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Review

Environmental Nano-remediation in Nigeria: A Review of its potentials

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ABSTRACT

Pollution of the environment is one of the most pressing problems confronting developing nations such as Nigeria and the world at large. Due to the unchecked quest for infrastructural and technological development, we have continuously explored and exploited our natural resources, paying little or no attention to the impact of these exploitations on our ecological environment. This negligence has resulted in some severe environmental degradation and the conventional methods previously employed in addressing these issues are no longer efficient, thus there is need for novel, innovative, advanced and efficient environmental remediation alternatives. Nanotechnology offers such alternatives and although most countries are embracing the idea, Nigeria is yet to fully explore this alternative. This paper seeks to throw more light on the application of nanotechnology as viable technique in remediating polluted soil and marine environment in Nigeria.

1. Introduction

Environmental degradation is one of the most widespread problems facing the world and it has increased over the years with grave and irreparable damage to the earth and human health as a result of man's quest to exploit the environment to meet his needs [1]. The negative consequences of over-exploitation of the human environment in Nigeria have led to environmental degradation which has posed significant challenges to sustainable development in the country [2]. Environmental degradation can negatively impact ecosystem functioning, human health and comfort, integrity of the built environment, security of states, stability of life support systems and even that of social and political systems [3]. The oil industry and other industrial activities are major contributors of environmental degradation with hazards such as greenhouse gases, poisonous chemicals (Trichloroethylene (TCE) and Polychlorinated Biphenyls (PCB)), chemicals produced as result of gas flaring, oil spillages (Total Petroleum Hydrocarbons (TPH)) and other activities [4, 5].

With the problems of environmental degradation on the increase in Nigeria, the conventional methods of environmental remediation are becoming less efficient and there is need to explore and embrace an alternative. This paper highlights the potentials of nanoparticles in treating contaminated soil and water. It is an informative tool for both academicians and professionals, shedding more light on innovative methods of mitigating environmental challenges. As we combat various environmental issues such as soil pollution, water pollution, etc., nanotechnology gives us a more efficient approach to dealing with these issues. The aim here is to create more awareness on the need for Nigeria as a country to explore the option of applying nanotechnology in environmental remediation, and the specific objectives are; to provide background information on nanotechnology, to review the advances made over the years in its applicability in environmental remediation, to analyse the potentials of some nanomaterials in treating soil and water and their advantages over conventional methods of treating soil and water, to review the current status of Nanotechnology in Nigeria.

In recent years, Nanotechnology has gained significant attention in the scientific and engineering community as it

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has facilitated the development of novel materials with focus on inherent characteristics for a specific purpose [6, 7]. In Environmental Engineering, it can be defined as the manipulation and control of matter on the nanoscale dimension by using scientific knowledge of various engineering and environmental applications [8]. It has immense agricultural and environmental applications which cut across various stages of agricultural production and environmental remediation. In agricultural production, Nanotechnology can be employed to increase the quality and quantity of crop yields, increase shelf life, enhance site-specific distribution, and ensure the absorption of nutrients and active ingredients [9]. In environmental remediation, nanotechnology involving the use of green plants and animals or metabolites of microorganisms provides an enviromentally safe means of remediation [10]. Nanotechnology was defined as the development and utilization of structures and devices with a size range from 1nm (molecular scale) to about 100 nm where new physical, chemical and biological properties occur as compared to their bulk counterparts, such as extremely small size, high surface area to volume ratio, surface modifiability and excellent magnetic properties [11]. Mansoori et al, [12], while taking cognizance of the benefits of conducting researches at nano-size, described it as an emerging field encompassing an immense array of growing technologies in nanoscale, which plays a significant role in the creation of innovative methods to develop new products, substitute existing production equipment and to reformulate new materials and chemicals with improved performance resulting in the consumption of less energy and materials, and reduction in environmental degradation as well as environmental remediation. Alagarasi [13], gave two main reasons why materials at the nano scale can have different properties as increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic properties.

1.1. Broad Classification of Nanomaterials

There are three distinct classification of nanomaterials; Origin, Material, and Dimension. These classifications are based on the source of material, the material content, and electron movement respectively [14, 8]. Table 1 depicts these three distinct classifications and their sub-division.

Table 1. Classification of Nanomaterials.

CLASSIFICATION OF NANOMATERIALS		
ORIGIN	1.	Incidental
	2.	Engineered
	3.	Natural
MATERIAL	1.	Carbon Based
	2.	Inorganic Based
	3.	Organic Based
	4.	Composite Based
DIMENSION	1.	Zero Dimension
	2.	One Dimension
	3.	Two Dimension
	4.	Three Dimension

Figure 1 shows the two major approaches in preparing nanoparticles; Top down and Bottom up processes. The more convenient method for producing nanoparticles on a commercial scale is to use a Bottom-up approach where a nanoparticle is grown from simple molecules.

