



Potentials of Nanoparticles for Soil and Water Remediation (A Review)

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Abstract: Soil and water are two basic components of the environment which are of paramount importance to man and to the survival of all living things. The scope of pollution associated with these two major components of the environment is of concern and the issues rely not only on control but how to remediate soil and water which have already been polluted. Therefore, this paper brings to limelight the most recent methods of environmental remediation. These methods involve the use of nanoparticles in environmental clean-up. The unique properties of nanoparticles such as photocatalytic properties, adsorption property and redox processes have been discussed in this paper. The paper also present how these unique properties of the relevant nanomaterials are utilized in their application for environmental remediation. The significance of some these nanoparticles for soil remediation are nanoscale zero-valent iron for the decomposition of halogenated organic pollutants, nanoscale calcium peroxide for the destruction of organic-oil pollutants and nanoscale metal oxides for the adsorption of heavy metals in soil and water. This paper also highlight the significance of titanium dioxide nanoparticles, carbon-based nanoparticles, and magnetic nanoparticles and dendrimers nanoparticles in surface, ground and waste water remediation. These methods are new in environmental clean-up and therefore, there is need for more research to investigate their properties in soil and water as well as their environmental impacts.

Key words: Adsorption Photocatalytic, Pollutant and wastewater

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Introduction

Nanoparticles (sometimes referred to as nanomaterials) are substances with size measuring between 1 and 100nm (Duran, 2008). Mansoori *et al.* (2008), define nanoparticles as substances that contain atoms or molecules bonded together with a radius of less than 200nm (<200nm). Mueller and Nowacks (2010) refer to nanoparticles as substance that have novel properties and functions because of their small size. Nanoparticles display unique and appealing physical and chemical properties that provide

opportunity for the use of these particles for environmental remediation. The size and shape of these particles are important properties that account for their dispensability and effective reactivity (Rizwan *et al.*, 2014, Sanchez, 2011). Nanoparticles can occur naturally from natural process and are present in air, water, soil and sediments. They can be produced for specialized materials and processes. Nanoparticles are also produced as by-products of industrial processes (Mueller and Nowack, 2010).

The unique properties of nanoparticles offer great potentials in the production, development and improvement of so many materials. These particles at the nanoscale level have been used in the development of many materials such as electronics, biomedical, pharmaceuticals, cosmetics and other materials applications, as well as in the developments of catalyst and in energy (Duran, 2008). In industries nanoparticles played significant role in the areas of sunscreen, magnetic recording tape, automotive catalyst supports, biolabeling, chemical-mechanical polishing, electro-conductive coatings, and optical fibres (Duran, 2008). Nanoparticles displayed enormous potentials in the area of environmental pollution control through, sensing, detections and treatment of environmental pollutants as well as in environmental remediation.

Properties of Nanoparticles

Nanoparticles display so many unique and appealing properties. Some of these properties are as follow:

1. The high reactivity of nanoparticles is attributed to their increase surface area per unit mass.
2. The high surface to volume ratio of the nanoparticles as a result of their smaller size has allowed quantum effect to come to play.
3. The reaction rates of nanoparticles are faster than the reaction rate of granular materials in the micrometre to millimetre range.
4. They show wider reactivity by attacking both organic and inorganic molecules.
5. Their smaller size and capacity to be suspended or dispersed allow them to travel faster than large macro-sized particles, achieving a wider distribution.

Application of Nanoparticles

The most common application of nanoparticles is in the area of environmental remediation. They have been widely used for the treatment of surface water, groundwater and waste water (Rizwan *et al.*, 2014). For example nanofiltrations, involving carbon nanotubes and TiO₂ nanoparticles have been used in purification, disinfection, and desalination of surface water (Theron *et al.*, 2008, Muller and Nowack, 2008 and Nowack, 2010). Nanoparticles zero-valent iron (nZVI) has been used for soil and sediment cleanup, as well as in groundwater remediation (Gomes *et al.*, 2013, Rizwan *et al.*, 2014). Nanoparticles are currently being used for cleanup against petroleum and petroleum products (hydrocarbon) pollution (Rizwan *et al.*, 2014). Calcium peroxides nanoparticles been recently applied in the remediation, of soil against oil spills and other organic contaminants, such as gasoline, heating oil, methyl tertiary butyl ether (MTBE), ethylene glycol and solvents (Karn *et al.*, 2009, Mueller and Nowack, 2010). TiO₂ nanoparticles been used for the photocatalytic break down of air pollutants, such as oxides of nitrogens (NO₂) volatile organic compounds, polychlorinated biphenyls (PCB), dioxins and other persistent organic pollutants (Rizwan *et al.*, 2014, Duran, 2008). These nanoscales particles are potentially used for the

remediation of uranium and heavy metal environmental pollution (Sanchez, 2011, Rizwan *et al.*, 2014). The capacity of nanoparticles to suppress environmental pollution to the barest level is of great potential to environmental management in the near future.

