Chapter 7
Nanotechnology for Water Remediation

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Contents

Abstract Scarcity of fresh drinkable water has escalated to be the one of the major global problem. Traditional wastewater treatment technologies are not adequate enough to produce safe water due to increasing demand of water coupled with stringent health guidelines and emerging contaminants. On that note, the advent of nanotechnology has given immense scope and opportunities for the removal of heavy metals, microorganisms and organic pollutants from wastewater and has emerged to be a very dynamic branch in the utilization of nanotechnology due to their unique physiochemical and biological properties compared to their bulk. Exploiting these properties of high specific surface area and surface reactivity have resulted in the excessive use and study of nanoparticles in wastewater remediation. The use of various nanomaterials, including carbon based nanomaterial, metal and metal oxides

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nanoparticles as were focused on, and their mode of action towards waste water remediation were discussed. Herein we tried to incorporate an overview of recent advances in nanotechnologies for water and wastewater treatment and understand various advantages, limitations and future direction.

7.1 Introduction

> "Water, water, everywhere, And all the boats did sink;
> Water, water, everywhere, Nor any drop to drink."
>
> –Samuel Taylor Coleridge

Water is the most essential substance for all form of life. Nearly 71% of earth's surface is covered with water but only 1% is available for drinking. Over 1.1 billion people lack supply of adequate drinking water and nearly 1.8 million children die every year from diarrhoea mainly due to water contamination (WHO, UNICEF 2010). It was estimated that by 2025, 50% of the world's population will be living in water-stressed areas. Again, due to the rapid pace of urbanization, heavy industrialization and changing lifestyles of people, more and more hazardous wastes, by-products have contaminated the natural water sources. The scarcity of pure drinkable water is now becomes the major global challenge for this century. Thus the use of nonconventional water sources (e.g. storm water, contaminated fresh water, brackish water, wastewater and seawater) can be an alternative to freshwater.

The traditional methods of water remediation have several drawbacks such as high-energy requirement, incomplete pollutant removal and generation of toxic sludge. Filtration can be used to remove the contaminants but that produces a highly concentrated sludge in one phase which is toxic and difficult to dispose. Thus, there is a real requirement for more efficient and less power consuming technology for treatment of municipal and industrial wastewaters. Among the various emerging technologies, nanotechnology has shown an incredible potential for the remediation of wastewater due to their unique properties (Sanchez and Sobolev 2010). Nanowires, nanotubes, films, particles, quantum dots and colloids are the different morphologies of nanomaterials which have at least one dimension less than 100 nm (Mihranyan et al. 2012). At this scale, materials often exhibit different physical, chemical and biological properties compared to their bulky counterparts (Qu et al. 2013). Due to their larger specific surface areas nanomaterials are excellent adsorbent of various types of pollutants. Surface engineering can also be incorporated to maximize surface reactivity. The higher surface area also enable them to catalyse the degradation, oxidation and reduction of contaminants at the surface. Therefore, along with high surface area, the selectivity of nanoparticles for specific water purification processes should stand on the chemical affinity, the surface charge density and the electron transfer ability. Nanomaterials also possess high mobility in solution and the whole volume can be quickly scanned with small amounts of nanomaterials due to their small size. Thus, a variety of efficient, eco-friendly and cost-effective both inorganic and organic nanomaterials with different techniques have been used and tested for the purification, disinfection, removal of heavy metals, degradation of organic compounds and pharmaceuticals. Again, the adsorbed species can be removed by applying mild (and affordable) gravitational (centrifugal) or magnetic force (in the case of magnetic nanoparticles).

Overall, with the emergence of nanoparticles a new domain has been introduces that can be exploited for better utilization in the wastewater treatment. Till date several nanomaterials have been developed that have shown promising result in wastewater treatment. These systems have potential to replace their conventional counterparts. But like every other systems, these nanotechnological systems also comes with few limitations that are needed to be looked upon in near future. In this chapter, we have tried to provide a thorough overview of different nanomaterial used in the wastewater treatment, their associated mechanisms, limitation and future direction. This chapter will serve a broader audience, a general introduction guide for non-experts in nanotechnological application and wastewater treatment to detailed analysis study with mechanism and examples.

7.2 Current Status

Nanotechnology has been extensively used for waste water remediation over the last decade. Several development has been made to modify the existing systems. We here in try to ensemble a comprehensive overview of several works related to the use of nanoparticles for the use of wastewater remediation. From the reports in literature till date, the use of nanomaterials in wastewater remediation can be mainly focused into four major categories (Fig. 7.1).

