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NANOPROCESS FOR WATER PURIFICATION

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ABSTRACT

Nanotechnology is an emerging science that has shown potential applications in solving current problems involving water quality. Nanomaterials are highly reactive, have a large surface area compared to their mass and can easily capture other particles. Hence nanotechnology is also used as an environmental technology to protect the environment through pollution prevention treatment and clean up. Additionally, nanotechnology-derived products can reduce both chemical and biological impurities in water treatment. This article summarizes in the area of nanomaterial synthesis and the origin of their reactivity at the nanoscale in environmental clean up like water purification. In addition, we discuss the limitations associated with the potential applications of nanomaterials for water purification.

Keywords: chemical and biological impurities, environmental technology, nanomaterials, potential applications, water quality

INTRODUCTION

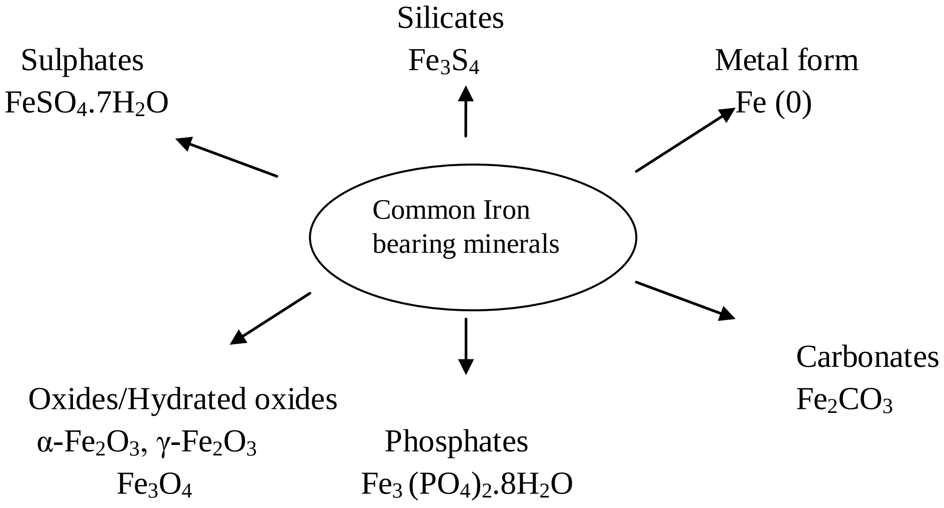
Environmental pollution is a serious day-to-day problem faced by the developing and developed nations in the world. Due to increased industrialization and urbanization a vast majority of water quality problems are caused by contamination, overexploitation or combination of the two, soil and water quality is slowly but declining everywhere. The common pollutants include toxic compounds like chlorinated and non-chlorinated aliphatic and aromatic compounds, dyes, detergents and surfactants, agro wastes like insecticides, pesticides and herbicides, disinfection byproducts, volatile organic compounds, plastics, inorganic compounds like heavy metals, noxious gases like NO_x, SO_x, CO, $NH_3$and pathogens like bacteria, fungi and viruses.

Clean water which is free of toxic chemicals and pathogens is essential for the very existence of life. Clean water is also a critical feedstock in a variety of key industries including electronics, pharmaceuticals and food. The world is facing formidable challenges in meeting the rising demands of clean water. In order to secure water resources water reuse is becoming more viable. One of the concerns with water reuse is the contamination with chemicals, bacteria and other pollutants. Various environmental technologies have been employed to remove the pollutants in water. Conventional water treatment plants are constructed based on three important assumptions. Firstly, the influent source waters entering the treatment plant is comprised of only naturally occurring chemical and biological contaminants. Secondly, they appear in the source waters mainly due to surface water runoffs, localized conditions existing in the source waters and cross contamination resulting from discharge of untreated sewage. Thirdly, the contaminants present in source water can be completely removed via a simple treatment following a sequence of steps inclusive of coagulation-flocculation, filtration and disinfection.[1] However, to date neither type of existing conventional treatment is universally applicable or highly effective. This suggests that there is a need for technological advancement in water treatment to benefit people in many countries.

