Biogenic Nanoparticles and their Environmental Applications in Bioremediation and Pollution Control

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Abstract:- ***Currently*, words derived from the prefix “nano,” has become increasingly common in scientific literature. Mainly in today’s science, this nano prefix has gained more popularity such that many nano words are being recently used and such include nanotechnology, nanoparticles, nanomaterials, nano encapsulation nanofabrication *et cetra*. Nanoparticles have particularly drawn worldwide attention due of their unique characteristics and uses. In nanoscience and nanotechnology, recent advances have also led to the development of novel nanoparticles, and this has eventually improved health potentials and environmental hazards. Research has also shown an increase of ecofriendly and environmentally sustainable approaches in the nanofabrication of metallic nanoparticles. Such increase is as result to minimize the negative effects of synthetic procedures, as well as their resulting toxic chemicals and other derivatives. Green and sustainable nanotechnological approach would be a search for various bioresources for the synthesis of nanoparticles. Therefore, microbiological resources such as bacteria, fungi, algae as well as plants are being sourced for the productions of low-cost, energy-efficient, and environmentally friendly iron nanoparticles. The current review outlines different reports on green syntheses of iron nanoparticles (such as zero valent iron (ZVI) and iron oxide (Fe_2O_3) NPs) with attention paid on their significant applications in environmental pollution control. It also summarizes the ecotoxicological impacts of green synthesized iron nanoparticles in opposition to non-green synthesized iron nanoparticles.**

Keywords:- *Iron Nanoparticles; Sustainable Green Nanotechnology; Environmental Pollution; Environmental Toxicology.*

I. INTRODUCTION

In response to growing urbanization and to effectively satisfy the increasing population of cities, massive industrialization quickly came to the rescue. The resultant industrial revolutions saw massive production of consumer goods fueled by increasing purchasing power. While the world was ready for the increased productivity, it was however not ready to handle the associated large of waste generated. Also, in a bid to satisfy growing demand, unsustainable exploitation of natural resources equally gave rise to polluted environment very far from its original condition. Amongst the pollutants that are of environmental and public health concerns due to their toxicities are: heavy metals, nuclear wastes, pesticides, green-house gases, and hydrocarbons. Growing concern over the health of the environment has caused policy makers to tighten environmental regulations to avert further degradation of the environment.

In spite of this, environmental pollution sites around the world are increasing in their numbers. It is reported that in the United States alone, approximately 350,000 sites are contaminated with various toxic compounds. And these sites are estimated to require more than 30 years of decontamination, with the cost reaching more than $8.3 billion/year according to private sources [1]. Numerous attempts have also been made at cleaning up polluted sites with varying degrees of success. One of the viable and ecofriendly ways of cleaning up polluted sites is through bioremediation.

Bioremediation is the process through which biological mechanisms are utilized in reducing concentration of pollutants to pre-contamination levels [2]. Based on site of application, bioremediation techniques can be either be *ex situ* or *in situ*. *Ex situ* bioremediation techniques involve remediation done by moving contaminated soils away from site of pollution to a different location before remediation can be carried out. While *in situ* techniques carry out the remediation process on site without need to move the contaminated substance to a new location. Pollutant type, level of pollution, environment type, cost, location, and environmental policies are usually are considered when selecting bioremediation techniques. Bioremediation remains an attractive remediation technique due to its comparatively low environmental footprints. Bioremediation is also known to be cost-effective as the resources needed to carry out bioremediation can easily be gotten in the environment.

Apart from bioremediation, current research seeks to develop new technologies that can fast-track decontamination while reducing cost is increasingly desired. In addition, some contaminants are reportedly recalcitrant to normal remediation techniques. For instance, several complex organic compounds, like long-chain hydrocarbons and organochlorines, are known to be resistant to both microbial and plant degradation. This has fueled the growing demand for new technologies to fast-track decontamination reduce their associated costs. Numerous bioremediation technologies are currently being considered, including *in situ* and *ex situ* technologies. But among them, nanotechnology seems to be getting growing attention in North America and Europe [1]. Use of nanomaterials, especially iron nanoparticles, has been receiving unparalleled research attention as a novel remediation technique.

