Original Article

Role of nanotechnology in water treatment and purification: Potential applications and implications

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Abstract

Nano-materials have gained special attention in water pollution mitigation researches since last decade. Two vital properties make nanoparticles highly lucrative as sorbents. On a mass basis, they have much larger surface areas compared to macro particles. They can also be enhanced with various reactor groups to increase their chemical affinity towards target compounds. Nanofiltration techniques are now widely used to remove cations, natural organic matter, biological contaminants, organic pollutants, nitrates and arsenic from groundwater and surface water. Nano-membranes are used to treat contaminated water by filtration or separation techniques. Nanosorbents are widely used as separation media in water purification to remove inorganic and organic pollutants from contaminated water. During the last decade, titanium dioxide (TiO_2) nanoparticles have emerged as promising photocatalysts for water purification. Consequently, different workers had adopted the methods such as chemical precipitation, sol–gel, vapour deposition, solvo thermal, solid state reaction etc. for the synthesis of some nanostructured mixed oxides, which can be effectively used for groundwater treatment. Nano-agglomerates of mixed oxides such as iron–cerium, iron–manganese, iron–zirconium, iron–titanium, iron–chromium, cerium-manganese etc. have been synthesized, thoroughly characterized in sophisticated instruments like SEM, TEM, FT-IR, AFM and successfully employed for water treatment. Among the available different technologies, adsorption is one of the best due to its easy handling, low cost and high efficiency. The environmental fate and toxicity of a material are critical issues in materials selection and design for water purification. The success of the techniques in field conditions is a factor of interdisciplinary works, which need successful collaboration of chemistry, material science and geology and bio-sciences.

1. Introduction:

Water is a mythical substance whose material existence is secondary compared to the symbolic value as it is manifested in our mind as the symbol of life. Sustainable supplies of clean water are vital to the world's health, environment and economy. Currently the human society is facing a tremendous crunch in meeting rising demands of potable water as the available supplies of freshwater are decreasing due to extended droughts, population growth, decline in water quality particularly of groundwater due to increasing groundwater and surface water pollution, unabated flooding and increasing demands from a variety of competing users. Water being a prime natural resource, a basic human need and a precious national asset, its use needs appropriate planning, development and management. Increasing population coupled with overexploitation of surface and groundwater over the past few decades has resulted in water scarcity in various parts of the world. Wastewater is increasing significantly and in the absence of proper measures for treatment and management, the existing freshwater reserves are being polluted. Increased urbanization is driving an increase in per capita water

consumption in towns and cities. Hence there is a need to recognize the requirement to manage existing water reserves in order to avoid future water strain. Today availability of safe drinking water is a concern. For almost all the water needs of the country, groundwater is by far the most important water resource. Worldwide, according to a United Nations Environment Programme (UNEP) study over 2 billion people depend on aquifers for their drinking water [1]. 40 per cent of the world's food is produced by irrigated agriculture that relies largely on groundwater [1]. Groundwater constitutes about 95 per cent of the freshwater on our planet (discounting that locked in the polar ice caps), making it fundamental to human life and economic development. However the ever increasing scarcity of groundwater coupled with diminishing water quality has posed a serious threat to the population especially the rural community and has forced everyone to look at treatment of groundwater because clean water is fast becoming an endangered commodity. The unabated use has taken a serious toll on the availability of groundwater resources and as such the world is facing a severe crunch in the availability of groundwater. So we have no other option to move from "groundwater development" to "groundwater management" which means that we have to move towards optimal usage of groundwater which would be sustainable in the long run. Today the onus is on everybody to provide safe drinking water and for that water treatment processes need to be developed that are easy to implement, cost effective and sustainable in the long run.

