Nanotechnology: Review on Emerging Techniques in Remediating Water and Soil Pollutions

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ABSTRACT: Environmental Pollution is becoming a global challenge in both developing and the developed countries, pollutants discharge from oil and gas industries and or agricultural practices continue effecting the health of human and other animal in an ecosystem in one way or the other. This necessitated the development of a techniques to clean up of the polluted environment. Remediation of pollutants relies mainly on using various techniques like physical, chemical and or biological methods for the removal of contaminants from different environmental media be it soil, water, and or air. These techniques have their own limitations as the toxicity of the degrading agents, time consuming and the fate of the environment after remediation matters a lot. Therefore, nanotechnology is gaining interest in remediating pollutions as nanoparticles are relatively cost effective, sensitive and selective and can be used as sensors to monitor toxins, organic contaminants and heavy metals in land, water and or air. The enhanced properties and effectiveness of nanotechnology-based materials makes them suitable for nano remediation. This review provides an overview of the nanomaterials: Organic based nanomaterials (Dendrimers), inorganic (TiO2, nZVI), carbon-based (Carbon nanotubes, (CNTs)), and composite-based materials) used in environmental remediation. These nanomaterials were reported to remediate different contaminants in the environment such as heavy metals, pathogens, pesticides, dyes, chlorinated organic compounds, and polycyclic aromatic hydrocarbons.

Environmental pollution raises concern in the past years due to increase in human activities on oil and gas industries, agricultural practices, industrialization and many more. These activities are the primary source of contaminations in water, air and land and as such have drawn major concern globally. Environmental pollution is one of the main challenges today's societies are facing, the risks associated with these pollutions may not be immediate, but do accumulate over time, posing harmful effects to the inhabitants (Neely *et al*., 1974). Water and soil pollutions are among the most serious forms of pollution that pose long-term damage to the environment, and the pollutants include petroleum products (Yunus *et al.,* 2012; Nnaji, 2017), pathogens (Kang *et al*., 2007; Cortes et al., 2009), heavy metals (Gao *et al*., 2009, Rizwan *et al*., 2014) and organic pollutants such as p-nitrophenol (Rizwan *et al*., 2014). These pollutants are usually laden with toxic contaminants that are deleterious to global health as they caused problems like neurological and mental disorder, organ dysfunction, cancer, and even death to some extents (WHO, 2013), diseases of the heart and cancer of the

lung (Yunus *et al.,* 2012), dysfunction of kidney, reproductive system, liver, brain and central nervous system (Chen and Lim, 2002). Hence the need for immediate response to curb the effects of such pollutants, this necessitates the development of ecofriendly approach and bioremediation come to play. Bioremediation is a process that involves in cleaning up of pollutants from environment using microorganisms (Nkereuwem *et al*., 2010), it is relatively ecofriendly and cost effective compares to chemical and physical methods of removing pollutions (Chibueze *et al*., 2016). This eco-friendly remediation approach gained interest as it reduces contaminants accumulations in the environments to the lowest level, hence minimizes the global environmental impacts induced by greenhouse gas emissions (Reddy and Adams, 2010). The ultimate goal of bioremediation is to effectively restore the polluted environments in an eco-friendly approaches and at a considerable low cost. However, bio remediation approach has its own limitations in combating pollutants concentration in an environment, that include time consuming, and some time poisoning the organisms used (Rickerby and