Nanotechnology involves matter manipulation at dimensions of the order of 10^{-9} m, using chemical and/or physical processes to create materials with desirable specific properties with wide-ranging applications [3].

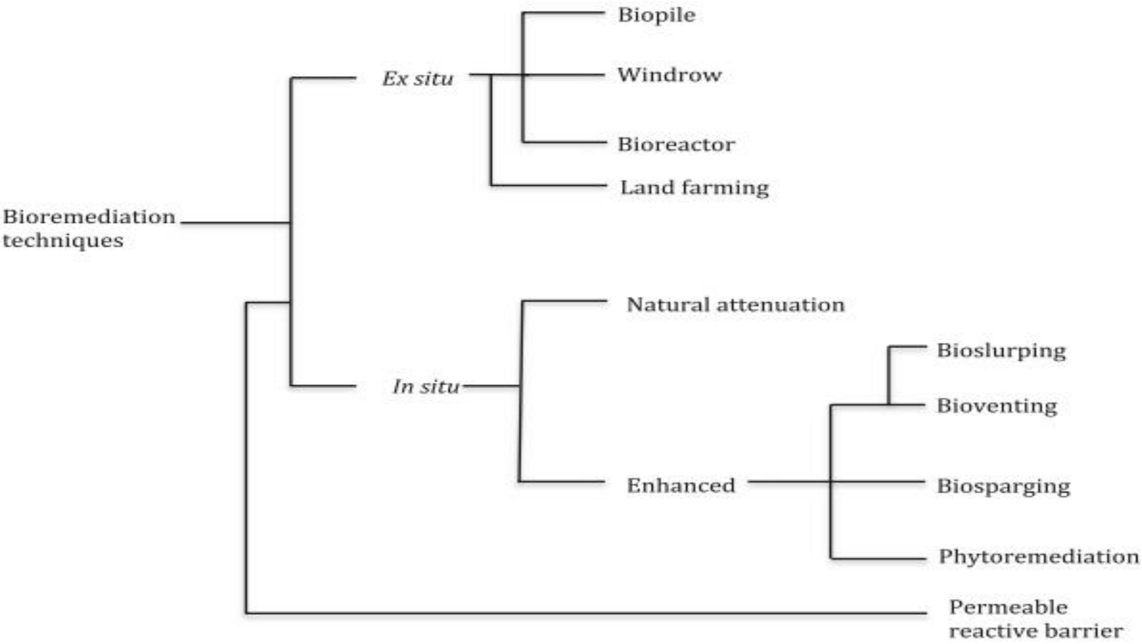

Figure 1: Bioremediation techniques [2].

A nanoparticle on the other hand is a microscopic particle with at least one of its dimensions being less than100 nanometers [4]. Unlike bulk materials, these particles possess special optical, thermal, electrical, chemical, and physical properties [5] which influences their variety of applications in environment, medicine, agriculture, chemistry, energy, ICT, heavy industry, and consumer goods [1]. Nanoparticles produced through conventional routes like attrition and pyrolysis frequently have high cost of manufacturing, defective surface formation, low production rate, and are energy-intensive [6]. While chemical methods (e.g., chemical reduction, sol gel technique, etc.) use toxic chemicals, with hazardous byproducts, and involving precursor chemicals contamination [7]. Hence, green and environment-friendly synthesis mechanisms for nanoparticle synthesis are desirable. And preliminary research outcomes have shown that nanoparticles can be synthesized from microorganisms and plants [8].

Currently, sustainability has gained significance, as captured in the sustainable development goals. This recent drive aims at reducing environmental risks associated with processes while reducing environmental impacts in the form of waste generation, greenhouse gas emissions, and natural resource consumption [9]. Bio-based methods like bioremediation have demonstrated sustainability great potential in remediation of contaminated sites. However, bioremediation takes enormous treatment time and might be ineffective when contaminant concentrations become toxic to biological agents. The integration of nanomaterials and bioremediation has huge potentials to become sustainable, efficient, and effective. This paper reviews the microbial and plant-based synthesis of iron nanoparticles and their environmental application in in bioremediation of contaminated sites. The paper also reviews toxicity of nanoparticles, interaction of nanoparticles with soil constituents, and the opportunities of integrating nanoparticles into bioremediation to overcome each technology's limitations.

