Chapter 13
Applications of Nanomaterials for Water Disinfection

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Abstract The presence of harmful pathogens in water is a major threat to human health when it comes to drinking water and hygiene. In addition to that, the emergence of new pathogens and antimicrobial resistance microbes will further challenge the operation of water treatment plants. Hence, there is a pressing need to develop cost-effective treatment technologies that will ensure safe and clean water supply for drinking and sanitation requirements. In recent years, nanomaterials have been extensively studied to inactivate waterborne pathogens. This chapter provides a short review of the applications of nanomaterials for disinfection against bacteria, protozoa, and viruses. The first section of the chapter briefly discusses the type of nanomaterials, synthesis protocols, and disinfection mechanisms. The subsequent section discusses some of the experimental studies related to the inactivation of bacteria, protozoa, and viruses using various nanomaterials. Challenges and limitations of nanomaterials in water treatment applications are also discussed towards the end of the chapter.

Keywords Pathogen · Disinfection · Nanomaterial · Water treatment · Drinking water

13.1 Introduction

Access to safe and clean drinking water is of paramount importance to humankind. One of the continuous threats to the supply of safe drinking water is the presence of microbial pathogens that could seriously affect public health and safety. The emerging and re-emerging nature of the pathogens can be attributed to the changes in demographics and human behavior, poor and improper maintenance of public health

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N. R. Maddela et al. (eds.), *Nanotechnology for Advances in Medical Microbiology*, Environmental and Microbial Biotechnology,
https://doi.org/10.1007/978-981-15-9916-3_13

utilities, microbial adaptation, and also by the impact of climate change and extreme weather events (Jones et al. 2008). A study analyzing the failure of the conventional water systems in developed countries revealed that malfunction of infrastructure and institutional practices led to frequent recurrence of microbial contamination in water supplies (Onyango et al. 2015). The effect of climate change on the rise of waterborne diseases can be directly correlated as extreme weather conditions such as floods and storms could pollute water bodies. For instance, there were reported cases of drinking water reservoir contamination by *Cryptosporidium* after heavy rainfall events (Saxena 2019). A *Campylobacter* outbreak in New Zealand affected nearly 5500 people as the groundwater supply was contaminated by seepage of sheep feces into a nearby aquifer following heavy rainfall (Gilpin et al. 2020). The contamination of water bodies by wastewater is another cause of concern for waterborne disease outbreaks. Numerous studies have shown that wastewater is the major source for fecal microorganisms, including emerging pathogens which when improperly handled contaminates the surface waters. As wastewater production and efficiency of treatment facilities vary across different regions, the presence of nutrients, chemicals, and pathogenic microorganisms needs to be adequately addressed to prevent environmental and health issues. Wastewater from household hosts a myriad of pathogenic microorganisms such as bacteria, viruses, and protozoa (Herschy 2012). Also, excess nutrition in the water bodies resulting from the industrial discharge of untreated wastewater can lead to algal bloom and eutrophication. This in turn causes the proliferation of pathogenic microorganisms and deteriorates the overall water quality (Roy et al. 2011). The presence of natural organic matter (NOM) in water supplies increases the microbial contamination risk as NOM shields microorganisms from conventional disinfection technologies and serves as a breeding medium for a large variety of other microorganisms (Gledhill 1987). Apart from these factors, the ability of the pathogen itself to evolve and develop antibiotic-resistant genes is posing innumerable challenges to the conventional disinfection process (Dungeni et al. 2010).

The United States Environmental Protection Agency Contaminant Candidate List 3 (CCL 3) identifies many waterborne pathogens that could compromise the safety and quality of the drinking water (“Final Contaminant Candidate List 3 Microbes: Screening to the PCCL” 2009). Common symptoms related to waterborne diseases are diarrhea, vomiting as well as eye, ear, skin, and/or respiratory infections. Some of the common pathogens that are found in water supplies are *Cryptosporidium, Legionella, Escherichia coli O157, Rotavirus, Hepatitis E virus, and Norovirus*. A survey by Moreira and Bondelind (2017) indicated that *Cryptosporidium, Norovirus, Giardia, Campylobacter,* and *Rotavirus* are among the most reported waterborne pathogens. *Shigella flexneri* is another common food and waterborne pathogen that has been reported in many different regions and is known to be resistant to most of the antibiotics (Nisa et al. 2020). The emergence of more new pathogens such as *Helicobacter pylori* (*H. pylori*) that could be potentially transmitted through water is also a growing concern in the water treatment sectors. Other pathogens that belong to the *Enterobacteriaceae* family such as *Klebsiella spp.* and

Salmonella spp. are also among the common cause of water supply contamination (Mehrad et al. 2015).

