

Silver–magnetic nanocomposites for water purification

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Abstract There is a need for protecting and tidying up the natural resources of water, largely polluted by human activities. Impure water leads to health issues, especially in rural areas. Though various techniques had been used for years to purify water, research is still carried out to find out advanced treatment protocols. Here we review the application of nanomaterials to disinfect and purify water resources. We present micro-organisms responsible for waterborne diseases; physical, chemical and biological treatment systems; and disinfection using silver–magnetic nanocomposites.

Keywords Waterborne infection · Pathogens · Water purification · Disinfectant · Nanomaterial · Silver–magnetic nanocomposite

Introduction

Water is a universal solvent and an important component of metabolic processes within the cells. Nowadays water is under serious threat due to rising heavy industrialization and population which resulted in microbial contamination and chemical pollution (Sarayu and Sandhya 2013; Qu et al. 2013) leading to waterborne diseases (Li et al. 2008).

In rural and remote areas of developing countries, drinking water is collected from natural water sources such as river, lake or pond which contain few amounts of pathogens that may increase during long-term storage due to lack of disinfectants (Wright et al. 2004; Quang et al. 2013). Discharges of wastewater in natural water systems cause pathogen cultivation (Joao PS Cabral, 2010). Also during floods, harmful microbes are transferred from contaminated sites such as domestic sewage route and wastewater treatment plant to residential areas; even drinking water treatment facilities cause fatal infections such as typhoid, cholera and malaria (Quang et al. 2013). World Health Organization (WHO) reported that at least one-sixth of the world population (1.8 billion people) lack access to safe water (WHO 2004a, b) and the main waterborne disease, diarrhoea, kills about 2.2 million people every year mostly children under age 5 (Mthombeni et al. 2012; WHO 2004a, b). This has led to a great challenge in providing safe and clean water to the society in twenty-first century (Sarayu and Sandhya 2013).

Micro-organisms responsible for waterborne diseases

Bacteria

Bacterial community are dominant in waterborne diseases and can produce infections even at smaller ranges of infective units, i.e. 10–200, through faecal–oral route (Barna and Kadar 2012). Detection and enumeration of all types of pathogen in water is very difficult. Hence, *E. coli* and faecal streptococci have been selected as the indicator micro-organism for faecal contamination. The assumption is that if the indicators are detected for pathogens,

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appropriate action may be required (Fawell and Nieuwenhuijsen 2003). *E. coli*, equipped with a couple of virulence factors, produces diversified diseases from short self-limiting diarrhoea to frequently fatal haemolytic uremic syndrome. Shiga toxin (STEC) or verocytotoxin (VTEC) or enterohaemorrhagic (EHEC) *E. coli*-producing strains cause most of the illnesses during waterborne outbreaks. Persons with diarrhoea usually recover completely, but children under 5 years and the elderly are more frequently endangered by a complication called haemolytic uremic syndrome (HUS), characterized by haemolytic anaemia and renal failure, that may occur in about 2–8% of infections (Barna and Kadar 2012). Enterotoxigenic (ETEC) strains of *E. coli* cause gastroenteritis in children below 5 years of age followed by watery diarrhoea, dehydration, malnutrition leading to, in certain cases, death. Enteroinvasive (EIEC) *E. coli*, similar to *Shigella*, causes dysentery accompanied by certain diseases such as abdominal cramps, fever, diarrhoea, bloody stools (Cabral 2010). *Salmonella* species, *S. typhi* and *S. paratyphi*, are the most common intestinal pathogen next to *E. coli* contributing to higher risk of infections and are responsible for enteric fever known as typhoid and paratyphoid fevers (Fawell and Nieuwenhuijsen 2003, Chouhan 2015). *Shigella*, with humans and primates as natural host, causes symptoms from mild abdominal discomfort to dysentery characterized by cramps, tenesmus, diarrhoea, fever via faeces-contaminated food or water and by hand-to-mouth infection. In genetically compromised patients, *Shigella flexneri* causes Reiter's syndrome. According to WHO (World Health Organization), in 108,000 cases a year, death can happen due to mucosal ulceration, dehydration and rectal bleeding especially among children in the developing world. (Barna and Kadar 2012).

Vibrio cholerae is responsible for an acute diarrhoeal disease known as cholera. Death happens in less than 24 h in untreated case due to vomiting and massive loss of fluid and electrolytes. It occurs in many forms such as sporadic, endemic, epidemic or pandemic. In India, large epidemic incident of cholera was recorded in different regions. In 1961, the pandemic conditions happened in Indonesia and spread to Hong Kong, Philippines and westwards finally invading India in 1964. By 1966, it had spread throughout the Indian subcontinent and West Asia. In 1970s, it extended to Africa and different parts of southern Europe. For the first time, cholera had invaded Central and South America by mid-1992 reporting over half a million cases and 5000 deaths (Ananthanarayan and Paniker 2002). Another important waterborne bacterium is *Helicobacter pylori* which colonizes various regions of the upper digestive system causing stomach and duodenal ulcers and certain stomachic cancers (Akhter et al. 2007; Peter and Beglinger 2007). The infection is surprisingly common,

and the bacteria are believed to colonize more than half of the world's population (Aziz et al. 2015). Many researchers reported that route of transmission of *H. pylori* is contaminated water (Aziz et al. 2015; Engstrand 2001; Bellack et al. 2006). This is because the people are obliged to rely on municipal water wells as their main supply for drinking and irrigation (Aziz et al. 2015).

Campylobacter jejuni is a bacterium targeting human gastrointestinal tract causing severe diarrhoea known as campylobacteriosis upon faecal-contaminated water intake. In severe cases, gastroenteritis would be accompanied by fever that lasts for 2–10 days. Water systems, when transformed into a trash of infected farm animals, remnants of slaughtered animals such as leftover meat, intestines, skin and other solid animal wastes, could turn into potential contaminants generating particular organism. When such water bodies are used up for drinking purposes directly, the disease tends to spread over the immune system (Dziuban et al. 2006). Legionellosis, another waterborne infection, is caused by a bacterial genus *Legionella* that harms the respiratory tract causing pneumonia-like symptoms along with loss of coordination. These organisms are found in warm water environments from water heating systems to fine mist. The world's biggest outbreak was experienced in Murcia, Spain, in 2001 with 449 confirmed cases (Jamie Bartram et al. 2007). A recent study showed that 87 cases, out of which 10 were fatal, of Legionnaires' disease were reported between June 2015 and January 2016 by the Michigan Department of Health and Human Services for the city of Flint, Michigan, and surrounding areas (<http://www.michigan.gov/mdhhs>). *Leptospira* is a Gram-negative bacterium causing a zoonotic disease referred to as leptospirosis. These microbial agents spread through water contaminated with rodent urine. The waterborne pathogen enters the human body through open wounds or through drinking and turns the body yellow, termed as Weil's disease, or the lungs would bleed, medically called as the severe pulmonary haemorrhage syndrome. Leptospirosis has various terms such as the seven day fever, harvest fever, field fever, rat catcher's yellow and cane field fever. Reports indicate that 80% of the population exhibited serologic evidences of leptospiral infection (Ningal et al. 2015).

Viruses

Viruses are the second most ubiquitous pathogen found in contaminated water. Among the various viral groups rotavirus, norovirus and adenovirus are the overwhelming majority of acute gastroenteritis diseases worldwide. The major route of spread for virus is contaminated water (Barna and Kadar 2012). Adenovirus is a double-stranded DNA virus whose serotypes multiply in small intestine and

shed through faeces. The infections are mild or asymptomatic, except for those acquired in early childhood and are second to rotavirus as a cause of childhood gastroenteritis (Barna and Kadar 2012; Puig et al. 1994). Severe diarrhoea is caused by rotavirus, a group of double-stranded RNA virus, reporting very high death rate of 527,000 in 2004 under 5-year-old children (WHO 2004a, b). Norovirus, single-stranded RNA viruses, is the most prevalent cause of gastroenteritis globally in children, adolescents and adults with an estimated 1 billion case of diarrhoea every year. This group of viruses reported 21 million illnesses, 70,000 hospitalizations and 800 deaths in USA (Barna and Kadar 2012). It mainly causes 1–3-day-long self-limiting diarrhoea after 24–48 h of infection, but severe symptoms may be manifested in early childhood and elderly persons. Around 30% of infections from norovirus are symptomatic, highly contagious, and less than twenty virus particles can cause an infection (Morillo and Timenetsky 2011).