Biosynthesis of Iron Nanoparticles

Biological synthesis of iron nanoparticles can generally be grouped into two including microbial and plant-based production of iron nano-particles.

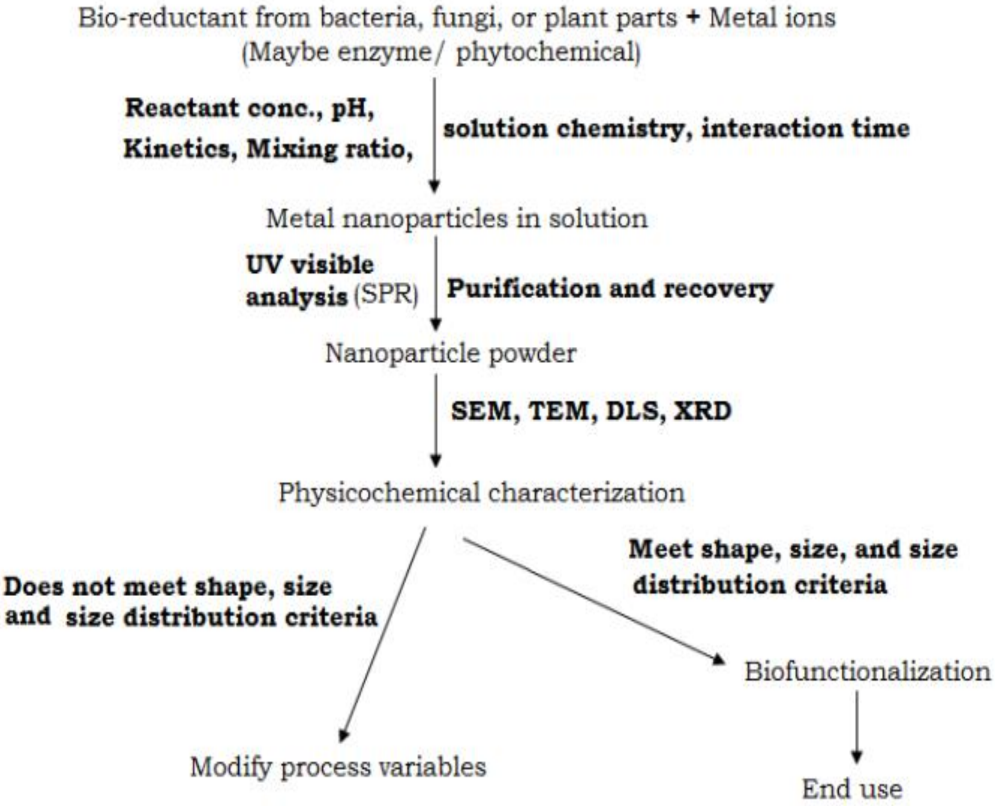

Figure 2: Generalized flow chart for nanobiosynthesis [5].

Synthesis by Microorganisms
Bacteria

Production of nanoparticles of iron normally involves iron-producing bacteria like *Actinobacter sp.* [10]. these bacteria have the ability of extracellular production of magnetic nanoparticles in the presence of aqueous ferric salts under prolonged aerobic conditions. Formation of iron nanoparticles is frequently associated with colour changes to dark brown and can be characterized using techniques like TEM, XRD, FTIR, magnetic measurements, etc. Using this process nanoparticles of different types like maghemite (γ-Fe_2O_3) and greigite (Fe_3S_4) by utilizing different iron precursor. The process is complex involving reductase enzyme synthesized by the bacteria, which induces extracellular reduction of Fe^{3+} into Fe^{2+}, thereby producing iron nanoparticles in the presence of ferric salts. Other types of bacteria equally used by researchers include *Thermoanaerobacter sp.* [11] and *Thiobacillus thioparus* [12].

