Chapter 19

Nanomaterials for removal of waterborne pathogens: opportunities and challenges

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1. Introduction

Water is the most basic and irreplaceable need of our ecosystem. Water is not only a universal solvent but also a vital resource for life to sustain. With an exponential rise in the anthropogenic activities and illicit management, water pollution has been spiraled and resulted in an escalation of waterborne diseases (WDOs) all over the world. The microbiological pollution in waterbodies is an issue of serious concern. According to reports of UNICEF in 1995 (The state of the world's children. Oxford University Press, Oxford), waterborne pathogens accounted for approximately 5 million deaths per year, out of which half was accounted for children. Waterbodies' surfaces and groundwater contain number of pathogens that may pose serious threat to human health. Thus, the need of water disinfection is an undeniable issue worldwide (Ong, 2016). Bacteria (*Burkholderia pseudomallei, Escherichia coli, Pseudomonas aeruginosa, Salmonella typhi, Vibrio cholerae, Yersinia enterocolitica, Plesiomonas, Campylobacter* spp., *Shigella* spp., etc.), cyanobacteria (*Microcystis, Anabaena, Planktothrix, Nostoc*), viruses (adenoviruses, enteroviruses, astroviruses, hepatitis A viruses, hepatitis E viruses, noroviruses, sapoviruses, rotavirus), prions, protozoa (*Acanthamoeba* spp., *Cyclospora cayetanensis, Entamoeba histolytica, Giardia intestinalis, Cryptosporidium, Balantidium coli, Isospora belli, Naegleria fowleri, Toxoplasma gondii*), cysts, fungi, helminths (*Dracunculus medinensis, Schistosoma* spp.), *Rickettsia*, etc., are variety of microbes proved fatal to human beings and pose serious threat to aquatic systems as well (Seo et al., 2012). Bacterial pathogens may lead to infections such as typhoid, cholera, intestinal infections, etc. On the other hand, cyanobacteria produce microcystins that may prove lethal to human systems. Virus pathogens cause serious health issues such as

conjunctivitis, throat sores, abdominal inflammations, rashes, fever, respiratory disorders, and enteric infections. Protozoan cells such as *Cryptosporidium* and *Giardia* are reported to cause human gastroenteritis, while fungal cells produce mycotoxins that induce inflammations in respiratory tracts and digestive systems (Kumar et al., 2014a,b). A detailed account of pathogens and disease related with them has been summarized in Table 19.1.

Every year millions of people lose their life because of these WDOs all around the world. Waterborne pathogens pose serious global challenges and around 800 million populations is diploid of safe and consumable water. Biological contamination of water needs to be curbed and water disinfection techniques are the methods to tackle these pathogens. The history of water purification dates back to around 1804 in Scotland where world's first citywide municipal water treatment plant was set up using sand filter technology. The earliest mode of disinfection was introduced by Humphrey Davy in 1814 using chlorine, which was further brought into application of water disinfection around 1902. Few years later, ozonation was introduced as new pathway for water disinfection. From then, treatment of waterborne pathogens has traveled a lot through. Even today chlorination is used as a method for water disinfection in not only many developing countries but also in the United States and some developed nations in Europe because of its simple application and cost-effectiveness. Extensive techniques have been implied for the termination of biological pollutants including physical processes such as adsorption, heating (boiling), distillation and filtration, biological processes in the form of activated sludge, chemical processes such as flocculation and chlorination, light irradiation, and photocatalysis. Disinfectants are not only limited to combat microbial pollution but they also help in eliminating taste and color, oxidize iron and manganese in waterbodies, and enhance coagulation and filtration activity. The inefficiency of common chemical disinfectants (chlorine, chloramines, ozone, chlorine dioxide, etc.) has steered need of more efficient systems for pathogenic inactivation. Also, the side products of these conventional disinfectants are haloacetic acids, chlorite, haloacetonitriles, dibutyl phthalate, and chloral hydrate formed because of the reaction between these disinfectants and natural organic materials and had been reported to be carcinogenic, teratogenic, and highly mutagenic (Sadiq and Rodriguez, 2004; Wei et al., 1994). The highest amount of disinfection by-product is chlorate followed by bromochloro-, bromodichloro-, dibromochloro-, and tribromo-acetic acid, trichloronitromethane, and chloral hydrate (Muellner et al., 2007). These conventional techniques for disinfection of water have been proved to be unsuitable in the long term. There are number of side effects and limitations that have been proposed for conventional techniques of pathogen inactivation. There are around 600 by-products of disinfection reported so far and all the conventional oxidants that are being used as disinfectant have been reported to produce side products that are very harmful for the living systems. The nonspecificity of conventional disinfectants poses another threat for the living

TABLE 19.1 Waterborne pathogens and related diseases (Kumar et al., 2014a,b).

Bacteria	
Burkholderia pseudomallei	Melioidosis
Campylobacter jejuni, Campylobacter coli, Escherichia coli, Yersinia enterocolitica	Gastroenteritis
Legionella pneumophila	Legionnaires' disease
Nontuberculous mycobacteria, Pseudomonas aeruginosa	Pulmonary disease, skin infection
Salmonella typhi	Typhoid
Salmonella enterica	Salmonellosis
Shigella spp.	Shigellosis
Clostridium botulinum	Botulism
Mycobacterium marinum	Marinum infection
Leptospira spp.	Leptospirosis
Viruses	
Adenoviridae virus, Enteroviruses, Astroviruses, Noroviruses, Sapoviruses, Rotavirus	Gastroenteritis
Poliovirus	Polio
Coxsackievirus	Meningitis
Hepatitis viruses A and *E*	Hepatitis
Coronavirus	SARS
Protozoa	
Acanthamoeba	Encephalitis
Cryptosporidium	Cryptosporidiosis
Cyclospora cayetanensis	Gastroenteritis
Entamoeba histolytica	Amebiasis
Giardia lamblia	Giardiasis
Naegleria fowleri	Primary amebic meningoencephalitis
Toxoplasma gondii	Toxoplasmosis
Helminths	
Dracunculus medinensis	Guinea-worm disease

TABLE 19.1 Waterborne pathogens and related diseases (Kumar et al., 2014a,b).—cont'd

Schistosoma spp.	Schistosomiasis
Taenia solium	Taeniasis
Ascaris lumbricoides	Ascariasis
Enterobius vermicularis	Enterobiasis
Fasciolopsis buski	Fasciolopsiasis

systems as higher doses are required to carry out disinfection (Lee, 2015). Limitations of current disinfectants can be listed as follows (Muellner et al., 2007):

- Tedious preparation and application because of their harmful and rapid degradation attributes.
- Short range of antimicrobial ability.
- Harmful by-products during and after their use.
- Harmful to human beings.
- Storage is arduous.
- Highly corrosive for any equipment or surface.
- Unsafe disposal.

These conventional techniques are not only slow but also some of them such as filtration creates lots of sludge, another toxic waste which needs to be disposed and tackled (Catalkaya et al., 2003). Adsorption has been the most common method for the removal of pathogens especially bacteria and fungi from the system because of their easiness and highly efficient features. Removal of viruses is a tough task as they are very small in size and thus easily pass through theses filters (20−90 nm). As time goes by, some of the pathogens such as *Cryptosporidium* and *Giardia* are reported to develop resistance to chemical disinfectants. It means high doses of these chemicals are required to kill these pathogens, as a result of which more and more disinfection by-products are added to system. A large extent of works has been already done for studying the adsorbents and their applications for pathogens removal in the past many years. However, issues such as high cost of equipment, separation challenges, disposal, and other reasons limit the application of adsorbents in removal of pathogens (Hao et al., 2010; Zhang, 2003). Till date no chemical disinfectant has been proved sufficient for complete sterilization and disinfection (Favero, 2007, pp. 31−50). Therefore, development of eco-friendly, highly robust, and advanced techniques with higher efficiency has become the need of time.

2. Nanomaterials

Nanomaterials refer to the class of materials that consist of particulate substances having any one of their dimension <100 nm at least (Laurent et al., 2010). Nanotoxicology is such an emerging branch of science that deals with interaction of nanomaterials and biological cells and their cytotoxic impacts. The properties of nanomaterials include large specific surface area, their crystalline structure, shape (that regulates most of its properties as well as their unique attributes), surface morphology, and assembling phenomena. The quantum effect in nanoparticles is responsible for their unusual physico-chemical properties such as thermal, electrical, or optical properties (Cheng, 2004). Their highly tunable synthetic pathways, sensitive characterization methods, and multiple action properties make them materials of advanced applications (Heiligtag and Niederberger, 2013). They have already been of great benefit in the field of catalysis and sensing because of their high reactivity and large surface area. Nanotechnology is steadily making its way into dealing with environmental pollution. Nanomaterials exhibit characteristics, such as strong adsorption, superior redox, and photocatalytic activity, thereby resulting in extraordinary prospective for removal of waterborne pathogens. In past years, it has emerged as highly advanced and robust method of wastewater remediation and created new pathways in achieving excellent results in water treatment technologies (Oves et al., 2015). For the application of nanomaterials as disinfectant, above limitations have to be overcome along with two basic and chief properties, i.e., stability of nanomaterials in aqueous solutions (physical and chemical stability should be taken care of) and photocatalytic nanoparticles must be active under solar irradiation for photoexcitation. The most important factor that controls the application of nanomaterial as antimicrobial disinfectant lies in the fact that it should show antimicrobial activity only and that it is harmless for human beings within a certain limit (Mahendra et al., 2009, pp. 157−166). The photocatalytic efficiency of nanomaterial is mainly ascertained by the interaction between their optical bandgap energy and the capturing of photogenerated charge carriers (Saeed and Khan, 2017). These nanomaterials provide a discrete, high-performance, and recyclable water cleaning system that reduces the cost of transport, water loss, and improves the quality. Another technique that may prove highly beneficial for pathogens removal is nanomembranes, which can be used for bacteria and viruses more than 50−60 nm in diameter. Many other advanced techniques that employ nanotechnology for treatment of pathogens have been discussed in this chapter with their limitations and plausible solutions. The application of nanomaterials largely depends on its physical properties, which is discussed point by point below.

2.1 Characteristics of nanoparticle

Nanomaterials are characterized on basis of their size, morphology, and the charge they bear on their surfaces. Many advanced microscopic techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are already available to determine their size distribution, average diameter, morphology of the nanomaterial surfaces, and their shape. These parameters play an important role in determining their physical stability and in vivo particle distribution which is mostly controlled by their size and surface charge (Bhatia, 2016, pp. 33−94). A deep insight into these physicochemical properties leads a vast understanding regarding the application of nanomaterials in various fields. Some of the important characteristics have been mentioned below:

(a) *Particle size*: Particle size holds important information of studying the cytotoxicity of nanoparticles, their biodistribution, and their retention the tissues. Smaller the size of nanoparticle, larger the surface area it possesses. The small size of nanomaterials facilitates its easier cell penetration (cell wall and cell membrane), thereby promoting cellular dysfunctioning. Cellular uptake of nanomaterials is inversely related to their particle size. Many advanced techniques are available, which helps in determining the size of the nanomaterials that are listed here:

Photon-correlation spectroscopy (*PCS*) or *dynamic light scattering* (*DLS*): It qualifies to be the most admired and speedy technique that determines the nano- and submicron ranges of Brownian nanoparticles in a colloidal suspension. The mode of determination of particle size involves Doppler shift due to Brownian motion of nanoparticles against monochromatic light beam (LASER). The interaction of light beam with particle results into shift in the wavelength of incoming light which is used to correlate the size and motion of the particle in the colloidal suspension (DeAssis et al., 2008).

