**Chapter 1**

INTRODUCTION

Water has always played a prominent role in human civilization. When people first began settling in one place and growing crops for sustenance, it was invariably near water sources like rivers, lakes or ground water springs. Water was needed for drinking, preparing food, bathing, cleaning, irrigating crops and a variety of other tasks, so it was important to have ready access to this resource. The water sources used for supplying water were not always clean and water was treated in one way or other to improve smell, taste and clarity or to remove disease causing pathogens, throughout the recorded history.

Water treatment describes those processes used to make water more acceptable for a desired end use. It may be for domestic, industrial processes, medical and many other uses. The goal of all water treatment processes is to remove existing contaminants so that the water becomes fit to use.

Water treatment includes treating water before its use and treating waste water generated after use. The latter includes sewage or domestic, agriculture or industrial waste water treatment.

Many methods are available for the above types of water treatment processes. All have their own merits and demerits, ease of use, economics, efficiency and end use which drive their selection.

In recent years nanotechnology has entered the sphere of water treatment processes. Many different types of nanomaterials are being evaluated and also being used in water treatment processes. Nanotechnology holds great promise in desalination, purification and waste water treatment. Desalination is a key market area. Vast majority of the world’s water is salt water, and though technology has existed for years that enables the desalination of ocean water, it is often a very energy intensive procedure and therefore expensive. However, as discussed below, nanotechnology applications can greatly reduce the costs of desalination. Nanotechnology is also being applied to the purification of water used for human consumption and in the production of ultrapure water required for certain manufacturing processes. Finally, as will be discussed below, nanotechnology has provided several applications that can be used to treat wastewater, making the recycling of water a viable and cost efficient way to address water supply shortages.

**Chapter 2**

Nanotechnology and its applications in Water treatment

2.1 Nanotechnology:

Nanotechnology is the study of manipulating matter at atomic and molecular scale. It deals with structures sized between 1 to 100nm and involves developing materials or devices with this size. Substances or materials generated having nanoscale dimensions are referred to as ‘nanomaterials’. There are generally two categories of nanomaterials: fullerenes and nanoparticles. [1]

A fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are called buckyballs. Cylindrical ones are called carbon nanotubes or buckytubes.The carbon nanotubes have a lenghth to diameter ratio of 132,000,000:1. Have diameter of order 1nm and length upto 18cm. They exhibit extraordinary strength and unique electrical properties. They are categorized as single walled and multiwalled nanotubes. [2]

A nanoparticle is a metallic, semiconductor or oxide particle having dimensions between 1 to100nm. They are having a large surface area, very reactive and exhibit different properties compared to the bulk material of the same substance. They exhibit very interesting mechanical, magnetic, optical, chemical and other properties.

2.2 Nanotechnology in water treatment:

Recent advances in nanoscale science and engineering are providing unprecedented opportunities to develop more cost effective and environmentally acceptable water purification processes. It is suggested that many of the issues involving water quality could be resolved using the products resulting from the developments in nanotechnology. Development of affordable novel technologies to desalinate water are among the most exciting and promising features of nanotechnology. Utilization of specific nanoparticles either embedded in membranes or on other structural media that can effectively, inexpensively and rapidly render unusable water is being explored at a variety of institutions. Innovative use of nanoparticles for the treatment of industrial waste water is another potentially useful application. Many factories generate large amounts of wastewater. Removal of contaminants and recycling of the water would provide significant reductions in cost, time and labour to industry. Aquifier and groundwater remediation are also critical issues becoming more important as water supplies steadily decrease and demand continues to increase. Here too nanotechnology is showing promising results.

Many types of nanomaterials are being evaluated and used in purification of water contaminated with toxic metal ions, radionuclides, organic and inorganic solutes, bacteria and viruses.

The classes of materials being evaluated as functional materials for water purification are metal containing nanoparticles, fullerenes, zeolites and dendrimers. These have a broad range of physicochemical properties that make them particularly attractive as separation and reactive media for water treatment. The nanoparticles and fullerenes have been discussed above.