In recent years, nanoscience and nanotechnology has introduced a new dimension to scientific discipline and technology sectors due to its ability to exhibit super functional properties of materials at mono-dimensions. There is a great potential to use this technology to clean up the contaminated sites and protect the environment from the pollution. This eco-friendly technology is considered to be an effective alternative to the current practices of site remediation. Nanoremediation methods involve application of reactive materials for the detoxification and transformation of pollutants. Nanomaterials will enable new means of reducing the production of wastes, using resources more sparingly, cleaning-up chemical and bacterial contamination, proving potable water and improving the efficiency of energy production and use. Several nanomaterials include magnetic nanoparticles, heterogeneous nanophotocatalysts and polymeric nanoparticles. Due to their strong magnetic properties, magnetic nanomaterials act not only as an adsorbent to remove target compounds from the contaminated water, but also as a magnetic element to attract and retain the nanoparticles, which can be removed from solutions. This magnetic separation, which may replace centrifuge separation technologies, has less complicated technical requirements and low generation cost, thus making this adsorption treatment economically attractive for individual users.[2] Many different nanomaterials have been evaluated for use in nanoremediation. They include nanoscale zeolites, metal oxides, carbon nanotubes, noble metals and titanium dioxide. This review focuses on various research works regarding the use of nanotechnology for environmental clean-up, particularly on their application in remediation of water.

Iron based technologies

Iron is the fourth most abundant element in the earth’s crust, and reactions involving iron play a major role in the environmental cycling of contaminants. Iron exists in the environment in two valence states- water soluble Fe (II) and highly water insoluble Fe (III). Zero valent Iron (Fe (0)) is also found under some specific and environmental conditions.



Various mineral forms of iron

In the environment, iron plays an important role in contaminant mobility, sorption and breakdown due to its role as an electron donor, and, in its various mineral forms, as a precipitant/ sorbent surface. Since early 1990s, the iron corrosion has been put into productive use in the treatment of hazardous and toxic chemicals. The use of iron-based technologies in contaminated water remediation is a rapidly developing field, with a range of techniques proposed which make use of iron as a reductant, precipitant and sorbent. The applications of iron-based technologies in contaminated water remediation can be broadly divided into two, based on the chemistry involved in the remediation process. Technologies which use iron as 1) a sorbent, precipitant or immobilizing agent 2)as an electron donor to convert contaminants into a less toxic form. The ability of iron, both of its zero valent form and as its Fe^{2+}, to reduce redox sensitive elements like Cr, Tc and to dechlorinate various organic contaminants has been successfully used. Reactions for Cr reduction and immobilization include:

$Fe^{2+} + CrO_4^- + 4H_2O \longrightarrow (Fe_x(Cr_{1-x})(OH)_3 + 5OH^-$ in which the toxic Cr (VI) can be reduced to Cr (III) form, which readily precipitates as $Cr(OH)_3$ or as a solid solution $(Fe_x(Cr_{1-x})(OH)_3$ (Puls et al.,1999).

Elemental iron slowly oxidizes to ferrous iron and releases two electrons. Contaminants such as polychlorobiphenyls, or PCBs, and chlorinated benzenes can accept the electrons and be reduced to hydrocarbon compounds. For example, tetrachloroethene (C2Cl4) can be reduced to ethene in accordance with the following stoichiometry:

$$4Fe^0 + C_2Cl_4 + 4H^+ \longrightarrow C_2H_4 + 4Fe^{2+} + 4Cl^-$$

Ferrous sulphate and Ferrous Ammonium Sulphate can also be used in treatment of contaminated water. Ferrous Sulphate is a traditional reducing agent for the treatment of metal industry process effluents. Ferrous Ammonium Sulphate has the advantage over ferrous sulphate of reacting relatively rapidly over neutral to alkaline pHs, avoiding the need for acidification.[3]The ability of iron to act as an electron donor or reducing agent is utilized in Fenton treatment technologies, where Fe^{2+} or Fe^0 can be used to reduce Hydrogen peroxide and generate the highly reactive OH radical.

$$\mathbf{Fe^0 + H_2O_2 \rightarrow Fe^{2+} + OH^-}$$

Fe^{2+} can then react with H_2O_2 in traditional Fenton's oxidation reactions

$$\mathbf{Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\circ}OH + OH^-}$$

