Application of Nanobiofertilization for Bioremediation and Ecorestoration of Polluted Soil/Farmland

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Abstract

Nanotechnology is a novel field of research that solves issues in relation to environmental contamination. It opens doors for an environmentally friendly substitutes without altering the ecosystem. The combination of the two methods, nanobiofertilization and bioremediation is a recently developed approach which gives hope for decontamination of the environment and restoring a livable future. It has proven to effectively absorb contaminates in a short period of time and in a friendlier manner. Microorganisms in nanobioremediation play an important role in the removal, detoxifying, degrading, and immobilization of pollutant into less toxic form. Bio- and phytoremediations are exclusively preferred approaches because of the edge it has over numerous methods like high waste cleaning abilities, its cheap, ecofriendly, and generally acceptable. This approach has exceptionally added to the tolerability and ecorestoration of the environment based on the upper hand it has over other innovations. More so, its efficacy signifies high level of pollutant removal and has lay out new prospect to tackle problem within the environment.

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Charles Oluwaseun Adetunji, Chukwuebuka Egbuna, Anton Ficai and Oluwatosin Ademola Ijabadeniyi (eds.) Handbook of Agricultural Biotechnology: Volume V Nanobiofertilizers, (1–36) © 2024 Scrivener Publishing LLC

Keywords: Nanobiofertilization, bioremediation, ecorestoration, pollution, nanobioremediation, nanoparticle

1.1 Introduction

Soil pollution poses a danger to livelihoods, quality of life, and sustainable development [1]. Therefore, safeguarding soil is imperative in the present time due to the pressures of a growing population and the reduction of cultivable land caused by human activities. Nanotechnological methods are emerging as one of the most modern approaches to restoring the environment, which can be utilized to eliminate various pollutants. The integration of nanoparticles with microorganisms enhances degradation of harmful contaminants in the environment [2].

Soil restoration is one primary field where nanotechnological approaches have been extensively utilized. Recently, nanobioremediation (NBR) has been used in addressing soil pollution via biodegradation using nanoparticles. Nanobioremediation is concerned with the integration of plants or microorganism with nanoparticles to eliminate pollutants in the environment [3] through various mechanisms, basically precipitation, adsorption, co-precipitation, and redox reactions [4]. This mechanism is facilitated as a result of their exceptionally large surface area of the particle [5]. By utilizing nanoparticles (NPs), hyperaccumulators and native soil microorganisms can enhance biodegradation processes, thus expanding the potential scope of restoration. This approach can be referred to as nanophytoremediation and microbe-mediated nanorestoration [6]. Given the rising costs of chemical and physical techniques, phytoremediation and bioremediation have gained ground. The reason nanoparticles is combined with bioremediation is because of their surface area being able to interact with the surroundings, enhancing the remediation process. Therefore, nanobioremediation aims to reduce the concentration of pollutants to an extent that is deemed safe, while also minimizing secondary environmental effects. Additionally, this reclamation approach is very effective, quicker, and eco-friendly compared to bioremediation methods [7]. Nanobioremediation (NBR) uses a technique that require the application of nanocatalyst to breakdown pollutants by enabling them to penetrate down into pollutants, thus carrying out the entire process safely without altering the environment [3]. The establishment of the connection between microorganisms and nanoparticles is crucial to effectively utilized the technique [8]. The surface covering, size, nature, and chemical makeup of nanoparticles influences the kind of interactions the exist between NPs, organisms, and pollutants. Additionally, the type of pollutants organism used and environmental factors are known to significantly affect the process [9]. Pollutants are usually dissolved, assimilated, and transformed as a result of the interactions between microorganism and nanoparticles [10]. However, interactions between NPs and biota may be harmful or stimulated, leading to either a positive or negative impact on the microbial performance in the NBR process [11].

1.2 Nanoparticles

Nanoparticles (NPs) are molecular aggregates with smaller sizes ranging from 1–100 nm, this alters their physico-chemical characteristics in comparison to the bulk materials [12]. Nanoparticle sizes define their characteristics [12]. Nanoparticles' small size and large surface area has aided its stability, surface modification, and biocompatibility [13]. Nanoparticles could either be in the form of rods, round, box, or triangular shapes [14]. Nanomaterials are essentially divided into three sorts primarily based on their materials [15] such as the inorganic (metallic, metallic oxide), carbon (nanotubes), and polymer. Polymer is most preferred because of their capacity to the identify and remove heavy metals [16]. Sensors are produced as a result of small size, which are used in controlled locations. Nanoparticles have gained more ground because of their efficacy, low cost, and are eco-friendly substitutes to perfectly eliminated toxic chemical substances, poisonous end product, and environmental clean-up [2]. Microorganisms have reportedly been used to manufacture different nanoparticle including gold, zinc, silver, copper, and iron [17]. Biosynthesis of nanoparticles is growing rapidly within nanotechnology because it employs numerous biological entities within the process [18]. Nanomaterials additionally can be engineered to broaden quite miniature, correct, and sensitive pollutants-tracking gadgets. Nanoparticles as sensor not only tract pollutants but also break them down to a less poisonous form [19]. The use of nanoparticles in site remediation has presented a great opportunity for the cleanup of the environment [20]. The involvement of nanoparticles in the breakdown and chemical reduction has created an avenue to control pollution. This particle is applicable in vast areas of bioremediation like in wastewater and hydrocarbon remediation [21].