Zeolites are microporous, alluminosilicate minerals commonly used as commercial adsorbents. Zeolites have a porous structure that can accommodate a wide variety of cations such as Na+, K+, Ca2+, Mg2+ and others. These positive ions are rather loosely held and can be exchanged for others in a contact solution. They can be acquired from natural sources or fabricated in laboratories. Synthetic zeoloites are usually made from silicon-alluminium solutions or coal fly ash and are used as sorbents or ion exchange media in cartridge or column filters. Nanoparticles of zeolites are being evaluated for the water treatment processes. [3]

Dendrimers are repeatedly branched, roughly spherical large molecules. It is symmetric around the core and often adapts spherical three-dimension morphology. A Dendron usually contains a single chemically addressable group called the focal point. The properties of dendrimers are dominated by the functional groups on the molecular surface. Dendrimers can be considered to have three portions a core, an inner shell and an outer shell. Ideally a dendrimer can be synthesized to have different functionality in each of these portions to control properties such as solubility, thermal stability and attachment of compounds for particular applications. Dendrimer based nanomaterials are being evaluated and are discussed later. [4]

**Chapter 3**

NANOMATERIALS IN WATER TREATMENT SYSTEMS

3.1 Nanofilters:

Membrane processes play an important role in water purification, since conventional water treatment techniques such as coagulation, flocculation, sedimentation, activated carbon adsorption are not always able to remove organic pollutants to prescribed specifications. Because membrane components are considered key components of advanced water purification and desalination technologies, there is a continuous search for new material and technology for membrane fabrication. In this regard nanomaterials (e.g. carbon nanotubes, dendrimers) are contributing to the development of more efficient and cost effective water filtration processes. Nanofiltration is one of the four membrane technologies, which utilize pressure to effect separation of contaminants from water streams. The other three are microfiltration, ultrafiltration and reverse osmosis. All of these technologies utilize semi-permeable membrane that have the ability to hold back (reject) dissolved and/or suspended solids from a water stream containing these contaminants. The characteristics of the four technologies are summarized in the table 2.1.

**Table 2.1** Comparison of membrane technologies. [5]

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Feature | Microfiltration | Ultrafiltration | Nanofiltration | Reverse Osmosis | |
| Polymers | Ceramics, Polypropylene,  Polysulfone,  Plyvinylidene  fluoride,  Polytetraflour-  Ethelyene,  Polyacrylonitrile | Ceramics,  Cellulosics,  Polysulfone,  Polyvinylidene flouride | Thin film cellulosics | Thin film composites, Cellulosics, Polysulfonated, Polysulfone. |
| Pore size range | 0.1-1.0 | 0.001-0.01 | 0.0001-0.001 | <0.0001 |
| Molecular weight cutoff range(daltons) | >100,000 | 2,000-100,000 | 300-1,000 | 100-300 |
| Operating pressure range (psi) | <30 | 20-100 | 50-300 | 225-1,000 |
| Suspended solids removal | Yes | Yes | Yes | Yes |
| Dissolved organics removal | Yes | Yes | Yes | Yes |
| Dissolved inorganics removals | None | Yes | Yes | Yes |
| Microorganism removal | Protozoan cysts, algae, bacteria | Protozoan cysts, algae, bacteria, virus. | All | All |
| Osmotic pressure effects | None | Slight | Moderate | High |
| Concentration capabilities | High | High | Moderate | Moderate |
| Permeate purity | High | High | Moderate-High | High |
| Energy usage | Low | Low | Low-moderate | Moderate |
| Membrane stability | High | High | Moderate | Moderate |
| Operating costs($1000 gal) | 0.50-1.00 | 0.50-1.00 | 0.75-1.50 | 1.50-5.00 |

A defining characteristic of the nanofilter membrane is that they reject multivalent ions to a significantly greater degree than monovalent ions. This characteristic is greatly exploited in rendering hard water soft. Water softening generally involves the removal of hardness ions, specifically calcium and magnesium. Because these ions are multivalent, they are preferentially removed by nanofilter membranes. Many institutions and countries are deploying desalination units using nanofilter membranes. Research is also being carried out.   
It has been reported that these technologies are being used in places such as Israel and in certain U.S. municipalities, notably in the Long Beach, California Municipal Water District. [6].

The particular advantage of the nanofilter membrane technology is that the nanofilter has a higher flux rate. This means that fewer membrane components are required and it operates at a lower pump pressure, thereby offering savings in pumping costs.

Additionally at nanoscale these filter membranes may be engineered with specific properties e.g. alumina nanofilms reduce fouling by providing an electropositive surface which repels many clogging agents. Similarly, nanoscale zeolite membranes are highly chemical, mechanical and temperature resistant with a large surface area and absorption capacity. Also, it has been reported that the membranes made of carbon nanotubes can be readily cleaned by ultrasonication and autoclaving and hence the problem of fouling of these membranes can be addressed to a greater extent. [7]

3.2 Nanosorbents:

Sorbents are used as separation media in water purification to remove inorganic and organic pollutants from contaminated water. Nanoparticles have two key properties that make them particularly attractive as sorbents. On a mass basis, they have much larger surface areas than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. Several research groups are exploiting the unique properties of nanoparticles to develop high capacity and selective sorbents for metal ions and anions.