According to the commitments to the Sustainable Development Goals, governments should take measures to considerably increase recycling and safe reuse of the wastewater by 2030 (Malik et al. 2015). In addition to that, there is a need for the transition to decouple the economic growth and development essentially with the consumption of finite resources like water, in achieving a circular economy (Shan et al. 2016). The United States Environmental Protection Agency (USEPA) has permitted the use of copper as an antibacterial agent due to its ability to generate reactive oxygen species to disinfect pathogens through chromosomal aberrations and oxidative damage to DNA (Environmental Protection Agency Federal Facilities Restoration and Office 2017). The efficiency of the water treatment process in removing pathogens is measured using Log Reduction Value (LRV). LRVs are generally monitored in water treatment plants from the entry point and after successive treatments,

$$\mathrm{LRV} = \log_{10}\left(\mathrm{C}_{\mathrm{in}}/\mathrm{C}_{\mathrm{out}}\right)$$

where C_{in} is the influent pathogen concentration and $\mathrm{C}_{\mathrm{out}}$ is the effluent pathogen concentration. (Bennett 2008).

In general, WHO recommends the LRVs for pathogens as follows: (1) enteric viruses (9.5-$\log_{10}$) (2) bacteria (8.5-$\log_{10}$), and (3) protozoa (8.5-$\log_{10}$). The determination of LRV for viruses is more complicated and only several countries have regulations to control the indicator viruses and on the LRVs (Ahmed et al. 2020).

Many different treatment processes are deployed in a water treatment plant as a multiple-barrier to remove and inactivate pathogens. This includes (1) pretreatment (such as roughing filters, micro strainers, riverbank filtration) (2) coagulation, flocculation, and sedimentation/flotation, and (3) filtration (granular media filtration, sand filtration, microfiltration, and ultrafiltration). These treatment processes are followed by disinfection steps that can be achieved using oxidizing compounds such as chlorine, chlorine dioxide, and ozone or by Ultraviolet light (UV). Conventional disinfection processes have their own merits and disadvantages. For instance, chlorination is effective in deactivating different types of pathogens and able to provide positive residual protection for a longer period. However, chlorination effectiveness is pH-dependent and could potentially create toxic disinfection by-products such as trihalomethanes. UV treatment, despite being excellent in eliminating pathogens by breaking the bonds of microbial nucleic acids, requires frequent maintenance and does not work well in turbid water. Therefore, there is a need for developing efficient processes for disinfection and microbial control. Nanomaterials with antimicrobial properties have huge potentials as viable technologies to inactivate pathogens in water supplies.

13.2 Application of Nanomaterials in Disinfection

In recent years, nanomaterials have been explored and utilized in different water treatment processes such as oxidation, adsorption, filtration, and disinfection. The exceptional properties of nanomaterials owing to its different shape and size along with others features such as (1) high efficiency, (2) high surface area, (3) durability, (4) ease of functionalization, and (5) antimicrobial structures have led to the development of various innovative water treatment technologies (Ibrahim et al. 2016; Bora and Dutta 2014; Gautam et al. 2019; Ul-Islam et al. 2017; Guerra et al. 2018; Punniyakotti et al. 2020).

There are a plethora of scientific studies related to the application of nanomaterials for disinfection purposes. One of the studies demonstrated excellent removal of *E. coli* K12, *P. mendocina,* and virus using polysulfonate ultrafiltration membranes impregnated with silver nanoparticles (Zodrow et al. 2009). In another study, carbon nanotubes were found effective in removing *E. coli* and *Staphylococcus aureus* and *Poliovirus sabin 1* (Srivastava et al. 2004). A photocatalytic material made of Al-doped $BiVO_4$ has a superior photocatalytic antibacterial property and was effective in controlling the growth of Methicillin-resistant *S. aureus* MRSA (Vicas et al. 2019). More studies related to microbial inactivation will be in the subsequent sections.

13.3 Types of Nanomaterials

Carbon nanotubes (CNT), graphene oxide (GO), and fullerenes are among the popular carbon-based nanomaterials that are used in water disinfection processes due to their excellent antimicrobial properties. Studies have confirmed that single-wall carbon nanotubes (SWCNT) inactivate *E. coli* by damaging its cell wall (Kang et al. 2007). Figure 13.1 shows the morphological degradation of *E. coli* after being exposed to SWCNT for 2 hours in saline solution (Ibrahim et al. 2016).