Morrison, 2007; Tripathi, *et al.,* 2018). This raises concerns again, hence the need to develop more efficient and cost effective approaches for remediating environmental pollutions. Nanotechnology is becoming an option in environmental remediation technology using various nanoparticles (Mueller and Nowack, 2010; Olyaie and Banejad, 2012; Pandey *et al.,* 2015; Guerra *et al.,* 2018; Tripathi *et al.,* 2018 and Isa *et al.,* 2019). Nanotechnology may be defines as understanding and controlling matter at dimensions between approximately 1- 100 nanometers, where unique phenomena enable novel applications (USEPA, 2011), it is a new technique in environmental remediation and termed as nano-remediation (Machado *et al.,* 2013), this technique has definitely identified as early as possible new areas of science and technology that have the potential to impact strongly on environment. When the environmental cleanup involves using nanoparticles or nanomaterials formed from living organism is termed as nano bioremediation (Yadav *et al.,* 2017). It has been used in remediating water and soil pollutants (Bottero *et al.*, 2006; Olyaie and Banejad, 2012) and has proven to be a new an effective strategy for cleaning up residual pollutants in a variety of environment into eco-friendly manner. The advantages of nanotechnology in environmental remediation include sensing, detecting, preventing and remediating pollutions (Durán, 2008), low cost, less time consuming and efficient (Li *et al.*, 2008), the fate of the environment after remediation and the toxicity of the degrading agent used (Olyaie and Banejad *et al.,* 2014) are need to be considered and as such, nanoparticles are nontoxic (Li *et al.*, 2008), and can diminishes pollution production (Watlington, 2005), hence are relatively safe to handle, this may help to reduce the impact of pollutions on an environments. Nano remediation is more sensitive and selective than conventional methods and can be used as sensors to monitor toxins, organic contaminants and heavy metals in land, water and air environments (Khin *et al.,* 2012). The goal standard of this review is to provide a comprehensive overview of some of the methods employed in nanotechnology in remediating environmental (water and soil) pollutions.

Why Nanoparticles over bulk particles? Research in nano sciences reported that many of the environmental challenges after remediation are usually being resolved using nonabsorbent, nanocatalysts, bioactive nanoparticles, nanopowder, nanotubes, magnetic nanoparticles, and nanoparticles (Mamadou and Savage, 2005; Savage and Diallo, 2005). Nanotechnology has several advantages that helps to improve the existing remediation techniques (Yunus *et al.,* 2012) and this creates new method that is better

than the current ones, this is possible due to the high surface area to-volume ratio of the nanoparticles which enable them to absorb maximum amount of pollutants, and their extremely small size also allow quantum effects to come to play (Hochella and Madden, 2005) and this make them accessible to contaminants hence prioritized in-situ over ex-situ form of remediation (Pandey *et al.,* 2016). Nanoparticles are more reactive than the bulk ones because of their increase surface area per unit mass (Rickerby and Morrison, 2007; Isa *et al.*, 2019). Nano science has being used in a variety of applications within the scientific, environmental, industrial, and medical arenas (USEPA, 2011).

Nano particles strategies in combatting pollutions: Nanotechnologies are expected to make a great contributions in curbing the effects of pollutions in an ecosystem using nano particles and nanomaterials, they are known to be incorporated into various materials to improve different properties (NRP, 2017). Controlling pollutions from their source of origin or limiting the process to a certain areas is a promising step, thus, the strategies employed by nanoparticles in controlling pollutions include: (1) Some nano particles like zero valent ions act as reducing agent by donating electrons to contaminants, this reduces them to a less toxic substances (Chuang *et al.,* 1995; Mueller and Nowack, 2010) then the insoluble substances would be precipitated (Helal *et al.*, 2016). (2) Nanoparticles may be engineered with specificity and affinity to a particular contaminants this helps to uptake the pollutants without subsequent release (Olyaie and Banejad, 2012). (3) Nanomaterials like dendrimers have interior voids which enable them to trap small substances (Zimmerman and Lawless, 2001; Triano *et al.*, 2015). (4) Little amount of energy can be used to degrade organic and inorganic contaminates (Nowack, 2008; Isa *et al.*, 2019). (5) Some nanoparticles interfere with DNA synthesis thereby destroying the bacterial cell wall (Thai *et al.*, 2010; Raj Kumar and Gopinath, 2017). (6) Prevent the formation of harmful intermediate and by products as well as preventing the release of contaminants at manufacturing sites (Pandey *et al.*, 2016).

Applications of nanotechnology in remediating water and soil pollutions using different nanoparticles: Nanoparticle (NPs) are classified into four different groups (USEPA, 2007; Jeevanandam *et al.,* 2018) they include: Carbon-based nanomaterials, Inorganic-based nanomaterials, Composite-based nanomaterials and Organic-based nanomaterials.