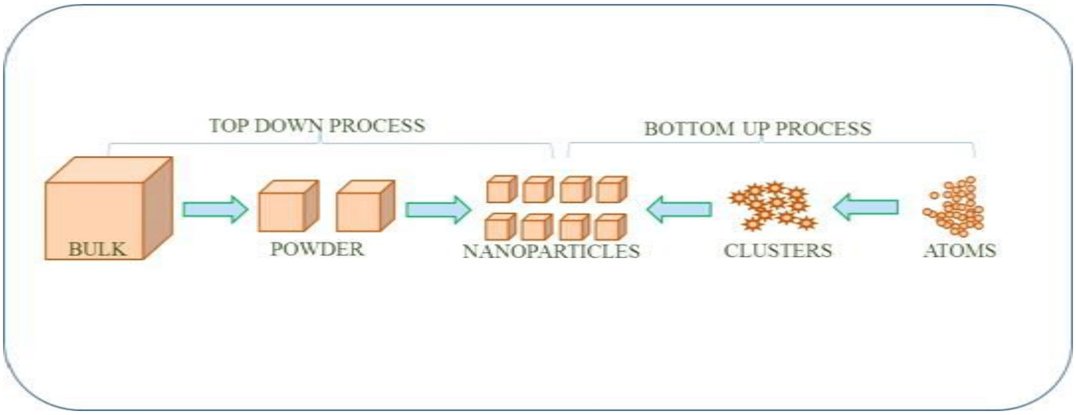

Fig 1. Approaches of Synthesizing Nanoparticles [15]

The top down approach employs physical processes such as crushing, milling, and grinding methods to break bulk material into smaller particles [16] Despite its ease of preparation, major drawbacks with this approach include formulation of unevenly shaped nanomaterials, difficulty in obtaining very small size nanoparticles, shortage of surface structure, and substantial crystallographic loss to the processed shapes [16, 17]. Various methods which employ this approach include Mechanical milling [18, 19, 20, 21, 22, 23, 24, 25, 26, 27], Laser ablation [28, 29, 30, 31], and Ion sputtering [32, 33, 34].

The bottom up approach is the most frequently used and it involves nanomaterials preparation based on particles formation from smaller molecules like joining of atoms and molecules with nanostructured building blocks of the nanoparticles first formed and then assembled to produce final nanoparticle [17]. Major advantages with this approach include better particle size distribution and morphology, and an environment friendly and economical process for nanoparticle production [16]. There are various methods which employ the bottom up approach in the synthesis of nanomaterials and they include chemical vapor deposition method [35, 36], thermal decomposition [37, 38], hydrothermal synthesis [39, 40], solvothermal method [41, 42], pulsed laser ablation [43, 44], templating method [45, 46], combustion method [47, 48], microwave synthesis [49, 50], gas phase method [51], conventional Sol-Gel method [52, 53], and green synthesis method [54, 55, 56, 57, 58].

In Environmental Engineering, Nanotechnology has great potential for improving environmental quality, reducing consumption of resources and energy, and allowing environmentally benign economic development [59]. Nanotechnology has great potential to remediate various environmental problems as well as to monitor environmental pollutants. Nanotechnology can help develop new, environmentally safe, and green technologies that minimize the formation of undesirable by-products or effluents. Nanotechnology is already being used to improve water quality and to assist in environmental clean-up activities. Their potential use as environmental sensors to monitor pollutants is also becoming viable. Research has shown that nanotechnology might be able to provide more sensitive detection systems for monitoring water and air quality, allowing for accurate, real-time, simultaneous sensing of a variety of compounds at low concentrations and measurements of environmental parameters [60]. The small size and wide detection range of the nano-sensors provide great flexibility in practical applications.

2. A Review of Literature

Over the years, significant progress has been made in the employment of nanotechnology for soil and water remediation. Pertinent literature covering a whole scope of environmental nano-remediation are reviewed and summarized in the following sections. The removal of Petroleum hydrocarbon, a major source of pollution in Nigeria, was investigated by Murgueitio, et al [61] using Iron nanoparticles. The good performance of iron nanoparticles in the study was attributed to their increased surface area, higher reactivity, and the possibility of in situ treatment. It was thus concluded that this technique may be efficaciously used in the remediation of water and soil contaminated with petroleum hydrocarbons in less time compared to a conventional bioremediation process as results indicated that the addition of iron nanoparticles produced strong reducing conditions, which accelerate removal of petroleum hydrocarbons. As a country with its economy highly dependent on oil production, oil spillage is a frequent occurrence and though nanotechnology has not been researched much for the treatment of total petroleum hydrocarbons (TPH) contamination. There is need for its investigation and trial here in Nigeria.

Trichloroethylene, a widely used solvent in the chemical industry and a chief contaminant of soil and water has been reported to be treated using iron nanoparticles [62, 63, 64]. Polychlorinated biphenyls (PCB) pose serious environmental challenges due to the persistence of these synthetic aromatic compounds and the lack of a cost-effective and sustainable remediation technology [65]. The treatment of PCB contamination using iron nanoparticles has also been investigated by several researchers [66, 65, 67].

Advances made in the application of nanotechnology for treating TPH, TCE, and PCB contamination are summarised in the table below.

Table 2. Applications of Nanotechnology in treating TPH, TCE and PCB.

