Review

Journal of
Nanoscience and Nanotechnology
Vol. 14, 1838–1858, 2014
www.aspbs.com/jnn

Nanotechnology-Based Water Treatment Strategies

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The most important component for living beings on the earth is access to clean and safe drinking water. Globally, water scarcity is pervasive even in water-rich areas as immense pressure has been created by the burgeoning human population, industrialization, civilization, environmental changes and agricultural activities. The problem of access to safe water is inevitable and requires tremendous research to devise new, cheaper technologies for purification of water, while taking into account energy requirements and environmental impact. This review highlights nanotechnology-based water treatment technologies being developed and used to improve desalination of sea and brackish water, safe reuse of wastewater, disinfection and decontamination of water, i.e., biosorption and nanoadsorption for contaminant removal, nanophotocatalysis for chemical degradation of contaminants, nanosensors for contaminant detection, different membrane technologies including reverse osmosis, nanofiltration, ultrafiltration, electro-dialysis etc. This review also deals with the fate and transport of engineered nanomaterials in water and wastewater treatment systems along with the risks associated with nanomaterials.

Keywords: Nanotechnology, Wastewater, Desalination, Decontamination, Disinfection.

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1. INTRODUCTION

Water covers one-third of the earth's surface; most of it is saline and unusable for human consumption, only 2.5 percent of the world's total water is fresh. Unfortunately, in addition to being scarce, fresh water is also very unevenly distributed, and more than half of the wetlands have disappeared from earth. Throughout the world, the biggest problem people face is inadequacy in access to clean and safe water. From the world's total estimated 6.5 billion population, 28 percent have Internet access while 15 percent don't have enough fresh water to live a normal healthy life. Seventy-one countries, including India, China, Israel, Thailand, and Morocco, are experiencing stress on their water resources. These countries are major producers of agricultural goods, and nearly two-thirds of them are facing the challenges of an increasing human population. Due to the loss of glaciers and reduction in snowmelt, developed countries such as North America and Europe are also facing water problems relating to irrigation, the municipal water supply, and hydroelectric and

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1533-4880/2014/14/1838/021 doi:10.1166/jnn.2014.9050

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thermo-electric plants.[1–3] The availability of clean, fresh water has become a basic necessity of mankind. An estimated 1.2 billion people do not have clean water to drink, whereas 2.6 billion people do not have water to fulfill their basic sanitation necessities.[1,4,5] The majority of these people live in Asia and Africa. Millions of people are suffering from diseases communicated by unsafe water and a million die due to it. Children under 5 years of age and elder groups are more prone to transmitted diseases. Due to contaminated water, around 4 billion diarrhea cases result in 1.8 million deaths per year.[6] Waterborne pathogens are the major cause of malnutrition in children resulting in several other diseases. Various recalcitrant pollutants (heavy metals, nitrosoamines and endocrine disrupters) from different sources enter into the water supply and, even if present in low concentration, have adverse effects on human health and the environment.[1,4,5,7–11]

Since the early twentieth century, conventional methods have been used for water treatment, which consist of coagulation, sedimentation, filtration, disinfection, decontamination and desalination. The above processes are chemically and operationally intensive and require large systems, infrastructure and engineering expertise, which make them burdensome, ineffective, time consuming and costly.[1,5,12] Further, the chemicals used for the chemical treatment of water involves chlorine, ammonia, hydrochloric acid, ozone, alum, permanganate, ferric salts, corrosion control chemicals, coagulants, filtration aids, ion exchange resins and residuals can contaminate freshwater resources to a great extent.[1] Water contains various contaminants at distant locations and hence the situation demands an effective, robust and low cost promising techniques that improve the water quality by decontamination and disinfection.

Nanotechnology offers a variety of promising solutions to filter out contaminants such as organic and inorganic solutes; heavy metals such as mercury, lead, arsenic, and cadmium; and biological toxins that causes water-borne disease such as cholera and typhoid. All existing technologies for water purification have many limitations, and nanotechnology contributes a scaffold for offering rapid detection and removal of contaminants by providing water treatment systems at low cost.[13]

