Nanotechnology in Groundwater Remediation

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Abstract- **Nanotechnology is a multidisciplinary field that has gained significant momentum in recent years. Nanoparticles are the key players that have promised many benefits through their nano-enabled applications in multiple sectors. This review summarizes the use of nanomaterials such as zero valent iron (nZVI) and carbon nanotubes (CNT) in environmental cleanup like ground water remediation for drinking and reuse. There are, however, concerns regarding the potential risks associated with the use of nanomaterials to the environment and human health. An understanding of the relationship between the properties of nanoparticles and their i*n vivo* effects would provide an effective strategy to tackle the deleterious effects.**

Index Terms- **Carbon Nanotube, Iron Nanoparticles, Nanoremediation, Toxicology.**

I. Introduction

In recent years, nanoscience and technology has introduced a new dimension to scientific disciplines and technology sectors due to its ability to exhibit super-functional properties of materials at nano-dimensions. There is a remarkable rise in research and development in all developed countries and many developing countries pertaining to this field. Organizations such as Universities, public research institutes and industrial R&D laboratories 1focus strongly on this new technology to benefit from its scientific and technological advantages [1]. Nanotechnology is a multidisciplinary field that applies engineering and manufacturing principles at molecular level [2]. In broad terms, nanotechnology is the development and use of techniques to study physical phenomena and construct structures in the physical size range of 1–100 nanometers (nm) as well as the incorporation of these structures into applications [3]. The past couple of decades have been dedicated to the synthesis, characterization, and application of nanomaterials

Nanotechnology has revolutionized a multitude of sectors such as the electronic, chemical, biotechnology and biomedical industries [4]. Whereas various industries produce different varieties of nanomaterials there are increasing efforts to use nanotechnology in environmental engineering to protect the environment by pollution control, treatment and as a remedial measure to long term problems such as contaminated waste sites [5]. This technique has proved to be an effective alternative to the conventional practices for site remediation. Further research has also been carried out and its application is found useful in the treatment of in drinking water.

Despite their potential benefits, there is a major concern over the exposure of humans and environment to nanoparticles that may exert deleterious effects. Toxicological risk assessment demands information on both exposure and uptake of nanoparticles and their immediate effects once they enter the human system. But, the available data on these topics are very limited to form conclusions and recommendations [6]. In response to these concerns, various scientific community is gaining knowledge in exposing their toxicological effects on human [7] and ecological health [8].This review focuses on various research and experimental works regarding the use of nanotechnology for environmental cleanup, particularly on their application in ground water and drinking water remediation with the help of nanoparticles such as Zero valent iron (nZVI) and Carbon Nanotubes (CNT). It also focuses on the deleterious effects of using these nanoparticles.

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II. Site Remediation

In response to a growing need to address environmental contamination, many remediation technologies have been developed to treat soil, leachate, wastewater and groundwater contaminated by various pollutants, using in situ and ex situ methods [9]. In particular, a contaminated site may require a combination of procedures to allow the optimum remediation for the prevailing conditions. Chemical, physical and biological technologies may be used in accordance with one another to reduce the contamination to a safe level. Hence, for a successful treatment, proper selection, design, and adjustment of the remediation technology's operations should be carried out based on the properties of the contaminants and soils and on the performance of the system [10]. Previously, conventional methods include primarily pump and treat operations. This method involves extraction of groundwater through wells and trenches and treating groundwater by above-ground (*ex situ*) processes such as air stripping, carbon adsorption, biological reactors or chemical precipitation [11]. But unfortunately, most of these methods produce highly contaminated waste which then has to be disposed off, resulting in high operation time [12].

