ISSN: 2501 - 2568 (2016) Volume 1, Issue 2, 141 - 164

Journal of Food Bioengineering and Nanoprocessing

open access journal

www.nanobiofoods.com

Review

received: 10.12.2015
revised: 15.02.2016
accepted: 20.04.2016
published: 02.06.2016

Drinking water purification through nanotechnology

Sapna Jain [1], **Mukesh Kumar Yadav** [2], **Ajay Kumar** [3,*]

[1] Department of Biotechnology, Motilal Nehru National Institute of Technology, Allahabad-211004, Uttar Pradesh, India
[2] School of Biosciences and Technology, Vellore Institute of Technology, Vellore- 632014 Tamil Nadu, India
[3] Department of Biotechnology, Rama University, Kanpur-209217, Uttar Pradesh, India

*corresponding author e-mail address: ***ajaymtech@gmail.com***

ABSTRACT

Nanotechnology holds great potential for cleaning of water resources. Clean water is not only essential to human health, but also is a critical feedstock in a variety of industries especially pharmaceuticals and food. Most of the countries are facing drinking water problems and about 35 percent of people in the developing countries die from water-related problems. Nanotechnology offers the possibility of an efficient removal of pollutants and microbes from water because the abiotic and biotic impurities most difficult to separate in water are in the nano-scale range. With the development of different nanomaterials possessing unique and enhanced properties, current problems involving water quality can be addressed and potentially resolved. Many nanomaterials with unique activity towards recalcitrant contaminants and application flexibility are under active research and development. In the recent years, a number of nanoparticles, nanomembranes and nanopowders have been used for the detection and removal of chemical and biological substances from water bodies. This review accentuates the application and working principles of different nanotechnologies including nanoparticles, nanostructured membranes (e.g. carbon nanotubes), nanoreactive membranes, nanocatalyst, nanosorbents and polymer-supported filtration of water. Some of the nanotechnologies, developed recently for water remediation have also been discussed. This review provides a detailed account on the potential of nanotechnology to significantly advance the availability of clean water along with the challenges and possible solutions to the challenges witnessed in the efficient harnessing of nanotechnology in meeting the ever increasing water requirements worldwide.

Keywords: *Water purification, nanoparticles, nano-structured membranes, nanocatalyst, nanosorbents.*

INTRODUCTION

Water is an elixir for sustainability of life on Earth. It has served as a pivotal component during the periods of origin, evolution, maintenance and continuity of life. Water is important for all living beings as it functions both as a universal solvent as well as an essential component of metabolic processes within the body. Owing to the vitality of water for life, approximately 70% of living beings body weight is water. Apart from playing an important role in the body, clean water is also important for food production and processing and for the manufacture of pharmaceuticals. Clean water represents prosperity, health, purity and many other attributes of not only a nation, but of the whole world (Pradeep and Anshup, 2009). Necessity of water for existence of life has driven man to develop methods for maintaining water purity and integrity. Despite of all the efforts being made during the past decade for meeting the needs of potable water around the world, 748 million people still do not have access to purified water as estimated by WHO in 2012 (WHO report, 2014). In developing countries, each year, approximately 1.8 million people die from diarrheal diseases, 90% of which are children, especially under age 5. It has been estimated that by 2025, 1800 million people will be facing water scarcity and two-thirds of the world population could be under stress conditions (Soumitra et al., 2012). The world is facing potable water crisis due to decreasing supplies of freshwater as a result of droughts, population growth and most importantly, pollution. Surface water and groundwater, the two basic sources of drinking water, get polluted by a wide range of industrial, municipal and agricultural derived pollutants. Water is contaminated with different types of pollutants such as microbes, disinfectants, inorganic chemicals, organic chemicals and in rare cases radionuclides, as well. The sources and adverse impact of different water pollutants are summarized in Table 1.

Table 1. List of water contaminants, their sources and effects on health (Drinking Water Contaminants, 2009).

Major Pollutant	Source	Health Effects
Micro-organisms		
Giardia lamblia	Human and animal fecal waste	Gastrointestinal illness
Cryptosporidium	Human and animal fecal waste	Gastrointestinal illness
Total coliforms (including fecal coliforms and *E. coli*)	Naturally present as well as from human and animal fecal waste	Not a health threat. But are indicator of presence of other bacteria
Legionella	Found naturally in water	Legionnaire's disease
Viruses (enteric)	Human and animal fecal waste	Diarrhea, gastrointestinal illness
Disinfectants		
Chloramines	Water additive used to control microbes	Stomach discomfort, eye/nose irritation, anemia
Chlorine	Water additive used to control microbes	Stomach discomfort, eye/nose irritation
Chlorine dioxide	Water additive used to control microbes	Anemia, affects nervous system of infants and children
Disinfectant Byproducts		
Trihalomethanes	Byproduct of drinking water disinfection	Liver, kidney or central nervous system problems; increased risk of cancer
Chlorite	Byproduct of drinking water disinfection	Anemia in infants
Bromate	Byproduct of drinking water disinfection	Increased risk of cancer
Haloacetic acids	Byproduct of drinking water disinfection	Increased risk of cancer
Inorganic Chemicals		
Arsenic	Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes	Skin damage or problems with circulatory systems and may have increased risk of getting cancer
Barium	Discharge of drilling wastes; metal refineries; erosion of natural deposits	Increase in blood pressure
Beryllium	Discharge from metal refineries, coal-burning factories, electrical, aerospace, and defense industries	Intestinal lesions
Chromium	Discharge from steel and pulp mills; erosion of natural deposits	Allergic dermatitis
Cadmium	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints	Kidney damage
Copper	Corrosion of household plumbing systems; erosion of natural deposits	Short term exposure: Gastrointestinal distress; Long term exposure: Liver or kidney damage
Cyanide	Discharge from steel/metal factories; discharge from plastic and fertilizer factories	Nerve damage or thyroid problems
Fluoride	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories	Bone disease
Lead	Corrosion of household plumbing systems; erosion of natural deposits	Infants and children: Delays in physical or mental development

Major Pollutant	Source	Health Effects
Mercury	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands	Kidney damage
Nitrate	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits	Blue-baby syndrome in infants
Nitrite	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits	Blue-baby syndrome in infants
Selenium	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines	Hair or fingernail loss, numbness in fingers or toes
Thallium	Leaching from ore-processing sites; discharge from electronics, glass, and drug factories	Hair loss; changes in blood; kidney, intestine, or liver problems
Organic chemicals		
Benzene	Discharge from factories; leaching from gas storage tanks and landfills	Anemia; decrease in blood platelets; increased risk of cancer
Carbon tetrachloride	Discharge from chemical plants and other industrial activities	Liver problems; increased risk of cancer
1,2-Dichloropropane	Discharge from industrial chemical factories	Increased risk of cancer
Polychlorinated biphenyls	Runoff from landfills; discharge of waste chemicals	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer
Pentachlorophenol	Discharge from wood preserving factories	Liver or kidney problems; increased cancer risk
Toluene	Discharge from petroleum factories	Nervous system, kidney, or liver problems
Radionuclides	Erosion of natural deposits	Increased risk of cancer
Pesticides	Farming, effluents, home use	Cancer, cardiovascular, nerulogical,, liver and kidney problems

The conventional technologies for water purification, such as activated carbon adsorption, solvent extraction and chemical oxidation are not only costly but also highly time consuming. Water bioremediation techniques, in spite of being environmental friendly, are time driven processes. The technologies developed so far usually are effective for a special type of pollution and no technology exist untill date that could clean all types of pollutants. Taking into consideration the inability of the current technologies to meet water demands of all water users, there is a clear need to devise innovative technologies to meet challenges regarding availability of safe drinking water in both developing and developed countries. Nanotechnology has been recognized as a promising technology for resolving a number of problems involving water purification and maintenance of its quality. According to U.S. National Nanotechnology Initiative (NNI), Nanotechnology is defined as the science of developing materials, devices and systems comprising of fundamentally different properties by exploiting unique properties of molecular and supramolecular systems at nano-scale (Savage et al., 2009). In simple words, the normal rules of physics and chemistry often do not apply when materials possess one or more of their dimensions under 100 nanometers. Due to this, many materials start to display unique and surprising properties. For example, gold turns into liquid at room temperature; silver exhibits enhanced antimicrobial properties while inert materials, such as platinum and gold become catalysts. These new properties open pathways for exciting fields of research and applications in area of water purification.