Nanotechnology is the manipulation of matter at the nanometer scale to create novel structures, devices and systems. At the nanoscale level, materials show different chemical, physical and biological properties than their normal sizes.[14] The surface area of particles increases with A decrease in particle size; so nanoparticles (NPs) exhibit different optical, magnetic and electrical properties in comparison to macroparticles.[15] Nanotechnology-based applications may enable us to boost drinking water by refined filtration mechanisms (carbon nanotube (CNT) membranes);[16–19] advanced detoxification of menacing pollutants (zero-valent iron NPs); detection of impurities and pathogens by nanosensors; catalytic degradation of water pollutants by titanium dioxide NPs; nanoporous polymers, nanoporous zeolites, and attapulgite clays for water treatment; and magnetic NPs for water purification and remediation.[20] Nanotechnology provides filters and membranes that are made from different nanomaterials such as CNTs, dendrimers, nanoporous ceramics (clays), nanofibers, zeolites and nanosponges. These nanomaterials offer high porosity, active sites for metal binding, a small size, regeneration after exhausting and faster removal of contaminants.[5,21,22] For detection, removal or detoxification of contaminants, we could develop multitasking filtration units. In the future, such membranes and filters may be very useful in treating and eliminating viruses in water.[13] Nanoabsorbents have been adopted for removal of micropollutants and heavy metals.[6] Magnetic nanoparticles (MNPs) easily bind with chemical contaminants and are currently used for the magnetic separations of chemical pollutants. Contaminants such as arsenic or oil bind to MNPs, which can be easily removed using a magnet resulting in an affordable method for water treatment.[13] CNTs adsorb heavy metal,[23] dyes[24] and organic compounds.[25] Small and portable nanosensors for detection of low concentration levels of biological and chemical contaminants with improved capabilities are being developed.[13] Nanophotocatalysts can chemically break down the organic contaminants and are self-regenerated and hence can be used again and again. Different nanomaterials such as ZnO, TiO_2, ZnO–CeO_2, and Degussa P25 TiO_2 NPs play an important role in the photodegradation of contaminants whereas the other current treatment techniques are ineffective or very expensive.[26–29] With the advancement of nanoscience, low cost filters, dynamic membranes and control on membrane fouling have enhanced the use of membrane bioreactors for industrial and municipal wastewater treatment.[30]

The release of NPs into bodies of water is now well known, but their interaction with aquatic organisms and the surroundings is of great concern because NPs may themselves be toxic and may transport toxins to the water system resulting in ecotoxicity. During recent years, many nanomaterials have been reported that cause acute toxicity to the aquatic organisms resulting in deaths. NPs may also have adverse effects on human health and the environment. This calls for developing proper strategies and guidelines for using nanotechnology in the public domain. In this review, we focused on the application of nanotechnology for water treatment and reuse: novel desalination, disinfection, contaminant detection, photodegradation of chemical contaminants, removal of heavy metals by nanoadsorption using different metals NPs and CNTs, nano-photocatalytic degradation of contaminates, microbial control in water distribution networks, fate and transport of engineered nanomaterials and the risks associated using nanotechnology in water and wastewater treatment.

2. DESALINATION

Earth is referred to as the "blue planet" because when viewed from space it appears blue due to the reflection from the oceans, which cover 71 percent of the earth's surface. The most formidable problem faced by the world is the global water scarcity. Out of the total amount of water, around 0.8 percent is fresh water, and extensive research has been conducted to figure out ways to meet the increasing water consumption needs with the use of sustainable technologies. It is estimated that by 2030, the water needs will increase from 4500 billion m^3 to 6900 billion m^3. There will be a shortage of water resources to meet future human needs. Desalination of saline water can provide the best solution to the above problem.[31] Desalination refers to the removal of salts and a few minerals from saline water to obtain fresh water through several processes or the removal of dissolved salts from saline water by using either membranes (chemical, mechanical and electrical mediated) or thermal processes. Evaporation of water over the oceans in a water cycle is a natural desalination process. Desalination is not a new technique. Challenges with desalination are its high cost, energy requirement, waste disposal and membrane fouling. Advances in nanotechnology are providing unprecedented opportunities to create more cost-effective and environmentally friendly water purification processes. Traditional water treatment methods are being replaced by new emerging technologies. Nanotechnology-based new methodologies for water desalination have been developed such as nanofiltration, solar desalination and membrane engineering. Worldwide, there are about 3,500 land-based desalination plants with a production capacity of about 3,000 million gallons per day (mg d) as compared to the early 1950s with 225 plants and about 27 mg d.[32] The new desalination technologies may emerge with time to meet the rising demand for fresh water. Over the years, a variety of desalting technologies have been developed, which primarily include thermal and membrane processes. The cost of desalination per produced water volume is somewhat inversely proportional to the production capacity of the plant. At present, the market is driven by the ebbing costs of desalination, which are due to the technological advances in the desalination process. With the latest advancement in technology, desalination of seawater to produce safe and clean water has evolved globally as a common solution for obtaining fresh water.