A common type of *in situ* or below-ground remediation method used for cleaning up contaminated groundwater is the permeable reactive barrier (PRB). PRBs are treatment zones composed of materials that degrade or immobilize contaminants as the groundwater passes through the barrier. They can be installed as permanent, semi- permanent or replaceable barriers within the flow path of a contaminant plume. The material chosen for the barrier is based on the contaminant(s) of concern [11]. One drawback of PRBs is that they can only remediate contaminant plumes that pass through them; they do not address dense non aqueous-phase liquids NAPLs (DNAPLs) or contaminated groundwater that is beyond the barrier.

III. NANOREMEDIATION

In recent years, nanoremediation has become the main focus of research and development. There is great potential to use this technology to clean up the contaminated sites and protect the environment from pollution. This eco-friendly technology is considered to be an effective alternative to the current practices of site remediation. Nanoremediation methods involve application of reactive materials for the detoxification and transformation of pollutants. These materials initiate both chemical reduction and catalysis of the pollutants of concern [5]. The unique properties of nanomaterials make them best suited for *in situ* applications. Their small size and novel surface coatings enable them to achieve farther and wider distribution when compared to large-sized particles [8].

The use of nanotechnology for site remediation could potentially provide a solution for faster and more cost-effective site remediation. Many different nanomaterials have been evaluated for use in nanoremediation. They include nanoscale zeolites, metal oxides, carbon nanotubes, noble metals and titanium dioxide. Of these, nanoscale zero-valent iron (nZVI) is currently widely used in groundwater remediation [5]. In addition to groundwater remediation, nanotechnology has also contributed towards reducing the presence of non-aqueous phase liquids (NAPL). For this purpose, a material utilizing nano-sized oxide is used *in situ* to clean up heating oil spills from underground oil tanks. Compared to previous remediation methods, this approach provided an overall reduction in the contaminant levels [13].

IV. NANOSCALE IRON NANOPARTICLE (NZVI)

Iron nanoparticles are an attractive component for nanoremediation. Iron at the nanoscale was synthesized from Fe (II) and Fe (III), using borohydride as the reductant. Nanoscale zero-valent iron particles range from 10 to 100 nm in diameter. They exhibit a typical core shell structure. The core consists primarily of zero-valent or metallic iron whereas the mixed valent [i.e., Fe (II) and Fe (III)] oxide shell is formed as a result of oxidation of the metallic iron. Iron typically exists in the environment as iron (II) - and iron (III)-oxides [14]. nZVI are generally preferred for nanoremediation because of large surface area of nanoparticles and more number of reactive sites than micro-sized particles [8] and it posses dual properties of adsorption and reduction, as shown in figure 1. This enables it to be used for the remediation of wide range of contaminants present *in situ*. Moreover, when zero valent iron was allowed greater access to the contaminant site, it was found to give out less amount of hazardous waste during the treatment process [15]. Zero valent iron can also be modified based on the contaminants present. It could be modified to include catalysts like palladium, coatings such as polyelectrolyte or triblock polymers [16] or can be encased in emulsified vegetable oil micelles [17].

In 2003, nanoscale iron particles were investigated for their effect on a number of common pollutants in groundwater and contaminated soil. The results showed that the nanoscale iron particles were highly effective for the transformation and detoxification of a number of pollutants especially chlorinated organic solvents, organochlorine pesticides and polychlorinated biphenyls (PCBs) [18].

The large specific surface area nanoparticles are significantly more active than larger particles of the same material to remove arsenic from ground water [19].This was evident as the nanoparticles were able to bind arsenic five to ten times more than micro-sized particles.