Fungi

Also, different fungi have been utilized in synthesis of iron nanoparticles. For fungi, their iron-producing process involve cationic proteins released by fungi, which can induce extracellular hydrolysis of anionic ferric and ferrous complexes at room temperatures. This causes crystalline magnetic particles to be formed showing ferrimagnetic transition signature. Fungi frequently used include *Fusarium oxysporum* and *Verticillium sp.* [13]. utilized *P. chlamydosporium*, *A. fumigates*, *A. wentii*, *C. lunata* and *C. globosum*, while [6] also used *Alternariaalternata* fungus. Nanoparticles produced from *Alternaria alternata* fungus was reportedly exhibited anti-bacterial activity against *B. subtilis*, *E. coli*, *S. aureus* and *P. aeruginosa*.

Algae

Algae have equally been used in synthesizing iron nanoparticles by different researchers. With algae, synthesis can either be carried out directly by the organism in question or its extracts can be used instead. [14] Was able to use extracts from a brown sea weed macroalgae, *Sargassum muticum* in producing cubic-shaped iron nanoparticles (Fe_3O_4 NPs). Their synthesis route involved a ferric chloride precursor in a one-step process that changed from yellow to dark brown on completion. For direct synthesis, [15] used a soil microalgae, *Chlorococcum sp.* Evidence of iron nanoparticles were confirmed using TEM which showed both intracellular and extracellular deposits of spherical iron nanoparticles on completion. Following FTIR analysis, it was reported that polysaccharides and glycoproteins in the algae in the form of carbonyl radicals and amines were responsible for formation of iron nanoparticles.

Synthesis of Iron Nanoparticles from Plant Biomaterials

However, synthesis of iron nanoparticles from microorganisms like bacteria, fungi and algae has been widely reported as slow, as it takes ample amount of time for significant quantities of iron nanoparticles to be produced through this route. Comparatively, plants are said to present a much quicker synthesis route than microorganisms [8]. This is reportedly due to the ability of plants to harbor higher concentrations and other desirable phytochemicals that help in nanoparticles synthesis. These phytochemicals are easily found in different parts of plants like leaves, fruits, stems and roots, thereby providing various options for synthesis of plant-based nanoparticles [16]. In addition, plant extracts equally possess the ability to stabilize produced iron nanoparticles and prevent them from agglomeration, which reduces their activity [5]. Due to the faster synthesis production route plants present for synthesis of nanoparticles, they have been touted to represent the biggest potentials for large-scale green production of iron nanoparticles [4].

Synthesis by leaf extract

Many researchers have reported synthesis of iron nanoparticles using various plant extracts. But the extracts from green tea (*Camellia sinensis*) accounts for a substantial number of plant-based iron nanoparticles production. The choice of green tea can be traced to the cheap availability of the plant and the presence of desirable nanoparticle-forming phytochemicals. The main phytochemical responsible for the formation of iron nanoparticles include a wide range of polyphenols present in green tea extracts. The polyphenols which are present in desirable concentrations are reported to function as both a natural reducing agent and a stabilizing agent. This means that synthesis of iron nanoparticles through this route does not require additional surfactants or polymers to cap synthesized iron nanoparticles. The potential capping ability of these polyphenols also serves to extend the viability of iron nanoparticles as they prevent the synthesized nanoparticles from oxidizing easily.

Researchers who have worked with green tea in synthesizing iron nanoparticles include but not limited to [17-21] etc. For instance, [21] studied the feasibility of producing iron nanoparticles from a number of different plants and concluded that oak, pomegranate and green tea produced extracts that were richest in polyphenols suitable for synthesis of nanoparticles. Other researchers have utilized other plants like Pattanayak and Nayak studied nanoparticle production capacity of neem tree (*Azadirachtaindica*). In another study, they also utilized different plants including mango leaves, green tea leaves, rose leaves, oregano leaves and curry leaves for production of iron nanoparticles. [7] have also utilised three different plants i.e., *Eucalyptus tereticornis*, *Melaleuca nesophila* and *Rosemarinus officinalis.* While [19] reported the synthesis of iron oxide nanoparticles using aqueous extract of *Hordeum vulgare* and *Rumex acetosa. Hordeum vulgare.* While [22] equally produced iron (III) oxide nanocrystals with leaf extract of Garlic Vine and extracts of *Tridax procumbens* plant has also been used in synthesizing iron nanoparticles.