In the presence of H_2O_2, Fe^0 is transformed into Fe^{2+}

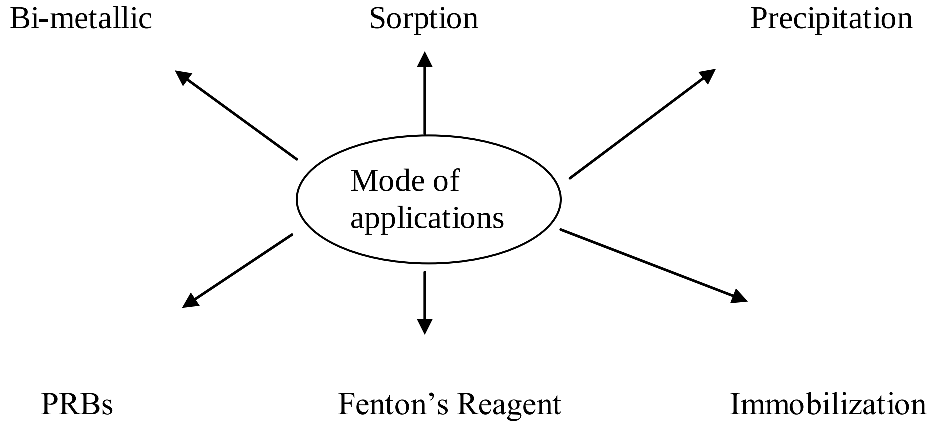
Fenton techniques show considerable efficiency in the remediation of pesticides, fuels, explosives etc.[4] observed a 90% reduction of chlorinated contamination in water. Fenton treatment can be applied for the removal of organic and inorganic contaminants in situ.

Of many iron-based materials, nZVI (nano Zero Valent Iron) are generally preferred for remediation because of large surface area of nanoparticles and more number of reactive sites than micro-sized particles[5] and it possess dual properties of adsorption and reduction. Solution-phase and Vapor-phase synthesis methods can be used for producing iron at nano-scale. Since vapor-phase synthesis normally yields relatively small quantities of particles, most of the synthesis approaches which are commercially available or normally used in laboratories, are solution-phase methods. Iron at nano-scale can be synthesized by solution-phase method is from Fe (II) and Fe(III) , using borohydride as a reductant:

$$\mathbf{4Fe^{3+} + 3BH_4^- + 9H_2O \longrightarrow 4Fe^0 + 3H_2BO_3^- + 12\,H^+ + 6H_2}$$

The excessive borohydride is typically needed to accelerate the synthesis reaction and ensure uniform growth of iron crystals. Synthesis at much lower concentrations and the use of ferrous iron has also successfully performed. Emulsification of nZVI is another novel modification of nZVI for active in situ remediation. This approach is adapted for emulsified oil flushing for DNAPLs (dense non-aqueous phase liquids), such as trichloroethane (TCE), which are hydrophobic. The emulsion is miscible with the contaminant, allowing an increased contact between TCE DNAPL and the ZVI present within the oil-emulsion droplet[6].

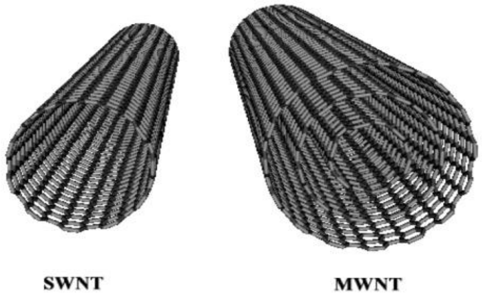
The use of iron as a permeable reactive barrier (PRB) has been the subject of considerable research and development since 1990s[7]. PRB is an engineered zone of reactive material, extending below the water table, designed to treat contaminated water. Contaminants passing through PRBs are either degraded or retained in the reactive barrier material. ZVI has been used particularly as a reactive media in a number of field-scale PRB systems particularly those designed to remediate chlorinated organic compounds, metal and radionuclide contaminants successfully[8]. PRBs containing nZVI may remove organic chlorinated compounds by reductive dechlorination[9], whereas metals, metalloids and radio nuclides can be removed by reductive precipitation, surface adsorption or complexation or co-precipitation with the Fe oxyhydroxides that form on the nZVI surfaces[10].Iron with other metals (bimetals) was used extensively for the remediation of contaminated water. Bimetallic nanoparticles consist of elemental iron in conjugation with a metal catalyst, such as platinum (Pt), gold (Au), nickel (Ni) and palladium (Pd)[11]. The combination of metals to form a nanoparticle increases the kinetics of redox reaction, therefore catalyzing the reaction. The most commonly used and commercially available bimetallic nanoparticles (BNPs) are the palladium and iron BNPs (Pd/Fe).The surface area normalized rate constant of BNPs of Pd/Fe was two orders of magnitude higher than that of nZVI. Pd/Fe BNPs are generally used in the removal of trichloroethane.