Remediating Material	Result	Source
	TPH	
Iron nanoparticles	85.94% and 88.34% removal of 9.32 mg/L and 94.20 mg/L of TPH respectively from contaminated water. 81.90% removal of 5000 mg/kg of TPH from contaminated soil after 32 hours.	[61]
Green mango peel-nano zerovalent iron (GMP-nZVI)	GMP-nZVI achieved a degradation efficiency of >90% over one week treatment of an oil sludge contaminated soil.	[68]

Granulated NaA zeolite nanoparticles (NaA-ZNPs), polyaniline membranes and nanocomposite membranes.	At optimal parameters, the hybrid system achieved a TPH removal efficiency of 99.83%.	[69]
Magnetite nanoparticle	At optimum conditions, a 74.20% TPH removal efficiency was achieved in contaminated soil slurries.	[70]
Granulated NaA zeolite nanoparticles (NaA-ZNPs)	A TPH removal efficiency of 97% and 88% was achieved for continuous and batch systems respectively.	[71]
Carbonaceous nanomaterials	The remediating technology reduced TPH from 2500 to 650 mg TPH kg^{-1} soil from soils containing recalcitrant, non-biodegradable fractions of TPH.	[72]
NaA zeolite nanoparticles (NaA-ZNPs)	A TPH removal efficiency of 92.3% was achieved for batch processing and a TPH removal efficiency of 87.4% was also achieved for continuous processing.	[73]
	TCE	
Nano zero valent iron-nickel composite (nZVI-Ni) and sodium persulfate (SPS)	At nZVI-Ni/SPS/TCE molar ratio of 4/4/1, 95% of TCE was removed efficiently within 120 min at 20 °C. In the presence of Tween-80, BRIJ-35 and TX-100 surfactants and nZVI-Ni/SPS/TCE molar ratio of 80/80/1, percentage removal of TCE was observed as 97.75%, 95.63% and 77.50%.	[74]
Sulfidated zero-valent iron nanoparticles (S-nZVI)	S-nZVI degraded TCE by the β-elimination pathway with ethene, ethane, and acetylene being the dominant reaction products. A 12-fold increase in the TCE removal and a 7-fold increase in the electron efficiency was obtained by amending nZVI with sulfide	[75]
Metal bionanohybrids (MeNPs@CALB)	The Cu_2O@CALB biohybrid containing Cu_2O nanoparticles exhibited excellent catalytic performance in TCE degradation by eliminating 95% (>125 ppm) in 10 min. Under sustainable conditions, Cu_2O@CALB showed excellent stability and recyclability by maintaining its effectiveness in more than 90% for three cycles.	[76]
Polyvinylpyrrolidone stabilized nanoscale zerovalent iron particles (PVP-nZVI)	PVP-nZVI dechlorination efficiency of TCE was observed as 84.73%. The efficiency by PVP-nZVI was about 20% higher when combined with SDS in comparison to CTAB. Therefore, application of PVP-nZVI with SDS represents a potential remediation approach for TCE contaminated soil	[77]
Sulfidated zero-valent iron nanoparticles (S-nZVI)	At a TCE concentration of 40 mg/L, S-nZVI concentration of 5 g/L and pH of 5.61, a TCE removal efficiency of 66% was observed after 8 h.	[78]
Ozone micro-nano-bubbles	The treatment significantly reduced the concentration of TCE in groundwater with an overall removal of 99% after six days. The final observed TCE concentration in the treated area was below the local permissible limit.	[79]
Nanosponge β-cyclodextrin (β-CD) polyurethane modified with phosphorylated multiwalled carbon nanotubes (pMWCNTs) and decorated with titanium dioxide and silver nanoparticles	TCE was effectively eliminated from model and real wastewater samples to low-level concentration. A short equilibrium contact time of 10 min was recorded for the removal of TCE with its adsorption attributed to hydrophobic interactions taking place through chemical adsorption and endothermic processes.	[80]
Sulfidated zero-valent iron nanoparticles (S-nZVI)	TCE dechlorination was largely dependent on Fe/S molar ratio and initial pH with higher TCE dechlorination obtained at Fe/S molar ratio of ~60 under alkaline condition. The enhanced TCE dechlorination was attributed to FeS presence on the surface of S-nZVI. Between the pH of ~5 to ~8, the solution experienced significant increase in TCE degradation by S-nZVI. This indicates S-nZVI has great potential for the remediation of groundwater (with typical pH ~ 8).	[81]

