with each other to create an improved, faster, and more environmentally benign remediation method (Kumar et al. 2021).

There are, however, specific merits as well as demerits associated with each advancement in the remediation process. As a result of the extensive literature survey, it can be concluded that integrating bioremediation and nanotechnology would be a viable alternative to conventional remediation technologies. Nevertheless, more research and development are needed to bring these types of sustainable technology to the market for full implementation. This current review paper makes an effort to integrate and summarise findings on the application of nano-bioremediation to alleviate the environmental agro-pollutants. Furthermore, it includes an in-depth discussion of the synthesis and mechanism/kinetics model, interaction with nanomaterials with other microorganisms, as well as their role in environmental remediation.

Mechanism and action of nano-bioremediation in soil

Nano-bioremediation is the process of employing nanoparticles/nanomaterial generated by plants, fungus and bacteria to remove environmental toxins (such as organic and inorganic pollutants) from polluted locations with the aid of nanotechnology. Apart from the many methods available for contaminated site remediation (such as chemical and physical remediation), bioremediation now provides an ecologically acceptable and cost-effective option for removing toxins from the environment (Yadav et al. 2017). Bioremediation encompasses bioaccumulation, biotransformation, biosorption, and biological stabilization, among others with the use of microbes, plants, and enzymes or combinations of them (Fernández et al. 2018). In one technique, nanoparticles can be used to treat soils contaminated with pollutants, while in another, they can be employed by combining phytoremediation with enzyme-based bioremediation (Sunanda et al. 2021). This challenge might be overcome by merging nanotechnology and biotechnology, in which nano-encapsulated enzymes transform complex organic molecules into simpler ones, which are subsequently quickly eliminated by bacteria and plants working together (Prasad et al. 2017). Figure 1 shows aspects of nano-bioremediation in agriculture soil in terms of applications. In case of agricultural soil, it works as remedial approach to remove inorganic, organic, and emerging pollutants. The same way it helps in soil health, growth of plants and also works to improve the degraded land.

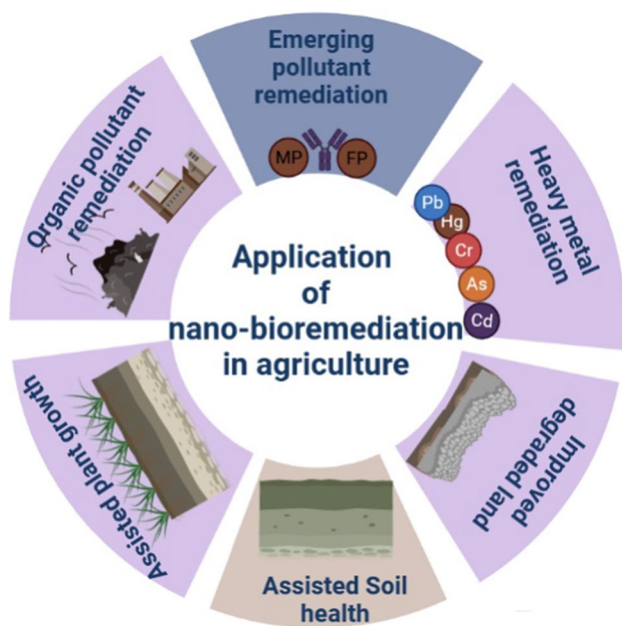


Fig. 1 Application of nano-bioremediation in agriculture soil

Bacteria have the ability to mobilize and immobilize metals, and in some cases, the microorganism that can decrease metal ions may also precipitate metals at nanoscale size. Bacteria are being investigated as a latent "biofactory" for the production of nanoparticles such as gold, silver, iron, zero valent iron, platinum, palladium, titanium dioxide,

cadmium sulfide, gold nanowire, titanium, selenium, magnetite, and zinc sulfide (Yadav et al. 2017; Ramezani et al. 2021). The utilization of microorganisms can act as catalyst because of their enzyme present for specific reaction to inorganic nanoparticle which is a new coherent biosynthesis approach for production of nanoparticles, which comprises application of polysaccharides, biodegradable polymers, microorganisms, enzymes, microbial enzymes, vitamins, and organic structures (Ramezani et al. 2021).

Preparation of nanomaterial

Only physical and chemical processes were previously used to create nanoparticles. In the search for more cost-effective and sustainable production of nanoparticle, microorganism and plants extracts were utilized. Table 1 represents the synthesis methods or procedures of different types of nanomaterial with suitable examples. Synthesis of nanomaterials from different methods of preparation is shown in Fig. 2. The biogenesis of nanoparticles follow a bottom-up process involving the primary reaction of reduction/oxidation. The reduction in metal compounds into their respective nanoparticles is usually mediated by microbial enzymes or phytochemicals with antioxidant or reducing properties. Nanomaterials are being produced in the millions of tons throughout the world, and this number is likely to skyrocket in the near future. The word "nanomaterial" refers to specially designed materials with at least one dimension between 1 and 100 nm (European Commission, 2011). Microorganisms such as bacteria,

Table 1 Synthesis of nanomaterial with different methods

Nanomaterials	Methods	Metals/metalloids/composites/microorganisms/polymers	References
Metal nanoparticles (NPs)	Photochemical Electrochemical Biochemical Thermochemical	Pt, Rh, Pd, Ir, Ag, Au, Cu, Co, Ni, FeNi, Cu ₃ Au, CoNi, CdTe, CdSe, ZnS	Das and Ansari (2009), Koul and Taak (2018)
Carbon NMs	Arc-discharge Laser ablation Chemical vapor deposition	Cylindrical nanotube	Rizwan et al. (2014), Prasad et al. (2017), Singh et al. (2020a, b)
Metal oxide NPs	Sol-gel Hydrothermal Reverse micelles method Solvothermal Electrochemical deposition	ZnO, Fe ₂ O ₃ , Fe ₃ O ₄ , MgO, BaCO ₃ , BaSO ₄ , TiO ₂	Newkome et al. (1985), Chauhan et al. (2012), Koul and Taak (2018)
Polymer NMs	Electrochemical Polymerization	Nanowire of polypyrrole, polyaniline, poly (3,4-ethylenedioxythiophane) dendrimers (PAMAM)	Rizwan et al. (2014), Prasad et al. (2017), K and V (2017)
Nanocomposite	Innovative	CNTs (fluoropolymers polycarbonates, polyethylene, glycol, polyester polyamides); epoxy composites	Prasad et al. (2017), Yadav et al. (2017), Benjamin et al. (2019), Singh et al. (2020a, b), Vázquez-Núñez et al. (2020)
Bio-nanomaterials	Biological	Viruses, plasmids, and protein NPs	Koul and Taak (2018), Bahrulolum et al. (2021)