Carbon-based nanomaterials: Carbon based nanomaterials composes mostly of carbon and are in

various shape. They are classified based on their shape and geometrical structures and include; nanohorns (horn-shaped) carbon nanotube (CNT) (tube-shaped), carbon nanospheres (fullerenes) (ellipsoidal spherical shape), and zero-dimension dots exhibited quantum character as carbon quantum dots (CQDs) (Khare *et al.,* 2019). They are macromolecules consisting of sheets of carbon atoms covalently bonded in hexagonal lattices (Niu and Cai, 2012) and are being incorporated into various materials to improve different properties (NRP, 2017).

Carbon nanotubes (CNTs): Carbon nanotubes (CNTs) are among the types of allotrope of carbon-based nanomaterials that have excellent electrical and mechanical properties (Khare *et al.,* 2019). CNT and nanocrystals have been reported by Kang *et al.*, 2007; Cortes *et al.,* 2009 Rizwan *et al.*, 2014 and Isa *et al.,* 2019 to have wide range of environmental applications such as those used as sorbent, antimicrobial and environmental sensors in remediating pollutants. They emerged in the field of nanotechnology due to their nanosize structure and novel properties. Attaching to a functional group, unique adsorption properties (Mansoori *et al.*, 2008), mesoporous structure and large surface area to volume ratio enable them to be used in adsorption of pollutants from drinking water (Savage and Diallo, 2005). Yu *et al.,* 2014 also

reported that hydrogen bonding, π-π interactions, hydrophobic effect, electrostatic interactions and covalent bonding are the mechanisms employed by CNT to adsorb organic compounds. They were reported to remediate various contaminants including soil toxic organic compounds (polychlorinated biphenyls and polycyclic aromatic hydrocarbons (Pan and Xing, 2010), organic and inorganic contaminants (Jin *et al.*, 2007) and Pathogenic microorganisms from waste water by depth-filtration mechanism (Mostafavi *et al.,* 2009). Two types of CNTs were reported namely: Single-Walled Carbon Nanotubes (SWCNTs) and Multi-walled Carbon Nanotubes (MWCNTs) (Chen *et al.*, 2015; Raj Kumar and Gopinath, 2017). Both SWCNTs and MWCNTs are unique macromolecules with thermal stability, one dimensional structure and special chemical properties (Firozjaee *et al.*, 2017). SWCNTs possesses antimicrobial properties which destroys the bacterial cell wall by interfering with metabolic reactions and or inhibit the DNA synthesis (Thai *et al.*, 2010; Raj Kumar and Gopinath, 2017) it also effectively adsorb the PCBs by reducing its bioavailability from sediment (Hua *et al.,* 2017). MWCNTs also has both antimicrobial and adsorption ability to remediate heavy metals (Raj Kumar and Gopinath, 2017; Correia, *et al.,* 2019), thereby reducing the risk of contaminants in soil (Josko *et al.*, 2013).
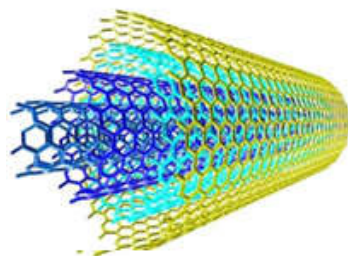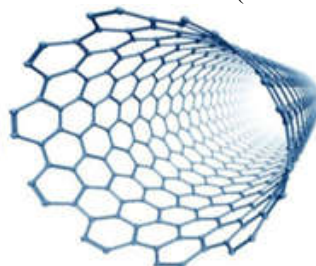

Fig 1. Represent Multi-walled Carbon Nanotubes (MWCNTs), while Fig **2** Represent Single-walled Carbon Nanotubes (SWCNTs)
(Source: Rafique *et al.,* 2016)

Inorganic-based nanomaterials: These are nano-materials that include metal and metal oxide nanoparticles and nanomaterials (Jeevanandam *et al*., 2018). While metal nanoparticles include Pt, Rh, Pd, Ir, Ag, Au, Cu, Co, Ni, FeNi, Cu_3Au, CoNi, CdTe, CdSe, and ZnS (Rizwan *et al.,* 2014), metal oxide nanoparticles are ZnO, Fe_2O_3, Fe_3O_4, MgO, $BaCO_3$, $BaSO_4$, and TiO_2 (Rizwan *et al.*, 2014) and semiconductors such as silicon and ceramics (Jeevanandam *et al.*, 2018).