1.2.1 Nanoparticles as Nano-Adsorbents

The nanomaterials work with greater achievements when taken up both inorganic and natural waste from water [22]. Nano-absorbents have been applied in many fields of life due to their unique chemical and physical properties [23]. Particles are able to stick to surfaces due to the property of adsorption. Physical adsorption is triggered by means of an interplay caused by Vander Waals force involving sharing of electron while in the chemical perspective, it takes place via a bond existing between the adsorbent and adsorbate and the fabric, the chemical adsorbed is hard to be removed. The process is irreversible while the physical is reversible [24]. In wastewater remedy, nanomaterial as an absorbent is environmentally friendly based on its pore and surface sizes, site of absorption, moderate temperature, and surface interaction properties. The capacity of the nanomaterial is based on its physical characteristics and shape [24]. There are four exclusive kinds of nano-absorbent which are: polymeric, carbon nanotube, zeolites, and metals [24]. Table 1.1 shows the list of nanomaterials, adsorbate and their adsorption capacity.

i. Carbon nanotube is circular, having excessive sorption and surface sites with one or more nanotube wall [25]. The water-resistant form of nanomaterials stops the reduction of its activity on the surface. The interplay between nanotube and metallic positive charge is a result of the electrostatic desirability and chemical bond [26], and this aids in waste removal from sewage [27]. Desalination by means of adsorption strategies nevertheless constrained due to excessive energy consumption and technical problems; however, the usage of long plasma altered carbon tubes remove pollutant and salts effectively in contrast to the ordinary absorbent when purifying wastewater [28]. The fundamental hinderance for its industrial scale utility is its manufacturing price.
ii. Nano polymeric adsorbent is the most enhanced approach than the traditional approach and has greater relevance in some situations [29] due to some interesting properties like pores arrangement, rigidity, surface attraction adaptability, and large surface area [30]. Carbon polymer, metal and metal oxide, graphene, and dendrimer are categorically formed based on the polymeric composition of the nanomaterial [31]. The makeup of dendrimer nanopolymer has an internal water-resistant portion which removes both inorganic and natural pollutant and a surface area that also removes heavy metals. Based on its molecule branched repeat structure, it is said to be the ideal nano-adsorbent polymer [32]. Elimination of negative

Table 1.1 The adsorbate capacity of some nanomaterials to pollution [34].

Nanoparticles	Adsorbate	Adsorption capacity (mg/g)	References
MgO	Cu, Cd, Pb, and Ni	135, 149.1, 149.9, and 148.6	[178]
TiO_2	Cd, Cu, Ni, and Pb	120.1, 50.2, 39.3, and 21.7	[178]
Amino functionalized Fe_3O_4 NPs	Cr and Ni	222.1 and 232.5	[179]
Al_2O_3	Cd, Cu, Ni, and Pb	35.9, 41.2, 47.9, and 118.9	[178]
Magnetite	Pb, Cu, Zn, and Mn	37.3, 10.8, 10.5, and 7.69	[180]
ZnO	Zn, Cd, and Hg	714, 387, 357, and 387	[181]
Au	Hg (0)	4065	[182]
Nano-hematite	Cr (VI)	6.33–200	[183]
Maghemite nanoparticle	Pb (II) and Cu (II)	68.9 and 34.0	[184]

charge (dye) and a positively charged copper in water is feasible due to the impact of chitosan (nanostructure of dendrimer) as well as the blended impact of branched molecule and ultra-filtration [33]. In wastewater treatment, polymer nano-absorbents are substitutes to that of the conventional reasons due to its effectiveness (99%), unhazardous and biodegradability.

iii. Zeolite is a type of nanomaterial that possesses high surface area covered with positive charges, water molecule, and an electrical resistant micro pore containing silica and alumina [35]. This nanomaterial is said to have higher attraction in the direction of the contaminant [36] and also prevents the growth of microorganism due to zeolite combination with silver [37]. Zeolite possesses a large variety surface of electrostatic covered with the aid of water and positive charges as an aluminum and silicate compound. Zeolite size is decreased to a nano zeolite (10–500 nm) using higher technology. It has top preference to motion in permitting water or ions to bypass thereby improving transformable desiccation and ion exchange and also very selective.

iv. Metals primarily are nano-adsorbent and have extra potential to dispose of heavy metals [38] and irradiation detail than the traditional technique using carbon. Metals can, without difficulty, be compressed without direct effect on the surface area and also have diffusion distance between two particles. The oxide of nanometals used in the treatment of surface water is nano-magnetite, which is diamagnetic in structure, *e.g.*, arsenic and nano iron hydroxide [α-FeO (OH)] [38], it can get rid of this compound from polluted water effectively like hydrocarbon containing chlorine by zerovalent nano-iron because it possesses a robust rating-resistance absorbent. Silver and titanium oxide have reportedly shown a broad range of antimicrobial activity [39]. For heavy metal high quality remediation, nano-adsorbents of metal oxide are particularly used while for the removal of metals, organic and water containing chlorine, zerovalent iron is used.

1.2.2 Nanobiofertilizers

Biofertilization is a process that involves the inoculation and cultivation of soil microbial population, so as to increase soil nutrient and crop productiveness [40]. Alternatively, biofertilizers are life microbes supplied to plants to increase yield by rapidly gaining nutrients directly [41]. Biofertilizers are applied to stimulate native hydrocarbon degrading microorganisms which includes bacteria and fungi, in the course of bioremediation [42]. Biofertilizer by and large consists of living preparation of advantageous microorganisms such as rhizobacteria, which include, *cyanobacteria*, *Rhizobium*, fungal mycorrhizae, *Azotobacter* bacteria, *Azospirillum*, potassium and phosphate-solubilizing microorganism like *Pseudomonas* species, *Bacillus* species, and different beneficial microorganisms [43]. These microorganisms promote the supply of nutrient to the crops with the aid of increasing organic nitrogen fixation and changing complex organic matter into less complex, thereby making them more handy to plant [44]. Nitrogen-solving bacteria release the nitrogenase enzyme machine which increases bioremediation process of crude oil-polluted soil [45]. The processes enhance soil enrichment. Additionally, it increases the remediation of hydrocarbon-contaminated media because it is renewable and ecofriendly. By enhancing hydrocarbon using bacteria, it will increase microbial populations within the soil.