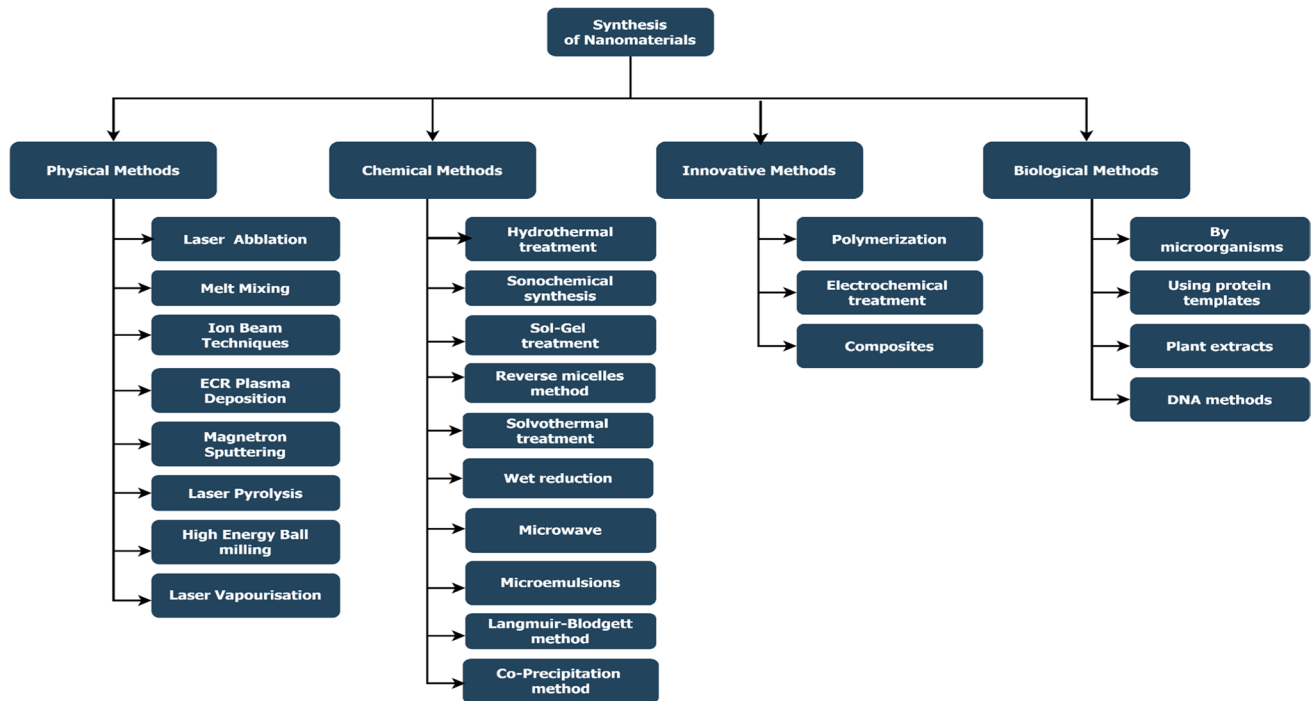


Fig. 2 Methods for synthesizing nanomaterials (Rizwan et al. 2014; Koul and Taak 2018; Singh et al. 2020b)

filamentous fungi, yeasts, algae, and actinobacteria can be employed for synthesis of biogenic nanoparticle in addition to vascular plants.

Botanical synthesis

Biosynthesis of nanoparticles by plants namely *Azadirachta indica*, *Catharanthus roseus*, *Aloe barbadensis*, etc., is gaining wide acceptance due to the single-step biosynthesis process, the unavailability of toxic elements, the presence of natural capping agents, and the presence of a wide variety of metabolites that may assist in reduction. Plants require a shorter incubation period for the reduction in metal ions than fungi and bacteria; hence, they are regarded superior candidates for nanoparticle synthesis (Table 2). In case of synthesis on industrial scale, plant tissue culture and downstream processing techniques generally used, though it depends on the metabolic status of the plant (Mura et al. 2013). Though effect of nanoparticles on contaminants diverges from plant to plant, but it depends on the physiological, biochemical, molecular mechanisms of the plant, and their interactions with contaminants and living organisms (Yadav et al. 2017).

Bacterial synthesis

Bacteria are being investigated as a latent "biofactory" for the production of nanoparticles such as gold (Au), silver (Ag), iron (Fe), zero valent iron (ZVI), platinum

(Pt), palladium (Pd), gold (Au) nanowire, titanium (Ti), titanium dioxide (TiO_2), selenium (Se), magnetite $\{\text{Fe}^{2+}(\text{Fe}^{3+})_2(\text{O}^{2-})_4\}$, cadmium sulfide (CdS), zinc sulfide (ZnS), and they can immobilize metals at the nanometer scale (Chauhan et al. 2012; Phumying et al. 2013; Ramezani et al. 2021; Wang et al. 2018; Xiao et al. 2017). It uses bacteria as a source of enzymes, microbial enzymes, vitamins, and polysaccharides for the formation of nanoparticles, and it follows an innovative rational biosynthesis approach that does not involve any toxic, harmful, or expensive chemical for stabilizing operations (Benjamin et al. 2019). Although it is devoid of other cellular proteins, the NPs produced by enzyme secretion have an edge in metal binding capacities, making them valuable in nano-bioremediation. The production of nanoparticles is influenced by a number of parameters, including microbe growth circumstances, chemical composition, cellular activity, and enzymatic activities. More in-depth research is needed to fully comprehend the chemical pathways and identify the enzymes and proteins involved in biosynthesis of nanoparticles.

Fungal synthesis

Yeast and filamentous fungi have long been utilized for nanoparticle synthesis, and they are a great source of extracellular enzymes that influence nanoparticle synthesis. In case of production of larger amounts of nanoparticles, filamentous



Table 2 Biosynthesis of nanomaterials with plants, bacteria, yeast, and filamentous fungi

Nanomaterials	Plant	Bacteria	Yeast and filamentous fungi	References
Gold and silver	<i>Hibiscus rosasinensis</i> , <i>Coriandrum sativum</i> , <i>Embllica officinalis</i> , <i>Diopyros kaki</i> (persimmon), <i>Citrus sinensis</i> , <i>Peltarogonium graveolens</i> , Phyllanthium Mushroom extract		<i>Verticillium</i> sp., <i>Fusarium oxysporum</i>	Shankar et al. (2003b, 2004), Ankamwar et al. (2005), Narayanan and Sakthivel (2008), Song and Kim (2008), Kasthuri et al. (2009), Philip (2009), Popescu et al. (2010), Song et al. (2010) MubarakAli et al. (2011)
Silicon-geranium	<i>Stauroneis</i> sp. <i>Freshwater diatom</i>			
Silver, nickel, cobalt, zinc and copper	<i>Helianthus annuus</i> , <i>Medicago sativa</i> , <i>Brassica mjuncea</i>	<i>Streptomyces griseus</i> , <i>Endophytic actinomycetes Ca-1</i>	<i>Fusarium culmorum</i> , <i>Alternaria alternata</i> , <i>Pleurotus sajor-caju</i> , <i>Trichoderma harzianum</i> , <i>Volvartella volvaceae</i>	Bali et al. (2006), Bharde et al. (2006), Gajbihiye et al. (2009), Philip (2009), Ponnurugan et al. (2016), Hassan et al. (2018), Chaturvedi et al. (2020)
Gold	<i>Syzygium aromaticum</i> L., <i>Medicago sativa</i> , <i>Camellia sinensis</i> L., <i>Chenopodium album</i> L., <i>Magnolia kobus</i> , <i>Juniperus communis</i> (Zimbora tea), banana peel, <i>Azadirachta indica</i> , <i>Mentha piperita</i> L., <i>Allium cepa</i> L., <i>Justicia gendarussa</i> L., <i>Sesbania grandiflora</i> L., <i>Mirabilis jalapa</i> L., <i>Macrotyloma uniflorum</i> , <i>Cinnamomum zeylanicum</i> , <i>Terminalia catappa</i> L., <i>Dyopiros kaki</i> , <i>Eucommia ulmoides</i> , <i>Mucuna pruriens</i> , <i>Amaranthus spinosus</i>	<i>Pseudomonas aeruginosa</i> , <i>Yarrowia lipolytica</i> NCIM3589 <i>Thermomonospora</i> sp., <i>Actinobacter</i> spp., <i>Bacillus subtilis</i> , <i>Escherichia coli</i> k12, <i>Lacticaseibacillus casei</i> (strain JCM1134), <i>Haloferax volcanii</i> , <i>Deinococcus radiodurans</i> , <i>Lactobacillus strain</i> , <i>Alkalothermophilic actinomycete</i>		Gardea-Torresdey et al. (2002), Sastry et al. (2003), Ankamwar et al. (2005), Bharde et al. (2007), Sintubin et al. (2009), Smitha et al. (2009), Song et al. (2009), Pimprikar et al. (2009), Ankamwar (2010), Raghunandan et al. (2010), Thirumurugan et al. (2010), Vankar and Bajpai (2010), Arulkumar and Sabesan (2010), Bankar et al. (2010), Mubarak Ali et al. (2011), Parida et al. (2011), Dwivedi and Gopal (2011), Fazaludeen et al. (2012), Konwar Boruah et al. (2012), Aromal et al. (2012), Das et al. (2012), Das and Velusamy (2014), Guo et al. (2015), Geraides et al. (2016), Kikuchi et al. (2016), Li et al. (2016), Markus et al. (2016), Wadhvani et al. (2016), Nadhe et al. (2020), Tariq et al. (2020), Costa et al. (2020), Wang et al. (2020)



Table 2 (continued)