Different types of nanomaterials and nanoparticles can be used in purification of water. Nanomaterials exhibit unique activity towards recalcitrant contaminants and due to their application flexibility, a large number of nanomaterials are under active research and development for remediation of industrial effluents, groundwater, surface water and drinking water. Recent advances have led to development of nanomaterials with enhanced reactivity, affinity, capacity, surface area, selectivity for heavy metals and other pollutants and improved sequestration properties. Nanomaterials and nanoparticles of utmost importance in water purification include, carbon nanotubes, zeolites, self assembled monolayer or mesoporous supports, dendrimers, single enzyme nanoparticles, zero-valent iron nanoparticles and nano-scale semi-conductor photocatalysts. The most promising antimicrobial nanomaterials are metallic and metal oxide nanoparticles, especially silver and titanium dioxides. Water purification and desalinization techniques cannot be totally efficient without any filtration procedures. A wide array of nanomembranes has been developed for the purpose. The two most studied types of nanomembranes include nanostructured filters and nanoreactive membranes (Cloete et al., 2010). Nanostructured filters generally deploy carbon nanotubes or nanocapillaries to form the basis for nanofiltration, whereas nanoreactive membranes utilize functionalized nanoparticles to aid the filtration process. Nowadays, researchers are also focusing on different materials and polymers for the formation of nanomembranes in order to overcome the biggest challenge of membrane fouling during water purification.

Nanotechnology applications in water purification can be categorized in three areas viz, treatment and remediation, sensing and detection of pollutants and prevention of pollution. The first area of application involves the use of advanced filtration materials that ensure increased water reuse, recycling and desalinization; adsorption of pollutants on nanoparticles and breakdown of pollutants by nanoparticle catalyst. The second area of nanotechnology application encompasses the development of new, highly sensitive and cost effective sensors for detection of chemical and biological contaminants even at extremely low concentrations. Within the third area, nanotechnology possesses the potential of facilitating the development of devices capable of continuous and online monitoring, which generate real-time measurements in least cost and maximum specificity. This review highlights the use of nanotechnology in water purification and remediation. The area of pollutants detection and sensing through nanotechnology is beyond the scope of this review.

NANOMATERIALS AND NANOPARTICLES USED FOR PURIFICATION

Nanomaterial is a term usually used to refer to materials which possesses external or internal dimensions in nano-scale and exhibit unique or additional properties as compared to coarser materials with similar chemical composition. Nanomaterials are of immense importance due to the fact that at nano-scale unique electrical, optical, magnetic and other properties emerge. These evolving properties hold the potential for great impacts in various fields such as medicine, electronics, cosmetics, sporting goods, tires and many more (Gaffet, 2008). The two reasons that explain why nanomaterials exhibit different properties at nano-scale include the relative surface area and the quantum effects. Nanomaterials have a greater surface area to volume ratio than their larger forms. This results in enhanced chemical reactivity and greater strength. At nano-scale, quantum effects are vital to determine the materials properties and characteristics. The history of nanomaterials started when nanostructures were formed in the early meteorites. The first scientific report of nanomaterial was the formation of gold particles by Michael Faraday in 1857. Nanomaterials can be nano-scale in one dimension (e.g. surface films), two dimensions (e.g. strands and fibers) or three dimensions (e.g. particles). They can exist in either single, fused, agglomerated or aggregated forms with a wide range of shapes such as tubular, spherical and irregular (Alagarasi, 2011). Various nanomaterials that exhibit high aspect ratio, adjustable pore size and increased reactivity through electrostatic, hydrophilic or hydrophobic interactions, find application in catalysis, sensoring, optoelectronics and adsorption. Nanomaterials with increased surface porosity are of extreme importance in desalination of water, removal of recalcitrant dyes, heavy metals and halogenated compounds (Das et al., 2014).

Nanoparticles can be defined as organic or inorganic solid particles of dimension in nanometer. They can be functionalized with various chemical groups to increase the affinity towards target compounds. They possess exotic catalytic, optical and electronic properties, which vary depending upon the manufacturing techniques used for controlling the size and shape of nanoparticles. This makes them suitable for the use in nano-scale structures, assemblies and devices.

Nanomaterials that are gaining widespread popularity for utilization in wastewater treatment are shown in Figure 1. A large number of nanomaterials occur naturally, but of particular interest are engineered nanomaterials that are designed for special use or commercial applications. However, the safety of engineered nanomaterials for water purification is still questionable. Recent advances in nanomaterial research for treatment of industrial wastewater involves degradation of organic dyes using manganese doped ZnO nanoparticles (Ullah and Dutta, 2008), nanofilteration of biologically treated effluents from paper and pulp industry (Manttari et al., 2006) and treatment of wastewater from molasses distilleries using nano-size pore membrane (Satyawali and Balakrishnan, 2008).

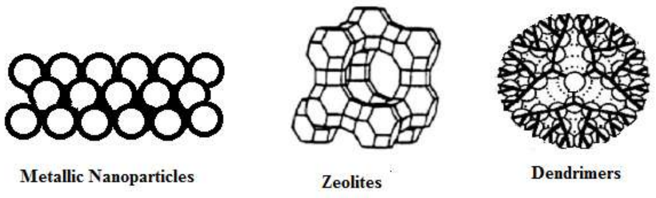
Metallic Nanoparticles
Zeolites
Dendrimers

Figure 1. Some of the most important Nanoparticles for Water Purification

Carbon Nanotubes

Carbon Nanotubes (CNTs) were first synthesized in 1991 by Iijima. CNTs are cylinder shaped macromolecules in which the tube walls are composed of a hexagonal lattice of carbon atoms and they are covered by half of a fullerene-like molecule at their ends (Ijima, 1991). Depending upon the number of hybridized carbon atom layers in the walls of CNTs, they are be classified as Single-Walled carbon nanotubes (SWCNTs) and Multi-walled carbon nanotubes (MWCNTs). SWCNTs are characterized by a cylindrical shape consisting of a single graphene shell, which has a diameter ranging from 0.3 to 3 nm, whereas MWCNTs are composed of a concentric arrangement of a number of cylinders that may possess diameters of up to 100nm (Balasubramanian and Burghard, 2005). CNTs exhibit tunable physical, chemical, electrical and structural properties, which forms the basis of their applications in addressing the problems regarding water shortage and water pollution. The fields of water treatment where CNTs based nanotechnologies find application, involves desalination of water, sorbents, catalyst, filter or membranes. In this section, we only discuss the use of CNTs as adsorbents. The applications of CNTs in membranes, catalysts and sorbents are discussed in detail later in this review.

Adsorption is one of the simplest and efficient methods for the removal of both organic and inorganic contaminants from drinking water. Activated carbon is the first generation carbonaceous adsorbent that is used widely because of its broad-spectrum pollutant removal capability, thermal stability and chemical inertness. However, certain limitations associated with activated carbon include difficulty in regeneration and slow adsorption kinetics. In order to overcome these problems, activated carbon fibers with pores that directly open on the surface of carbon matrix were developed as second generation carbonaceous adsorbent. These fibers offer shortened diffusion distance for pollutants to adsorption sites, thus enhancing the adsorption kinetics. CNTs are like miniaturized activated carbon fibers in which all adsorption sites are located on the inner or outer layer surface. With the improved adsorption kinetics and tunable surface chemistry, CNTs have the potential to be developed as third generation carbonaceous adsorbent (Liu et al., 2012). CNTs have been used successfully as adsorbents for toxins and herbicides in water. CNTs have higher dioxin removal efficiency as compared to that of activated carbon (Long and Yang, 2001). Due to increased discharge of nitrogen- and phosphorus-containing wastewater into lakes and rivers, cyanobacterial blooms have become quite a concern for the environmental safety. Studies have demonstrated that CNTs can be used to adsorb microcystin, the most prevalent toxin produced by cyanobacterial blooms (Falconer, 1999; Haider et al., 2003). As compared to the traditionally used adsorbents for water treatment, such as wood-based activated carbon, kaolinite, talc and sepiolite, CNTs with diameters ranging from 2 to 10 nm are four times more efficient in adsorbing microcystin (Yang et al., 2006). This suggests that CNTs may be a promising nanomaterial for the removal of microcystins from the drinking water.