2.1. Different Energies and Processes Involved in Desalination

2.1.1. Mechanical Process

By using a mechanical process, filtration and evaporation processes occur. Filtration of seawater by using a membrane is one of the popular methods of desalination; e.g., reverse osmosis (RO). Water is forced through a membrane that is selectively permeable, allowing only water, and not salts, to pass. In mechanical vapor compression, the seawater is first evaporated and then compressed using mechanical forces.

2.1.2. Thermal Process

The thermal process is used to mimic the hydrological cycle through which water evaporates from the bodies of water and is transported to land in different forms of precipitation. Thermal energy is supplied to the bodies of water to heat and finally vaporize the water. Evaporation of water results in separation of pure water vapors from dissolved salts and other impurities. Based on evaporation, four types of distillation are available: solar distillation, multi-effect distillation, multi-stage flash distillation and thermal vapor compression. After evaporation, the water vapors condense back to liquid, resulting in pure distilled water. If seawater is allowed to freeze, the pure water crystallizes forming ice and leaving behind dissolved salt and other impurities. Freeze desalination requires less energy than any distillation process and has the potential to purify a wide variety of waste streams. Using these basic processes, numerous distillation units have been developed and are in use worldwide.

2.1.3. Electrical Process

The process of transport of salt ions from seawater through a selective membrane to concentrate solutes and water into another cell under the influence of an applied electric field is called "electrodialysis of seawater." A systematic configuration of electrodes, a dilute feed stream and concentrate stream compartments forms a complete electrodialysis (ED) cell. The ED process is different from other distillation techniques, because the dissolved species are moved away from the feed stream rather than the reverse.

2.1.4. Chemical Process

A chemical process of ion exchange is also used for desalination. In ion exchange, undesirable ions in the feed water are exchanged for desirable ions as the water passes through granular chemicals, called "ion exchange resins." For example, for the production of ultra-pure water in industries, in the home and municipal water treatment plants, cation exchange resins are used to remove calcium and magnesium ions from hard water. Resins will need to be replaced much earlier, if the concentration of dissolved solids in the feed water is high. The cost of resin is very high and due to the rising costs for resins, ion exchange is now competitive with RO and ED only in treating relatively dilute solutions containing a few hundred ppm of dissolved solids.

2.2. Membrane Technologies for Desalination

A membrane is a thin layer of porous material that permits water molecules to pass through it, but synchronously restricts the passage of larger and unwanted elements such as bacteria, viruses, salts and metals. Membranes use either pressure-driven forces or electrical technologies. Pressure-driven membrane technology is a perfect method for the water purification to any desired quality. Membrane is the essential component of this technology. The membrane act as a barrier between two homogenous phases. It shows selective permeability to some solutes. Separation of solutes is achieved when a driving force is applied. The force could be a concentration gradient (Δc), pressure gradient (Δp), electric field gradient (ΔE) or temperature gradient (ΔT).[33]

RO uses the osmosis phenomenon, i.e., the osmotic pressure difference between the pure water and the salt-water to remove salts from water. Common membranes used in RO are cellulose acetate, aromatic polyamide, polypiperzine-amide, polybenzimidazoline, polyoxadiazole, polyfurane, polyether-polyfurane, sulfonated polysulfone, polyamide via polyethylenimine, polyvinylamine, polypyrrolidine, polypiperazine-amide, cross-linked fully aromatic polyamide and cross-linked aralkyl polyamide.[34] Reverse-osmosis typical seawater recoveries are between 35–50 percent.[1] The remaining salt solution, now concentrated brine, is discharged back to the sea. This is a critical environmental drawback to RO and also limits its use to coastal areas, since brine from brackish groundwater desalination cannot be disposed of inland in an economical manner. RO cannot achieve this high recovery due to hydraulic pressure limitations of the pumps and membrane housings.[35] To reduce the price of present desalination technologies, it is wise to target technologies that are less expensive. Energy usage is the most important contributor to the price of desalination.[35,36] Thus for making desalination more affordable, subtraction in energy usage is the main aim. Today RO is the leading seawater desalination technology. It has outdistanced conventional thermal technology with new technologies such as Brine Conversion System (BCS),[37] ED,[38,39] Bipolar Membrane Electrodialysis, (BPME),[40] membrane distillation,[41,42] forward osmosis (FO)[35,43] and capacitive deionization.[44]