Scanning electron microscopy: It is the most customary method to ascertain shape, size, and surface morphology of the nanoparticles. They help in directly visualizing the morphology of nanomaterials; however, their information about size distribution and average population tends to be of limited benefit. The technique is costly and time-consuming and requires complementary information for the data accuracy (Molpeceres et al., 2000) (Fig. 19.1).

Transmission electron microscopy (*TEM*): It provides image, diffraction patterns, and spectroscopic data of the material. High-resolution TEM imaging can be coalesced to nanodiffraction, atomic resolution electron
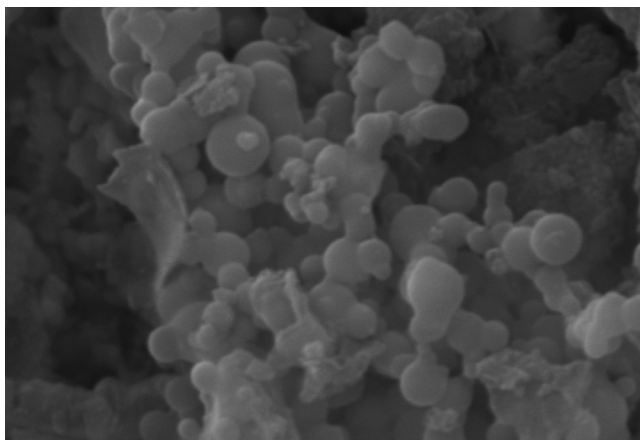
FIGURE 19.1 A scanning electron microscopy image of silica nanoparticles.

energy-loss spectroscopy (AREES), and X-ray energy-dispersive spectroscopy (X-ray EDS) techniques to investigate their properties in advancement. They have much more advancement when studying biological sample as compared to thick-stained section studies.

Atomic force microscopy: The technique is also known as scanning force microscopy (SFM). A probe tip of atomic scale is used to physically scan samples at submicron level. The method holds an advantage above every morphological study process. The study of biological samples in AFM requires no specific treatment and therefore easily provides details for biological and delicate polymeric samples. It provides the most accurate data for size, size distribution, and morphology and hence is most suitable method for studying the interaction of nanomaterials with biological samples (Polakovic et al., 1999; Cho et al., 2013).

Other techniques include differential centrifugal sedimentation (DCS) and nanoparticle tracking analysis (NTA), which are new methodologies based on high resolution and are quite useful for biological systems such as proteins, DNA, and RNA (Sikora et al., 2016).

(b) *Morphology and surface area*: X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique for analyzing exact elemental ratio, composition, and bonding nature of elements in the nanomaterials. Their vibrational characteristics can be studied by FTIR and Raman spectral analysis. The fingerprint region of these spectral data provides exact information of the nanomaterial and peak shifts are important revealing factor for detecting the extent of functionalization. The surface area of nanomaterials is studied by Brunauer−Emmett−Teller (BET) technique. The large surface area of nanomaterials makes them available to diverse

applications ranging from catalysis, medical, and environmental to many other advanced technologies (Saeed and Khan, 2017).

(c) *Surface charge and surface hydrophobicity*: The interaction of nanomaterials with the biological system is largely determined by their surface charge and intensity. The surface charge is indirectly determined through zeta potential measurement. Zeta potential plays an important role in determining the stability of colloids (nanoparticle) as well as knowing the intensity of electrostatic attraction between biomolecules and the nanoparticles. High value of zeta potential in either direction (positive or negative) is an indicator of high stability of the colloidal solution.

Surface hydrophobicity can also be determined with zeta potential values. Besides, other methods for the determination of hydrophobicity include hydrophobic interaction chromatography, biphasic partitioning, probe adsorption, and contact angle measurements. The latest advancement in the field of studying surface hydrophobicity involves X-ray photon correlation spectroscopy, which determines surface hydrophobicity as well as identifies chemical groups (or functional groups) also on their surface (Scholes et al., 1999; Pal et al., 2011).

(d) *Electronic and optical properties*: The electronic properties of nanomaterials also control most of its optical properties. The optical properties of nanoparticles are mostly dependent on its size and surface property. Nobel metal nanoparticles show strong absorption in UV-visible region. Localized surface plasma resonance (LSPR) is the phenomenon that provides a deep insight of electrooptic property of the nanomaterials. Optical property determination is an important factor in determining the photocatalytic activity and hence the application of the nanomaterials. A core analysis of photocatalytic activity helps in deducing the mechanism for photochemical reactions. Using the basic principles of photochemistry (Grothus-Draper's law, Beer−Lambert law), the characterization of optical properties can be largely done. UV-visible diffuse reflectance spectroscopic (DRS) measurement technique is on such method that assists in determining the photoactivity of nanomaterials in terms of absorbance, reflectance, luminescent, or phosphorescent properties. Besides DRS, photoluminescence and null ellipsometer are other means to derive optical properties of these nanoparticles. UV-Vis DRS also helps in determining the bang gap in semiconductor nanomaterials. Bandgap lets us know the photocatalytic activity and material conductivity of these nanomaterials.

(e) *Magnetic and mechanical properties*: Magnetic activity of certain nanomaterials is another important benefit and can be applied in field of catalysis, biomedical techniques, and MRI as well as water remediation. The uneven distribution of electrons leads to formation of magnetic moment in these nanomaterials. The mechanical strength of nanomaterials is measured in terms of modulus, stress, strain, adhesion, or friction.

Mechanical properties are necessary for studying effect of porosity, particle size, filled composites, and polymer-based nanocomposites of various kinds of nanomaterials. Magnetic properties of some metals are visible at nanoscale such as for Au or Pt. Ferromagnetism is observed in case of nano-Pt and nano-Pd due to structural changes (Alagarasi, 2009, pp 45−60).

2.2 Types

2.2.1 Naturally occurring nanomaterials

Nanoparticles are not actually human inventions. Their presence in nature dates back to the time of origin of Earth. Various geological and biological activities have added variety of nanoparticles into the system. Naturally occurring peptides, celluloses, chitins, and many other such biological nanoparticles have been studied for their applications in various fields. Peptides are the class of biomolecules that form the protein structures in living systems. Cellulose nanoparticles are most promising biopolymers in nanotechnology. Their high mechanical strength and robustness make them a perfect material for nanomembranes. The surface of cellulose can easily be functionalized and therefore can be switched for variety of purposes (Moon et al., 2011). Chitins β-(1−4)-poly-N-acetyl-D-glucosamine are most abundant polysaccharides derived from many organisms including some fungi and insects. They can be easily processed into membranes and nanofibers. Chitin nanoparticles (50−100 nm) were prepared from acid hydrolysis and ultrasonication of chitin (Barikani et al., 2014). Chitosan is a naturally obtained material from the arthropod shells, crustaceans, fungi, and algae and has been reported for its antimicrobial activity. It is the second largest naturally occurring biopolymer after cellulose. They are nontoxic, mucoadhesive polymers formed by deacetylation of chitin. Chemically, chitosan is similar as cellulose with a β-(1−4) glycoside bonded 2-amino-2-deoxy-D-glucose monomers. Chitosan is potential bactericide against a range of pathogens especially Gram-negative bacteria (Chung et al., 2003). Chitin and chitosan have widely been applied to fabricate nanopolymer scaffolds in many nanomembrane-based antimicrobial systems (Don et al., 2005). Curcumin nanoparticles (2−40 nm) obtained from wet milling technique was effective against *Staphylococcus aureus, Bacillus subtilis, E. coli, P. aeruginosa, Penicillium notatum,* and *Aspergillus niger* (Bhawana et al., 2011).

Antimicrobial peptide nanoparticles were synthesized through biomineralization reactions with higher stability and less chances to be inactivated, for example, cationic decapeptide, KSL (KKVVFKVKFK) 10, isolated from a combinatorial peptide array was active against *E. coli, S. aureus, S. epidermidis,* and *Calbicans albicans* (Eby et al., 2008).

2.2.2 Metals and their oxide-based nanomaterials

This class of nanomaterial constitutes primarily of nanoparticles synthesized from metals, their oxides, or sulfides precursors. The most important constituents of nanoparticle in this group consist of metals from the transition series. Noble metals such as Ag, Au, Pd, and Pt show an extensive range of application when used in nanorange. Their high optoelectronic activity due to the LSPR makes them an outstanding photocatalytic system (Khan et al., 2019).

The photocatalysis involves generation of electron−hole pair in conduction bands. The holes (h^+) are captured by water molecules and cause splitting of water molecules and formation of hydroxyl radicals (OH•). These radicals are highly oxidizing and have tendency to degrade wide range of organic pollutants and microbial cells. Ag and titania nanoparticles have been studied widely in regard to their environmental applications and they have proved of great efficiency in waste treatment methods. Titania has been extensively studied for its antimicrobial activity and solar irradiation was enough to kill bacterial cells (*E. coli*) at a very fast rate following first-order kinetics (Wei et al., 1994). Iron-based nanoparticles have also been studied for their disinfectant properties and many interesting results have been obtained there. They are cost-effective and recyclable which puts them as an excellent mode of disinfection (Zhang, 2003).

Manganese oxide (MnO, Mn_3O_4, Mn_2O_3, and MnO_2) NPs, cerium oxide NPs, magnesium oxide NPs, and ZnO are examples of some other metal oxide nanoparticles that may be used as disinfectant either photocatalytically (generating reactive oxygen species [ROS]) or by destructing cell membranes (Fei and Li, 2010, pp. 287−314).

