

NANOTECHNOLOGY FOR WATER PURIFICATION: APPLICATIONS OF NANOTECHNOLOGY METHODS IN WASTEWATER TREATMENT

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1 Introduction

Water is the most important asset of human civilization, and potable water supply is a basic human necessity. However, we are far from meeting global demands; this problem will only increase with time (Hillie and Hlophe, 2007). Demand escalates due to population growth, global climate change, and water-quality deterioration (Ali and Aboul-Enein, 2004; Nemerow and Dasgupta, 1991; Tchobanoglous and Franklin, 1991).

Only 2.5% of the world's oceans and seas harness fresh water, FW (salts concentration of <1 g/L). However, 70% of fresh water is frozen as eternal ice. Only <1% of FW can be used for drinking. Globally, >700 million people do not have access to potable water (WHO, 2014). This problem is severe in developing nations and sub-Saharan African countries. Therefore, water treatment must be implemented in these affected places. Available technologies for water treatment are reaching their limits in providing sufficient quality to meet human and environmental needs (Qu et al., 2013a). Therefore, reuse, recycle, and repurpose are the “needs of the day.”

Water contaminants may be organic, inorganic, and biological. Some contaminants are toxic and carcinogenic (Ali and Aboul-Enein, 2006; Ali et al., 2009; Laws, 2000) and have deleterious effects on humans and ecosystems (Ali, 2012). Some heavy metals are notorious water pollutants with high toxicity. Arsenic is one of the deadliest elements, well known since ancient times. Other heavy metals water pollutants with high toxicity are cadmium, chromium, mercury, lead, zinc, nickel, copper, and so on; they have serious toxicities (Ali, 2012). Nitrates, sulfates, phosphates, fluorides, chlorides, selenides, chromates, and oxalates show hazardous effects at high concentrations; these ions also change the taste of water. For example, high levels of fluoride in water causes fluorosis. Organic pollutants, such as pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, and greases are associated with toxicities (Damià, 2005). Emerging contaminants include pharmaceuticals and personal care products (PPCPs) (Carballa et al., 2007; Ellis, 2006; Mohapatra et al., 2014). PPCPs are usually resistant against natural biodegradation. The general origin of such compounds is household and hospital water, which contains metabolized and nonmetabolized (1) drugs, (2) drugs products, (3) additives to detergents, and (4) packaging. PPCP concentration ranges from ng/L up to µg/L, in water. Therefore, conventional water treatment provides unsatisfactory results, because treatment facilities are not equipped to remove stable low-concentrated pollutants.

Produced water containing hydrocarbons necessitates measures that are fast and simple. For instance, according to Gouma and Lee (2014), the petroliferous shale production in the USA will amount to 5 MIO barrels/d by 2017. Hydraulic fracturing (fracking) of shale or rocks are used to recover oil under high pressure. The US's mining-holes (1 MIO) produce 3.29×10^3 m³ of produced water (frac-water) per year.

Aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes, labeled as BTEX are the most predominant components in produced water among other volatile contaminants. These volatile organic compounds can easily evaporate when water is exposed to the atmosphere. BTEX chemicals are toxic and have carcinogenic persistent contaminants. The current maximum contaminant levels (MCL, µg/liter = ppb) for BTEXs in potable water are: benzene 5; toluene 1,000; ethylbenzene 700; xylenes (total) 10,000. Since customary procedures of water purification (filtration, flocculation, and sedimentation) do not remove organic compounds at low concentrations, eliminating BTEX pollutants is challenging. Working expenses depend on various factors, but eventually are dictated by the cost

of the media and means used, the cost of their arrangement, and distribution.

Microbes are responsible for several waterborne diseases. Natural organic matter (NOM) is one of the principal characteristics of water quality, and it determines the strategy of purification. Sometimes NOM is represented by total organic carbon and dissolved organic carbon (Matilainen et al., 2011). NOM is omnipresent from remains of animal or plant origins. It negates the effectiveness of certain techniques—flocculation, carbon adsorption, or filtration. Even worse, NOM produces undesirable oxidation products during chlorination treatment. NOM serves as a breeding medium for a large variety of other microorganisms stimulating growth of bacteria in an aquatic habitat. Given that NOM is various, it is not possible to remove all related objects from the environment, disfavoring water authorities. NOM pollution in the surface and ground water makes it unfit for drinking (Gledhill, 1987).

The global population is expected to reach 7.9 billion by 2020, and therefore the world may encounter severe water scarcity. Therefore, it is necessary to remove these pollutants from contaminated water to provide good health to the public (Dyson, 1996). Different methods are available for water purification (Gupta et al., 2011a,b; Gupta and Nayak, 2012; Saleh and Gupta, 2012; Saleh et al., 2011). The most important methods are screening, filtration, micro- and ultrafiltration, crystallization, sedimentation, gravity separation, flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electrodialysis, electrolysis, adsorption, setting-out, centrifugal and membrane separation, fluidization, neutralization and remineralization, reduction and oxidation, and so on (Ali, 2012).

Any of the above methods can be combined depending on the type of contaminated water and prospective purpose (Fig. 2.1) (Stackelberg et al., 2004). These methods work well, but recent notorious anthropogenic pollutants (result of modern human life style) pose a challenge to purify/treat the contaminated water. Table 2.1 summarizes major limitations associated with conventional methods (Das et al., 2014). A literature survey reveals no single method sufficient to remove all pollutants from water. High operational costs prevent use of sophisticated techniques. Moreover, efficiency of the treatment plants decreases during the removal of contaminants. Thus, the existing technologies are not “100%” effective to supply potable water (Upadhyayula et al., 2009). New and improved technologies for water purification are, therefore, extremely important.

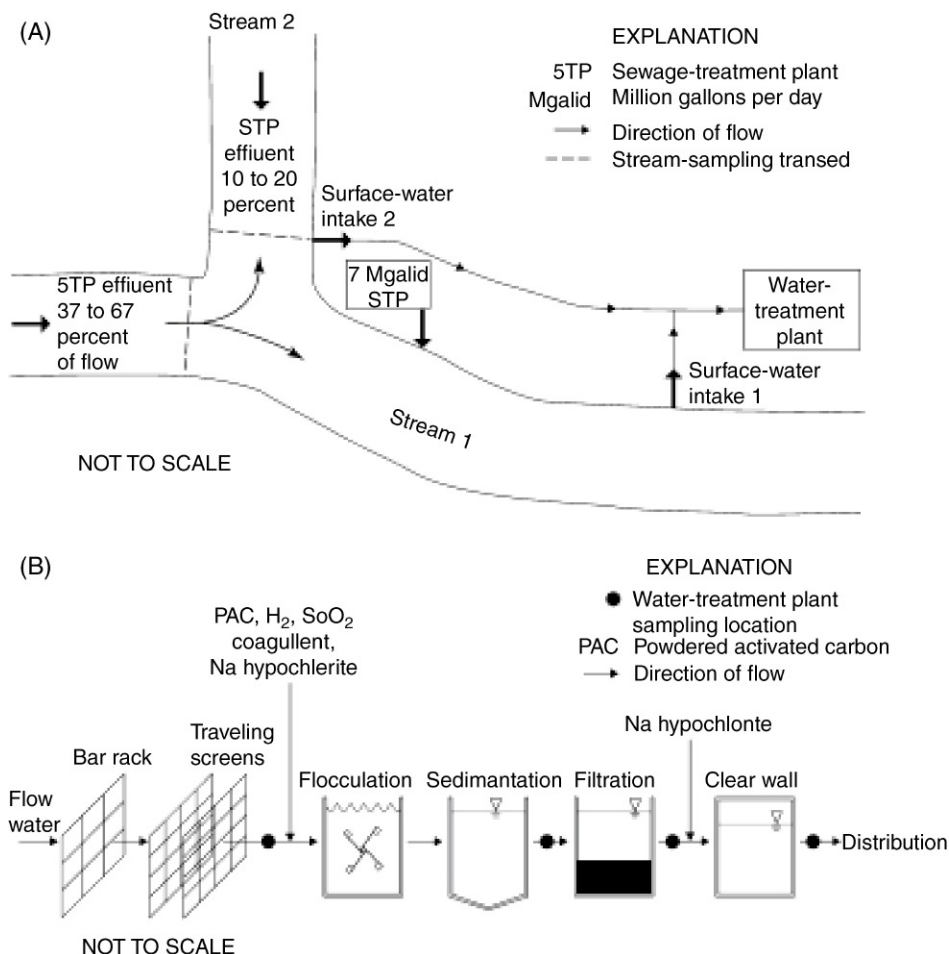


Figure 2.1. Schematic diagram showing (A) location of stream sampling sites, surface-water intakes, and drinking-water-treatment plant, and (B) physical and chemical processes used in drinking-water-treatment plant. From Stackelberg, P.E., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Henderson, A.K., Reissman, D.B., 2004. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant, *Sci. Total Environ.* 329, 99–113, Copyright © 2004, Elsevier.

2 Importance of Nanotechnology in Water Purification

Nanotechnology provided innovative solutions for water treatment. Nanomaterials are fabricated with features, such as high aspect ratio, reactivity, and tunable pore volume, electrostatic, hydrophilic, and hydrophobic interactions, which are useful in adsorption, catalysis, sensing, and optoelectronics

Table 2.1 Major Limitations Associated with Conventional Water Purification Methods

Conventional Methods	Limitations
Distillation	Most contaminants remain behind and require high amounts of energy and water. Pollutants with boiling point $> 100^{\circ}\text{C}$ are difficult to remove
Chemical transformation	Excess reagents are required. Product may be a low-quality mixture and cannot be released into environment. Inactive in harsh conditions. This is not highly selective method
Coagulation and flocculation	This is a complex and less-efficient method and requires alkaline additives to achieve optimum pH
Biological treatment	Microorganisms are sensitive to environmental factors and difficult to control. Intermediates damage the microbial cells. This is not cost effective. Time consuming
Ultraviolet treatment	Expensive method and inactivated by water cloudiness and turbidity. Ineffective for heavy metals and other nonliving contaminants removal
Reverse osmosis	This method removes minerals from water which is unhealthy, and the treated water will be acidic. This method cannot remove volatile organics, chemicals, chlorine, chloramines and pharmaceuticals. Requires high energy
Nanofiltration	This technique requires high energy, and pretreatment. Limited retention for salts and univalent ions. Membrane fouling will occur with limited lifetime and expensive
Ultrafiltration	This method will not remove dissolved inorganics. Requires high energy. Susceptible to particulate plugging and difficult to clean
Microfiltration	Cannot remove nitrates, fluoride, metals, sodium, volatile organics, color, and so on. Requires regular cleaning. Membrane fouling will occur. Less sensitive to microbes, especially virus
Carbon filter	Cannot remove nitrates, fluoride, metals, sodium, and so on. Clogging occurs with undissolved solids. Susceptible to mold. Requires frequent changing of filters

(Das et al., 2014). Nanotechnology-enabled processes are highly efficient, modular, and multifunctional in nature, and they provide high performance, affordable water and, wastewater treatment solutions. Materials consisting of nanoobjects are durable and instantiated by high specific surface (S_{BET}). In other words, a huge surface to volume ratio controls the interaction with pollutants and/or bacteria (Qu et al., 2013b). Nanotechnology-enabled processes for the water treatment constitute major challenges to existing methods. Nanotechnology can also be extended to the purification and utilization of unconventional water sources in an economic way.