Another study claimed that the antimicrobial properties of SWCNT could be attributed to its -OH and -COOH surface groups (Arias and Yang 2009). Graphene Oxide (GO), made up of a monolayer of tightly packed carbon treated with hydroxyl, epoxyl, and carboxyl groups, has been widely studied in the field of disinfection. GO inactivates microbes by forming cell-GO aggregates and disrupting the membrane of microbes using its sharp nanowalls edges (Dizaj et al. 2015). Fullerenes, made up of carbon atoms, have excellent antimicrobial activity against *E. coli, Salmonella*, and *Streptococcus spp*. The antimicrobial mechanism of fullerenes involves the inhibition of the bacterial energy metabolism by disrupting the oxygen uptake as well as by damaging the cell membrane (Tegos et al. 2005). C60 and C70 fullerenes have shown good results against viruses and bacteria by cleaving their genetic material (Chae et al. 2014). Fullerol was studied extensively for water treatment applications, especially against MS2 bacteriophage, which has similar morphology of *hepatitis A*

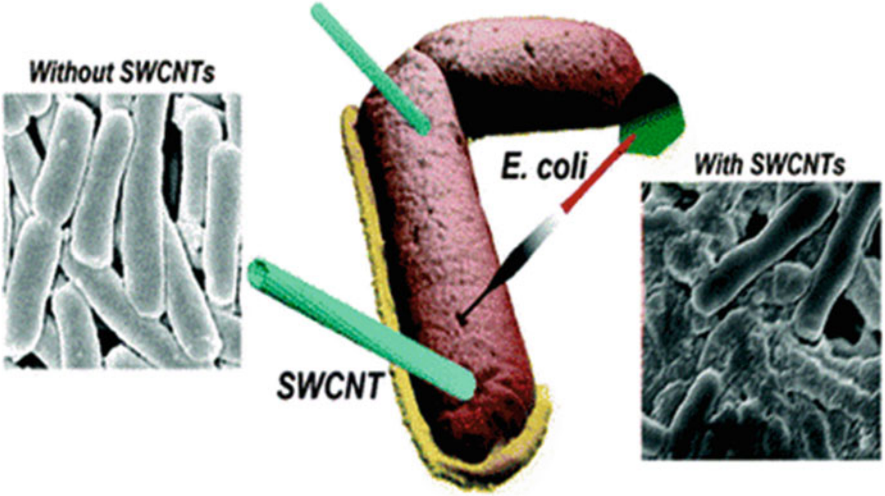

Fig. 13.1 SEM images of punctured *E. Coli* after exposure to SWCNT

virus and *poliovirus*. In the presence of fullerol and UV light, excellent inactivation of MS2 bacteriophage was achieved (Badireddy et al. 2007).

Metal oxide-based nanomaterials have been attracting major interest in recent decades due to their numerous applications, especially in the environmental remediation field. Titanium dioxide, TiO_2 is among the popular metal oxides that are well known for its antimicrobial properties. Under UV/visible light exposure, TiO_2 generates reactive oxygen species that destroy cellular membranes, DNA, and proteins. Other excellent candidates are Zinc oxide (ZnO) and Copper (II) oxide (CuO) and Magnesium oxide (MgO). ZnO has shown 100% inhibition, antibacterial and antibiofilm activities against *Staphylococcus aureus* and *Pseudomonas aeruginosa* (Akhil et al. 2016). CuO nanosheets showed antibacterial activity against *Enterococcus faecalis* and *Micrococcus luteus* along with its good reusability and photo corrosion and inhibition properties (Fakhri et al. 2018). Ag@TiO_2 nanoparticles under UV light irradiation showed complete disinfection of *E. coli* at a 0.4 g/L catalyst loading rate (Sreeja and Vidya Shetty 2016).

13.4 Nanomaterial Synthesis Methods

Chemical methods such as coprecipitation, hydrothermal, facile hydrothermal, and microwave-assisted approaches are widely adopted in synthesizing various types of nanomaterials. This method is generally simple, tunable, and can be scaled up for mass production (Hyeon 2003). The hydrothermal technique is one of the commonly used chemical methods for the synthesis of nanomaterials. It promotes chemical reaction under elevated temperature and pressure where the properties and

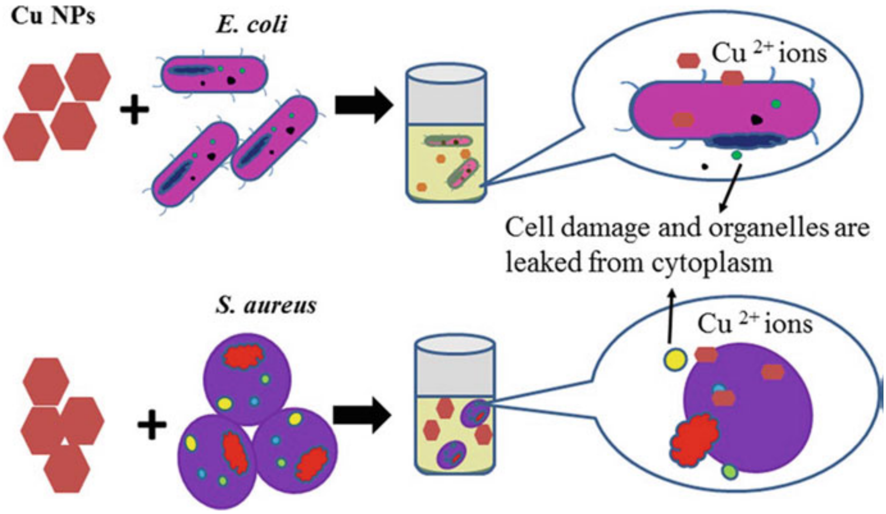

Fig. 13.2 Schematic representation of Cu NPs on Gram-positive and Gram-negative bacteria

characteristics of nanomaterials can be tuned by varying the reaction pressure and temperature of an autoclave reactor. It is a highly preferred method due to its capability to operate across different solvent, operating pressure, and temperature to manipulate the critical point of the substances used in the reaction (Rane et al. 2018).