Nanoparticles Remediation

Nanoparticle remediation or Nano remediation involves the use or application of nanoparticles for environmental clean-up. These particles are currently being explored to remove pollutants from contaminated environment. Nanoparticles are used to treat surface water, groundwater, waste water and in the remediation of soil, sediments, air and other environmental materials (Crane and Scott, 2012, Mueller and Nowack, 2010). Two methods are involved in environmental remediation using nanoparticles. These methods are:

1. **Adsorptive method** which act through adsorption involving *in situ* sequestration of contaminants by adding binding agents or *ex situ* extraction of contaminated solution, which is then treated with adsorbents, as in Nanofiltration. The nanomaterials used are iron oxides, and dendrimers. The method is used to remove organic pollutants, metals and arsenic.
2. **Reactive method** which act through redox-reaction involving *in situ* reaction of nanomaterial with target contaminant or *ex situ* extraction of contaminated solution, which is then treated with reactants, as in TiO₂ photo-oxidation. Other nanomaterials that used the redox process are nanoscale zero-valent iron (nZVI) and nanoscale calcium peroxide, which are used to removed halogenated organic compounds, metals, nitrates, arsenate and oil from contaminated soil or water (Mueller and Nowack, 2010).

Potentials of Nanoparticle in Soil Remediation

The soil is not only a home for living organism or place on which living organism live and obtain their food, but also a reservoir for other substance that pollute and contaminate the soil. The substances that contaminate the soil are of different origins and from various sources. The most important thing is to eliminate these pollutants, in order to make the soil safe for other uses. One way of removing these contaminants involve the use of nanoparticles to remediate the soil.

Iron based nanoparticles for soil remediation

Iron based nanoparticles remediate the soil through the process of adsorption or redox reaction. Iron based nanoparticles have been employed in the treatment of contaminated soils, sediments and solid wastes through remediation (Mansoori *et al.*, 2008). Zero-valent iron nanoparticles have proved effective in removal of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCB) from soil (Mueller and Nowack, 2010). Dehalogenation of chlorinated hydrocarbons has been achieved by the use of zero-valent iron nanoparticles as reactive material (Schrack *et al.*, 2004). The removal and sorption of arsenic from contaminated soil has been successful with zero-valent iron nanoparticle (Mansoori *et al.*, 2010). Zero-valent iron nanoparticles stabilized with carboxy methyl cellulose (CMC) is used to reduce Cr(VI) in soil (Mansoori *et al.*, 2010). Enhanced emulsified zero-valent iron nanoparticle improves *in-situ* dehalogenation of dense, non-aqueous phase liquid, containing trichloroethene from soil (Mansoor *et al.*, 2008).

Calcium peroxide nanoparticle and soil remediation

One important nanoparticle for the remediation of soil is calcium peroxide nanoparticle. This nanoparticle has recently been used for environment remediation of soil against oil

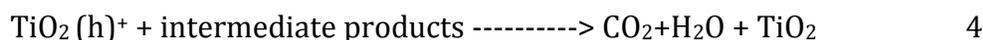
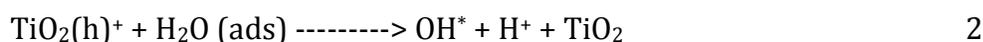
spills (karn *et al.*, 2009). Calcium peroxide nanoparticle is currently being used as an oxidant in environmental clean-up of soils containing various organic contaminants such as petrol, kerosene, methyl tertiary butyl ether, ethylene glycol and solvents. The oxygen produced in the reaction of calcium peroxide nanoparticle with water leads to an aerobic environment that supports natural bioremediation by aerobic organism present in the soil (Mueller and Nowack, 2010).

Potentials of Nanoparticles in the Remediation of Water

Nanoparticles have been extensively used in the remediation of water from various sources. They have been widely used in the area of surface water treatment, wastewater treatment and groundwater treatment (Mueller *et al.*, 2012, Theron *et al.*, 2008, Chong *et al.*, 2010). Various nanoparticles materials are used for water remediation.