India is a vast country having diversified geological, climatological and topographic set-up, giving rise to divergent groundwater situations in different parts of the country. Unsustainable uses of resources and indiscriminate applications of pesticides, fertilizers, industrial pollutants are continuously disturbing the status of purity of groundwater. Shallow aquifers generally suffer from agrochemicals, domestic and industrial waste pollution. Major water pollutants include microbes (like intestinal pathogens and viruses), nutrients (like phosphates and nitrates), heavy metals and metalloids (like arsenic, lead, mercury), organic chemicals (like DDT, lubricants, industrial solvents), oil, sediments and heat. Virtually all industrial and goods-producing activities generate pollutants as unwanted by-products. Heavy metals can contaminate the aquifer and subsequently can bioaccumulate in the tissues of humans and other organisms. For example, more than 100 million people are living in the arsenic affected districts of India and Bangladesh. 9 districts out of 19 in West Bengal, 78 blocks and around 3150 villages are affected with arsenic-contaminated groundwater [2]. Pollutants can take years to reach the aquifers, but, once it reaches the water source, it is very difficult and costly to remove the pollutants. More than 80% of sewage in developing countries is discharged without proper treatment which can pollute the river systems, lakes and coastal water bodies [3].

In the present context the recent advancement of nanoscale science and engineering is opening up a hitherto unknown and novel gateway to the development and deployment of water purification processes which are in tune with the above mentioned parameters. Nanoscience is the study of phenomenon and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale [4]. Nanotechnology is the design, characterization, production and applications of structures, devices and systems by controlling shape and size at nanometer scale. In recent years, a great deal of attention has been focused onto the applicability of nanostructured materials as adsorbents or catalysts in order to remove toxic and harmful substances from wastewater [5]. Nano-materials had gained special attention since last decade because the materials of such kind posses unique properties than the bulk materials. Like different nano materials, single and multi metal or doped metal oxides are also subject of much interest since that materials posses high surface-to-volume ratio, enhanced magnetic property, special catalytic properties etc [6]. Consequently, different methods viz. chemical precipitation, sol-gel, vapour deposition, solvo thermal, solid state reaction etc were adopted for the synthesis of specified oxides by various workers [7]. Nano-enabled technologies for water treatment are already on the market. Nanofiltration currently seeming to be the most mature and eco-friendly technology and many more are on their way of development and applications. The environmental fate and toxicity of any material are critical issues in choice of materials for water purification. Nanotechnology while being questionably better than other techniques used in water treatment, the knowledge about the environmental fate, transport and toxicity of nanomaterials is still inadequate.

The high surface area and surface reactivity compared with granular forms enable the nanoparticles to remediate more material at a higher rate and with a lower generation of hazardous by-products. Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nanosorbents, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, nanotubes, magnetic nanoparticles, granules, flake, high surface area metal particle supramolecular assemblies with characteristic length scales of 9-10 nm including clusters, micromolecules, nanoparticles and colloids have a significant impact on water quality in natural environment [8]. The defining factor which characterizes the capability of nanoparticles as a versatile water remediation tool includes their very small particle sizes (1–100 nm) in comparison to a typical bacterial cell which has a diameter on the order of 1 μm (1000 nm). Hence nanoparticles can be transported effectively by the groundwater flow [9]. They can also remain in suspension for sufficient time in order to launch an in situ treatment sphere. As a result, nanoparticles can be anchored onto a solid matrix such as a conventional water treatment material like activated carbon and/or zeolite for enhanced water treatment [9].

2. Role of nanomaterials in water treatment and purification:

Nanomaterials are fast emerging as potent candidates for water treatment in place of conventional technologies

which, notwithstanding their efficacy, are often very expensive and time consuming. This would be in particular, immensely beneficial for developing nations like India and Bangladesh where cost of implementation of any new removal process could become an important criterion in determining its success. Qualitatively speaking nanomaterials can be substituted for conventional materials that require more raw materials, are more energy intensive to produce or are known to be environmentally harmful. Employing green chemistry principles for the production of nanoparticles can lead to a great reduction in waste generation, less hazardous chemical syntheses, and an inherently safer chemistry in general. However, to substantiate these claims more quantitative data is required and whether replacing traditional materials with nanoparticles does indeed result in lower energy and material consumption and prevention of unwanted or unanticipated side effects is still open to debate. There is also a wide debate about the safety of nanoparticles and their potential impact on the environment. There is fervent hope that nanotechnology can play a significant role in providing clean water to the developing countries in an efficient, cheap and sustainable way. On the other hand, the potential adverse effects of nanoparticles cannot be overlooked either. For instance the catalytic activity of a nanoparticle can be advantageous when used for the degradation of pollutants, but can trigger a toxic response when taken up by a cell. So this Janus face of nanotechnology can prove to be a hurdle in its widespread adoption. However as mentioned before nanotechnology can step in a big way in lowering the cost and hence become more effective than current techniques for the removal of contaminants from water in the long run. In this perspective nanoparticles can be used as potent sorbents as separation media, as catalysts for photochemical destruction of contaminants; nanosized zerovalent iron used for the removal of metals and organic compounds from water and nanofiltration membranes.