Reduced graphene oxide (rGO) supported bimetallic Iron/Nickel nanoparticles	Pure nZVI showed good dechlorination ability with 51% of TCE dechlorinated within 60 min. The immobilization of nZVI onto rGO decreased the specific surface area to $102m^2g^{-1}$ but enhanced the dechlorination efficiency of TCE to 61% after 60 min of incubation.	[82]
Ozone micro-nano-bubbles	Based on field tests performed in a TCE-contaminated site, an overall removal rate of 99% was achieved after six days of treatment.	[83]
Biochar supported carboxymethyl cellulose-stabilized nanoscale iron sulfide (CMC-FeS@biochar) and Corynebacterium variabile HRJ4	TCE dechlorination to cis-1,2-dichloroethene (cis-DCE) and acetylene through hydrogenolysis and β-elimination, respectively was achieved within 12h by CMC-FeS@biochar. Further addition of HRJ4 strain resulted in the effective degradation of the residual TCE, cis-DCE and acetylene to ethylene. The chemical and biological process yielded Acetylene and ethylene as main products respectively.	[84]
Nano zero-valent iron on reduced graphene oxide, functionalized by polydopamine (nZVI-PDA@rGO). Nano zero-valent iron supported on solely reduced graphene oxide (nZVI-rGO)	At a Pootassium monopersulfate dosage of 0.3mM and catalyst dosage of 50 mg L^{-1}, a TCE removal of 45.0% and up to 99.6% was observed for nZVI-rGO and nZVI-PDA@rGO respectively.	[85]
Bentonite supported Fe/Ni bimetallic nanoparticle (BNF)	Complete degradation of 0.1 mM TCE was observed in 25 min at pH=8.2 with 1 g/L of BNF and 5 mM of peroxymonosulfate.	[86]
Cu\\Ni bimetallic cathode with nanostructured copper array	An optimum electrodeposition time of 10 min was achieved for coating copper as a uniform nanosheet array on the nickel foam substrate surface. The highest TCE removal was observed using this cathode. At the same passed charge of 1080C, TCE removal increased from 33.9 ± 3.3% to 99.7 ± 0.1% with the increasing operation current from 5 to 20 mA cm^{-2}, while the normalized energy consumption decreased from 15.1±1.0 to 2.6±0.01kWh $log^{-1}m^{-3}$	[87]
Polydopamine enabled palladium loaded nanofibrous membrane	Excellent dechlorination performance was shown by the Palladium loaded nanofibrous membrane in aqueous solution with a degree of up to 96.5 (± 0.32) % with high recyclability	[88]
Surfactant-enhanced polyethylene glycol nanoscale zero-valent iron (PEG-4000-nZVI)	Optimal operational parameters were observed at PEG-4000-nZVI dosage 1.0 g/L, cationic hexadecyl trimethyl ammonium bromide/anionic sodium dodecyl sulfate (CTAB/SDS) concentration equal to the critical micelle concentration CMC, SDS concentration was 2.0 × CMC, CTAB was concentration 1.0 × CMC and the vibration speed 150 r/min. At these conditions, the removal efficiency of trichloroethylene in a soil-water system reached 100% after 4 h.	[89]
Graphene-based bimetallic Fe/Ni nanoparticles and Boron-doped reduced graphene oxide (B-rGO)	The graphitic backbone and bimetallic nanoparticles interaction led to a fast and low-resistant electron transport in B-rGO/Fe/Ni, which enhanced the dechlorination efficiency and rate of TCE. At pH between 4 and 7, a rapid and complete hydrodechlorination of TCE by B-rGO/Fe/Ni which followed the Langmuir–Hinshelwood kinetics was achieved.	[90]
Au–pd bimetallic alloy nanoparticle-decorated $BiPO_4$ nanorods ($BiPO_4$/Au-Pd)	82.3% TCE removal efficiency was achieved by $BiPO_4$/Au-Pd within 50 min.	[91]
Polyvinylpyrrolidone stabilized nanoscale zerovalent iron particles with Ni (PVP-nZVI-Ni)	Complete TCE removals of up to 10 cycles of repeated TCE dechlorination was achieved with negligible leaching of Ni (<0.1ppm) from the catalytic nanoparticle surface. A reaction kinetics of k_{obs} = 5.702 h^{-1} for TCE reduction was obtained. Ethylene	[92]