A RO seawater desalination system has many advantages such as using less installation space and saving energy and has become the standard technology to obtain freshwater from seawater. By raising system recovery, Toray, a leading company in membrane technology have developed a new RO seawater desalination system called a brine conversion two-stage sea water reverse osmosis (SWRO) system (BCS) that provides 60 percent recovery of freshwater for 3.5 percent seawater.[37,45,46] BCS includes many other technologies such as high-membrane technology (UTC-80BCM operates with 8–10 MPa), anti-biofouling technology (MT-901), energy recovery and system configuration. A pilot plant has been operated successfully at Toray's Ehime plant site since 1997. The first commercial plant with total capacity of 4500 m^3/d (1.2 mg d) has been started successfully in March 1999 in Mas Palomas (Spain).[37]

Membrane fouling is a big problem in RO desalination. Poly amino polyether methylene phosphonate (PAPEMP) is a unique inhibitor for membrane fouling. The inhibitor is effective for controlling calcium sulfate, calcium carbonate, magnesium hydroxide, barium and strontium sulfates, silica/silicate and other various metal hydroxides deposits. It can eliminate or minimize the use of acid, which in turn will protect equipment from corrosion and provide operator safety.[47] Development of thin film nanocomposites has occurred by application of mixed matrix membrane technology to polyamide RO membranes; i.e., a combo of organic and inorganic material combining the benefits such as good permselectivity and a high packing density of polymeric membrane coupled with superior thermal, chemical and biological stability of inorganic membranes.[34,48] Titanium oxide and zeolite NPs are incorporated in the interfacially formed separating layer in these membranes. These increased permeability, enhanced flux and have lower fouling surfaces.[34,48]

Nanofiltration (NF) in combination with RO is used for desalination. An NF membrane due to larger membrane pore size (0.05 μm to 0.005 μm) requires less pressure (70 and 140 psi) in comparison to RO. NF is used to remove cations, organic pollutants, biological contaminants, natural organic matter, minute quantities of U (VI), arsenic and nitrates from groundwater and surface water.[32] ED is an affordable technology for the desalination of seawater, or brackish water. In comparison to RO, it is low cost and also treats the waste stream that is generated by various membranes technologies used in desalination. Biopolar membrane electrodialysis (BPMED) has increased the potential of ED by acidifying/alkalizing a salt without salt introduction. A bipolar membrane (BPM) is a composite ion exchange membrane that consists of two layers—a cation exchange layer and an anion exchange layer—that are joined through an intermediate layer. A BPM provides excellent efficiency in the conversion of selective industrial wastes into useful products. In membrane separation performance, a key role is played by hydrophilicity and pore structure. Polysulfone (PSu)-based BPM shows better performance over PSDVB (polystyrene cross-linked with divinyl benzene) based membranes. PSu-based BPM gives higher current efficiency and requires low power.[31]

Forward osmosis (FO) is a process that utilizes an osmotic pressure gradient to create the driving force, instead of using hydraulic pressure for water transport through the flat sheet cellulose tri-acetate membrane. FO may be facile to desalinate saline water at a noticeably reduced cost. Similar to RO, a semipermeable membrane is present which allows water, but not salt, to pass through. Water automatically transports across the membrane by osmosis. Osmotic driving forces in FO are significantly greater than the hydraulic driving forces in RO, potentially leading to higher water flux rates and relatively high salt rejection.[35] FO has not been fully established due to the lack of a suitable draw solution and an appropriate membrane. A desirable draw solution solute must have a high osmotic efficiency to be highly soluble in water and have a low molecular weight to develop a high osmotic pressure. Higher osmotic pressure leads to higher water flux, mostly a concentrated ammonium bicarbonate solution is used. Upon heating, ammonium bicarbonate decomposes into carbon dioxide and ammonia gases, which are separated and recycled as draw solutes.

For brackish water desalination, RO and ED are both competitive in price. On a large scale, brackish water at well-operated, centralized RO or ED plants can be most economically desalinated (e.g., 1 mg d, or larger) at an overall cost (including both capital and operating costs) of about $1.50 to $2.50 per 1,000 gallons; whereas for seawater, large scale distillation and RO together cost about $4 to $6 per 1,000 gallons. On a global scale, around 7,500 desalting plants in operation produce several billions of gallons of water per day. Fifty-seven percent of distillation plants are in the Middle East and 12 percent of the world capacity is produced in the United States, where most of the plants are located in the Caribbean and Florida. Saudi Arabia's desalination plants account for about 24 percent of total world capacity.[32]

Solar energy is available almost everywhere so it should be used to desalinate sea water. The only problem with solar thermal desalination is space availability. The solar water distillation works on a simple principle of evaporation; distillation replicates the way nature makes rain. The sun's energy is used to evaporate water into water vapor and condense on the collection surface. Impurities such as salts and heavy metal are removed by this process. Solar stills and multi-effect humidification systems are available for this purpose.[32] In remote areas with access to saline lakes and aquifers, solar thermal distillation play a significant role.