As the chemical synthesis methods have its drawbacks such as (1) requiring expensive chemicals, (2) hazardous solvent, (3) and waste disposal issues, there is a need to develop more environment-friendly synthesis methods (Chen et al. 2007). Green chemistry principles are now being explored to synthesize nanomaterials using extracts of plants, fruits, and fungi (Prasad 2014, 2016, 2017; Prasad et al. 2016, 2018a,b; Srivastava et al. 2021). This method is non-toxic, low cost, and reduces the usage of harmful substances. For instance, copper nanoparticles can be synthesized in a greener way by mixing copper chloride solution and leaf extracts of *Cardiospermum halicacabum,* (commonly known as balloon vine). The green-synthesized Cu NPs liberate their cations (Cu+) into the growth medium stick on the cell membrane of cells because of electrostatic attraction and leads to cell death as shown in Fig. 13.2 (Punniyakotti et al. 2020).

Silver nanoparticles (AgNPs) have also been synthesized using a facile method with the extracts of *Excoecaria agallocha* (*E. agallocha*), a mangrove tree leaf (Bhuvaneswari et al. 2017). The synthesized AgNPs were pure, stable, and displayed excellent cytotoxic properties. In another study, Ag NPs were synthesized using Ives cultivar (*Vitis labrusca*) pomace as reducing and stabilizing compounds and were capable of reducing 47% of *E. coli* in the raw wastewater (Raota et al. 2019).

13.5 Mechanism of Inactivation by Nanomaterial

Inactivation of pathogens by nanomaterials involves the combination of different mechanisms. MS-2 phage and *E. coli* were inactivated differently when photocatalytic TiO_2 was used (Cho et al. 2005). MS-2 phage was mainly inactivated by the formation of free hydroxyl radicals in the bulk phase, while *E. coli* was targeted by the surface and free hydroxyl radicals as well as by other reactive oxygen species. Ag NPs inactivate pathogen using several mechanisms. Apart from releasing silver ions that are capable of altering enzyme activities and interfering with DNA replications, Ag NPs can also accomplish its activation by forming free radicals on the cell wall of the pathogens that would result in the damage of cellular membranes (Saleh 2017; Prasad and Swamy 2013; Aziz et al. 2014, 2015, 2016). Similarly, ZnO nanoparticle can achieve its antimicrobial activities using its superior photoconductivity properties resulting from UV illumination as well as by damaging the cell walls using its morphology (Sirelkhatim et al. 2015; Bhuyan et al. 2015). Like other nanomaterials, carbon nanotubes also inactivate microbes using several mechanisms such as by damaging DNA, disrupting the cell wall, and transmembrane electron transfer (Liu et al. 2018).

13.6 Bacterial Inactivation Using Nanomaterials

The current disinfection technology such as chlorine can effectively control pathogens but forms disinfection by-products, which causes harmful effects on human health. Therefore, there is a need for an ideal disinfectant with broad antimicrobial property. Therefore, NPs and nanomaterials could be a better alternative for pathogen removal.

Copper NPs (CuNPs) are among the excellent antibacterial agents against various pathogens such as *E. coli, P. aeruginosa,* and *S. aureus* species (Yadav et al. 2017). In one of the studies, the antimicrobial performance of a cellulosic paper coated with CuNP against *E. coli* was evaluated. Their study showed that CuNP embedded paper achieved up to 8.8 log reduction value. It was also shown that the leaching of copper from the paper substrate was only 0.14%, thus indicating the robustness of their facile deposition method. The direct contact between CuNP and *E. coli* during the filtration process was postulated as the main mechanism of inactivation (Dankovich and Smith 2014). In a recent study, copper oxide nanoparticles were synthesized using *Citrus aurantifolia* leaves to evaluate the antimicrobial performance against *S. aureus* and *E. coli*. The results indicated that *E. coli* was more susceptible to copper oxide nanoparticles and the inactivation mechanism was attributed to the presence of amine groups and large surface area of the nanomaterial (Rafique et al. 2020).