	and ethane were observed as intermediate and main transformation product respectively.	
Nanoscale ZnO/polybutadiene rubber composite (ZBRC)	A synergistic increase in the removal of 1,1,2-trichloroethylene (TCE) via the coupled reaction processes (i.e., sorption, photolysis, and photocatalysis) was achieved as sorption of TCE to the ultraviolet(UV)-transparent polybutadiene rubber took place, and was coupled with the heterogeneous photocatalytic reactions with nanoscale ZnO particles on the surface of ZBRC.	[93]
Starch supported Fe/Ni nanoparticles	To obtain maximum TCE removal efficiency, the optimum conditions was an initial TCE concentration 100.0 mg L^{-1}, pH of 5.77, and Fe^0 dosage of 1.67 g L^{-1}. The experimental efficiency of TCE removal was 94.87% at these conditions.	[94]
Zeolite supported nano zero valent iron copper bimetallic composite (Z-nZVFe-Cu)	Using Z-nZVFe-Cu as a heterogeneous Fenton like catalyst, a degradation efficiency of more than 95% was observed for TCE.	[95]
Nanofer zero-valent iron (ZVI) coated with tetraethyl orthosilicate in the presence of Cu(II)	10mg of nanofer ZVI degraded 63% of TCE in the presence of Cu(II) and degraded 42% of TCE in the absence of Cu(II).	[62]
Surfactant modified nanoscale zero-valent iron	0.1 g/L concentration of iron nanoparticles degraded fully 10mL of TCE in 500mg of soil after 456 hours	[63]
Iron oxide nanoparticles	TCE degradation as high as 100 % (with about 91% dechlorination) was achieved. TCE dechlorination was also achieved in real groundwater samples.	[64]
	PCB	
Carboxymethyl-β-cyclodextrin functionalized titania magnetic nanoparticles (CM-β-CDFe_3O_4@ TiO_2)	CM-β-CDFe_3O_4@TiO_2 achieved an 83% degradation yield of PCB at a temperature of 25 °C and time of 16 min.	[96]
Nanoscale zero valent iron (nZVI) and bacterial mixed culture (BMC)	The combination of nZVI and BMC achieved a 78% degradation of PCBs, with the addition of non-ionic surfactant Triton X-100.	[97]
Fe/Pd bimetallic nanoparticles	After 4h of treatment, the catalytic membrane achieved a dechlorination efficiency of up to 93% with by-products such as tetrachlorobiphenyl (PCB-52) and dichlorobiphenyl (PCB-2).	[98]
Modified nanoscale zero-valent iron	The degradation efficiency of PCB after 24 h of reaction was 11.9% by S-nZVI, 14.3% by nZVI and 33.2% by carboxymethylcellulose stabilized nZVI (CMC-nZVI)	[99]
Nanoscale zero valent iron (nZVI)	nZVI achieved a degradation efficiency of 70% at a temperature of 75°C.	[100]
$CuFe_2O_4$ nanoparticles activated peroxymonosulfate (PMS)	At a pH of 7.0 and temperature of 25 °C, 0.2mM of PMS in the presence of 0.1 g L^{-1} nano-$CuFe_2O_4$, degraded 89% of 0.5 mg L^{-1} PCB in 8 h.	[101]
Carbon-modified titanium oxide (CM-n-TiO_2) nanoparticles	At a pH of 5 and CM-n-TiO_2 loading of 0.5 g L^{-1}, complete removal of PCB was achieved after 15 min of irradiation.	[102]
Nanoscale zerovalent iron (nZVI) supported on porous carbon (PC)	The composite achieved a dechlorination rate of 86% after 6 days at room temperature.	[103]
Nanoscale zero valent iron (nZVI) and biosurfactant enhanced soil washing method	7.5 g/kg soil of nZVI with 0.5% of crude biosurfactant solution achieved an 80% removal rate of PCB.	[66]
Carbon-modified titanium oxide (CM-n-TiO_2) nanoparticles	Photocatalytic degradation of polychlorinated biphenyls (PCBs) in seawater was successfully achieved at laboratory level with UV light and at pilot-plant scale under natural solar radiation. The	[104]

	best degradation rate was obtained at pH5 and CM-n-TiO_2 loading of 0.5 g L^{-1}	
Electric current and iron nanoparticles	PCB removal percentage of 83% with direct current and 29% without was achieved for a 258 μg kg^{-1} contaminated soil.	[65]
Iron nanoparticles	A minimum of 95% total destruction efficiency of PCB was achieved.	[67]

2.1. Problems Associated with Conventional Methods of Environmental Remediation

Several conventional methods have been deployed over the years for soil and water treatment and they include; Chemical, Physical, Biological and Thermal remediation [105]. These methods have certain drawbacks as outlined below.

Chemical remediation which involves the treatment of pollutants in contaminated soil and water using chemicals is usually associated with by-products that are hazardous to the ecosystem, high cost and inability to treat large amounts of pollutants [105]. Physical remediation can be described as a process which involves the physical removal of contaminated soil or water, treatment of contamination and the subsequent return of the media to the original site. Its effectiveness is quite limited when applied to dense non-aqueous phase liquids (DNAPLS) and there is usually by-product (aqueous effluent) which needs further treatment or disposal. Biological remediation involves the use of biological agents to convert environmental contaminants into less toxic or more easily biodegradable substances is. Advantages of this method include safety, cost-effectiveness and ease of administration. However, at sites with high concentrations of pollutants like heavy metals, polycyclic aromatic hydrocarbons and salt, the effectiveness of bioremediation is hampered due to the toxicity of these pollutants to the bioremediating microorganisms [106]. Thermal remediation involves the application of heat for treating contaminated soil and water, it is usually done at high temperatures (750 to 1200°C) and so it is a costly process which may also produce unwanted by-products.

2.2. Application of Nanotechnology in Soil and Water Treatment

Nanotechnology has been deployed successfully in environmental remediation; it can be used in disinfection, desalination, removal of heavy metals and ions, and the removal of organic contaminants. Pandey and Fulekar [107] illustrated the key role environmental nanotechnology plays in current environmental engineering and science, and how the nanoscale has stimulated the development and use of novel and cost effective technologies for remediation, pollution detection, pollution monitoring and remediation of pollutants. Nanomaterials present enhanced reactivity and thus better effectiveness when compared to their bulkier counterparts due to their higher surface-to volume ratio. In addition, nanomaterials offer the potential to leverage unique surface chemistry as compared to traditional approaches, such that they can be functionalized or grafted with functional groups that can target specific molecules of interest (pollutants) for efficient remediation. Further, the intentional tuning of the physical properties of the nanomaterials (such as size, morphology, porosity, and chemical composition) can confer additional advantageous characteristics that directly affect the performance of the material for contaminant remediation. The rich surface modification chemistry along with the tuneable physical parameters of the nanomaterial offer significant advantages over conventional methods for addressing environmental contamination