Treating industrial wastewater with nanomaterials is also important and widespread. The remediation technologies available now are effective, but they are costly and time consuming. Nanotechnologies are advantageous in treating wastewater, since they eliminate contaminants and help in the recycling process to obtain purified water. This leads to reduction in labor, time, and expenditure to industry solving various environmental issues (Kanchi, 2014).

It should be noted that nanomaterials for purifying drinking water must be environment-friendly and nontoxic. Unsafe particles can cause severe injury to vital organs upon contact with the human body. Due to dimensional features nanoobjects may translocate to various organs, which aggravates the danger of biological damage. Thus, before introduction into the industry, toxicity performance tests must strictly be included into safety data sheets, SOPs, and other related normative documents. This chapter reviews an overview of nanotechnology applications in water and wastewater treatment.

3 Applications of Nanotechnology in Water or Wastewater Treatment

Nanomaterials are typically less than 100 nm in dimension and contain materials with novel and significantly changed physical, chemical, and biological properties (Theron et al., 2008). Materials of this scale contain novel size-dependent properties, which are different compared to their larger counterparts. Desirable nanomaterial properties, such as high surface area for adsorption and high reactivity toward photocatalysis should also have good antimicrobial properties for disinfection and also to control biofouling, should have superparamagnetism for particle separation, should contain optical and electronic properties, and should have good sensing nature to measure water quality (Qu et al., 2013a). Some nanotechnology applications for water and wastewater treatment are discussed in the following sections (Table 2.2) (Gehrke et al., 2015).

3.1 Nanoadsorption

Adsorption is a surface process wherein pollutants are adsorbed on a solid surface. Adsorption takes place in general by physical forces, but sometimes this can be attributed to weak chemical bonds (Faust and Aly, 1983). The efficiency of conventional adsorbents may be restricted by their surface area, and

Table 2.2 Overview of Different Nanomaterials in Water and Wastewater Treatment

Nanomaterial	Properties/Applications	Limitations
Nanoadsorbents	Have high specific surface and very good adsorption capacity Used to remove organic and inorganic contaminants, and bacteria	High production costs
Nanometals and nanometal oxides	Contain high specific surface area and short intraparticle diffusion distance, compressible without change in the surface area, abrasion resistant, magnetic, and photocatalytic in nature Used to remove heavy metals and radionuclides Used in media filters, slurry reactors, powders, and pellets	Less reusable
Membranes and membrane process	Highly reliable and mostly automated process. Applied in all fields of water and waste treatments	Requires high-energy source
Photocatalysis	Photocatalytic activity in UV and possibly visible light range, low human toxicity, high stability, and low cost	Reaction selectivity
Disinfection and microbial control	Strong and wide-spectrum antimicrobial activity, low toxicity to humans, ease of use	Lack of disinfection residue

the lack of selectivity (Qu et al., 2013a). Usually nanoadsorbents are used to remove inorganic and organic pollutants from water and wastewater. The unique properties of nanoadsorbents, such as small size, catalytic potential, high reactivity, large surface area, ease of separation, and large number of active sites for interaction with different contaminants make them ideal adsorbent materials for the treatment of wastewater (Ali, 2012). Carbon-based (Chowdhury and Balasubramanian, 2014; Gao et al., 2011; Jurado-Sanchez et al., 2015; Lubick, 2009; Sui et al., 2012) nanoadsorbents, metal-based (>99.5% purity) (Das et al., 2012; Zhang, 2003) nanoadsorbents, polymeric nanoadsorbents, magnetic or nonmagnetic (Arshadi et al., 2015; Chen et al., 2014; Rafiq et al., 2014) oxide composite, and zeolites are currently used nanoadsorbent technologies in the treatment of water (Gehrke et al., 2015).

Adsorption efficiency of target compounds hinges on the water used. With the increasing concentrations of any substances (natural or anthropogenic) in water, the capacity for the specific compound is reduced because of competitive binding with the surface sites.

3.1.1 Carbon-Based Nanoadsorbents

3.1.1.1 Removal of Organic Contaminants

Carbon-based nanoadsorbents, such as carbon nanotubes (CNTs) are cylindrical. CNTs are explored as substitutes for activated carbon. CNTs are categorized as single-walled nanotubes and multiwalled nanotubes (MWCNTs) depending on their preparation. CNTs contain a high specific surface area with highly assessable adsorption sites. Their surface chemistry can also be modified accordingly (Yang and Xing, 2010). The hydrophobic surface of CNTs makes them form loose bundles/aggregates in aqueous medium, which reduces the active surface area. These aggregates are high-energy sites for the adsorption of organic contaminants in water (Pan et al., 2008). The reason for the adsorption of bulky organic contaminants by CNTs is the availability of larger pores in bundles and more accessible sorption sites (Ji et al., 2009). CNTs can also adsorb polar organic molecules because of diverse contaminant-CNT interactions in the form of hydrophobic effect, π - π interactions (with polycyclic aromatic hydrocarbons), hydrogen bonding (with acids, amines, alcoholic functional groups), covalent bonding, and electrostatic interactions (with positively charged organic contaminant molecules, such as antibiotics) (Chen et al., 2007; Ji et al., 2009; Lin and Xing, 2008; Yang and Xing, 2010).

3.1.1.2 Removal of Heavy Metal Ions

Surface-oxidized CNTs using hydrogen peroxide, KMnO_4 , and nitric acid are used in the removal of Cd^{2+} from aqueous solutions (Li et al., 2003a). The oxidation of CNTs may have high adsorption capacity for metal ions with faster kinetics. The surface of oxidized CNTs contains functional groups, such as carboxylic acid, hydroxyl, and carbonyls (Fig. 2.2) (Vuković et al., 2010). These groups have good adsorbing capacity for heavy metal ions

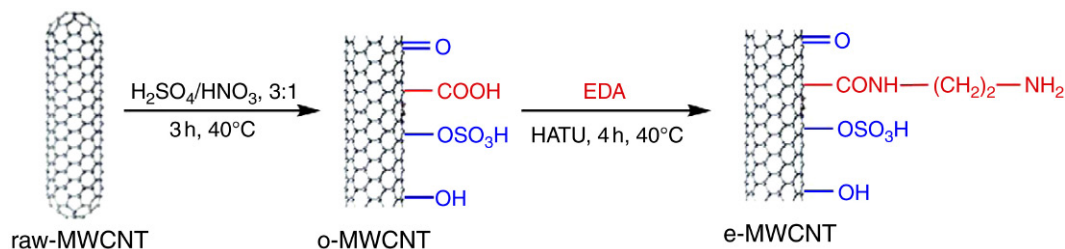


Figure 2.2. Functionalization of MWCNT for the removal of heavy metals (Vuković et al., 2010).

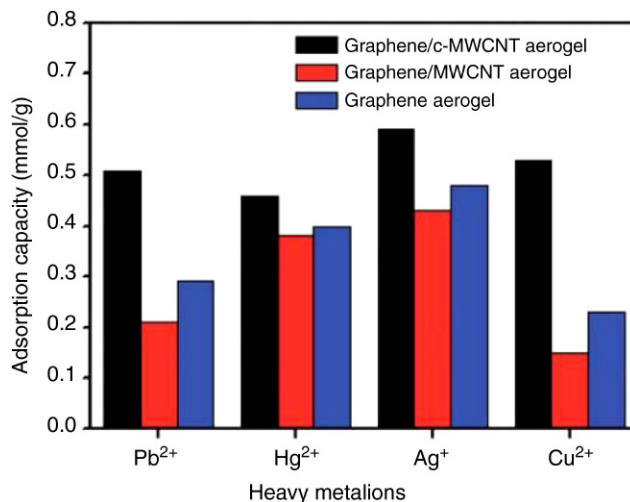
when the pH is above the isoelectric point of the oxidized CNT (Datsyuk et al., 2008; Li et al., 2003b; Musameh et al., 2011; Peng and Liu, 2006; Lau et al., 2015; Liu et al., 2012). Many other studies have been reported that CNTs are very good adsorbing nanomaterials for heavy metal ions, such as Cu^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+} (Li et al., 2003a; Lu et al., 2006). A sponge made of CNTs with a dash of boron showed a very good adsorbing capacity for oil from water. These sponges are reusable once the oil is removed from them, and they are promising in the removal of oil spills for oil remediation (Hashim et al., 2012).

Even though CNTs have significant advantages, they have certain limitations even in water treatment by the adsorption method. The use of CNTs on an industrial scale for wastewater treatment plants is not expected due to high production costs (De Volder et al., 2013). Toxicity of CNTs is well known since their discovery in the early 1990s (Iijima, 1991), and many reports are available regarding health concerns (Bottini et al., 2006; Muller et al., 2006). Another limitation is that CNTs show a coagulation phenomenon with some organic contaminants and algae, and lose their nanoidentity/structure (Ali, 2012).

Regeneration of CNTs after their use as adsorbents can be achieved by altering the pH toward acidic. The regeneration will not change CNTs adsorbing capacity for metal ions. It has been reported that Zn^{+2} adsorption by CNTs decreases only 25% after the tenth regeneration, while activated carbon loses its activity almost 50% after its first regeneration (Lu et al., 2006).

In combination with graphene, aerogels of acid-treated MWCNTs exhibit improved absorbance of heavy metals from aqueous solutions (Fig. 2.3) (Sui et al., 2012). To depend upon types of MWCNTs used—pristine or acid treated (c-MWCNT)—there is a substantial difference in absorbance capacities. Aerogels containing acid-pretreated MWCNTs represent higher values of capacities in contrast to CNT-free graphene or pristine MWCNT-graphene hybrid samples. This was supposed to have been due to electrostatic interactions revealed by oxygen-based groups on the pore surface of graphene-c-MWCNT sample—carboxyl groups located on the edges of graphene sheets and walls of c-MWCNTs.