Nanocrystalline zeolites have the ability to remediate water containing cationic species such as ammonium and heavy metals, as well as chemicals, such as 137Cs and 90Sr. These radioactive species are found in nuclear plant waste water and polluted ground water. [8]

Along with these the carbonaceous nanomaterials i.e. fullerenes, serve as high capacity and selective sorbents for organic solutes in aqueous solutions.

3.3 Nanocatalysts and redox active nanoparticles:

Nanoparticles have great potential as water-purification catalysts and redox active media due their large surface areas and their size and shape dependent optical, electronic and catalytic properties. They can chemically degrade pollutants instead of moving them somewhere else, including pollutants for which existing technologies are inefficient or prohibitively expensive. Researchers from Indian Institute of Science, Bangalore are using the nanotitanium oxide particles for this very purpose. TiO2 particles are very versatile and can serve both as oxidative and reductive catalysts for organic and inorganic pollutants. It has been reported that the removal of total organic carbon from waters contaminated with organic wastes was greatly enhanced by the addition of TiO2particles. [7]

Nanoscale zerovalent iron (Fe0) and bimettalic Fe0 have emerged as effective redox media for the detoxification of organic and inorganic pollutants in aqueous solutions. These nanomaterials have larger surface areas and reactivity than bulk Fe0 particles. It has been reported by Zhang[9] that these nanoscale Fe0  and Fe0 /Pt0, Fe0 /Pd0, Fe0 /Ag0, Fe0/ Ni0 and Fe0/ Co0  particles can reduce a variety of organic pollutants(e.g., chlorinated alkanes and alkenes, chlorinated benzenes, pesticides, organic dyes and nitro aromatics) and inorganic anions(e.g., nitrates) in aqueous solutions, to less toxic and recalcitrant byproducts.

Dendrimer encapsulated nanocatalysts (DEN’s) are also being evaluated for water treatment. Dendrimer nanocatalysts containing silver, palladium and platinum is reported to

**Table 3.1:** Nanotech products in market [10]

|  |  |  |  |
| --- | --- | --- | --- |
| Product | How it works | Importance | Developers |
| Nanorust to remove arscenic | Magnetic nanoparticles of iron oxide suspended in water bind arscenic, which is then removed with a magnet | India, Bangladesh and other developing countries suffer thousands of cases of arscenic poisoning each year, linked to poisoning of wells. | Rice University, United States. |
| Desalination membrane | A combination of polymers and nanoparticles that draws in water ions and repels dissolved salts. | Already in the market, this membrane enables desalination with lower energy costs than reverse osmosis. | University of California, Los Angeles and NanoH2O |
| Nanofiltration Membrane | Membrane made up of polymers with a pore size ranging from 0.1-10nm | Field tested to treat drinking water in China and desalinate water in Iran. Using this membrane requires less enrgy than reverse osmosis. | Sachen Industries, Korea. |
| Nanomesh waterstick | A straw like filtration device that uses carbon nanotubes plaed on a flexible, porous material. | The waterstick cleans the water as it is drunk. Doctors in Africa are using a prototype and the final product is said to be available at an affordable cost in developing countries. | Seldon Laboratories , United States. |
| World Filter | Filter using a nanofibre layer, made up of polymers, resins, ceramics and other materials that remove contaminants. | Designed specifically for the household or community level use in developing countries. The filters are effective, easy to use and require no maintenance. | KX Industries, US |
| Pesticide Filter | Filter using nanosilver to adsorb and then degrade three pesticides commonly found in the Indian water supplies. | Pesticides are often found in the developing countries water supply. This pesticide filter can provide a typical Indian household with 6000 liters of clean water over one year. | Indian Institute of Technology, Chennai, India and Eureka Forbes Limited, India. |

have been prepared. The average sizes of nanoparticles ranges from 1.2 to 7.5nm. These DEN’s have been subsequently used in reduction of 4-nitrophenol.

Another set of nanoparticles - the magnetic nanoparticles have large surface areas relative to their volume and can easily bind with chemicals. In water treatment applications, they can be used to bind with contaminants, such as, arsenic or oil and then be removed using a magnet. Several companies are commercializing such technologies and researchers are frequently publishing new discoveries in this area.

3.4 Bioactive Nanoparticles:

A variety of strong oxidants (e.g., chlorine) are used as disinfectants for pathogens (e.g. bacteria and viruses) in water treatment. Because these compounds tend to generate toxic disinfection by products such as trihalomethanes, haloacetic acids and aldehydes, alternative disinfectants are critically needed to comply with certain safe drinking water rules. Nanomaterials are providing unprecedented opportunities to develop chlorine free biocides. It has been reported by Stoimenov et.al [11] that MgO nanoparticles are very effective biocides against Gram-positive and Gram-negative bacteria and bacterial spores.