In water treatment, harmful pollutants in water can be converted into harmless chemicals through chemical reactions. For example, Trichloroethene, a dangerous pollutant commonly found in industrial wastewater, can be catalysed and treated by nanoparticles. Nano-wires made of potassium manganese oxide have been developed which can clean up oil and other organic pollutants while making oil recovery possible [108]. These nanowires form a mesh that absorbs up to twenty times its weight in hydrophobic liquids while rejecting water with its water repelling coating. Since the potassium manganese oxide is very stable even at high temperatures, the oil can be boiled off the nanowires and both the oil and the nanowires can then be reused. Carbon nanotubes have exceptional absorption and water treatment capabilities and have a higher rate of organic contaminant removal when compared to activated carbon due to their large surface areas and other factors. They have been used as sorbents for chlorophenols, herbicides, etc. [109]

Seymour [110] depicted the beneficial uses of Nanotechnology for chemical and physical processes of groundwater remediation of toxic chemicals in the subsurface, emphasizing the need to improve the efficiency of remediation technologies already present, and to possibly design new treatment processes. Nanotechnology also has the potential to contribute to long-term water quality, availability, and viability of water resources, through advanced filtration that enables more water reuse, recycling, and desalinization. For example, nanotechnology-based flow-through capacitors (FTC) that desalt seawater using one-tenth the energy of state-of-the art reverse osmosis and one-hundredth of the energy of distillation systems have been designed. The projected capital and operation costs of FTC-based systems are one-third less than conventional osmosis systems [111].

In soil treatment, pressure or gravity can be utilized to apply a colloidal solution or aqueous slurry of nanoparticles to the contaminated soil [112]. The widely investigated biocompatible technologies for removal of heavy metals from soil are adsorption and stabilization or immobilization of heavy metals in soil by nanoparticles [113]. Nanoparticles are generally injected into the soil and they remain suspended making a decontamination zone. The small size of the nanomaterials increases their mobility and deliverability in soil, and the heavy metals are stabilized or converted to less toxic species in soil. Nanotechnology has become a reliable means to remediate heavy metal contaminated soil. Most of the studies are conducted in laboratory scale, and therefore, much effort should be given to the field-scale remediation.

2.3. Environmental Remediation Use of Nano Zerovalent Iron (nZVI)

The most extensively applied nanoparticle in the removal of pollutants from soil and water is nanozerovalent iron (nZVI), due to its properties and effectiveness of application as well as its cost effectiveness of production. The use of nanoscalezerovalent iron (nZVI) to remediate contaminated groundwater has received a great deal of research attention in the past decades, due to its potential for broader application and higher reactivity compared to other traditional remediation techniques [114]. Due to their large surface area and reactivity, nZVI have emerged as an effective redox media for reducing a variety of organic pollutants such as PCBs, pesticides, organic dyes, chlorinated alkanes, and alkenes in water/wastewater, they provide an effective way of in situ remediation of water and industrial effluent. The nZVI particles can be used to treat contamination by incorporating the particles in a permeable reactive barrier [114]. Once the barrier is designed and installed, groundwater will flow through the barrier where the contaminated groundwater is treated and clean water will continue its path.

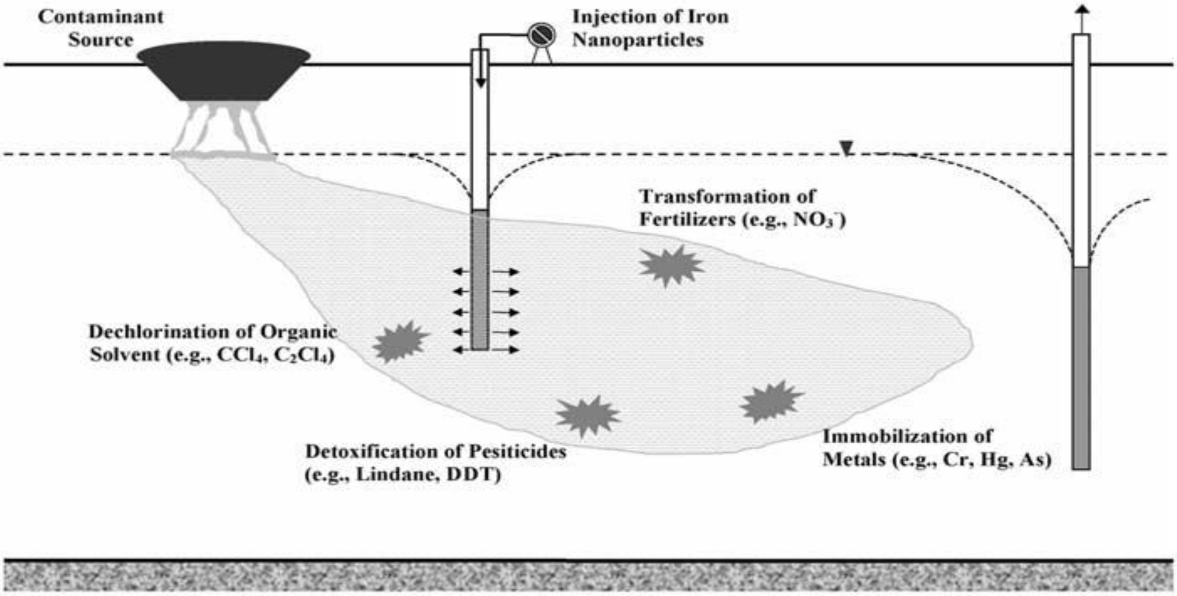

Fig 2. In-situ Application of Iron Nanoparticles [115]