Various modes of applications of nZVI

Carbon nanotubes

In recent years, nanotechnology has introduced different types of nanomaterials to the water industry and has produced some promising outcomes. With emergence of nanoscience and technology in the last decade, research has been initiated to exploit the unusual and unique properties of carbon nanotubes (CNTs). CNTs are very thin; hallow cylinders made of carbon atoms. They are about 10,000 times thinner than human hair. CNTs, a new form of carbon, are attracting great research interest due to their exceptional adsorption, mechanical properties, unique electrical properties and high chemical and thermal stability mainly because of their extremely small sizes, uniform pore distribution and large specific surface area[12]. CNTs are nanomaterials that are rolled into a tube and are classified as single-walled carbon nanotubes (SWNTs), a single pipe with a diameter from 1 to 5 nm and multi-walled carbon nanotubes (MWNTs) with several nested tubes, at lengths varying from 100 nm upto several tens of micrometers. The SWNTs bundles have their adsorption sites inside the tubes, the interstitial triangular channels between the tubes, or the grooves formed at the contact between adjacent tubes on the outside of the bundle. For MWNTs, adsorption can occur in the aggregated pores, inside the tube, or in the external walls. Since their discovery, CNTs have attracted great attention due to their unique properties. CNTs can be synthesized by chemical vapor deposition (CVD) process. The characteristics of CNTs synthesized by this process depend upon the type of catalyst and carrier gas used[13].A novel silica template-mediated approach for synthesis of nanoporous carbon using CVD was proposed by Ryoo et al[14].The resulting high surface area materials with uniform pores were suitable for wide range of applications such as adsorbents, catalytic supports etc. The dye adsorbing capacity of such nanoporous carbon was found to be 10 times higher than that of commercial activated carbon.



Classification of CNTs

The hexagonal arrays of carbon atoms in the graphite sheets of CNTs surface have a strong interaction with other molecules or atoms, which make CNTs a promising adsorbent material substituted for activated carbon in many ways[15]. These are utilized for the removal of heavy metals, metalloids, organic and biological impurities. Nanotube surfaces are chemically modified to enhance the adsorption of contaminants. The functionalization with various groups such as –OH, -COOH, $-NH_2$ etc. and introduction of nanopores in activated carbon by chemical oxidation (by HNO_3, $KMnO_4$, H_2O_2, NaOCl, H_2SO_4, KOH, and NaOH etc.) and heat treatment was another approach for synthesis of nanoporous carbon which increases their water solubility and biocompatibility. Heavy metal adsorption on CNTs has been shown to depend on surface functional groups, specific surface area, and solution components. The most important factor is the surface functional group, which generates oxidized acids. It is well known that oxidation treatment by nitric acid causes an increase in cation exchange capacity. Due to their porous structure, CNTs are found to have much higher adsorption than that of carbon black with the same surface area of CNTs. The researchers assert that CNTs are effective adsorbents for environmental applications when compared to other adsorbents. The unique properties of CNTs like high chemical and thermal stability were utilized for the treatment of natural organic matter (NOM) which produces carcinogenic agents, thus maintain high water quality. CNTs have significantly higher dioxin removal efficiency than that of activated carbons. CNTs are good fluoride adsorbents and their fluoride removal capacity is superior to that of an activated carbon filter. Adsorption of 2,3-dichlorophenol was found to be dependent on the mass of MWCNTs , concentration, solution pH and adsorption temperature. The amino functionalized MWCNTs can be used to produce filtration membranes for the removal of heavy metals from industrial waters.

Li et al.[16] found that the metal ion sorption capacities of the MWNTs were 3-4 times larger than those of powdered activated carbon and granular activated carbon, two commonly used sorbents in water purification. Peng et al.[17] have recently developed Cerium-oxide supported on carbon nanotubes which are effective sorbents for As (V). Li et al.[18] reported that MWNTs were better sorbents of volatile organic compounds (VOCs) than carbon black in aqueous solutions. Fuget su et al.[19] has prepared cross-linked alginate vesicles encapsulated inside MWCNTs which have high sorption capacity for water soluble dyes. CNTs have also unique strength in adsorption of biological contaminants because of their structural and functional properties. Anti-microbial effect of CNTs is due to their fibrous shape[20]. The groove edges of CNT bundles and the external surface area of outermost nanotubes are potential adsorption sites and provide large pore spaces that will be fully utilized by micro-organisms. Thus with respect to adsorption of biological contaminants on CNTs, accessible external surface area and presence of aggregated pores with volumes greater than mesopore are considered important. The microbial cytotoxic property of CNTs has a partial influence on concentration of bacteria. Thin fibers of CNTs impinge bacterial cell surface, disrupt the intracellular metabolic pathways and subsequently, the internal contents are released due to the cell rupture caused by oxidative stress after impingement[21].The size and length of the tubes, dispersivity, amorphous nature and number of layers (single or multi walled) are identified to influence the cytotoxic properties of CNTs[22]. Bacterial adsorption on CNTs is characterized by having three unique features: 1) microbial adsorption capacities on CNTs are higher than any other commercially available adsorbent media. 2) CNTs express selective adsorption of bacteria, a feature which is generally not seen in other adsorbents. 3) Adsorption kinetics of bacteria on CNTs is almost instantaneous. The pristine modified CNTs prohibit the growth of pathogens on their surface and might probably contribute to self-cleaning efficiency of the CNT absorption filters. Pristine CNTs exhibited antimicrobial characteristics over wide range of micro-organisms including a) bacteria e.g. *Micrococcus lysodeikticus*, *Streptococcus mutans*, *E.coli*, *Salmonella* and bacteria endospores [22-24]. b) Protozoa species e.g., *Tetrahymena pyriformis*,[25] c) viruses, e.g., *MS2 bacteriophage* [26-27.]