Nanomaterials	Plant	Bacteria	Yeast and filamentous fungi	References
Silver	<i>Elettaria cardamomom</i> , <i>Nerium indicum</i> , <i>Ficus indica</i> , <i>Parthenium hysterophorus</i> , <i>Clerodendrum serratum</i> , <i>Pelargonium graveolens</i> , <i>Azadirachta indica</i> , <i>Ocimum</i> sp., <i>Desmodium triflorum</i> , <i>Pterocarpus santalinus</i> , <i>Brassica juncea</i> , <i>Clerodendrum inerme</i> , <i>Pongamia pinnata</i> , <i>Euphorbia hirta</i> , <i>Rumex hymenosepalus</i> , <i>Grewia flaviscences</i> , <i>Carica papaya</i> (fruit), <i>Gliricidia sepium</i> , Aloe vera extract, <i>Capsicum annum</i> , <i>Coriandrum sativum</i> , <i>Tephrosia tinctorial</i> , <i>Avicennia marina</i> , <i>Cerriops tagal</i> , <i>Rhizophora mucronata</i> , <i>Opuntia</i> , <i>Sonchus asper</i>	<i>Bacillus cereus</i> , <i>B. subtilis</i> , <i>Oscillatory willetii</i> NTDMO1, <i>Pseudomonis stuzeri</i> , <i>Corynebacterium</i> , <i>Escherichia coli</i> , <i>B. thuringiensis</i> <i>Ureibacillus therosphaericus</i> , <i>Lactobacillus</i> strain, <i>Staphylococcus aureus</i> L. <i>acidophilus</i> , L. <i>acidophilus</i> 58p. <i>Brevibacterium casei</i> , <i>Bacillus licheniformis</i> D4hbl, <i>Pseudomonas deceptionensis</i> DC5, <i>Pseudomonas fluorescens</i> CA 417, <i>Sporosarcina koreensis</i> DC4, <i>Pseudomonas rhodesiae</i> , <i>Pseudomonas poae</i> CO, <i>Streptomyces capillispiralis</i> Ca-1, <i>Haloalkaliphilic Streptomyces</i> sp.	<i>Yeast strains</i> MKY3, <i>Cortiolus versicolor</i> , <i>Phanerochaete chrysosporium</i> , <i>Cladosporium cladosporioides</i> , <i>Aspergillus flavus</i> , <i>Fusarium semitectum</i> , <i>F. oxysporum</i> , <i>Extremophillic yeast</i> , <i>Pleurotus sajor-caju</i> , <i>Aspergillus niger</i> , <i>A. oryzae</i> , <i>Trichoderma viride</i> , <i>Fusarium solani</i> , <i>P. nagiovense</i> A112	Dameron et al. (1989), Klaus et al. (1999), Joeger et al. (2000), Klaus-Joeger et al. (2001), Ahmad et al. (2003), (2011), Shankar et al. (2003a, b), Kowshik et al. (2003), Zhang et al. (2005), Vigneshwaran et al. (2006), (2007), Chandran et al. (2006), Li et al. (2007), Basavaraja et al. (2008), Mohanpuria et al. (2008), Gade et al. (2008), (2010), Ganesh Babu and Gunasekaran (2009), Gurunathan et al. (2009), Ingle et al. (2009), Balaji et al. (2009), Jain et al. (2009, 2010), Nanda and Saravanan (2009), Nithya and Ragunathan (2009), Parashar et al. (2009), Pugazhenthiran et al. (2009), Saifuddin et al. (2009), Sanghi and Verma (2009), Shekhawat and Arya (2009), Sintubin et al. (2009), Kalishwaralal et al. (2010), Binupriya et al. (2010), Philip (2010), Sathyavathi et al. (2010), Thakkar et al. (2010), Thirumurugan et al. (2010), Tripathy et al. (2010), Raut et al. (2010), Juibari et al. (2011), Mallikarjuna et al. (2011), Mano Priya et al. (2011), Mourato et al. (2011), Mubarak Ali et al. (2011), George et al. (2012), Gnanadesigan et al. (2012), Gnanajobitha et al. (2012), Selvi and Sivakumar (2012), Sunkar and Nachiyar (2012), Umashankari et al. (2012), Gopinath et al. (2013), Priya Dhas et al. (2013), Rodriguez-León et al. (2013), Verma et al. (2013), Maliszewska et al. (2014), Priyadharshini Raman et al. (2015), Rajaram et al. (2015), Sana et al. (2015), Garmasheva et al. (2016), Jo et al. (2016), Shanthi et al. (2016), Singh et al. (2016), Hossain et al. (2019), Ibrahim et al. (2020), Fouda et al. (2020), Marathe et al. (2021)
Gold nanowires		<i>Rhodospseudomonas capsulate</i>		He et al. (2008)



Table 2 (continued)

Nanomaterials	Plant	Bacteria	Yeast and filamentous fungi	References
Palladium	<i>Cinnamomum camphora</i> L., <i>Gardenia jasminoides</i> Ellis., <i>Glycine Max</i> L., <i>Chlorella vulgaris</i> , <i>Origanum vulgare</i> L., <i>Anogeissus latifolia</i> , <i>Cinnamomum zeylanicum</i> Blume	<i>Desulfovibrio desulfuricans</i> NCIM 8307		Nair and Pradeep (2002), Jia et al. (2009), Sathishkumar et al. (2009), Yang et al. (2010), Kumar Petla et al. (2012), Arsiya et al. (2017), Rafi Shaik et al. (2017), Korra and Rastogi (2018)
As-S nanotubes		<i>Shewanella</i> sp.		Jiang et al. (2009)
ZnS		Sulfate reducing Bacteria, <i>Desulfobacteriaceae</i>		Labrenz et al. (2000), Mandal et al. (2006), Murugadoss et al. (2009), Sharma et al. (2009a, b), Popescu et al. (2010), Chauhan et al. (2012)
Iron, Iron oxide	<i>Psidium guajava</i> , <i>Vaccinium corymbosum</i> , <i>Eichhornia crassipes</i> , L. Alston, <i>Ramalina sinensis</i> , <i>Vaccinium Floribundum</i> , <i>Aloe vera</i> , <i>Mentha spicata</i> L.,	<i>Shewanella oneidensis</i> , <i>G. sulfurreducens</i> , <i>Geobacter</i> sp.,		Perez-Gonzalez et al. (2010), Iwahori et al. (2014), Prasad et al. (2014), Watts et al. (2015), Xiao et al. (2016), Mukherjee et al. (2016), Wei et al. (2017), Manquian-Cerdá et al. (2017), Abril et al. (2018), Kamath et al. (2020), Arjaghi et al. (2021), Shukla et al. (2022)
nZVI, nZVAg	<i>Eucalyptus globules</i> , <i>Ficus benjamina</i> , Oak, mulberry	<i>Pseudomonas</i> , <i>E. Coli</i> , <i>B. Subtilis</i> , <i>B. Subtilis-niger</i> , <i>P. Fluorences</i> , <i>Aspergillus versicolor</i> , <i>B. Cereus</i> , <i>Sphingomonas</i> sp.	<i>Aspergillus versicolor</i>	Diao and Yao (2009), Chen et al. (2011), Kim et al. (2012), Fajardo et al. (2013), Madhavi et al. (2013), Chaitawiwat et al. (2016), Poguberović et al. (2016), Al-Qahtani (2017), Slijepčević et al. (2021)
CdS		<i>Klebsiella aerogens</i> , <i>Clostridium thermoaceticum</i> , <i>Escherichia coli</i> , <i>Lactobacillus acidophilus</i> DSMZ 20079 T, <i>Shewanella oneidensis</i> MR-1, <i>Pseudomonas aeruginosa</i> JP-11, <i>Rhodopseudomonas palustris</i>	<i>Schizosaccharomyce pombe</i> , <i>Candida glabrata</i> , <i>Fusarium oxysporum</i> ,	Dameron et al. (1989), Holmes et al. (1995), Ahmad et al. (2002), Sweeney et al. (2004), Mandal et al. (2006), Bai et al. (2009), Raj et al. (2016), Xiao et al. (2017), Riaz et al. (2020)
PbS		<i>Anaerobic granular sludge</i> , <i>Citrobacter freundii</i> Y9, <i>Shewanella loihica</i> PV-4	<i>Rhodospiridium Dibovatum</i> , <i>Torilopsis</i> sp.	Kowshik et al. (2003), Seshadri et al. (2011)
Selenium		<i>Quercus glauca</i> , <i>Azadirachta indica</i> , <i>Diopyros kaki</i> , <i>Octimum sanctum</i> L		Jain et al. (2015, 2016a, b), Wang et al. (2017, 2018)
Platinum				Song et al. (2010), Soundarrajan et al. (2012), Karthik et al. (2016), Thirumugan et al. (2016)
CdS quantum dots				Kowshik et al. (2003)
Stable silver			<i>Schizosaccharomyces pombe</i> <i>A. terreus</i> , <i>A. fumigatus</i> , <i>A. nidulans</i> <i>Aspergillus flavus</i>	Bhainsa and D'Souza (2006), Neveen (2013)



Table 2 (continued)

	Nanomaterials	Plant	Bacteria	Yeast and filamentous fungi	References
Magnetite		<i>Aloe vera</i>	<i>Magnetospirillum magneticum</i> , Sulfate reducing bacteria		Gericke and Pinches (2006), Mohanpuria et al. (2008), Phumying et al. (2013)
Bioactive				<i>Lichen fungi (Usnea longissima)</i>	Shahi and Patra (2003)

fungi could be employed as a source since it secretes higher volume of proteins which translates into better nanoparticle production efficiency (Koul and Taak 2018). One of the key disadvantages of employing filamentous fungi is that it produces nanoparticles at a significantly slower rate than plant synthesis, owing to the creation of enzymes that catalytically decrease salt metallic solid nanoparticles. In terms of nanoparticle synthesis, filamentous fungi offer an advantage over other biological systems owing to an environmentally acceptable approach with a large variety of species, simple culture methods, reduced time, and increased cost-effectiveness (Sunanda et al. 2021). Yeast strains also have certain advantages over bacteria in terms of synthesis, such as quick growth with the use of basic nutrients and enzymes, and the use of yeast in the manufacture of metallic nanoparticles is being studied. Table 2 contains a list of diverse plants, bacteria, yeast and filamentous fungi that are employed in the processing and manufacture of nanomaterials.