Nanofertilizer can be described as nanoparticles encapsulated substances which slowly supplies nutrients to crops. Nanofertilizers are enclosed nanomaterials which apply nourishing substances at a slow pace to plants. They are usually enclosed with a skinny shielding nanopolymer sheet and supplied as nanoparticles [46]. A combination of nutrients is supplied to crops for increase and add up to the performance of traditional fertilizers [47]. The nano-coating seen covering fertilizer particles, can keep it indestructible on plant surface due to a better external rigidity [48]. They increase or can improve the overall performance of conventional fertilizers [47]. For example, nano-coatings on fertilizer particles can firmly keep the material on the plant because of its better surface tension [48]. The effectiveness of nanofertilizers relies upon three factors: intrinsic factors, extrinsic factors, and channel of administration. Intrinsic elements encompass the technique of instruction of nano-formulation, particle length of nano-formulation, and surface coating. In the same vein, extrinsic elements encompass soil intensity, soil pH, soil texture, temperature, organic be counted, and microbial activity, which may additionally affect the capacity use of nanofertilizers [49].

Furthermore, the portal of administration/mode of application via plant roots or leaves (foliar), additionally plays a sizeable function in the absorption, behavior, and bioavailability of nanofertilizers. The organization of nanofertilizers into micronutrients, macro- and nanomaterials nutrient-loaded was identified [50]. Among the three classes, nanomaterials or nanocarriers of nutrients are more well-known in contrast to nanomaterials made of nutrients. The benefit of the use of nutrients-loaded nanomaterials is that they are safe and eco-friendly. Although, fertilizers encapsulated in the nanocarriers can launch fertilizers in a particular manner according to their requirement. Diverse kinds of nanomaterials had been used for encapsulation and managed launch of fertilizers, which include polymeric nanoparticles, carbon-based totally nanomaterials, nanoclays, mesoporous silica, and one-of-a-kind nanomaterials [51]. Controlled-launch nanocarriers have moreover been employed for a lot of distinct purposes together with insecticides, heavy metals, and meals and drug delivery [52].

Nanobiofertilizers is prepared by enclosing biological nutrients with a particular nanoproduct to a micro-size of 1–100nm. It incorporates both nanofertilizer and microorganisms or plants [53]. Several characteristics of nanofertilizer such as minimal nutrient and better efficient usage, increase crop yield, minimal disturbance of soil, and gradual application, have made it more preferable as compared to the traditional [54]. Increased nutrient utilization efficiency, reduced nutrient demand on broad usage, price effectiveness, rapid bulk manufacturing, sustainable fertilization, and environmentally friendly aspects are the key characteristics of nano-biofertilizers [53, 55]. Metal nanoparticles containing metals (zinc, gold silver, titanium, palladium, nickel, etc.) are produced by a variety of microbial cells as possible biomanufacturers in a safe and cheap way with exact dimension, shape configuration, and uniformity of the particles [56].

1.2.3 Biosynthesis of Nanoparticles

Nanomaterial synthesis occurs using biological innovations that are safe, economical, and convey minimal contamination. There are different processes involved in the synthesis of nanoparticle like bottom-up, top-down, and biological methods. The technique is based on grinding substances into small sizes and the nanoscale properly prepared and arranged are termed top-down processes. Challenges of this technique is less size manipulation and higher impurities [57]. The bottom-up technique initiates at very simple degree, the use of atomic or molecular stage using chemical reactions to build up nanoparticles. Being a chemically managed method, consequently, this technique has an advantage of managing the particle lowering and lowering the impurity in a higher manner [58]. Bottom- up is currently a successful method used for the manufacturing of nanonutrient because it is able to produce nanoparticles in a stable physical-chemical conditions following a uniform selected nanopreparation. Similarly, to top-down and bottom-up techniques, NPs can additionally be synthesized biologically by plants, fungi, yeast, and bacteria. The most favorable characteristics of NPs are managed toxicity and particle size [59].

Numerous microorganisms and few plants are responsible for the biological synthesis of nanoparticles. Their magnitude and stable state have made them more preferred than traditional manufactured nanoparticles [60]. Microorganisms with absorption pollutant concentration capacity the environment, have the potential of been an arbitrator for the synthesis of nanoparticles [61]. The two types of nanofabrics, natural (polymer, lipids, nanocarbon tube) and inorganic (zinc oxide, titanium oxide, and silver oxide) differ in the kind of physical and chemical techniques used. More so, Ag, Au, magnetic (magnetite maghemite), and alloy are the basic types of nanomaterials [47].

1.2.4 Microbe-Mediated Synthesis

Nanoparticles are obtained from microbes via specific strategies, inside and outside the cell. During the biological synthesis of nanoparticle inside the cell of microorganisms using a unique system of transportation, the cation and anionic metallic ion on the walls of the cell, is moved to anionic cell wall through charge transfer interplay. The charge in the cell decreases during metabolism with the help of enzymes (nitrate reductase) to produce metallic nanoparticles after its movement inside the microbial cell [62]. The processes for the synthesis of nanoparticles outside the cell employs the enzyme nitrate reductase to transform the metallic ion to nanoparticles [63]. The synthesis that occurs outside the cell is very fascinating since it involves biological nanoparticle manufacturing procedure that demands steeply-priced, little time in regaining nanoparticles present inside the cell [64]. The biosynthesis of nanoparticles using microorganisms is very convenient because they grow rapidly, easy to grow, and evolve under favorable environmental conditions. This is known as biological or green synthesis [65].

Microorganisms that are known with the ability of decreasing metal nanoparticles possess diverse constituents like proteins, enzymes, and other living materials, and are broadly exploited as nanomanufactures of metal nanoparticles [66]. Twelve bacteria supernatants containing auxin complex were used to synthesize iron and manganese nanoparticles, and were tested as plant nano fertilizer [66]. Microalgae responsible for manufacturing of microparticles inside and outside microbial cells interrelate with metal precursors in the medium when growing. Microalgae are isolated and washed within the cell after the synthesis [67]. Fungal as a flexible organic gadget can form metallic nanoparticles each inside and outside the cell. Many fungi are known for manufacturing of various metallic nanoparticles of various shapes and dimensions because of their huge kind of scattering and due to reality of desiring them over other microbial structures [68]. Sedefoglu *et al.* [69] used *Ganoderma lucidum* extract to physiologically generate ZnO nanoparticles.