Silver nanoparticles

Water is the common breeding ground for many micro-organisms. The greater water-borne threat to human health is bacterial contamination of drinking water sources leading to outbreak of diseases. The removal or inactivation of micro-organisms is the last step in the treatment of waste water. Many chemical and physical agents such as chlorine and its derivatives, ozone, $AgNO_3$, UV light are commonly used for disinfection of water[28] which reacts with various constituents in natural water to form disinfectant byproducts

(DBPs), many of which are carcinogens. DBPs will be formed when chemical oxidants are used in water treatment. Furthermore, the resistance of some pathogens, to conventional chemical disinfectants requires high disinfectant dosage, leading to higher DBP formation.

The rapid growth of nanotechnology has opened significant interest in the environmental applications. The use of metal nanoparticles for disinfection is expected to play a crucial role in water purification because of their high reactivity due to the large surface area to volume ratio. These nanoparticle scan either directly by interacting with the microbial cells, e.g. interrupting trans membrane electron transfer, disrupting/penetrating the cell envelope, or oxidizing cell components, or producing secondary products(e.g. reactive oxygen species or heavy metal ions) that cause damage. The antibacterial properties of silver compounds and silver ions have been historically recognized and applied in a wide range of applications from disinfecting medical devices and home appliances to water treatment.

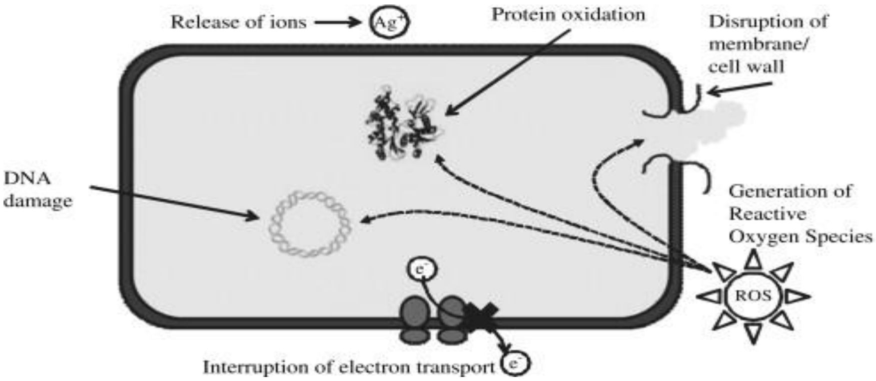
AgNPs exhibit additional antibacterial capabilities which are not exerted by bulk or ionic silver. Current AgNPs used for disinfection in different forms include: metallic silver nanomaterials[29], silver-impregnated zeolite powders and activated carbon materials[30], dendrimer-silver complexes[31], polymer-silver nanoparticle composites[32], silver-titanium dioxide composite powders[33] , AgNPs coated onto polymers like polyurethanes[34] etc. The most common method of preparation of silver nanoparticles is chemical reduction of a silver salt dissolved in water with a reducing agent such as $NaBH_4$, citrate, glucose, hydrazine and ascorbate etc [35-36]. Since the use of chemical reducing agents for silver nanoparticle synthesis is often considered toxic, the green synthesis methods for silver nanoparticles such as polysaccharides, polyphenols, irradiation, biological reduction are used[37].