Figure 2.3. Binding capacities of graphene-MWCNTs for heavy metals (Pb^{2+} , Hg^{2+} , Ag^{+} , Cu^{2+}). From Sui, Z., Meng, Q., Zhang, X., Ma, R. Cao, B., 2012. Green synthesis of carbon nanotube-graphene hybrid aerogels and their use as versatile agents for water purification. *J. Mater. Chem.* 22, 8767–8771, Copyright © 2012, Royal Society of Chemistry.



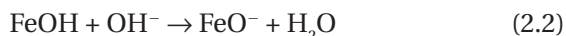
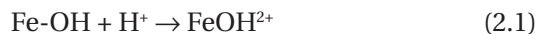
3.1.1.3 Metal-Based Nanoadsorbents

Metal-based nanoadsorbents, such as iron oxide, titanium dioxide, zinc oxide, and alumina are used in heavy metal removal during water decontamination. They are effective and low-cost materials. The mechanism of action is that the oxygen in metal oxides complexed with heavy metals dissolves in contaminated water (Trivedi and Axe, 2000). As the particle size decreases, the adsorption capacity increases several fold. For example, 300 and 20 nm magnetite particles have similar degrees of adsorption for As(III). When the particle size is reduced to less than 20 nm, the specific area of the nanoparticles increases, and the adsorbing capacity for arsenic increases three times (Auffan et al., 2008). This is because of the “nanoscale effect” of the magnetite, in which surface structure creates new adsorption sites for metal ions (Auffan et al., 2009).

Magnetic nanoadsorbents (MNPs), such as maghemite ($\gamma\text{-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and spinel ferrites ($\text{M}^{2+}\text{Fe}_2\text{O}_4$, where M^{2+} : Fe^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Mg^{2+}) are very good adsorbing materials for the collection and removal of toxic elements from contaminated water. Environmental benefits lie in their magnetic nature. They can be easily separated from reaction media by application of an external magnetic field. Ample reports are available in the literature for the use of these MNPs for the removal of a variety of elements, such as arsenic, chromium, cobalt, copper, lead, and nickel in their ionic forms (Badruddoza et al., 2013; Lei et al., 2014; Ngomsik et al., 2012; Tan et al., 2014; Tu et al., 2012).

Such magnetic oxide nanomaterials modified by functional groups— $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2/\equiv\text{SiCH}_3$ and $(\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2/\equiv\text{SiC}_3\text{H}_7)_{7-n}$ —are shown to act as adsorbents of undesired biopolymers from water (Melnik and Zub, 2012).

The iron oxide surfaces are covered with $-\text{OH}$ groups. This is because of adsorbed H_2O or structural features. Hence, the surface is not inert:



The functionality can be varied in relation to the nature of both oxide and pH. In this respect FeOH^+ or FeOH^{2+} ($\text{pH} < 7$) and $\text{Fe}(\text{OH})_2^0$, $\text{Fe}(\text{OH})_3^-$, FeO^- ($\text{pH} > 7$) are predominant on surfaces of iron oxides (Chowdhury et al., 2012). Such dependences become agents for different removals of chromium(IV) from water.

Maghemite nanotubes have been used for the removal of Cu^{2+} , Zn^{2+} , and Pb^{2+} from water (Roy and Bhattacharya, 2012).

The use of magnetite nanorods was reported for the removal of heavy metal ions, such as Fe^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , and Cu^{2+} from aqueous solutions (Karami, 2013). In the same study, when compared to nanotubes, the nanorods had higher adsorption capacity for Zn^{2+} and Pb^{2+} but lower adsorption capacity for Cu^{2+} . Water soluble magnetite superparamagnetic nanoparticles had fast and selective for the adsorption of Hg^{2+} (Qi et al., 2014). The study on the role of nanohematite as an adsorbent for the removal of heavy metal ions was carried out using spiked tap water. The nanohematite particle surface contains hydroxyl groups, which allows for the adsorption of specific heavy metal ions. This model also proves that the adsorption of Pb^{2+} , Cd^{2+} , and Cu^{2+} is endothermic, and Zn^{2+} is exothermic (Shipley et al., 2013).

The application of paramagnetic ferrite-based nanoparticles (CuFe_2O_4) makes possible adsorption of oxidized forms of As—As(V) in the form of arsenate salts from contaminated groundwater (Tu et al., 2012). This feature aids in a rapid recovery (20 s) by force of magnetic field.

Another metal oxide, TiO_2 , was studied for the removal of arsenic. Luo et al. acquired wastewater from copper smelting industry that contained an average concentration of 3310 mg L^{-1} As(III), 24 mg L^{-1} Cu, 5 mg L^{-1} Pb, and 369 mg L^{-1} Cd. The authors successfully removed arsenic in less than 1 h to 100 mg L^{-1} from the initial concentration 3310 mg L^{-1} . They have used TiO_2 for almost 21 successive cycles after its regeneration (Luo et al., 2010).

Magnesium oxide (MgO) was noticed due to its signaled removal properties against inorganic micropollutants, such as As(V) and heavy metal ions. Flower-like nanoforms of MgO ($S_{\text{BET}} = 72 \text{ m}^2/\text{g}$) are high-efficiency adsorbents of Cd^{2+} and Pb^{2+} with maximum capacities of 1.98 and 1.5 g/g (pH = 7), respectively. The XRD studies bear record to ion exchange mechanism between both types of metal ions and Mg^{2+} : $\text{MgO} + \text{M}^{2+}(\text{Cd}^{2+}/\text{Pb}^{2+}) = \text{PbO}/\text{CdO} + \text{Mg}^{2+}$. The growth of Mg^{2+} during the adsorption process does not, however, exceed the World Health Organization limit (450 mg/L) (Cao et al., 2012). The adsorption capacity of porous MgO nanowires toward As(V) was shown to be at 384.6 mg/g (Jia et al., 2013). In this case, the ionic exchange does not take place on the surface of MgO. Although the shape of 1-D MgO had been saved, new “plates” of magnesium arsenate were formed on the surface of nanowires. Thus, a chemical interaction occurs during As(V) adsorption without any loss of Mg^{2+} into water.

By conjugation of MgO and TiO_2 into a dual nanocomposite, the adsorbing effectiveness of metal oxides goes together with

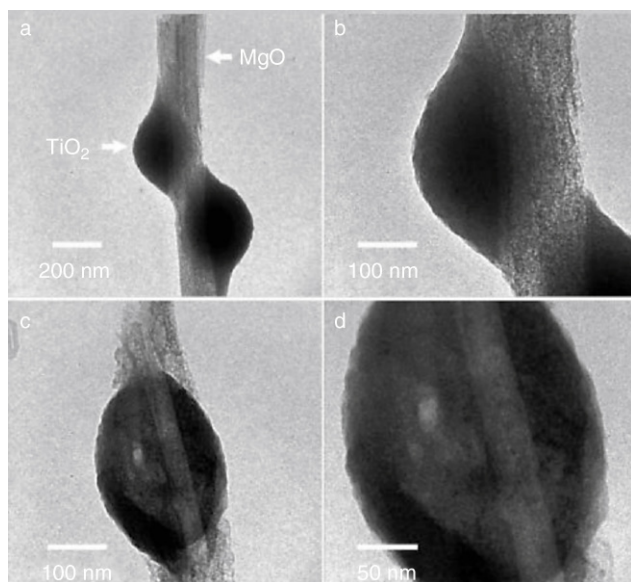


Figure 2.4. TEM images of the necklace-like MgO/TiO₂ heterojunction structures. From Jia et al. (2014), Copyright © 2013, Royal Society of Chemistry.

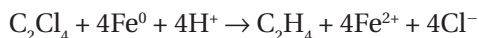
strongly marked photocatalytic activity (Fig. 2.4). Videlicet, As(V) removal via MgO and photocatalytic degradation of model compound (methylene blue, MB) induced by TiO₂ all complement each other despite low specific surface area ($S_{\text{BET}} = 76 \text{ m}^2/\text{g}$). The highest capacity to adsorb As(V) was 217.8 mg/g (almost 1.8 times less than that of flower-like MgO). This is because of titanium phase introduction. Presence of arsenic did not influence the photocatalytic decomposition of MB (100% oxidation in 25 min). But, the dye reduced removal of arsenic due to possible competitive adsorption of oxidized products of MB on MgO surface.

ZnO nanoadsorbents were used to remove Zn²⁺, Cd²⁺, and Hg²⁺ ions from aqueous solutions in a study reported in the literature. These metal ions adsorbed onto ZnO nanoparticles at different concentrations, however, Hg²⁺ had highest adsorbing capacity. The reason may be that Hg²⁺ has the smallest hydrated ionic radii compared to other metal ions in the study (Sheela et al., 2012). Alumina nanoadsorbents can be prepared at low cost. They have high surface area and good thermal stability. They have been used for the removal of cadmium, chromium, copper, lead, and mercury metal ions (Pacheco and Rodriguez, 2001).

Metal-based nanoadsorbents are one of the highly efficient nanoadsorbents for the removal of heavy metal from water and wastewater. They have their own advantages, such as faster kinetics, high adsorption capacity, and preferable nanomaterials for heavy metal removal (Hua et al., 2012).

Long reactive iron nanoparticles (10–100 nm) as reducing materials demonstrate effectiveness as detoxicants of chlorine-containing compounds (pesticides, organic solvents, and polychlorinated biphenyls) (Fig. 2.5) (Zhang, 2003).