Nanoparticles for surface water remediation

Titanium dioxide (TiO₂) nanoparticle has been widely used in water treatment because of its semiconducting, photocatalytic, energy converting and electronic properties (Mansoori *et al.*, 2008). The application of titanium dioxide (TiO₂) as a photocatalyst in water treatment results from its semiconducting property, making it an excellent material for removal of different organic pollutants. Titanium dioxide (TiO₂) display excellent performance in surface water treatment in the area of purification, disinfection and desalination (Theron *et al.*, 2008). The target contaminants in surface waters include heavy metals, organic contaminants and pathogens. In the presence of sunlight (ultraviolet light) titanium dioxide (TiO₂) produces highly reactive hydroxyl radicals, which can oxidize contaminants. The hydroxyl radical thus produced are used for water treatment, in a methods generally referred to as advanced oxidation processes. The main reactions that occur are as follow:



Titanium dioxide (TiO₂) is not recommended for underground *in situ* remediation, as there is no light to support the reaction. The most striking properties of titanium dioxide are its chemical stability and insolubility in water. One advantage with titanium dioxide is that it is inexpensive and easy to obtain. The disadvantage associated with titanium dioxide (TiO₂) is the wide band gap energy (3.2eV) that requires the use of UV light, instead of visible light only, for photocatalytic activation. Titanium dioxide (TiO₂) has been modified by doping with metals, nitrogen or carbon to enhance the efficiency of its photocatalysis, so that a greater portion of photons in the visible light spectrum are used for photocatalysis (Theron *et al.*, 2008).

Carbon based nanoparticles for surface water remediation

Carbon based nanoparticles show exceptionally unique properties and functionalities which are potentially utilized in the remediation of industrial effluents, surface water, drinking water and ground water. Carbon-based nanoparticles such as nanocrystals and carbon nanotubes (CNT) have displayed a broad range of environmental applications as

sorbent materials, high-flux membrane, depth filters, antimicrobial agents, environmental sensors, renewable energy technologies and in pollution prevention strategies (Rizwan *et al.*, 2014). The exceptional behaviours demonstrated by carbon nanotubes such as high thermal and electrical conductivities, high strength, high stiffness, and exceptional absorption properties account for its potential application in remediation process (Ralph, 2003).

The high adsorption capability of carbon nanotubes has been applied in the removal of heavy metals from water (Mansoori *et al.*, 2008). Single-wall carbon nanotubes (SWCNT), multi-wall carbon nanotube (MWCNTS) and hybrid carbon nanotubes (HCNTS) have been used in the removal of organic pollutants from water (Rizwan *et al.*, 2014). Sodium hypochlorite purified single-wall carbon nanotubes (SWCNTS) and multi-walls carbon nanotubes have been used to adsorb and remove zinc from water. Fluoride has been adsorbed and removed from drinking water by amorphous Al_2O_3 supported carbon nanotubes ($\text{Al}_2\text{O}_3/\text{CNTS}$). Similarly, aligned carbon nanotubes have also been used for the adsorption of fluoride from drinking water (Mansoori *et al.*, 2008). Carbon nanotubes (CNTs) modified with cyclodextrins (Co) such as CD-CO-hexamethylene-I toluene-diisocyanate polyurethanes have been developed and successfully applied in removing organic contaminants from water. Polymeric carbon nanotubes incorporated with calixarenes and thiacalixarenes have been tested for removing both organic pollutants (P-nitrophenol) and inorganic pollutants (Cd^{2+} and Pb^{2+}) from water (Rizwan *et al.*, 2014). Multiwall carbon nanotubes have also been used to remove nickel ion from water (Kandah and Meunier, 2007).

Dendrimers for surface water remediation

Dendrimers are highly branched polymers with relatively monodispersed macromolecules and controlled composition, with architecture comprising of nanoparticles features (Mansoori *et al.*, 2008). A dendrimer consists of three main components, (i) a central core, (ii) interior branch cells or radial symmetry, and (iii) a terminal branch cell or peripheral group (Under *et al.*, 2013). In dendrimers small molecules are linked together to produce larger polymeric molecules. Dendrimer nanostructure can be designed in such a way that it can enclose metal ions and zero-valent metals, enabling them to dissolve in suitable media or bind to appropriate surface (Mansoori *et al.*, 2008).