2.2.3 Carbon-based nanomaterials

The backbone of these nanomaterials comprises of carbon and found in variety of shapes such as hollow tubes (carbon nanotube, i.e., CNT), sheets (graphene, graphene oxide, i.e., GO), and spheres (such as fullerenes). They serve as an excellent material for water treatment over other macromolecules because of their higher ratio of surface area by volume. There are varieties of methods to synthesize these nanomaterials such as laser applications, discharge tubes, and chemical vapor deposition techniques (Kumar and Kumbhat, 2016, pp. 189−236). The carbon-based nanomaterials may be functionalized or non-functionalized with hydroxyl (−OH) and carboxylic acid (−COOH). The functional groups are attached through covalent or noncovalent interactions and tend to increase the dispersion in water as compared to their non-functionalized graphene as well as increase their adsorption properties (Kuila et al., 2012; Upadhyayula et al., 2009). Functionalization serves two major prerequisites for their environmental application, i.e., (1) it increases the hydrophilicity of carbon-based nanomaterials such as CNTs, GO, etc., making

them more stable and highly dispersed in aqueous media, which leads to exposing microbes and contaminants to a larger surface area, and (2) it allows tuning the surface of nanomaterial according to the sorbate for higher electrostatic interaction with sorbent (Vuković et al., 2011). CNTs are synthesized as single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). Some of the factors that affect the activities of these nanomaterials include pH, functional groups, ionic strength of the solution being used, and presence of organic matters (Smith and Rodrigues, 2015). CNTs are highly flexible and hence are very suitable to capture bacterial cells. Their flexibility (both SWNTs and MWNTs) has been experimentally verified on *Streptococcus mutans* bacterial colony, where the growth was stagnated on introduction of these CNTs (Akasaka and Watari, 2009). Fullerol suspension inactivated bacteriophage MS2 by photosensitization (Badireddy et al., 2007). Graphenes can be used as hydrogels, thin film membranes, recoverable nanocomposites, or electrodes in the treatment of microbial contamination of wastewater. They wrap around cell or enter cell membrane and interact with, leading to cell disruption and cytotoxicity (Zeng et al., 2017).

2.2.4 Newly structured and engineered nanomaterials

This class of nanomaterials includes synthesis of such nanomaterials which are comprised of two or more than two nanomaterials and whose properties can be tuned according to their applications. Nanocomposite materials having at least one of the component falls in the nanoscale or multidimensional nanoparticles are major components of such engineered materials. They are mainly designed to attain special functionalities such as improved mechanical strength, stability in solution, enhanced light absorption, and thermal conductivity or specific electronic properties. They have been identified to play major role in advanced biomedical techniques, functional nanocomposites, and nanoenergy. The nanocomposites may contain natural, carbon-based, or metal-based nanoparticles mixed with ceramics, polymers, or metals (A). Polyurethane-coated AgNPs, polypropylene filters coated with nanosilver particles (45 nm), and many such polymer composite show antimicrobial activities which have been discussed in detail further.

2.3 Application in contaminated water treatment

Nanomaterials of various chemical composition, shape, and dimensions have been studied for pathogen inactivation, contaminant removal and transformation, and membrane separations, for the enhancement of existing water treatment technologies. These studies indicated varying activity levels and prove to be very reliable in future (Mauter et al., 2018). Nanotechnology in past few years emerged as highly advanced and reliable technique in many areas including water treatment units. Exploiting nanotechnology in treatment

of contaminated water has been proved to be breakthrough in water purification. Their application ranges from detection, monitoring, and possible solutions of eradication of waterborne pathogens (Anjum et al., 2016a). Their extremely small size (1−100 nm) and larger surface area make them highly reactive, thereby providing greater activity for treatment of polluted water. Nanomaterials hold a wide range of application in today's world. They may be utilized as attached to a substrate, i.e., immobile or free nanoparticles. Nanosilver (AgNP), CNTs, nano-TiO$_2$ (P-25), and many others such as nanomaterials form an integral part of daily life. Their application has not only been restricted to research and pharmaceuticals but also now their application has extended to electronic devices, catalysis, fillers, etc. Current research fields focus on more and more implementation of nanotechnology for the solid waste management and wastewater treatment because of their miscellaneous antibacterial activity. Their small size and large surface areas tend to increase their chemical activities. The removal of heavy metals such as mercury, cadmium, thallium, and lead has been extensively targeted in the role of nanotechnology as water treatment technology. It has also been hinted that there is less chance of developing resistance toward these nanomaterials as compared to classical antibiotics (Pal et al., 2007). Silver nanoparticles, silica-based nanocomposites, TiO$_2$ nanoparticles, and carbon-based nanomaterials have proved their outstanding role in the treatment of pollutants in aqueous systems. Silver nanoparticles show an excellent bactericidal property (Weir et al., 2008). Noble metal nanoparticles show an excellent result for the disinfection of *E. coli*. SWNTs and MWNTs have been reported to be excellent filter for virus adsorption and inactivation than other routine filters. Nanofiltration membrane technologies are even effective for pathogens such as *Cryptosporidium* oocytes that have been major concerns in some developed nations also (Anderson et al., 2011). Some of the advantage that lies in implying nanotechnology for water treatment includes point-of-use techniques, time economy, high efficiency, simple treatment methods, and space saving (Nassar, 2013, pp. 52−65).

3. Mechanism of cytotoxicity of nanomaterials

The interaction between cell and nanomaterials follows various routes and mechanism of action. Deducing the mechanism of cellular uptake or binding of a nanomaterial plays a crucial role in deciding the mode of action of them on pathogens. Two major ways in which antimicrobial nanomaterials work include direct interaction with cell, disrupting its transmembrane or destructing the cell envelope or generation of reactive species or metal ions that hinder the cell activity, and destroying the microbial cells. A significant pathway for nanocytotoxicity includes generation of ROS that creates oxidative stress in cellular structures. This may lead to failure of cell to sustain its redox regulated physiological functions normally. These results into series of

events such as generation of protein radicals, formation of lipid-based peroxidases, cleaving of DNA strands, changes in nucleic acid, production of redox-sensitive transcription factors, and many other functions that lead to cell death and genotoxicity (Meng et al., 2009). Studies suggested that size and bactericidal activity of bacteria is inversely related to each other and nanoparticles ranging from 1 to 10 nm diameter showed very high antibacterial activity (Scholes et al., 1999). According to toxicological data, the toxicity of NMs depends on various factors such as degree of nanoparticles dispersion into the aqueous systems, degree of aggregation of nanoparticles, presence of other oxidizing species, coatings on the nanoparticles, exposure time, temperature, pH, etc. (Jeevanandam et al., 2018). The antimicrobial mechanism is exact and different prepositions have been made regarding their mode of action. Few suggested mechanisms include (1) disrupting cell membranes, (2) disturbing purine metabolism, (3) damaging of DNA or protein damaging, (4) effects on respiratory mechanisms, (5) oxidative stress through ROS, and (6) effecting DNA replication (Khan and Malik, 2019).

3.1 Naturally occurring nanomaterials

Naturally occurring nanomaterials have also been reported to show antimicrobial activity. Certain peptides, chitosan, and cellulose have been studied extensively for their antimicrobial action. The low cost or production and low-tech disinfection make them a promising natural nanomaterial disinfectant. The natural peptides cause osmotic puncture of bacterial cells by creating nanoscale passages in their cell membranes (Gazit, 2007). These peptides can easily be engineered into various nanostructures, and their size, shape, morphology, functional groups, and other features may be tuned according to the antimicrobial applications.

Other class of antimicrobial nanoparticles of natural origin is chitosan, which is obtained from arthropod shells. Many researchers have successfully synthesized their nanoparticles as these materials have noticeable antimicrobial activities ranging from bacteria and viruses to fungi. These nanoparticles show higher toxicity toward fungi, viruses, and Gram-positive bacteria in comparison to Gram-negative bacteria (Qi et al., 2004; Rabea et al., 2003). Presence of biomolecules such as lipids, proteins, microbial cells, pH, and degree of polymerization, etc., play a major role in determining the concentration required (18−5000 ppm) for its effect on microbial cells.

Two major pathways for chitosan-based antimicrobial activities were proposed. The first one involves electrostatic interaction between cell membranes (negatively charged) and chitosan particles (positively charged), which leads to higher penetrability of the membranes and thereby enhancing the outflow of cell organelles. At higher pH (>6), chitosan or such other nanoparticles lose their protonation tendency and hence become less effective. Derivatives of chitosan such as N,N,N-trimethyl chitosan, N-propyl-N,N-

dimethyl chitosan, and N-furfuryl-N,N-dimethyl chitosan tend to have higher antimicrobial activity and can perform at high pH also (Qi et al., 2004; Holappa et al., 2006).

Second mechanism is the inactivation of enzymatic activities of the microbial cells because of the trace metal chelation with chitosan. Some reports suggested the inhibition of RNA synthesis by chitosan due to its binding with DNA after it penetrates the cell wall in some fungal cells (Rabea et al., 2003). Some researchers have successfully synthesized nanocurcumin, which possess antibacterial properties. The nanoparticles attach to the surface of cell wall, damage them, enter into the cell, damage cell organelles, and cause cell death. Curcumin nanoparticles also disrupt the cell structure by combining with cell, destroying the peptidoglycan layers, and entering the cell (Bhawana et al., 2011).

3.2 Metals and their oxide-based nanomaterials

Nanometals such as nano-copper (CuNP), nano-silver (AgNP), nano-gold (AuNPs), nano-palladium (PdNP), nano-aluminum, nano nickel, etc., oxides of metals such as nano-TiO_2, nano-ZnO, nano-ZrO_2, nano-V_2O_5, nano-Fe_2O_3, nano-SnO_2, and nano-CdO, and metal sulfides such as nano-CdS and nano-ZnS show an extensive antimicrobial activity. They not only generate ROS that inactivates viruses or bacteria but also cleaves their DNA and RNA. They disrupt the structural integrity of the microbial bodies by interacting with the cell membrane and cell wall, which disturbs the energy transduction due to the leakage of their intracellular components (1.1.1). Cerium dioxide (CeO_2), titanium dioxide (TiO_2), silver (Ag), and gold (Au) nanoparticles have been some of the most common metal nanoparticles that have been studied for antimicrobial activities in wastewater at treatment plants as well as ordinary conditions to find the mode of their action (García et al., 2012; Ravishankar Rai and Jamuna Bai, 2011).

Titania is the most common and easily available nanoparticle that has high efficiency for pathogens inactivation in water. TiO_2-based disinfection techniques mainly involve formation of ROS (OH• and peroxide radicals) between 300 and 390 nm wavelength irradiation. Microorganism inactivation by TiO_2 depends on certain factors such as nanoparticle concentration, type of microbe, wavelength of radiation and its intensity, O_2 concentration, pH, ROS, and the retention time of active species (Kikuchi et al., 1997; Alrousan et al., 2009).

CeO_2 (ceria) nanoparticles show three kinds of interactions with microbes: adsorption, oxidoreduction, and toxicity. Positively charged ceria NPs bind to outer lipid polysaccharides of the cell membrane which are negatively charged, thereby undergoing reduction and creating an oxidative stress and destructing the cellular functioning (Thill et al., 2006; Dowding et al., 2013).

Silver nanoparticles (AgNPs) has been extensively studied for their antimicrobial activities and show different pathways for action either through

nanoparticles or silver ions: binding with enzymes through thiol functional groups and deactivating them; preventing DNA replication by binding with it; forming ROS; modifying cell membrane permeability; and disrupting electron transport (Sondi and Salopek-Sondi, 2004) (Fig. 19.2).