Studies of adsorption properties of CNTs at the molecular level have revealed that many driving forces act simultaneously, including hydrophobic effect, π- π electron-donor acceptor interaction, hydrogen bonding and electrostatic interactions. Due to the hydrophobicity of CNTs outer surfaces, they possess strong affinity to organic chemicals such as phenanthrene, pyrene (Yang et al., 2006) and naphthalene (Gotovac et al., 2007a). Other factors that influence the adsorption of organic pollutants on CNTs involve nano-scale curvature and chirality of graphene layers. Depending upon the nano-scale curvature, significance difference between the adsorption capacities of phenanthrene and tetracene has been observed by (Gotovac et al., 2007b). An *ab initio* study of benzene adsorption on CNTs showed that the adsorption energies varied with the chiral angle of CNTs (Tournus et al., 2005). The adsorption ability of CNTs is also governed by aggregation tendency which is further dependent on the morphology difference in CNTs. The presence of strong van der waals forces along the axial length and decrease in number of walls also makes CNTs prone to aggregation. This explains why SWCNTs form more aggregated structures as compared to MWCNTs.

The processes, such as air oxidation or acid oxidation, can be used to introduce functional groups (-OH, -C=O, and -COOH) onto the CNTs surfaces. These functional groups enhance the hydrophilic behavior of CNTs and make them more suitable for adsorption of polar and relatively low molecular weight pollutants involving phenol (Lin and Xing, 2008) and 1,2-dichlorobenzene (Peng et al., 2003). The surface functionalization of CNTs is also crucial for the adsorption of metal ions (Rao et al., 2007). In addition to the use of CNTs as direct adsorbents, CNTs can also be deployed as scaffold for various macromolecules or metal oxides with intrinsic adsorption ability. CNTs have been used as scaffold for removal or adsorption of pollutants such as europium (Chen et al., 2009), methyl orange (Zhu et al., 2010) and chromium (Di et al., 2006), where CNTs are decorated with iron oxide, chitosan and ceria nanoparticles respectively. The adsorption capacity of CNTs may be further increased by utilizing their electrical properties with the help of electrochemical processes (Li et al., 2011). The excellent properties of CNTs, especially mechanical flexibility and thermal stability render them with promising application potential in water treatment. However, there are several issues that are yet to be addressed before CNTs can be applied in water treatment plants on mass scale. These issues involve cost, excessive pressure drop due to small particle size, reusability, recovery of spent CNTs and possibility of leakage into the environment.

Zeolites

Zeolites may be defined as inorganic crystalline porous materials, which possess highly ordered structure. They are commonly comprised of silicon (Si), aluminium (Al) and oxygen (O) (Breck, 1974). Zeolites exhibit certain physicochemical properties, such as high mechanical resistance, high surface area and chemical resistance, which make them suitable for use in catalysis, separation, and ion-exchange (Tavolaro et al., 2007). The conventional methods for the synthesis of zeolites are successful only in producing zeolites that are 1 to 10 μm in size. With the development of newer methods for their synthesis during the past decade, it has been possible to synthesize nano-scale zeolites with discrete, uniform crystals ranging from 5 to 100 nm (Bell et al., 2006; Ding and Zeng, 2007). The nanocrystalline zeolites have a greater external surface area, less likely to form coke and smaller diffusion path lengths as compared to micron-scale zeolites (Song et al., 2005a). Zeolites exhibit a low Si/Al ratio and thus possess a high ion-exchange capacity. The Si/Al ratio of zeolites can be altered both during and after synthesis. Also, if the Al content of the zeolites is reduced, they become more hydrophobic in their adsorptive characteristics (Tavolaro et al., 2007).

Zeolite nanoparticles can be synthesized by laser-induced fragmentation of zeolite Linde type A (LTA) micoparticles with the help of a pulse laser. The formation of zeolite nanoparticles occurs due to absorption of the laser at impurities or defects within the zeolite microcrystal generating thermoelastic stress that results in breakdown of microparticles into nanoparticles. Studies have proved that the nanoparticles have a wide range of size and morphology distribution. Large nanoparticles (>200 nm) tend to have irregularly shaped crystals whereas small nanoparticles (<50 nm) are typically spherical, amorphous and dense (Tiwari et al., 2008). The amount of fragmentation and structural damage to the crystal may be controlled by increasing or decreasing the laser energy density irradiating the sample. The optimal laser processing conditions are 355 nm and 10 mJ/pulse laser energy for Zeolite LTA samples (Nichols et al., 2006).

Zeolites act as effective sorbents and ion-exchange media for metal ions. NaP1 zeolites have been used to eradicate heavy metals from different types of wastewaters. They can be easily synthesized by alkaline hydrothermal activation of coal fly ash in 1-2 M sodium hydroxide (NaOH) solution (Moreno et al., 2001). Certain surface modified zeolites (SMZ) have also been developed for the purpose of wastewater treatment. For example, SMZ are used for remediation of water polluted with radioactive species ^{137}Cs and ^{90}Sr in nuclear plant wastewater, SMZ can be used for the adsorption of tetrachloroethane from groundwater and removal of benzene, toluene, ethylbenzene and xylene (BTEX) hydrocarbons from oilfield wastewater (Bowman, 2002)

Nanocrystalline NaY zeolites that are able to absorb comparatively more toluene and nitrogen dioxide have been proposed for commercial applications (Song et al., 2005b). Nanocrystalline Zeolite Socony Mobil-5 (ZSM-5), with a particle size of 15 nm, have been found to adsorb approximately 50% more toluene than ZSM-5 samples with larger particle sizes (Song et al., 2004). For advanced application in water treatment, nanocrystalline zeolites are still under active research.

Single Enzyme Nanoparticles (SENs)

With the advances in nanotechnology, it has been possible to stabilize enzymes in the form of single-enzyme nanoparticles (SENs). Chymotrypsin was the first model enzyme to be assembled as SENs by Kim and Grate (2003). The steps involved in the synthesis of SENs are enzyme surface modification, vinyl polymer growth from the enzyme and finally, orthogonal polymerization takes place by silanol condensation reactions, which results in the cross-linking of the attached polymer chains into a network around the enzyme (Kim and Grate, 2003). The organic/inorganic network of nanometer-scale thickness not only stabilizes the enzyme, but also it is quite porous to allow substrates access to the active sites of the enzyme. Studies have identified that the catalytic stability and activity of chymotrypsin are not lost in the form of SENs and also there is an increase in the half-life of chymotrypsin activity in the form of SENs. Recently, only the chymotrypsin and trypsin enzymes are under research for the formation of SENs with application in water treatment, but this technology can be applied to any enzyme. Thus, SENs may be used in devising promising decontamination methods for a wide range of organic pollutants (Kim and Grate, 2005). However, issues such as enzyme stability, lifetime and cost-effectiveness are firstly to be addressed for large scale purposes.

Nano-scale Biopolymers

Different types of protein-based nano sized biomaterials can be designed with the advancements in genetic and protein engineering. At molecular level, it is now possible to regulate the size, composition and functions of the biopolymers encoded by synthetic gene templates. Nano-biopolymers can be designed with a number of tunable and metal binding properties (Kostal et al., 2005). Different metal-binding functionalities can be provided by joining a number of selected metal-binding proteins to the nano-biopolymers. Such multi-functionalized nano-biopolymers have enhanced specificity and affinity as compared to the chemical sorbents (Kostal et al., 2003). It is an extremely cost-effective approach. as large quantities of biopolymers can be synthesized by overexpression in *Escherichia coli*.

Elastin-like polypeptides (ELP) have come into view as a promising technology for remediation of heavy metals from aqueous wastes. ELPs are biopolymers containing repeating units of pentapeptide Val-Pro-Gly-Val-Gly and are structurally quite similar to the mammalian protein elastin. ELPs possess the ability to undergo reversible phase transition under different values of temperature, pH and ionic strength. These properties are ideal for the metal-polymer complexes recovery (Urry et al., 1992). The chain length and peptide sequence can be varied in order to control the phase transition temperature. The tuning of process temperature leads to formation of reversible network between the individual polymers; this eventually enables the recovery of sequestered metals by precipitation. Once the metals are extracted, the aggregated polymers are re-solubilized and re-used for more remediation cycles (Kostal et al., 2005). It is quite easy to modify the metal-binding capability of the biopolymers. It has been demonstrated that ELP containing a terminal hexahistidine domain show increased cadmium-binding capacity (Kostal et al., 2001). ELPs have been functionalized with different moieties for different applications. ELPs have been fused with synthetic phytochelatin metal-binding domain (Lao et al., 2007) and MerR (a bacterial metallo-regulatory protein) for remediation of chromium and mercury (Kostal et al., 2003) contaminated water respectively.