Kinetics and models for nano-bioremediation of contaminants

A proper interaction between nanomaterials (NMs), living organisms and contaminants takes place during whole nano-bioremediation process. A set of parameters influence on each of the component which have physical, chemical, and biochemical interactions among them (Fig. 3) (Taylor et al. 2012; Tang et al. 2016; Tan et al. 2018; Vázquez-Núñez et al. 2020). In this complex interaction phenomena nanomaterial depends on size and shape, surface coating of material, and its chemical nature; contaminants depends upon its concentration in soil, level of toxicity, and its compounds stability. Due to nanomaterial and contaminant interactions from both side, living organisms undergo biocidal (BC) or biostimulation (BS) effect, which impacts its remedial performance in bioremediation process. Sorption is a critical step in the nano-bioremediation process. Sorption is the process of a pollutant interacting with a sorbent at the surface, and the pollutant then penetrating deeper layers of the sorbent to produce a solution (Vieira and Volesky 2000). To understand the nature of the adsorption processes employing NMs, a substantial amount of studies have been conducted (Hu et al. 2006; Wang et al. 2011; Sebeia et al. 2020). On other side, contaminants get adsorbed through adsorption process with the influence of temperature, pH, media. Mechanistic, thermodynamic and kinetic investigations are, therefore, required to describe the behavior of the nanomaterial when it comes into contact with contaminants. The Langmuir, Freundlich and Temkin isotherms, as well as the Dubinin–Radushkevich models, are some of the models that describe the nature of involving the biological material in remediation processes (1–12) (A.O.D 2012;



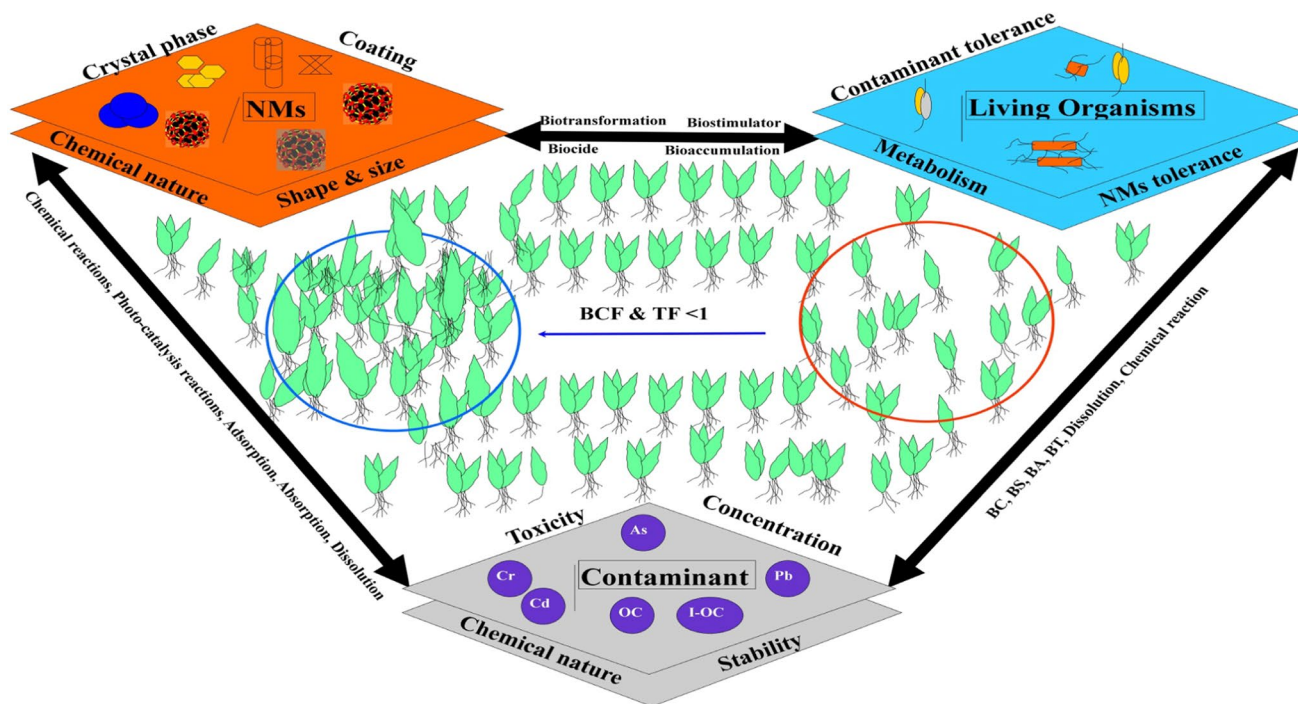


Fig. 3 Schematic diagram depicting the nano-bioremediation of contaminants (Taylor et al. 2012; Tang et al. 2016; Tan et al. 2018; Vázquez-Núñez et al. 2020); BCF (Bioconcentration factor), TF (Translocation factor)

Olalekan et al. 2013; Dada et al. 2013; Pathak et al. 2015; Matouq et al. 2015).

According to the Langmuir isotherm, a monolayer adsorption occurs on a uniform surface that has a finite number of adsorption sites, and the adsorbate cannot transigrate along the surface plane. This isotherm is presented by Eq. (1) (Langmuir 1916, 1918)

$$q_e = \frac{q_m b_0 C_e}{1 + b_0 C_e} \tag{1}$$

The linear model is expression as (Eq. 2):

$$\frac{C_e}{q_e} = \frac{1}{q_m b_0} + \frac{C_e}{q_m} \tag{2}$$

where q_e —quantity of contaminants absorbed (mg/g), C_e —equilibrium liquid-concentration (mg/g), b_0 —Langmuir isotherm constant (L/mg), q_m —maximum adsorption capacity (mg/g).

Langmuir model can also be used as equilibrium parameter or separation factor “ R_L ” for interpreting the adsorption behavior of the nanoparticles system (Eq. 3) (Weber and Chakravorti 1974).

$$R_L = \frac{1}{1 + b C_0} \tag{3}$$

where C_0 is the initial concentration of adsorbate (mg/L). The irreversibility ($R_L = 0$), linearity ($R_L = 1$) and viability ($0 < R_L < 1$) of the sorption process is determined by the values of R_L .

A Freundlich isotherm achieves multilayer coverage of an adsorbent by means of transmigration interaction. It suggests that model is applied to the absorption characteristics on heterogeneous surfaces. This isotherm is presented by the following empirical equation as follows (Eq. 4) (Freundlich 1906).

$$Q_e = k_F C_e^{1/n} \tag{4}$$

where K_F and n are the freundlich constant and heterogeneity factor, respectively.

Linearized illustration of the isotherm provided as (Eq. 5):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

Temkin model assumes that the heat energy of sorption process decreases with the coverage of the adsorbent surface and its interaction with adsorbate molecules. This isotherm equation and linear form of the model expressed in following Eqs. (Eqs. 6, 7) (Temkin and Pyzhev 1940):

$$q_e = \frac{RT}{b_E} \ln K_T C_e \tag{6}$$

$$q_e = B \ln K_T + B \ln C_e \quad (7) \quad \text{Photocatalysts (NPs)} + h\nu \rightarrow e^- + h^+ \quad (13)$$

$$B = \frac{RT}{b} \quad (8) \quad h^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \quad (14)$$

$$\text{where } B \text{ is the Temkin isotherm constant (Eq. 8), } K_T \text{ is the} \quad h^+ + \text{OH}^- \rightarrow \text{OH}^\bullet \quad (15)$$

Temkin equilibrium binding constant (L/mg), R = universal gas constant (8.314 J/mol.K), T = Temperature at 298 K.