Mg (OH)$_2$ nanoparticles were also reported for their antibacterial activity. These nanoparticles either directly enter into the cell wall and cause damage to cell membrane or adsorb water molecules on the surface of nanoparticles and increase the concentration of hydroxyl ions (due to high pH of nanoparticles) at the surface, thereby destroying the membrane of pathogens coming in contact with it (Dong et al., 2010; Moritz and Moritz, 2013; Hossain et al., 2014). ZnO nanoparticles and ZnO nanorods have also been reported to show antibacterial activity against *E. coli* DH 5α bacterial strains (Zhang et al., 2008; Rodríguez and Elimelech, 2010). Possible pathway for antimicrobial activity includes generation of peroxide or some other radicals and damage of cell membrane due to them. High concentration and small particle size favors the antimicrobial activities of ZnO nanoparticles. The bactericidal tendency of ZnO is largely because of production of ROS (peroxy, oxy, and hydroxyl radicals) and blocking of cell activity due to deposition of nanoparticles on the cell membrane as well as cytoplasm (Raghupathi et al., 2001; Applerot et al., 2010; Zhang et al., 2010a) (Fig. 19.3).

3.3 Carbon-based nanomaterials

The carbon-based nanomaterials serve as an excellent and highly tunable structure that can be modified in various forms to attain desired role in water treatment. They serve as an excellent antimicrobial agent when compared to traditional or conventional adsorbents because of their larger surface area and high surface area-by-volume ratio (Kang et al., 2007). The surface area of
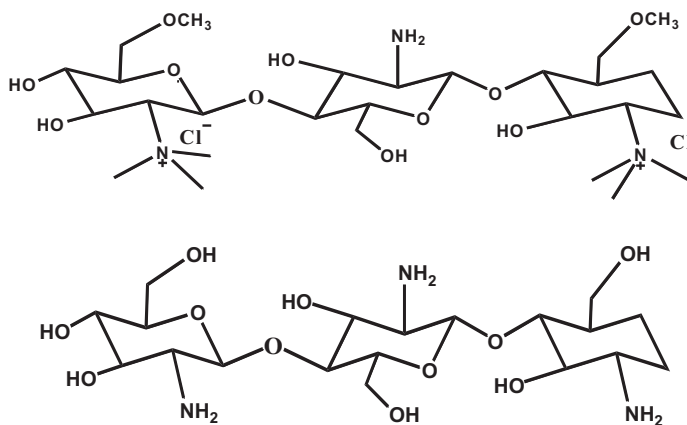

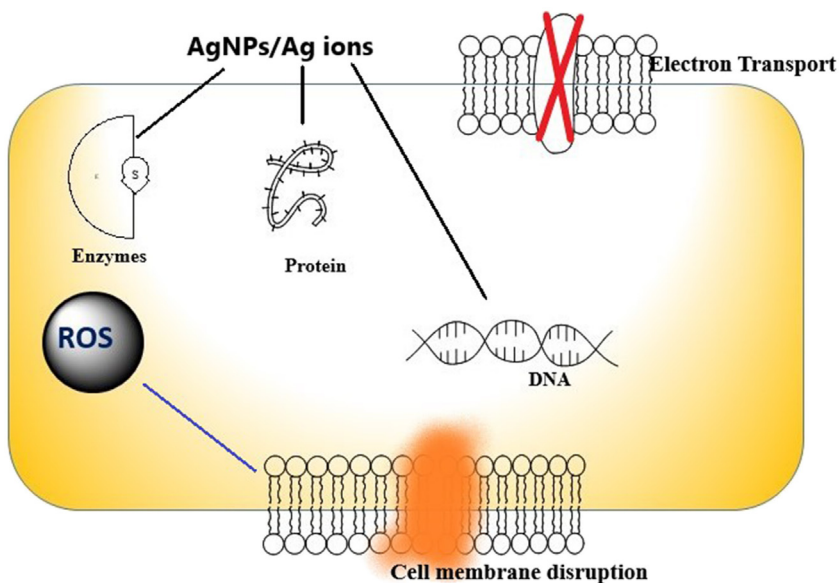**FIGURE 19.2** Structure of chitosan and its amino derivative.

FIGURE 19.3 A general representation of mode of action of silver nanoparticles.

SWNTs is around 407 m^2/g, which can remove bacterial and virus contaminants up to 3.18×10^{12} CFU/mL and 107—108 PFU/mL, respectively (Brady-Estévez et al., 2008). Moreover, SWNT shows specificity to certain bacteria that increase their application for on point use as sensor and also developing filters. Affinity of SWNT for *B. subtilis* is 27—37 times higher than conventionally used powdered activated carbon. Bacterial biofilm formation of *E. coli* and *B. subtilis* can be reduced significantly by applying SWNT and GO coatings (Rodrigues and Elimelech, 2010). The factors that control the cytotoxicity of carbon-based nanomaterials mainly include shape, size, surface area, functional groups, surface charge, and their chemical constituents. Larger surface area of these nanomaterials promotes their higher antimicrobial activity. The dispersed samples of CNTs showed more toxicity as compared to the aggregates of CNTs and activity of these CNTs increases two- to threefolds on adding functional groups to these nanotubes for bacterial species such as *S. aureus, E. coli,* and *B. subtilis* (Murugan and Vimala, 2011; Mauter and Elimelech, 2008).

For the rod-shaped CNTs, the diameter of the tubes play an important role in determining their antibacterial activity, which is why MWNTs show less antimicrobial activities than SWNTs. The larger diameters of these MWNTs tend to reduce the antimicrobial activity of nanotubes. The sharp endings of SWNTs cause cell membrane puncturing on interacting with the microbial cell. The smaller diameter of them pushes the bacterial cell to produce more

stress-related gene products (Kang et al., 2007). Experiments on the expression of genes showed that mechanism for membrane damage, repair and lipid recycling, such as the fatty acid β-oxidation, glycolysis, and fatty acid biosynthesis pathways were highly enunciated in the presence of SWNT as compared to that of MWNT. The studies further stated fatty acid uptake from neighboring media is due to the β-oxidation of fatty acids. These fatty acids were obtained from the lipid breakdown. These lipids discharged into the media by cell membrane disruption or cell death in the presence of SWNT. The fatty acid biosynthesis pathway is regulated by the synthesis of new lipid molecules which are to be incorporated into the cells for cellular mechanisms such as cell growth or membrane repairing caused by the nanomaterial. Cells need to produce more and more energy under the stress situations. In the presence of SWNTs, it was observed that cells showed high rate of glycolysis (the energy producing phenomena) to combat the stress created on the cell due to these SWNTs. Cell also needs high amount of acetyl-CoA, which are by-product of glycolytic pathways, to synthesize fatty acids to repair damaged cell membranes (Kang et al., 2008).

Other findings suggest that in carbon nanomaterials in the form of sheets such as GO or graphene, the cell damage is mainly caused because of higher edge-to-weight ratio. This leads to physical damage to the cell as well as bacterial cell inactivation by the sharp edges of these sheets (Liu et al., 2011; Chen et al., 2014). SEM images revealed the engulfing of these cells by the graphene sheets and stopping the flow of nutrients to bacterial cells. The graphene sheets are much larger in size as compared to bacterial cell and envelope them, thereby cutting off the nutrient supply. Therefore, it can be deduced that size plays a major role in determining the cytotoxicity of graphene and GO (Mejias Carpi et al., 2012).

Besides above research findings, the most significant and widely studied cytotoxic process involves the generation of harmful ROS. Formation of toxic peroxides ($H_2O_2^-$) and superoxides (O_2^-) due to carbon-based nanomaterials creates toxic reactions within the bacterial cells. These ROS disrupt the cell functioning by oxidizing the fatty acids in cell membranes and destructing the cells. The higher activity of genes such as superoxide dismutase and catalase in these bacterial cells to detoxify these harmful ROS confirmed this pathway of bacterial inactivation. DNA damage and repair system were also activated in presence of these nanomaterials. The large surface area-by-volume ratio of graphene sheets and other carbon-based nanomaterials serves as an excellent sorbent for bacteria and viruses. SWNT-based filters have been developed to adsorb these microbes into the micropores of the materials (Yang et al., 2010).

The whole cytotoxicological mechanism for bacterial and virus inactivation by carbon-based nanomaterials can be summarized under three basic points, i.e., cell membrane damage, oxidative stress, and sorption phenomenon (Kang et al., 2008; Liu et al., 2011; Chen et al., 2014; Mejias Carpi et al., 2012).

3.4 Newly structured and engineered nanomaterials

The cytotoxicology of advanced newly structured nanomaterials depends on their compositions. As these specially designed materials comprise of two or more materials with desirable properties, provide them uniqueness in physicochemical behavior and hence are more advanced method of disinfection. This class of nanomaterials mainly comprises of nanocomposites. Nanocomposites are the materials having one of the compositions in nanoscale (10−100 nm). There are classified into many categories and have variety of mode of actions. Their action involves combination of two or more mechanism pathways. For example, we use a TiO_2/GO nanofiber it will adsorb the pathogen as well as shows bactericidal activity photocatalytically. Similarly the use of magnetic nanoparticles (MNPs) over cellulose acetate serves the dual purpose of removal and killing of pathogens. The next Section is an attempt to cover all such advanced nanomaterials with novel properties that can be applied to decontamination process and hence can be used at macro level.

4. Applications of nanomaterials in waterborne pathogens treatment

4.1 Magnetic nanoparticles

MNPs have been proved to be of vast application in the field of medical applications such as MRI (magnetic resonance imaging), drug delivery, identifying biological species, and various therapies. Their high surface volume ratio and magnetic characteristics can make them efficient disinfectant material when grafted with suitable polymers and also raises their adsorbent property. The easy separation of magnetic nanomaterials facilitates recycling of these materials and hence provides additional benefit over other engineered nanomaterials. Fe_3O_4 and Fe_2O_3 are widely used MNPs that have proved their high efficiency against range of bacteria and viruses once they are functionally modified with biocompatible organic or inorganic moieties. One such antibacterial nanomaterial is quaternized poly(2-(dimethylamino)ethyl methacrylate), i.e., PQA modified magnetite nanoparticles. They are easily recyclable and can be separated from water after the action on pathogens by applying external magnetic fields. The reported efficiency of this nanomaterial was found to be around 100% for *E. coli* (Dong et al., 2001). Another such antimicrobial nanomaterial is amine-functionalized (AF) magnetic Fe_3O_4/SiO_2, which were found extensively effective against bacteria and viruses in water (bacteriophage f_2, poliovirus, *S. aureus, E. coli, P. aeruginosa, Salmonella, B. subtilis*). The effectiveness largely depends on surface charge and hydrophobicity of pathogen as well as the material. Pathogen surfaces are negatively charged due to phosphates and carboxyl groups over envelopes covering them and their isoelectric point ranges from 4.0 to 6.0. On the other hand, isoelectric

point of amine-functionalized nanomaterial is around 9.0. It was suggested that it was pure electrostatic interaction that prompted pathogen removal with efficiency of 92%−93% (Zhan et al., 2014). Quaternary ammonium compounds coated with Fe_3O_4 nanoparticles serve as dual purpose to treat heavy metal removal as well as bacterial disinfection through quaternary compounds destroying microbial cells and magnetic material to eliminate heavy metals (Zhang et al., 2015). Chitosan-oligosaccharides coated Fe_3O_4 bonded with cell wall at specific sites and were removed applying magnetic field. The nanoparticles show less agglomeration and are stable over a wide range of pH (Shukla et al., 2015). Functionalization with amine group reported to increase the effectiveness of pathogen removal by 2−3 times compared to Fe_3O_4/SiO_2. Amino acid (arginine, lysine, and poly-L-lysine) functionalized Fe_3O_4 nanomagnets were found effective against both Gram-positive (*B. subtilis*) and Gram-negative (*E. coli*) and antimicrobial efficiency was around 95% (Jin et al., 2014).