Inactivation of mixed *E. coli* and *Bacillus spp.* culture using TiO_2 Degussa P-25 in a coaxial photocatalytic reactor illuminated with neon lamps showed that *E. coli* was more susceptible than the *Bacillus sp.* It also showed that higher microbe inactivation was achieved at elevated dissolved oxygen levels (Rincón and Pulgarin

2005). Another study investigated the inactivation of *M. smegmatis* using nine different TiO_2 nanotubes electrodes impregnated with Ag nanoparticles. It demonstrated that inactivation efficiency as high as 99.6% was achieved after 30 minutes of visible light exposure while full activation was attained within three minutes of using UV light (Brugnera et al. 2014). In another study, Ag/TiO_2 nanofiber membranes developed showed excellent filtration and antimicrobial properties (Liu et al. 2012). The membrane was able to inactivate 99.9% of *E. coli* within 30 min of solar irradiation. Bacteria regrowth test using the Kirby–Bauer approach confirmed the antimicrobial nature of the membrane where no regrowth of *E. coli* was observed. Similar findings were observed, where the addition of silver improved the photocatalytic performance of TiO_2. However, excessive addition of silver could be detrimental as this could reduce the active site available for photocatalytic reactions (Taylor et al. 2011).

AgNP decorated GO nanocomposite synthesized using a facile and green method showed good antibacterial property when tested against Gram-negative *E. coli* ATCC 25922 and Gram-positive *S. aureus* ATCC 6538. The synthesis of AgNP–GO was made by suspending GO in deionized water along with $AgNO_3$ with further addition of 1 mM glucose and 4% starch as a reducing agent and stabilizer, respectively. The undesired agglomeration of silver nanoparticles was overcome in this study by using GO as a support media. SEM microscopy analyses confirmed the substantial deformation in the shape and size of *E. coli* and *S. aureus after* being exposed to AgNP–GO, hence suggesting that the inactivation of the pathogen was likely due to the damage of cell walls (Shao et al. 2015).

In another investigation, the effect of capping agents such as ethylene glycol (EG), gelatin, polyvinyl alcohol (PVA), and polyvinylpyrrolidone (PVP) on the microbial activities of ZnO NPs was evaluated. The experiments were conducted using *Staphylococcus aureus* and *Pseudomonas aeruginosa* where the bacterial cells were exposed to ZnO NPs synthesized using different capping agents for four hours under dark and light conditions. The results indicated that most of the capping agents except for PVP yielded in lower inactivation when compared with pristine ZnO NPs (synthesized without any capping agent). Their results were also in agreement with many other findings that confirmed the higher inactivation activity of ZnO with the presence of light (Akhil et al. 2016).

Cerium oxide (CeO_2) nanoparticle is another promising nanomaterial that is being actively studied due to its photocatalytic and antimicrobial properties. CeO_2 nanoparticles, synthesized using *Calotropis Procera* flower extract, showed efficient antimicrobial activity against Gram-positive and Gram-negative bacteria such as *Bacillus subtilis, Staphylococcus saprophyticus, E. coli,* and *Pseudomonas aeruginosa*. This study showed that the prepared CeO_2 NP was effective against these bacteria and it was noted that higher inhibition activity was achieved against Gram-negative bacteria. The antimicrobial characteristics of CeO_2 NP were attributed to the huge surface area and surface reactivity of the nanomaterial (Muthuvel et al. 2020).

The antimicrobial property of monoclinic bismuth vanadate (m-$BiVO_4$) octahedral nanostructures was investigated using *E. coli* as an indicator of bacteria (Sharma et al.