The nZVI due to its high activity towards persistent organic contaminant degradation and heavy metal removal has also attracted applications in industrial waste water treatment. Enhancement of nZVI’s catalytic activity can also be pursued by employing different surface modification strategies and by conjugating or hybridizing with other carbonaceous or metallic nanomaterials. Nanohybrid formation has multifaceted advantages towards its redox activity increases, electronic property alterations, providing with higher surface area, and better adsorption capabilities.

Use of nZVI particles in advanced oxidation processes (AOPs) such as the Fenton Process have shown an advantage over conventional method which requires around 40 to 80 ppm of ferrous ion in the solution and this value is above the standards. In addition, the application of homogeneous AOPs to treat large quantity of water may produce large amount of sludge in the final neutralization step. In order to avoid these disadvantages, nano-zero valent iron (nZVI) could be used as an alternative way to induce Fenton oxidation. Several studies have shown that nZVI is very effective for the degradation of halogenated solvents such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes and other polychlorinated hydrocarbons in groundwater [116]. Zero-valent iron nanoparticles has also shown to be effective against some pesticides, heavy metals, and dyes. They can be distributed into the subsurface using a variety of carrying fluids. Among the most common are water, nitrogen gas, and vegetable oil. Slurries of water and nZVI powder can be injected into the contaminated zone using nitrogen gas as a carrier. This helps the iron powder disperse in the subsurface and create contact between the contaminants and the iron. Alternatively, nZVI can be mixed with vegetable oil and water to create an emulsion, which is then injected into the contaminant zone.

The practical applicability of ZVI lies in the fact that it can easily get oxidized to +2 and +3 oxidation states and in the process reduce other organic as well as inorganic impurities. Elemental iron slowly oxidizes to ferrous iron and releases two electrons. These electrons begin to function in a variety of reactions that lead to the transformation of target contaminants. It is intended that toxic contaminants (e.g., tetrachloroethylene, tricholoroethylene) would be reductively dechlorinated to an essentially nontoxic mixture of ethane, ethene, and acetylene. Elemental iron can be oxidized by many substances in the environment in accordance with the following oxidation half reaction (equation 1);

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad 1$$

Contaminants such as polychlorobiphenyls (PCBs), and chlorinated benzenes can accept the electrons and be reduced to hydrocarbon compounds. For example, tetrachloroethene (C_2Cl_4) can be reduced to ethene in accordance with the following stoichiometry (equation 2):

$$C_2Cl_4 + 4Fe^0 + 4H^+ \rightarrow C_2H_4 + 4Fe^{2+} + 4Cl \quad 2$$

These reactions proceed in two known pathways: Beta-elimination pathway, in which the formation of partially dechlorinated products such as dichloroethene and vinyl chloride (VC) is avoided, and trichloroethene (TCE) is transformed directly to ethane via the production of some short-lived intermediates, such as chloroacetylene and acetylene; and Hydrogenolysis or sequential degradation pathway, which occurs when one chlorine atom is removed in each step, so that TCE degrades to cis-1,2 DCE, then to VC, and finally to ethene and ethane. It is believed that chlorinated solvents degrade primarily through the beta-elimination pathway when exposed to iron [117]. Beta-elimination is the preferred pathway because it occurs under abiotic-reducing conditions and degrades TCE without producing the environmentally persistent intermediate products DCE and VC.

Besides toxic chlorinated compounds such as TCE, nZVI has been shown to be able to degrade other compounds found at contaminated sites such as the organic contaminant trinitrotoluene (TNT), dichlorodiphenyltrichloroethane (DDT) pesticides, heavy metals (Hg, Ni, Cd, etc.), organic dyes (chrysoidin), and inorganic anions.

2.4. Bimetallic Nanoparticles

The limitations associated with monometallic nanoparticles including their propensity toward aggregation and their low stability. Often, different stabilizers and surfactants are employed to increase the stability of nanoparticle solutions; however, the addition of a second metal to the formulation can enhance the solution stability of the material and obviate the need for stabilizers and surfactants [118]. Improved stability can contribute to increased efficiency and capacity, and can accelerate the degradation rate of contaminants. Bimetallic nanoscale particles increase the kinetics of the redox reactions involved in contaminant remediation, and thus perform as a catalyst to this reaction. Palladium and iron Nanoparticles are commercially available and currently the most commonly used in site remediation. Some noble metals (i.e., resistant to corrosion and oxidation in moist air) can be combined with nZVI to catalyzedechlorination and hydrogenation reactions with contaminants, therefore resulting in a more efficient remediation method. For instance, in their study of the effects of the addition of Pd to nZVI particles, [119] described an enhanced rate of dehalogenation of chlorinated organic compounds, albeit at a higher cost due to the expense of elemental palladium.