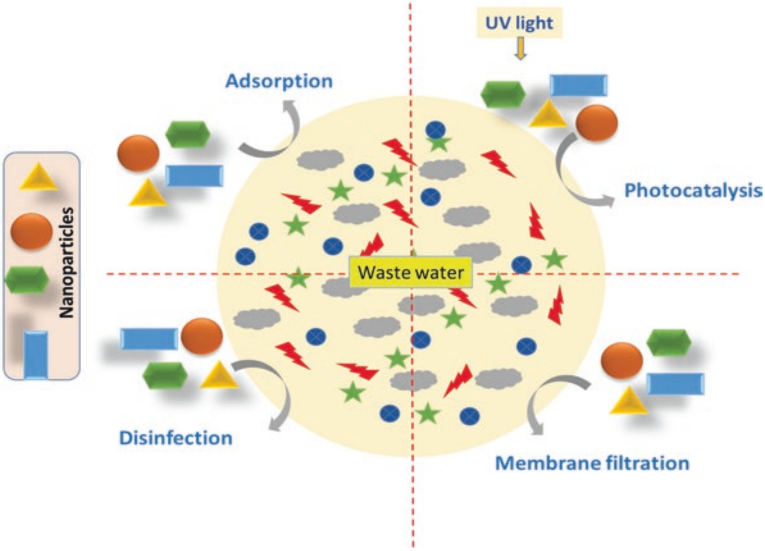

Fig. 7.1 Schematic representation of the use of nanotechnology in wastewater treatment

(a) Adsorption onto nanomaterials
(b) Photocatalytic water treatment using nanomaterials
(c) Disinfection of water with nanomaterials
(d) Nano membrane filtration

An attempt is made to incorporate the recent development and mechanisms associated to each categories in a chronological manner. At the end we have also stated the limitations of the use of nanotechnology in wastewater remediation, conclusion and its future direction.

7.2.1 Adsorption onto Nanomaterials

Adsorption is considered as one of the most promising methods for the removal of contaminants from wastewater where the sorbate i.e. water pollutants are adsorb onto the surface of the sorbent due to certain attractive forces. Both non-covalent (physiosorption) and covalent (chemisorption) forces may involve in the adsorption process. The nanoparticles are highly efficient and studied for their adsorption properties due to their large surface areas and short intraparticle diffusion distance (Kalfa et al. 2009). Besides that, high surface energy and size dependent surface structure at the nanoscale may create highly active adsorption sites, resulting in higher surface-area-normalized adsorption capacity. The ease of surface modification also allow selective adsorption of particular contaminants onto the surface of the nanoparticles. Once the contaminants are adsorbed onto the surface, it can also be desorbed by modulating the solution conditions such as pH, temperature etc. [Saikia et al. (2011, 2013), Saha et al. (2011)]. Desorption of the contaminants from the surface unlocks the reusability of these nanomaterials and reduces the overall treatment costs. Apart from the modulation in size and shape, the porosity of these nanoparticles can also tuned to controlled. Porous nanomaterials (e.g., electrospun activated carbon nanofibers) have tunable pore size and structure to allow control of adsorption kinetics (Shi et al. 2008). Nano-adsorbents consist of different nanomaterials and are broadly classified into various categories like metallic nano-particles, nanostructured mixed oxides, magnetic nanoparticles and metallic oxide nanoparticles (Al_2O_3, TiO_2, MnO_2, ZrO_2, ZnO, MgO, CeO_2), based on their role in adsorption process (Gupta et al. 2015). Another new series of carbonaceous nano-materials (CNMs) which includes carbon nanotubes, carbon nano-particles and carbon nanosheets have also been assimilated into this category. Besides this, different silicon based nano-material are also used as nano-adsorbents such as silicon nanotubes, silicon nanoparticles and silicon nanosheets (Anjum et al. 2016). Moreover, nanoclays, polymer-based nano-materials, nanofibers, and aerogels are highly efficient for heavy metals removal from wastewater. Size, surface chemistry, agglomeration state, shape and fractal dimension, chemical composition, crystal structure and solubility are the various factors which control the adsorption properties. Interestingly, some of these nanosorbents are already in the market in various water purifiers.