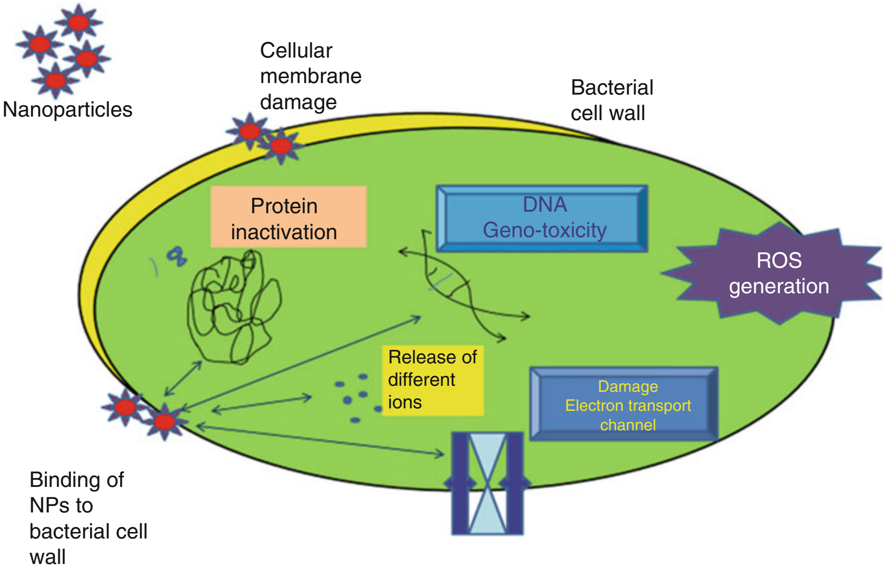

Fig. 13.3 Antimicrobial mechanism of nanoparticle

2016). It was found that exposure to m-$BiVO_4$ led to cellular disintegration where complete inactivation of *E. coli* was achieved after 8 hours of exposure to 80 ppm of m-$BiVO_4$. In another study, a one-pot hydrothermal approach was adopted to synthesize Al:$BiVO_4$ by adding 1% aluminum oxide powder (w/v) to the precursor solutions that comprised of bismuth nitrate and ammonium vanadate. The resultant nanoparticles exhibited higher bacteria inactivation than the pristine $BiVO_4$ even at the lowest Al concentration of 0.02 g/L. It was postulated that the addition of Al lowered the bandgap energy and improved the charge transfer characteristics of the material, thus leading to the enhancement of photocatalytic efficiency (Vicas et al. 2019). Figure 13.3 shows the various inactivation mechanisms of bacteria by nanoparticles. Nanoparticles bind to the surface of the bacterial cell wall and deploy various mechanisms to inactivate cells. This includes (1) releasing of ions to disrupt the cell function (2) puncturing of the cell wall (3) binds with DNA and causes genotoxicity, and (4) generation of reactive oxygen species (ROS) that led to oxidative stress (Chaudhary et al. 2020; Prasad 2019a,b; Prasad et al. 2020).

In a very recent study, photocatalytic activity of a WO_3/ZrO_2 was improved using ruthenium (Ru), a rare transition metal. By coating the Ru/WO_3/ZrO_2 on aluminum plates, they were able to reuse the synthesized materials for extended disinfection cycles where the catalyst inactivated more than 90% of Gram-negative (e.g., *Shigella, Salmonella, Vibrio parahaemolyticus,* and *Vibrio cholerae*) and Gram-positive bacteria (e.g., *Enterococcus*) within 120 min of exposure (Fouad et al. 2021). They reported that the holes and hydroxyl radicals played a prominent role in activating the microbes with negligible contribution from superoxide radicals. This study also reported that a high concentration of NOM (e.g., 28.7 mg/L) in water

Table 13.1 Nanoparticle or nanomaterial used for the removal of bacteria

Nanoparticle type / nanomaterial used	Concentration used	Susceptible pathogens and mechanism	Refs.
Zinc oxide	100 mg/L	*S. aureus*, *P. aeruginosa*, and *E. coli* inhibited to 100% by the production of ROS	(Akhil et al. 2016)
Ag/TiO_2 nanofiber membrane	–	*E. coli* inactivated up to 99.9% in 30 min using solar light	(L. Liu et al. 2012)
TiO_2 photocatalysis	–	*E. coli, S. typhimurium*, and *S. sonnei*	(Moncayo-Lasso et al. 2012)
TiO_2, Pt–TiO_2, and Ag–TiO_2—photocatalysis	–	*E. coli*	(Taylor et al. 2011)
Ti/TiO_2–Ag—photocatalysis	–	100% inactivation of *Mycobacterium smegmatis* using UV for 3 min	(Brugnera et al. 2014)
TiO_2 nanowires on fabrics	–	100% inactivation of *E. coli* and *S. epidermidis* under visible light for 15 min	(Xu et al. 2018)
Films of TiO_2 and TiO_2/Ag	4% w/w	100% inactivation of fecal coliform using UV irradiation for 6 min	(Domínguez-Espíndola et al. 2017)
SnO_2-doped nanomaterials	–	*E. coli, P. aeruginosa, S. aureus, L. monocytogenes, B. subtilis, S. typhi, and T. viride*	(Pandiyan et al. 2019)
Modified core shell Fe_3O_4–SiO_2–NH_2	–	93.4% *S. aureus*, 97.4% *B. subtilis*, 95.1% *E. coli*, and 90.1% of *P. aeruginosa* and *Salmonella*	(Zhan et al. 2014)
Fe_3O_4@CTAB	–	99% inactivation of *E. coli* and *B. subtilis* within 60 min	(Jin et al. 2015)
AgNPs-loaded Clay	0.1 mg/L	Removal up to 90% *Salmonella spp*, 80% of *E. coli*, *Klebsiella pneumonia*, and *Shigella flexneri*, and 70% *Klebsiella aerogenes* at 2 h exposure Time	(Kassem et al. 2019)
Hybrid polyaniline/graphene/CNT		Up to 99.5% removal of *S. aureus* and 99.2% for *E. coli*	(Hussein et al. 2018)
$BiVO_4$ QDs/g-C_3N_4 and $AgVO_3$ QDs/g-C_3N_4	–	Removal up to 87.5% and 96.4% against *Salmonella* under visible light for 10 min	(Wang et al. 2018)

led to poor inactivation of microbes. This was due to the absorbance of light energy by NOM, adsorption of NOM on the catalyst surface that affects the production of reactive oxygen species (ROS) and finally scavenging of ROS by the NOM itself. Some of the other types of nanomaterials and nanoparticles used in the investigation of pathogenic bacterial removal along with their mechanism are provided in Table 13.1.