Self-assembled monolayer on mesoporous supports (SAMMS)

Self-assembled monolayers on mesoporous supports (SAMMS) may be described as functionalized nanoporous ceramics that act as excellent sorbent materials (Mattigod, 1999). SAMMS are produced through surfactant-templated synthesis which is followed by calcination for the removal of surfactant. Nanoporous ceramic oxides are produced with a large surface area and a high density of sorbtion sites. The overall structure of the ceramic is similar to a hexagonal honeycomb and the monolayers that are formed in between the porous surfaces adsorb and bind to molecules. The selectivity of these ceramics towards a pollutant can be increased by their functionalization with molecular self-assembly (Fryxell et al., 2005).

With the assistance of surface chemistry, it has been possible to develop different classes of SAMMS for selectively binding to a specific target. Different types of SAMMS along with their target species are summarized in Table 2.

Table 2. Different type of self-assembled monolayer on mesoporous supports (SAMMS)

Type of SAMMS	Target Species	Reference
Metal-capped ethylenediamine (EDA) SAMMS	Chromate and Arsenate	Kelly et al., 2001
Copper-Ferrocyanide-EDA-SAMMS	Radiocaesium	Lin et al., 2001
Phosphonate and Hydroxypyridinone functionalized SAMMS	Actinides and Lanthanides	Lin et al.,2005
Thiol SAMMS	Metallic cations such as Ag (I), Cd (II), Pb (II) and Cu (II)	Mattigod, 1999

Zero-valent Iron Nanoparticle (nZVI)

Iron nanoparticles are gaining considerable importance for applications in groundwater treatment and remediation. Of utmost importance are the zero-valent iron nanoparticles (Fe^0; nZVI) in which reactivity of core-shell nanoparticles is due to oxidation of the Fe^0 core (Nurmi et al., 2005). nZVI exhibit higher reactivity as compared to the micro-scale particles as they have greater density and higher intrinsic reactivity of their reactive surface sites (Zhang et al., 2003). During the past decade, a number of methods have been developed for the production and modification of nZVI particles (Sun et al., 2006). Studies have demonstrated that nZVI particles can be used for the transformation of various environmental contaminants, such as polychlorinated biphenyls (He and Zhao, 2005), inorganic ions, such as nitrate and perchlorate (Choe et al., 2000), chlorinated organic compounds (Cheng et al., 2007) and heavy metals, such as lead, copper, nickel and chromium (Li and Zhang, 2006). For treatment, nZVI particle-water slurries are injected under pressure to the contaminated plume. The particles remain in the suspension for extended periods of time in order to establish an *in situ* treatment zone. nZVI particles can also be fused to solid matrix, such as activated carbon and/or zeolite for better wastewater treatment (Zhang, 2003). For efficient reduction of contaminants, pH and dose of nZVI particles are critical factors in addition to large surface area. In general, acidic pH and a high dose of nZVI particles have been found to be associated with increased reaction rate (Yang and Lee, 2005). nZVI nanoparticles form large flocs in the surrounding media due to agglomeration as a result of extremely high reactivity. This leads to significant loss in reactivity; hence, various particle-stabilizing methods have been developed for proper dispersion of the nZVI particles in order to increase their efficiency. nZVI particles has been stabilized using cetylpyridinium chloride (Chen et al., 2004) and carboxymethyl cellulose (Xu and Zhao, 2007). The stabilized nZVI particles show much better reactivity and reaction kinetics as compared to the unstabilized ones and thus may be potentially used for *in situ* remediation of groundwater or industrial wastewater.

Bimetallic Iron Nanoparticle

The reactivity of iron decreases with time due to formation of layers of oxide on the particle surface during the reaction or when nZVI particles come into contact with air (Li et al., 2006). The efforts made to increase the reactivity and functionality of nZVI particles have led to the finding of bimetallic iron nanoparticles that contain palladium (Pd^0) or nickel (Ni^0) along with iron (Fe^0). Bimetallic iron nanoparticles have been showed to increase the dehalogenation rate of trichloroethylene by a factor of 30, as compared to nZVI particles. Bimetallic iron nanoparticles have been synthesized through co-reduction of the precursors of the two metals (Schrick et al., 2002) or deposition of second metal on the surface of iron particles after their production.

In the bimetallic particle system, Fe acts as the reducing agent whereas the metals, such as Ni or Pd, act as catalyst in presence of hydrogen produced from reduction of water. Ni has weaker catalytic activity as compared to Pd, but its good corrosion stability and lower cost makes it more appropriate for applications in wastewater treatment. Bimetallic nanoparticles can be used for faster and increased hydrodechlorination of chlorinated organics (Shin and Keane, 1999), chlorinated alipahtics (Schrick et al., 2002), chlorinated aromatics (Wei et al., 2006) and polychlorinated biphenyls (He and Zhao, 2005).

The exact mechanism behind the increased reactivity of bimetallic iron nanoparticles is not properly understood. It has been proposed that the formation of galvanic cells takes place in the coupled bimetallic particles when nZVI particles are attached to a noble metal. Lim et al., (2007) have studied the effectiveness of bimetallic Ni/Fe nanoparticles against brominated organic compounds (BOCs), an important class of disinfection by-products generated during water chlorination. They concluded that bimetallic particles were more reactive for dehalogenation of the brominated methane as compared to the micro-scale Fe available commercially.

The post-coating of second metal on surface of iron particles has been reported to be better than the method of co-reduction for generation of highly reactive bimetallic Ni/Fe nanoparticles. In order to avoid the agglomeration of nanoparticles, water-soluble starch (0.2% by weight) can be deployed as a stabilizer (He and Zhao, 2005).

Metal and Metal Oxide nanoparticles

Nano-scale metals such as silver, gold, titanium, iron and zinc, as well as their oxides are extremely useful in mitigation of environment (Das et al., 2014). Titanium nanoparticles have been effectively used against micropollutants that are involved in various redox reactions (Kamat and Meisel, 2003). Silver (Ag) nanoparticles are used in the disinfection of biological contaminants, such as viruses, bacteria and fungi. Gold (Au) and silver nanoparticles are also useful in the removal of inorganic heavy metals from wastewaters (Khin et al., 2012). Several researchers have evaluated the use of gold nanoparticles as biocides (Baker et al., 2005; Kim et al., 2007; Shrivastava et al., 2007). Au and Ag nanoparticles are more effective against gram-negative bacteria as compared to gram-positive bacteria and their effect is dependent on dose, size and shape (Madigan and Martinko, 2005; Pal et al., 2007). In general, Ag nanoparticles of less than 10 nm are highly toxic to bacteria such as *Escherichia coli* and *Pseudomonas aeruginosa* (Xu et al., 2004; Gogoi et al., 2006). The shape of the nanoparticles also governs their biocidal action. The truncated triangular Ag nanoparticles showed the strongest biocidal action as compared to spherical or rod-shaped nanoparticles. It has been observed that Ag nanoparticles act against certain viruses by binding preferentially to the virus' gp120 glycoproteins (Elichiguerra et al., 2005).

The nanoparticles act against microbial cells either directly, by interrupting transmembrane electron transfer, disrupting/penetrating the cell envelope, or indirectly by oxidizing cell components, production of reactive oxygen species or dissolved metal ions that cause damage. The mechanism of action of Ag nanoparticles against microbial cells is not yet fully understood. There are several mechanisms that have been proposed to explain the antimicrobial activity of Ag nanoparticles: (1) Ag nanoparticles penetrate inside the cells and cause DNA damage; (2) the release of Ag^+ ions is toxic to cells (Morones et al., 2005); (3) adherence of nanoparticles to the surface results in alteration of membrane properties. The lipopolysaccharide molecules can be degraded by Ag nanoparticles by forming pits, thereby increasing the membrane permeability (Sondi and Salopek, 2004). Ag nanoparticles have also been reported to interact with thiol groups in proteins, resulting in inactivation of respiratory enzymes (Matsumura et al., 2003).