These contaminants, preadsorbed on zero-valent Fe, accept electrons, which provokes the reduction process with formation of ethene:



Monodisperse nanosilver bioconjugate particles (15 nm) synthesized using fungal mycelia (*Rhizopus oryzae*) are efficacious

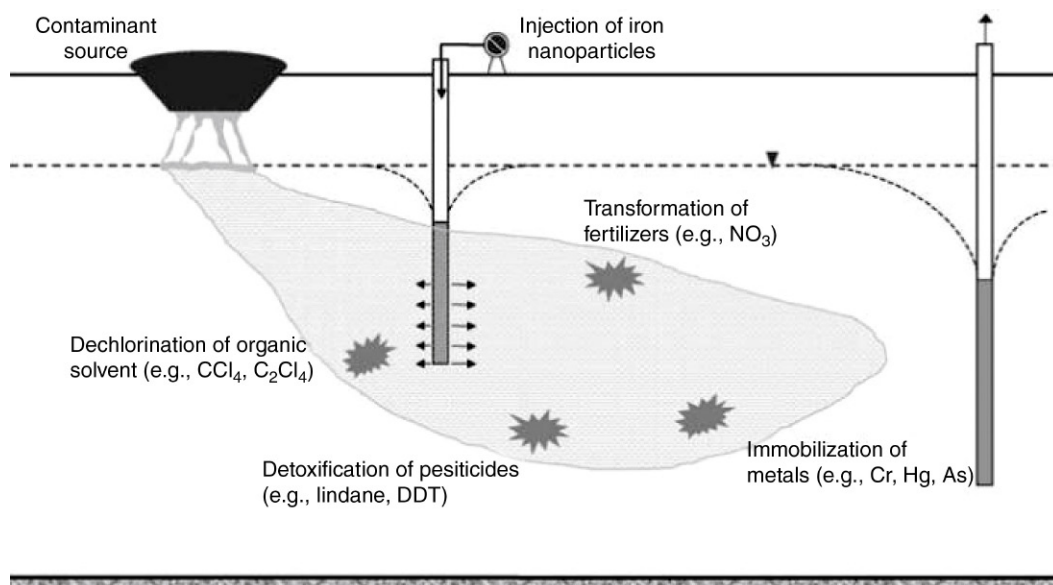


Figure 2.5. Nanoscale iron particles for in situ remediation. From Zhang, W.-X., 2003. Nanoscale iron particles for environmental remediation: an overview. *J. Nanopart. Res.* 5, 323–332, Copyright © 2003, Springer.

adsorbents and antimicrobial agents. The concentrations of studied pesticide (parathion and chlorpyrifos) were significantly reduced (85–99%) in contrast to gamma-hexachlorocyclohexane (γ -BHC), whereas only 16% of absorbance occurred. In addition, the amount of *Escherichia coli* (initial concentration—60 cell/mL) was not sufficient to be detected after treatment. Such a difference can be explained by means of the HSAB theory, that is, with the affinity of sulfur atoms of parathion and chlorpyrifos to Ag. Hence, hard Cl-atoms in γ -BHC cannot redound to an effective adsorption onto nanosilver particles.

Metal-based nanoadsorbents can be regenerated by changing the solution pH. Also, after several reuses and regeneration the adsorbing capacity of these nanoadsorbents is not altered. However, in some cases the adsorbing capacity is reduced after regeneration due to the formation of aggregates by van der Waals and other forces (Pan et al., 2008).

3.1.2 Polymeric Nanoadsorbents

Polymeric nanoadsorbents gained interest recently. They are used either as a system into which inorganic nanosized materials can be inserted or as a bed or template to prepare nanoparticles (Khajeh et al., 2012). The most important advantage of the

polymer-inorganic nanoadsorbents is their good adsorption capacity and very good thermal stability over a wide range of pH. Further, the resistance of polymeric groups and their linkages to acid and base hydrolysis is an added advantage (Kaya et al., 2011; Khajeh et al., 2012). Some recent examples are discussed. Fe_3O_4 magnetic nanoparticles (Fe_3O_4 MNPs) modified with 3-aminopropyltriethoxysilane (APS) and copolymers of acrylic acid (AA) and crotonic acid (CA) as polymer shells ($\text{Fe}_3\text{O}_4\text{@APS@AAco-CA}$ MNPs) were prepared. The use of a polymer shell prevented interparticle aggregation and improved dispersion stability of the nanostructures. The polymer modified MNPs successfully removed heavy metal ions, such as Cd^{2+} , Zn^{2+} , Pb^{2+} , and Cu^{2+} from aqueous solution with high maximum adsorption capacity at pH 5.5. This nanoadsorbent could be reusable in at least four cycles (Ge et al., 2012). In another study, a bimetal doped micro- and nanomultifunctional polymeric adsorbent for the removal of fluoride and arsenic(V) was developed (Fig. 2.6). The polymer was prepared by suspension

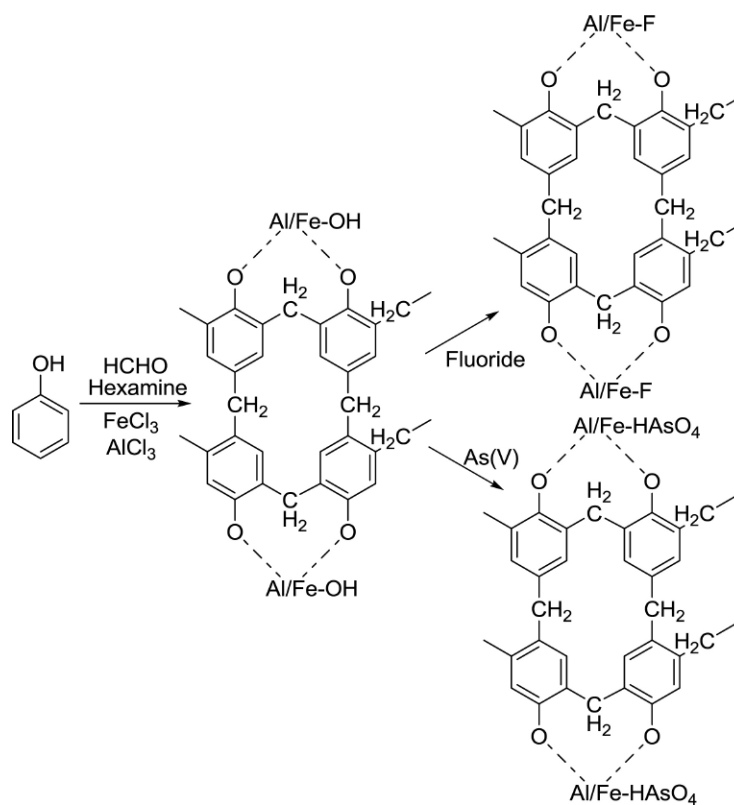


Figure 2.6. Metal-doped phenolic polymeric beads for the removal of fluoride and arsenic (Kumar et al., 2011).

polymerization. During polymerization Al and Fe salts were incorporated to obtain a bimetal-doped nanoadsorbent. The synthesized Fe-doped nanoadsorbents had very good adsorption for arsenic, compared to fluoride, whereas Al-doped nanoadsorbents showed good adsorption toward fluoride compared to arsenic (Kumar et al., 2011).

A polymeric hybrid sorbent (ZrPS-001) was fabricated for enhanced sorption of heavy metal ions, such as lead, cadmium, and zinc ions from aqueous solution by impregnating $\text{Zr}(\text{HPO}_3\text{S})_2$ (i.e., ZrPS) nanoparticles within a porous polymeric cation exchanger D-001. The negatively charged groups bound to polymeric matrix D-001, resulting in preconcentration and permeation enhancement of target metal ions prior to sequestration. The nanoparticles are expected to sequester heavy metals through an ion-exchange process (Zhang et al., 2008).

Even though, polymeric nanoadsorbents are excellent materials with respect to their structures, pore sizes, and tunable functional groups, for the removal of heavy metals from water/wastewater the ability to make them selective for a given pollutant is a difficult task. The adsorbing capacities of these materials is rather low, and regeneration is required at high cost (Pan et al., 2008).

3.2 Membranes and Membrane Process

A membrane is a porous thin-layered material that allows water molecules to pass through it, but at simultaneously restricts the passage of bacteria, viruses, salts, and metals. Membranes use either pressure-driven forces or electrical technologies. Pressure-driven membrane technology is a perfect method for water purification to any desired quality (Kumar et al., 2014). Membrane separation processes are increasingly advanced methods for the treatment of water and wastewater. Membranes separate substances depending on pore and molecule size. It is a reliable and automated process for wastewater treatment (Gehrke et al., 2015). The challenge of membrane technology is the inherent tradeoff between membrane selectivity and permeability. This technique requires high-energy consumption due to the pressure-driven process. Fouling of membranes makes the process very complex and also reduces the life time of membranes and membrane modules (Qu et al., 2013a). The performance of the membrane system depends on the type of membrane material. Functional nanomaterial inclusion into membranes is definitely advantageous in the improvement of membrane permeability, fouling resistance, mechanical, and thermal stability.

3.2.1 Nanofiber Membranes

Electrospinning is a simple, inexpensive, and efficient technique to fabricate nanofibers. These nanofibers contain high surface area, porosity, and form nanofiber mats with complex pore structures. The physical and chemical parameters of electrospun nanofibers can be easily manipulated for different applications. Nanofiber applications have been documented in the literature. Preparation, characterization of nano fibers, and their suitability for air and water filtration applications have been presented in the literature (Ahmed et al., 2015; Balamurugan et al., 2011; Feng et al., 2013; Nasreen et al., 2013; Subramanian and Seeram, 2013). This class of membranes removes micron-sized particles from water without any significant fouling (Ramakrishna et al., 2006). Thus, nanofibers can be used in pretreatment prior to ultra filtration or reverse osmosis. Electrospinning is a widely employed technology in air treatment, not so common in wastewater treatment (Ramakrishna et al., 2006).

An electrospun nanomembrane can eliminate bacteria or viruses by size exclusion. However, the utilization of these membranes incurs difficulties because of smaller pore sizes for appropriate removal of viral agents. At such a scale, size of pores will essentially depress the onrush of water. To the contrary, a novel composite cellulose-based membrane to remove microorganisms (99.9999% removal of *E. coli*) maintaining the water stream was developed (Sato et al., 2011). Positive charged fibers trapped the negatively charged viruses. This rate of activity is in keeping with requirements specified by the National Sanitation Foundation Standard (max. 2 CFU/mL).

Poly(acrylonitrile-co-glycidyl methacrylate) nanofibers (100 nm in diameter) were surface functionalized with protein. Biofunctionalization made these nanofibers slightly bigger in diameter to 126 nm. The bionanohybrid electrospun nanofiber membranes undergo conformational change upon wetting during filtration and increase of pH to above the isoelectric point of the protein. This leads to the emergence of the hidden functional groups, molecules (thereby protein swelling) and nanosolids to be filtered. Moreover, swollen protein makes a higher steric hindrance, facilitating the capturing of the nanosolids, such as metal ions (Elbahri et al., 2012).