Enzymes are protein in nature, they connect with nanomaterials by blocking cellular touch using stereo-electronic obstruction and also decrease surface strength. Enzyme plays an important role in the biological synthesis both in and outside the cell [70]. They have a special property as a catalytic substance, make nanomaterials more adjustable and different in breaking down processes and in the maintenance of power production. The plant extract or constituent like flavonoids and microbial cells are often used for the production of nanoparticles with an appropriate solvent, using a safe biological approach [71]. Enzymes produced by bacteria *B. licheniformis*, (nitrate reductase) is responsible in decreasing silver to silver nanoparticle via energy transfers and other factors like nicotinamide adenine dinucleotide phosphate (NADPH) [72].

Enzymes produced from *Rhodopseudomonas capsulate* are involved in decreasing gold to gold nanoparticles with an enzyme called

NADH-dependent reductase via the transfer of energy. Also, gold is decreased to gold nanoparticle by *Fusarium oxysporum*. The enzymes involved in the external synthesis of nanoparticle in fungi are cellobiohydrolase D, glucosidase, and Acetyl xylan esterase [73]. Other organisms reportedly used in decreasing gold to gold nanoparticle are *Rhodococcus* species, *Thermomonospora* species [74], *Verticillium* sp [73].

1.2.5 Plant-Mediated Synthesis

Plants are known to manufacture large amounts of bimolecular reducing agent because they are readily available. Extracts from wide variety of plant substances (stalks, leaflets, roots, blooms and fruits) were used to synthesize metal nanoparticles [75]. When the concentrate is obtained through different steps such as washing, air drying, heating, and filtering, medium containing the metallic salt is added to the filtrate and incubated for the production of nanoparticle of metals [76]. Phytochemicals (terpenoids, flavones, quinones, ketones, and aldehydes) are also present in the concentrate of flora. Metallic ion is transformed into nanoparticles as a result of energy transfer that takes place in the solution containing extract. Concentrates contain a decreasing agent that acts as a capping agent to stabilize metal NPs while they are produced [77]. Plant substances have higher advantages as biological synthesizer of microparticles than living organisms. *Azadirachtaindica* leaves have been used by microparticles of zinc oxide with a round physical appearance as concentrate. Absorbance was noticed at a dimension of 50 nm, height of 365 nm using ultraviolet (UV)-visible light [71]. Looking at the production of nanocomposites, bean seed was used to determine to what extent this particle could trigger germination. It was concluded that plants applied with zinc oxide had an increased rate in the germination of seeds with observable tall roots and shoot of about 237% and 168%, respectively, while unapplied plants showed low germination rate. Also, the fruit peel of *Citrus medica* L concentrate was used as a decreasing agent for the production of titanium oxide nanocomposites for increased yield of plants [78].

1.3 Nanobiofertilization in Bioremediation

Bioremediation is a natural and economical approach that employs the use of plant or microorganisms in the cleaning up of contaminant in the environment [79]. This approach used in cleaning up of heavy metals in the soil, are often times influenced by environmental factors where remediation is to take place and it often consumes time [80]. The process of bioremediation involves the conversion of contaminants to H_2O, CO_2, and methane as byproducts through mineralization and detoxification [10]. Microorganisms have the ability to modify nearly all organic materials, utilizing catalytic mechanisms and exhibiting a wide range of diversity [81]. Microbes-facilitated nanoremediation, which is an innovative and effective method that decomposes and purifies the environments from poisonous contaminants via enzymatic activity released from microbes [82].

Table 1.2 shows the list of microorganisms used for nanobioremediation of contaminants. Nanoremediation substantially increases soil and water standard by reducing waste which affects excessive output and vegetation, and influences continuity of native microorganisms [83]. This environmentally friendly approach is used to eliminate long existing

Table 1.2 Nanobioremediation of contaminants using various microorganisms.

Microorganisms	Contaminants	Nanomaterials	Degrading ability	References
Pseudomonas stutzeri NA3	Anthracene, pyrene, and benzo(a) pyrene (BaP)	Fe	85%	[83]
Bacillus cereus	Phenanthrene, anthracene	graphene oxide	52.7%	[83]
Microbe consortium	PAHs	$Ag_3PO_4@Fe_3O_4$	49.83%	[93]
Mycobacterium vanbaalenii PYR-1	Phenanthrene	Single-walled carbon nanotubes	59.5%/42.4%	[94]
Rhodotorula sp. NS01	Benzo[ghi] perylene (BghiP)	ZnO NPs	63.83%/60%	[95]
Methanosarcina and *Methanosaeta, Pseudomonas, Cloastridia,* and *Synergistetes*	Pyrene	FeS or magnetic carbon	77.5% and 72.1%/40.8%	[96]

pollutants that are within the environment in large amounts. The potential of microbes to breakdown and transform pollutants was reportedly recognized [84]. Microorganisms ideally are built up with an enzyme system to utilize environmentally harmful waste as their source of food and energy. These microbes have the ability to take up and decrease the concentration of metallic ions in the environment. Enzymes, in combination with metals, produce valuable NPs for nanobioremediation [85]. There are two stages involved in clean up using microbial cells [86]. The first stage is the inorganic stage, where waste undergo light activated catalysis, adsorption, absorption, and dissolution [87]. The second stage involves biological methods like biostimulation, and transformation helps in the removal of these pollutants [88]. The large surface aera and small dimension of nanocomposites enable rapid adsorption of waste over the exterior area. Numerous studies have reported catalytical characteristics of different nanoparticles combined with microbial cells, which have resulted in the reduction of harmful pollutants [89].