Rigid-star amphiphiles and ceramic membranes also show good performance in contaminant rejection.[41] Aquaporins, also known as "water channels" or "ion channels," are specialized protein channels present in the biological cells that immediately transport water/ions selectively across the cell membrane. Aquaporins have a few angstroms' core of hydrophobic channels to transport water, and orientation of the molecules in single-file fashion occurs inside the pore due to the presence of the H-bond interaction with functional groups on the channel walls. Due to the loss of their hydration sphere and a decrease in entropy, the free energy associated with penetration of ions into a channel largely increases resulting in effective ion removal.[49] The presence of the bacterial water-channel protein Aquaporin Z imparts an 800-fold increase in water permeability; rejecting salts, urea, glucose and glycerol.[50] A de novo synthesis of ion channels for making a synthetic analog to aquaporin has also motivated research on engineered membranes with ion selectivity and high water flux.[5, 51, 52] Mimicked aquaporin porous inorganic membranes such as CNTs with hollow graphite cores and metal oxide frameworks have been modified to provide a water channel-like function; i.e., water transport occurs in a single-file fashion.[54, 55] A higher salt rejection (97.69 percent as compared with 96.19 percent) was achieved and a nearly double water flux (44 Lm^{-2} day^{-1} bar^{-1} as compared to 26 Lm^{-2} day^{-1} bar^{-1}) was obtained by using CNT/polymeric membranes.[34] To control the ion transport in a much better manner, nanofabrication approaches are applied to ion-selective membranes: either they are biased externally or incorporated with fixed ionic charges resulting in the exclusion of ions from the pore interior.[49] In self-assembled polymer vesicles, which are made up of tri-block co-polymer, poly(2-methyl-2-oxazoline)-block-poly(dimethylsiloxane)-block-poly(2-methyl-2-oxazoline), aquaporins were incorporated and in comparison to available thin film composite (TFC) RO membranes, improvement in permeability was reported when a permeability test using stopped-flow light-scattering experiments was carried out. Aquaporins represent an ideal opportunity for ultra-pure water production as these allow only the passage of water molecules from it.[34] Worldwide-developed nanotechnology-enabled filtration membranes are listed in Table I.

2.3. Key Issues in Desalination

2.3.1. Pretreatment Before RO/FO/NF/ED

The feed water normally requires pretreatment before it is subjected to any desalination process. The type of desalination process used and quality of the feed water

Table I. Nanotechnology-based filtration membranes developed worldwide.

	Organization	Country	Type of technology
1.	Banaras Hindu University	India	Carbon-nanotube-based filters devised to remove contaminants
2.	Argonide	United states	Oxidized aluminum nanofiber filters developed on glass fiber substrate
3.	Rensselaer Polytechnic Institute	United States	Carbon-nanotube-based filters devised to remove contaminants
4.	SolmeteX	United States	Heavy metal binding resins developed that remove metals such as mercury, arsenic, cyanide and cadmium from water
5.	North West University Potchefstroom	South Africa	Nanomembrane filtration technologies
6.	Filmtec Corporation	United States	Nanomembrane filtration technologies
7.	The Stephen and Nancy Grand Water Research Institute	Israel	Reverse osmosis filtration technologies
8.	Long Beach Water Department	United States	A relatively low-pressure, two-staged nanofiltration process.
9.	University of Stellenbosch Institute for Polymer Science	South Africa	Nanomembrane filtration technologies

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determines the level of pretreatment required. Pretreatment processes usually include coagulation, settling, treatment with activated carbon to remove organics, dechlorination, disinfection to kill microorganisms, filtration and addition of acids and polymer-based additives to forbid scaling. Pretreatment expenses may account for 3–30 percent of the total cost of desalination.

2.3.2. Post Treatment of Water

The post treatment of the product water is required in some cases depending on its intended use and quality. The post-treatment processes usually include carbon dioxide removal, chemical addition, pH adjustment and disinfection. Post treatment is an important step to making water suitable for drinking and other purposes. For example, water produced after ion exchange and distillation may corrode the metal pipes because it has a very low mineral content. Post-treatment is needed to improve both taste and quality.