The marketed nanofiber filter, NanoCeram (Argonide Corporation, Sanford, FL, USA) is a fiber with a small diameter and large surface area (300–600 m²/g). This fiber is scalable to kilogram through a sol-gel reaction. The resulting product is white, free-flowing made up of nanofibers (~2 nm) in diameter and ~10–100 nm length. They aggregate and can be embedded in glass

and cellulose sheets, and may be used in ultra filtration. The fibers are free flowing, but gets rid of dirt, bacteria, viruses, and proteins through Columbic interactions. NanoCeram can be applied in commercial/industrial water treatment as a microbiological sampler or as a stand-alone filtration device (Karim et al., 2009). Membranes made of hydrophobic nanofiber materials might become very appropriate for separation of organic solvents, leading to higher flux efficiency (Feng et al., 2013).

3.2.2 Nanocomposite Membranes

Nanocomposite membranes are promising filtration units; they may be fabricated from mixed matrices and surface-functionalized membrane. Mixed matrix membranes use nanofillers, and most are inorganic. They are mixed to a polymeric or inorganic oxide matrix, and have substantial surface area (Gehrke et al., 2015). Hydrophilic metal oxide nanoparticles (Al_2O_3 , TiO_2 , and zeolite), antimicrobial nanoparticles (nano-Ag and CNTs), and (photo)catalytic nanomaterials (bimetallic nanoparticles, TiO_2) are some of the nanomaterials used for such applications (Qu et al., 2013a).

Addition of hydrophilic metal oxide nanoparticles into the membrane reduces fouling. Such addition of metal oxide nanoparticles (alumina, silica, zeolite, TiO_2 , etc.) to polymeric membranes increases membrane surface hydrophilicity, water permeability, or fouling resistance (Bae and Tak, 2005; Bottino et al., 2001; Maximous et al., 2010; Pendergast and Hoek, 2011; Pendergast et al., 2010). Also, these inorganic nanoparticles enhance the mechanical and thermal stability of polymeric membranes by reducing the negative impact of compaction and heat on membrane permeability. Also, these inorganic nanoparticles enhance the mechanical and thermal stability of polymeric membranes by reducing the negative impact of compaction and heat on membrane permeability.

Nanocomposite membranes are made up of ordered mesoporous carbons as nanofillers fabricated as thin-film polymeric matrices. They are semipermeable, the top surface used in reverse osmosis. Atmospheric pressure plasma converts hydrophobic mesoporous carbons to a hydrophilic one. Small percentage of hydrophilic mesoporous carbons increases the hydrophilicity; resulting in increased pure water permeability (Kim and Deng, 2011). Thin-film nanocomposites made from polyamide and nano-NaX zeolite (40–150 nm) were reported. They were coated by interfacial polymerization using trimesoyl chloride and *m*-phenylenediamine monomers over porous polyethersulfone. This membrane shows good permeability to pure water, leaving contaminants behind the membrane (Fathizadeh et al., 2011).

Nano-Ag and CNTs prevent membrane biofouling. Inhibition of bacterial attachment or biofilm formation was observed with doping or surface grafting of nano-Ag on polymeric membranes (Mauter et al., 2011; Zodrow et al., 2009) and also inactivation of viruses (De Gussemme et al., 2011). However, authors do not mention membrane long-term efficacy against biofouling. It has been reported that direct contact of CNTs inactivate bacteria (Brady-Estévez et al., 2008). High bacterial inactivation (>90%) was observed with polyvinyl-*N*-carbazole-SWNT nanocomposite at 3 wt.% of SWNT (Ahmed et al., 2012). However, long-term filtration experiments are required to determine the impact of fouling on the antimicrobial activity of CNTs.

Photocatalytic nanoparticles inserted into membranes perform a physical separation process, and the photocatalyst contaminate degradation. Photocatalytic TiO₂ nanoparticles were grafted on metallic filters through dip coating. Combination of foul repellent and photocatalytic nanocoatings degrades unwanted substances forming a dense cake. However, such surface activation is limited to inert materials, polymeric membranes would degrade during the oxidation process (Gehrke et al., 2012).

Nanoscale metallic iron (nZVI) or zero-valent iron (ZVI) has been extensively studied for two decades for the treatment of ground water and also wastewater polluted with different organic and inorganic contaminants (Crane and Scott, 2012; Guan et al., 2015). When these nano-ZVI and noble metal supported on nano ZVI incorporated in to polymeric membrane system for the degradation of contaminants, such as chlorinated compounds, nano ZVI serves as electron donor and noble metals catalyze the degradation reaction (Qu et al., 2013a; Wu et al., 2008).

3.2.3 *Thin-Film Nanocomposite Membranes*

Thin-film nanocomposite (TFN) membranes are a new category of composite membranes prepared by an interfacial polymerization process. Nanoparticles are incorporated within the thin layer of the polymer to improve the properties of the interfacially polymerized layer (Lau et al., 2015). Nanomaterials, such as nano-zeolates, nano-Ag, nano-TiO₂, and CNTs were incorporated as nanoparticles into active thin layers of thin film composite (Lau et al., 2015; Qu et al., 2013a).

Zeolite-polyamide nanocomposite thin films were prepared by interfacial polymerization, which results in reverse osmosis membranes with improved permeability and interfacial properties when compared to similarly formed pure polyamide thin films. In this study water permeability increased up to 80% compared

to thin-film composite membrane, with the NaCl rejection largely maintained up to 94% (Jeong et al., 2007). In another study, zeolite-polyamide TFN membranes for reverse osmosis process were prepared and achieved upon usage for salt rejection (32 g/L) up to 99.4% compared to regular reverse osmosis membranes (Kurth et al., 2011; Lind et al., 2010). This technology is now commercially available; LG NanoH₂O, Inc. successfully conducted a field test of a TFN element and reported that the water flux of the TFN membrane was twice the flux of the polyamide membrane and achieved salt rejection >99.7% (Lau et al., 2015). The unique crystal structure of the zeolite molecular sieve particle is responsible for the improvement in the water flux through its internal pore structure (Lind et al., 2009). Also, hydrophilicity and negative charge of zeolite nanoparticles can cause greater affinity toward water molecules and increased repulsions of anions due to coulombic effects (Jeong et al., 2007).

In a study, incorporation of appropriate amounts of nano-TiO₂ into the thin-film composite active layer resulted in increase in the membrane rejection for salts while maintaining the permeability. In another study, a TFN nanofiltration membrane was developed by the incorporation of aminosilanized TiO₂ nanoparticles. Aminosilanized TiO₂ nanoparticles had good dispersion inside the polyamide skin layer by reducing their surface energy. At ultra-low concentration (0.005 wt.%), the functionalized TiO₂ nanoparticles improved NaCl rejection up to 54%. For higher concentrations of TiO₂ nanoparticle incorporation into thin layers, increased water flux up to twofold was observed compared to thin film composite membrane with negligible rejection loss (Rajaeian et al., 2013).

The incorporation of Ag nanoparticles into TFN membrane has also been reported. Ag nanoparticles can deactivate microorganisms during the filtration process and also reduce membrane biofouling. TFN membranes containing Ag nanoparticles in the thin layer improved water permeability and also demonstrated antibacterial effects on the growth of *Pseudomonas aeruginosa* (Kim et al., 2012).

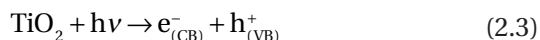
CNTs also found application in TFN membranes. Introduction of carboxyl-functionalized MWCNTs into thin-film composite structure can improve both membrane antifouling property and chlorine resistance (Zhao et al., 2014). The better antifouling property of TFN membrane was due to the improved surface hydrophilicity and greater negative surface charge upon addition of MWCNTs. Further, this membrane was reported to exhibit better chlorine resistance when evaluated either in dynamic or immersion mode, owing to the protection of amide linkage by electron-rich MWCNTs.

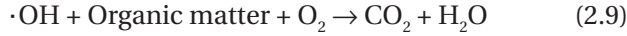
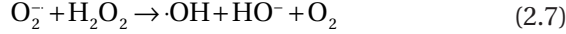
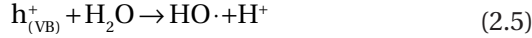
3.2.4 Aquaporin-Based or Biologically Inspired Membranes

Aquaporins are pore-forming protein channels. They are ubiquitous in living cells. Under specific conditions they regulate water flux to reject most ionic molecules (Gehrke et al., 2015; Tang et al., 2013). They are selectively permeable to water; ideal material for making efficient biomimetic membranes for water purification. Aquaporins are unstable, so incorporated into small vesicles embedded in a matrix (Gehrke et al., 2015; Tang et al., 2013). Aquaporin Inside (Aquaporin A/S, Copenhagen, Denmark), first commercial membrane with embedded aquaporins. They withstand pressures up to 10 bar, and water flux rate $>100 \text{ L}/(\text{hm}^2)$. One of the example of using this product is in desalination (Gehrke et al., 2015). The experiments of (Kumar et al., 2014) show that aquaporins have exceptional water permeability. Their observations lead to postulate desalination membranes with vastly improved performance. In a study, aquaporins form self-assembled polymer vesicles forming dense hydrophobic polymer layer. It provides a nanostructured selective barrier, with significant mechanical strength (Xie et al., 2013). Recent literature concerning membrane nanotechnologies has indicted that aquaporin-based bioinspired membranes offer the best chance for revolutionary performance, but they were also seen as the furthest from commercialization (Pendergast and Hoek, 2011).

3.3 Photocatalysis

Photocatalysis is an advanced oxidation process employed in the treatment of water and wastewater. This technique is based on the oxidative elimination of micropollutants and microbial pathogens (Friedmann et al., 2010; Gehrke et al., 2015). Most organic pollutants can be degraded by heterogeneous photocatalysis (Chong et al., 2010; Fujishima et al., 2008; Gaya and Abdullah, 2008; Lazar et al., 2012). TiO_2 is a validated photocatalyst as it is readily availability, safe, and inexpensive (Qu et al., 2013a). When TiO_2 is irradiated by UV light in the range of 200–390 nm, electron-hole pair (e^- - h^+)s is photoexcited. They move into the conduction (CB) and valent (VB) bands, which results in charge separation for an effective photocatalytic function depending on redox potential of a substrate. Therefore, the biodegradability of heavily decomposable substances can be increased in a pretreatment step.





Since, the band gap (E_g) of TiO_2 undertakes broadening (ΔE_g) within the nanorange ($d = 1 \div 12$ nm), more possible organic substrates can be involved in redox processes according to the necessary criteria of photocatalysis:

$$E_{CB} < E_{A/A^-}^0$$

$$E_{VB} > E_{D/D^+}^0$$

where E_{CB} and E_{VB} , the energy edges of conduction and valence bands, respectively; E_{A/A^-}^0 and E_{D/D^+}^0 , the standard potentials in respect to reduction and oxidation of an acceptor (A) or a donor (D). Another requirement to a photocatalyst is correspondence of its band gap to redox potential of $H_2O/\cdot OH$ couple ($OH^- \rightarrow \cdot OH + e^-$, $E^0 = -2.8$ V). This figure resolves the case for TiO_2 ($E_g = 3.2$ eV).