2.5. Environmental Impacts of Nanoremediation

It is important that the materials used for the remediation of pollution are not another pollutant themselves after they have been employed. Target-specific capture, cost effectiveness, facile synthesis, green chemistry, non-toxicity, biodegradability, recyclability, and the potential for recovery after use (regeneration) are some of the key challenges that must be considered when developing and deploying new materials for environmental remediation. Despite the potential advantages of the nanomaterials mentioned above, the potential risks they pose may include;

- Dispersal ability in the environment which may involve long range transport
- Ecotoxicity which includes inhalation, ingestion and dermal contact by humans with nanoparticles which has the potential to instigate various diseases
- Persistence in environmental media
- Bioaccumulation in living organisms

Patil, Shedbalkar, Truskewycz, Chopade, & Ball [120] suggested the following mitigation measures to counter the environmental risks posed by the use of nanomaterial for environmental remediation:

- Use of green synthesis for Nanomaterials
- Use of microbes for synthesizing Nanomaterials
- Use of biomarkers and methods for monitoring the fate and transport of Nanomaterials.

2.6. Status Quo of Nanotechnology and Environmental Nano-Remediation in Nigeria

In spite of the essential benefits of nanoscience and technology, Nigeria is yet to key into nanotechnology initiative and strategy towards improving her socio-economic development and transformation [121]. The benefits and opportunities these evolving technology offers are enormous, and have led to high expectations in the academics, industries and even government. Nnaji [105] described Nigeria as a nanotechnology dormant nation, still largely at the demonstration of interest stage while smaller and less rich countries like Nepal, Bangladesh and Sri Lanka are seriously pursuing research in Nanotechnology. Nigerian government interest in advancing nanotechnology is based on the 2012 Science, Technology and Innovation (ST&I) Policy of the Federal Ministry of Science and Technology which addresses new and emerging technologies like nanotechnology in item 12. However, significant research has not been conducted in nanotechnology and only a few institutions like the National Agency for Science and Engineering Infrastructure (NASENI), University of Ibadan, University of Nigeria and Obafemi Awolowo University, Ile-Ife are known to engage in appreciable nanotechnology research [105].

The nanotechnology research group (*NANO+*) at Ladoke Akintola University of Technology, Ogbomoso, Nigeria has been at the fore front on efforts to promote the use of nanotechnology in Nigeria by organizing conferences and national workshops on the synthesis, characterization and applications of nanoparticles. Despite these efforts, it is evident from available research statistics that there are little or no impact researches in nanotechnology being carried out in Nigeria over the years.

In the area of nanoremediation, researches are few and little information exists on the research and use of nanoremediation by public and private institutions [105]. Researches in recent times have largely focused on the extraction of nanomaterials with very few going further to investigate its application. Industrial pollution of the Nigeria environment is a topical issue which has led to avoidable human, material and economic losses to the governments at all levels, communities and industries. Most companies appreciate the dire need for sustainability in their operations and have carried out several remediation efforts. However, the use of conventional remediation technologies which may be expensive and tedious for oil polluted environment have limited or partial effectiveness and this calls for more novel and innovative technologies that will lead to the successful and cost effective remediation of polluted marine and soil environment.

3. Conclusion and Recommendations

3.1. Conclusion

Environmental degradation is evident in Nigeria as a result of the nation's dependency on exploitation of the environment to meet its needs. The conventional methods of remediation have proved to be less effective and efficient in addressing this problem and as such there is need to chart an alternative course. Nanotechnology offers such alternative with the potential to not only reduce the overall cost of cleaning up large-scale contaminated soil and water, but also to minimize cleanup time, eliminate the need for treatment and disposal of contaminated soil and diminish the concentration of some contaminants to near zero level. In soil and water treatment, nanomaterials offer the potential to leverage on unique surface chemistry as compared to traditional approaches, such that they can be functionalized or grafted with functional groups that can target specific pollutant molecules of interest for efficient remediation. The most extensively applied nanoparticle in the removal of soil and water contaminants is nanozerovalent iron (nZVI), due to its properties and ease of application as well as its cost effectiveness of production. But despite the benefits of nanotechnology and its growing awareness in other countries, available research statistics show that Nigeria is yet to fully key into this emerging technology with very little research done in the area over the years. The statistics corroborates Nnaji's assertion of Nigeria as a Nanotechnology dormant country. This paper has successfully depicted the problems of conventional methods of remediation, the advantages of nanoremediation and current status of nanotechnology in Nigeria.

3.2. Recommendations

The potential benefits of nanotechnology and its advantages over conventional methods of environmental remediation cannot be overlooked, especially in a country ravaged by environmental degradation such as Nigeria. It is therefore pertinent to recommend as follow;

- Environmental Stakeholders (Government Agencies, Industries, Tertiary and Research Institutions) should dedicate more funds to researches in Nanoremediation
- Academicians should stimulate more interest in their graduate students to undertake researches in Nanoremediation
- For every Nanoremediation research undertaken, there should be result dissemination and Environmental Impact Assessment (EIA) to ascertain its level of impact on the ecosystem.

Conflict of Interest

The authors declare that they have no conflict of interest.

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