Other functionalized MNPs such as carboxyl (succinic acid), ethylene diamine or thiol-coated Fe_3O_4, and polyethylene glycol (PEG)-coated Fe_3O_4 showed antimicrobial activity by trapping through surface and damaging cell wall of bacterial pathogens such as *E. coli*. The hydrophilic MNPs interacts with polar head of lipids membranes resulting in cell death due to depolarization and structural disintegration (Singh et al., 2001). Poly(hexamethylene biguanide) modified magnetite, gentamycin, vancomycin functionalized Fe/Pt MNPs, some Co-based MNPs, etc., were also studied for their bactericidal actions but showed efficiency less than amine, carboxyl, or thiols functionalized MNPs. Graphene/Fe_3O_4 nanocomposites were reported to showed antibacterial activity against wide range of pathogens including bacteriophage *ms2, S. aureus, E. coli, Salmonella, E. faecium, E. faecalis, Shigella*, etc. (Zhan et al., 2015). SWNTs-iron oxide nanoparticles are shown antibacterial activities against various strains of *E. coli* (Engel et al., 2018).

Next in line for MNPs includes cobalt oxide NPs, which were studied for antimicrobial activity in water treatment techniques. AF-$CoFe_2O_4$ was studied in capturing *E. coli*. The hydrophilic MNPs bind to the polar head of lipid membranes and work at a pH range of 4−12 (Bohara et al., 2014, 2017; Jin et al., 2014). These nanomaterials serve an additional advantage of easy separation after the use.

4.2 Nanostructured membranes

Nanostructured membrane technology is one the recent development in the field of pathogens removal from water. They have advancements such as surface functionalization, highly permeable structures and resistance to fouling (Pendergast and Hoek, 2011). Their efficiency, easy and cost-effective designing, and low space requirement make them stand apart and much better than other treatment processes. Some of the common types of

nanostructured membranes includes zeolite-coated ceramic membranes, reactive/catalytic ceramic membranes, inorganic−organic membranes, thin film nanocomposite membranes, biologically inspired membranes, vertically aligned nanotube membranes and isoporous block copolymer membranes (Pendergast and Hoek, 2011). Nanomaterial coupled membranes systems were found to be more effective and highly advanced. Researches on such systems not only were biocidal against bacterial cells but they also acted on virus systems. One such progress in this area was electrospinning of carbon fiber cloth with polymers, for example, PANI/PAN/AgNWs-CC nanomembranes. This nanocomposite was highly effective in filtering off *E. coli* and *S. aureus* completely without application of external voltage and the AgNWs acted in complete inactivation of bacterial cells within few hours. The electrospinning technique provide a suitable route for modification of pore size as per the requirements and maintain flux amount and prevent fouling as compared to traditional methods of filtration. Electroporation and generation of ROS are the proposed mechanism of action of such nanofilters. Such composite filters serve the dual purpose of pathogen removal by physical membrane filtration and their inactivation through electrochemical disinfection. Some of the major benefits of these polymer-based membranes includes low cost of energy requirements, highly efficient removal of bacteria and its inactivation, and small disinfection contact time, and amount of silver released was very low and up to the standard criteria of 15 ppb. Some experiments carried after coupling membranes with P-25 showed effectiveness against bacteriophage MS2 (Zheng et al., 2017). Novel nano-thorn TiO_2, titanate porous nanotube membranes, and TiO_2 nanowire-based ultrafiltration membranes were also good in preventing membrane fouling and fighting the microbes (Bai et al., 2010; Zhang et al., 2009a,b).

Surface coating of membrane-based filters with graphene and PVK-GO showed an increased antibacterial activity against Gram-negative (*E. coli*) and Gram-positive (*B. subtilis*) (Musico et al., 2014). Other such nanostructured membranes that have proved effective in water disinfection are Polysulfone/AgNPs, AgNPs/PU, AgNW/CNT, Ag/CNT/PU sponges, MWNTs filters, AgNPs coated polypropylene filters, etc. (Wen et al., 2017; Heidarpour et al., 2010, 2011; Jain and Pradeep, 2005; Mangayarkarasi et al., 2012). Fabricating CNT hollow cylinders with radially aligned CNTs produced advanced reusable, thermally and mechanically stable nanomembranes which were found to be effective against bacteria (*E. coli* and *S. aureus*) and Poliovirus sabin 1 in contaminated water (Srivastava et al., 2004). Anodic MWNTs have also been developed that can remove and inactivate bacteriophage MS2 and *E. coli* (Vecitis et al., 2011; Rahaman et al., 2012).

Some other nanofilters include mesoporous Ag/Al (OH) three foam filters with alkali and polyols modified surface for removal of bacterial contaminants from secondary effluents (1.1.35). Coating of polyurethane with AgNPs is newly devised technique to slow down AgNP consumption in bactericidal

activity. TiO_2/modified nylon 6/AgNP mats and immobilized TiO_2 biofilms is very potential and cost-effective filter introduced recently (Pant et al., 2001). Nanomembrane composed of γ-Al_2O_3/TiO_2 nanocrystallites was found to be 100% effective for microbial disinfection (Shayesteh et al., 2016). Ceramic filters impregnated with AgNPs was applied for point-of-use removal of *Cryptosporidium parvum* (Abebe et al., 2015)

Chitosan nanoparticle loaded with secondary metabolite of *Streptomyces* is an example in bioinspired nanoparticles, which was used in membrane filters and was successful in removing pathogens from the water (Rajendran et al., 2015).

Protozoa can be efficiently removed using membrane-based reactors (MBRs) made up of polyvinylidene fluoride (PVDF), polyamide (PA), or cellulose acetate (CA). The major drawback associated with them is the need of proper disinfection of reactors post their application. Membrane-based bioreactors can prove as single step and highly efficient in terminating range of bacteria, viruses (noroviruses, adenoviruses), and protozoa from the water (Yao et al., 2009; Hai et al., 2014).

Clogging of pores and biofouling are two major problems that can be solved by the application of these advanced membrane systems.

4.3 Bioactive nanoparticles

Bioactive nanoparticles consist of such nanoparticles that have proved to be highly efficient biocide as compared to the conventional biocides. One such nanoparticle consists of MgO nanoparticles that show high affinity for Gram-negative bacteria such as (*E. coli* and *B. megaterium*) and *B. subtilis* bacterial spores (Koper et al., 2002). They deeply affect the functioning of the cell membranes and causes cell death. AgNPs are also important in this class of bioactive nanomaterials because of their direct interaction with cell membranes and protein structures. Comparative studies between GO coated and noncoated AgNPs showed that addition of GO increased the bactericidal efficiency of these nanoparticles (Karnib et al., 2013). AgNP electrospinning over cellulose acetate and ascorbic acid reduced silver nitrate in DAXAD 19 (polymerized sodium salt of alkylnapthalene sulfonic acid) are such nanocomposites that have been found effective biocides against Gram-positive and Gram-negative bacterial cells such as *E. coli, S. aureus, V. cholerae, Salmonella typhus, Klebsiella pneumoniae*, and *P. aeruginosa* (Son et al., 2004). In addition to silver nanoparticles some other metals, metal oxides and sulfides have been reported to show antibacterial activity. Nanoparticles such as TiO_2, Cu, CuO, ZnO, CeO_2, and CdS have also shown an effective antibacterial activity (Jones et al., 2008; Kang et al., 2008; Thill et al., 2006; Yoon et al., 2008; Prasse and Ternes, 2010, pp. 55−79).

Monodispersed copper nanoparticles (CuNPs) ranging from 2 to 5 nm were incorporated into sepiolite (magnesium phyllosilicate) and were found to be

effective against *E. coli* and *S. aureus* (Esteban−Cubillo et al., 2006). Cu-doped SiO_2 was tested for antibacterial activities against variety of bacteria, fungi, and yeasts such as *S. aureus, E. coli, Enterobacter cloacae, Penicillium citrinum*, and *C. albicans* at varying compositions and antibacterial activities were seen (Kim et al., 2006). Co-doped ZnO nanoparticles have been applied in targeting waterborne bacterial treatment. They showed an active antibacterial property against *S. dysenteriae, S. typhi, V. cholerae*, and *E. coli* with or without sunlight (Oves et al., 2015; Padmavathy and Vijayaraghavan, 2008). Exfoliated graphite/Se/ZnO acted as photocatalyst for dyes as well as antibacterial agent when studied for *E. coli* and *Enterobacter* (Sonde et al., 2017). Researchers working on cytotoxicity of Fe (III) oxide found that zero valent and divalent iron is much toxic when studied on *E. coli* because of their oxygenation tendency which destroys the cells. They create an oxidative stress by generating ROS and disrupting ion exchange across the cell membranes (Auffan et al., 2008). Iron-based nanoparticles also showed antimicrobial activities especially zero valent iron was found to be active against Gram-positive bacteria as well as fungus with 100% efficiency against *B. subtilis* and *P. fluorescens*. The best part of using zero valent iron nanoparticles (NZVI) is that it ends up as iron oxide or iron hydroxides which are already present in environment and form an important part of mineral systems (Diao and Yao, 2009; You et al., 2005). Some of the researchers suggested NZVI to be quite effective in dealing with *S. typhimurium phage* 28B from contaminated water (Rad, 2014, Thesis Chapter, 44 pages). ZnO NPs and its derivatives were found to much effective as compared to other six common metal oxide NPs including TiO_2 (Jones et al., 2008).

Biologically originated chitosan nanoparticles or copper loaded chitosan nanoparticles and Chitosan NPs-AgNPs have been reported as antibacterial substances. Their positive surface charge and small size makes them stable in biological systems and they tend to bind with negatively charged bacterial membranes (study on *S. choleraesuis, M. smegmatis, P. aeruginosa, S. typhi, and S. aureus*) and causes cell leakage through membrane disruption (Qi et al., 2004; Sonawnae et al., 2012). Prodigiosin impregnated cellulose matrix has been found to remove *E. coli* (97.31%) and *B. cereus* (97.33%) (Arivizhi-vendhan et al., 2015).