2.3.3. Energy Recovery and Cost

Seawater desalination by RO has become an easy-on-the-pocketbook option for areas where natural freshwater resources are diminishing in quality and quantity. This transformation is possible due to advances in low-energy seawater reverse osmosis (SWRO) membranes, potent energy recovery devices (ERDs) that transfer energy from the high-pressure concentrate stream to the membrane feed and improvements in the efficiency of HP pumps. ERD and HP pumps enable the build-up of small-scale seawater desalination plants that are more efficient in comparison to large plants and cut down the cost also.

2.3.4. Brine Disposal

Brine disposal is also an important factor due to environmental and economic issues. The flora and fauna are very sensitive to the increase in salinity of local seawater. Thus, proper engineering should be made before brine disposal.

3. DECONTAMINATION

3.1. Biosorption

Unfortunately, water is polluted with various toxic substances such as arsenic, mercury, fluoride, lead, chromium, halogenated aromatics, nitrates, and phosphates. These pollutants are harmful even if present in trace amount. The discharge of medicine and cosmetics into bodies of water is also playing a major role in water pollution.[5] Due to continuous increase in the number and amount of water pollutants, new methods for the detection and removal of water pollutants are urgently needed. Heavy metals such as Hg, Pb or As enter the water from both natural (forest fires, volcanic eruptions, metal-rich soil) and anthropogenic sources (mining, biomass burning, pharmaceuticals, chemical manufacturing, coal burning, paper industries, gold-silver mining).[56–58] Increased deposition of heavy metal affects the natural biogeochemical cycles and are of serious concern because of their non-biodegradable nature. Biomagnification leads to an increase in the concentration of heavy metals in the food chain.[59] Thus, there is a demand for their removal and for the development of ecofriendly techniques. Various techniques such as RO, ultrafiltration, ED, chemical precipitation, and ion-exchange are involved in the removal of heavy metals but these techniques have disadvantages such as high energy requirements, incomplete metal removal and production of harmful waste products.[60, 61]

Biosorption is a promising substitute for heavy metal removal from water. Biosorption is a physico-chemical interaction that occurs between a metal and microbial cell.[62] Biosorption comprises two words: "bio" for biological entity and "sorption" for adsorption of heavy metal ion. Biological entities such as algae,[63] fungi,[64] yeasts,[65] exhausted coffee,[66] cork biomass,[67] waste tea,[68] seaweed,[69] mustard seed cakes,[70] and bacteria[71] are used to adsorb heavy metals ions present in water. Biosorption is a biological approach for treating water from contaminates, and it involves two phases: a solid phase (sorbent; biological material) and a liquid phase comprising a dissolved species (sorbate; metal ion). The sorbent attracts and binds to the sorbate due to its higher affinity for sorbate. This continues until an equilibrium is attained between the two. An abundance of solute molecules in the solution creates a driving force, and the heavy metals get adsorbed on the biomass surface. In this way, biosorption takes place. The mechanism for biosorption falls into two categories: metabolism dependent and non-metabolism dependent. The location of the sorbate species falls into three categories: extracellular accumulation/precipitation, cell surface sorption/precipitation and intracellular accumulation. Transport of the adsorbed ions across the membrane occurs in the same manner by which the metabolically important ions (sodium, potassium, and magnesium) are transported. The mechanisms involved in transportation are physical adsorption, ion exchange and complexation.[60] Table II lists the different biological species used to remove various heavy metals.

3.1.1. Biosorption Procedure

The origin of the biomass is a primary factor for selection. One can select biomass from activated sludge, microorganisms from their natural habitat, agricultural products, sea weeds and molds. After proper selection, the biomass is pretreated by using various methods such as heat treatment (for exposing additional metal binding sites), employing alkalis, acids, enzymes (for destroying unwanted components) and washing with a detergent. The next essential step is immobilization of the biomass, which increases the shelf life of the biosorbents and makes them more convenient for use. The commonly used immobilization matrix are calcium alginate,[90] polyurethane,[91] silica[92] and polyacrylamide.[93] For lowering the cost and recovery of metals, desorption is required. The process of desorption should yield the metal in a concentrated form, should not cause any damage or physical change to biomass and, restores the biosorbent close to its original state for efficient reuse. For removing metals from biomass, dilute mineral acids such as HCl, H_2SO_4, or HNO_3 are used.[94–96]

Table II. Different biological species that has been used to adsorb various metals, along with references.