To date, several mechanisms have been postulated for the antimicrobial property of silver nanoparticles :(1) adhesion of nanoparticles to the surface altering the membrane properties: AgNPs interact with the bacterial membrane and are able to penetrate into the cell. AgNPs have been reported to degrade lipopolysaccharide molecules, accumulate inside the membrane by forming pits and cause increase in membrane permeability and cytoplasm leakage[38]. (2) dissolution of AgNPs releases antimicrobial Ag+ ions: The possible mechanisms for the oxidative dissolution of AgNPs have been reported by Choi et al[39] and Asharani et al[40].

$$4Ag^{+} + O_2 + 2H_2O \rightarrow 4Ag^{+} + 4\,OH^{-} \qquad \text{(Choi et al)}$$

$$2Ag + H2O2 + 2H+ \rightarrow 2Ag+ +2H2O \qquad \text{(Asharani et al)}$$

Ag+ has known antimicrobial properties. Ag+ interact with thiol groups in proteins, resulting in inactivation of respiratory enzymes and leading to the production of reactive oxygen species (ROS) [41] (3) generation of ROS which cause DNA damage: ROS species are natural byproducts of the metabolism of respiring organisms. Excess ROS production can lead to breakdown of mitochondrial function or cause DNA damage[42].

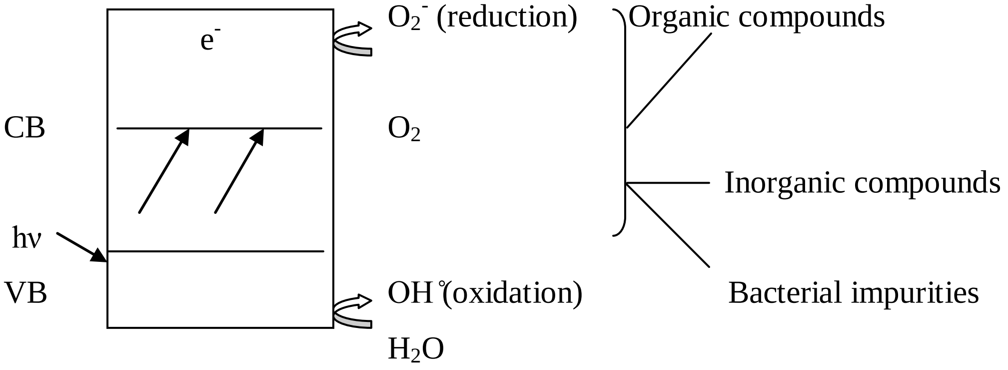


Various mechanisms exhibited by antimicrobial nanoparticles

The factors influencing AgNP toxicity are particle size, shape, crystallinity, surface chemistry, capping agents etc. The environmental factors include pH, ionic strength, macromolecules divalent cations and presence of ligands. The decrease in particle size increases the specific surface area of AgNPs which has a higher number of atoms exposed on the surface available for redox, photochemical, biochemical reactions in addition to physico-chemical interactions with cells. AgNPS are effective biocides against 1) bacteria such as *E.coli, S.aureues, B. subtillis, Klebsiella mobilis, Staphylococcus* epidermis etc [43-44]. 2) fungi such as *A.niger, candida albicans, saccharomyces cerevisia, penicillium citrinum* [45-46] 3) virii such as *HIV-1, Hepatitis B, Syncytial virus.* [47-49]

TiO_2

TiO_2 is the most commonly used semiconductor photocatalyst which has been applied for various photocatalytic reactions for its high efficiency, low cost, physical and chemical stability, widespread availability and non-corrosive properties. The applicability of TiO_2-based heterogeneous photocatalysis has been used extensively for environmental decontamination purposes[50]. TiO_2 nanoparticles can serve both as oxidative and reductive catalysts for organic and inorganic pollutants. It can be successfully used for treating water contaminated with dissolved metals such as Ag, Au, Hg, Cr, Pt, Cu, Ni etc.[51] TiO2 nanoparticles can also completely degrade the organic pollutants into harmless inorganic substances such as CO_2, H_2O etc.[52] under moderate conditions, and would not bring any other serious secondary pollution. According to Pirkanniemi and Sillanpaa [53], the overall heterogeneous photocatalysis can be summarized into the following five steps: 1) reactant diffusion to catalyst surface, 2) adsorption of the reactant onto the surface, 3) chemical reaction on the catalyst surface, 4) desorption of final products of the catalyst surface, 5) diffusion of final products from the catalyst surface. Heterogeneous photocatalysis process is a combination of charge transfer features, electronic structures, excited life spans and light absorption effects. The energetic and charge transfer processes involved in a photocatalytic process can be illustrated in the given figure.