Magnesium oxide (MgO; periclase) have also been reported to act as biocide against *E. coli*, *Bacillus megaterium* and *Bacillus subtilis* spores (Stoimenov et al., 2002). MgO nanoparticles with size 8 nm are found to be most active against bacterial cells.

Metallic nanoparticles are also being immobilized in different matrixes because of their high antibacterial activity, chemical stability, low toxicity and thermal resistance. Recently, copper monodispersed nanoparticles incorporated into sepiolite has been demonstrated to function as biocide against *E. coli* and *S. aureus* (Esteban-Cubillo et al., 2006).

TiO_2 and ZnO are other important metal oxide nanoparticles that find application in water treatment. They are most widely used as nanocatalysts and are described later in Section 5 of this review.

Toxicity of Nanomaterials

In spite of the several advantageous properties of nanomaterials that make them potentially useful for water treatment, there are a number of disadvantages of nanomaterials that hamper their large scale application. First is the instability of the particles, it is quite challenging to maintain the active metal nanoparticles due to their rapid kinetics. Certain nanomaterials have poor corrosion resistance, high solubility and may undergo transformation. Nanoparticles are sometimes encapsulated into some matrix in order to retain their nano-size. Various metal nanoparticles can act as strong explosives when they come in contact with oxygen. The recycling and disposal of nanomaterial is another important issue as no hard-and-fast policies have been developed for safe disposal of nanomaterials.

The most important concern is the toxicity of nanomaterials to the living organisms. Nanomaterials can generally consider harmful as they become transparent to the cell-dermis. Nanomaterials have also been shown to be carcinogenic, genotoxic and cytotoxic (Bhabra et al., 2009; Trouiller et al., 2009; Yang et al., 2009). Recently, various animal models and cell culture have been used to study the toxicological effects of nanomaterials. There are two important mechanisms proposed untill date that explains the specific toxicity of nanoparticles: (1) Metallic nanoparticles can generate significant amount of reactive oxygen species or free radicals that can damage the cell membrane. This can induce inflammation and fibrosis. They can also damage the DNA and trigger cancerous process. (2) Nanomaterials may adsorb various biologically active molecules, such as factors required for cell growth. If inhaled, nanoaparticles due to their low mass get entrapped inside lungs. Titanium oxide exhibits significant pulmonary toxicity when it is nano-sized. Nanoparticles can cross different biological barriers to spread inside the body and accumulate in certain organs or cells. Nanoparticles have been documented to show toxicity to lungs, heart, reproductive system, skin and kidney at cellular level (Gaffet E.).

Due to limited data available on nanoparticle-specific toxicity, it is difficult to quantitatively assess the risk associated with different substances. Also, the route of exposure used for toxicity assessments is often not representative of occupational exposure.

SYNTHESIS OF NANOPARTICLES

There are two approaches for the synthesis of nanoparticles: bottom-up and top-down approaches. The fundamental idea behind the two approaches is depicted in Figure 2. Bottom-up approach aims at arranging molecules to form complex structures with exciting and useful properties, on the contrary, top-down approach involves disassembling or break down of larger structures by use of ultrafine grinders (Tiwari et al., 2008). Other approaches for production of nanoparticles include methods based on equilibrium or near-equilibrium thermodynamics, such as methods involving self-organization or self-assembly. These methods are sometimes also referred to as biomimetic processes (Alagarasi, 2011). Some of the important methods for production of nanoparticles are briefly explained as under.

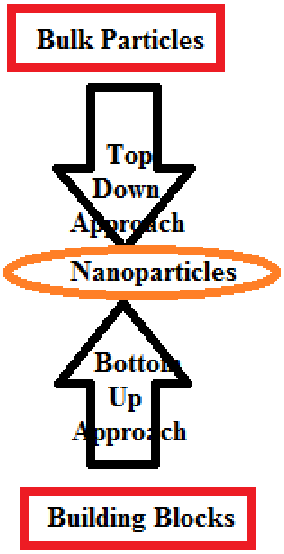

Figure 2. Schematic representation of preparative methods of Nanoparticles

Self-assembly

Self-assembly is an important process in which building blocks are organized into ordered, macroscopic structures, either through direct specific interactions, or indirectly by using an external field or a template. Self-assembly is usually associated with thermodynamic equilibrium, whereby the organized structures are governed by a minimum free energy of the system (Grzelczak et al., 2010). Manipulation of physical, chemical conditions such as pH, temperature and concentration of different solutes can also induce self assembly of molecules to form nanoparticles (Graveland and Kruif, 2006).

Mechanical grinding

Mechanical grinding is an inexpensive, top-down method for the synthesis of nanocrystalline nanomaterials. In this method, energy is imparted to a course-grained material to bring about the reduction in particle size (De Castro and Mitchell, 2002). Mechanical grinding is achieved by employing planetary balls, high energy shaker or tumbler mills. The energy transferred from the steel balls depends on the rotational speed, size, number of the balls, grinding time and atmosphere. Two serious drawbacks of this method are contamination from the grinding media and restriction for the production of non-oxide materials. Hence, this requires that the grinding process must take place in an inert atmosphere and the powder particles must be handled in a suitable vacuum system (Alagarasi, 2011).

Gas phase synthesis

Gas phase synthesis methods are very quick, cost effective and elegant methods as they allow ways to control process parameters in order to manage the size, shape and chemical composition of nanomaterials. These methods have much higher deposition rate as compared to vacuum-based techniques and also nano-scaled powders of high purity with a narrow particle size distribution. Parameters that influence the production process are reaction temperature, pressure, precursor material, method of precursor delivery, mass flows of reactants and carrier gas, type of carrier gas and reactor geometry (Tse and Kear, 2008). Most of the synthesis routes are dependent on the production of small clusters that can agglomerate to form nanoparticles. Condensation takes place only when the vapors are saturated and homogenous nucleation in the gas phase is utilized to form particles. This can be achieved by a number of processes, such as heating the desired material in a heat resistance furnace, flame assisted ultrasonic spray pyrolysis, gas condensation processing, chemical vapor condensation, microwave plasma processing and particle precipitation aided chemical vapor condensation (Alagarasi, 2011).

Sol-gel Synthesis

The sol-gel process is characterized by evolution of inorganic network through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). These colloids are generally synthesized by utilizing metal or metalloid elements as precursors and these elements are enclosed by various reactive ligands. Sol-gel processing involves the hydrolysis and condensation of alkoxide-based precursors. The fundamental reactions involved in the hydrolysis and condensation of metal alkoxides M(OR)z are described in Figure 3. The starting material is firstly processed to produce a dispersible oxide which forms a sol in contact with water or dilute acid. Gel is obtained by the removal of liquid from the sol. The particle size and shape are controlled by the sol/gel transition. Finally, the oxide is produced by the calcination of the gel. The flowchart of the steps involved in the sol-gel process is shown in Figure 4.

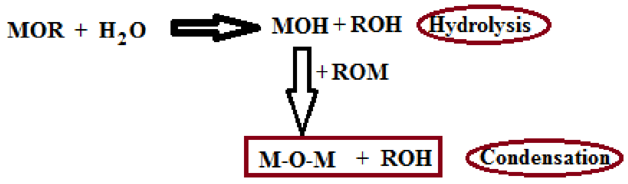

Figure 3. Reactions involved in the hydrolysis and condensation of metal alkoxides M(OR)z

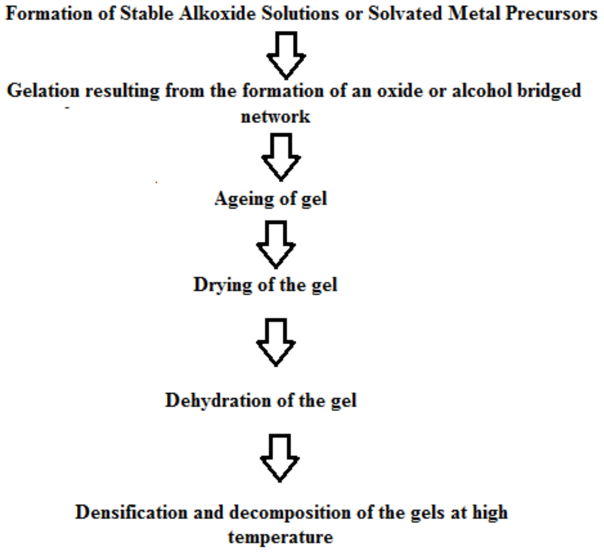

Figure 4. Steps involved in the sol-gel process.