Microorganisms	Metal Adsorbed	Ref.
Chlorella emersonii	Cd	[72]
Sargassum muticum	Cd	[73]
Ascophyllum sargassum	Pb, Cd	[74]
Ulva reticulate	Cu(II)	[75]
brown sea weeds	Cr	[76]
Ecklonia species	Cu(II)	[77]
Phanerochaete chrysosporium	Ni(II), Pb(II)	[78]
Aspergillus niger	Cd	[79]
Aspergillus fumigatus	Ur(VI)	[80]
Aspergillus terreus	Cu	[81]
Penicillium chrysogenum	Au	[82]
Saccharomyces cerevisiae	Ur	[83]
Saccharomyces cerevisiae, Kluyveromyces fragilis	Cd	[84]
Saccharomyces cerevisiae	Hg(II) and methyl mercury	[65]
Bacillus polymyxa	Cu	[85]
Eschereria coli	Hg	[86]
Eschereria coli	Cu, Cr, Ni	[87]
Bacillus coagulens	Cr(VI)	[88]
Pseudomonas species	Cr(VI), Cu(II), Cd(II), Ni(II)	[89]

3.2. Nano-Adsorption

Adsorption is a surface phenomenon whereby molecules of a substance (adsorbate) adsorb on some solid surface (adsorbent). Various factors affecting adsorption are temperature, the nature of the adsorbate and adsorbent, the presence of other impurities, particle size, contact time and chemical environment. Nanomaterials have proved to be excellent adsorbent materials due to their exotic properties that include small size, catalytic potential, high reactivity, larger surface area and a large number of active sites for interaction with various impurities. These properties contribute toward their exceptional adsorption capacities.

Mercury is a highly toxic substance. Its harmful effects were first reported in 1956, when accumulation of methyl mercury caused Minamata disease in fishes present on the sea coast of the city of Minamata.[97, 98] Mercury is carcinogenic and neurotoxic, and can lead to memory loss and decreased fertility rate in adults.[99, 100] Worldwide, mercury contamination has been reported in numerous countries, including the United States, Canada, Germany, Great Britain, Australia, China, India, Israel, Japan, Korea, and Kazakhstan.[101, 102] The maximum permissible limit for mercury discharge set by the World Health Organization (WHO) is 0.001 mg/l, whereas it is 0.01 mg/l in India. In the industrial areas of India, its concentration ranges between 0.058 to 0.268 mg/l, which is a shocking rate.[103, 104] Common methods used for removal of mercury-contaminated water are adsorption, ion exchange, precipitation, membrane filtration and bioremediation.[104, 105] For mercury removal, silver NPs supported on activated alumina and protected by mercaptosuccinic acids provide a practical solution. At 5–6 pH and room temperature, a high removal ability of mercury is achieved: 0.8 g Hg^{2+} removal per g of Ag.[104] Alumina-supported gold NPs are excellent candidates for removal of Hg(0) from water. Before this, mercury (Hg^{2+}) must be reduced to Hg(0) by $NaBH_4$.[105] The reduction potential for Hg^{2+} and Ag^{+} are 0.85 V and 0.80 V respectively. For bulk silver, Hg^{2+} does not show high reactivity, but for nanosized silver the reactivity increases with decreased reduction potential due to the decrease in size.[106]

The iron oxide (α-Fe_2O_3) NPs have been used to purify the water from aluminum (Al^{3+}), arsenic (As^{3+}), cadmium (Cd^{2+}), cobalt (Cd^{2+}), copper (Cu^{2+}) and nickel (Ni^{2+}). Through experiments, it has been observed that iron oxide NPs are more effective for removal of As^{3+} and Cu^{2+} than other metals. Maximum adsorption is achieved for all the metals within just 5 minutes. It was found that at low pH, the iron NPs are positively charged and negatively charged at relatively high pH. So the metals are repelled and thus removed due to electrostatic repulsion.[107]

Magnesium oxide is an efficient chemisorbent for organophosphorus, chlorocarbons and acidic gases.[108] It is used in waste treatment plants, as additives in paint products and in catalysis.[109] The most important aspect of MgO is its ability to remove fluoride from drinking water. Nano MgO is a powerful candidate for defluoridation of polluted drinking water as it is independent of normal pH variations found in drinking water.[110] Nanomagnesia (3–7 nm) synthesis by a self-propagated combustion route provides the best choice by lowering its synthesis cost.[111] Fluoride removal by nanomagnesia followed a pseudo-second-order kinetic equation. A proposed household defluorination unit was effective in removing fluoride and controlling the pH below the permissible limit. The total dissolved solid level is reduced after treatment.[110]