Bacteria is known to have the the capacity to carryout bioremediation. Aerobic and anaerobic bacteria have developed a strategy to obtain energy from almost all pollutants using oxidizing agents. Several types of bacteria including *Bacillus*, *Escherichia*, *Micrococcus*, *Pseudomonas*, *Rhodococcus*, *Streptomyces*, and *Sphingobium*, *Desulfotomaculum*, *Clostridium*, *Thauera*, and *Desulfovibrio* [8, 90–92], can either by itself or in combination are involved in the cleaning up of oxygenic compounds.

1.3.1 Mechanism of NPs-Microbes Interaction in Pollutant Bioremediation

Nanoparticles can interact with adsorbed pollutants within the environment. The particle dimension and its large surface area make them react with contaminants easily. This particle size enables the particle to penetrate and percolate the holes within the soil via Brownian motion thereby improving the contact of the pollutant and the NP [97]. Soil float is capable of moving nanoparticles. It can remain within the environment until it comes in contact with the contaminant and degrade it through a variety of mechanisms [98] that enhances soil treatment. The uptake and breakdown of pollutant in an increased rate is based on microbial combination with microparticle. The bacteria release unique enzymes that are immobilized in NPs thereby dissolving the pollutant, making them reachable to the nanoparticles for degradation or the microorganism can extracellularly break them down effectively. The increase in the continuous degradation of toxic pollutant in the environment is a result of the interplay and depth of nanoparticles and microbial cell [97]. The mechanism involved in the breakdown of pollutant when the nanoparticle adsorbs the contaminant into the microbial cell is by catalytic binding to pollutant thereby changing its structure. The problem with the less stable form of nanoparticles is solved by molecular technique and produce biological nanocomposites with maintained dimension. The bonding of the adsorbed nanoparticle-pollutant and microbial cell is made feasible because of the presence of lipopolysaccharides and protein S-layer. The composition of lipopolysaccharides sugar affects the formation of biofilm this is fabricated with the aid of aggregation of various microorganisms which involves a variety of components such as polysaccharide substances, DNA and proteins e.t.c which helps to attach with strong substratum [99]. Biofilm and microbial development increases by hindering flagellar gene transcription consequences in no-motile organisms. Although, biofilm was said to have increased hydrophobic polycyclic aromatic hydrocarbons breakdown [100]. The combination of adsorbed phenanthrene and nanoparticles bond externally to microbes and increase adsorption of the composite, amplify transformation of bacteria. The anionic and cationic electrostatic interaction within lipopolysaccharides and nanoparticles are important [97]. For example, the shape of graphene oxide quantum dots, particular to isolate *B. cereus*, from contaminated soil was discovered to have inspired multiplication bacteria and hydrocarbon breakdown. The change that occurred in microbial cell as a result of subjection to graphene oxide quantum dots were continuous and was passed on to the next generation [101]. Conjugative techniques were used to remove chlorinated aliphatic hydrocarbons and acceptable dosage kept [102]. *Sphingomonas* species and zerovalent iron oxide nanoparticles are made up of loss or gain of electrons processes (decomposition). Polybrominated diphenyl ethers was reported to decrease the complexity of the compound to less toxic form using zerovalent iron oxide nanoparticles [103]. Microorganism will be additionally broken-down without any problem by the produced by-products. The exterior layer and holes of nanoparticles on which contaminants are taken up, plays an important role in nanobioremediation technique and becomes achievable for microbial decomposition [104]. The kinetic and mechanistic models which selects adsorption isotherm to explain the number of adsorbed wastes to an absorbent using Pseudo-first and second-order fashions [105] and Langmuir-Freundlich models, were reported [106].

1.3.2 Plant and Nanoparticle-Based Interaction Mechanism in Pollutant Bioremediation

From an ecological point of view and one among restoring degraded soils, cleaning up of environment polluted with heavy metals is a pressing problem that requires addressing straight away [107]. The application of hyperaccumulation systems based on plant and NPs for the cleanup of diverse HMs from infected sites. The type of soil and amount of contaminant present in soil influences the rate at which hyperaccumulating plant can be utilized to remediate the site [108]. The soils pH, of CO_2 to O_2 ratio, microbial group adjustment, the ability of redox, and electrical density slope determines the metal availability in the rhizosphere [109]. The plant is affected by the rhizosphere based on the kind of exudate and the structure of root present [108].

Rhizofiltration and survival strategies of heavy metals were used by plants (*Alternanthera pungens*, *Pedioplanis burchelli* and *Amaranthus spinosus*) species to cope in the present of the pollutant within the environment [110]. Despite the accumulation of huge quantity of pollutant in soil by hyperaccumulating plant, they are moved and accrued to an organ structure at the top of the soil while non-hyperaccumulating plant species show no inhibitory effect [111]. Plant hyperaccumulators' activity in opposition to heavy metals (HMs) has been verified by using viable phytoremediation strategies consisting of phytostabilization, phytoextraction, and rhizodegradation [112]. Hyperaccumulator plants having a bioconcentration component (BCF) of greater than 1 against heavy metal is controlled by plant stability and extraction activities [109]. Kisku *et al.* [113] reported to have observed plant stability and extraction activities of *Parthenium hysterophorus*, *Sacrum munja*. The researcher found the BCF and TF (translocation feature) of more than 1 for Cr, Ni, Cd, and Pb, specifying a plant stability activity which has similar time to those of BCF greater than 1 and a TF less than 1 for Zn and Mn, suggesting a plant extraction technique for heavy metals.

In the rhizosphere of the soil, contaminant is metabolized by microorganism for energy and nutrients sources. This process is called rhizodegredation. Microorganisms are capable of converting dangerous pollutants into riskless and harmless products [114]. The process in rhizodegradation is activated by microorganisms, when plant root liberates inherent carbon like alcohol, sugar, and acid as more nutrients to them [115]. For contaminant removal, several techniques that utilize adsorbing materials, oxidation-reduction reactions, biological, and plant remediation have been employed [116]. Plant remediation is an extensively explored approach, where nanoparticles are combined to treat contaminated environment. Materials used for adsorption (NPs, biochar) are lately accessible for the clearing off of vast array of contaminants in the soil. They have various advantages such as large exterior layer, extra interplay area, fast absorption ability, and are less expensive [117]. In summary, combining adsorbent materials with plant with high accumulative ability, is a reliable method for decontamination of environment.