Mechanism of photocatalytic effect of TiO_2

When electrons are excited by the light of energy equal to or exceeding its band gap energy, they are promoted from the valence band to the conduction band, leaving positive holes in the valence band. These electrons and holes are capable of reducing and oxidizing compounds at the TiO_2 surface, respectively. If electrons and holes do not recombine to produce heat, they can follow the reductive and oxidative pathways indicated by the reactions. In addition, these holes often react with water or hydroxyl ions adsorbed to TiO_2 producing hydroxide radicals, which then oxidize adsorbed organics. The TiO_2 occurs in rutile, anatase and brookite phases but the anatase phase of TiO_2 is photocatalytic active:

:

$TiO_2 – h\nu \rightarrow TiO_2 (h^+ + e^-)$ electron-hole pair formation

$e^- + h^+ \rightarrow$ heat recombination

$e^- + M^{n+} \rightarrow M^{(n-1)}$ reduction

$h^+ + H_2O\ (ads) \rightarrow \cdot OH + H^+$ oxidation of adsorbed water

$h^+ + 2OH^-\ (ads) \rightarrow \cdot OH + OH^-$ oxidation of hydroxide ions

$\cdot OH + R\ (ads) \rightarrow \cdot R(ads) + H_2O$ organic oxidation

$\cdot R(ads)\ (\cdot OH, \cdot R(ads)) \rightarrow$ products termination

Nano-TiO_2 is normally synthesized using various titania precursors such as titanium tetra-iso-propoxide [54], tetra butyl titanate [55], titanium tetrachloride [56]. Different starting materials can influence the morphology of the nano-TiO_2 produced such as specific surface area, crystalline phase and crystallite size that plays an important role in the photocatalytic degradation of organic pollutants. Doping techniques have been applied in photocatalysis to overcome the limitations of nano-TiO_2 such as a wide band gap, ineffectiveness of photocatalysis under the sunlight and thermal stability[57]. It is well known that small crystallite size, high percentage of the anatase phase and high specific surface area of nano-doped TiO_2 increases the photocatalytic degradation efficiency. Many dopants such as metals, transition metals, metalloids, non-metals, halogens can be successfully used. Zang et al[58] produced a Mn-doped TiO_2 in which the band gap of the photocatalyst was narrowed due to the formation of an impurity level near the bottom of the conduction bands. Sakthivel et al[59] investigated the performance of TiO_2 after supplementing with platinum dopant which act as an electron trap in the formation of TiO_2, decreasing its surface area. Non-metal dopants including carbon, nitrogen and sulphur are able to improve the morphology and photocatalytic performance of TiO_2[60]. Doping with non-metal anions broadens the band gap of TiO_2 in its electronic structure and affects the red-shift in the absorption spectra of nano-doped- TiO_2. Thus various photocatalytic, photochemical and the photoelectrochemical properties of TiO_2 are enhanced by shifting the wavelength sensitivity of TiO_2 from UV region into the visible light region[61]. Halogen dopants such as Iodine, Bromine and Flourine improve the morphology and the photocatalytic performance of TiO_2[62]. Wang et al[63] successfully prepared single anatase phase of Iodine-doped TiO_2 which hindered the growth of crystal particles by enhancing the energy barrier mutual diffusion between grains. Boron is known as metalloid compound that can be doped in TiO_2 which inhibits the growth of crystalline TiO_2 and thus increases the surface area as well as inducing the crystalline process [64].

The removal of total organic carbon from water contaminated with organic wastes is greatly enhanced by the addition of TiO_2 nanoparticles in the presence of UV light shown by Chitose et al[65]. Kabra et al [66] reviewed the utilization of photocatalysis in the treatment of water contaminated by organic and inorganic pollutants. From their results, TiO_2 nanoparticles degrade organic compounds e.g. chlorinated alkanes and benzenes, dioxins, furans, PCB etc. and also reduce toxic metal ions such as Cr (VI), Ag(I) and Pt(II) in aqueous solutions under UV light. Ashasi et al [67] synthesized N-doped TiO_2 nanoparticles that were capable of photo degrading methylene blue under visible light. A wealth of information on TiO_2 photocatalytic inactivation of bacteria has been acquired[68]. TiO_2 can kill both Gram-negative and Gram-positive bacteria. More recently, nano-sized TiO_2 was also reported to kill viruses including poliovirus1 [69], Herpes virus[70], Hepatitis B virus[71] etc. The antibacterial activity of TiO_2 is related to ROS production, especially hydroxyl free radicals and peroxide formed under UV-A irradiation via oxidative and reductive pathways respectively[72].