3. Mechanisms of removing pollutants from wastewater by nanomaterials:
Nanosorbents:

Two vital properties make nanoparticles highly lucrative as sorbents. On a mass basis, they have much larger surface areas compared to macro particles. They can also be enhanced with various reactor groups to increase their chemical affinity towards target compounds [10]. These properties are increasingly being exploited by workers to develop highly selective and efficient sorbents for removal of organic and inorganic pollutants from contaminated water. Many materials have properties dependent on size. Hematite particles with a diameter of 7 nm, for example, adsorbed Cu ions at lower pH values than particles of 25 or 88nm diameter, indicating the enhanced surface reactivity for iron oxides particles with decreasing diameter [11].

Peng et al. (2005) have developed a novel sorbent with high surface area (189 m^2/g) consisting of cerium oxide supported on carbon nanotubes (CeO$_2$-CNTs). They showed that the CeO$_2$-CNT particles are effective sorbents for As(V) [12]. This goes to show that how chemically modified nanomaterials can enhance the adsorption capacity of a traditional substance. Deliyanni et al. (2003) have also synthesized and characterized a novel As(V) sorbent consisting of akaganeite [β-FeOOH] nanocrystals, for the removal of metals and other inorganic ions, mainly nanosized metal oxides [13]. Equilibrium adsorption of As(III) and As(V) by nanocrystalline TiO$_2$ occurred within 4 hours and the adsorption followed pseudo-second-order kinetics in experiments conducted by Peng et al. (2005) [12]. Bang et al. (2005) reported that equilibrium was reached in 63 minutes for adsorption of As(V) adsorption and 240 minutes for adsorption of As(III) [14]. Manna et al. (2004) investigated the removal of As(III) using a synthesized crystalline hydrous titanium dioxide. They found that 70% of As(III) adsorption occurred within the first 30 minutes of contact time [15]. Nano-agglomerates of mixed oxides such as iron–cerium, iron–manganese, iron–zirconium, iron–titanium, iron–chromium, cerium–manganese etc. have been synthesized and successfully employed for pollutant removal (i.e. arsenic, fluoride etc.) from aqueous solutions [16]. Metals such as zinc and tin possess similar reduction capabilities of iron [16]. Like iron, these metals are converted to metal oxides in the decontamination process. Other metals have been combined with iron as well to produce similar results. Both iron-nickel and iron-copper bimetallic particles have been demonstrated to degrade trichloroethane and trichloro--ethene [17]. Another example is iron-platinum particles, which possess similar capabilities in degrading chlorinated benzene [17]. The photo-oxidation of As(III) to As(V) in the presence of TiO$_2$ and light and subsequent adsorption into TiO$_2$ has also been reported. Bissen et al. (2001) have showed that photo-oxidation of As(III) to As(V) occurs within minutes [18]. No reverse reaction of As(V) to As(III) was observed, and while As(III) was oxidized by UV light in the absence of TiO$_2$, the reaction was way too slow to be feasible in water treatment. The reaction rate did not depend on the pH of the solution [18]. Peng et al. (2005) reported that rapid photo-oxidation of As(III) to As(V) occurred in the presence of sunlight, nanocrystalline TiO$_2$, and oxygen. In natural groundwater, Peng et al. believed that oxidation of As(III) to As(V) and subsequent adsorption of As(V) onto TiO$_2$ would completely eradicate arsenic at slightly acidic pH values [12].

Carbon is a versatile adsorbent that is heavily used in the removal of various pollutants including heavy metals from aqueous solutions. Graphene is the latest member of the carbon family in research and is believed to be one of the most potential materials for water treatment [19]. Graphene is a flat, sp^2-hybridized, two-dimensional honeycomb arrangement of carbon atoms with single carbon atom thickness [20]. Graphene and its composites offer utility in several applications due to its unique two-dimensional nature and associated band structure. Features like large surface area and presence of surface functional groups make them attractive adsorbent candidates for water purification [21]. RGO-magnetite and GO-ferric hydroxide composites were used for the removal of arsenic from water [22,23]. Iron based oxides and hydroxides are already

proved as effective materials for removing arsenic from drinking water [24]. RGO and GO supported materials have higher binding capacity compared to those free nanoparticles. Interestingly, reduced graphene oxide also has antibacterial property and this property may help in preventing the development of biofilm on the filter surface due to bacterial growth, which can cause unwanted tastes and odors or prematurely clogging of filters [25].