Synthesis from other plant parts

Apart from leave extracts, iron nanoparticles have reportedly been synthesized using other plant parts. [23] Produced palladium and iron NPs using fruit extracts of *Terminalia chebula.* In another study they also used fruit extracts of *Passiflora tripartitavar* mollissima in synthesizing iron nanoparticles. In addition, [24] utilized seed extracts of *Syzygium cumini* as reducing agent and sodium acetate as stabilizing agent for the synthesis of iron oxide nanoparticles. [25] Found that the biomass of alfalfa (*Medicago sativa*) could be used in producing iron nanoparticles. [26] Have also explored the possibility of using sorghum bran for the synthesis of iron metallic nanoparticles. And [27] utilized waste plantain peel extract for production of iron nanoparticles. In addition, [28] equally successfully synthesized hematite $\alpha\text{-}Fe_2O_3$ nanoparticles by hydrothermal synthesis using green tea (*Camellia sinensis*) leaf extract. While, [29] also synthesized iron nanoparticles by the same method using aloe vera plant extract.

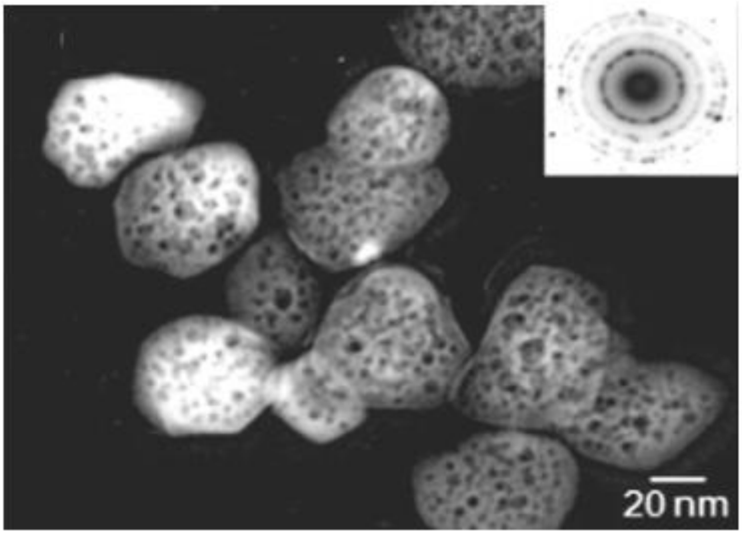

Figure 3: TEM image of α-Fe2O3 NPs synthesized by green tealeaves [4].

Possible Mechanism of Nanoparticles Synthesis

According to [8], the mechanism of iron nanoparticles synthesis using living organisms like plants and microorganisms is yet to be fully understood. But given decades of research into iron nanoparticles production from plants and microorganisms some form consensus can be established. For microorganisms, the best acceptable mechanism is the influence of desirable enzymes secreted by the organisms which help in reducing iron in the presence of iron salts. A number of iron-reducing microorganisms exist including the well-known *Actinobacter sp.* with this ability. This explains why these organisms have found ready application in the synthesis of iron nanoparticles. The ability to secrete enzymes which catalyze redox reactions that terminate with reduction of iron from a high valency to a lower positive valency seems to be a requisite requirement for any microorganism that produces iron nanoparticles. Any microorganism that falls into this category can potentially be used for synthesis of iron nanoparticles.