Because AgI and silver nanoparticles have been used as antimicrobial compounds in various biomedical products and applications, it has been reported that several investigators are evaluating use of silver nanoparticles as biocides. Silver nanoparticles have been found to be effective nanoparticles against both Gram-positive and Gram-negative bacteria including *Staphylococcus aureus, Escherichia coli, Klebsiella pneumonia* and *Pseudomonas aeruginosa.*

**Chapter 4**

RISKS, CHALLENGES AND OPPORTUNITIES

Some researchers have called for more research on potential health and environmental risks of using nanotechnology for water treatment. For example, there are concerns that the enhanced reactivity of nanoparticles makes them more toxic. Their small size also means they could be hard to contain, so can more easily escape into the environment and potentially damage aquatic life. The full effects of exposure to nanomaterials, from handling them at water treatment facilities to drinking them in treated water are not known. But a distinction can be made between active and passive nanoparticles, in terms of risk assessment. Passive nanoparticles, such as, coating are likely to present no more or less a risk than active nanoparticles, which can move around the environment leading to risks associated with control and containment.

Another key challenge is the integration of the nanomaterials into existing water purification systems. Many laboratory investigations and pilot plant studies are needed to integrate the novel nanostructured and reactive nanomembranes into existing water purification systems. However it is reported that nanosorbents(e.g. inorganic nanocrystals, carbonaceous nanoparticles, and zeolites), redox active nanoparticles(e.g. Fe0 and bimettalic Fe0 ) and bioactive nanoparticles (e.g. MgO and Ag) can be readily integrated into existing water plants.

Nanomaterials are the drivers of the nanotechnology revolution. The bottleneck to the applications of nanotechnology to water purification will be the availability of the suppliers who can provide large quantities of nanomaterials at economically viable price. It has been reported through a study conducted by Fredona Group[7] that in coming years larger quantities of carbon nanotubes, fullerenes and dendrimers will be available as these nanomaterials become key components of electronic products, drug delivery systems, batteries, fuel cells, etc.

CONCLUSION

There is an overwhelming demand for new technologies that can improve the cleanliness and reliability of water, whether it be for human consumption or for agricultural or industrial applications. As noted, there are several promising commercial applications of nanotechnology in the process of being developed and brought to market. However, before these technologies can make the leap from the laboratory to the mass market, they will need to clear the hurdles of public acceptance and economic feasibility. Many of these applications are still in their infancy and will require further testing to prove their reliability. Furthermore, implementing many of these technologies will require additional capital investment by existing water treatment centers to upgrade equipment and train personnel. However, though the proponents of nanotechnology face a challenge in convincing private and public entities to incur the up-front costs of adopting these new water purification technologies, nanotechnology holds out the promise of long-term benefits in the form of decreased costs of purifying the world’s water supplies and the enormous savings that would accompany reliable access to potable water in those areas of the world that currently suffer from lack of adequate drinking water and basic sanitation services.

References:

1. Nanotechnology. (Last modified on 11/03/2011). URL:

en.wikipedia.org/wiki/Nanotechnology. Accessed on 12/03/2011.

1. Fullerene. (Last modified on 09/03/2011). URL:

en.wikipedia.org/wiki/Fullerene. Accessed on 12/03/2011.

1. Zeolite(Last modified on 01/02/2011) URL:

en.wikipedia.org/wiki/Zeolite. Accessed on 12/03/2011.

1. Dendrimers.( Last modified on 01/02/2011) URL: en.wikipedia.org/wiki/Dendrimers. Accessed on 12/03/2011.
2. Peter S. Cartwright. Nanofiltration, When it works for the whole house. URL: <http://www.wcponline.com> /pdf/Nano.pdf.
3. John Loncto, Marlan Walker and Lynn Foster(2007). Nanotechnology in Water Industry.*Nanotechnology Law and Business,* June 2007, pp: 157-159.
4. Nora Savage and Maadoe S. Diallo.(2005). Nanomaterials and water purification: Oppurtunities and challenges*. Journal of Nanoparticle Rsearch* ,2005,pp 7: 331-242.
5. Katherine Watlington for U.S. Environmental Protection Agency. Emerging Nanotechnologies for Site Remediation and Wastewater Treatment. August 2005, pg 35.
6. Zhang W.X. 2003, Nanoscale iron particles for environmental remediation*. J .Nanoport.* Res.5, pp323-332.
7. David Grenshaw(2009).Nanotechnology for clean water treatment: Facts and figures. 6-May-2009. URL:www.SciDirect.net
8. Stoimenov P.K., R.L. Klinger, G.L. Marchin & K.J. Klabunde, 2002. Metal oxide nanoparticles as bactericidal agents. *Langmuir*  2002, 18, pp 6679-6686.