Polio and hepatitis viruses are certain viruses transmitted by faecal–oral route through contaminated food and water (Ananthanarayan and Paniker 2002). The polio virus enters through ingestion, multiplies in the intestinal tract and sheds through faeces. Gastrointestinal illness is the least characteristic disease they can cause. The wide array of symptoms occurs through neurological, cardinal, conjunctival, respiratory, then enters into central nervous system (CNS), multiplies in the neurons, destroys them and causes flaccid paralysis, leading to polio myelitis (Barna and Kadar 2012; Ananthanarayan and Paniker 2002). This virus is highly resistant to phenolic disinfectant; however, chlorination destroys the virus in water, but organic matter delays inactivation. Poliomyelitis is similar worldwide and paralysis is exclusively seen in children. In the early incidence, paralytic poliomyelitis in India was 20–40/100,000 population per year, an estimated 200,000 children developing paralysis annually (Ananthanarayan and Paniker 2002). The incident is soon to be eradicated by the routine vaccination processes.

Viral hepatitis is caused by hepatitis viruses of different types such as A, B, C, D, E and G. The term hepatitis refers to liver infection by such viruses (Ananthanarayan and Paniker 2002). They are very contagious, and their spread has a distinct pattern depending upon general hygiene circumstances. Waterborne spread of these viruses is well documented, with major drinking waterborne outbreaks of hepatitis E in Asia (Barna and Kadar 2012; Bloch et al. 1990; Jothikumar et al. 1993). Type B hepatitis viruses are the most widespread and the most important of viral hepatitis. More than third of the world's population is estimated to be infected by hepatitis B virus (HBV). The World Health Organization (WHO) estimates that HBV

infection causes more than a million deaths a year worldwide (Ananthanarayan and Paniker 2002).

Human polyoma virus (HPyV) is a potential viral pathogen present in the human gastrointestinal tract. Water reservoirs get contaminated due to discharge of human solid wastes which carry this organism from the gut. The name *polyoma* means numerous tumours in Latin, meaning the virus create tumours within the body. Infection starts primarily in the respiratory tract, and in acute conditions, the kidneys are affected (Hewitt et al. 2013). The virus also has the capacity to traverse through blood brain barrier into central nervous system leading to progressive multifocal leukoencephalopathy (PML) by destroying oligodendrocytes. Several studies also suggest that virus participates in causing colorectal cancer and in malignant colon tumours (White et al. 1992; Theodoropoulos et al. 2005).

Protozoa

Protozoa are diverse group of unicellular eukaryotic organisms, some of which are waterborne pathogens causing illness in humans. High mortality rate has been reported globally due to inadequacy of vaccines and medicines for most protozoan infections. *Entamoeba histolytica* is one of the most commonly known protozoa that causes amoebiasis, also known as amoebiasis, present worldwide (<http://www.ncbi.nlm.nih.gov>; Beeching and Gill 2014). The symptoms of this include abdominal pain, bloody diarrhoea or severe colitis with perforation and tissue death leading to peritonitis. If the intestinal lining is affected, then it could lead to amoebic colitis or amoebic bloody diarrhoea, and if it reaches the blood stream, then it leads to amoebic liver abscess (Farrar et al. 2013).

Cryptosporidium is the most harmful protozoan causing waterborne diseases in the developed and developing countries (Barna and Kadar 2012) as it is highly resistant to most of the disinfectants (Lin et al. 2013). Due to the presence of a rigid outer wall, the organism is 240,000 times more resistant to chlorination than *Giardia* (Rodgers et al. 1995). It is present in the oocysts of infected animals including humans and remains in water until it finds a new host for survival. Symptoms include watery diarrhoea and weight loss and can recur for up to 30 days. An outbreak in Milwaukee affected around 4,03,000 persons leading to death of immunocompromised patients and healthy people who consumed protozoan-contaminated water (Mac Kenzie et al. 1994; Fawell and Nieuwenhuijsen 2003).

Giardiasis is the second most common pathogenic protozoan infections caused by *Giardia* in humans in worldwide after *Cryptosporidium*, and it can be found in the digestive tract of almost every animal—including humans.

Giardia is capable of surviving long environmental exposure in the form of resistant cyst. Giardiasis is the most frequent intestinal disease worldwide caused by a protozoan, estimated to cause about 280–300 million cases a year (Barna and Kadar 2012; Esch and Petersen 2013). Untreated water, poor disinfection, pipe breaks, leaks, groundwater contamination, campgrounds are certain disease causing reasons in drinking water systems which happen to be same source of water for both humans and wildlife. Symptoms of individuals infected with this protozoan include diarrhoea, loss of appetite, bloating, and excessive flatulence and burping (Dziuban et al. 2006).

Cyclospora cayetanensis that causes gastrointestinal infection specifically termed as cyclosporiasis is spread through water contaminated with faeces and sewage (Talaro and Talaro 2002; Dziuban et al. 2006). Watery stools, cramps and fever are the indications within a week when the organism infects small intestine and invades mucosal layer (Dziuban et al. 2006). Recent studies by the Centers for Disease Control and Prevention (CDC) in 2015 notified 358 ill persons with confirmed *Cyclospora* infection (<http://www.cdc.gov/parasites/cyclosporiasis>). *Encyphalitozoon intestinalis* is waterborne protozoan that causes gastrointestinal tract infection called microsporidiosis and is transmitted through contaminated water. The infection eventually leads to diarrhoea and circulates to the ocular, genitourinary and respiratory tracts (Lanternier et al. 2009).

Parasites

Macro-organisms residing in animal and human intestines—parasites—also are responsible for waterborne illnesses as micro-organisms through contamination of water by faecal materials while drinking. Schistosomiasis, a parasitic disease caused by *Schistosoma* sp., generally released from freshwater snails, is spread by contact with contaminated fresh water. The disease is common in developing countries among children, farmers, fishermen and people using unclean water for household purposes (<http://www.who.int/mediacentre/factsheets/fs115/en/>).

This illness is mostly found in Africa, Asia and South America. As of 2012, it affected almost 210 million people worldwide (Fenwick 2012) and estimated 12,000 to 200,000 people died from it each year (Lozano et al. 2012). The indicator of the diseased individual is a distended belly, and other symptoms include bloody stool or blood in urine. If untreated, the protozoan can infect liver and kidney and also cause infertility and bladder cancer (<http://www.who.int/mediacentre/factsheets/fs115/en/>).

Dracunculiasis is an infection caused by a nematode worm, *Dracunculus medinensis*. This is spread through drinking water containing water fleas (*Cyclops* species) that

have the nematode larvae in their gut. After the organism enters the body, it migrates through the intestinal wall into the tissues and develops into adult worms (<http://www.who.int/topics/dracunculiasis/en/>). The female worms move through the subcutaneous tissue causing severe pain and emerge out of the skin of the feet producing oedema, blister and ulcer accompanied by fever, nausea and vomiting (Dziuban et al. 2006). When these female worms come in contact with water, the larva is discharged and starts a new life cycle. In 2015, there were 22 reported cases of the disease, and in the first half of 2016, there were 7 confirmed cases. No drugs are available to treat this disease (<http://www.who.int/topics/dracunculiasis/en/>).

Ascariasis is another dangerous disease which is caused by the roundworm *Ascaris lumbricoides*. Infection occurs by intake of food or water contaminated with *Ascaris* eggs from faeces (Hagel and Giusti 2010). In 85% of the cases, symptoms were not exhibited especially when the worms were lesser in number (Dold and Holland 2011). Symptoms during the onset of illness may include shortness of breath and fever, followed by abdominal swelling, abdominal pain and diarrhoea. The most infected age group is that of children showing symptoms such as poor weight gain, malnutrition and learning problems (Dold and Holland 2011). About 0.8–1.2 billion people are affected worldwide with ascariasis, with the most heavily affected populations in sub-Saharan Africa, South America and Asia (Keiser and Utzinger 2010). As of 2010, about 2700 deaths a year was recorded, down from 3400 in 1990 (Lozano et al. 2012).

Fasciolopsiasis is waterborne protozoan illness caused by the intestinal fluke, *Fasciolopsis buski*, considered as the largest intestinal fluke to be found in humans. It is endemic in India, China and Malaysia. These parasites can thrive in aquatic plants such as water spinach. When such plants are eaten raw or improperly cooked, they transfer to human intestines where they cause diarrhoea, abdominal pain, anaemia and allergies (Keiser and Utzinger 2009). *Echinococcus granulosus* is another parasite that causes disease by spreading through drinking water contaminated with faeces containing eggs. Symptoms include liver enlargement, hydatid cysts press on bile duct and blood vessels. If the cysts break open, they can cause anaphylactic shock (<http://www.who.int/mediacentre/factsheets/fs377/en/>).

Types of water purification system

Purification of drinking water is not a new technique; water treatment processes had been pointed out in the ancient period of civilization. For example, early Sanskrit writings outlined several methods for purifying water such as crude sand and charcoal filters (*Sushruta Samhita*), and the first

desalination was scientifically tested by Sir Francis Bacon in 1627 using sand filter (Pradeep 2009). Various events involved in the history of water purification are shown in Table 1.