For plants-based synthesis of iron nanoparticles, similar consensus has equally been established. Various researchers have singled out complex polyphenols and similar phytochemicals present in plants in desirable concentrations as being responsible for the formation of iron nanoparticles in plants. According to [25], who used tannin powder as plant-based reagent for the synthesis of iron nanoparticles, the presence of phenolic-OH groups and ortho-dihydroxyphenyl groups were found to be responsible for iron nanoparticles formation. In the process tannins are first oxidized to quinines and the precursor iron salt is simultaneously reduced to iron oxide nanoparticles. Other secondary metabolites present in plants that can equally be used include flavonoids, tannic acid, terpenoids, ascorbic acids, carboxylic acids, aldehydes and amides. In addition, many reducing sugars present in plants can also be used for the synthesis of iron nanoparticles. These phytochemicals are said to possess special redox properties which make them able to reduce salts of iron to their corresponding iron nanoparticles. Not only do they serve as reducing agents for the redox reactions, they equally serve as stabilizing and capping agents for the synthesized iron nanoparticles.

Environmental Applications of Iron Nanoparticles

There are several green approaches to synthesize iron-based nanomaterials using different bio-chemicals and bio-reducing agents. Iron nanomaterials are significantly important for abatement of environmental pollution such as degradation of organic dyes, chlorinated organic pollutants and heavy metals removal, e.g., arsenic. Details about environmental applications of greener iron nanoparticles are as follows.

Removal of Heavy Metals

Heavy metals like elemental arsenic and chromium are sometimes found as contaminants like drinking water sources. Numerous researches have demonstrated that injestion of these heavy metals are poisonous to human health. One of the frequently used purification processes for such contaminated water sources is to pass the contaminated water through filtration beds made of various adsorbents. Due to the large surface area of nanoparticles, they have found application as adsorbents for these heavy metals. Owing to the special order of packing found in nanoparticles they can selectively allow water molecules to easily pass through while trapping the heavy metals. Given ample time the product of such purification process is portable water that is fit for drinking without adverse side effects. Researchers like [30-33], etc have been able to synthesize iron nanoparticles and successfully applied them to removal of elemental chromium as biosorbents.

Wastewater Treatment

Sometimes the water to be treated is not drinkable but effluents from processing plants like mines and chemical plants. Some effluents of mines contain heavy metals like mercury, which if not properly managed find their way into natural water bodies like streams and rivers. Also, depending on the type of chemical plant, effluent water discharge might contain dyes and other harmful substances. Iron nanoparticles have also found application in treatment of these effluents. One good area that iron nanoparticles have found use is in the dechlorination processes. Iron nanoparticles have also been used in degradation of dyes as can be found in effluent water from cotton processing plants. A number of researchers have also successfully utilized iron nanoparticles in treatment of different types of wastewaters.

For instance, [24] utilized biosynthesised iron nanoparticles for treatment of eutrophic waste water. Chitosan-capped iron nanoparticles with acceptable stability have also been utilized separation of arsenic from water by batch and column experiments. The possible mechanism for degradation of dye by iron nanoparticles was given by [26], who produced iron nanoparticles from sorghum bran and applied the synthesized iron nanoparticles in degradation of bromothymol blue. They suggested that the degradation of bromothymol blue was catalyzed by the presence of hydrogen peroxide through an oxidative degradation mechanism. It starts with the generation of highly oxidative OH $^{\cdot}$radicals when $Fe^{2+}$is oxidised by H_2O_2 into Fe^{3+}. The generation of radicals further accelerates the decomposition of H_2O_2 and, iron nanoparticles were able to rapidly degrade bromothymol blue. Researches carried out using different types of iron nanoparticles from various synthesis routes have also confirmed this mechanism.

Groundwater Treatment

Due to human activities on land, some contaminants find their way downwards towards aquifers and other groundwater sources. Some of these contaminants could be leachates from landfill sites, underground disposal of oil and gas drilling wastes or leakages from underground special storage tanks. Through crevices and fractures in the soil, these contaminants travel both under gravity and concentration gradients until they intercept underground water sources. Sometimes their descent is actually aided by downward capillary movement of rainwater. One of the ways of remediating polluted groundwater is through the use of permeable reactive barriers made of iron nanoparticles.