Nanomaterials of metal and non-metal oxides are extensively used for hazardous pollutants removal from wastewater. The natural high abundance of iron and the low cost synthesis process of ferric oxide nano particle have made it widely applicable for various reasons (Li et al. 2006). Iron-based nanoparticles are mainly applied for the removal of different dyes [(Saha et al. 2011; Istratie et al. 2016)] heavy metals from water due to its large surface charge, redox potential and its reusability (Li et al. 2003). Several factors like pH, temperature, adsorbent dose and incubation time, are also important for the adsorption process. Normally, to increase the adsorption of Fe_2O_3 nano-particles, its surface is modified with various additives such as -aminopropyltrimethoxysilane (Palimi et al. 2014). Nanoscale zero valent iron (nZVI) has other properties also, like it can catalyse the reduction of heavy metal ions, such as hexavalent chromium to trivalent form which results in the separation of Cr as insoluble hydroxides. However, nZVI has a strong tendency to coalesce to form large aggregates due to the magnetic properties and quick oxidation of metallic iron. This in turn blocks the surface active sites, decreases the reaction rate, and often leads to fast inactivation. Therefore, the ability to manipulate aggregation and oxidation is critical for developing cost-effective applications of nZVI. But, at the same time, oxidised iron is released to the solution which has its own demerit. Thus, to overcome this issue, a protective layer for the iron nanoparticle surface is employed. Chitosan-coated ZVI nanoparticles are known for their potential to role in removing Cr(VI) from water by its reduction to Cr(III) and the simultaneous formation of a precipitate with Fe(III). Again, magnetic NPs such as Fe_3O_4 and γ-Fe_2O_3 are popular in terms of their high reactivity, abundance and low cost, ease of separation and reusability, and environmental friendliness. But due to their high reactivity in an aquatic environment, the magnetic NPs are sensitive to corrosion which reduces its life-span. Thus, they are mostly coated with mesoporous silica, porous carbon, HA, thiosalicylhydrazide etc.

Besides the oxides of iron, manganese oxide (MnO), zinc Oxide (ZnO) and magnesium oxide (MgO). NPs are too effective for the removal of heavy metals like arsenic, zinc, cadmium. All of these have very high BET surface areas with different nanostructures. MnO NPs are frequently modified as nanoporous/nanotunnel manganese oxides and hydrous manganese oxide (HMO) for the water remediation. Similarly, nano assemblies, nanoplates, microspheres with nano-sheets and hierarchical ZnO nano-rods are used for wastewater treatment.

Carbon nanotubes are also extremely effective for the adsorbing various organic pollutants as they possessed higher surface area and can interact with the pollutants through various interactions such as hydrophobic interaction, π-π interaction, covalent interaction, hydrogen bonding and electrostatic interactions. It is interesting that, the external surface, inner site, interstitial channel, and peripheral groove of the carbon nanotubes constitute four possible sites where adsorption could take place (Das et al. 2017). Moreover, they are also hollow from inside which allow adsorption of nanosized particles. Thus, organic molecules with C=C bonds or benzene rings, polycyclic aromatic hydrocarbons (PAHs) and polar aromatic compounds are easily got adsorbed to the carbon nanotubes surfaces (Yang and Xing 2010). Similarly, organic compounds which have -COOH, -OH, $-NH_2$ functionalities are also adsorbed to the carbon nanotubes surface due to the formation of hydrogen bonds with the graphitic carbon nanotubes surface (Yang et al. 2008). Electrostatic attraction is also possible between positively charged organic contaminants with electron rich carbon nanotubes at suitable pH. But, poor dispersion ability, difficulty in separation and small particles size are few drawbacks of carbon nanotubes as adsorbent. Thus, normal carbon nanotubes are constantly modified with various technologies in order to achieve better efficiency. Formation of multi-wall carbon nanotubes (MWCNT)s and introduction of magnetic properties are a few examples of such modifications. Yang et al. had reported a polyacrylamide (PAM) functionalized MWCNTs which selectively adsorb Pb(II) and humic acid (HA). Again, Cyano (CN) functionalized carbon nanotubes are excellent adsorbent for phenol-type water pollutants which includes 4-chlorophenol, 2,4-dichlorophenol (DCP), 1-naphthol and 2 naphthol etc. The modified magnetic carbon nanotubes have high dispersion ability and can be easily removed from wastewater or used medium by using magnet. Again, acid treatment, metals impregnation and functional molecules/group grafting of carbon nanotubes has significantly enhanced its BET surface area, surface charge, dispersion and hydrophobicity, consequently their adsorption potentials are also increased. Common inorganic acids like HCl, HNO_3, H_2SO_4 are used for the surface modification which introduces oxy functional groups. Such carbon nanotubes are highly effective for the removal of heavy metals ions such as Cd(II), Cu(II), Pb(II) and Hg(II) from wastewater. This also removes the impurities present on carbon nanotubes.