13.7 Inactivation of Protozoa by Nanomaterials

Some of the common waterborne protozoa that affect the water industries are *Cryptosporidium, Giardia, Cyclospora, Acanthamoeba,* and *Isospora*. Inactivation of *E. histolytica* and *C. parvum* cysts using silver and copper oxide nanoparticles was investigated and the study indicated that high inactivation was achieved for both the cysts after three hours of exposure (Saad et al. 2015). The inactivation of these parasites also increased with the concentration of NPs and exposure time. Post-treated SEM images of the parasites confirmed the structural damage in the cell wall of *C. parvum.* A study that investigated the efficacy of Ag NPs in inactivating *C. parvum* concluded that lower nanoparticles and ions concentration affect the cell viability while higher concentration led to oocyst rupture (Cameron et al. 2016). Another study investigated the effect of different dosages of silver nanoparticles (Ag NPs) (0.05, 0.1, and 1 mg/L) on the mortality of *Cryptosporidium parvum* (CP). The result indicated that a 97.2% drop in oocyst count was obtained when *C. parvum* was exposed to 1 ppm Ag NPs for 30 minutes. The inactivation of these protozoa was also possible at a much lower concentration of 0.05 ppm Ag NPs. However, at least four hours of exposure time was required to achieve over 90% inactivation efficiency (Hassan et al. 2019). In one of the studies, the performance of TiO_2 slurry under simulated solar radiation in inactivating *Cryptosporidium parvum* oocysts was compared between distilled water and simulated sewage effluent (Abeledo-Lameiro et al. 2016). This study reported that more than 95% of *C. parvum* can be inactivated in distilled water after five hours of exposure to 100 mg/L TiO_2 under simulated solar irradiation. In contrast, the inhabitation was significantly lower in the simulated wastewater effluent under similar operating conditions. The presence of scavengers such as carbonates, bicarbonates, and organic carbon in the wastewater effluent could potentially reduce the photocatalytic activity of TiO_2 and led to the poor inactivation efficiency. In another study, oocysts viability was studied by exposing them to solar radiation in the presence of 100 mg/L of TiO_2 and/or 50 mg/L of H_2O_2. The results showed a strong reduction in oocytes in the water samples with TiO2/ H_2O_2 up to 99.5% after exposure to sunlight, thus proving TiO_2 as one of the best photocatalytic disinfection agents against *C. parvum* (Abeledo-Lameiro et al. 2017). A study on the inactivation of *C. cayetanensis* oocyst at different doses of Magnesium oxide nanoparticles (MgO NPs) (1.25–25 mg/mL) revealed that exposure to MgO Nps induced morphological changes to the protozoa where cell wall damage/ rupture and leakage of oocysts content were observed. This study also claimed that antimicrobial properties of MgO Nps were controlled by the size of the nanomaterials where smaller dimension led to high inactivation efficiency. Longer exposure time also led to higher mortality of *C. cayetanensis* oocyst (Hussein et al. 2018).

13.8 Inactivation of Virus by Nanomaterials

Apart from bacteria and protozoa, the presence of viruses in water bodies poses a great danger to public health. The World Health Organization (WHO) recommends monitoring the microbial quality of wastewater and food using indicator organisms (e.g., fecal indicator bacteria (FIB) and bacteriophages) and reference pathogens (e.g., HNoV) in the position of measuring all of the human pathogens that can be possibly present. Some of the common nanomaterials used for disinfection include carbon nanotube, graphene, nano ZnO, nano Ni, nano Fe_3O_4, and nano TiO_2–anatase where MS2 phage is commonly used as a virus indicator.