Several nanoparticles such as activated carbon and GO-based systems were found active against bacteria such as *Aeromonas* spp., *P. aeruginosa,* and *E. coli* present in water supply systems (Qunilivan et al., 2005). Carbon and graphite oxide−based nanoparticles disrupt and kill bacterial cells by oxidizing the glutathione in some of the bacterial species (Shaobin et al., 2011). SWNTs as nanofilters have been remarkably effective against bacteriophage MS2 and are easy to produce, operate, and can be regenerated by heat or chemical treatments (Brady-Estévez et al., 2008, 2010).

4.4 Dendrimer-enhanced ultrafiltration

Dendrimers are monodispersed macromolecules synthesized under controlled composition and designing methods. Dendrimer-based filters provide an extraordinary opportunity in the field of antimicrobial activity. Not only have they proved to be efficient in fighting the water hardness, but also they established as an excellent filter for toxic metal ions, organic and inorganic contaminants, radioactive wastes, bacteria, and viruses. They are available in various polymeric forms which are monodispersed and extensively branched like randomly hyperbranched, dendrigraft, dendrons, etc. Dendrimers are made up of three units: core, interior branch cells, and terminal branching cells, size of which ranges from 1 to 20 nm (Ottaviani et al., 2000). Dendrimers show an additional benefit for fighting drug-resistant bacteria by following different mechanisms of action. Dendrimer-immobilized biocides are very effective and easy to separate from the systems. Their potency was found to be more than their counterpart small molecules or particles. They have been expected to possess more active time and are less toxic (Diallo, 2014). Dendrimers are very useful as carrier of antimicrobial nanoparticles as they possess a hollow cavity and the surface can be modified for a range of microbes. PAMAM dendrimer (core made of alkyl diamine, exterior made of primary amine, and branches of tertiary amine) based silver nanocomposite is one such material that shows an effective antimicrobial activity against waterborne pathogens such as *S. aureus, P. aeruginosa,* and *E. coli* (Balogh et al., 2001; Savage and Diallo, 2005). High positive charge on biocide dendrimers binds with negatively charged bacterial cell wall through electrostatic interaction and disintegrates the bacterial cell membranes. Biocidal dendrimer attached to antimicrobial terminals such as phospholipids replaces Ca^{2+} and K^+ and neutralizes the surface charge or reverses it. At high concentration they denature membrane proteins and destabilize membrane (bacteriostatic effect) and at extremely high concentration they completely break the cell membrane leading to cell death (bactericidal effect) (Chen and Cooper, 2002). Quaternary ammonium salt functionalized or phosphonium dendrimers of polycarbonates, poly(amidoamine), and poly(propylene imine) were reported by some groups against *E. coli* and *S. aureus* (Xue et al., 2015; Chen et al., 2000). The low stability and less knowledge of dendrimers, however, limit its application as biocidal materials.

4.5 Photocatalytic inactivation by nanoparticles

Photocatalytic activity of nanoparticles is due to the interaction between light and metallic nanoparticles. Photocatalysts are the semiconductor devices that have tendency to degrade a variety of chemicals (organic, petrochemicals, pharmaceuticals, etc.) and disinfect range of pathogens (bacteria, virus, fungi, and protozoan cells). Advance oxidation processes (AOPs) appeared as an

outstanding application of photocatalysis in disinfecting water. The process of photocatalytic inactivation mainly depends upon nature, morphology and concentration of the catalyst (Sondi and Salopek-Sondi, 2004). Metal oxide nanoparticles such as zinc oxide (ZnO), titania (TiO_2), zinc stannate (Zn_2SnO_4), and tungsten oxide (WO_3) based semiconductor materials have been reported for their antibacterial activities (Baruah and Dutta, 2011; Baruah et al., 2012). Titanium dioxide (TiO_2) has been validated to be the most common photocatalytic nanoparticle to inactivate pathogens in aqueous systems. Pathogen inactivation depends upon many factors, such as concentration of photocatalyst, microbe, intensity of light and its wavelength, degree of hydroxylation, pH, temperature, O_2 supply and ROS, and retention time. Ag/TiO_2 has been reported for high antimicrobial activity even at 425 nm (Akhavan, 2009) and effective against bacteriophage MS2 (Liga et al., 2011). Ag@ZnO core–shell nanoparticles have been developed to be used against *E. coli* and were found to be recyclable and reused for around three cycles. They have been practically applied to pond water and municipal water too for studying their activity (Das et al., 2017). Pt/TiO_2 are found to be effective against pathogens like *E. coli, Lactobacillus acidophilus* and *Saccharomyces cerevisia*e in UV-region (Matsunaga et al., 1985); TiO_2/MWCNTs (*B. cereus* and *E. coli*); nano-TiO_2/acetyl cellulose, carbon-doped TiO_2 and N-doped TiO_2 *(L. monocytogenes, E. coli)*; S-doped TiO_2 (*Micrococcus lylae*); Zr-doped titania, and hydroxyapatite supported Ag/TiO_2 were reported to be successful in inactivation of endospores of *B. cereus* and *E. coli* (Lee et al., 2005; Matsunaga et al., 1988; Reddy et al., 2007; Mitoraj et al., 2007; Swetha et al., 2010; Wong et al., 2006; Yu et al., 2005). Enhanced cytotoxicity was reported in Pt(II) and Pt(IV) doped TiO_2, which can clearly be understood from the fact that Pt ions have been known for their inhibitory actions on DNA, RNA, and protein synthesis (Asliyuce et al., 2012). Reports on antimicrobial activities of Au–TiO_2 nanoparticles are also present and have been found effective not only against pathogens but also organic contaminants (Ayati et al., 2014).

The other metal oxide–based nanoparticle includes zinc oxide (ZnO). It has a wide bandgap similar to TiO_2 and has been studied widely. However, its photocatalytic activity largely depends on its calcination temperature that regulates its agglomeration property. ZnO/ZnS/PANI nanocomposite killed *E. coli* in sunlight and in visible range (Anjum et al., 2016b). At higher temperature the material is highly agglomerated and hence photocatalytic activity is largely affected.

CdS nanoparticles are such another photocatalysts that have tendency to inactivate pathogens in waterbodies. They have bandgap of 2.42 eV and can function below wavelength less than 495 nm. As the bandgap is still higher and photocatalytic activity is largely in UV region of light, these nanomaterials are doped with some other active material to bring their activity in visible region. Such nanocomposite materials show a decrease in bandgap and higher photoactivity even in visible region. Ag, Si, Mn, Co, Cu, anions such as nitrogen, etc. Besides these metal-based nanoparticles, laponite nanodiscs

loaded with Si(IV) phthalocyanine dihydroxide (photosensitizer) was also applied as photocatalytic materials. They were found to be active against resistant Gram-positive pathogens (Grüner et al., 2015). Other issues that need to solved are posttreatment separation of nanomaterials and presence of extracellular polymeric materials (EPS). While the former increases the chances of nanotoxicity, the latter has potential to reduce the photocatalytic efficiency because of competition with bacterial cell for ROS (Chaturvedi et al., 2012). Few points that are necessary to keep in mind while applying photocatalysis and setting photocatalytic reactors are robustness of the process, cost-effectiveness, high sustainability, low risk while exposure, safe photocatalysts, and less chance of catastrophic effects if something goes wrong (Dimapilis et al., 2018).
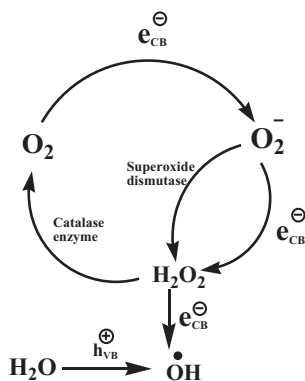
Mitoraj et al. (2007).

Photocatalysis can be represented by these basic set of equations:

$$M \xrightarrow{\text{light}} e^{\ominus}_{CB} + h_{VB}$$
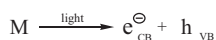
The electron generated in conduction band shows the following set of reactions:

$$O_2 \xrightarrow{e^{\ominus}_{CB}} {}^{\bullet}O_2^{\ominus}$$

$$2H^+ + {}^{\bullet}O_2^{\ominus} \longrightarrow H_2O_2$$

$$H_2O_2 \xrightarrow{e^{\ominus}_{CB}} {}^{\bullet}OH + {}^{\ominus}OH$$

$$H_2O_2 + {}^{\bullet}O_2^{\ominus} \longrightarrow {}^{\bullet}OH + {}^{\ominus}OH + O_2$$

$$4H^+ + {}^{\bullet}O_2 \longrightarrow {}^{\bullet}OH_2$$

$${}^{\bullet}OH_2 \xrightarrow{e^{\ominus}_{CB}} HO_2^{\ominus}$$

$$H^+ + HO_2^{\ominus} \longrightarrow H_2O_2$$

$$2{}^{\bullet}OH_2 \longrightarrow O_2 + H_2O_2$$
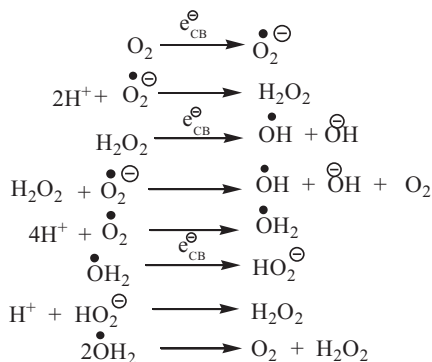
The holes thereby generated leads to following oxidation reaction:

$$h^+ + H_2O \longrightarrow H^+ + \overset{\bullet}{O}H$$
$$h^+ + \overset{\ominus}{O}H \longrightarrow \overset{\bullet}{O}H$$

The reaction ends up in:

$$\overset{\bullet}{O}H + \overset{\oplus}{H} + e^{\ominus} \longrightarrow H_2O$$
$$1/2\ O_2 + 2H^+ + 2e^{\ominus} \longrightarrow H_2O$$
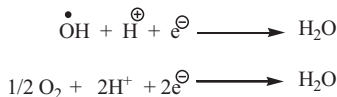
Baruah et al. (2015), Gaya et al. (2008), and Fujishima et al. (1972).

4.6 Molecularly Imprinted Polymers

Molecularly imprinted polymers are kind of affinity ligands that bind specifically to a molecule or a substrate to form complexes through ionic, covalent, hydrogen bonding or ligand exchange. They are also known as "Plastic Antibodies" and highly specific for binding with the target molecules. They are less prone to chemical or biological damage and hydrophobic in nature which leads to less chances of reversibility of binding of target with them (Wangchareansak et al., 2014; Volkert and Haes, 2014; Asliyuce et al., 2012). MIPs have been developed in form of nanocomposites have been applied as adsorbents. Designing of MIP is done such that binding is reversible to prevent damage of MIP on binding with target. Recently researchers developed surface-imprinted polymers that binds with influenza virus H5N1 (Wangchareansak et al., 2014). APTES-based MIP integrated on surface plasmon resonance (SPR) chip with microfluids was assessed for binding with *E. coli* bacteriophage MS2 (Altintas et al., 2015). The drawback with MIPs the release of residual template molecules during adsorption phenomena and still there is need of water soluble MIPs (Nnaji et al., 2017, pp. 129−167).