Water purification techniques generally are categorized into three main groups, namely physical, chemical and biological. Physical methods include boiling (Somani and Ingole 2011), filtration, adsorption, distillation (Sharma and Bhattacharya 2016), ultraviolet, ultrasound and reverse osmosis (Mthombeni et al. 2012; Zhang et al. 2012). Chemical methods followed are precipitation and coagulation (Sharma and Bhattacharya 2016), chlorination (Mthombeni et al. 2012), ozone (Mthombeni et al. 2012; Zhang et al. 2012), electrochemical and catalytic process (Sarayu and Sandhya 2013; Pradeep 2009; Sharma and Bhattacharya 2016), use of hydrogen peroxide, use of metallic ions and iodine (Somani and Ingole 2011). Biological methods to purify water are phytoremediation and bioremediation using micro-organisms (Sharma and Bhattacharya 2016).

Physical methods

Boiling

This is the most common, simple and basic method of disinfecting water. During boiling, the temperature is raised to its boiling point and maintained for 15–20 min to kill the bacterial cultures (Somani and Ingole 2011). The process could be utilized only for household purpose and is unsuitable for large-scale water usage or supply.

Filtration

Filtration is done to purify water using filtering material and has been practiced over 200 years using sand which is referred to as sand filtration or slow sand filtration (SSF). This is a potential technique in controlling pathogens in large- and small-scale water supplies (Li et al. 2008; Ephrem Guchi 2015). This process is advantageous for it requires neither electricity nor any chemical agents. The raw water to be purified enters the filter and moves through the sand bed due to gravity, which requires 3–12 h, depending on the applied filtration rate (Bahgat et al. 1999). Sand filtration, though an easy technique, is a slow process. To replace it, membrane filtration techniques had been introduced for filtering drinking and sewage water. Depending on the size of the particles removed, membrane filtration can be categorized into nanofiltration, ultrafiltration, microfiltration and reverse osmosis. Membrane filters can trap particles larger than 0.2 μm including *Giardia* and *Cryptosporidium* but cannot remove minerals and ions dissolved in drinking water such as phosphorous, nitrates and heavy metal ions (Padmaja et al. 2014).

Microfiltration and ultrafiltration membranes have a pore size in the range of >10 and 1–100 nm, respectively, whereas porosity of membranes of nanofiltration and reverse osmosis range between ~ 1 and <1 nm. The membranes are generally based on natural and synthetic polymers such as cellulose acetate, cellulose triacetate, polysulphone, polyamide (Sharma and Bhattacharya 2016). Membrane filtrations commonly use a membrane pore size approximately 0.002–0.1 micron with an operating

Table 1 Important milestones of water purification in the history (Pradeep 2009)

Year	Event
1804	Set-up of world's first citywide municipal water treatment plant (Scotland, sand filter technology)
1810	Discovery of chlorine as a disinfectant (H. Davy)
1852	Formulation of Metropolis Water Act (England)
1902	Use of chlorine as a disinfectant in drinking water supply (calcium hypochlorite, Belgium)
1906	Use of ozone as a disinfectant (France)
1908	Use of chlorine as a disinfectant in municipal supply, New Jersey
1916	Use of UV treatment in municipal supplies
1935	Discovery of synthetic ion exchange resin (B. A. Adams, E. L. Holmes)
1959	Discovery of synthetic reverse osmosis membrane (S. Yuster, S. Loeb, S. Sourirajan)
1965	World's first commercial RO plant launched
1974	Reports on carcinogenic by-products of disinfection with chlorine Formulation of Safe Drinking Water Act (USEPA)
1975	Development of carbon block for drinking water purification
1998	Drinking Water Directive applied in EU
2003	Report on use of noble metal nanoparticles for the degradation of pesticides (A.S. Nair, R. T. Tom, T. Pradeep)
2007	Launch of noble metal nanoparticle-based domestic water purifier (T. Pradeep, A.S. Nair, Eureka Forbes Limited)

UV Ultraviolet, RO reverse osmosis, USEPA US Environmental Protection Agency, EU European Union

pressure of approximately 200–700 kpa. Reverse osmosis (RO) is usually used for domestic water treatment to remove salts, microbial pathogens and chemical toxins such as pesticides, organic contaminants and dyes. In this process, crude water is forced (with pressure) through a dense membrane filter that ceases the passing of impurities (Sharma and Bhattacharya 2016). Though these filters remove bacterial agents, viral particles pass through them which are a perilous demerit of this process (Somani and Ingole 2011). This disadvantage had to be abolished using cost consuming ozonation or chlorination processes.

Distillation

Distillation is a process of water purification where heat is applied to separate non-preferred chemicals such as lead, calcium, magnesium and to destroy microbial cells. The basic principle is that the input of heat energy raises vapour pressure. When the vapour pressure reaches its surrounding pressure, the liquid mixture boils and distillation occurs because of the differences of volatility in the mixture. As distilled water is void of minerals, it is not suitable for drinking purposes (Sharma and Bhattacharya 2016).

Adsorption

In this physical mode of water purification, dissolved contaminating materials bind to porous surface of the solid adsorbents (Jiuhui 2008). It is based upon the surface phenomenon and is the result of surface energy. Adsorbents or porous solids such as activated carbon, silica gels, aluminas, zeolites, ion exchange resins contain pores with varied diameters but size as tiny as a fraction of a nanometre is advantageous (Ali and Gupta 2007; Sharma and Bhattacharya 2016). The adsorbent systems are added directly to the water supply. In general, all microporous materials can be utilized as adsorbing materials, but those that are highly microporous and controlled are most preferred. Atoms on the surface of the porous materials are filled with other atoms, but not completely surrounded by them, and also have physical attractive forces acting on, which can be physisorption (originates from van der Waals forces) and chemisorptions (originates from covalent forces) (Sharma and Bhattacharya 2016).

Ultraviolet treatment

In the widely used physical technique, ultraviolet (UV) light configured inside a low-pressure lamp is utilized to seep through the water to be purified. As the sample experiences the radiations, the biological contaminants are lysed due to the damage in their genetic components (Nicki

Pozos et al. 2004; Sharma and Bhattacharya 2016). The range of wavelength from 2500 to 2650 Å exhibit maximum destruction efficiency and can achieve disinfection of about 99.99% (Somani and Ingole 2011). A major drawback is the non-capability of the process to remove dissolved chemicals and other particulate matter from water.

Ultrasound

In this process, the mechanical vibration of ultrasonic waves damage cellular structures of bacteria (Sharma and Bhattacharya 2016), but they themselves have no germicidal effect (Dadjour et al. 2006). Ultrasonic waves of frequency 400 kHz have been demonstrated to provide complete sterilization in 60 min. A drastic decrease in bacterial number is observed within 2 s (Somani and Ingole 2011). However, regrowth of the micro-organisms is also possible which is a significant disadvantage this method.

Chemical methods

Precipitation and coagulation

It is the simplest chemical method to purify water systems. Precipitation is the method of removing contaminants from the solution by adding agents so that insoluble solids as a precipitate appear. When the ions in the solution exceed that of the respective solids, precipitation happens. Coagulation is the process in which particulates settle at the bottom when chemicals are added, and thus, contaminants are removed. These techniques are also performed to remove impurities such as heavy metals, phosphorus, fluorides, arsenic, cyanide compounds from water (Eikebrokk et al. 2006; Sharma and Bhattacharya 2016). Certain coagulants used in clarification of water are alum, $\text{Ca}(\text{OH})_2$, Na-aluminate, ferric chloride (FeCl_3) and ferric sulphate, CaCl_2 , lime (Sharma and Bhattacharya 2016). Synthetic and natural polymers can also be utilized for precipitation (Brostow et al. 2009). The synthetic polymers include polyacrylamide, polyethylene oxide, poly(diallyl dimethyl ammonium chloride), poly(styrene sulphonic acid) and examples for natural polymers are starch, guar gum, alginate, glycogen, dextran. Though these processes are easy to carry out, this method is expensive due to the involvement of excess quantity of chemicals and sludge removal and disposal.

Ozone

Ozone, O_3 , is an unstable form of oxygen and protective layer of UV radiation. Treating water with ozone is also a

common method of water purification techniques next to the UV treatment. To purify drinking water, ozone is utilized as an effective disinfectant. It readily gives up oxygen, thus acting as a powerful oxidizing agent. Ozone possesses more superior bactericidal properties than chlorine (Camel and Bermond 1998), oxidizing the organics in bacterial membrane, weakening the cell wall ultimately leading to cellular rupture. It is efficient in removing tastes, odour, colour, iron and manganese; and not influenced by pH and temperature. Ozone can be transported and stored with ease, and even if the treatment is overdosed with ozone, water remains unaffected (Somani and Ingole 2011). Despite the advantages, in a report by Sharma and Bhattacharya (2016), it is denoted that ozone treatment have certain limitations; for example, it is a significant air pollutant, explosive, and an irritant to skin, eyes, respiratory tract and mucous membrane.