Principally, persistent compounds, such as antibiotics or other micropollutants may be eliminated through photocatalysis during polishing. UV-A radiation is $\sim 5\%$ of the total sunlight. This low photon efficiency limits its industrial use (Gehrke et al., 2015).

In general, activation of TiO_2 is carried out by a UV lamp, but a sunlight source or visible light lamps are also permitted. KRONO Clean 7000 (Kronos Inc., Cranbury, NJ, USA) a photocatalyst, band gap shifted to lower energy; this renders using broader spectrum in sunlight (Gehrke et al., 2015).

To enhance photocatalytic properties of titania, which consist of improving activity or red-shift for energy saving, modification techniques have been explored. For example, the consociation of nanosilica (high thermal and chemical stability) and nanotitania (n-semiconductor) gives rise to new active surface sites. Catalytic properties of silica/titania nanocomposites considerably depend on TiO_2 content and distribution. Jung and Park (2000) stated that photocatalytic activity of SiO_2/TiO_2 enhance significantly in compared to TiO_2 . The highest performance was found at Ti/Si ratio = 70/30. Maximal photocatalytic activity was observed in thin composite films of SiO_2/TiO_2 at $C_{SiO_2} = 5$ mol.%. It is the authors' opinion that such a phenomenon deals with the size reduction of crystallites accompanied with the expansion in the number

of OH-groups on the film surface (Yu et al., 2002). According to Gao and Wachs (1999), direct contact between TiO_2 and SiO_2 enables generating of new characteristics and changes in reactivity of the surface. Such changes are provoked by the formation of Ti–O–Si bonds—their amount is directly proportional to TiO_2 concentration.

Doping of nanotitania makes possible improvement in photocatalytic properties. Inherently, dopants can be metal ions (Choi et al., 1994; Czech et al., 2015; Nazarkovsky et al., 2014), nonmetals (Takeshita et al., 2006; Zaleska et al., 2008); or other semiconductors (Hou et al., 2007; Wu, 2004; Wu and Ritchie, 2008; Zhou et al., 2008). For instance, tungsten trioxide and some fullerene derivatives, such as Fullerol and C60 encapsulated with poly(*N*-vinylpyrrolidone) and composites with TiO_2 show photocatalytic effects under visible light irradiation (Meng et al., 2011, 2013). But, they generate $^1\text{O}_2$ that contains low oxidation potential compared to TiO_2 . Another study shows that to enhance the performance of TiO_2 nanoparticles, TiO_2 nanotubes, and 25–40% doping with noble metals are more efficient, reducing the e^-/h^+ pairs recombination (Lazar et al., 2012). A recent review covers effect on water purification by different operating parameters, such as TiO_2 loading, pH, temperature, dissolved oxygen, contaminant type, concentration, light wavelength, and intensity (Chong et al., 2010).

Many research groups have been investigating the combination of separation and catalytic processes using a membrane photocatalytic reactor to purify water and retain catalytic particles (Azrague et al., 2007; Gehrke et al., 2015; Ollis, 2003). When using highly efficient nanoparticles, suitable filtration system should ensure complete removal of these toxic nanoparticles. Hence, the technology is expensive and energy inefficient—use of high-pressure pumps. A good solution is that photocatalytic nanoparticle immobilization on defined materials uses suitable coating methods, such as physical or chemical vapor deposition, and wet chemical coating method. Microfilters provide both mechanical filtration and chemical decontamination. Dirt particles and larger microorganisms are eliminated by microfiltration membranes at the same time that viruses, spores, and contaminants are also degraded (Gehrke et al., 2015).

In one study, TiO_2 nanoparticles and bactericidal silver-coated metallic filters were reported. The authors used dip coating, chemical, and physical vapor deposition to produce photocatalytic thin coatings, maximum thickness 500 nm. Photocatalyst surfaces were less effective than corresponding nanoparticle suspensions, due to lesser surface area (Gehrke et al., 2012). Purific Water (Holiday, FL, USA) combined water treatment process with photocatalysis,

and ceramic membrane filtration. The filtration assembly has the capacity of >4 million cubic meters per day. They were successful in degrading 1, 4-dioxane (<http://www.purifics.com/>).

Photocatalysis shows a substantial potential as a low-cost, environmental friendly, and sustainable water-treatment technology. Yet, there are some technical challenges for its large scale application, such as (1) catalyst optimization to improve quantum yield or to utilize visible light; (2) efficient photocatalytic reactor design and catalyst recovery/immobilization techniques; (C) better reaction selectivity (Qu et al., 2013a).

3.4 Antimicrobial Nanomaterials in Disinfection and Microbial Control

Current disinfection methods applied in the treatment of drinking water can effectively control the microbial pathogens. Research conducted in the past few decades, however, discloses a dilemma between effective disinfection and formation of harmful disinfection by-products (DBPs) (Li et al., 2008). The commonly used chemical disinfectants in the water industry are chlorine, chloramines, and ozone. They can react with other constituents in the water and generate harmful DBPs. Most are carcinogenic (Hossain et al., 2014). There were more than 600 DBPs, such as halogenated DBPs, carcinogenic nitrosamines, bromate, and so on, reported in the literature (Krasner et al., 2006). UV-disinfection processes have come out as an alternative for oxidative disinfection, since they generate fewer DBPs, while the required high dosage for certain viruses, such as adenoviruses. All these limitations urge the development of alternative methods that can enhance the robustness of disinfection while avoiding DBP formation (Li et al., 2008).

The ideal disinfectant should have the following properties (modified from Hossain et al., 2014):

1. very-broad antimicrobial activity at ambient temperature within short time;
2. cannot produce any harmful by-products during and after their use;
3. does not affect human health;
4. inexpensive and easy apply for the intended use;
5. easy to store, highly soluble in water, and must not be corrosive for any equipment or surface; and
6. amenable to safe disposal.

Materials, such as nano-Ag, nano-ZnO, nano-TiO₂, CNTs, and fullerenes exhibit antimicrobial properties without strong oxidation; they have lower tendency to form DBPs (Li et al., 2008;

Hossain et al., 2014). Brief updates regarding these nanomaterials and their antimicrobial actions are discussed in the following sections.

3.4.1 Antimicrobial Action of TiO_2 Nanoparticles

TiO_2 is a very common nanoparticle type to inactivate microbes in drinking water, surface water, wastewater, and other sources (Brame et al., 2011; Dimitroula et al., 2012; Friedmann et al., 2010; Hossain et al., 2014; Li et al., 2008; Liga et al., 2011; Markowska-Szczupak et al., 2011; Matin et al., 2011; Ng et al., 2013; Pleskova et al., 2011; Simon-Deckers et al., 2009). The antibacterial mechanism of TiO_2 is due to reactive oxygen species (ROS) generation, especially hydroxyl-free radicals and peroxides formed under UV-A irradiation via oxidative and reductive pathways, respectively (Kikuchi et al., 1997; Li et al., 2008). Generated ROS destruct the cell membrane, damaging DNA and protein, releasing hazardous ions for cell malfunction, disrupting electron transfer, and hampering respiration process (Hossain et al., 2014) (Fig. 2.7).

Strong absorbance of UV-A furnish activation of TiO_2 under solar irradiation, significantly enhancing solar disinfection.

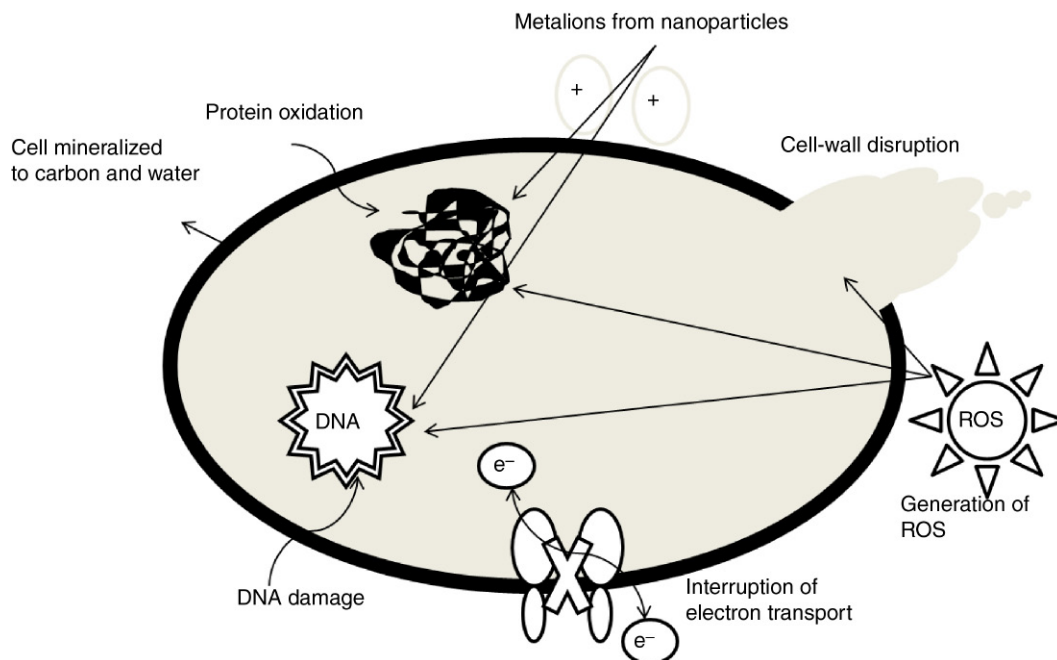


Figure 2.7. Different mechanisms of antimicrobial activities showed by nanomaterials.

However, TiO_2 -based solar disinfection is a very slow process that may be a small fraction of UV-A in solar radiation. Therefore, successful research on metal or nitrogen doping to improve visible light absorbance of TiO_2 or UV-A activity is critical to the application of TiO_2 solar disinfection. Bacterial death was observed even in the dark by this nanomaterial, indicating the involvement of other unknown mechanisms (Adams et al., 2006; Li et al., 2008).