D-R isotherm gives an idea about the nature of the adsorption process either physical or chemical and it does not hypothesize a homogenous surface or constant absorption potential (Hutson and Yang 1997). Dubinin–Radushkevich isotherm can be expressed as (Eq. 9)

$$q_e = (q_m) \exp(-k_{ad})\epsilon^2 \quad (9) \quad \text{O}_2\text{adsorption : } \text{O}_2(\text{ads}) + e^- \rightarrow \text{O}_2^{\bullet-} \quad (16)$$

where q_e signifies the quantity of adsorbate species adsorbed in adsorbent dose (mg/g), q_m is the theoretical isotherm saturation capacity (mg/g), k_{ad} represents D-R coefficient (mol²/kJ²).

ϵ is the polyani potential which is obtained from Eq. (Eq.10):

$$\epsilon = RT \ln \left[1 + \left(\frac{1}{C_e} \right) \right] \quad (10)$$

where R signifies the gas constant (0.008314 kJ/mol/K), T is the absolute temperature in Kelvin,.

Linear for of D–R isotherm can be expressed as (Eq. 11):

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (11)$$

However, as discussed above that the D–R isotherm can be use in defining the nature of the adsorption process through the relationship with apparent energy (E) parameter (Eq. 12) (Igwe and Abia 2006).

$$E = \frac{1}{\sqrt{2k_{ad}}} \quad (12)$$

Adsorption is regarded as following a chemisorption mechanism when the parametric value of E is between 8 and 16 kJ/mol while a value below 8 kJ/mol is indicative of a dominance of physisorption.

The photocatalytic activity of nanomaterials is mostly determined by light absorption, charge transport, and separation on the catalyst surface (Bhattacharjee et al. 2022). Photocatalysts reaction with light results formation of anionic electron-oxidative hole pairs, which later gets separated (Eqs. 13, 14). As h^+ (hole) further reacts with water molecules redox active species and subsequently hydroxyl radicals have been formed (Eq. 15). On the other side superoxide radical anion is formed with the reaction with anionic electron (Eq. 16).

$$\text{Organic} + \text{OH}^\bullet + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Other degradation product} \quad (19)$$

Furthermore, strong oxidants like hydroxyl ($\cdot\text{OH}$) and perhydroxyl ($\text{HOO}\cdot$) radicals are formed with the reaction of water and superoxide anion ($\text{O}_2^{\bullet-}$) radicals (Eqs. 17, 18) (Fujishima et al. 2008). Aqueous medium contains organic contaminants which are effectively degraded by these radicals (Rana et al. 2018). The reactions that follow show a mechanism that is similar to the photoelectronic breakdown of organic contaminants (Eq. 19). Contaminants may be reduced by photocatalytic reactions, depending on the type of the NMs. The resulting compounds may be bio-transformed by biotic systems, by lowering contaminants concentrations in the environment. In addition, certain enzymes produced by living organisms can degrade many types of pollutants (Peixoto et al. 2011). Apart from other entities, NPs can reach contaminated zones due to their small size, hence expanding the application areas of nano-bioremediation technologies, which is an advantage over conventional remediation strategies (Sohail et al. 2019). Several contaminants which are removed by the application of nano-bioremediation (nanoparticles and bioagents) are shown in Table 3. Other factors to consider are the standardization of techniques for testing nanomaterials toxicity in soil and water, the explication of their relationships with biotic and abiotic components, and the applicable regulatory context in which these materials might be employed (Ramírez-García et al. 2018). Finally, in regard to synergistic applications of nanomaterials over the long-term, collateral effects of nanomaterials on microorganisms, and trophic transfer of nanomaterials in the food supply chain, future research should focus on the selection of NPs and living organisms (Vázquez-Núñez et al. 2020).



Table 3 Removal of contaminants through nano-bioremediation techniques

Nanoparticle	Bioagent	Contaminant	Remark	References
Magnetic Fe ₃ O ₄ nanoparticles	<i>Pseudomonas delafieldii</i>	Dibenzothiophene	The bio-desulfurization of dibenzothiophene was higher in the magnetic nanoparticle-coated microbial cells than in the uncoated or celite-coated cells. It has also been discovered that it may be reused up to five times	Shan et al. (2005)
Pd (0) nanoparticles	<i>Shewanella oneidensis</i> MR-1	PCBs	Around 90% of PCBs were efficiently dechlorinated by the bio-Pd produced by the microbial reduction, resulting in less hazardous by-products	Windt et al. (2005)
Fe ₃ O ₄ nanoparticles/gellan-gum gel beads	<i>Sphingomonas</i> sp. strain XLDN2-5 cells	Carbazole	Microbial cells immobilized in Fe ₃ O ₄ nanoparticles/gellan gum gel beads decomposed carbazole more efficiently than free cells or cells that were not magnetically immobilized. When this integrated system was recycled, it revealed signs of increasing deterioration	Wang et al. (2007)
Pd/nFe	Laccase derived from <i>Trametes versicolor</i>	Triclosan	The remediation of triclosan was accomplished entirely by the use of Fe nanoparticles. The laccase released by the <i>T. versicolor</i> strain, on the other hand, transformed the degraded by-products into harmless compounds	Bokare et al. (2010)
Bio-Pd nanoparticle	<i>C. pasteurianum</i> BC1	Cr (VI)	<i>Clostridium pasteurianum</i> converted Pd (II) ions to Pd nanoparticles, which persisted in the form of bio-Pd in the organism's cell membrane and cytoplasm. The Cr (VI) reduction process was effectively catalyzed, and hydrogen gas was created as well	Chidambaram et al. (2010)
nZVI	<i>Dehalococcoides</i> sp.	TCE	This research found that nZVI increased methanogen metabolic activity while deactivating dechlorinating bacteria; yet, after a lag period, the dechlorinating bacteria were able to eliminate TCE and produce ethene as a by-product	Xiu et al. (2010)



Table 3 (continued)

Nanoparticle	Bioagent	Contaminant	Remark	References
Pd/nFe	<i>Sphingomonas wittichii</i> RW1 (DSM 6014)	2,3,7,8- tetrachlorodibenzo- p-dioxin (2,3,7,8-TeCDD)	The very lethal dioxin isomer is naturally refractory, and it could not be readily degraded by a single approach. The degradation was achieved by progressively utilizing Pd/nFe nanoparticles and the <i>Sphingomonas</i> strain	Bokare et al. (2012)
nZVI	<i>Sphingomonas</i> sp. PH-07	Polybrominated diphenyl ethers (PBDEs)	Effective for PBDEs breakdown via reductive debromination and biological oxidation. This technology might lead to a remediation strategy for highly halogenated contaminants in the environment	Kim et al. (2012)
Carbon nanotubes	<i>Shewanella oneidensis</i> MR-1	Cr (VI)	The MR-1 strain that was immobilized by CNT infused CA beads was able to remove four times more Cr (VI) than free cells, CNTs, or CA beads	Yan et al. (2013)
Fe ₃ O ₄	<i>Sphingomonas</i> sp. XLDN2-5 cells	Carbazole	The Fe ₃ O ₄ nanoparticles linked to the bacterial strain's surface, degraded at the same rate as free cells, yet they were very reusable. Another benefit of employing magnetic nanoparticles is that they may be isolated from microorganisms with the help of external magnet sources	Li et al. (2013)
Nano sponge	Two organo-clays (Dellite 67G and Dellite 43 B)	Triclopyr (3,5,6-Trichloro-2-pyridinyloxyacetic acid)	Removal capacity of Cyclodextrin-based, highly cross-linked polymers is around 92% in Triclopyr contaminated soil	Baglieri et al. (2013)
nZVI	<i>Paracoccus</i> sp. strain YF1	Nitrate	Lower concentrations of nZVI (50 mg/L) accelerated denitrification while generating little microbial toxicity, but larger concentrations (1000 mg/L) considerably retarded denitrification	Liu et al. (2014)
Nanotubes	Enzyme organophosphate hydrolase-MWNTs paper	Organophosphates and heavy metals Triclopyr	CNT, single-walled CNT, and multi-walled CNT shows low removal efficiency (~22%)	Fosso-Kankeu et al. (2014), Mechrez et al. (2014)
nZVI	Oak and mulberry leaf extracts	Cu and Ni	Mulberry-nZVI and Oak-nZVI were effective in transforming labile metals (Cu, Ni) bound to Danube river sediments to stable fractions	Slijepčević et al. (2021)