TiO₂ Nanoparticles: Nanoparticles have unique properties compare to their bulk counterpart, such properties include high reactivity attributed to their increase surface area per unit mass, wider reactivity

i.e. attacking both organic and inorganic molecules and large surface area to volume ratio which allows quantum effect to come to play (Isa *et al*., 2019). These novel properties warrant them to be the most suitable for remediating environmental pollutions. TiO_2 has been frequently investigated metal-based nanoparticles for remediating environmental pollution with nontoxicity, low-cost, photo catalytic and energy converting properties (Li *et al*., 2008), TiO_2 were reported to purifies water (Adesina, 2004; Kabra *et al.,* 2004 and Obare and Meyer, 2004; Li *et al.*, 2008), remediate Cr (VI), Ag (I), Pt (II), chlorinated alkanes, benzenes, dioxins and furans and polychlorinated biphenyls etc (Savage and Diallo, 2005), pesticides, dyes, toxic compounds from the waste water

(Meghmala *et al.,* 2019) and act as antioxidant, antibacterial and cytotoxicity activity against Mg 63 osteosarcoma cell lines (Chatterjee *et al.,* 2016), extraction of heavy metals from the surface of water (Quetel *et al.,* 2010) thus, TiO_2 have wide applications in environmental remediation.
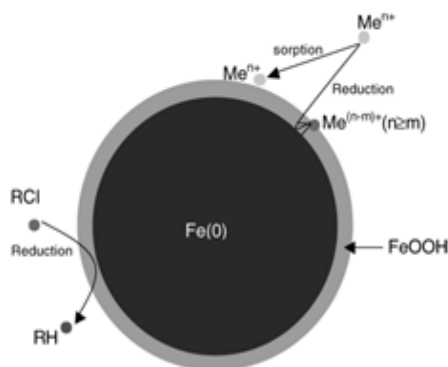

Fig 3 Zero valent Iron nanoparticles (Source: Li *et al.,* 2006)

Zero-Valent Iron (ZVI):Among numerous nanoparticles evaluated for the purpose of environmental remediation, zero valen iron (ZVI) nanoparticles gained momentum in the recent past, and were reported to be one of the most abundant element on earth (Deng et al., 2000). They have been thoroughly studied due to their great reduction potential towards chlorinated contaminants, and have higher sorption capacity and reaction rates compare to bulk particles approximately 25-30 times faster (Mueller and Nowack, 2010). They remediate various toxics contaminants in groundwater, soils, sediments and aquifers (Cundy et al., 2008) like chromate, nitrate, selenate, perchlorate and arsenate (Cao et al., 2005; Nowack, 2008), pesticides, fertilizers and dyes in the soil (Zhang, 2003), Cr (VI) in contaminated water and soil (Medina-Pérez et al., 2019), polycyclic aromatic hydrocarbons (Chang et al., 2007), As (III) Rizwan et al., 2014), Cd and Pb from polluted soils (Helal et al., 2016) and polychlorinated biphenyls (Varanasi et al., 2007).

ZVI act as effective redox media compared to their bulk counterpart for the detoxification of organic and inorganic pollutants from aqueous environments (Savage and Diallo, 2005), hydrocarbon compounds (Cheng and Wu, 2001; He and Zhao, 2005; Wei et al., 2006 and Zhu et al., 2006), their mechanism of action include, the ion act as reducing agent by donating electrons to the contaminants, thereby reducing them to a less toxic substances (Chuang et al., 1995; Mueller and Nowack, 2010) following this, the insoluble substances would then be precipitated (Helal et al., 2016). Mueller and Nowack, 2010 reported that ZVI nanoparticles remediate various forms of organic

pollutants in the soil and groundwater as shown in figure 2. This graphical representation shows that ZVI nanoparticles can be injected into well 1 to form a reactive barrier between contaminated and treated ground water, in well 2 mobile nZVI are injected to form a plume, while the incorporation of nanoparticles in to the top soil degrade the pollutants/contaminants as shown in well 3.