3.4.2 Antimicrobial Action of Ag Nanoparticles

Silver has been known for its antimicrobial action since ancient times. It has a wide range of industrial applications in healthcare and external medicine (Hua et al., 2012). In recent times nano-Ag has been widely used as an antimicrobial nanomaterial. They are the material of choice for water decontamination, due to the following: significant and broad antimicrobial activity, safety, and easy to fabricate. Nanosilver releases silver ions in water (Qu et al., 2013a; Xiu et al., 2011, 2012) binding to $-\text{SH}$ groups in vital enzymes and damaging them (Liau et al., 1997; Qu et al., 2013a). Silver ions interfere with DNA replication and induce structural changes in the cell envelope (Feng et al., 2000; Qu et al., 2013a). Toxicity of nano-Ag depends rate of release of silver ions. Size, shape, coating, and crystallographic facet influences the release kinetics of silver ions. Presence of ubiquitous ligands reduces its bioavailability, and reduces its toxicity (Qu et al., 2013a; Xiu et al., 2011). In another study they show sublethal doses of silver ions favors *E. coli* growth. Suggesting these strategy could hit back if not designed properly (Qu et al., 2013a; Xiu et al., 2011). Commercial devices, such as MARATHON and Aquapure systems utilizing nano-Ag are already available. Nano-Ag was incorporated into ceramic microfilters as a barrier for pathogens, which can be employed in remote areas of developing countries (Peter-Varbanets et al., 2009).

3.4.3 Antimicrobial Action of ZnO Nanoparticles

Zinc oxide nanoparticles have been used in sunscreen lotions, coatings, and paints due to their strong UV absorption capacity and transparency to visible light (Franklin et al., 2007; Qu et al., 2013a). ZnO nanoparticles show very good antibacterial activities on a broad spectrum of bacteria. However, the antibacterial mechanism of ZnO nanoparticles is unclear, since researchers have obtained opposite results, for example, the particles size effect was established in Jones et al. (2008), but that was not consistent in Franklin et al. (2007). The reason was suggested to be the

photocatalytic generation of H_2O_2 responsible for antimicrobial action of ZnO. Even though, both Zn^{+2} ion and ZnO nanoparticles show antibacterial activity. Aquatic organisms can be highly sensitive to dissolved zinc (Franklin et al., 2007). In view of its easy dissolving nature, ZnO applications in drinking water purification are limited.

3.4.4 Antimicrobial Action of Carbon Nanotubes

CNTs show antimicrobial property upon direct contact with cells (Vecitis et al., 2010). Graphene and graphite materials also exhibit similar mechanisms (Liu et al., 2012). Short, dispersed, and metallic CNTs with small diameters are more lethal (Qu et al., 2013a). CNTs effectively removes bacteria by size exclusion, and viruses by depth filtration (Brady-Estévez et al., 2008). Retained bacteria are quickly inactivated by CNTs; MWNTs directly oxidize adhering bacteria and viruses. They decontaminate water within seconds by using small intermittent voltage (Rahaman et al., 2012; Vecitis et al., 2010).

3.5 Nano Antimicrobial Polymers

Polymeric nanoparticles kill microorganisms either by releasing antibiotics, antimicrobial peptides, and antimicrobial agents or by contact-killing cationic surfaces, such as quaternary ammonium compounds, alkyl pyridiniums, or quaternary phosphonium. Different antibacterial mechanisms are reported to show how these cationic groups are able to disrupt bacterial cell membrane. The main mechanism is that the hydrophobic chains of certain lengths will penetrate and burst the bacterial membrane. It has been shown that high levels of positive charge are capable of conferring antimicrobial properties irrespective of hydrophobic chain length, perhaps by an ion exchange mechanism between the bacterial membrane and the charged surface (Beyth et al., 2015; Jain et al., 2014).

Nanopolymeric antimicrobial materials show long-term antimicrobial activity. They are nonvolatile and chemically stable. They can bind to the surface of interest and hardly permeate through biological membranes (Kenawy et al., 2007). Polycationic antimicrobials contain high surface density of active groups, which result in higher antimicrobial activity. Quaternary ammonium compounds possess a broad spectrum of antimicrobial activity against both Gram-positive and Gram-negative bacteria. Polyamines that have been reported as being highly effective antimicrobial nanoparticles are quaternary ammonium

polyethylenimines, which have a broad range of bacterial targets when incorporated into various polymeric matrixes (Shvero et al., 2015).

3.5.1 Chitosan-Based Nanoparticles

Chitosan is obtained from chitin in shells. It show antibacterial activity and is a natural polymer. The nanoparticles of chitosan or its derivatives have a broad spectrum of antibacterial, anti-fungal, and antiviral activities (Chirkov, 2002; Li et al., 2008; No et al., 2002; Qi et al., 2004; Rabea et al., 2003). The nanoparticles of chitosan are more effective against fungi and virus compared with bacteria (Rabea et al., 2003). Among bacterial strains the antimicrobial activity of chitosan is higher for Gram-positive bacteria than for Gram-negative bacteria (Don et al., 2005; No et al., 2002). Minimum inhibitory concentrations from 18 to 5000 ppm were reported for the chitosan nanoparticles depending on the organism, pH, molecular weight, degree of polymerization, and the presence of lipids and proteins (Don et al., 2005; No et al., 2002; Rabea et al., 2003).

The main antimicrobial mechanisms of chitosan are the positively charged chitosan particles that interact with negatively charged cell membranes, causing an increase in membrane permeability and eventually rupture and leakage of intracellular components (Qi et al., 2004). The antibacterial action of chitosan derivatives containing quaternary ammonium groups, such as *N,N,N*-trimethyl chitosan, *N*-propyl-*N,N*-dimethyl chitosan, and *N*-furfuryl-*N,N*-dimethyl chitosan are stronger than those of chitosan, and they increase with decreasing pH (Ji et al., 2009; Li et al., 2008).

Nanochitosan has potential drinking water disinfection applications as an antimicrobial agent in membranes, sponges, or surface coatings of water storage tanks. Nanochitosan shows superiority over other disinfectants due to its broader spectrum of activity against bacteria, viruses, and fungi, and less toxicity toward animals and humans. However, chitosan is an effective disinfectant only at acidic pH; this is due to its solubility and the availability of charged amino groups (Li et al., 2008; No et al., 2002; Rabea et al., 2003). This limitation can be overcome by preparing water-soluble chitosan derivatives.

3.5.2 Nanopolymers-Based Water Purification Systems

N-bromohydantoin/uracil-conjugated polystyrene beads were prepared by the authors and studied controlled release of bromine in water purification systems (Farah et al., 2015a,c).

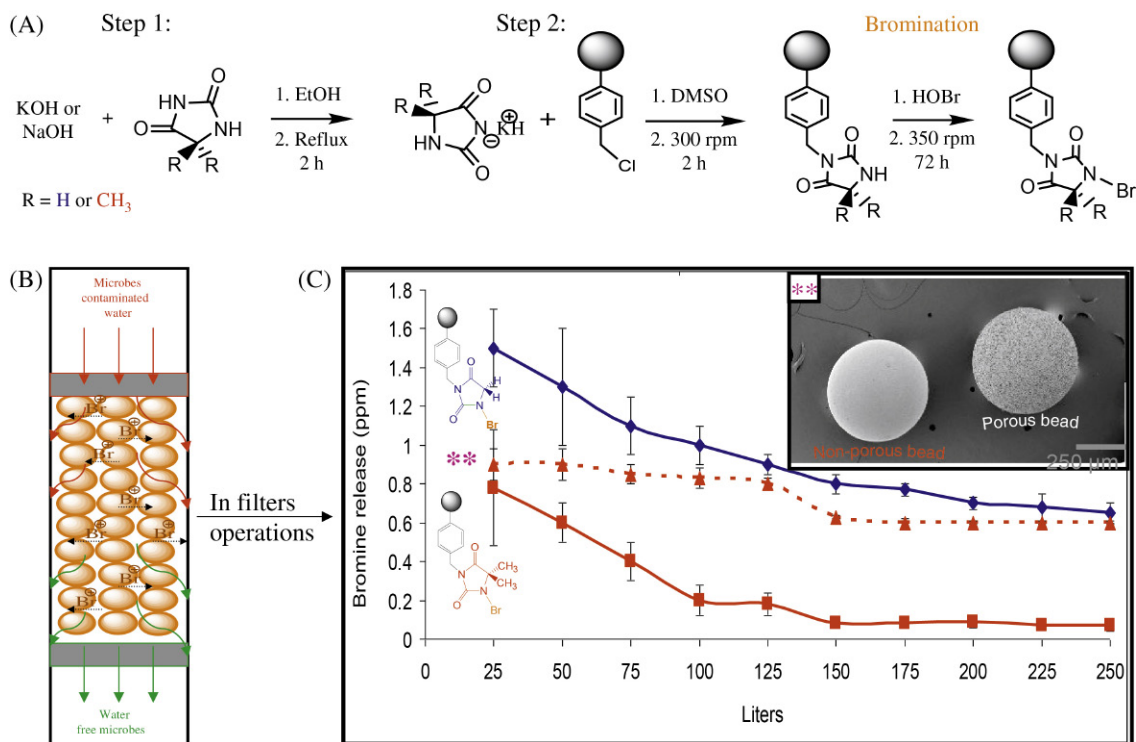


Figure 2.8. (A) *N*-bromo-hydantoin synthesis by conjugation to micronsized beads followed by bromination; (B) filters loaded with *N*-bromo-hydantoin/5,5'-dimethylhydantoin-polystyrene beads; and (C) in filters operations: hypobromous release from different beads having different nanomicro characteristics affecting oxidative halogen releasing profiles from polymeric beads/surfaces (Farah et al. 2015a).