Chlorination

Chlorination has been the major disinfectant process for domestic drinking water since many years (Nieuwenhuijsen et al. 2000a, b). The most common strong oxidants, chlorine and its compounds such as chloramine or chlorine oxide are used in this technique (Sharma and Bhattacharya 2016). Chlorine effectively kills various waterborne pathogens that can cause typhoid fever, dysentery, cholera and Legionnaires' disease. The mechanism of action of chlorine is to rupture the microbial cell membrane and release cell inclusions that resulted in cell death in a short time span. Recent reports revealed that the parasitic protozoans *Cryptosporidium parvum* and *Giardia lamblia* have emerged as formidable waterborne pathogens. These protozoa are remarkably resistant to chlorine disinfection imposing a greater challenge to researchers and threat to public (<http://www.scientificamerican.com>).

Catalytic process

Photocatalytic method Photocatalysis is the phenomenon of overcoming the activation energy or temperature of a chemical reaction by light. Advanced oxidation processes paired with sunlight is effective to treat water by generating hydroxyl or OH radical. This method can be used to break down a wide variety of organic materials, inorganic molecules, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses and chlorine-resistant organisms) and used along with precipitation or filtration and can also remove metals such as mercury (Ahmed et al. 2013). Upon UV irradiation, photocatalytic reactions are initiated by the absorption of illumination with photoenergy equal to or greater than the band gap of the semiconductor. It results in electron-hole (e^-/h^+) pairs, and it

participates in the redox reaction with the adsorbed pollutant species in water. Apart from the reaction, the semiconductor also oxidizes water to produce OH rapidly reacting with the contaminants. Certain heterogeneous photocatalysts employing semiconductor catalysts such as titanium dioxide (TiO_2), zinc oxide (ZnO) and ferric oxide (Fe_2O_3) have significant capacity to degrade pollutants in water. Metal oxides are also used for this purpose as they are more resistant to poisoning and deactivation (Sharma and Bhattacharya 2016). The limitation of this method is that the metal catalyst has to be removed intermittently from wastewater.

Hydrogenation of nitrate The hydrogenation via catalytic method is one of the promising techniques for removal of nitrate from water. The process requires low or ambient temperatures with active catalysts. The reaction occurs with reduction of nitrate to products such as nitrogen dioxide (NO_2^-), nitrogen monoxide (NO), nitrous oxide (N_2O) and gaseous form of nitrogen (N_2). Supported bimetallic catalyst (viz. Pd/Cu, Pd/In and Pd/Sn) is an efficient catalysts for this technique. Apart from Pd, the other metals such as Cu, In, Sn and Co serve as precursors for the first reduction step to convert nitrates (NO_3^-) into nitrogen dioxide (NO_2^-). During this process, nitrogen (N_2) and ammonia (NH_4^+) are formed as end products where the former is harmless but the latter is considered as a hazardous aquatic pollutant (Sharma and Bhattacharya 2016). The toxic by-product ammonia is formed by a side reaction due to over hydrogenation (Soares et al. 2010).

Electrocatalytic oxidation In this process, the oxidation occurs through surface mediator on the anodic surface (Mohana and Balasubramanian 2006). The rate of oxidation depends on temperature, pH and diffusion rate of generating oxidants in indirect electrolysis. It is different from electrolysis where direct oxidation of pollutants takes place and rate of oxidation depends on electrode activity, pollutants diffusion rate and current density. The electrocatalytic materials used in this process are Ru/Pb/Sn oxide and Pb/PbO₂ coated with Ti (Sharma and Bhattacharya 2016). This method is widely applicable for removal of dyes and nitrates but does not show much effect on eradicating microbial cells.

Bioremediation

Bioremediation is the process of removing heavy metals, organic pollutants, pesticides and dyes using plant extracts and microbial organisms. Scanty reports have been reported on removal of micro-organisms using this technology. Water hyacinth (*Eichhorniacrassipes*), pennywort (*Hydrocotyle umbellata* L.), duckweeds (*Lemna minor* L.) and

water velvet (*Azollapinnata*) are some of the plant materials used for water treating (Sharma and Bhattacharya 2016). Microbial engineered community system are also used for purifying water through this process in which fungi, bacteria or microalgae is grown on supporting material to form biofilm (Lariyah et al. 2016) and use for bioremediation. Xie et al. (2005) tested the performance of biological pretreatment in Yellow River, China, by using bioceramic filter (BF) and Moving Bed Biofilm Reactor (MBBR) and reported effective removal of diatoms and cyanobacteria.

Disadvantages of conventional methods

Chemical physical disinfectant such as chlorine dioxide, chlorine (in the form of gas or hypochlorite), chloramines, ozone and UV are commonly employed in water purification (Zhang et al. 2012). These methods can actively kill the micro-organisms and effectively control the spreading of pathogens. Nevertheless, resistance of some pathogens include *Cryptosporidium* and *Giardia* to the chemical methods needs over dosage which are reacted with various constituents of natural water resulting in formation of harmful disinfection by-products (DBPs) which are highly carcinogenic (Quang et al. 2013; Mthombeni et al. 2012; Lin et al. 2013; Ahmed et al. 2013). Many literatures indicate that more than 600 DBPs have been recorded (Mthombeni et al. 2012; Krasner et al. 2006).

Disinfection by-products (DBPs) in drinking water are of considerable interest due to their association with bladder and rectal cancer. Chlorine the most common disinfectant and existing as hypochlorous acid and hypochlorite in water (range 0.2–1 mg/L) reacts with humic and fulvic acids to form halogenated organic compounds such as trihalomethanes (THMs), haloacetic acids (HAAs), chlorophenols, chloral hydrate and haloacetonitriles (HANs). Certain volatile compounds namely chloroform, bromodichloromethane (BDCM), chlorodibromomethane (CDBM) and bromoform could also be formed. The formation of such compounds relies upon chlorine dose, type of treatment, pH, temperature, residence time and bromine levels (Nieuwenhuijsen et al. 2000a). Most other disinfection by-products occur at trace concentrations (usually <1 µg/l). Disinfection by-products (DBPs) play a very adverse role in reproduction, leading to reduction in body weight and survival of the offspring, congenital malformations of cardiovascular and nervous systems. Trihalomethanes are the DBPs that are generally measured and most prevalent (Nieuwenhuijsen et al. 2009). Neural tube defects, urinary system defects and ventricular septal defects due to chlorination by-products were investigated by Hwang and Jaakkola (2003) and Hwang et al. (2008). High doses of

chlorodibromomethane (CDBM) resulted in decreased litter sizes and pup viability (Borzelleca and Carchman, 1982). Klinefelter et al. (1995) reported that bromodichloromethane (BDCM) can cause sperm abnormalities indicated by decreased sperm motility in male rats. Testicular damage in rats with disruption of spermatogenesis and motility was experienced when exposed to a strong toxicant, brominated acetic acid (Toth et al. (1992) and Linder et al. 1997). Hunter et al. (1996) found changes in neural tube development when they exposed mouse embryos to HAAs. Neural tube and craniofacial defects have been found when treated with dichloroacetic or trichloroacetic acid in rats (Smith et al. 1989a, b). Some of the disinfection by-products (DBPs) and their adverse effects on laboratory animals are shown in Table 2. Pilot-scale disinfection cannot be implemented with ultraviolet purification and reverse osmosis (Li et al. 2008; Mthombeni et al. 2012). Moreover, other physical, chemical and biological processes have own disadvantages that are tabulated in Table 3.