Sol-gel process is gaining popularity as it can also be used to synthesize non-metallic inorganic materials at low temperature. However, there are certain difficulties that are yet to overcome for the large-scale use of this process. Firstly, the production rate of nanopowders is very low in this process. Secondly, it is quite cumbersome to control the growth of the particles and then to stop the newly formed particles from agglomerating.

Laser ablation

Laser ablation is a process that employs laser beam as the primary excitation source of ablation for generating clusters directly from a solid sample. This method is quite efficient for the production of ceramic particles and coatings as it provides the possibility to form thick films. This process has been used to synthesize ZrO_2 and SnO_2 nanoparticulate thin films and nanoparticles from lithium manganate, silicon and carbon. The formation of nanoparticle takes place by liquefaction that generates an aerosol; this is followed by the solidification of the droplets. The solidification or cooling of the droplets results in formation of fog. Finally, the formation of micrometer sized particles is favored by the general dynamics of both the aerosol and the fog. Highly porous thick films can be produced by the use of laser spark atomizer and the porosity can be modified by manipulating the flow rate of carrier gas (Alagarasi, 2011).

Microbial Synthesis and Biomass reaction

With the recent advancements, it has been possible to deploy living cells to produce nanoparticles. For instance, *Aspergillus fumigans* has been used to produce silver nanoparticles extracellularly (Bhainsa and Souza, 2006). Many other fungal, as well as bacterial species have also been used to synthesize gold and silver nanoparticles. Certain living plants that have the potential to take up and sequester heavy metals can also be used for the production of useful metallic nanoparticles. Gold nanorods and nanoparticles have been produced by incubating dead oat stalks in an acidic aqueous solution of gold ions (Bhattacharya and Gupta, 2005).

Other Methods

Some of the other methods for production of nanoparticles are sonochemical processing, microemulsion processing and cavitation processing. Sonochemical processing is an acoustic cavitation process that can produce a temporary localized hot zone with very high temperature gradient and pressure. The sonochemical precursors get destructed by these sudden changes in temperature and pressure and leads to formation of nanoparticles (Suslick et al., 1996). The process of hydrodynamic cavitation involves generation of nanoparticles through creation and release of gas bubbles inside the sol-gel solution. The sol-gel solution is mixed by rapidly pressurizing it in a drying chamber and exposing it to cavitational disturbances along with heating at high temperature (Sunstrom et al., 1996). The so-formed hydrodynamic bubbles lead to nucleation, consequently growth and quenching of the nanoparticles occur. The size of the particle can be directed by changing pressure as well as the retention time of solution in the cavitation chamber (Tiwari et al., 2008).

NANOFILTRATION PROCESSES

Nanofiltration processes are gaining widespread popularity for generation of safe drinking water from surface water, groundwater and brackish water (Ventresque et al., 2000).

Nanofiltration is defined as a separation process in which particles and dissolved molecules smaller than 2 nm are rejected (Das et al., 2014). Nanofiltration membranes were developed as an intermediate between ultrafiltration and reverse osmosis during the 1970s and 1980s (Eriksson, 1988). Nanofiltration is one of the most convenient and efficient techniques that possess the potential to be integrated in a number of industrial effluent treatment plants (Bruggen et al., 2008). Nanofiltration is advantageous over methods such as flocculation, sedimentation, distillation, pervaporation activated carbon, chlorination/ozonation, UV light, electrodialysis and coagulation in that it is effective against a wide spectrum of pollutants. Additional advantages include: chemical free operation, effective against resistant microbes, low cost and energy consumption, easy scale up, highly automated process control, smooth hybridization with other processes thus, they are ideal for plants with space restrictions. This technology is used for the removal of pollutants such as alkylphenols, bisphenol-A, phthalates, pharmaceuticals and many more (El Saliby et al., 2008).

A major drawback of membrane filtration processes is membrane fouling i.e. the accumulation of rejected materials on the membrane. Fouling results in clogging of pores and consequently, there is decrease in the flux. It poses a serious problem that challenges the vitality of appropriate utilization of membrane processes. The recent advancements in the nanostructure science have paved the way for the development of highly efficient and cost effective membranes. Nanomaterials most widely used in formation of membranes include carbon nanotubes, nanoparticles and dendrimers. Untill date, two types of water filtration membranes have been manufactured from nanomaterials viz. nanostructured membranes and nanoreactive membranes.

Nanostructured Membranes

The use of nanostructured materials for improving the efficiency of membrane filters is envisioned to gain more popularity in the near future. This technology holds unlimited benefits that occur from generating membranes with better performance in terms of removal of biological and organic pollutants, as well as metal selectivity. Nanostructured membrane is a term used to define any membrane with engineered nano-sized structures. Nanostructured membranes can be used to reject macromolecules, bacteria, suspended particles, colloids, multivalent ions, viruses and a number of organic and inorganic substances, such as pesticides and certain pharmaceuticals. The rejection of multivalent ions is greater than that of monovalent ions. Thus, nanostructured membranes find applications in treatment of industrial effluents and landfill leachate. Several studies have been conducted to study the effectiveness of nanostructured membranes for treatment of industrial wastewater (Mueller et al., 2006). Nanostructured membranes may be combined with different treatment steps, such as other types of membranes or conventional methods in order to reduce the cost, energy use or membrane fouling and to ensure total eradication of undesired substances. Nanostructured membrane can be used for water desalination and allows the recycling of wastewater by removal of even trace contaminants. In 2007, BCC research estimated that the market of nanofiltration membranes was $89.1 million in 2006 and was expected to reach $390 million by 2014 (Gagliardi, 2007).

Nanostructured membranes can be made from a ceramic material or from polymers. The ceramic membranes are more resistant to mechanical forces, chemicals and temperature. Thus, they can be easily sterilized for multiple applications. Various membrane nanotechnologies that hold potential for replacement of conventional reverse osmosis membranes include inorganic-organic nanocomposite membranes; hybrid-protein-polymer biomimetic membranes and carbon nanotube membranes.

Nanocomposite membranes

Nanocomposite materials are produced by the introduction of nanoparticulate materials into a macroscopic sample material (Komarneni, 1992). These nanocomposite materials exhibit extremely enhanced properties which forms the basis of their application in water treatment. Zeolite-polyamide thin film nanocomposite (TFN) membranes have been synthesized through interfacial polymerization (Jeong et al., 2007). TFN membranes are ideal for designing of nanofiltration membranes as the nanoparticle and polymer phases can be independently designed to impart a wide range of new functionalities and separation performance. TFN membranes have been functionalized with silver and titanium nanoparticles with the aim of generating nanofiltration membranes that have antimicrobial properties and are ultraviolet-active (Lee et al., 2007; Lee et al., 2008).

Hybrid-Protein-Polymer Biomimetic Membranes

Biomimetic membranes are designed with the objective to mimic the highly selective and specific transport of solute and water across biological membranes. The fundamental approach is to form biomimetic membranes that incorporate active transport proteins, isolated from cultured cells, within a vesicular or planar lipid bilayer or a synthetic stable analog such as ABA triblock copolymer monolayers (Ho et al., 2004). The protein may facilitate diffusion, co-transport or counter-transport in the presence of light energy, chemical energy or concentration gradients (Xi et al., 2005). The most promising approach for water treatment is the development of aquaporin (AQP) protein-based biomimetic membranes. Molecular dynamic simulations have been used to study osmotic and diffusion permeability coefficients for water through AQP by applying chemical potential and hydrostatic pressure differences across a single protein respectively (Zhu et al., 2004). Biomimetic membranes possess high selectivity and have good chances of further development to emerge as bio-inspired water purification membranes.

Carbon Nanotubes (CNTs) Membrane

Nanostructured membranes based on CNTs are remarkably important as CNTs membranes offer high flux, high selectivity and low fouling. The molecularly smooth hydrophobic graphitic walls, extremely high aspect ratios and nano-scale inner dimensions of CNTs make them ultra-efficient to transport water molecules at a much faster rate with very little absorption. SWCNTs possess excellent antimicrobial activity (Kang et al., 2007). Direct contact of microbial cells results in severe membrane damage and subsequently, death of cells. SWCNT filter have been showed to have high bacterial retention whereas MWCNT filter have high viral removal capacity even at low pressure ranges (Brady-Estevez et al., 2010a). In order to obtain mixed advantages, SWCNT-MWCNT hybrid filters have been designed to achieve both bacterial and viral retention at low pressure (Brady-Estevez et al., 2010b). The capacity of CNT filters to remove viruses can be significantly increased by applying external electric field (Rahaman et al., 2012). The major advantage of CNT filters over all other conventional filters is that they can be cleaned repeatedly by ultrasonication and autoclaving.