Active bromine release from the beads into the running water and the antimicrobial efficiency were examined against *E. coli* and MS2. This resin exhibited excellent antimicrobial properties; 6- and 4-log reduction for *E. coli* and MS2, respectively, were obtained for all tested points during 250 L. Moreover, beside the effect of the *N*-haloamine structure on lasting disinfection activities, bead's nanomicro characteristics were found critical for oxidative halogen release control: rate stabilization and modulation, extension and consequently influences antimicrobial activity. This aspect is important, since the rate of halogen release influences antimicrobial activity and subsequently the material usage for different applications, Fig. 2.8B and C (Farah et al., 2015a). Bromine% of the reported materials after release study indicated the capability of antimicrobial hypobromous release for extra hundreds of liters. *N*-bromo-dimethylhydantoin with low crosslinked beads maintained their activity for 550 L. This brominated resin should be considered in filters for

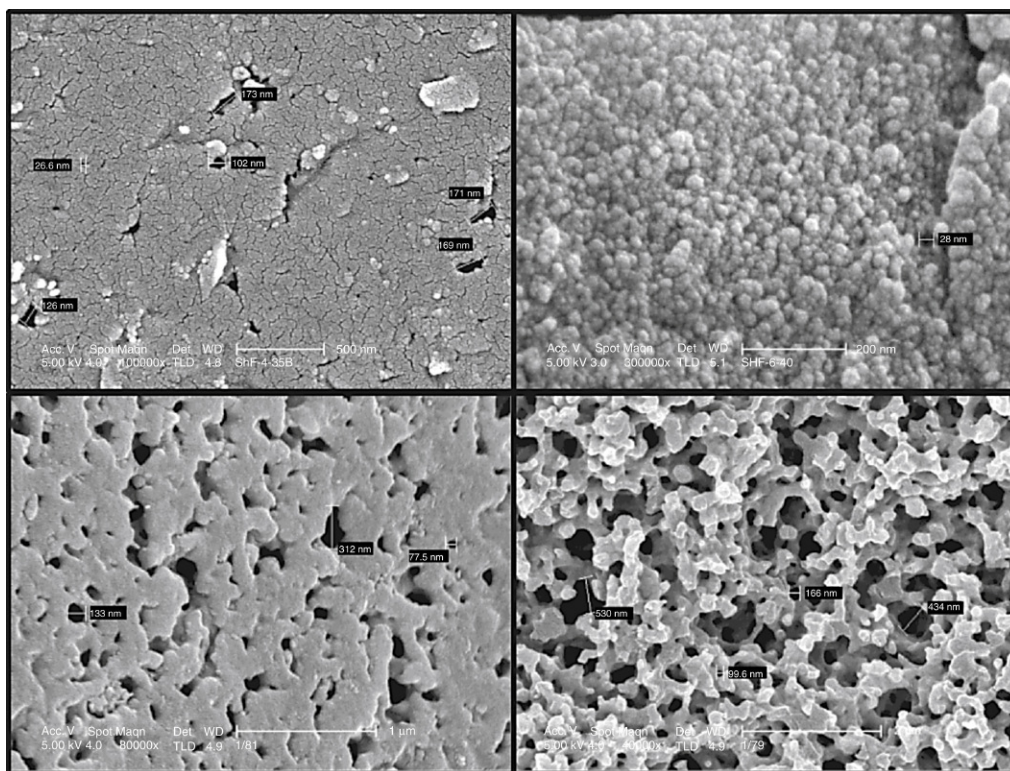
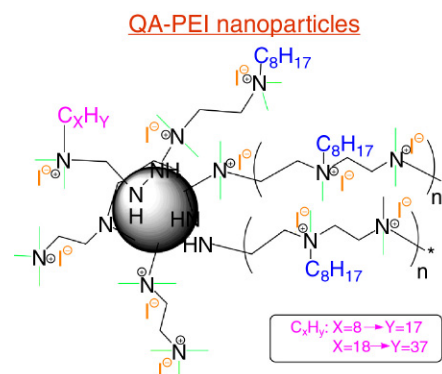


Figure 2.9. Representative photos of the nanopores onto the brominated-hydantoin beads surface or inside were found to play a critical role in oxidative halogen release control: rate stabilization and modulation, extension and consequently influences antimicrobial activity (Farah et al. 2015a).

decontamination of drinking water (Aviv et al., 2015). These materials were found to have great potential due to ability to decontaminate large volumes of contaminated water, low costs, and bromine rechargeability (Farah et al., 2015a,c) (Fig. 2.9).

Quaternary ammonium polyethylenimine nanoparticles (QA-PEI NPs) of C8 chain alkylated, and C18 modified were prepared (Fig. 2.10), and these nanoparticles were embedded into polyethylene vinyl acetate and polyethylene methacrylic acid coatings (Farah et al., 2013; Yudovin-Farber et al., 2010). These coatings were tested for their antibacterial activity against representative bacteria, *E. coli*, *P. aeruginosa*, *Staphylococcus aureus*, and heterotrophic plate count. Study was performed in both static and dynamic modes. The authors anticipated that these QA-PEI NPs will find application in water purification systems as disinfectants and for

Figure 2.10. Chemical structure of C8/C18 alkylated QA-PEI crosslinked nanoparticles.



preventing the accumulation of microorganisms onto device surfaces as well as in bioadhesives and self-sterilizing surfaces (Farah et al., 2015b).

4 Regeneration of Nanoparticles

Regeneration of nanoparticles in water purification is one of the crucial aspects, since it controls the economy of water-treatment technology. pH-dependent solvents play crucial roles in regeneration of nanoparticles. They can also be achieved by applying a separation device or immobilizing nanomaterials in the treatment system. Membrane filtration is promising for the regeneration and reuse of nanomaterials due to its chemical use. Ceramic membranes are always advantageous, as they are more resistant to UV compared to polymer membranes (Qu et al., 2013a). Raw water pretreatment is very important to reduce turbidity; otherwise the suspended particles are retained by membranes, and they decrease the efficiency of the treatment. Immobilization is another technique for nanomaterials. But, current immobilization techniques have not been very successful. Development of simple and low-cost methods is required to immobilize nanoparticles without affecting their efficiency. Magnetic separation is another option for the separation of magnetic nanoparticles.

Nanomaterials coated on treatment system surfaces are released in a relatively quick and complete manner. Nanomaterials embedded into a solid matrix have slow release until they are disposed of. Identification of a nanomaterial release is a major technical hurdle for risk assessment, and it remains challenging. The details regarding different detection techniques are mentioned in the literature (Qu et al., 2013a; Silva et al., 2011; Tiede et al., 2008). According to the literature, nanoparticles can be regenerated and used for water treatment, which makes them economically viable materials. The regeneration capacity of nanoparticles may be considered an extra advantage for their popularity in wastewater treatment. However, only very few methods are available for the detection of nanomaterials in complex aqueous matrices. They are highly sophisticated, expensive, and have many limitations. Currently, rapid, sensitive, and selective nanomaterial analytical techniques are in great demand.

Management of used nanoparticles and recovered pollutants is one of the most important aspects. Everyone is aware of pollutant hazards and nanotoxicology; proper disposal must be carried out by the users. The best way is to recycle the nanoparticle and exhausted nanoparticles may be in the manufacturing of bricks,

stones, and so on. Different regenerated materials may be recycled for manufacturing various commodities. The recovered organic contaminants should be treated as priority pollutants (Ali, 2012).

5 Safety, Toxicity, and Environmental Impact of Nanomaterials

Due to our current poor understanding of the fate and behavior of nanoparticles in humans and the environment, toxicity is becoming one of the urgent issues of nanotechnology. The main concerns related to nanotechnology are the hazardousness of nanoparticles and the exposure to risk (Gardner and Dhai, 2014). Biological and chemical effects on humans or the environment is the first major issue. The second is of leakage, spillage, circulation, and concentration of nanoparticles that might cause a hazard to humans or the environment (Gardner and Dhai, 2014). Properties, such as size, shape, reactivity, and so on, are making these nanomaterials very useful. The same properties can also make them harmful to the environment and toxic to humans (Hillie and Hlophe, 2007). The entry of nanoparticles into our body is possible through the skin, inhalation, ingestion, and so on. After reaching the bloodstream, they can travel to various body parts, such as the brain, heart, liver, kidneys, spleen, bone marrow, and nervous system (Ali, 2012). The toxicity of nanoparticles is due to their properties and can lead to high chemical reactivity and production of ROS. Production of ROS is possible from CNTs and metal oxides. The ROS generated will cause oxidative stress, inflammation, which results in damage to proteins, membranes, and DNA (Nel et al., 2006). There is a possibility that nanoparticles can adsorb on the body surface and alter the mechanisms of enzymes and certain proteins (Hubbs et al., 2011). Nanoparticles show their toxicity in the environment by agglomeration. Environmental risk analysis of nanoparticles is mentioned in the literature (Grieger et al., 2012). Knowledge of hazards and exposure risks of nanoparticles to the ecology is less among the scientific community, so risk assessment and management is crucial (Gardner and Dhai, 2014). The challenge is to resolve problems before nanoparticle usage starts on a large scale in water purification. There must be safety evaluation, large-scale production facilities, safe disposal of wastes, and energy efficiency. These are the major challenges that may cause delay in the large-scale application of nanotechnology in water purification (Gardner and Dhai, 2014). However, the behavior of nanoparticles inside the body is still a major question that needs to be addressed.

6 Limitations and Research Needs

Water/wastewater-treatment processes by nanotechnology show great promise in laboratory studies. Some of these technologies are marketed, and others require significant research before they can be scaled up. Their commercialization is challenging; we need to overcome many technical hurdles; make them cost effective, and safe. Research is needed before full-scale operation of nanotechnology for treating natural and wastewaters. Studies should be conducted under realistic conditions to assess the efficiency of available nanotechnology to validate the nanomaterial-enabled sensing. Another research need is to measure the long-term efficiency of available technologies, which are conducted on a laboratory scale. Commercialization of these technologies is possible only by their long-term performance in the treatment of water and wastewater. Also, adoption of an innovative technology strongly depends on the cost effectiveness and potential risks involved. At the moment, the cost of nanomaterials is very high, with few exceptions, such as nano-TiO₂, nano-scale iron oxide, and polymeric nanofibers. Cost effectiveness can be achieved by regeneration and reuse of these nanomaterials (Qu et al., 2013b). Since these materials are nanoscale, risk assessment and management is a challenge. Researchers should understand the potential hazards of these materials in the treatment of water and wastewater.

7 Conclusions

Today we need water purification technologies that provide high-quality drinking water, remove micropollutants, and intensify the industrial processes. Nanotechnology provides the opportunity; unique properties of nanoparticles are ideal candidate for developing rapid water-treatment technology. Nanoparticles may eliminate metal ions, anions, organic compounds, and microorganisms. Nanoparticle doses required for the water treatment are low, making their application relatively economical.

Different nanotechnologies are reviewed in this chapter. A few technologies are in laboratory research stage, some reached to pilot testing, and some are commercial. Among these technologies, nanoadsorbents, nanomembranes, and nanophotocatalysts are most promising. Although, these technologies have been commercialized, their potential has not been reached for large-scale use in wastewater treatment.

Risk assessment of recovered pollutants and exhausted nanoparticles still remains significantly unexplored. Therefore,

ecofriendly waste management methods are required to avoid hazards and toxicities. The future of the nanoparticles in water treatment is quite progressive, but it requires collaborative efforts of academic and industrial resources to materialize a fast, economical, and feasible water-treatment technology. It will be possible by working together to solve water contamination globally.

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