Nanomaterials as disinfectants

Though the organic materials sterilize water effectively, their use in drinking water is limited due to doubtful safety when compared with organic or inorganic disinfectant especially heavy metal ions. Nanomaterials are the choice of alternate disinfectant because of their excellent adsorbents, catalysts and sensor properties due to their large surface area (Li et al. 2008). They are discovered as an important material in the development of nanotechnology which can be used in plentiful industrial, scientific and technological applications. Nanomaterials are simply defined as small particle between 1 and 100 nm in size at least one dimension (Qu et al. 2013). At this smaller size, these materials often possess novel size-dependent properties different from their large counterparts, many of which have been explored for applications in water and wastewater treatment (Qu et al. 2013). They form aggregates in solution due to van der Waals forces and high surface energy. The antimicrobial nature of silver has received special attention because of the increasing general demands for hygiene in public health care (Sureshkumar et al. 2010). Higher antibacterial activity of silver is a result of their nanometre size based on silver mass content (Sureshkumar et al. 2010). Moreover, these have good chemical and thermal stability and do not result in drug resistance of bacteria (Zhang et al. 2012). Nanosilver is capable of destroying Gram-positive bacteria such as *Bacillus*, *Enterococcus*, *Listeria*, *Staphylococcus* and *Streptococcus* and Gram-negative bacterial genera namely *Acinetobacter*, *Escherichia*, *Pseudomonas* and *Salmonella*. Strains resistant to antibiotic compounds can be effectively

Table 2 Various disinfection by-products and their adverse effects on reproductive system

S. no.	Disinfection by-products	Dosage level	Effects	References
1	Total trihalomethanes (TTHMs)	>100 µg/l	Birth outcomes such as birth weight, low birth weight and preterm birth	Bove et al. (1995)
2	Chloral hydrate	55 and 188 mg/kg	Decreased sperm motility in male rats at highest dose only	Klinefelter et al. (1995)
3	Trihalomethanes: chloroform	100–400 mg/kg orally	Reduced foetal body weight at highest dose, evidence for foetotoxic response, no teratogenic effects	Ruddick et al. (1983)
4	Bromoform	200 mg/kg	Pregnancy loss, reduced foetal body weight and crown–rump length at high dose	Murray et al. (1979)
5	Bromodichloromethane (BDCM)	25–75 mg/kg	Foetal resorption at 50 and 75 mg/kg doses. No effect on duration of gestation, pup survival, weight and morphology	Narotsky et al. (1997)
6	Chlorodibromomethane (CDBM)	685 mg/kg	Decreased litter size, and pup viability at high dose, slight depression of foetal weight	Borzelleca and Carchman (1982)
7	Trichloroacetic acid (TCAA)	330–1800 mg/kg	Increased embryonic resorption, reduction in body weight and increase in cardiovascular malformations at all doses. Skeletal malformations found at highest dose only	Smith et al. (1989a)
8	Dibromoacetic acid (DBAA)	0–270 mg/kg/day	Reduced epididymal sperm counts and sperm motility, morphological changes	Linder et al. (1994)
9	Dibromoacetic acid (DBAA)	1250 mg/kg/day	Sperm motility and morphology effected	Linder et al. (1994)
10	Dibromoacetic acid (DBAA)	0–250 mg/kg	Reduction in sperm motility and sperm count at highest dose only and moderate changes at lower doses	Linder et al. (1995)
11	Dichloroacetonitrile (DCAN)	1–55 mg/kg	Increased foetal resorption and reduction in foetal body weight with increasing dose. Cardiovascular, skeletal, and urogenital malformations >45 mg/kg	Smith et al. (1987)
12	Trichloroacetonitrile (TCAN)	1–555 mg/kg	Increased foetal resorption and reduction in foetal body weight with increasing dose. Cardiovascular and urogenital malformations at >15 mg/kg	Smith et al. (1989a)
13	TTHM	60 µg/l	Low birth weight and preterm delivery	Gallagher et al. (1998)

killed by silver nanoparticles (Prociak et al. 2014). In our previous research, we have successfully synthesized silver using exopolysaccharide from a novel strain of Gram-negative soil bacterium *Pseudomonas fluorescens* CrN6 (KF359766.1) which demonstrated excellent bactericidal activities of silver against *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, *Escherichia coli*, *Salmonella typhi* and *Candida albicans* (Sirajunnisa and Surendhiran 2014). Hence, silver can be used as alternate disinfectant for killing pathogenic micro-organisms in an effective manner. Another main advantage of using nano-material as disinfectant is that it can be reused in many repeated cycles, is not a strong oxidant, is inert in water and does not produce harmful non-degradable by-products (Li et al. 2008).

Water purification by silver–magnetic nanocomposite

Several nanoparticles including silver (Ag), titanium (TiO₂), zinc (ZnO), magnetic, carbon nanotubes are employed in water purification system (Li et al. 2008). Among various types of nanomaterials, silver is well recognized as promising antimicrobial agents (Li et al. 2008; Sureshkumar et al. 2010; Mahmoudi and Serpooshan 2012) because it appears to be independent of bacterial strain particularly methicillin-resistant *Staphylococcus aureus* (MRSA), ampicillin-resistant *E. coli*, a common water contaminant, erythromycin-resistant *Streptococcus pyogenes* and vancomycin-resistant *Staphylococcus aureus* (VRSA) (Sarayu and Sandhya 2013; Reidy et al. 2013), *Pseudomonas aeruginosa* (Morones et al. 2005),

Table 3 Advantages and disadvantages of different conventional water purification

Methods	Mechanism	Advantages	Disadvantages	References
<i>Physical treatment</i>				
Boiling	High temperature	Short period	Only applicable for domestic purpose	Somani and Ingole (2011)
Membrane filtration	Water moves across membrane contains pores that filter microbes and unwanted products	Non-pollution, safety and reliability, effective for complete removal of dissolved ionic particles (cation and anions), heavy metals, etc.	Removal of low molecular weight ionic contaminations, large membrane areas are required to satisfy capacity requirements for low concentration (and sparingly conductive) feed solutions	Sharma and Bhattacharya (2016)
Reverse osmosis	Flow of water across semi-permeable membrane on application of pressure	Removes total dissolved solids (TDS), heavy metals, fluoride, pesticides, micro-organisms	Low recovery, brine disposal, high maintenance (membrane change in 3 years), need pretreatment	Pradeep (2009)
Adsorption	Dissolved contaminants adhere to the porous surface of the solid particles, e.g. activated carbon, silica gels, aluminas, zeolites and ion exchange resins	Activated charcoal is effective for trapping carbon-based impurities, chlorine, as well as colours and odours and long life	Frequent filter changes often required and can generate carbon fines; removal of Se, Sb, Pb and Bi from the water is also possible, preparative aspects needed very precise control, ion exchange resin-treated water contains sodium, which cannot be recommended for the diet requiring low sodium intake, if resin is not sanitized or regenerated regularly, bacterial colonies proliferate on resin surfaces and can contaminate drinking water	Sharma and Bhattacharya (2016)
Ultrasound	mechanical vibration can damage cellular structures of bacteria	Needs very short time, eco-friendly	Regrowth of the micro-organisms is possible	Somani and Ingole (2011)
Ultraviolet	Works on the generation of free radicals from UV lamp	Broad range micro-organism removal, high filtration capacity	Effectively degrades only micro-organisms, high costs	Pradeep (2009); Fawell and Nieuwenhuijsen (2003)
Electrodialysis	Charge separation on application of electric field	High total dissolved solids removal efficiency (–90%)	Proportional increase in cost with total dissolved solids, does not remove: pesticides, micro-organisms	Pradeep (2009); Fawell and Nieuwenhuijsen (2003)
Distillation	Reduced pressure evaporation of water followed by condensation	Removes a broad range of contaminants, reusable, cost not proportional to total dissolved solids	Regular maintenance, volatile organics are not removed	Sharma and Bhattacharya (2016)
<i>Chemical treatment</i>				
Chlorine, chloramines, chlorine dioxide and ozone	Kills micro-organisms by destructing their cell membrane or nucleic acids	Kills broad range of micro-organisms such as bacteria, virus, fungi and protozoa	Produce harmful disinfection by-products (DBPs) which produces cancers of the bladder, colon, breast, testes and rectum and adverse birth outcomes such as spontaneous abortion, low birth weight and sperm count decline. Produce chlorine smell and does not remove solid materials	Pradeep (2009); Nieuwenhuijsen et al. (2000a)

Table 3 continued

Methods	Mechanism	Advantages	Disadvantages	References
Precipitation and coagulation	Positive charges to neutralize the negative charges on the particles	Very simple method, Effective for the removal of As, Cd, Ba, Cd, Cr, Pb, Hg, Se, Ag, etc.	Requires continuous supply of huge chemicals, disposal of coagulation/precipitation sludge is a concern	Sharma and Bhattacharya (2016)
Ozone		Good disinfection method, Ozone acts over 3000 times faster than chlorine, requiring shorter contact time and dosage than chlorine with the ability to kill 99% of all waterborne pathogens	Significant air pollutant, explosive, and an irritant to skin, eyes, respiratory tract and mucous membrane	Padmaja et al. (2014); Sharma and Bhattacharya (2016)
Photocatalytic method	Photodegradation by generation of OH radical using UV light	Operational process is simple, reactions can occur in ambient condition as well as no consumable chemicals are required, reusability of the catalyst as it is unchanged during the process	Post-separation of the semiconductor catalysts after water treatment is important and failing results in catalyst poisoning, the catalysts with their fine particle size and large surface area to volume ratio create a strong catalyst agglomeration tendency during the operation	Ahmed et al. (2013); Sharma and Bhattacharya (2016)
Hydrogenation of nitrate	nitrate is reduced to NO_2^- , NO , N_2O , N_2 and NH_4^+	The method can be of single operation mode, addition of other chemicals can be avoided	Increase in pH in the reaction medium forms ammonia in dissolved condition, which is more harmful than nitrate	Sharma and Bhattacharya (2016)
Electrocatalytic oxidation	Oxidation of through catalytic anodic surface	High pollutant degradation, easy control and low cost, it can be easily controlled by putting on/off the power, it has the potential to eliminate different types of pollutants as well as bulk volume	High operating cost due to the high energy consumption during operation, electrode fouling may also occur on the surface of the electrodes, requires a separation step to recover the metallic species	Martinez-Huitle and Ferro (2006); Sharma and Bhattacharya (2016)
<i>Biological method</i>				
Bioremediation	Phytoextraction, rhizofiltration, biotransformation/ biodegradation, adsorption using microbial biofilm	Cost-effective, eco-friendly, it can avoid chemical disinfection water treatment processes	Seasonal growth of the plants, biomass disposal	Rai (2009); Sharma and Bhattacharya (2016)