These barriers are selectively permeable to different substances depending particle size. They are designed in a way that the dichlorination and heavy-metal trapping capacities of iron nanoparticles are fully utilized when the barriers are strategically placed in the trajectory of groundwater [2].

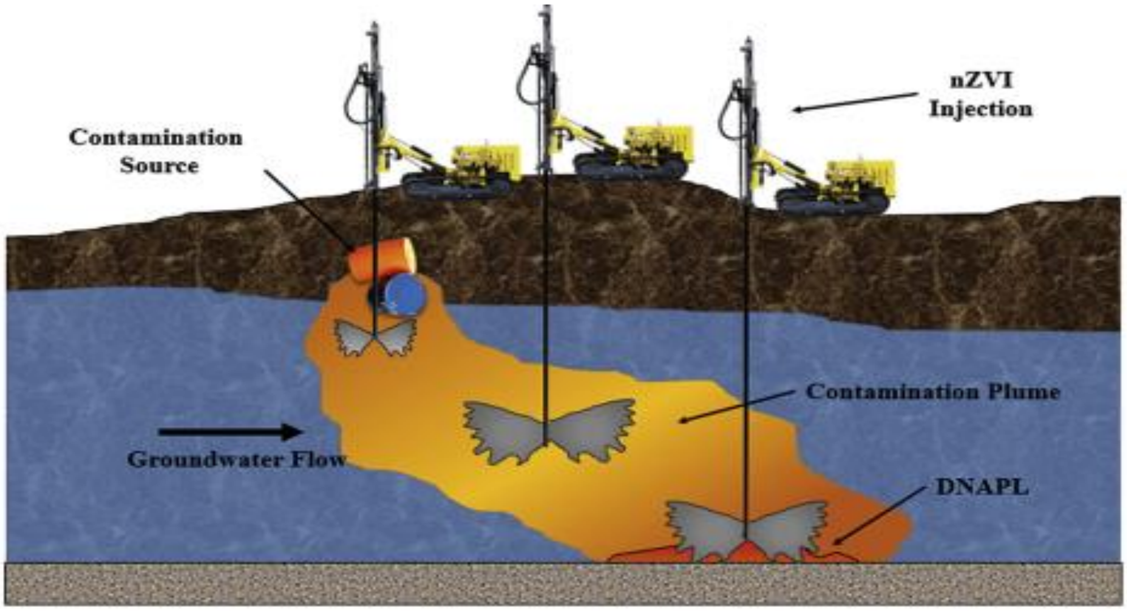

Figure 4: Use of iron nanoparticles in groundwater treatment [1].

Environmental Impact of Iron Nanoparticles

In spite of the numerous advantages and applications of iron nanoparticles there is great concern about its potential toxicity. Given the sheer number of possible applications and types of iron nanoparticles, this area still remains largely under-researched. Results of preliminary research in this area, however, reveal mixed results pertaining to the toxicity of used iron nanoparticles both in the environment and on living species. While there is ample evidence that introduction of iron nanoparticles induces negative oxidative stress, some applications of iron nanoparticles have reported positive results in terms of enhancement. This oxidative stress has been traced to the release of reactive oxygen species (ROS) as byproducts of the redox reactions involving reactive iron nanoparticle species.

Another explanation for the contradictory results can be traced to the fact all iron nanoparticle are not equally reactive. This has led some researchers to study the relationship between iron nanoparticle oxidative state and cytotoxicity. To this end, [34] compared the cytotoxic impacts of nZVI and iron oxide nanoparticles (magnetite and maghemite) towards gram negative bacteria *E. coli*. They found out that the toxicity of zero-valent iron nanoparticles was higher than the toxicity of iron oxide nanoparticles. They suggested that the toxicity was linked to generation of oxidative stress from reactive oxygen species when iron nanoparticles are oxidized. The ROS involved include unstable superoxide radicals, hydroxyl radicals and freely diffusible and relatively long-lived hydrogen peroxide, which stick to cell membrane and while disrupting cell processes.