Aligned CNT membranes have been designed to function as high-flux desalination membranes. Holt and co-workers have designed sub-2 nm aligned CNT membranes through catalytic chemical vapor deposition followed by laser etching to uncap the nanotubes. These membranes possess comparatively high water permeablities (Holt et al., 2006).

There are four approaches for the synthesis of CNT based membranes (Soumitra et al., 2012). (1) Carbonaceous materials can be deposited inside pre-existing ordered porous membranes, such as anodized alumina. Membranes produced using this approach, are termed as template synthesized CNT membranes. (2) The membranes produced depending on the interstice between nanotubes in a vertical array of CNTs are referred to as dense-array outer-wall CNT membranes. (3) Open-ended CNT membranes can be produced by encapsulation of vertically aligned CNTs with a space-filling inert polymer or ceramic matrix followed by opening up the CNT tips using plasma chemistry. (4) Mixed-matrix membranes are comprised of nanotubes as fillers in a polymer matrix (Holt et al, 2006).

Membrane fouling can be controlled by tuning the membrane surface chemistry. Generally, an increase in surface hydrophilicity offers better resistance to fouling as many organic foulants are hydrophobic. The hydrophobic nature of CNTs can be changed by treating them with acid. CNTs can be functionalized with various functional groups, such as isophthaloyl chloride groups (Qiu et al., 2009) and amphilic-polymer groups with protein-resistant ability to increase their hydrophilicity (Liu et al., 2010). Polysulfone membranes blended with CNT are more hydrophilic due to the presence of carboxylic groups (Choi et al., 2006). The antibacterial properties of CNTs impart biocidal properties to the membrane, thus resulting in better resistance to biofouling (Tiraferri et al., 2011).

Limitations

There are certain challenges associated with the use of nanostructured membranes that require further research and development. These include: (1) increased flux or reduced pressure, (2) reduction of membrane fouling, (3) even pore size distribution, (4) increased lifetime and membrane selectivity, (5) increased membrane resistance, (6) reduction of membrane fouling and scaling and (7) precise modeling and simulation of membrane performance. However, there are no concerns on adverse effect of nanostructured membranes on human health or ecosystem. Moreover, nanostructured membranes can be employed to filter unwanted nanoparticles in wastewater treatment plants.

Nanoreactive Membranes

Nanoreactive membranes can be described as membranes functionalized with discrete nanoparticles. This type of filtration is also termed as nanoparticle enhanced filtration. Nanoparticles with potential of application in water purification or treatment cannot be directly added to water due to the risk of health and environmental hazards. Thus, a superior approach is to immobilize nanoparticles on or within a solid matrix, such as membranes. The membranes resulting from immobilization of nanoparticles possess better separation performance, interfacial properties and chemical, thermal or mechanical stability.

Alumina ultrafiltration membranes fabricated with alumina nanoparticles (A-alumoxane) have been showed to exhibit selectivity towards different synthetic dyes, such as Direct Red Blue 81, Direct Blue 71 and Direct yellow 71 (DeFriend et al., 2003). Novel nanofiltration membranes have been fabricated by deposition of 4.5 – 5.0 layer pairs of poly(styrene sulphonate) or poly(allylamine hydrochloride) onto porous alumina (Stanton et al., 2003). These membranes show high retention of divalent cations, such as [Ca (II) and Mg (II)] and Cl^-/SO_4^{2-}. Methods have been developed for attachment of polyelectrolytes or polyamines on membrane internal pore surfaces. Polyamines contain multi-functional chelating groups that form strong and stable interactions with metal ions (Rivas et al., 2003). Homopolymers of amino acids have been effectively used for sorption of metals (Ritchie et al., 2001). Membranes have been prepared by deposition of multi-layers of charged polypeptides [poly(L-glutamic acid) or poly(L-lysine)] inside the pores of functionalized polycarbonate track-etched membrane (Hollman and Bhattacharyya, 2004).

Nanoreactive membranes have also been produced by incorporation of zero-valent iron (nZVI) nanoparticles into cellulose acetate films (Wu et al., 2005). For this purpose, nZVI nanoparticles are synthesized in a water-oil microemulsion, mixed with a cellulose acetate-acetone solution and then formed into a porous membrane by phase inversion. This membrane is effective for dechlorination of halogenated organic compounds, such as trichloroethylene (TCE). Alumina and polymeric membranes have been altered by gold nanoparticles via layer by layer adsorption of polyelectrolytes and citrate-stabilized gold nanoparticles. These modified membranes have been found to reduce approximately 99% of 0.4 mM 4-nitrophenol to 4 aminophenol (Dotzauer et al., 2006). Bimetallic Pt/Fe nanoparticles have been incorporated into cellulose acetate films for production of redox reactive membranes that are effective against TCE (Meyer et al., 2004). Recently, TiO_2 nanowire membranes have been successfully fabricated which have the property of filtering organic contaminants and their oxidation simultaneously. This membrane exhibits excellent anti-fouling ability (Zhang et al., 2008).

Nanoreactive membranes are also being promoted by various water treatment companies. For instance, Agromide, Pittsburgh has a product named as Nanoceram which is a purifier that uses 2 mm diameter alumina nanofibres to remove 99.9% of bacteria, virus and protozoa from water (Smith, 2006)

Polymer-supported filtration of water

Dendrimers form the basis of polymer-supported filtration of water for the removal of toxic metal ions, radionuclides, organic and inorganic solutes, bacteria and viruses. Dendrimers consist of a central core, repeating units and terminal functional groups. They are highly branched macromolecules with controlled composition, monodispersity and structural design (Bosman et al., 1999). The nature of the repeating units determines the interior microenvironment while in the external medium, the chemical behavior of dendrimers is determined by the external groups (Frechet and Tomanlia, 2001). There are different types of dendritic polymers, which include random hyper-branched polymers, dendrigraft polymers, dendrons and dendrimers. These are soft nanoparticles with size ranging from 1 - 20 nm and can be used as high capacity and recyclable water-soluble ligands. Apart from their use in filtration, dendritic polymers can be used to form scaffolds and templates for the preparation of redox and catalytically active nanoparticles. They have also been used as delivery vehicles for antimicrobial agents, such as Ag(I) and quaternary ammonium chlorides (Chen and Cooper, 2002)

Hyper-branched polymers are formed by one-step reaction involving polydisperse polymers of a non-perfectly symmetric shape. These polymers maintain most of the architectural attributes and properties of dendrimers (Yates and Hayes, 2004). Cyclodextrins are defined as polysaccharide oligomers that possess a truncated-cone shape forming a well-defined cylindrical cavity (Del Valle, 2004). The cavity is lipophilic in the interior and has the capacity to encapsulate various different organic compounds with proper geometry and polarity resulting in formation of stable inclusion complexes. The outer surface of cyclodextrins has a number of hydroxyl groups, which can be deployed for further functionalization. These can be used for a number of purposes, such as removal of pesticides (Sawicki and Mercier, 2006) and organic contaminants from water (Arkas et al., 2005).

NANOCATALYST AND NANOSORBENTS

Recent advances in nanotechnology are evident of the fact that many of the issue related to drinking water could be resolved or ameliorated by nanotechnology. Nanoparticles have great potential to function as water-purification catalyst and redox active media. Such nanoparticles are termed as nanocatalysts. Nanosorbant are one of the important developments of nanotechnology. Nanosorbants are used to remove organic and inorganic pollutants from contaminated water.