Vibrio cholera (Morones et al. 2005), *Bacillus subtilis* and *HIV-1* (Elechiguerra et al. 2005) and other microbes. Nano-materials have to be retrieved and reused to retard the cost which could be achieved through a separation device or immobilization on various platforms such as resins and membranes to avoid further separation. However, immobilization techniques usually result in significant loss of treatment efficiency. Hence, immobilization techniques have to be designed to overcome such disadvantages. One such possible option is low-field magnetic separation for magnetic/silver nanocomposites (Qu et al. 2013).

The separation of silver from the water purification column is difficult due to its nanosize, for which simple and effective separation methods at low concentration in liquids have to be derived. Therefore, nanosilver disinfectant should be coated onto any one of the supporting materials. A variety of approaches including chromatographic techniques, cloud

point extraction, centrifugation and filtration have been developed for extraction, separation, concentration of silver nanoparticles from aqueous media, but they possess certain disadvantages for example filtration is most common technique but problematic due to low sample recovery and frequent changing of filters (Mwilu et al. 2014). Many researchers used different doping materials such as cation resin beads (Mthombeni et al. 2012), silica beads (Quang et al. 2013; Reidy et al. 2013), BiOI (Zhu et al. 2012), polyurethane foams (Phong et al. 2009), Fe_3O_4 (Feng et al. 2014), poly(vinyl pyrrolidone)-catechol-coated iron oxide (Mosaiab et al. 2013), magnetic particles (Sureshkumar et al. 2010; Reidy et al. 2013; Mwilu et al. 2014), alginate beads (Bloch et al. 1990) for supporting nanosilver. The incorporation of silver into different matrices has been intensively studied in order to extend their effectiveness (Sureshkumar et al. 2010). Among various supporting materials, magnetic

substance is the choice of doping material, due to their supermagnetism properties and can readily be attracted by an external magnet. Magnetic materials act as good sorbents for valuable separation/concentration method for trace amounts of silver nanoparticles (Mwilu et al. 2014).

In recent years, magnetic nanoparticles have gained widespread attention due to their magnetic behaviour, controlled size and more chemical reactivity (Ambashta and Sillanpää 2010). These are used for targeted delivery of silver in medicinal and disinfection applications and due to the magnetic properties of iron oxide they can be transported to a certain location for controlled release (Reidy et al. 2013). The magnetic coated Ag could be separated easily because of the ease of direction of magnetization. They can be easily separated after water treatment using external magnetic rod. Sharma et al. (2009) and Tuutijarvi et al. (2009) reported that various metal ions such as chromium (Cr-VI), copper (Cu-II), cobalt oxide (CO-II), arsenic (As-V), and mercury chloride (Hg-II) were easily separated using magnetic nanoparticles. Therefore, separation by magnetic adsorbents has opened a new field in engineering separations applications.

Use of magnetic absorbents for the dehalogenation of hydrocarbons and transformation and detoxification of various common environmental contaminants in water such as chlorinated organic solvents, organochlorine pesticides, trinitrotoluenes, phenols and herbicide molinate, amino carboxylic acids and p-hydroxybenzoic acid are an added advantage. The inorganic anionic contaminants such as nitrates (NO_3^-), dichromate ($\text{Cr}_2\text{O}_7^{2-}$) could also be degraded using iron nanoparticles (Ambashta and Sillanpää 2010; Xian 2003; Feitz et al. 2005; Cundy et al. 2008). Mwilu et al. (2014) recovered >99% of silver using external magnetic from the tap water and this experiment were further evidenced by inductively coupled plasma mass spectrometry (ICP-MS). Chang and Chen (2009) reported that high degradation efficiency was found with gold doped with magnetic particles when compared with naïve gold for the degradation of organic compounds such as phenols and amines as compared to other support-based systems. Uses of silver-coated magnetic particles not only deactivate the micro-organisms but also remove various contaminants present in drinking water. Overall process involved in water purification using silver–magnetic composite and its separation after treatment is shown in Fig. 1.

Mechanism of inactivation of micro-organisms by silver nanoparticle

Several antimicrobial mechanisms have been published including extracellular inactivation such as damage of the peptidoglycan layer, lipopolysaccharide layer, phospholipids bilayer and intracellular inactivation such as protein

damage and suppression of RNA, DNA replication of micro-organisms (Sarayu and Sandhya 2013; Qu et al. 2013). Table 4 indicates various nanomaterials and their different antimicrobial mechanisms as given by Sarayu and Sandhya (2013), Qu et al. (2013), Reidy et al. (2013). In the mechanism of extracellular inactivation, nanosilver first adheres on the surface of micro-organisms and alters their membrane properties (Reidy et al. 2013). The small size and extremely large surface area of enable them to make strong contact with the micro-organism surface (Wong and Liu 2010). They are reported to degrade lipopolysaccharide molecules, accumulate inside the membrane by forming “pits”, and cause large membrane permeability (Li et al. 2008; Sondi and Sondi 2004). Li et al. (2005) described susceptibility of cell membrane to the radical attack of the and is very porous in nature thus can allow the passage of hydroxyl radicals and superoxides and can further attack the cell membrane which resulted in release of cell inclusions leads to cell death.

In the intracellular inactivation, the particles penetrate into the cytoplasm (Reidy et al. 2013), bind with DNA and stop its replication, thus decreasing the proliferation of bacteria (Li et al. 2008; Reidy et al. 2013; Wong and Liu 2010) and inhibiting the bacterial multiplication. Silver nanoparticle cations bind to thiol groups of bacterial proteins disturbing their enzyme activity and lead to cell death as stated by Cao et al. (2010) and Radzig et al. (2013). The silver nanoparticle also inhibits the activity of adenosine triphosphate (ATP) present in micro-organisms. It is reported that proton electrochemical gradient happens in bacteria and respiratory processes maintain the system. Electrochemical gradient helps in the adenosine triphosphate (ATP) synthesis when protons enter the cell via (ATPase). When these processes are ceased, then all essential energy-dependent reactions halt; therefore microbial cells die (Cao et al. 2011). The mechanism of various target sites of silver nanoparticle is clearly shown in Fig. 2 as illustrated by Zhang (2013).

Gong et al. (2007) synthesized the bifunctional Fe_3O_4 –Ag nanoparticles possessing super paramagnetic and antibacterial properties against *E. coli*, *S. epidermis* and *B. subtilis*. Radzig et al. (2013) investigated on antibacterial effects of silver nanoparticle of diameter 8.3 nm on Gram-negative bacteria such as *E. coli* AB1157, *P. aeruginosa* PAO1 and *S. proteamaculans* 94, strongly killing them at the concentrations of 4–5, 10 and 10–20 $\mu\text{g}/\text{ml}$, respectively. Pucek et al. (2011) experienced that nanocomposites of iron oxide and silver showed much lower minimum inhibitory concentration (MIC) on inhibiting ten tested bacteria and four fungal species. Wang et al. (2011) studied the effect of chemically synthesized on different bacteria namely *B. cereus*, *E. coli*, *P. aeruginosa* and *E. cloacae*. From this study, it was found that *B. cereus* and *E. cloacae*

Fig. 1 Silver–magnetic nanocomposite involved in water purification. Wastewater is treated with synthesized silver–magnetic nanocomposite which after treatment is removed using a magnetic rod to obtain nanoparticle-free purified drinking water