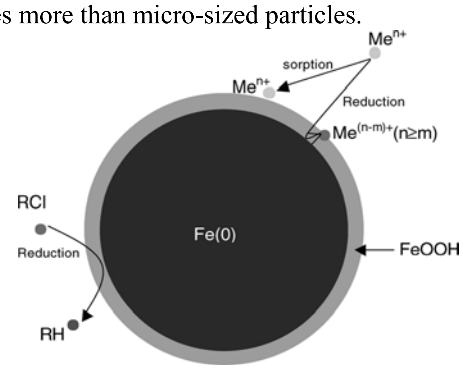

Fig.1 Schematic diagram of Zero valent Iron

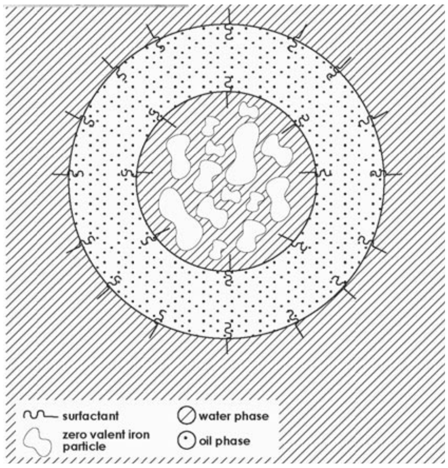

Fig. 2. Magnified Image of an Emulsified Zero Valent Iron (EZVI)

To remove the contaminants, the super paramagnetic property of iron nanoparticle was manipulated and retrieved using a magnetic field without the negligence of being released into the environment. Laboratory tests have indicated that in excess of 99% of arsenic in water samples can be removed using 12nm diameter iron oxide nanoparticles [20].

For the treatment of trichloroethane (TCE), a hazardous organic contaminant present in water, the surface of the zero valent iron nanoparticle is modified to contain an oil-liquid membrane. This oil-liquid membrane which is generally composed of food-grade surfactant, biodegradable oil and water is hydrophobic and forms an emulsion with ZVI. This is termed as emulsified zero valent iron (EZVI) [21]. Since all DNAPLs (dense non-aqueous phase liquids), such as the trichloroethane are hydrophobic, the emulsion is miscible with the contaminant, allowing an increased contact between TCE DNAPL and the ZVI present within the oil emulsion droplet [22]. Whereas the ZVI in the emulsion remains reactive, the chlorinated compounds are continuously de-chlorinated within the aqueous emulsion droplet which produces a concentration gradient within the oil membrane, which in turn acts as a driving force to allow additional TCE migration into the membrane and additional degradation is carried out. A potential benefit of EZVI over NZVI for environmental applications is that the hydrophobic membrane surrounding the NZVI protects it from other groundwater constituents, such as some inorganic compounds, that might otherwise react with the NZVI, reducing its capacity or passivating the iron. [23].

Another type of nanoparticle used for environmental application in the Bi metallic nanoparticle (BNP).Bi metallic nanoparticle consist of elemental iron or other metals in conjunction with a metal catalyst, such as platinum (Pt), gold (Au), nickel (Ni), and palladium [22]. The combination of metals to form a nanoparticle increases the kinetics of oxidation-reduction (redox) reaction, therefore catalyzing the reaction.

The most commonly used and commercially available BNPs are the Palladium and Iron BNPs (Pd/Fe). The surface area normalized rate constant of BNPs of iron combined with palladium (NZVI/Pd) was two orders of magnitude higher than that of MZVI [24]. Palladium and Iron BNPs are generally used in the removal of TCE (Trichloroethane). In one of the studies, palladium converts TCE into ethane with minimal formation of vinyl chloride and other chlorinated intermediates that often occur with anaerobic bioremediation and with iron metal [25].

A. Risks

Apart from using nZVI for various classes of contaminants, there is little information or research being conducted based on the potential toxicological effect they might pose. There are insufficient data on the potential for accumulation of nanoparticles in environmentally relevant species [26] and there have been few studies on the effects of many nanoparticles on environmental microbial communities [3]. Under standard environmental conditions i.e., using aerated water and pH ranging from 5 to 9, Fe2+ will readily and spontaneously oxidizes to form Fe3+ and precipitate out of the groundwater as insoluble iron oxides and oxy-hydroxides.