Nanomaterial	Mechanism involved	contaminants remediated	Ref.
Iron, Fe (0)	precipitation, Immobilization, Sorption, Fenton's reagent, PRBs, Bimetallic	DNAPLs such as TCE, Organic chlorinated compounds, metals, metalloids, radionuclides etc.	[3,4, 6,10]
CNTs SWNTs MWNTs Functionalized-CNTs	adsorption, filtration membranes antimicrobial	metals, metalloids, organic & biological impurities etc.	[14,15,18]
Silver, Ag (0)	antimicrobial, disinfection by generation of ROS	bacteria, fungi, virii etc.	[41]
TiO_2	photocatalysis, oxidative & reductive catalysis, antimicrobial	organic compounds, toxic metals, bacteria, virii etc.	[47, 62,64]

Limitations of nanotechnology in water purification

Applications of nanomaterials are of definite advantage in many functional areas including water treatment. Although nanoparticles provide high specific surface area, a primary reason for their high reactivity, aggregation in water negates this benefit. Release of nanomaterials into the environment can have broader impacts on our ecosystem. It is therefore critical that researchers in this area to address questions such as

- What are the most environmentally benign methods for producing nanomaterials?
- What is the behavior of nanomaterials in environment and where these mostly end up in the environment?
- What are the toxic effects of nanomaterials when they interact with the organisms?

Unfortunately, there is an insufficient data on the potential for accumulation of nanomaterials in environmentally relevant species and there have been few studies on the effects of many nanoparticles on the environmental communities. The properties that can be harmful to the environment are the very same properties that are advantageous and exploited during treatment and remediation processes. For instance, the catalytic properties of nanoparticles that induce the degradation of pollutants can also induce a toxic response when taken up by the cells. The factors and processes affecting ecotoxicity are complex, and the impact of manufactured nanoparticles on organisms is determined by a range of properties, including dissolution, aggregation, surface properties, the characteristics of exposure environment and the biochemical and physiological traits of the organism being exposed[73].

Retention of nanomaterials is critical not only because of the cost associated with loss of nanomaterials, but also, and more importantly, because of the potential impacts of nanomaterials on human health and ecosystems[74]. The increased mobility of nZVI on its surface modifications would allow efficient remediation; it could also result in the possibility of nanomaterials migrating beyond the contaminated plume area, discharging to drinking water wells during the remediation process. Bulk TiO_2 particles are known to be harmless to humans and animals. Although nanoscale TiO_2 was classified recently as a possible carcinogen if inhaled[75] its potential injestion via water is not expected to be a major concern, as reflected by its use in toothpaste and sunscreens. Researchers found that CNTs, if inhaled in large proportions could be as danger as asbestos. According to Lam and his co-workers, CNTs are light and could get air borne and when they enter into lungs, lesions were formed and toxicity greater than that of quartz was observed[76]. The toxicity of well dispersed CNTs is less compared to CNT agglomerates[77]. In CNT agglomerates, the fraction of non-CNT soot like particles is higher than well dispersed CNTs which is believed to be one of the main reasons for increased toxicity of agglomerated CNTs. The negative health impact of Ag^+ is darkening of skin and mucous membrane due to long term exposure to high silver concentration. Nevertheless, available information is insufficient to determine the highest allowable concentration of a particular nanomaterial in drinking water.

The matter of determining the substance as dangerous involves not only in determining the material's toxicity, but also to what degree the material will come into contact with the living cells. When materials are persistent and resist degradation, they may be present in the environment for long periods and have a greater chance of integrating with the living environment. Further research is needed to develop and understand the mechanism affecting the fate and transport of manufactured nanoparticles and their interaction with other organisms and how these interactions are influenced by different environmental variables. All these improvements can increase the ability to remediate more of the hazardous waste sites and minimize potential harm.

CONCLUSIONS

Emerging nanomaterials and the technologies will create tremendous opportunities for improvement and accessibility of water treatment technologies. The problems and challenges are multidisciplinary and begin with accurately understanding the potential for the environmental releases of nanomaterials and continue throughout characterizing environmental behavior, fate and bioavailability. In order to prevent any potential adverse environmental impacts, proper evaluation of these nanomaterials needs to be addressed before used on a mass scale. Future research addressing scalability, economics and safety of these systems is likely to overcome many of the current limitations and create opportunities to revolutionize drinking water treatment.

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