4.7 Bioinspired nanoparticles

To overcome the plausible toxicity of nanomaterials, a new realm of nanomaterials has been introduced known as bioinspired materials. These nanomaterials are classified into two basic categories: biomimics and biotemplates. It employs the application of biological methods of nanomaterial synthesis and is eco-friendly and highly adaptable (Bhattacharya et al., 2014). The most commonly synthesized bioinspired nanoparticles is AgNPs and mediated through various biomolecules such as carbohydrate (chitosan, glycogens, polysaccharides), plants (*Cinnamon, Allium cepa, Mentha,* etc.), fungi (*Aspergillus, Fusarium, Candida guilliermondii, Trichoderma viride, Phoma sorghina, Penicillium* sp.), and bacterial cells (*K. pneumoniae, Pseudomonas,*

Streptomyces, Bacillus) (Zinjarde, 2012; MubarakAli et al., 2001; Sonar et al., 2017). Carbohydrate-based AgNPs range from 6 to 13 nm and were highly effective against *E. coli, S. aureus, B. subtilis, P. aeruginosa, C. albicans,* and some Gram-negative bacteria while that synthesized using fungi were from 3 to 50 nm (some between 550−650 nm and 10−100 nm also) and were quite effective against bacterial cells mentioned above as well as *S. typhi* also. Plant-inspired AgNPs were synthesized using parts of plants (barks, leaves, fruit peels, callus) such as *Cinnamon zeylanicum* bark powder; *Sesuvium portulacastrum* callus and leaves; leaf extracts of *Acalypha indica, S. portulacastrum, Eucalyptus citriodora, Ficus bengalensis, Solanum torvum, Allium cepa, Garcinia mangostana, Mentha piperita;* fruit peels of *Musa paradisiaca* and *Citrus sinensis*; and *Curcuma longa* tuber. Such bioconjugated nanoparticles were studied for antimicrobial activity and highly effective against *E. coli, S. aureus, V. cholerae, P. aeruginosa, Aspergillus flavus, S. typhimurium, C. albicans, C. lipolytica, E. aerogenes, Klebsiella* sp*., and Shigella* sp*, B. subtilis, Fusarium,* and *A. niger* (Sathishkumar et al., 2009, 2010; Nabikhan et al., 2010; Krishnaraj et al., 2010; Ravindra et al., 2010; Govindaraju et al., 2010; Saxena et al., 2010; Veerasamy et al., 2011).

Other vastly studied nanoparticle is gold nanoparticles (AuNPs). Recent development in these is use of *Mentha* for reduction of HAuCl$_4$ to AuNPs and their antibacterial activity was found highly effective against *E. coli*. Next variant in bioinspired AuNPs synthesis is use of banana (*Musa paradisiaca*) peel extract and the nanoparticle was highly effective against *Candida albicans, Shigella, Citrobacter koseri, E. coli, P. vulgaris* and *Enterobacter aerogenes* but ineffective against *Klebsiella* and *P. aeruginosa.* Fungi (*Candida guilliermondii, Penicillium* sp.), bacteria (*Shewanella oneidensis*) and yeast (*Rhizopus oryzae*) had also been employed in biosynthesis of AuNPs and found to show antimicrobial activity against *S. cerevisiae, S. aureus, E. coli,* and *C. albicans* (Mishra et al., 2011; Suresh et al., 2011; Maliszewska and Puzio, 2009).

Bioinspired nanomaterials establish properties such as less toxicity, high selectivity, and specific targeting and disinfecting efficiencies (Constantin and Neagu, 2017). Polydopamine attached to porous nanofibrous polyacrylonitrile substrate and doped with AgNPs reduced by polydopamine was applied as bioinspired material for disinfection of *B. subtilis* (Wang et al., 2017).

The biological origin of nanoparticles can be useful in many ways. The chemical need will be reduced and also the cost-effectiveness adds some other benefit.

4.8 Nanofibers

Electrospun fibers and nanofibers have been identified as active disinfectants against submicron level particles (Xu et al., 2008). Nanofibers are created by applying high voltage to charged liquid or melt using high-voltage supplier

through a capillary. They have high surface-to-volume ratio and micron level pore size. Various active antimicrobial nanofibers have been developed in recent years. NanoCeram alumina fibers are electropositive and remove bacteria by size exclusion method. They are much robust and resistant to clogging than most of ultrafiltration membranes (Tepper, 2002). The formation of antimicrobial nanofibers mainly depends upon surfactants and polymers used (Botes et al., 2010, p. 196). One of them includes PAN/GO/CNT-based nanotubes systems for water disinfection, developed using ultrasonicated mode of synthesis and was studied for antimicrobial activities against *E. coli* and *S. aureus* (Hussein et al., 2018). Poly (4-vinylpyridine) grafted PU fibers functionalized with hexyl bromide was used as disinfectant against *S. aureus* and *E. coli.* Polycarbonate (PC)/chloroform solution of benzyl triethylammonium chloride (BTEAC), Nylon 6 nanofibers with N-halamine additives, Chitosan with PAA and PEGDA were shown to inhibit bacterial cells such as *S. aureus, E. coli* and *K. pneumonia* with approximately 80%−99.7% efficiency in filtration (Kim et al., 2007; Tan and Obendorf, 2007; Don et al., 2005). Poly[(dimethylimino) (2-hydroxy-1,3-propanedily)chloride] functionalized nanofibers resulted in much antibacterial activity against Gram-positive *S. aureus* than Gram-negative *E. coli* (Daels et al., 2011). Poly(ethylene oxide) nanofibers coated with AgNPs via electrospunning predominantly antimicrobial activity against *S. aureus* and *K. pneumoniae* (Kim et al., 2009). Quaternary amine functionalized chitosan (N-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan) electrospun by PVA and cross-linked to glutaraldehyde was prepared to impart antiviral property (tested for porcine parvovirus, PPV and Sindbis virus, SDV) and stability in water to chitosan nanoparticles (Mi et al., 2014). β-Cyclodextrin/cellulose acetate nanofibers and chitosan (CTS)-based nanofibers loaded with AgNPs and AgNPs/Fe NPs were found to be effective against *B. cereus, E. coli, K. pneumonia, P. aeruginosa, K. oxytoca, P. mirabilis, S. boydii,* and *S. sonnei* (Nthunya et al., 2016, 2017).

4.9 Nanosorbents

Advancements have been made in the recent adsorption techniques by using nanoadsorbents. The smaller size and larger surface are facilitates high chemical reactivity as well as adsorption capacity of these nanomaterials. They consist of metallic nanoparticles, mixed oxide nanoparticles, magnetic NPs, etc. CNTs, silica nanotubes (SiNTs), carbon nanosheets, etc., also fall under this category. Their functionality is mainly controlled by various factors such as size, surface morphology, crystal structure, shape, and solubility. Tricalcium phosphate nanoparticles mixed with DNA solution before applying to target cell population showed effectiveness against virus sorption (Link et al., 2007). SWNTs are reported to be better nanosorbents for bacteria (*B. subtilis*) than any other conventional or any other common adsorbents. Their fibrous

structuring and easily accessible surface makes them 37 times better adsorbent for bacteria as well as cytotoxins (Ahmad et al., 2016). Nano-SiO_2-AgNPs was proposed as new antifouling adsorbent where Ag reduction was protein-mediated against *E. coli and P. aeruginosa*. It was reusable, high adsorbing, eco-friendly, cost-effective, high yielding, and even removed dye from the solution (Das et al., 2013). Reusable adsorbent "pebbles" made of nano-cellulose AgNPs are found to completely remove heavy metals, dyes and pathogens were made, and efficiency was reported to be above 95% (Suman et al., 2015).

Clay-based nanoadsorbents can widely be used for range of microbes such as chitosan/bentonite/AgNPs or chitosan/bentonite/ZnO NPs. Such nanomaterials serve dual purpose, i.e., adsorption as well as killing of microbial cells such as *V. cholerae* (Unuabonah et al., 2017).

5. Limitations and upcoming challenges

Advanced nanomaterials also demand a deep insight into their potential side effects on human health. The toxicity study of nanomaterials is also an important aspect that needs to be covered while exploring their benefits in water contaminant removal. Monitoring of NPs and nanomaterials is a challenge and need more advancements in tracking their motion in systems. In vitro assessments have already been done and reported by many research groups that examined the effects of nanomaterials on cells in terms of toxicity and carcinogenicity (Drasler et al., 2017; Liu, 2006). The adversity of the nanomaterials lies in their novel and exotic physicochemical properties. As the nanoparticles are nanoscale materials, their properties vary much from their macroscale properties. Deriving the toxicity of nanoscale materials on basis of their macrocounterparts is not justified. Nanomaterials tend to aggregate in aqueous solutions and the property of these aggregates is quite different from nanoparticles which must be taken into account (Butt et al., 2013). Proactive research is needed before commercially applying them and to ensure sustainable technology for nanomaterials development (Colvin, 2003). Fundamental knowledge of the material and side effect is an indispensable need before its application as disinfectant. Human and other living systems are directly or indirectly exposed to these nanoparticles through soil, air, or aquatic systems. Time needs development of frameworks to monitor the flow of these nanomaterials into living systems. The nanoscience application in environmental remediation will further increase the degree of exposure deliberately. The biggest hindrance that lies in application of nanomaterials is absence of standard protocol that regulates its use (De Faria et al., 2014, pp. 363−405). The basic issues regarding nanomaterials include stability, economic, safety, and aggregation (Khan and Malik, 2019). The field of nanotoxicology is still in its infant state and needs a lot of advancements. Most of the toxicity studies have been performed under standard conditions and the

instrumental analysis takes natural interferences into account also (Baruah et al., 2016). The major challenges in econanotoxicity are toxicity assessment at functional level, detection and differentiation of nanomaterials from natural colloids, and tracking the nature of nanoparticles in the environment (Maurer-jones et al., 2013). The synthesis of nanoparticles is highly advanced technology and need standard methods, thereby increasing the cost of production which is an important point needed to be tackled and the issue of their point-of-use application rather than long distance transport can be matter of serious concern too (Li et al., 2008, pp. 465−494). Technological advancements are still lagging behind when it comes to removal of these nanomaterials from the treated water.

5.1 Mode of application and side products of degradation

Suspended nanoparticles tend to coagulate or precipitate in the presence of salts. Other problem arises with the coated nanoparticle is the fact that their bioavailability is quite relegated. The reactive species generated during photocatalysis are envisaged to be consumed by competing species such as organic molecules present in the system. Obstruction at the surface of nanomaterials may also reduce their activity to disinfect microbes. Dead cells and other soluble side products may hamper the active site at the surface of the antimicrobial nanomaterials. These depositions can further lead to formation of biofilm, thereby completely blocking their antimicrobial activity. While some nanomaterials are easy to synthesis and cost-effective, many promising nanomaterials (such as carbon-based) have very high cost and long route of synthesis which creates another issue with their potential application in water treatment.