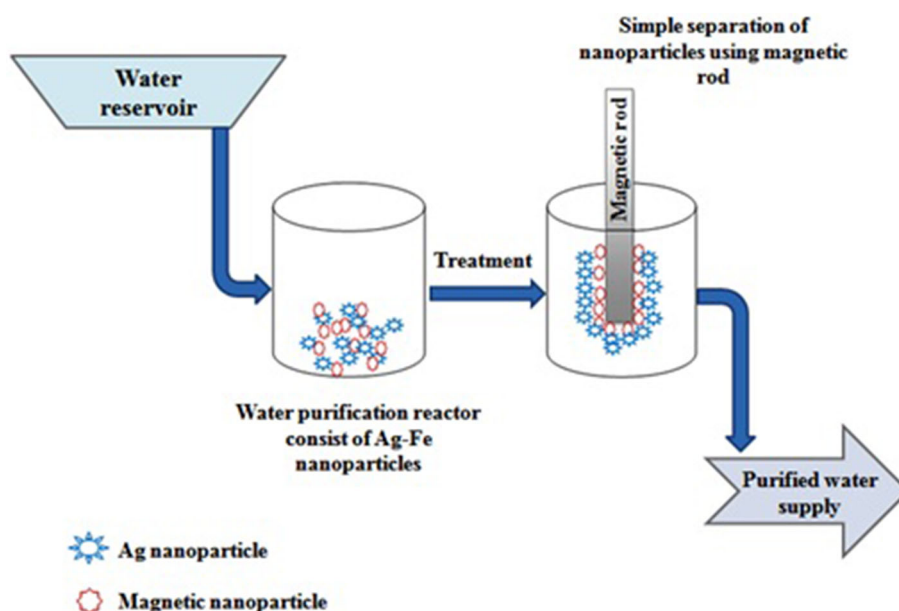


Table 4 Various nanomaterials and their different antimicrobial mechanisms

Nanomaterials	Antimicrobial mechanisms
Nano-Ag	Release of silver ions, protein damage, suppression of RNA, DNA replication, membrane damage, intracellular molecules inactivation, inhibition of ATP synthesis
Nano-TiO ₂	Production of ROS
Nano-ZnO	Release of zinc ions, production of H ₂ O ₂ , membrane damage
Nano-MgO	Membrane damage
Nano-Ce ₂ O ₄	Membrane damage
nC ₆₀	ROS-independent oxidation
Fullerol and aminofullerene	Production of ROS
Carbon nanotubes	Membrane damage, oxidative stress
Graphene-based nanomaterials	Membrane damage, oxidative stress

RNA Ribonucleic acid, DNA deoxyribonucleic acid, ATP adenosine triphosphate, ROS reactive oxygen species

were completely killed at the incubation time of 6 h, whereas *E. coli* at 24 h. Another study was conducted by Quang et al. (2013) for water disinfection using silver coated with silica beads and *E. coli* as model organism. They inactivated <99% *E. coli* with a contact of several seconds by 4.5 g/L of silver.

In recent study conducted by Feng et al. (2014), Ag(II)O–Fe₃O₄ hybrids synthesized through mechanochemistry were analysed for its sterilization property against *Staphylococcus aureus* and *Escherichia coli*. This composite showed 99.9% bactericidal activity against both types of bacteria at the mass ratio of Ag(II)O to Fe₃O₄ as 1:2 and 2:1 at the concentration of 10 mg/L. Zhu et al. (2012) effectively demonstrated the disinfectant activity of

Ag nanoparticle under photocatalytic process for *E. coli* 8099. In this study, Ag nanoparticle was coated with BiOI ethylene glycol by a solvothermal process and this composite kills almost 99.99% within 10 min irradiation and measurement of released K⁺ further confirmed that the cell membrane of *E. coli* was destructed in the photocatalytic disinfection by the silver nanoparticle/bismuth oxyiodide (BiOI) as evidenced by transmission electron microscope (TEM) analysis. Similarly Phong et al. (2009) reported 100% complete killing of bacteria such as *E. coli* and *B. subtilis* using silver-coated polyurethane foams as disinfectant for water treatment.

Size and shape of the silver nanoparticle play a very important role in inactivation of micro-organisms. The

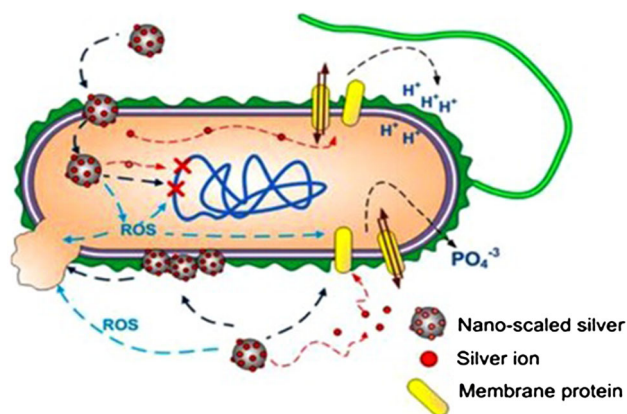


Fig. 2 Interactive mechanism of nanosilver with bacterial cell (Zhang 2013). Nanoparticle binds to cell and disintegrate cell wall interrupting permeability and destroying respiration leading to cell death. Also, nanosilver could impart oxidative stress and disrupt DNA by producing reactive oxygen species. Another mode of interaction is that the silver ions can breakdown ATP synthesis within the cell and cease DNA synthesis, thus acting as a bactericidal agent

viruses are very smaller than the bacterial cells; hence, silver must be synthesized in the range from 1 to 10 nm in size. So it can easily bind with the virus' gp120 glycoproteins and destroys them (Elechiguerra et al. 2005). In the study of Choi and Hu, (2008), Ag nanoparticles less than 5 nm easily penetrate inside the bacterial cell and damages the DNA when compared to the larger sizes of silver nanoparticle. Triangle-shaped nanosilver nanoplates produce more microbial death than the rod-shaped and sphere-shaped ones; this is due to more reactive planes (Choi and Hu 2008), which binds multiple target sites on surface of micro-organisms.

Methods of preparation of silver–magnetic nanocomposites

Many methods have been employed to develop silver–magnetic nanocomposite for various applications. Several investigations report on preparing silver–magnetic nanocomposite using various methods. Alzahrani (2015) reported on production of silver–magnetic nanocomposite for eosin dye wastewater treatment by adding magnetic nanoparticles with 0.1 M silver nitrate solution and 1% sodium carbonate as the enhancer of reduction. The crude nanocomposite pellet was dried at 80 °C for 24 h, calcinated in a furnace at 400 °C for 6 h, washed with distilled water and dried at room temperature for 12 h in a vacuum desiccator. In a method by Sureshkumar et al. (2010), magnetic nanoparticles were synthesized by precipitation method. The nanofibrous bacterial cellulose (BC) was homogenized with a ferric and ferrous mixture. Precipitated magnetic nanoparticles were incorporated into

bacterial cellulose present in dopamine solution under alkaline pH and coated with an adherent self-polymerized polydopamine layer. The nanocomposite was prepared in such manner as polydopamine layer is highly capable of reducing silver salt to silver ion. The nanocomposite acted as bactericidal agents against *Escherichia coli* and *Bacillus subtilis*.

The silver–iron nanocomposite can also be produced using chemical co-precipitation technique, which was experimented by Levitin et al. (2015). To a volume of silver nitrate ($AgNO_3$) solution, 0.05 M iron sulphate or ferrous sulphate ($FeSO_4$) and 0.1 M ferric chloride ($FeCl_3$) were mixed together and added along with 10% mass fraction of glucose solution in the presence of ammonia at pH ranging between 10 and 12 with temperature being increased gradually to 60–70 °C for 40 min to obtain light brown from black precipitate indicating the formation of nanocomposite. Iglesias-Silva et al. (2007) prepared silver-coated Fe_3O_4 nanoparticle using a two step protocol. A microemulsion method was used to the synthesis of Fe_3O_4 nanoparticle and then separately coating with silver. The amount of silver nitrate ($AgNO_3$) used was calculated assuming a complete covering of the magnetic cores (of 9 nm size) with a 2 nm silver shell. Glucose was employed as a mild reducing agent to ensure a controlled shell growth of silver onto iron particles and avoiding the formation of new silver nuclei. These conditions promoted the reduction of $Ag(I)$ ions adsorbed onto Fe_3O_4 particles at room temperature which were confirmed by the black Fe_3O_4 particles turning brownish. Liu et al. (2008) synthesized Ag/Fe nanocomposite by reverse micelles followed by a direct coating method in dimethylformamide (DMF). The iron nanoparticles were dispersed in 70 mL anhydrous dimethylformamide through mechanically stirring for 10 min. 0.46 g sodium borohydride ($NaBH_4$) and 4.0 g silver nitrate were dissolved into 10 mL DMF in separate flasks. After sodium borohydride ($NaBH_4$) solution was added into the suspension of iron nanoparticle, silver nitrate solution was dropped into this intermixture and stirred for an hour at Ar atmosphere. The final powder with 10% iron was separated with magnet field, washed several times with ethanol to procure pure product and dried for using it in various biological applications.