However, due to higher cost of carbon nanotubes s, graphene oxide nanosheets have emerged as alternative absorbents to both metal and organic contaminants. Graphene is one of the allotrope of carbon having special features that make it highly favorable for several environmental applications. Chemical oxidation of graphene has produced two-dimensional graphene oxide nanosheets. Few selective hydrophilic groups like hydroxyl and carboxylic acids are also induced in graphene oxide to increase the adsorption of heavy metals. But, it did not require any further acid treatment to enhance the adsorption capacity. Electrostatic, π bonding (cation–π and anion–π), and Lewis acid–base interactions (i.e. chelating) are the major determinant forces for inorganic water pollutant adsorption onto graphene and graphene oxide, while organic water pollutants are adsorbed through π–π, hydrophobic, electrostatic, and hydrogen bonding. Besides the metal ions, graphene based materials are also explored for the adsorption of anionic contaminants. Fluoride, perchlorate are the various anions adsorbed efficiently on the graphene based materials. Again graphene oxide and their composites are highly effective for the removal of cationic dyes while graphene and its composites are mainly effective anionic dyes.

Nano polymers i.e. nano cellulose and dendrimers are also explored as adsorbent for waste water treatment. Biocompatibility, biodegradable, and cost-effective, these are the best characteristics of nano cellulose. Dendrimers are effective in adsorbing both organic and inorganic pollutants. The hydrophobic organic compounds are adsorbed on the hydrophobic core of dendrimer while the interior and exterior branches can be attract metal and/or ionic pollutants through electrostatic and/or hydrogen bonding. And the best part is that, desorption from dendrimers require only a change in pH of the solution. Overall, nano adsorbents are easy to synthesized their high adsorption capacity and effective regeneration and reuse (after desorption of contaminants) make them a potentially superior candidate for wastewater treatment. Scheme 2 elaborates different factors and interactions responsible for the efficient utilization of nanoparticles for waste water remedy. Different surface forces (electrostatic, hydrogen bonding etc.) are responsible for the interaction and binding of the pollutants onto nanoparticle surface. The solubility or dispersibility of the nanoparticle in different media containing the pollutants also determine the efficiency of the nanoparticle. Different chemical factors, such as oxidation and reduction potential of nanoparticles and the ability to form e^-/h^+ pairs (as in case of photocatalyst) also plays a crucial role in waste water remediation by nanoparticles. The aggregation and accumulation reduces the performance of nanoparticles as a whole by reducing the effective surface area.

7.2.2 Photocatalytic Water Treatment Using Nanoparticles

In photocatalytic water treatment a nano-catalyst harness the energy from light (generally UV) and uses the energy to degrade or break wide variety of organic materials – organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses and chlorine resistant organisms), inorganic molecules such as nitrous oxides (NOx). The main principle of photocatalysis lies in oxidation of these organic materials, water pathogens and disinfection by-products. Photocatalyst generates highly reactive transitory species (i.e. H_2O_2, OH, O_2, O_3) that leads to the degradation of these organics into readily biodegradable compounds, and eventually convert them to carbon dioxide and water. These falls under the broad spectrum of Advanced Oxidation Processes (AOP), which generates highly reactive and oxidizing hydroxyl radicals (•OH), regarded as the major responsible species for the degradation of organic pollutants in wastewater (Kuwahara et al. 2010). Figure 7.2 gives an overall graphical representation of the fate of pollutants in presence of TiO_2 nanoparticles.

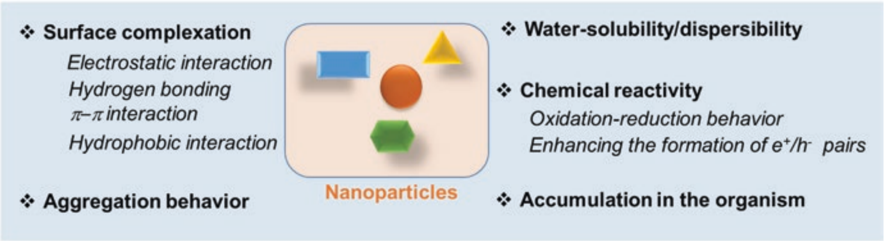

Fig. 7.2 Properties and interactions of nanoparticle responsible for waste water remediation