Dendrimers: These include nanomaterials made usually from organic matter, excluding carbon-based or inorganic-based nanomaterials. They are nano-sized polymers consisting of branched units and their interior cavities can be used for drug delivery (NRP, 2017). The surface of a dendrimer has numerous chain ends, which can be adapted to perform specific chemical functions, this property makes it useful as catalysts (Gangadhara, *et al.,* 2012).

Dendrimers in nano remediation: Dendrimers are highly structured macromolecules composed of a central core connected to two or more repetitive branching units (Triano *et al.,* 2015), they are characterized by their sphere-like bifurcated, three-dimensional structure (Frechet *et al.,* 2001) and are mono disperse polymers with specific size, solubility, porosity, high degree of molecular uniformity and highly functional terminal groups on their surface (Newkome *et al.,* 2006; wang *et al.,* 2008).

Dendrimers were reported to be used in remediating environmental pollutions (Savage and Diallo, 2005; Triano, 2015; Pawlaczyk *et al.,* 2018; Fernanda *et al.,* 2018) like Pb (IV) from polluted soil (Xu and Zhao 2006), organic compounds (Diallo *et al.*, 1999), manganese, nitrate, iron, arsenic, heavy metals, CO, SO2, aliphatic and aromatic hydrocarbons, pharmaceuticals, bacteria, parasites and viruses, etc. (Guerra *et al.,* 2018). PAMAM dendrimers remediate soil and water contaminated with metal ions such as $Cu2^+$ (Xu and Zhao, 2005; Guerra *et al.,* 2018).

Composite-based nanomaterials: These are materials that combine nanoparticles with other nanoparticles or with other materials. They are composite in which at least one of the phases shows dimensions in the nanometers ranging between 1 to 100nm (Cônsoli *et al.,* 2019). Nano-composite may be polymer based or non-polymer based nano materials (Pandya, 2015), the incorporation of nanomaterials into composites enhances mechanical, thermal and barrier properties of a material (NRP, 2017). The improvements in these properties have resulted into an interest in nanocomposite been used in various industrial applications as found in environmental cleanup.
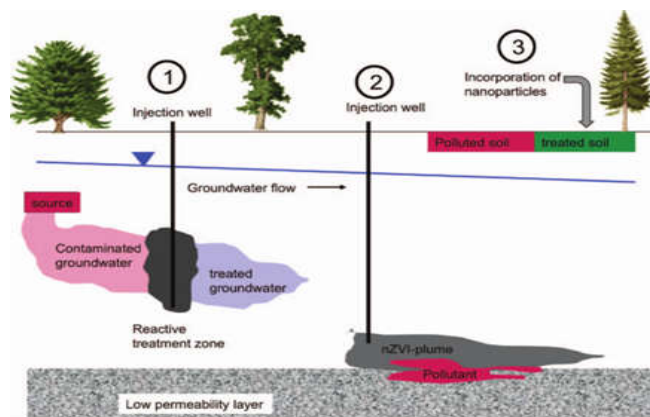
Fig 4 In situ technologies used to treat polluted ground water and Soils: (Source: Mueller and Nowack, 2010)

Table 1: A brief summary of application of nanotechnology in soil and water remediation