1.4 Application of Nanobiofertilization in Bioremediation

There are several ways in which this technique is applicable such as:

1.4.1 Heavy Metals Removal

Pollutants are escalating within surroundings because of human lifestyle that disrupts the ecosystem.

The harmful impact of Pb, Cd, and As on living components within the surroundings at small quantity, affect the living system [118]. Microbes-facilitated remediation toxic pollutants confirm abilities of microbial cells in cleansing of soil. The efficacy of NPs in biological remediation was demonstrated when environmentally friendly synthesized silver (Ag) NPs, in conjunction with *Bacillus cereus* and assisted with alumina, proved active in neutralizing heavy metals, particularly chromium (Cr) and lead (Pb), in pharmaceutical waste effluents [119]. The method of bacterial-mediated nanoparticles-adsorbents proved successful in eliminating approximately chromium 98.13% and lead 98.76% of heavy metals released as waste effluents. The tendency of using *Escherichia coli* and metal NPs in a mutually beneficial way for the cleaning metals like cadmium and lead in the environment was also explored [120]. Application of iron nanoparticle synthesized from *Chlorococcum* sp. showed a great reduction of Cr (VI) of approximately 92% at a concentration of 4 mg/L to Cr (III) [121].

Nanoparticles of iron fabrication by algae, assisted by biological material from their cells, exhibited greater stability, reactivity, and efficiency in depleting toxic pollutants in the environment. *L. sphaericus* produced an excellent stabilizer, electron donor and coating agent, providing multiple receptor sites for various metallic ions as an exopolysaccharides (EPS) biofilm [122]. The biofilm showed an increased capacity to assimilate Cr (VI) when fabricated with magnetic oxide. Furthermore, the on-side transformation of hexavalent chromium, Cr (VI) to Cr (III) by a synthesized Pd nanoparticles from Pd (II) ions mediated by *Clostridium pasteurianum*, showed feasible cleanup, and consequently resulted in the generation of hydrogen gas [123]. The clean-up capacity of Cr (VI) significantly increased to 7.2 g, highlighting the advantages of nano-enzymes compared to conventional *in situ* biological stimulation approach. The bacterial cells demonstrated decrease of organic Cr (VI) to soluble Cr (III) in wastewater [124]. Zinc oxide (ZnO) nanoparticles produced by *B. cereus and L. macroides* fabricated with zinc oxide were successful in eliminating Cu, Cd, Cr, and Pb [125]. Bacteria resistant metal, *B. cereus* strain (XMCr^{-6}) decreases Cr^{+6} to Cr^{+3}. An attractive force was demonstrated on the surface of bacteria cell by Cr^{+3}. CrO nanoparticles was formed as a byproduct when reacted with oxygen [126]. Seshadri *et al.* [127] reported *Rhodosporidium diobovatum* with ability to synthesis PbS NPs. It revealed fungi capacity to degrade Pb (II) ions into less harmful and beneficial state. *Pseudomonas aeruginosa* have demonstrated to be efficient in reducing Cd and increase the synthesis of cadmium sulfide (CdS) NPs [128]. Also, the combination of *L. casei* and selenium nanoparticles removes cadmium from polluted soil and water. The combination effect of cadmium uptake was 65% with *L. casei*, which was greater than *L. casei* when used alone (43%–78%) [129].

Mariannaea sp was used for the synthesis of nanoparticles [130]. Fungi have been useful in the cleanup of harmful contaminant via the uptake of metallic ion since they are involved in the production of nanoparticles [131]. Fungi materials, type of metallic ions, and surrounding conditions influence the biosorption ability [132]. *Microbacterium* sp was revealed to synthesize nickel oxide NPs and used to eliminated nickel from wastewater [133]. Also, nickel was decreased by *Hypocrealixii* and synthesizes nickel oxide nanoparticles from pollutant for subsequent uses [134].

1.4.2 Removal of Hydrocarbon

Several researchers have reported that microorganisms can effectively remediate persistent organic pollutants, such as hydrocarbons. It has been discovered that *Sphingomonas* sp. can be used as a biofunctionalized tool to stabilize bimetallic (Pd/Fe) nanoparticles with carboxymethyl cellulose (CMC). This nanocomposite has shown success in removing gamma-hexachlorocyclohexane (γ-HCH), also known as lindane, which is a common beauty product ingredient [135].

In a study conducted to remove Aroclor 1248, a specific type of polychlorinated biphenyl (PCB), its treatment with bimetallic (Pd/Fe) nanoparticles in an oxygen-free environment resulted in significant de-chlorination and conversion of the contaminant into biphenyls. The resulting biphenyls were then progressively bioremediated using *Burkholderia xenovorans*, leading to a catalytic reduction of Aroclor 1248, from 33.8×10^{-5} µg/g to 9.5×10^{-5} µg/g [136].

The nanoremediation process facilitated by *Bacillus licheniformis* was assessed for the biofunctionalization of $Zn_5OH_8C_{12}$-modified Fe_2O_3 nanoparticles with *B. licheniformis* to decompose crude oil into biodegradable substances. Moreover, it presents potential advancements in the use of biological surface-active agent for effective natural bioremediation contamination [137]. The combination of *Alkaligenes faecalis* and iron oxide nanoparticles to increases remediation of polluted soil [138]. More so, combining different concentrations of *A. faecalis* with iron oxide nanoparticles at a dosage of 200 mg, effective remediation of crude oil pollution was achieved. Ansari *et al.* [139] reported that the electronic charge interplay of attractive nanoparticles modified by *Rhodococcus erythropolis* resulted in a significant 56% reduction in the dibenzothiophene (DBT) hydrocarbon component through bio-desulfurization. This validates the advantage of using magnetic nanoparticles modified by *R. erythropolis* instead of solely relying on individual components for bioremediation.