Table 3 (continued)

Nanoparticle	Bioagent	Contaminant	Remark	References
Pd/nFe	<i>Burkholderia xenovorans</i> LB400	Polychlorinated biphenyl (PCB) Aroclor 1248	Bi-, tri-, tetra-, penta-, and hexachlorinated biphenyls were efficiently dechlorinated into biodegradable intermediates by Pd/nFe nanoparticles, which were then quickly degraded by <i>Burkholderia xenovorans</i>	Le et al. (2015)
nZVI-C-A beads	<i>Bacillus subtilis</i> , <i>E. coli</i> , and <i>Acinetobacter junii</i>	Cr (VI)	Removal efficiency is around 92% of Cr (VI) with the application of nZVI entrapped calcium alginate beads	Ravikumar et al. (2016)
TiNPs	Dead yeast biomass	Cr (VI)	High remediation efficiency (99.92%) with removal capacity of 162.07 mg/g. It follows langmuir adsorption process with pseudo-second order kinetics	
nZVI	nZVI combination with a second metal or microorganisms	PCB	High removal efficiency (78–99%) of PCB with rapid reaction time	Jing et al. (2018)
Multi-walled carbon nanotubes immobilized	<i>Saccharomyces cerevisiae Rhizobium</i> sp.	Cr (VI)	Removal capacity Cr (VI) is around 24.82–31.6 mg/g. Sorption experiment follows langmuir adsorption process with pseudo-second order kinetics	Sathvika et al. (2018)
Bimetallic iron-based NPs	Tobacco plants	hexabromocyclododecane (HBCD)	Removal efficiency is around 27% in case of HBCD contaminated soil	Le et al. (2019)
Polyvinylpyrrolidone (PVP)-coated iron oxide NPs	<i>Halomonas</i> sp.	Pb, Cd	Due to this integrated strategy, metal removal was enhanced, and metal remediation durations were also reduced (approx. 100% removal of Pb after 24 h, of Cd after 48 h)	Cao et al. (2020)



Nano-bioremediation for heavy metals and other pollutants

In recent years, carbon nanotubes (CNTs) have been utilized for remediation of wastewater contaminated with heavy metals. There are mainly two types of carbon nanotubes: single-walled and multi-walled (Martel et al. 1998). CNTs are able to treat heavy metal wastewater much better than other treatment methods due to their rapid adsorption kinetics associated with high specific surface area and high adsorption capacity which is more prominent in heavy metal ions such as Mn^{7+} , Ti^{+} , Cu^{2+} , Pb^{2+} , and Cr^{7+} (Pu et al. 2013; Yadav and Srivastava 2017). CNT surfaces may be modified by heat treatment and chemical modification or endohedral filling to increase their adsorption properties toward heavy metals through introduction of functional groups such as COOH, NH, OH (Kumar et al. 2021).

A study was conducted that examined the use of a graphene oxide (rGO) modified electrode that contains Au nanoparticles (rGO-Au NPs). The nanoparticles were synthesized using a vegetable extract from *Abemoschus esculentus* as a reducing agent and sensing of toxic metal ions such as Cd^{2+} , Pb^{2+} , Cu^{2+} , and Hg^{2+} were detected simultaneously. Several bacteria were introduced such as *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Rizobium gallium*, and *Staphylococcus aureus* for their high adsorptive potential for bioremediation of the toxic metal ions and these were reported to scavenge heavy metal ions effectively (Gnanaprakasam et al. 2016). Cao and his team demonstrated in a seminal paper that polyvinylpyrrolidone-coated iron oxide nanoparticles were useful for metal removal, specifically Cd^{2+} and Pb^{2+} , through bacterial interaction with *Halomonas* sp. The treatments included a bacteria and nanoparticle both individually and in combination. After 24 h of treatment, Cd was removed with the removal efficiency of 100% in the combined treatment. After 48 h, the percentage remained the same. The removal of Cd and Pb was found to be 60% and 80% for treatments with only NPs, respectively. Whereas, by *Halomonas* sp., the removal of Cd rose to 80%, while treatment of Pb showed the same removal as for NPs, i.e., 80% (Cao et al. 2020).

The possibility of making iron nanoparticles from natural consortia that can adsorb arsenic, copper, zinc, and chromium from wastewaters was reported in a recent study (Castro et al. 2018). Biogenic Fe–Mn oxides (BFMO) synthesis was carried out using the soil bacterium *Pseudomonas* sp. QJX-1 isolated from manganese mines. These oxides were found to oxidize and adsorb arsenic. This allows for adequate As(III) and As(V) adsorption and oxidation (Bai et al. 2016). The use of sulfate-reducing bacteria (SRB) to treat wastewater containing chromium

has also been demonstrated. The bacteria rely on organic compounds as a carbon source to be able to remove sulfate and COD from wastewater. As a result of experiments conducted at optimized conditions on synthetic wastewater, 81.9% of COD, 89.2% of Cr^{7+} , and 95.3% of sulfate were removed (Verma et al. 2015). Biogenic manganese oxide (BMO) derived from *Pseudomonas putida* MnB1 has been used to remove heavy metals from the environment. With regard to adsorbing heavy metals, BMO have shown superior performance compared with chemically synthesized manganese oxide (birnessite). It is amorphous, small size, and the large surface area makes BMO an excellent adsorbent. Compared to birnessite, BMO adsorbs zinc, lead, and cadmium at a rate 7–8 times higher, and when the pH and temperature are changed, BMO adsorbs heavy metals even more powerfully (Zhou et al. 2015). Recent reports have found that nanoparticle synthesis through biogenic method utilizing *Citrobacter freundii* Y9 are effective in remediating Hg contaminated soil (Wang et al. 2017). Combined elements of mercury and selenium form HgSe, an inert and chemically inert compound that is less toxic than mercury and selenium alone. Furthermore, nano-selenium has the ability to capture mercury in anaerobic and aerobic conditions. Immobilizing mercury using nano-selenium is an effective way to remediate soils that are contaminated with mercury.

Nano-bioremediation for organic contaminants (including pesticides and herbicides) in soils

Le et al. (2015) investigated the degradation of Aroclor 1248-containing solutions which is a polychlorinated biphenyls (PCB) with nZVI (1000 mg/L) followed by biodegradation with *Burkholderia xenovorans*. Following the application of nZVI, the researchers obtained an 89% degradation of the congeners. Following that, Biphenyls formed by bacterial metabolism after PCB dechlorination showed a biodegradation rate of 90%. The nZVI was found to have no toxic effects on microorganisms in this study. Also, Bokare and his team investigated the feasibility of combining bioremediation and reductive processes using nanoparticles in a triclosan (5 g/L) contaminated solution. A sequential degradation was promoted by exposing the contaminant to anaerobic dechlorination using Pd/Fe nanoparticles. Following that, a further remediation step involves oxidizing the by-products with *Trametes versicolor* laccase. As a result, triclosan was completely dechlorinated and its by-products completely oxidized 20 min after application (Bokare et al. 2010). Another experiment conducted by Bokare and his team combined the use of Pd/Fe nanoparticles and *Sphingomonas wittichii* to remediate a



2,3,7,8-tetrachlorodibenzo-p-dioxin-contaminated solution. A dechlorination process was carried out in an anaerobic environment with 2,3,7,8-tetrachlorodibenzo-p-dioxin via Pd/Fe nanoparticles, yielding 100 percent dechlorination in just 10 h. As a result of dechlorination, the residual by-product (dibenzo-p-dioxin) could not be remedied by nanoparticles, but was degraded completely through microbial metabolism (Bokare et al. 2012). Singh and his team investigated the integrated remediation of Lindane-contaminated soil. Using CMC-Pd/Fe nanoparticle the researchers evaluated how *Sphingomonas* sp. behaved when exposed to different concentrations. The researchers discovered that nanoparticle suspensions containing 40 mg/L of nanoparticles produced the best results for microbial growth. Combining the two systems (biotic and abiotic) resulted in a contaminant degradation rate of 99 percent in 6 days, a result that was far superior to either treatment alone (Singh et al. 2013).