Nanostructured metal oxides semiconductors have gained a considerable attention of the scientists in photocatalysis developing wastewater treatment technologies due to their excellent band gap properties which upon irradiation of light generates electron-hole (e^-/h^+) pairs that lead to the cascade process of waste degradation. Other elements of theses nanostructured semiconductors such as (i) inexpensiveness; (ii) lower to no toxicity; (iii) exhibition of tunable properties that can be modified such as by size reduction, maximizing reactive facets, doping, or sensitizers; (iv) capacity of extending their use without substantial loss in photocatalytic activity, also render their use in waste water treatment. Nanostructures of metal oxide semiconductors like titania (TiO_2), zinc oxide (ZnO) are the most two promising candidates till date. Size and geometry plays a prominent role for these materials in its solid-phase transformation, sorption, and (e^-/h^+) dynamics. Faster recombination of the e^- and h^+ lowers the efficiency of TiO_2. This recombination can be lowered by decreasing TiO_2 particle size which enhances interfacial charge carrier transfer (Zhang et al. 1998). However, there should be a fine tuning in the optimal size within the nanometer range to get maximum efficiency, as lowering the size to several nanometers also leads to more surface recombination of the e^- and h^+. Similarly, increase in the particle size for ZnO with high calcination temperature decreases the photocatalytic degradation efficiency (Hayat et al. 2011). Geometry also plays a pivotal role in the efficiency of these nanocatalyst. TiO_2 nanotubes were found to be more efficient than TiO_2 nanoparticles in decomposition of organic compounds due to the shorter carrier-diffusion paths in the tube walls and faster mass transfer of reactants toward the nanotube surface (Macak et al. 2007). A general mechanism (Fig. 7.3) comprising a series of chain oxidative and reductive reactions occur at the TiO_2 surface as follows:

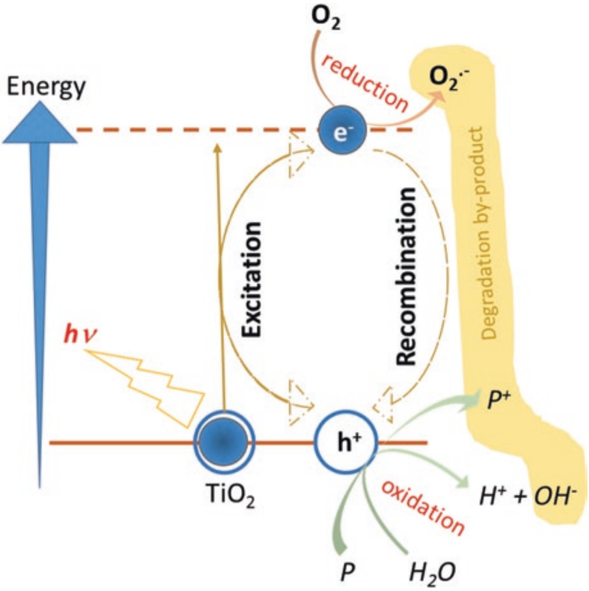

Fig. 7.3 Fate of pollutant (P) with the interaction of TiO_2, upon irradiation of light and the formation of e+/h− pairs. (Adapted from, Chong et al. 2010)

$$\text{Photo excitation}: \mathrm{TiO_2} + h\nu \rightarrow e^- + h^+ \tag{7.1}$$

This e^- and h^+ gets trapped in the conduction band and valence band respectively and these trapped carriers are surface bounded and do not recombine immediately after photon excitation. When a scavenger molecule such as O_2 accepts the trapped e^- in the conduction band and gets reduced to form the O_2^-

$$\text{Scavenging of} e^- \text{by} O_2 (\text{reduction}): O_2 + e^- \rightarrow O_2^{\cdot -} \tag{7.2}$$

Pollutant molecule (P) can also combine with the surface trapped holes (h^+) and oxidise to for intermediate degradation product (P^+)

$$\text{Combination withh}^+ (\text{oxidation}): P + h^+ \rightarrow P^+ \tag{7.3}$$

This P^+ intermediate recombines with the O_2^- radicals to give final degradation products. In parallel various other reactions also propagate which scavenges the excited e^- and h^+ to form OH^-, $OH^\cdot$ and $HOO^\cdot$ species that eventually gives the degradation products.