Chi et al. (2012) prepared the nanocomposite for catalytic reduction of 4-nitrophenol using in situ wet chemistry route. Iron oxide (Fe_3O_4) on silicon dioxide (SiO_2) spheres were dispersed into 0.03 M silver ammonium nitrate ($Ag(NH_3)_2NO_3$) solution under mechanical stirring at room temperature. By electrostatic attraction between $[Ag(NH_3)_2]^+$ ions and the negatively charged Si–OH groups, $[Ag(NH_3)_2]^+$ ions adsorbed onto the surfaces of silica spheres in around 30 min. The solution was added into 15 mL of ethanol containing polyvinylpyrrolidone

(PVP) (0.1 g), followed by heating by reflux at 70 °C for 4 h. The final products were magnetically separated, washed several times with a recycle of ethanol and deionized water and dried at 50 °C for 12 h. Feng et al. (2014) produced silver oxide–iron oxide ($\text{Ag}_2\text{O}-\text{Fe}_3\text{O}_4$) hybrids by mechano-chemistry method reporting its antibacterial properties. Silver submicron particles were prepared by chemical oxidation and magnetite nanoparticle by chemical co-precipitation using Fe^{2+} and Fe^{3+} ions. The silver particles were mixed with iron magnetite nanoparticle in different mass ratios and were ground with a high energy ball mill at the same conditions for 6 h and 2000 rpm. The mass ratio of grinding balls to milling materials was 1:1. This nanocomposite showed 99.99% of bactericidal activity against *Staphylococcus aureus* and *Escherichia coli*.

Recently Ivashchenko et al. (2016) fabricated silver/magnetic nanocomposites for antibiotic therapy against pathogenic bacteria. Magnetite powder was produced by a thermochemical technique based on thermal decomposition and reduction of iron oxalate in a gaseous atmosphere (450–470 °C, 2 h) created in an oven by the addition and subsequent chemical decomposition of hydrocarbons such as paraffin and stearin. Magnetite nanopowder was pre-treated in 0.1 M iodine solution, magnetically separated and rinsed thrice with distilled water. The magnetite powder was then treated in a solution of silver nitrate, followed by circumfusion with 1% ascorbic acid solution under mechanical stirring (1 h). Finally, the magnetite nanopowder was magnetically separated, washed with distilled water and dried at 50 °C.

Characterization of silver–magnetic nanocomposites

Formation of a nanocomposite is primarily characterized and detected by the change in the colour of the solution. The observation of specific colour is due to the excitation of surface plasmon resonance. When the frequency of the electromagnetic field becomes resonant with the coherent electric motion, absorption happens bringing out the colour during visualization (Sirajunnisa and Surendhiran, 2014). The formation of coloured particles is to be then confirmed using an UV–Vis spectroscopy, which is a simple procedure with the principles of optical properties. Sharp absorption peaks are obtained for metallic ion formed during each investigation. These peaks are formed due to free electron density leading to high plasmon frequency (Dallas et al. 2011).

To obtain a good understanding of characteristic features of nanocomposite, the size of the particles and the

morphology should be studied. It should be analysed with different techniques namely transmission electron microscopic (TEM), scanning electron microscopic (SEM) analyses. Transmission electron microscope is a good tool for analysing the size and shape data as it gives away the real images from which size of the particle can be calculated. In addition, compositional analysis was performed using energy-dispersive X-ray analysis (EDAX). For phase identification and the structural analysis of the silver–magnetic nanocomposite, an X-ray diffraction (XRD) instrument can also be utilized (Alzahrani 2015). Functional groups can be elucidated by Fourier transform infrared spectroscopy (FTIR) analysis. Ivashchenko et al. (2016) to confirm morphological changes of silver and magnetic by scanning electron microscope (SEM) and high-resolution transmission electron microscope (HR-TEM) before and after formation of nanocomposite. The scanning electron microscope (SEM) and high-resolution transmission electron microscope (HR-TEM) measurements showed that silver clusters grew on the magnetite surface and increased particle size variation from 5–10 nm to 40–50 nm in size. Levitin et al. (2015) characterized silver–magnetic nanocomposite in an effective manner using X-ray analysis and scanning electron microscopy. Through characterization, it was found that nanocomposite as a “core–shell” permits magnetic controllability of the magnetite core with bactericidal and bacteriostatic properties of the silver shell which finds its perfect application in pharmacy and in discovering and designing of medicine. Sureshkumar et al. (2010) described the characteristics features of polydopamine magnetic bacterial cellulose–silver nanocomposite (PMBC-Ag) using scanning electron microscope (SEM) and X-ray diffraction (XRD) pattern. In the scanning electron microscope analysis, at initial step they analysed the BC alone and observed the structure which is highly porous with a 3-D ribbon-like nanofibrillar network. The diameters of the fibrils range from 20 to 30 nm and a length ranging several micrometres. Energy-dispersive X-ray spectroscopy (EDAX) analysis confirmed the presence of metallic silver. Four major peaks 38.2°, 44.4°, 64.6° and 77.5° corresponding to the crystal planes (111), (200), (220) and (311), respectively, were observed through X-ray diffraction (XRD) analysis for polydopamine magnetic bacterial cellulose–silver nanocomposite (PMBC-Ag) which indicates the face-centred cubic (fcc) structure of the silver nanoparticle. These simple and instant characterization studies are very useful for confirmation of nanocomposite particle formation and it may be extended to the preparation of other magnetic metal nanocomposites for various applications.

Table 5 Various companies manufactured nanotechnology-based water purifier (Pradeep 2009)

Product Name	Nanomaterial used	Contaminants removal
Aquaguard Gold Nova, Eureka Forbes Limited (Launch: 2007, India)	Silver nanoparticle supported on alumina	Pesticides and halogenated organics
Adsorbisia, Dow Water Solutions (Launch: 2005, USA)	Titania nanoparticles	Arsenic and disinfection
AD33, Adedge Technologies, Inc. (Launch: 2002, USA)	Iron oxide nanoparticles	Heavy metals including arsenic, lead, chromium, zinc, copper
Nanoceram, Argonide (Launch: 2006, USA)	Electropositive alumina nanofibers on a glass filter substrate	Disinfection, natural organic matter, turbidity, salt, radioactivity, heavy metals
ArsenX, SolrneteX, Inc. (Launch: 2004, USA)	Hydrous iron oxide nanoparticles on polymer substrate	Arsenic, vanadium, chromium, uranium
Nanopore, Nanovation AG (Launch: 2003, Germany)	Membrane filters based on ceramic nanopowder supported on alumina	Disinfection

Research needs for commercialization

On the basis of the complete literature survey, this review article reveals that silver–magnetic composite is highly suitable for purification of drinking water system. Table 5 shows the various companies manufacturing nanotechnology-based drinking water purifier (Pradeep 2009). Though these companies are manufacturing their water purification system using nanotechnology, they are produced in very smaller-scale type. Purifics Photo-CatTM is the only company that operates water purification system by treating the capacity of high as 2 million gallon per day with a small footprint of 678 ft². There are two major research needs for large-scale applications of nanotechnology in water treatment. First, the performance of treating real natural water needs to be tested as it contains more turbidity. Moreover, the long-term efficacy of these nanotechnologies is largely unknown as most laboratory studies were conducted for relatively short period of time. Research addressing the long-term performance of water and wastewater treatment nanotechnologies is in great need (Qu et al. 2013). Secondly, cost associated with manufacturing of water purifier with nanotechnology must be affordable to public; hence, low cost must be implemented. More importantly the potential impacts of nanomaterials on human health and ecosystems must be considered, as nanotoxicity studies increase in the past few years. It may also escape from the treatment system and enter water that may harm consumers. Bulk titanium dioxide (TiO₂) particles (>100 nm) are known to be harmless to humans and animals, although nanoscale titanium dioxide (TiO₂) was classified recently as a possible carcinogen (Li et al. 2008). Therefore, research has to be focused on economic analysis of commercialization of nanotechnology for purifying drinking water and has to evaluate the safety aspects of such system for human, animal and ecosystems.

Conclusion

Treating wastewater efficiently has become a trivial task for the society as all the natural water resources are getting contaminated with the industrial effluent and sewage lines, directed into aquatic systems, due to burgeoning globalization. Common treatments such as physical and chemical methods impose malicious threat to humans and ecosystems. To overcome the toxic effects of these technologies, the advent of nanomaterials has proved to be an alternate and better technique for wastewater management. This article covered the negative aspects of routine treatments of contaminated wastewater to pure water, use of nanotechnology in waste purification, mechanisms of killing the potent pathogenic organisms and the need for researchers to commercialize the nanomaterials, to disinfect water for humans to intake, economically. The unique features of the nanomaterials as nanocomposites could be considered to be an effective disinfectant due to their nanosize and protect the aquatic ecosystem, thus serving in wastewater purification.

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