Fullerol nanoparticles under UVA irradiation were reported to have achieved 4-log removal of MS2 bacteriophage. It was confirmed that the generation of superoxide and singlet oxygen during the photosensitization reaction played a key role in MS2 inactivation (Badireddy et al. 2007). A part of the study conducted by Brady-Estévez et al. (2008) investigated the removal of MS2 bacteriophage using single-walled carbon nanotube (SWNT) filter. This study demonstrated that the viral particles were completely removed using a 6-μm thick SWNT layer at a loading of 0.8 mg/cm^2. The researchers suggested that the high filtration efficiency was due to the effective filtration depth of the SWNT layer. In another investigation, the effectiveness of polymeric graphitic carbon nitride (g-C_3N_4) in inactivating MS2 bacteriophage was evaluated (Li et al. 2016). The photocatalytic experiments conducted under the visible light irradiation showed that at a concentration of 150 mg/L, the material was able to achieve an approximately 8-log reduction within six hours of exposure. However, g-C_3N_4 loading needs to be optimized as an excessive amount could negatively affect the photocatalytic reactions. Viral regrowth studies also confirmed that MS2 bacteriophage was completely inactivated as no regrowth was observed after 72 hours of incubation. The photocatalytic performance of Cu–TiO_2 nanofibers in inactivating bacteriophage f2 showed more than a 5-log reduction of bacteriophage f2 within four hours of exposure under visible light (Zheng et al. 2018). The inactivation efficiency was relatively unaffected when the pH of bulk water was varied between 6 and 9. Bacteriophage f2 inactivation increased with the addition of catalyst but tapered off as the catalyst loading reached 75 mg/L. It was mentioned that excessive addition of catalyst would result in turbid water and eventually led to a poor photocatalytic reaction. Some of the other types of nanomaterials and nanoparticles used in the investigation of viral removal along with their mechanism are provided in Table 13.2 below.

13.9 Limitation of Nanomaterial

Despite showing huge potentials in solving many water treatment problems, the risk associated with nanotoxicity needs to be effectively assessed. The toxicity of nanomaterials is governed by its shape, size, concentration, and reactivity (Sarkar

Table 13.2 Nanoparticle or nanomaterial used for the removal of virus

Nanoparticle type/ nanomaterial used	Susceptible pathogens and mechanism	Refs.
Cu–TiO_2 nanofibers/ photocatalysis	Bacteriophage f2 and its host *E. coli* 285 under visible light irradiation	(Zheng et al. 2018)
Magnetic Fe_3O_4–SiO_2–NH_2 nanoparticles	76.7% of bacteriophage f2 and 81.5% Poliovirus-1	(Zhan et al. 2014)
g–C_3N_4/EP composite nanomaterial	Complete inactivation of 8-log *E. coli* and MS2 within 3 and 4 h of visible light irradiation	(Zhang et al. 2020)

et al. 2019). Exposure to nanomaterials can lead to severe health and environmental problems. Owing to their nanoscale nature, nanomaterials can penetrate and disrupt cell walls, interact and bind with proteins, cause organ damage as well as triggering undesirable immune responses (Naqvi et al. 2018). CNT and metal oxide-based nanomaterials are known to create oxidative stress to cells by generating reactive oxygen species (Metzel 1990). Fullerenes have been reported to cause ecotoxicity to bacteria, daphnia, earthworms, fish, and human cell lines (Hlongwane et al. 2019). It was also reported that the growth of marine algae was reduced by 50 to 75% due to the exposure to ZnO NPs (Miller et al. 2010). A toxicology study on the effect on CuO and ZnO NPs on crustaceans and protozoans indicated that the presence of solubilized ion was likely the root cause for toxicity (Blinova et al. 2010). Another study demonstrated that flat shape Ag NPs is more toxic to embryos of zebrafish than Ag NP of spherical shape (Abramenko et al. 2018). A geno and ecotoxicities study on *D. magna* revealed that Ag Nps caused damage to DNA and could have genotoxic potential towards *Daphnia* (Park and Choi 2010). The utilization of nanomaterials in water treatment processes requires more extensive testing and investigations to gain a deeper understanding of the nanomaterial leaching and its and toxicology effects.

Apart from toxicity, recovery of nanomaterial from the treated water matrices is another practical limitation that needs to be overcome for successful implementation in the field. Other key challenges include aggregation and leaching of nanoparticles. The stability of nanomaterials could be also compromised by the water quality parameters such as pH, turbidity, temperature, dissolved organic carbon, and alkalinity.

13.10 Conclusion

Pathogens are usually found in wastewater and have a detrimental effect on human health. Unlike chemical emerging pollutants, whose effects on humans at low concentrations are yet to be established, most pathogenic contaminants are known to cause a wide range of waterborne diseases that have adverse effects on humans. Despite the advancements in monitoring and microbiological detection technologies, waterborne pathogens continue to pose risks. This is evident from the increasing number of infectious disease cases caused by unidentified or known microorganisms in the last few decades worldwide (Kot et al. 2015). It is of great importance that water treatment plants are equipped with the best available technologies and regularly monitored to ensure that they are free from harmful microorganisms. Nanomaterials with antimicrobial properties have huge potential in activating waterborne pathogens as demonstrated by various studies. However, there are some concerns and limitations that need to be addressed. It is essential to develop nanomaterials with a wide range of properties that are capable of treating various kinds of pathogens and emerging chemicals at different water matrices. Extensive studies related to the stability and toxicity of nanomaterials at a large pilot scale are required to completely de-risk the technology.

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