Modulating the size and the geometry may not be enough to improve the requisite efficiency in photolysis kinetics or photolytic range. Each nanomaterial have an effective absorption range of optimal wavelength of light that corresponds to the band gap of the material. The associated energy to the wavelength should be greater than or equal to band gap to excite the electron and initiate the photocatalysis cascade. For TiO_2, the band gap ranges from 3.2 eV (anatase) to 3.0 eV (rutile) and the light wavelength translates to less than 400 nm, limited to irradiation wavelengths in the UV region in the solar spectrum. And also the solar spectrum consist of only 3–5% in this UV range. Therefore, the efficiency of such photocalyst (TiO_2) to use the solar energy is limited. Thus the need to extend the excitation range of TiO_2 to include the visible solar light has been investigated. Various methods for modification of the catalyst include dye sensitization, doping metal impurities, hybrid nano-particles or composites using narrow band-gap semiconductors, or anions (Ni et al. 2007). Dye sensitization is done by using a dye molecule that harness the solar energy and get excited. The excited dye molecule than provide the additional electrons to the TiO_2 for enhancing the formation of e^+/h^- pairs (Vinodgopal et al. 1996). Noble metal or metal ions doping reduce the e^+/h^- recombination because the photo-excited electrons tend to migrate to the noble metals with lower Fermi levels while the holes stay in TiO_2 and this increase the charge separation and photocatalytic efficiency (Ni et al. 2007). Use of anions also decreases the band gap energy and subsequently transfers the exited electron to semiconductor under illumination of solar radiation (Fujishima et al. 2008). Also, doping with anions such as (N, F, C, S etc.) in the crystalline lattice of TiO_2 drastically shift the photo-responsiveness into the visible spectrum [(Asahi et al. 2001; Torres et al. 2004; Hattori et al. 1998; Ohno et al. 2004)]. Amongst all these anions, N-doped TiO_2 shows the higher feasibility under visible light but the e^+/h^- recombination is increased (Torres et al. 2004). Therefore coupling such system with other technology such as noble metal for trapping the electron shall eventually increase the photochemical efficiency (Ni et al. 2007). Crystallographic facets can also promote the photocatalytic activity of TiO_2. Using capping agents such as fluorides the percentage of high energy facets that has more efficient photcatalytic activity, can be increased from 10% to up to 89% (Han et al. 2009).

All these methodologies are used to increase the efficacy and photolytic efficiency of various nanomaterials. Overall the efficiency of a photocatalytic water treatment process strongly depends on the configuration and operation parameters of the photoreactor. The photocatalytic water treatment applications have almost become a mature market either be it a small scale photocatalytic systems with artificial UV-light or be a large scale solar treatment plant or pilot projects in developing countries.

7.2.3 Disinfection of Wastewater with Nanomaterials

Disinfection is one of the most used effective technique for waste water purification. But there is an urgent need to overcome the limitation and hazards posed by the conventional disinfection techniques that leads to the formation harmful disinfection byproducts (DBPs). Although effective in controlling microbial pathogens, conventional use of chemical disinfectants such as chlorine, chloramines and ozone can react with various constituents in natural water to form DBPs. The strong oxidation tendency of these conventional disinfectants leads to the formation of numerous DBPs. Various nanoparticles have shown excellent disinfectant properties without creating such DBPs pushing the reliability and robustness of disinfection to new heights. These nano-disinfectants are relatively milder oxidants and inert in water (Adhikari et al. 2014). The mechanism of such nanoparticle induced disinfectants are different than the conventional disinfectants. These nanoparticles can either directly interact and disrupt or penetrate with the cellular membrane and interrupt the electron transfer mechanism or initiate reactive oxygen species (ROS) production that causes the cell damage (Li et al. 2008).

Silk polymeric peptide nanoparticles that were found to be effective antimicrobial use forms nano-scale channels in bacterial cell membranes, which causes osmotic collapse and cell death (Gazit 2007). Chitosan nanoparticles are also exhibits antimicrobial activity. The proposed mechanism for chitosan is that the positively charged chitosan particles interacts with negatively charged cell membranes and increases the membrane permeability leading to rupture and leakage of intracellular components (Qi et al. 2004). Amongst various nano-disinfectant nano-Ag is currently the most widely used antimicrobial nanomaterial due to its strong antimicrobial activity, broad antimicrobial spectrum, low human toxicity (Xiu et al. 2012). The bactericidal property of Ag nanoparticle is also found to be size and shape dependent. Smaller Ag nanoparticles (8 nm) were most effective, compared to larger particle size (11–23 nm) (Morones et al. 2005). Also, truncated triangular silver nanoplates with a lattice plane as the basal plane displayed the strongest biocidal action, compared with spherical and rod-shaped counterparts, against the gram-negative bacterium Escherichia coli (Pal et al. 2007). Nano-Ag initiate different mechanisms by its release of silver ions that induce binding to proteins and enzymatic damage, suppress DNA replication and membrane damage (Kim et al. 2007; Liau et al. 1997; Danilczuk et al. 2006). Apart from the photocatalytic degradation of harmful organic and inorganic molecules, TiO_2 exhibits broad biocidal properties. The antibacterial activity of TiO_2 is related to ROS production, especially hydroxyl free radicals and peroxide that is formed upon UV (Kikuchi et al. 1997). Furthermore, Ag doping of TiO_2 enables visible light excitation of TiO_2 which results in great improvement in bacterial inactivation of bacteria under visible light (Seery et al. 2007; Sökmen et al. 2001; Sung-Suh, et al. 2004).