Combination of enzyme laccase from fungi, a conjugate found with greater capability for degradation than when used individually, and it also increased their stability. The magnetic nanoparticles layered with polyallylamine hydrochloride and functionalized by *Alcanivorax borkumensis* offered a chance for effective breakdown of hydrocarbons [140].

Unique characteristics of the biofilm (*i.e.*, intracellular fat formation) of *A. borkumensis* and the presence of biosurfactant micelles ensure the possibility of hydrocarbon decomposition.

A study by Kim *et al.* [103] reported a collaborative effect of nano zerovalent iron (nZVI) with *Sphingomonas* sp. as an efficient pair towards the removal of bromine atoms and gradual degradation of polybrominated diphenyl ethers in water. On the other hand, the degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin hydrocarbon by the combinative action of bimetallic nanoparticles and *Sphingomonas wittichii* was acknowledged [141].

1.4.3 Removal of Colored Dyes

Colorants have been widely acknowledged as a crucial constituent for production industries, such as textiles and beauty products. They are predominantly discarded as liquid waste into the environment, posing a threat to the environment [142]. The effective photocatalytic remediation of methylene blue and removal of waste containing harmful colorants resulting in significant reductions of pollutant was demonstrated by silver nanoparticles derived from *Caulerpa racemosa* and *Chlorella pyrenoidosa* [143]. The removal of Congo red colorants used on spun wool from polluted water have been utilized by silver nanoparticle produced from *Bacillus pumilis* [144]. The main priority for eliminating Congo red colorants was based on cleansing and light susceptibility. Ag NPs recovery was prioritized for the prevention of soil damage. More so, *Caulerpa serrulate* was reported to produce Ag NPs used for degradation of Congo red colorants [145].

Methyl orange dye is a pollutant in effluent. Due to the acidic sensitivity of the colorants, it is rarely used in textile industries except for cotton materials. Methyl orange colorants is effectively broken down by a combination of *Cellulosimicrobium* sp., *Micrococcus lylae*, and *Micrococcus aloeverae* to produce titanium dioxide nanoparticles. Its degradation takes place in a bioreactor affected by ultraviolet irradiation [146]. Microorganisms associated with rhizosphere root showed the potential and efficacy to produce nanoparticles. Methyl orange colorants underwent light activated catalytic breakdown of approximately 99%. Light activated catalytic procedure is importance for a protected ecosystem and a satisfactory cleanup system.

The effectiveness in degrading methyl orange colorant under UV irradiation when using silver nanoparticles produced by the algae *Hypnea musciformis* (Wulfen) J.V. Lamouroux was reported [147]. Azo colorant is an artificial pigment used for fabric, writing paper, and preprint. Lead nanoparticles produced from *Klebsiella oxytoca* biologically decrease Azo dyes [148]. The collaborative effect of *Chlamydomonas reinhardtii* with polysulfone nanofibrous that is biologically synthesized, eliminates sensitive pigments from effluent. Organic dyes are eradiated by excellent enzymatic reactions of Ag and Au nanoparticles. Au NPs are used as sorbents for organic dyes. Since Au NPs possess surface organic molecules and are produced from fungus *Cladosporium oxysporum* AJP03, they significantly improved the sorption of rhodamine-B organic colorant [149]. Nanoparticles reduces the time for dye removal while enhancing the reaction rate [150].

1.4.4 Removal of Antiseptics and Antibiotics

The repeated liberation of effluent is regarded as a grave worry. Effluent primarily from homes and factories discharges contaminated the surroundings and contributed to the proliferation of multidrug-resistant microorganisms in effluents [151]. However, the potential for eradicating them through the NBR approach was assessed based on numerous research studies. The effectiveness of platinum and palladium nanoparticles synthesized from bacteria *Desulfovibrio vulgaris* in eliminating wastewater constituting drug factory component was documented. Similarly, 1,2,4-triazole, which is utilized in various clinical applications due to its extensive range of ring system compounds, was examined. Additionally, a component used to manufacture antiseptic (picric acid) has led to contamination of surrounding in solution. For effective nanobioremediation of picric acid in the environment, Fe_3O_4 nanoparticles incorporated into multiwalled carbon nanotubes to create a robust nanomaterial is fabricated from *Pseudomonas aeruginosa* [152]. Silver and gold nanoparticles were produced from *Turbinaria conoides*, a type of algae that has proven to be an effective antimicrofouling agent [153]. *Trametes versicolor* is known to biologically modify bimetallic nanoparticles to eliminate triclosan in water waste [141] since it was discovered to be associated with cancer and have been frequently utilized as drugs and disinfectants. *Sargassum bovinum* produces Pd nanoparticles which is used to effectively eliminate hydrogen peroxide from factory wastewater via electrochemical reducing reaction. Although hydrogen peroxide is used as a constituent of the pharmaceutical industry, they are a contaminant that is needed to be removed [154]. Magnesium oxide nanoparticles produced by *Candida* sp. is used for wastewater treatment and breakdown Cefdinir [155]. Many bacteria such as *Bacillus* and *Pseudomonas* spp are known to biologically synthesize manganese oxide nanoparticles which was observed to effectively eliminate 1,2,4-triazole from effluents [156]. The ability of organic manganese oxide nanoparticles to eliminate various persistent pollutants by biological treatment of effluent from factories has been confirmed.

1.4.5 Nano-Phytoremediation of Polluted Soils

Nano-phytoremediation is a technique for the restoration of pollutants and impurities using artificially created nanoparticles derived from plants. Plants act as natural purifiers for the soil by absorbing various types of substances and purging them. Phytoremediation, a term derived from Greek, refers to the process of restoring or fixing environmental issues through the use of plants [157]. The effectiveness of nanobioremediation is also influenced by the characteristics of the plants. To achieve optimal results, a plant should exhibit rapid growth and high biomass production, possess a well-developed and extensively branched root system, demonstrate the ability to tolerate and accumulate pollutants, have a high capacity for hyperaccumulation, be easily genetically manipulated, and be non-consumable by humans. In nanophytoremediation, flora that takes-up pollutant within tissue cells, break them down to detoxify the environment [2].