One of the most important applications of dendrimers is in environmental remediation. These nanostructures have been used in water treatment and in the removal of organic pollutants through simple filtration with TiO_2 porous ceramic filters (Rizwan *et al.*, 2014, Duran, 2008). Polyamidoamine (PAMANI) dendrimers have been effective in the removal of copper from water with subsequent regeneration of the dendrimer from the dendrimer Cu(II) complexes by ultrafiltration. Water insoluble diaminobutane poly(propylene imine) dendrimers were used to remove organic pollutants such as polycyclic aromatic hydrocarbons from water and produced ultra-pure water (Mansoori *et al.*, 2008). A dendrimer can be modified to produce a hybrid organic and inorganic filter module of high mechanical strength with high surface area (Guo *et al.*, 2012).

Titaniumdioxide (TiO_2) and wastewater remediation

Titaniumdioxide (TiO_2) is at the fore front in terms of wastewater treatment (Chong *et al.*, 2010). Surface modification of titanium dioxide nanoparticles have enhanced its surface chemistry leading to more surface adsorption and improved photocatalytic activities. The two forms of titanium dioxide (TiO_2) rutile and anatase were both used to remove phenol

from waste water. Immobilized titanium dioxide (TiO₂) nanoparticles have been used to remove butachlor (N – butoxymethyl -2-chloro-2, 6-diethyl(acetanidide) from waste water (Mansoori *et al.*, 2008). The use of immobilized titanium dioxide (TiO₂) in environmental remediation is significant because of its easy recovery.

Magnetic nanoparticles for waste water remediation

The response of materials to external magnetic fields differs depending on a number of factors, such as the atomic and molecular structures of the material, and the net magnetic field associated with the atoms. The magnetic movement in an atom comes from three basic areas, (i) the electron orbital motion, (ii) the change in orbital motion due to external magnetic field, (iii) and the spin of the electrons. Hund's rule indicates that electrons in atoms appear in pairs and that the paired electrons must have opposite spins which cancel their magnetic fields. Materials with unpaired electrons will have magnetic property and will be attracted to an external magnetic field based on these materials are classified into diamagnetic, paramagnetic and ferromagnetic. The ferromagnetic materials respond strongly to magnetic fields and retain their magnetic properties, in the absence of the external magnetic field. The magnetic property of these materials results from the presence of magnetic domains within their atoms and as a result transition metal ions such as iron, manganese, nickel and cobalt are ferromagnetic. (Mansoori *et al.*, 2008). Magnetic nanoparticles have different applications depending on the size and subsequent change in magnetic property.

One significant application of magnetic nanoparticle is in the area of magnetic separation, making it possible to separate specific substance from a mixture of different other substance. In a process referred to as “magnetically assisted chemical separation (MACS)” magnetic nanoparticles can be fixed to specific molecules, which can subsequently be isolated from waste water (Mansoori *et al.*, 2008). The toxic Cr (VI) ion have been removed and recovered from wastewater using nanoparticle adsorption and magnetic separation techniques. Magnetite magnetic nanoparticles have shown selective adsorption for Cr (VI) ion from waste water containing other ions such as Na⁺, Ca²⁺, Mg²⁺, Cu²⁺, Ni²⁺, NO₃⁻ and Cl⁻. Magnetic chitosan at pH range of 3-7 and temperature between 20-45°C is fast and efficient in the removal of Co (II) ion. Nickel ion has been removed from aqueous solution using magnetic alginate microcapsules (Mansoori *et al.*, 2008). Different kinds of magnetic nanoparticles were also employed for the removal of organic pollutants from aqueous solution (Mansoori *et al.*, 2008).

Nanoparticles and Groundwater Remediation

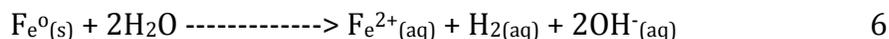
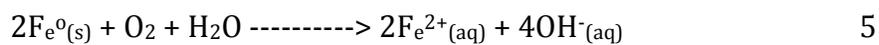
Nanoparticles are presently the most promising and emerging approach to groundwater remediation. These materials are currently gaining recognition of wider commercial application in ground water treatment (Bardos *et al.*, 2014, U.S EPA, 2014, Lowry, 2007). Nanoparticles are effectively used for *in situ* treatment of ground water by injecting the nanoparticles into a contaminated aquifer through injection well. The particles are then transported by ground water flow to the source of contamination. When these nanoparticles interact with the contaminants they sequester them through adsorption or redox reaction. The contaminants are immobilized or degraded to less harmful compounds (Lowry, 2007).