Considering the level of toxicity of iron nanoparticles under aerated and dearated conditions [35-36], studied the anti-bacterial effects of iron nanoparticles under aerobic and anaerobic conditions. Both groups of researchers were able to demonstrate that the toxicity of zero-valent iron nanoparticles were found to be lower in aerobic conditions compared to anaerobic conditions. This behaviour they suggested was not unrelated to the formation of a protective iron oxide layer. In contrast, Fe^{2+} nanoparticles were found to be more toxic under aerobic conditions than under anaerobic conditions. For both types of iron nanoparticles reported cytotoxicity was in the form of physical damage and cell inactivation caused by the penetration of cell membrane by the iron nanoparticles.

Also, negative effects of iron nanoparticles have also been reported by researchers. [36] Investigated the effects of nZVI on antioxidant enzymatic activities and lipid peroxidation in Medaka (*Oryziaslatipes*). Their results showed histopathological changes and morphological alterations were observed in gills and intestine of adult fish. Similarly, [37] evaluated the chronic toxicity effects of iron oxide (Fe_2O_3) nanoparticles (500 mg/L) on certain haematological, ion regulatory and gill Na+/K+ ATPase activity of an Indian major carp, *Labeorohita*. They reported toxicityeffects were observed by the significant increase in reactive oxygen species (ROS) production, lipid peroxidation, protein carbonylation, ubiquitin conjugates and DNA damage.

Meanwhile, [38] reported that iron nanoparticles had no significant cytotoxicity impacts on bryophytes (*Physcomitrella patens*). Similar results were observed in another study iron nanoparticles were exposed to seeds; iron nanoparticles could not show any detrimental impacts on seed germination at lower concentration of iron nanoparticles (0–5000 mg/L) [100]. Studies show that many factors affect the behaviour of iron nanoparticles when they are released into the environment. Given the fact that synthesized iron nanoparticles could easily be oxidized, the effect of age on the toxicity of iron nanoparticles have also been studied by different researchers. [39] Studied the toxicity impacts of residual aged nZVI on metal contaminated soil. Heavy metal (Pb, Zn) polluted soils properties were evaluated after a leaching experiment. No negative effects on physico-chemical soil properties were observed after aged nZVI exposure.

Another to be considered in the determination of toxicity of iron nanoparticles is the synthesis route used for the production of iron nanoparticles. It has been reported that nZVI synthesised using green tea, since it is much smaller in size, has been shown to be nontoxic to human keratinocytes when compared to nanoparticles synthesized using the borohydride reduction process. To combat the toxicological issues, research has advanced production of green nanomaterials, and studies have revealed that biosynthesised nanoparticles are less toxic than engineered nanoparticles.

II. CONCLUSION AND FUTURE PERSPECTIVE

This review focused on the production of iron nanomaterials through microorganisms and plants and their use for remediation of environmental pollutants. From the study, it was revealed that apart from popular plants like green tea, other types of plants can equally be used in synthesizing iron nanoparticles. While the possible mechanism for the iron nanoparticle synthesis was explored. Also, the potential toxicity of iron nanoparticles in various applications was equally ascertained with mixed results. The toxicity was found to not only depend on the type of iron nanoparticle, but also the type of application. Specifically, it was found that zero-valent iron nanoparticles were more reactive and toxic than their iron nanoparticle counterparts. Overall, biosynthesized iron nanoparticles were found to be less toxic compared to engineered iron nanoparticles.

Despite the amount of research efforts already expended studying nanoparticles and iron nanoparticles in particular, more research is however still needed. There is an obvious need to better understand the phytochemistry of iron nanoparticles biosynthesis. Furthermore, considering the enormous potential uses of iron nanoparticles, their toxicity to both plant and animal life needs to be fully understood. Considering the application of iron nanoparticles in remediation of environmental pollution, a synergetic relationship between nanotechnology and bioremediation (nano bioremediation) is hereby suggested. This is borne out of the fact that each bioremediation technique has its own weaknesses. But a combined approach involving nanotechnology and biotechnology could overcome this limitation: complex organic compounds would be degraded into simpler compounds by nano encapsulated enzymes, which in turn would be rapidly degraded by the joint activities of microbes and plants.

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