S/No	Types of nanoparticles	Type of pollutants remediated	References
1	**Carbon-based nanomaterials**	organic and inorganic pollutants	(Jin *et al.*, 2007).
		Fluoride from drinking water	(Mansoori *et al.*, 2008)
	Carbon Nanotubes (CNTs)	Polychlorinated biphenyls, polycyclic aromatic hydrocarbons	(Pan and Xing, 2010)
	MWCNTs	Microorganisms, heavy metals	(Raj Kumar and Gopinath, 2017)
		heavy metals in soils	(Correia, *et al.*, 2019),
	SWCNTs	Microorganisms	(Raj Kumar and Gopinath, 2017)
		Polychlorinated biphenyls (PCBs) (Hua *et al.,* 2017)	(Hua *et al.,* 2017)
2	**Inorganic-based nanomaterials**	chlorinated alkanes, benzenes, dioxins and furans, polychlorinated biphenyls, Cr (VI), Ag (I) and Pt (II)	(Savage and Diallo, 2005)
		Microorganisms	(Chatterjee *et al.,* 2016).
	TiO_2 Nanoparticles	pesticides; dyes; toxic compounds from the waste water	(Meghmala *et al.,* 2019)
		Heavy metals	(Quetel *et al.,* 2010)
3	**Organic-based nanomaterials**	$Cu2^+$ from polluted water and soil	(Xu and Zhao, 2005;Guerra *et al.,* 2018)
	Dendrimers	Pb (IV) from polluted soil	(Xu and Zhao 2006),
		Manganese, nitrate, iron, arsenic, CO, SO2, aliphatic and aromatic hydrocarbons, pharmaceuticals, bacteria, parasites and viruses, etc.	(Guerra *et al.,* 2018).
		organic compounds	(Diallo *et al.*, 1999),
		ions, gaseous molecules, low molecular weight organic compounds	(Zimmerman and Lawless 2001; Triano *et al.,* 2015)
4	**Composite based nanoparticles**		(Arabi *et al.,* 2019; Khare *et al.,* 2019),
	carbon nanotubes+ ZnO nanoparticles	Congo red dye from aqueous environments	
	Polymeric CNT+		(Rizwan *et al.,* 2014)
	Calixarenes and thiacalixarenes	Cd^{2+}, $Pb2^+$ and P- nitrophenol from water.	
	Ceramic filters+ Poly (amidoamine) and poly (ethyleneimine) dendrimers	Pesticides and polycyclic aromatic hydrocarbons from water	(Arkas *et al.* 2006),
	nZVI+ noble metals	Organic chlorine and hydrogen	(Karn *et al.,* 2009)

Composites based nanomaterials can be used to develop various and efficient sensors to detect very low concentrations of chemical compounds in a polluted environments, for example, carbon nanotubes loaded with ZnO nanoparticles (Composite) can be used to reduce Congo red dye from an aqueous environment (Arabi *et al.,* 2019; Khare *et al.,* 2019)**,** Polymeric CNT incorporated with calixarenes and thiacalixarenes remediate inorganic pollutants such as Cd^{2+} and Pb^{2+} and organic ones such as P-nitrophenol from water (Rizwan *et al*., 2014)**.** Ceramic filters when impregnated with Poly (amidoamine) PAMAM and

poly (ethyleneimine) dendrimers remediate pollutions such as pesticides and or polycyclic aromatic hydrocarbons from water (Arkas *et al.*, 2006), nZVI can be combined with some noble metals to catalyze dechlorination and hydrogenation reactions with contaminants Karn *et al.,* 2009.

The downside of nanoparticles: It is being realized that nanoparticles are being released into the environment (Wilson, 2018), these nanoparticles may get into the environments through a varieties of known and unknown sources (APHL, 2015). Toxicologist geared up to develop an approach that understand how nanoparticles disperse into the environments and their potential toxicity due to the way they behave (Wilson, 2018), Research has shown that nanoparticles when inhaled, may interact with biological system due to their smallness in size, solubility and large surface area (USEPA, 2017), this may end up binding to proteins in the blood and as such stimulate or sometime suppresses immune responses (Dobrovolskaia and McNeil, 2007). Due to negative impact imposed by nanoparticles, Mueller and Nowack, 2010 reported that most of the nanoparticles require verification of their efficacy and safety in the field as they have been successfully demonstrated in the laboratory scale, this might probably be the reason why few nanotechnological applications for environmental cleanup have been commercialized for now. Many risks associated with nanoparticles are not known at this time, but as more is learned about their transformational behaviour, the number of possible hazardous may escalate over time.

Conclusion: Nanotechnology offers an effective alternative approaches to an existing remediation in environmental pollutions, and the superior performance is due to the novel properties of the nanoparticles. This work put together the most recent techniques applied in remediating soil and water pollution. These techniques are considered to be most efficient and cost effective so far. Organic, Inorganic, carbon-based and nano-composite nanomaterial are among the different types of nano-materials that can be successfully employed for a variety of applications in environmental remediation.

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