Zero-valent iron (ZVI) for groundwater remediation

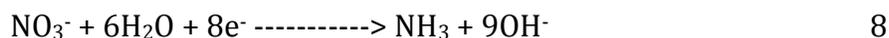
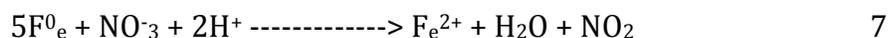
Zero-valent iron is the most widely used nanoparticle for ground water remediation and has significant benefits (Nowack, 2008, Tratnyek and Johnson 2006, Klimkova *et al.*, 2008),

Nanoscale zero-valent iron (nZVI) may be mixed or coated with another metal, such as Pd, Ag, or Cu, that act as catalyst in what is called a bimetallic nanoparticle (Karn *et al.*, 2009). It may also be emulsified with a surfactant and an oil, creating a membrane that enhance the nanoparticle's ability to interact with hydrophobic liquids and protects it against reaction with materials dissolved in water (Crane and Scott, 2012; U.S. EPA, 2012). Nanoscale zero-valent iron has been shown to be effective in the remediation of groundwater in porous soil (Mueller and Nowack, 2010). The highly toxic, mobile and predominant species of arsenic (As (III) and As (V) has been removed from ground water by nanoscale zero-valent iron (nZVI) (Rizwan *et al.*, 2014).

Several studies indicated that nZVI as a reactive barrier is very effective in the reductive degradation of halogenated solvents, such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes and other poly chlorinated hydrocarbons in ground water (Mueller and Nowack, 2010). Pd/Au nanoparticles have also been used to remove chlorinated compounds from ground water (Mansoori *et al.*, 2008). Emulsified modified zero-valent iron (EZVI) has been used in, *in situ* dehalogenation of dense, non-aqueous phase liquids (DNAPLs) containing trichloroethene (TCE) from groundwater (Mansooro *et al.*, 2008). The use of zero-valent iron (ZVI or Fe⁰) for *in situ* remedial treatment has been expanded to include all different kinds of contaminants (Mansoori *et al.*, 2008). Zero-valent iron (ZVI) removes contaminants by reductive dechlorination or by reducing to insoluble form, in the case of metal ions. It can also undergo redox reaction with dissolved oxygen in water.



Nitrogen oxidant also reacts with zero-valent iron, as illustrated by the de-nitrification of nitrate (NO₃⁻)



Nanopowder of zero-valent iron (ZVI or Fe⁰) was used for the removal of nitrate in water (Mansoori *et al.*, 2008). Nanoscale zero-valent iron (nZVI) appears to be useful for degrading organic pollutants as well as immobilizing or removing metals (Karn *et al.*, 2009, Theron *et al.*, 2008). Nanoscale zero-valent iron (nZVI) and other nanoparticle materials that do not require light can be injected underground for *in situ* ground water remediation within the contaminated zone.

Nanoparticles Toxicity

There is upraising concerns in connection with the use of nanoparticles and nanomaterials in environmental remediation. These concerns are based on possible toxicity and ecotoxicity of these nanoscale particles due to their large mobility, small size, insolubility and reactivity (Duran, 2008, Mueller and Nowack, 2010). The decreasing size of nanoparticles and their reactivity are two properties that account for their toxicity as smaller particles are often more toxic than larger ones (Oberdorster *et al.*, 2007). The smaller size of these particles make it possible for nanoparticles to be ingested, inhaled,

adsorbed through the skin and to be taken up by a wide variety of mammalian cell types (Oberdorster *et al.*, 2007). A lot of research is still going on to unveil the unknown about the toxicity of nanoparticles to humans and its effect on the environment (Nowack and Bucheli, 2007).

Conclusion

Presently, there is growing concern on the state of the environment as regarding to environmental pollution, as enormous amount of pollutants are released into the environment on daily basis from various sources. These pollutants contaminate the soil, water and air rendering them unfit for use. The advent of nanoparticles has opened a new leaf in environmental clean-up. The unique properties of these nanomaterials have been utilized in their application for environmental remediation. The search for a more potent, nontoxic and environmentally friendly nanoparticles is a continuous process and remains pertinent in this our present time. The use of nanoparticles for water and soil remediation is an underdeveloped area of research that calls for attention. The photocatalytic property, adsorption property and the redox processes of the relevant nanoparticles can be improved and enhanced by modifying and developing the existing nanoparticles and in the synthesis of new nanomaterials with exceptional properties to meet up with the current challenges of nanoparticles-materials in environmental remediation.

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