Kim and her team investigated the effect of combining nZVI and diphenyl ether with the bacteria *Sphingomonas* sp. PH-07 on the biodegradation of polybrominated diphenyl ethers (PBDEs). They found that PH-07 is capable of growing at 5 g/L nZVI concentrations and has the ability to biodegrade PBDEs (Kim et al. 2012). Furthermore, utilization of nZVI nanomaterials as part of bioremediation, electrokinetic remediation and chemical oxidation has assisted in the cleanup of heavily polluted sites (Fan et al. 2016). In their report, nZVI-assisted dechlorination was followed by a biosurfactant-based soil washing procedure to eliminate polychlorinated biphenyls (PCBs) from soil contaminated by transformer oil. Aside from direct dechlorination, it was discovered that nZVI greatly improved efficiency of soil washing in oil and soil phases by lowering the interfacial tension between them, and 90 percent of PCBs were removed. A combination of treatments with nZVI, surfactants, electrokinetic treatments has previously been reported to pretreat sites of contaminated with heavy metals, polychlorinated biphenyls (PCBs), pesticides and chlorinated volatile organic compounds (cVOCs) (de Lima et al. 2012; Bhattacharya et al. 2016). The reactivity of nZVI is affected by natural organic matter (NOM), such as fulvic acids and humic acids, as they compete with pollutants for the reactive sites on the surface of nZVI where reactions occur. However, some have argued that NMs are ineffective in bioaugmentation because they inhibit microbes living in polluted environments (Nzila et al. 2016; Amoatey and Baawain 2019). However, it should be noted that NMs can reduce microbial diversity and abundance after a few days, but they can return again after a few weeks. Furthermore, although NMs decreased enzyme concentrations involved in ecological processes, they began to increase again after the first few days of the experiment. There is an indication that NMs have a priming effect initially, but because of their resilience, ecological balance returns shortly thereafter. It has been reported, however,

that high CNT concentrations inhibit bacterial growth and microbial activity, while low CNT concentrations lead to greater biodegradation by causing bacteria to grow and over-express degradation genes (Zhang et al. 2015). Because of its large surface area, NM could help to overcome limitations in microorganism immobilization and entrapment during bioaugmentation strategies (Nzila et al. 2016).

With the introduction of the basic idea of how nanoparticles interact with microbes, different nanoparticles have been fabricated using biological entities. It has become the focus of "green nanotechnology" to immobilize microbes on nanoparticles with desirable characteristics, and their use in environmental remediation combines both technologies into an innovative, hybrid approach that could open up new approaches to sustainable pesticide mitigation. Different nanoscale structures are used here to enhance the degradation of pesticides from polluted sites by simultaneously or sequentially combining with microbes. Reátegui and his team employed whole cell immobilization techniques to degrade pesticides. To remove the pesticide, they used recombinant *Escherichia coli* cells that expressed the long-lasting atrazine-dechlorinating enzyme. To encapsulate cells in a porous gel, siliconized silica nanoparticles (SiNPs) were used. By silanizing nanoparticles with methyltrimethoxysilane (MTMS) and polyethylene glycol, a porous gel was created which served as a cross-linker. Stability testing was carried out at 23 and 45 °C, respectively. In the higher temperature range, gel displayed a good structural rigidity. The degradation of the pesticide by encapsulated cells was three times more efficient than that of free cells (Reátegui et al. 2012).

Zhuang et al. (2015) used *Streptomyces* sp. N01 immobilized on bamboo-carbon supported Fe₃O₄ nanoparticles (Fe₃O₄/BC) to break down the heterocyclic aromatic organic compound quinoline. It was found to be effective at quinoline concentrations of 100–400 mg L⁻¹, pH levels of 5–10, and temperatures of 20–45 °C. When temperature and pH were changed, Fe₃O₄/BC immobilized cells demonstrated greater pesticide concentration tolerance. In the ninth cycle, pesticides were removed at an 85.3 percent rate. Hou and his team observed that aniline-degrading *Rhodococcus rhodochrous* cells immobilized on Fe₃O₄ nanoparticles were capable of degrading chlorophenols (CPs) which is an organochloride of phenol utilized for a variety of purposes such as antiseptics, disinfectants, pesticides and wood preservatives. Immobilization of *Rhodococcus rhodochrous* DSM6263 strain was carried out with k-carrageenan. In this study, 2,3-dichlorophenol, 4-chlorophenol and their mixture were efficiently degraded by cells immobilized by k-carrageenan in combination with 9 g L⁻¹ Fe₃O₄ nanoparticles, indicating a higher degradative efficiency than free cells. With these immobilized cells, the process could be repeated for a minimum of six times (Hou et al. 2016). Khataon and Rai (2018)



isolated two *Bacillus* sp. capable of degrading atrazine, *B. badius* and *B. ensimensis*. Atrazine's biodegradation in various environmental conditions was studied using free and α -Fe₂O₃ immobilized cells. In order to immobilize these bacterial isolates, α -Fe₂O₃ magnetic nanoparticles were developed because free cells of microbes were rarely able to degrade atrazine. SEM images revealed that immobilized bacterial cells were completely held on to and spread across the surface of α -Fe₂O₃ magnetic nanoparticles. In comparison with free cells, immobilized α -Fe₂O₃ cells degraded by 90.56 percent after 20 days.

Advances in nano-bioremediation and crop productivity

Nano-bioremediation is defined as the method wherein environmental contaminants including heavy metals, organic and inorganic pollutants are removed from polluted sites by using nanoparticles/nanomaterials produced by plants or microorganisms such as fungi, bacteria through nanotechnology. Nano-bioremediation is gaining popularity as a flexible utility for long-term environmental cleanup (Koul and Taak 2018). Currently, bioremediation provides an environmentally useful and economically feasible option to remove pollutants from the environment, following latest advancements (Ken and Sinha 2020). Microbes, plants and enzymes-mediated remediation are the three fundamental methods used in bioremediation. Nano-bioremediation is one such technology that employs physiochemical and biological approaches and is now being researched in several polluted areas. Nanomaterials are utilized in the nano-bioremediation process to break down pollutants to a level that is suitable for biodegradation, and then the contaminants are biodegraded. NPs that are biologically produced from plant extracts or microbes are utilized in nano-bioremediation to clear away polluted water and land locations. Nanomaterials have developed as a viable alternative to conventional methods of treatment in the last two decades due to their high efficacy, cost-effectiveness, and environmental friendliness (Dastjerdi and Montazer 2010). The first nanoparticles to be utilized for environmental cleanup were iron NPs (Tratnyek and Johnson 2006). For the treatment of polluted soil or groundwater remediation, several potential iron-based solutions are available. Zero-valent iron NPs have been demonstrated to successfully remediate acidic water polluted with heavy metals by solubilizing the heavy metal contaminants on their interface, making them a viable and necessary technique of nano-remediation (Iravani 2011; Saif et al. 2016). Because of their exceptional ability to destroy organic dyes, Zn NPs have been widely studied and examined by scientists all over the world. Because Zn NPs are semiconductor photocatalysts, they may completely degrade

a broad range of substances, including dyes, phenols, and pharmaceuticals (El-Kemary et al. 2010). Noble metallic nanoparticles, such as gold and silver, offer a broad range of uses, the most notable of which is the decomposition of organic dyes (Rajeshkumar and Santhiyaa 2018). Copper nanoparticles have also been demonstrated to be effective at degrading organic pigments (Marcelo et al. 2018).

Nanotechnology also improves the effectiveness of phytoremediation (Zhu et al. 2019). Organic contaminants like atrazine, chlorpyrifos and molinate can be eliminated by nano-sized zero-valent ions, as reported by (Ghormade et al. 2011) Ghormade and his team. In enzymatic bioremediation, nanoparticles can also be employed in combination with phytoremediation (Singh 2010). Microbial and plant degradation are especially resistant to some organic substances that are complex in nature such as organochlorines and long-chain hydrocarbons. This limitation might be overcome by linking nanotechnology and biotechnology, for example, complex organic substances would be reduced into simpler compounds by nano-encapsulated enzymes, which would then be promptly broken down by microorganisms and plants functioning together. Carbon nanotubes have also been shown to be particularly successful in the treatment of polluted water due to their high affinity and adsorption properties for pollutants (Kitching et al. 2014). Excellent thermal and chemical stability of carbon nanotubes makes them a viable alternative to activated carbon for the detoxification of various organic and inorganic pollutants such as zinc, lead, and chromium (Hu and Xia 2018). Even though nano-remediation helps in treating the mine water, there are still a number of safety problems that need to be resolved. Various eco-remediation nano-applications are rapidly progressing from trial to full-scale success in addressing ecologically hazardous chlorinated areas. Nanoscale TiO₂, carbon nanotubes, dendrimers, swellable organically modified silica (SOMS), and metallo-porphyrinogens are nanoproducers for *in situ* and *ex situ* remediation of pollution (Shi et al. 2015; Wang et al. 2017). During photo-catalysis, TiO₂ nanoparticles can treat a variety of chemical fertilizers, herbicides, insecticides, and pesticides, and are being explored for *ex situ* handling of diseased groundwater reservoirs (Pandey 2018). The kinetics of the redox reaction is increased by biologically produced iron, copper and titanium nanomaterials in conjunction with a metal precursor including gold, nickel, Pt, and Pd. Pd NPs have the ability to catalyze the conversion of trichloroethene to ethane while avoiding the formation of an intermediate by-product, vinyl chloride. Palladium-Osorb, a parallel metal-glass fused material, has been experimentally verified and employed for *ex situ* cleanup of chlorinated volatile organic compounds (Song et al. 2009). Silica NPs are used for lead remediation (Ma et al. 2018), zinc NPs for carbon disulfide removal from the air, and nano-crystalline hydroxylapatite for the removal of lead and cadmium, zero-valent