Ongoing studies are evaluating surface coatings and other modifications that would maximize subsurface mobility of nZVI [27]. Whereas increased mobility would allow more efficient remediation, it could also result in the possibility of the nanomaterials migrating beyond the contaminated plume area, seeping into drinking water aquifers or wells or discharging to surface water during the remediation process. Nanoparticles may have a negative impact on human health when nanoscale particles are inhaled, absorbed through skin or ingested [26]. Because of their small size, the particles have the potential to migrate or accumulate in places that larger particles cannot. One such area is the alveoli of lungs, hence potentially increasing toxicity [28].

Problems of toxicity and safety have limited the use of nanotechnology for remediation by some private-sector companies. A work done by DuPont, for example, has ruled out the use of nZVI for site remediation at any of its sites until problems concerning fate and transport have been more thoroughly researched. Their research has cited questions of post remediation persistence and potential human exposure to the particles as areas of particular concern during nanoremediation [29].

V. Carbon nanotubes (CNT)

In recent years, nanotechnology has introduced different types of nanomaterials to the water industry and has produced some promising outcomes .Since its discovery, carbon nanotubes have attracted great attention due to its unique properties. CNTs are nanomaterials that are rolled into a tube and are classified as single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNTs).

According to the carbon atom layers in the walls of the nanotubes [30]. Removal of contaminants and recycling of the purified water would provide significant reductions in cost, time and labor to the industry and result in improved environmental stewardship [31]. One such nanomaterial is the carbon nanotube (CNT). These nanosorbents are increasingly attractive since their discovery, due to their exceptional adsorption properties, their ability to be attached to a functional group to increase the affinity towards the target molecule [31].

The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface have a strong interaction with other molecules or atoms, which make CNTs a promising adsorbent material substituted for activated carbon in many ways [32]. They are utilized for the removal of heavy metals like Cr^{3+}, Pb^{2+}[33], and Zn^{2+} [34], metalloids such as arsenic compounds [35], organics, biological impurities [31], and removing many kinds of organic and inorganic pollutants such as dioxin [36] and volatile organic compounds[37]. On comparing CNTs with other adsorbents, the researchers assert that nCNTs are effective adsorbents for environmental applications [9]. The carbon nanotubes (CNTs) are unique and one-dimensional macromolecules that posses high chemical and thermal stability [38]. This property of the nanoparticles have been manipulated for the treatment of natural organic matter (NOM) which could produce carcinogenic agents [39] and even enhance the bacterial regrowth and bio-film formation [40]. Hence, thermally treated CNTs were employed for the treatment of natural organic matter to realize effective absorption. Thus, CNTs posses all the essential properties to maintain water of high quality. Here we look at various methods in which CNTs can be used effectively to retrieve the various types of contaminants present in water for drinking and for reuse.

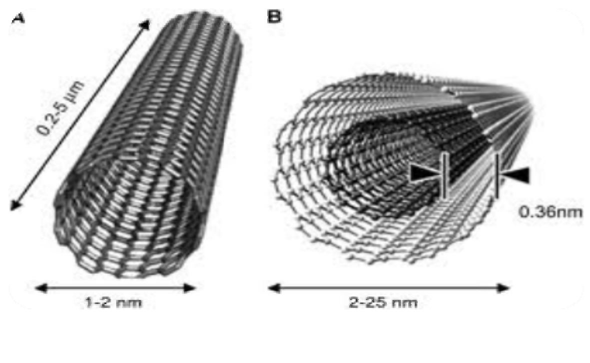

Fig. 3. A schematic Representation of Carbon Nanotube and Multi walled Carbon Nanotube

For ground water remediation, there are stringent regulation methods. Any increase in the discharge of heavy metals into the aquatic environment is toxic as they can accumulate in the living tissues. Hence they have to be removed from water. This is done using multi-walled carbon nanotubes (MWCNTs). To increase the absorption capacity of MWCNTs, it is oxidized with nitric acid resulting to which a higher level of adsorption was achieved. According to Li and co-workers (2003), the sorption of Pb (II), Cu (II) and Cd (II) on to MWCNTs were 3-4 times larger than those of powdered activated carbon and granular activated carbon which are the two conventionally used sorbents in water purification.