Similarly, another nanomaterial having identical band gap chemistry to TiO_2 has been extensively used for its bactericidal properties. ZnO nanoparticles also has a high UV absorption efficiency and exhibit strong antibacterial activities on a broad spectrum of bacteria (Jones et al. 2008). Incorporating palladium onto ZnO nanoparticles have also shown an enhancement in the antibacterial properties at removal of E. coli from water (Khalil et al. 2011). Intracellular accumulation of nanoparticles, cell membrane damage, H_2O_2 production and release of Zn^{2+} ions are believed to be responsible for the efficacy of ZnO nanoparticle as a broad spectrum bacteriocide (Sawai 2003; Huang et al. 2008). Another class of nanomaterial, fullerene (a derivative of C_{60}), has demonstrated a potent broad spectrum antibacterial activity. Although intrinsically insoluble, this class of nanomaterial can be derived to increase the water solubility (Lyon et al. 2008). Carbon nanotubes dispersion has also been enhanced by using surfactants or polymers to elucidate their antibacterial response. carbon nanotubes causes cell membrane perturbation and induce oxidative stress to eradicate bacteria (Vecitis et al. 2010).

7.2.4 Nanomembrane in Wastewater Treatment

The basic principle of membrane filtration is to apply semi-permeable membranes to remove undesired molecules from water and to make it reusable. Thus, such membranes must be water permeable and less permeable to solutes or other particles. Membrane technology deals with the various materials and techniques to improve membrane performance, reduce membrane fouling, minimizing energy requirement to achieve higher efficiency. Compared to other available membranes processes like microfiltration, ultrafiltration, reverse osmosis; nanofiltration has the advantage of functioning relatively at low pressure (Gehrke et al. 2015). Thus, nanofiltration is highly effective for the separation of contaminants from surface water where the osmotic pressure is low. Its pore size selectively rejects heavy metals and all other organic compounds but allows monovalent salts like sodium chloride to pass through it. nanofiltration will completely remove all microorganisms from water and also reduces hardness of water. Reverse osmosis is very efficient for retaining dissolved inorganic and small organic molecules. More than the size of the ion, it is the electrostatic interactions between the charged membrane and the charged species which play an important role in their permeation across the membrane (Shi et al. 2008). Thus, the salts containing divalent sulfate anions are better rejected by the membrane than salts with a monovalent chloride anion. These characteristics make nanofiltration membranes extremely useful for selective removal of solutes from complex process streams (Qu et al. 2013; Jagadevan et al. 2012).

Carbon nanotubes are also used for the synthesis of polymer composite membranes. Such composite have various features such as low mass density, extremely high strength and tensile modulus, high flexibility and large aspect ratio, which enhance its performance. Base on the variation in synthesis, the structure may contain single walled carbon nanotubes (SWCNTs) or MWCNTs. Carbon nanotubes membranes are hydrophobic in nature and possess high mechanical strength. There are two major types of carbon nanotubes membranes such as vertically aligned (VA) and mixed matrix (MM)/ thin film composite (TFC) membranes. Most of the studied VA- carbon nanotubes membrane have similar pore sizes to that of ultrafiltration and microfiltration membranes. Nanofibres are highly efficient for nanofiltration which have effective diameters in the range of 1–200 nm. Electrospinning is an efficient and inexpensive way to make such nanofibers using various materials like polymers (both natural and synthetic such as polystyrene (PS), poly (vinyl chloride) (PVC), polyvinylidene fluoride (PVDF), polybenzimidazole (PBI), poly(vinyl phenol) (PVP)), inorganic materials (e.g., some metal oxides), which form nanofiber mats with complex pore structure (Wegmann et al. 2008; Ramakrishna et al. 2006). Higher porosity and surface to volume ratio are the major advantages of this technique. Fibers thus produced are orders of magnitude thinner than the conventionally used methods. The fiber diameter (Anjum et al. 2016) governs the surface area to volume ratio and affects membrane porosity, which can be controlled by varying the process parameters such as solution concentration, applied voltage, surface tension, and spinning distance. Such nanofiber membranes are already in market for air filtration applications, but their potential in water treatment is still largely unexploited. They are highly efficient for the removal of micron-sized particles (heavy metals such as nickel, cadmium, copper and chromium) without significant fouling. Thus, such electrospun membranes are used prior to the ultrafiltration or reverse osmosis. More importantly, the membrane properties such as hydrophilicity, porosity, pore size, mechanical stability and charge density can be tuned easily which make it highly attractive and widely applicable for waste water treatment.