Nanofiltration:

Membrane processes such as nanofiltration (NF) are emerging as key contributors to water purification [26]. Nanofiltration membranes (NF membranes) are widely used in water treatment for drinking water or wastewater treatment. It is a low pressure membrane process that separates materials in the 0.001-0.1 micrometer size. NF membranes are pressure-driven membranes with properties between those of reverse osmosis and ultra filtration membranes and have pore sizes between 0.2 and 4 nm. NF membranes have been shown to remove turbidity, microorganisms and inorganic ions such as Ca and Na. They are used for softening of groundwater (reduction in water hardness), for removal of dissolved organic matter and trace pollutants from surface water, for wastewater treatment (removal of organic and inorganic pollutants and organic carbon) and for pretreatment in seawater desalination. Bruggen & Vandercasteele (2003) have studied the use of nanofiltration to remove cations, natural organic matter, biological contaminants, organic pollutants, nitrates and arsenic from groundwater and surface water [27]. Favre-Reguillon et al. (2003) found that nanofiltration can be used to remove minute quantities of U(VI) from seawater [28]. Mohsen et al. (2003) have evaluated the use of nanofiltration to desalinate water [29]. They found that nanofiltration in combination with reverse osmosis could effectively render brackish water potable. An improvement in water quality was shown by Peltier et al. (2003) for a large water distribution system using nanofiltration [30]. Carbon nanotubes filters are also gaining prominence in water treatment processes. Srivastava et al. (2004) recently reported the successful fabrication of carbon nanotube filters [31]. These new filtration membranes consist of hollow cylinders with radially aligned carbon nanotube walls. They showed that the filters were effective at removing bacteria (Escherichia coli and Staphylococus aureus) from contaminated water. The carbon nanotube filters are readily cleaned by ultrasonication and autoclaving.

Nanoceramic filters are a mixture of nanoalumina fiber and micro glass with high positive charge and can retain negatively charged particles. Nanoceramic filters have high efficiency for removing virus and bacteria. They have high capacity for particulates and less clogging and can chemisorb dissolved heavy metals [4].

Nanoscale Zerovalent Iron:

Iron nanoparticles are quite useful component for nanoremediation. Iron at the nanoscale was synthesized from Fe (II) and Fe (III), using borohydride as the reductant. The size of the nanoscale zero-valent iron particles are 10-100 nm. in diameter. They have 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. Nanoscale Zerovalent Iron is generally preferred for nanoremediation because of large surface area of nanoparticles and more number of reactive sites than microsized particles and it posses dual properties of adsorption and reduction [32].

The use of Nanoscale Zerovalent Iron (nZVI) for groundwater purification has been the most widely investigated environmental nanotechnological technique. It has been established that nanoscale metallic iron is very effective in destroying a wide variety of common contaminants such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides and dyes [9]. The basis for the reaction is the corrosion of zerovalent iron in the environment:

$$2Fe^0 + 4H^+ + O_2 \longrightarrow 2Fe^{++} + 2H_2O$$
$$Fe^0 + 2H_2O \longrightarrow Fe^{++} + H_2 + 2OH-$$
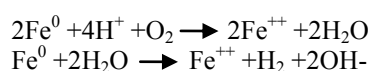
It has been found that nZVI can reduce not only organic contaminants but also inorganic anions like nitrate, perchlorate, selenate, arsenate, arsenite and chromate. The reaction rates for nZVI are several times faster and also the sorption capacity is much higher compared to normal granular iron. nZVI is also capable in removing dissolved metals from solution, e.g. Pb and Ni. The metals are either reduced to zerovalent metals or lower oxidation states [33]. Typically, nZVI can be prepared by using sodium borohydride as the principle reductant. For example, $NaBH_4$ (0.2 M) is added into $FeCl_3.6H_2O$ (0.05 M) solution (1:1 volume ratio). Ferric iron is reduced by the borohydride according to the following reaction [34]:

$$4Fe^{3+} + 3BH^{4-} + 9H_2O \rightarrow 4Fe^0\downarrow + 3H_2BO^{3-} + 12H^+ + 6H_2$$
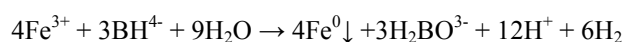
Permeable Reactive Barrier (PRB) technology is a novel groundwater remediation method which enables physical, chemical or biological in situ treatment of contaminated groundwater by means of reactive materials [35]. Granular ZVI in the form of reactive barriers has been used for many years at numerous sites all over the world for the remediation of organic and inorganic contaminants in groundwater [11]. In recent years nZVI have gained ground as attractive candidates using this technology. The reactive materials are placed in underground trenches downstream of the contamination zone forcing it to flow through them and by doing so, the contaminants are treated without water excavation. Generally, this cost-effective removal technology causes less environmental harm than other methods.

4. Removal of nanoparticles after water treatment:

The use of nanoparticles in environmental applications will invariably lead to the release of nanoparticles into the environment. Assessing their potential risks in the environment requires an understanding of their mobility,

bioavailability, toxicity and persistence. Little is known about the possible exposure of aquatic and terrestrial life to nanoparticles in water and soil. The rapidly growing use of engineered nanoparticles in a variety of industrial scenarios and their potential for wastewater purification and drinking water treatment raise the inevitable question how these nanoparticles can be removed in the urban water cycle. Traditional methods for the removal of particulate matter during wastewater treatment that have been in vogue include sedimentation and filtration. However, due to the small sizes of nanoparticles the sedimentation velocities are relatively low and significant sedimentation will not occur as long as there is no formation of larger aggregates [36]. Common technologies such as flocculation might be inappropriate to remove nanoparticles from water, which points to the need of finding new solutions to the problem. Till now, membrane filtration (e.g. nanofiltration and reverse osmosis) has been already applied for the removal of pathogens from water [37]. Hence, this technique can also be used for the removal of nanoparticles. Most nanoparticles in technical applications today are functionalized in nature and therefore studies using virgin nanoparticles may not be relevant for assessing the behaviour of the actually used particles. Functionalization is often used to decrease agglomeration and therefore increase mobility of particles. Unfortunately little is known to date about the influence of functionalization on the behaviour of nanoparticles in the environment.

5. Conclusion:

While nanotechnology is considered to be the new buzzword by many in the scientific community, information regarding the subject remains largely dispersed and fragmented due to the relative novelty of the technology. But the increasing trends of researches which have been discussed so far have made it clear that nanotechnology holds an immense potential to be developed into a very potent water treatment tool of the 21st century. In fact nanomaterials and their various incarnations are the drivers for the nanotechnology revolution. Nanoparticles in particular will have important impacts on various fields of environmental technology and engineering not least in water treatment. However most of techniques for the treatment of wastewater involving nanotechnology so far have only been investigated in laboratory scale and not all of them are likely to be feasible alternatives for existing treatment technologies mainly perhaps due to economic reasons. This makes it difficult to predict what the future holds for us at this stage concerning this nascent technology. Also the incorporation of nanomaterials into existing water purification systems is another key challenge. Membrane processes such as RO, NF are becoming the standardised water purification techniques for public utilities and industry because they are flexible, scalable, modular and relatively easy to operate and maintain. Thus further laboratory investigations and pilot scale testing will be needed to integrate novel nanostructured membranes into existing water purification systems. Also the environmental fate and toxicity of a material are areas of concern in material selection and design for water purification. Not much is known about the environmental fate, transport and toxicity of nanomaterials. Thus it should be borne in mind that nanotechnology can become a double edged sword and each positive and desired property of nanomaterials could pose a risk to the environment. Thus a careful weighing up of the opportunities and risks of nanotechnology with respect to their impact on the environment is therefore needed. No systematic investigations regarding the stability of nanomaterials in natural and engineered environmental systems have been carried out till date to the best of our knowledge. On a positive note, due to their extremely high potential in combination with the high specificity, nanoparticles can be developed into ideal candidates for water treatment and may contribute to solving future challenges in the area of water treatment technologies. Thus nanotechnology holds a lot of promise in the remediation of groundwater and for this there is further scope in research and development.

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