Carbon-based nanomaterials may directly or indirectly enter the system and show damaging effects on aquatic ecosystem. The long exposure time and interactions with polysaccharides or other biomacromolecules imbalance the ecosystem (Warheit, 2006).

Particle size in case of metal nanoparticles has to be regulated, for example, in AgNP small size and large volume not only increases the inactivation efficiency but also tends to enhance loss of silver as silver ions. It is therefore needed to combat the rate of silver loss to provide enough time for inactivation of microbial cell as well as provide longer life to AgNP-based disinfecting techniques.

Small size of nanoparticles facilitates its high mobility in porous media; therefore, translocation of nanoparticles into various cells and tissues is an issue of important concern and has to be combated. The metal-based nanoparticles are easily introduced to the living system by their use as disinfectant and may cause potential health issues. Nanoparticles are reported to induce autophagy in many cell types due to cellular response for nanoparticles and can cause cancerous tissues or cell damage (Peynshaert et al., 2014).

Nano-TiO$_2$ was experimentally studied to induce cytotoxicity in rat neuroglia cells as a part of inflammatory response (Liu et al., 2013).

Disposal of wastes generated along with nanoparticle is also a matter of serious concern.

5.2 Nanotoxicity and its effects

Although proven to be of great advantages, there has been certain level of toxicities associated with nanoparticles and other nanomaterials. Elementary knowledge of nanotoxicity is an important need of time to prevent their ill effects. Engineered nanomaterials are directly introduced to the system through environmental treatment of various systems and hence enters in soil and aquatic systems (Saeed and Khan, 2017). Unwanted dispersion and disposal of waste have been various possible routes through which nano-material is introduced into the system during waste management. Nano-material surface having the tendency to modify continuously has been an issue of serious concern for the stakeholders and researchers to a major extent. With the immensely strong potential exhibited by these nanomaterials in the field of environmental science, with a thrust upon water treatment applications, there lies an extensive possibility that they will be exposed to the living system too. This creates a serious concern over their long-term effects on the living systems (Tomar and Kumar, 2017). Ecotoxicity of NPs and nanomaterials being studied and investigations are going on over the effects of nanomaterials on various phyla. Some of the researchers have deduced that the formation of ROS and oxidative stress can cause damage even to the human cells. Auto-phagy or lysosomal dysfunctions can be other way by which a cell may trap nanoparticles by detecting them as foreign particles and creating cell damages (Stern et al., 2014).

Studies on carbon-based nanomaterials revealed many of their cytotox-icological effects on human beings and other mammals. The cytotoxic prop-erties of these materials are mainly controlled by their size, shape, and doses of their application. The information on the effect of carbon-based nanomaterials is quite limited in comparison to their effect on microbes and their antimi-crobial activities. As suggested, earlier smaller sheets tend to have more cytotoxic effect as compared to their larger counterparts. In vivo studies over mice revealed their accumulation in the lungs and kidney tissues, and the limit value for toxic dose was reported to be around 0.4 mg (Wang et al., 2001).

CNTs (SWNT and MWNT) are likely to be accumulated inside the human cells and create oxidative stress inside the cells and reduce cell life. Higher dose or contact time may result in exposure of these materials in the human epidermal keratinocyte cells that has been confirmed through studies. Not only had this higher dispersion of CNTs but also resulted in greater exposure of cell toward cytotoxicity or inflammations. Similar to CNTs, sheet structures such as graphene or GO have adverse effects on human fibroblast cells even at very

low concentration (>20 μg/mL) and reported to cause cell deformation and untimely cell death, with its effect extending from cytoplasm to lysosomes, mitochondria, and reaching to nucleus. Recent findings suggested that out of all carbon-based nanomaterials, SWNTs have been found to show highest level of toxicity when compared with MWNTs, graphene, and GO (Pinto et al., 2013; Zhang et al., 2010b). Studies suggest that hampering of metabolic activity of microbes at high concentration of carbon-based nanomaterials may disturb the biogeochemical cycle of nutrients and affect the nutrient balance of nitrogen, phosphorus, and carbon, etc. Insufficient data are available on lingering effect of nanomaterials as well as their acute impact on the system in which they are used. Biosynthesis of new nanomaterials from the existing ones may also be an alarming situation as many works have also been conducted on the role of microbes as biocatalyst.

Metal nanoparticles have high affinity for proteins depending on their shape, size, and surface morphology, as well as functionalization and free energy (Saeed and Khan, 2017). MNPs can induce toxic cellular reactions and produce lethal effects on cells as compared to the micromagnetic materials. Some experiments that were conducted on studying the effects of titania, fullerenes, and polystyrene NPs showed that they do not create much toxicity in abiotic conditions but are highly toxic and create tremendous amount of oxidative stress under biotic conditions by formation of ROS (Xia et al., 2006). Reports are available on nanocytotoxicity of nano-TiO_2 on algae and daphnids that may affect the aquatic life and lead to imbalance the aquatic ecological balances (Hund-Rinke and Simon, 2006).

The effect of nanomaterials is not limited to animal world but it extents up to the plants. A variety of reports have been presented on the uptake of nanoparticles, their translocation in the plant body, and their consecutive side effects. Studies on AgNPs, ZnO NPs, silica NPs, fullerenes, etc., uptake by plants and algae showed their toxicity effects as well as interfered with seed germination (Zhang et al., 2001). They inhibit the metabolic pathways and prevent cell growth or functioning. This arises as important issue to be dealt with as these nanomaterials may enter food chain and lead to biomagnifications.

5.3 Plausible solutions

Research is still being carried out to find cheap and time economic mode of production of nanomaterials so that their application can be extended to a greater scale. A clear risk assessment and risk management systems should be developed before the application of these materials into the systems (Berekaa, 2016). Any new nanomaterial should be examined for cytotoxicity under REACH (Registration, Evaluation, Authorization, and Restrictions of Chemicals) framework before the introduction (Handy and Shaw, 2007; Handy et al., 2008; Hansen, 2009). Use of easily available, cheap precursors or natural

sources can be convincing mode for price drop of them. Polymer-based nanocomposites show more activity and less amount of nanomaterials (e.g., PVK-SWNT) can also be a leap in the field of nanomaterial application with the higher antimicrobial activity. The cytotoxicity of carbon-based nanomaterial can be curbed by blending them with biocompatible polymers to produce their nanocomposites (Ahmed et al., 2012). A reduction in cyto-toxicity from 40% to 20% was reported for PEG or bovine serum albumin−coated GO, PEG-based SWNTs nanomaterials showed drop from 80% to 20% and similar effects were observed for graphene (reduction from 15% to 7.5%); however, they showed higher antimicrobial activity than the pure carbon-based nanomaterials (Li et al., 2014; Zhang et al., 2001). To prevent the leaching out of metal nanoparticles or such small nanoparticles, it is better to coat them with polymers such polyurethane, PEG, PVA, etc. Combustion can be one of the methods that may be used in case of carbon-based nanomaterials discarded in bulk amount (Bystrzejewska-Piotrowska et al., 2009). The size correlation with toxicity can be an important step in finding the nanocytotoxicity and risk analysis of nanomaterials before their applications (Sayes and Warheit, 2009).

Recycling of metal-based nanoparticles can be a step to fight with the generated wastes and it can prove economic also as most of the metals are very expensive. Irreversible aggregation and dissolution of nanomaterials and then processing the resultant materials is an innovative method suggested by some research groups (Sanchez et al., 2011). Application of biomimetic methods such as aquaporins can be helpful in reducing the toxicity effects of nanomaterials. Multifunctional nanomaterials that combine two or more nanomaterials to treat varieties of pollutants can be one possible solution for reducing the amount of exposure of nanomaterials.

Bioaccumulation using plants or fungi can be one of the better solutions for removal of nanoparticles from water, soil, or air. Some of the steps that can help in monitoring the NPs translocation include studying the exact conditions under which the nanomaterials will be used and studying their effects. Combining two or more analytical techniques is also one of the proposed methodologies for tracking the nanomaterials (Kumar et al., 2014a,b). Tech-nologies are needed to prevent leaching out of nanomaterials into the system after use as disinfectants. Magnetic nanomaterials can be used as suitable method for disinfection as their removal is much easier by simple application of magnetic field. Their recyclability adds an extra advantage for their application as disinfectant (Li et al., 2008). Models should be developed to track the discharge, translocation, transformation, agglomeration, and uptake of nanoparticles within the environment (Bridle et al., 2015). A global awareness is the need of the time for knowing the toxicity of nanomaterials as well as focus on safe and eco-friendly nanomaterials is to be developed with time.

6. Summary

The coming time needs more and more advancements in water treatment technology, with the ever increasing world's population. Waterborne pathogens create a major hindrance in the way of pure water availability. Earlier methods of disinfection defined above hold many of its own drawbacks and some of the pathogens have already developed resistance against these conventional methods. Nanomaterials application in water treatment and contaminant removal holds a highly daunting and promising future than their traditional counterparts, wiping out limitations and side effects of conventional methods. Metal oxide NPs, fullerenes, photocatalysts, nanomembranes, and other such technologies ensure a long-term solution biological contamination of water. Combination of two or more nanomaterials can serve as multipurpose solution to eradicate pathogens as well as dissolved and undissolved impurities. Many of these nanomaterials have also high adsorbent properties, which establish new pathways for development of hybrid system for water treatment techniques. Many carcinogenic chemicals will be discontinued after their cost-effective establishment as water treatment units. The future of safe drinking water can be thrusted up on these "tiny particles." The tailoring nature of these nanomaterials let the researchers develop more and more sustainable and robust technology.

However, every technology comes with certain drawbacks. As discussed above, there are some of the major areas of concerns in the nanotechnological applications. Such issues need a deeper insight and should be properly dealt with. More and more focus on eco-friendly nanomaterials should be made so as to have a perfect technique to combat water crisis. Methods should be developed with small cost of production and less amount of chemicals required. Biosynthesis and biopolymers or bionanoparticles can play an important role in this regard. Nanomaterials with least effect on human and ecology are still to be designed for using them substantially in daily life. Lab to field applications and the studying effect of these nanoparticles in the living system should be taken care of.

Abbreviations

AgNWs Silver nanowire AgNWs
BSA Bovine serum albumin
CFU Colony-forming unit
DBP Dibutyl phthalate
DCS Differential centrifugal sedimentation
DRS Diffuse reflectance spectroscopic
GO Graphene oxide
PAA Polyacrylic acid
PAMAM Poly(amidoamine)
PAN Polyacrylonitrile
PANI Polyaniline

PEG Polyethylene glycol
PEGDA Poly(ethylene glycol) diacrylate
PFU Plaque-forming units
PU Polyurethane
ROS Reactive oxidative species
SWNT Single-walled nanotubes

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