Again, nanomaterials may also be composite into polymeric or inorganic membranes which thereby promote it for multifunctioning. Various hydrophilic metal oxide nanoparticles (e.g., Al_2O_3, TiO_2, and zeolite), (Arancibia-Miranda 2016), antimicrobial nanoparticles (e.g., nano-Ag and carbon nanotubes), and (photo) catalytic nanomaterials (e.g., bi-metallic nanoparticles, TiO_2) are used for this purpose (Gehrke et al. 2015). The use of hydrophilic metal oxide nanoparticles reduces fouling by increasing the hydrophilicity of the membrane. Similarly, use of alumina, zeolite and TiO_2 to polymeric ultrafiltration membranes has increase membrane surface hydrophilicity, water permeability, or fouling resistance. Again incorporation of antimicrobial nanomaterials such as nano-Ag and carbon nanotubes are known to reduce membrane biofouling.

7.3 Limitation of Nanoparticles Used in Wastewater Treatment

All the nanomaterial studied, poses excellent physiochemical properties such as size, shape, surface to volume ratio, that make them a superior candidate in substituting conventional counterparts and has been a hot topic in the field of research for numerous application. Pivoting on these properties nanoparticle has also emerged as one of the most advanced processes for wastewater treatment. Although, there are several challenges and short comings for the use of nanoparticles in waste water treatment that restrict down the large scale commercialization of such systems. Some of the major concerns are (1) dispersion (2) retention and recovery (3) loss of activity over time (4) realistic condition efficacy (5) cost balance and (6) lesser known downhill toxicity of nanoparticles. Dispersion of these nanoparticles to their individual nanometric range are requisite for their optimal performance, but when introduce to water or wastewater conditions most of these nanoparticles tend to aggregate thus leading to settling or reducing their effective surface area and decrease performance. Aggregation is also aggravated by presence of some salt and ions in the solution (Lyon et al. 2008). Retention, recovery and reuse of these nanoparticles are important for cost effective measure and also for potential impacts on human health and ecosystems (Wiesner et al. 2006). Immobilization and membrane filtration methods are applied for the retention of nanoparticles which limits the effective dosage of the applied nanoparticles by the available surface area in the reactor and hence lowers the overall disinfection efficiency. Loss of activity over time and less number of efficiency cycle has also hampered the use of nanoparticles. For instance, Ag nanoparticles possess excellent bactericidal properties but its activity deteriorates with time due to the loss of Ag^+ ions (Chaturvedi et al. 2012). Although doping resolves some of the issues of inactivation of nanoparticles by inhibiting e^-/h^+ recombination, still the effectiveness of such system deteriorates over time. Apart from these the waste-degradation efficiency for most of the studies are done in a laboratory environment under simulated conditions. Whereas, in reality the waste-water situation is too complex and contains lots of different complexing ions and molecules. Most of these nanoparticle systems tends to show a better efficacy in simulated conditions but their performance decrease when translated to a real wastewater system. Apart from few metal oxide nanomaterial the synthesis and characterization of nanoparticles are very expensive. The recovery and reusability is imperative for these nanoparticles. Leakage of nanoparticles into water bodies may lead to harmful effect in human and marine ecosystem. The intrinsic toxicity of such nanoparticles is not clear. Although the short term exposure of some nanoparticles seem non-toxic but may have long term damaging effect. NPs may induce stress and lead to chronic inflammation (Mohd Amil Usmani 2017). Dissolution of nanomaterials in the water may also release metal ions that may have detrimental effects. Therefore, it is crucial for detailed understanding of these limitations and mitigating potential byproducts and hazards associated with these nanoparticles for a broader applicability and acceptance of nanotechnology in waste-water treatment.

7.4 Conclusion

Exploiting and redirecting the unique properties of nanoparticles towards waste-water treatment have proven promising. Different remediation process such as adsorption, photocatalysis, disinfection and membrane separation have been successfully utilized to get maximum efficacies out of theses nano-constructs. The domain of these nanoparticles are ever increasing, with the persuasion of lot of active research and developments throughout the world. Novel materials are being develop for better performance and better properties than their counterparts. Overall, these nanoparticles are potential upgradation than their conventional systems in waste-water treatments but they too have limitations that need further analysis. Majority of these systems are shown to be highly effective, but the study conditions are reported in a laboratory setup in simulated conditions. Real waste-water system studies would be more beneficial to assess their efficacies. Cost analysis of these nanoparticles from synthesis and characterization to purification, retention and recovery needs to be thoroughly evaluated to keep the cost underline for largescale utilization. Collaboration between different sectors from research labs to the person in field application can help reduce the cost to a larger extent. Further studies are required for better understanding of the working mechanism of such nano-constructs and its downstream effects on human health and ecosystem. Looking forward to the superior potential of these nanoparticles, future research resolving these limitations and improved understanding of the process mechanism will eventually lead to successful applications of innovative nano-constructs for wastewater treatment.

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