1.4.6 Removal of Organic Pollutants

Toxic chemicals derived from natural sources pose a significant danger to farmland, the environment, and human well-being. These harmful substances are primarily emitted from industrial activities and used as chemicals in agriculture [158]. The implementation of phytoremediation is consistently regarded as a cheap and efficient method to address toxic chemicals [159]. Previous studies have documented application of nanomaterials in phytoremediation, efforts targeting poisonous substances, trichloroethylene, endosulfan, and trinitrotoluene [160]. SiO_2, a biologically produced nanoparticle of Fe (namely *Ficus*-FeNPs) and Ag (*Ipomoea*-Ag and *Brassica*-AgNPs) were effectively able to eliminate chlorfenapyr at 93.7%, 91.30%, and 92.92%, respectively. *Populus deltoides* augment absorption of trichloroethylene with fullerene nanoparticles (2 and 15 mg/L), it was said to have increased uptake by 26% and 82%, respectively [161]. Cyclic organic compounds have been validated as tenacious contaminant. These pollutants have affinity for lipids, so they tend to pile-up and increases in fatty tissues of various microbial cell in the food web of marine or land environment. Phenols, polycyclic aromatic hydrocarbons, organochlorine insecticides, and polychlorinated biphenyls are all example of tenacious pollutants environment [162].

1.4.7 Removal of Heavy Metal

Nano-phytoremediation is an efficient approach for utilization of nanoparticles to increase phytoextraction [163]. Contaminants that necessitate reduction via breaking down processes employ iron nanoparticle as a potent reducing agent [164]. In phytoremediation of various contaminants, zerovalent iron exhibits immense ability as it is a reductant electron donor. Using zerovalent iron at low concentration for the treatment of plants, have demonstrated high buildup at 1175.40 g with 100 mg/kg of zerovalent iron. While greater quantity, 500–1000 mg/kg of zerovalent iron nanoparticle induce pressure in *Lolium perenne*, consequently curtailing Pb sorption [165]. At concentrations of 100, 500, and 1000 mg/kg, zerovalent iron can adsorb Cd in plants root, leaves, and stem of *Boehmeria nivea L.*, ranging from 16% to 50%, 29% to 52%, and 31% to 73%, respectively [166]. Another investigation reveals that the TiO_2 nanoparticles of 100, 200, and 300 mg/kg introduced into the soil exhibited increase in Cd accumulation by 1.9-, 2.1-, and 2.6-fold in plants shoots and 2.5-, 2.6-, and 3.3-fold in plants roots, respectively. However, Singh and Lee [64] reported that the maximum accumulation of Cd per pot was 1534.7 mg. *Acaulospora mellea* plant significantly facilitated movement of toxic metal pollutant and the concentration for zerovalent iron ranges between 50 and 1000 mg/kg [167]. Conclusively, the vulnerability to toxic metal contaminants poses significant threat to plant and also human health [168].

1.5 Environmental Distress

Environmental pollution is a grave concern and numerous methods are being utilized and others are currently being experimented with to address the contamination in the ecosystem [169, 170]. Nanobioremediation is used to convert harmful contaminants into less toxic forms using nanoparticles. Despite significant advancements in nanotechnology due to its exceptional properties, negative consequences of NPs in the environment have also been observed.

Nanoparticles do not help in biological augmentation process, afterward, they prevent native or indigenous microorganisms in polluted sites [171]. Zerovalent iron can cause difficulty in soil by blocking the flow of water [172]. This happens when the nanoparticles commence coating the particles of soil, assembling in a manner that attracts other suspended soil particles. This straining effect blocks pores of soil, hindering the movement of substances. Carbon nanotubes were established to slow break down processes by inhibiting microbial proliferation and activity [173]. A number of microbial cells are present in water bodies, so it is natural for nanoparticles to come in contact with microbes once they are released into the water. Zerovalent iron directly interacts with bacterial cells and it leads to oxidative stress and destruction of the cell membrane. The current research demonstrates the destruction of internal components and disruption in connection linking external and internal environments of microbial cell [174]. Oxidative properties of a catalyst in liquid are altered by carbon nanotubes, which have detrimental effects on microorganisms [175]. Reactive oxygen is known to be utilized by graphene oxide without causing harm to microbes. When silver nanoparticles are used in large amounts, the enzyme function is slowed down while the genes for resistance are increased [176]. Nanoparticles are detrimental to microbial activity primarily involving the destruction of cell membranes and the induction of oxidative stress [177]. Also, nanoparticles can affect aquatic life by making recovery difficult as these nanoparticles not only cause cellular damage but also harm genes and disrupt reproduction.

1.6 Conclusion

Nanotechnology have contributed massively in various sectors to enhance performance in bioremediation processes and ecorestoration of contaminated soils. In various reviews, much attention has been on the advantages of nanoparticles in pollutant removal although regarding its safety to human and its environment has caused concern. Nanotechnology has given a robust key to the difficulty encountered in connection to pollution issues like in hydrocarbon and heavy metals pollutant which has unfavorable effect to the environment. Nanobioremediation has dispensed an environmentally friendly substitute for ecosystem sustainability without causing distress to the environment. Most microbes and plants recognized as 'hyper accumulators' have shown to have great potential in amassing large contaminants. Nanoparticles formed from microbes and plants have been used to remove pollutants from highly contaminated sites and clean up the environment via bioremediation. The major problem that affects applying nanotechnology is their market. Therefore, the utilization of this technology and biologically producing NPs on a larger scale should be continuous and increasing. The acceptance and alteration of this innovation will increase the time and effectiveness of bioremediation. Government and researchers should work as a team in order to give birth to nanobiotechniques in industries.

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