Some studies showed that un-derivatized CNTs tend to be water insoluble and toxic. Carbon nanotubes, in order to be highly dispersed in water and to be easily separated from their dispersion for their re-use, are functionalized with various functional groups (e.g. hydroxyl, carboxyl, amines, etc.) to increase their water solubility and biocompatibility in some cases [41, 42]. In 2006, Jin and co-workers functionalized MWCNTs with Fe nanoparticle for their effective disposal of aromatic compounds which are considered as carcinogens. In addition to this, to make CNTs water soluble, it is made to decompose thermally with azodiisobutyro nitrile (AIBN) and refluxed with sodium hydroxide to form nanoparticle functionalized water-soluble MWNTs (Fe-MWNTCH2COONa). According to the analytical data the adsorbed percentages of benzene, toluene, dimethylbenzene and styrene were found to be 79%, 81%, 83% and 88% respectively, which showed that Fe-MWNT-CH2COONa can be used as a potential sorbent for the removal of benzene and its aromatic compounds. Fe-MWNT-CH2COONa could also be reused due to their exceptional magnetic separation capability [43].

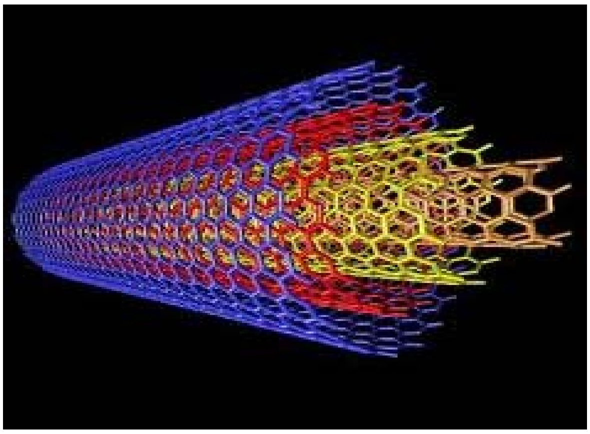

Fig. 4. Schematic Representation of Multi Walled Carbon Nanotube (MCNT)

A. Risks

The design and synthesis of biocompatible carbon nanotubes (CNTs), on the other hand, are very challenging. Only a few peer-reviewed studies of the toxicity of CNTs have been published by various researchers [44], [45], [46]. However, it has to be pointed out that metal-containing particles also exhibit a size dependent toxicity [47]. Thus, a key challenge will be to gain regulatory and public acceptance for using nanomaterials in water purification because of their unknown toxicity and environmental impact. Scientists have found that carbon nanotubes, if inhaled in large proportions, could be as dangerous as asbestos [48]. Researchers found carbon nanotubes causing the same kind of damage as asbestos in mice. According to Lam and its co-workers, CNTs are light and could get air borne and when it enters the lungs, lesions were formed and toxicity greater than that of quartz was observed [44]. Another set of experiments reveal that exposure to nanotubes on mice could cause mesothelioma, a cancer which affects the lung lining. All these factors have affected the use of these nanomaterials in nanoremediation by various organizations. Hence extreme degree of safety and caution must be maintained when carrying out experiments using carbon nanotubes (CNTs).

VI. CONCLUSION

The aim of this review is to give an overall perspective of the use of nanoparticles to solve potential issues such as treatment of contaminated water for drinking and reuse more effectively, than through conventional means. Nanoremediation has the potential to clean-up large contaminated sites in-situ, reducing clean up time and eliminating the need for removal of contaminants and hence reducing the contaminant concentration to near zero.

As highlighted, a great degree of care needs to be taken if it has to be implemented in real life scenarios to avoid deleterious effects. The success of the technique in field conditions is a factor of interdisciplinary work that is involved. The collaboration of chemistry, material science and geology is one of the key challenges of this research.

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