nano-iron, carbon nanotubes, fullerenes, TiO₂ and ZnO NPs, and bimetallic nano-metals for DDT, carbamates, and heavy metals such as chromium, lead, arsenic, and cadmium from soil (Lárez Velásquez 2018). The incorporation of biologically generated Iron NPs and Iron-Pd NPs in the remediation of dyes, hydrocarbons, 2,3,7,8-tetrachloro dibenzo-p-dioxin, pesticides, trichloroethylene, polychlorinated biphenyls, and Lindane, among other things, has become more widespread (Asmel et al. 2017). Biogenic uranite nanoparticles were utilized for the bioremediation of uranium (Bargar et al. 2008). Heavy metals, namely Cu, Zn, Pb, and Ni, were deposited in biologically produced nanoparticles from *Gundelia tournefortii*, *Centaurea virgata*, *Reseda lutea*, *Scariola orientalis*, *Eleagnum angustifolia*, *Bacillus* sp., and *Noaea mucronata* (Sinha et al. 2011; Ingle et al. 2014).

A few chemicals in the agricultural system, such as pesticides, degrade slowly or are chemically stable in nature, so they remain in the environment for longer periods of time and lead to serious consequences. However, by using nanoscience, these hazardous and toxic derivatives can be degraded under certain circumstances. They may penetrate the food chain if they are not decomposed, posing a major health risk. Agriculture nanotechnology has taken a positive stride in this regard in recent years. For example, in polluted soil, a nanoparticle-water slurry can be combined, and over time, these particles will diminish the toxicity of pesticides that are slow to degrade or resistant. Plant-derived nanometric lignocellulosic materials have led to a new market place for creative and value-added nanoscale materials and products, such as nano-sized cellulose crystals utilized as ultra-light augmentation in polymeric matrixes (Dasgupta et al. 2016). These can be implemented in food as well as other packaging, manufacturing and body components of transport vehicles. Because we can extract nano-lignocellulosic components from lignin- and cellulose-based agricultural residues, nano-lignocellulosic materials are the ideal solution to manage agricultural wastes (Brinchi et al. 2013).

Commercialization of nano-materials for restoration of contaminated agricultural land

The "Environmental Remediation Market with COVID-19 Impact Analysis by environmental medium (soil & groundwater), Technology (Bioremediation, Pump & Treat, Soil Vapor Extraction, Chemical Treatment), Site Type, Application, and Region—Global Forecast to 2026" reported that the market for environmental remediation is predictable to reach USD 158.8 billion by 2026, up from USD 104.6 billion in 2021, at an 8.7 percent CAGR over the forecast horizon. By 2026, bioremediation technology is expected to rationalize the majority of the environmental remediation

market. Due to the growing demand for this methodology for the remediation of both soil and groundwater, the bioremediation section is supposed to prompt the market for environmental remediation during the baseline period. Increasing government initiatives for environmental safety; a rising emphasis on the development of environmental friendly enterprises, and rapid population growth and industrialization in developing countries are key elements which drive this market's growth. In the midst of COVID-19, the development of sophisticated remediation technologies and the steady expansion of the oil and gas industry caused a heavy demand for environmental remediation for productive industrial activities.

The global agricultural land is projected to produce nearly 99 percent of our food, as well as textiles, timber, and raw materials of industrial significance. However, anthropogenic activities have led to the contamination of agricultural land due to the release of organic pollutants such as pesticides, fertilizers, plastics, bisphenols; inorganic pollutants like heavy metals and metalloids, and other pollutants including personal care products, pharmaceuticals, surfactants, nanoplastics, etc. (Marziali et al. 2021). Engineered nanoparticles (ENMs) are now being explored as a way to enhance agricultural soil quality and, as a result, promote sustainable agriculture. ENMs are particularly reactive due to their tiny size and wide surface area, and they exhibit a range of features such as improved cation exchange capacity, sustained release of nutrient in the soil that make them useful in soils application (Thul et al. 2013). Chemical reductant-based nanoparticles such as nano-zerovalent iron (nZVI), manganese (Mn), thiosulfate (S₂O₃⁻²), molybdenum sulfides (MoS₂), zinc (Zn), hydrogen peroxide (H₂O₂), and iron sulfide (FeS) are effective at transforming, degrading, and detoxifying organic and inorganic soil pollutants. Adsorption, immobilization, ion exchange, complex formation, reduced dehalogenation, and SN2 nucleophilic substitution were the basic mechanisms (Wang et al. 2017; Chen et al. 2020; Zhou et al. 2021). nZVI is one of the most effective technologies that has been used to create permeable barriers or restore soil *in situ* by removing several pollutants. Nano form of ZVI has also been shown to be very successful in eradicating organic chemicals from the soil, particularly chlorinated solvents (e.g., TCE), in real-world applications at military-based locations across the United States and Europe (Viskutyte et al. 2014). The utilization of flower-like MoS₂ nano-hybrid has been proved to be effective in removing Hg(II) and Pb(II) from soil (Wang et al. 2020). Other interesting nanoscale materials including the self-assembled monolayers on mesoporous supports (SAMMS) have been reported to remove non-polar pollutants like polyaromatic hydrocarbons (PAHs) from soil (Brandl et al. 2015). Metal oxides-based nanoparticles such as oxides of Mn, Zn have greater capabilities to detoxify contaminated soil. Mn oxide is being applied for



the detoxification of contaminated land due to its interesting properties such as large specific surface and low pH. However, Mn oxide-based nanomaterials are not desirable for the pollutants with reduced species (e.g., Cr^{3+} versus Cr^{6+} ; their application is restricted only to the pollutants with oxidized chemical species, e.g., As^{3+} versus As^{5+}) since Mn oxides have strong oxidative characteristics (Villalobos et al. 2014). In comparison with Mn oxides, biogenic nanostructured Mn oxides are more productive, cost-effective, and environmental-friendly materials. They have been reported to be successful in restoring arsenic-contaminated soil (Wang et al. 2020). Zn oxide nanoparticles have been reported to reduce both cadmium and arsenic contamination in paddy (Ma et al. 2020). With adsorption and degradation efficiencies of up to 80% and 99%, respectively, carbon-based materials such as biochar, graphene, activated carbon, single and multi-walled CNTs have been proven to be effective in extracting both organic and inorganic contaminants from soil (Gopinath et al. 2021). Biochar/Fe components have been utilized in soil restoration via three different mechanisms—adsorption, reduction and oxidation (Lyu et al. 2020). For the treatment of Cd^{2+} and Pb^{2+} polluted soils, a new thiol-modified rice straw biochar was produced by esterification with-mercaptoethanol. Rice straw preferentially adsorbed Cd^{2+} over Pb^{2+} , lowering Cd availability by up to 40% while allowing Pb to be immobilized to a limited extent (Fan et al. 2020). Nano-sized biopolymers have been described as a flexible category of materials that may be employed in a variety of applications, particularly soil conditioners. However, there's limited information on the application of nanotechnology in soil restoration and hence this deserves further investigation.

Conclusion

The biosynthesis of nanoparticles is a slow process compared with physical and chemical processes. Further studies should focus on reducing the reaction time for the synthesis of nanoparticles, which will enhance the attractiveness of the process. In addition, it is crucial to determine and isolate the compound(s) that results in metal reduction during synthesis so that the process can be more efficient. Nanobioremediation-based approaches have been established as an effective treatment for a number of environmental contaminants, including micropollutants. Nevertheless, these studies are confined to laboratory conditions, so their efficacy in soil, wastewater treatment plants remains to be further explored. The creation of intermediate complexes led to toxicity in aqueous systems when nanoparticles are utilized to remediate environmental contaminants. Therefore, it is mandatory to check the genesis and fate of these compounds at miscellaneous points during the treatment procedure, as well as to take adequate steps to remove them.

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Declarations

Conflict of interests All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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