The discovery of photocatalytic splitting of water on titanium (IV) dioxide (TiO_2) electrodes is the root to the notion of applying TiO_2 as homogenous photocatalyst for the remediation of groundwater and wastewater (Kositzi et al., 2004; Prieto et al, 2005). The photoexcitation of TiO_2 photocatalysts requires light with energy greater than its band-gap energy leading to production of electrons in the conduction band and positive holes in the valence band. The adsorbed oxygen species are the traps for electrons and consequently, unstable superoxide species are formed. The hydroxyl ions and water get trapped into the holes, leading to the formation of hydroxyl radicals that act as strong oxidizing agents. The hydroxyl ions and superoxide species so generated react with molecules that are adsorbed on the photocatalyst surface. This facilitates the hydroxylation, oxidation and finally mineralization to carbon dioxide and water (Carp et al., 2004). The most investigated semiconductor photocatalysts for water purification include metal oxides, such as TiO_2, ZnO, SnO_2, WO_3 or chalcogenides e.g. CdS, ZnS, ZnSe, CdTe (Carp et al., 2004). TiO_2 is the most commonly used photocatalyst for water treatment due to their low cost and resistance to corrosion. The only limitation of this technology is the requirement of ultraviolet light irradiation for photocatalytic activation (Dvoranova et al., 2002). Several approaches have been developed in order to decrease the band-gap energy of TiO_2 photocatalysts. These include sensitizing with adsorbed dyes (Moon et al., 2003) or by semi-conductors with lower band-gaps (Yu et al., 2003a), reductive hydrogen plasma treatment (Palmer et al., 2002; Yu et al., 2003b) and transition metal doping (Nahar et al., 2006). The photocatalytic activity of metal-doped TiO_2, depends on the nature and concentration of the dopant ion, preparation methods and calcinations processes. The synthesis of visible light-activated TiO_2 nanoparticles has attracted significant interest in the recent years. TiO_2 nanoparticles with TiO_2 modified by ruthenium-complex sensitizers and platinum deposits have been generated. Under visible lights, these nanoparticles have enhanced rate of reductive dehalogenation of trichloroacetate and carbon tetrachloride in aqueous solutions (Bae and Choi, 2003). The TiO_2 nanoparticles and nanocrystals can be used for water purification or they can be incorporated in a suitable nanocomposite with the help of several traditional grafting, impregnation and precipitation methods (Yang et al., 2006; Zhang et al., 2005). The impregnation methods are preferred over other methods as it prevents agglomeration of the TiO_2 particles and also facilitates the separation and recovery of the catalysts following treatment. The tubular arrays of meso- and microporous molecular sieves composed of TiO_2 nanoparticles, supported by mesoporus silica have also been used for water remediation from aromatic pollutants in the presence of UV light (Lopez-Munez et al., 2005)

Over the past decade, scientists have exploited unique properties of nanoparticles to develop high capacity and selective sorbents for metal ions & anions. Li et al (2003) have reported maximum sorption capacity for Pb(II) 97.08 mg/g, for Cu (II) 24.49 mg/g and for Cd (II) 10.86 mg/g at room temperature and pH 5. They also found that MWCNTs having 3-4 time better capacity of sorption than powdered activated carbon and granular activated carbon.

Qi and Xu (2004) described sorption of Pb (II) on to chitosan nanoparticles, prepared by ionic gelation of chitosan and tripolyphosphate. Pb(II) have maximum sorption capacity of 398mg/g with phosphate functionalized chitosan nanoparticles. A novel sorbant with high surface area (189 m^2/g) consisting of cerium oxide supported on carbon nanotubes (C_eO_2-CNT_s) have been developed by Peng et al (2005). They showed that C_eO_2-CNTs particles are effective sorbents for As(V). They also found that addition of two divalent cations [Ca(II) and Mg (II)] (in range of 0 to 10 mg/l) resulted in substantial increase of amount of sorbtion of As(V) (from 10 to 82 mg/g).

Akaganeite [β-FeO (OH)] nanocrystals have been proposed as novel sorbents for As (V) (Deliyanni et al., 2003), Cr (VI) (Lazaridis et al., 2005). For metal ions, zeolites are effective sorbent and ion-exchange media. NaP1 zeolite ($Na_6\ Al_6\ Si_{10}\ O_{32} . 12H_2O$) have high density for Na ion exchange site. Synthesis of NaP1 zeolite can be done by hydrothermal activation of Fly ash at 150^0C with low Si/Al ratio in 1.0 – 2.0 M NaOH solution.

NaP1 zeolites are widely used as ion exchange media for removal of the heavy metals from acid mine waste water (Moreno et al., 2001). Synthetic NaP1 zeolites can remove Cr (III) and Cd (II) from electroplating waste water (Alvarez-Ayuso et al., 2003). Toxic metal ions can also be removed by self-assembled monolayer on mesoporous supports (Yantasee et al., 2003). These are made up of mesoporous ceramics which contain very large surface area (~1000m^2/g) with high density of sorption site that increase their selectivity towards target pollutants. For organic solutes in aqueous solution, carbonaceous nanomaterials have highly selective capacity as sorbent. Magnun and co-workers synthesized activated nanoporous activated carbon fibers (ACFs) with average pore size of 1.16 nm and surface area ranging from 171 to 483m^2/g (Mangun et al., 2001). The study of sorption isotherms of Benzene, Toluene, xylene and ethyl benzene on ACFs at 20^0C, has shown that the sorption isotherms are adequately described by a Freundlich equation. ACFs have better sorption than granular activated carbon. CNTs also possess tremendous sorption properties. It has been reported that MWCNTs are better sorbents of volatile organic compounds than carbon black in aqueous solutions (Li et al., 2004). MWCNTs encapsulated inside cross-linked alginate vesicles are found to have high sorption capacity and selectivity for soluble dyes, such as ethidium bromide, acridine orange, eosin (Fugetsu et al., 2004). Fullerenes can also serve as sorbents for polycylic aromatic compounds (PAHs), such as naphthalene (Cheng et al., 2004).

CHALLENGES AND FUTURE PROSPECTS

While a considerable amount of attention has been concentrated on the development and potential benefits of nanomaterials in water purification, concerns have also been identified regarding the toxicity of nanomaterials to humans and environment. Studies have successfully proven that the properties that enable nanomaterials to be used in water treatment are also responsible to cause health and environmental problems. The assessment of the harmful effects of nanomaterials is extremely difficult, as no proper methodologies or tools have been developed for the purpose so far. Not only this, there are also no strategic frameworks available for risk assessment, risk research and risk management.

Another important challenge includes the integration of nanomaterials into existing water purification systems. The scarcity of natural water threatens the advancement and social security of many nations around the world, thus it is envisioned that exploitation of nanoparticles for water recycling, remediation and seawater desalination will be more pronounced in the near future. Consequently, the production of nanostructures, modified nanostructures and nanocomposites will also increase in order to devise fast, cost effective and low-energy consuming methods for treatment of wastewater.

It is important to develop water purification methods based on nanomaterials in such a way that ensures that the nanomaterials are reaching their full potential and they are as safe as possible. Effective and reliable methods are needed to be developed for anchorage of nanoparticles to reactor surfaces, or to the selective layer of filtration membrane. It is also crucial to design strategies for separation and retention of suspended nanoparticles in order to reduce cost associated with premature material loss. This involves development of better surface coating techniques with the help of nanoparticle surface functionalization, impregnating nanoparticles into filter packing materials and minimizing membrane fouling by the nanomaterial suspension. In the field of water purification through nanotechnology, future researches would be concentrated on addressing the economics, scalability and safety of nanomaterial-based systems and to resolve many other current limitations. Efforts have to be made in order to create opportunities to revolutionize drinking water treatment through nanotechnology.

SUMMARY

The application of nanotechnology derived products in the treatment of contaminated water can be summarized under three categories. First is the adsorption of pollutants on the nanoparticles. Second is the nano-scale filtration techniques and third is the breakdown of contaminants by nanoparticle catalysts. Recent advances suggest that most of the issues related to water quality can be resolved using products resulting from development in nanotechnology.

The nanomembrane based technology, such as nanocomposite membranes, protein-polymer membranes and CNT membranes hold great promise to improve the energy efficiency of membrane-based filtration processes. Nanoparticle-based products that decrease the amount of toxic substances to sub-ppb levels can help in maintaining the water quality standards and health advisories. In addition to providing advantages to the developed nations, nanomaterials based technologies would also benefit developing nations. Innovative use of nanoparticles for treatment of industrial wastewater is one of the most significant advantages as this technology reduce cost, labor and time. Nanotechnology for water purification will play an extra-ordinary role in ensuring water-security and consequently, food security of the world.

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Conflicts of Interest

The authors declare no conflict of interest.

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