CNTs were first reported by lijima in 1991.[112] CNTs are hollow cylindrical rolled sheets of graphite with outer diameters in the nanometer range (1–100 nm) and lengths of a few centimeters. These have unique electrical properties, exceptional adsorption and mechanical properties, a large specific surface area and high chemical stability.[113–116] CNTs are of great interest for researchers as an adsorbent. CNTs are relatively new adsorbents that can adsorb trace pollutants from wastewater. CNTs have an exceptional sorption capability due to their high surface-to-volume ratio and controlled pore size distribution. Researchers found that both the surface functional groups and the nature of the sorbate determines the adsorption capacity of CNTs.[117] The adsorption of polar compounds is favored by the presence of functional groups on the CNT surface such as carboxylic, lactonic and phenolic groups[117, 118] and involves chemical interactions whereas adsorption of non-polar compounds is favored by unfunctionalized CNTs[117, 119, 120] and involves physical interaction. A porous structure and certain functionalities provide them higher adsorption than other forms of carbon. Functionalization of CNTs by oxidation boost their adsorption by introducing new functional groups on the surface such as –OH, –COOH and $>C{=}O$.[121, 122] Amino-functionalized multi-walled CNTs (MWCNT) showed best adsorption capacity for Cd^{2+}.[123] Single-walled CNTs (SWCNTs) are also efficient in removing viruses at higher ionic strengths.[124] Several reports are available that reflect the use of CNTs for heavy metals removal such as Pb^{2+},[125, 126] Cu^{2+},[126, 127] Ni^{2+},[128] Zn^{2+},[129] Cd^{2+},[130] arsenate,[131] fluoride,[132] thallium,[133] and organic compounds such as xylene,[134] dioxin,[135] trihalomethanes,[136] 1,2-dichlorobenzene,[137] and 2,3-dichlorophenol.[138] In 2001, Long and Yang first reported that CNTs are more efficient for removal of dioxins than activated carbon.[139] In 2003, Peng et al. first reported the removal of 1,2-dichlorobenzene from water by using graphitized and as-grown CNTs as adsorbents.[137] For removal of direct dyes, numerous adsorbents such as algal,[140] compost,[141] wheat shells,[142] bentonite,[143] soy meal hulls,[144] Fe(III)/Cr(III) hydroxide,[145] biogas residual slurry,[146] almond shells,[147] coir pith,[148] and orange peel[149] have been examined. In 2008, Kuo et al. reported the adsorption of direct dyes such as C.I. Direct Yellow 86 (DY86) and C.I. Direct Red 224 (DR224) from aqueous solutions using CNTs.[150] For Ni(II) removal from wastewater various adsorbents such as olive stone waste,[151] bagasse,[152] activated carbon,[153] husk of Lathyrus sativus,[154] crab shells[155] and mordenite[156] have been reported as reasonable adsorbents with some limitations because of their low adsorption capacities. In 2008, Wang et al. reported the adsorption of Ni(II) on oxidized MWCNTs.[128] MWCNT-zirconia nanohybrids were reported for removal of fluoride[157] and arsenic[158] from drinking water. The importance of this nanohybrid lies in the fact that its sorption capacity was independent of pH over a wide range. Adsorption is explained by the Langmuir and Freundlich models. However the rate of arsenic removal by MWCNT–ZrO_2 was two to three times slower than that for iron-coated MWCNTs but its adsorption capacity was nearly two to five times higher. In 2013, Pu et al. first reported the adsorption and desorption of thallium ((I) on MWCNTs[133]). The adsorption of Tl(I) on MWCNTs is pH and ionic strength dependent.

3.3. Nanoscale Photocatalysis

Wastewater effluents from factories, industries, laboratories and domestic sources discharge wastes containing various organic compounds such as pesticides, herbicides, azo dyes, and phenols.[159–162] These contaminants not only harm microorganisms and aquatic life, but also cause serious threats to human beings.[163] Prior to disposal discharged wastes need to be treated properly to reduce their harmful effects. These toxicants contaminate the drinking water when they enter the ground and surface water.[164] Human ingestion of chlorophenol via orally, dermally, or through the respiratory tract has been established by tracking the high levels of chlorophenols in urine.[159] Volatile organic chemicals cause specific diseases of the liver, heart, stomach, erythrocytes, and also cause damage to the brain.[165] Nitrobenzene mild exposure may cause mild irritation to skin or eyes; however, excessive exposures can result in methemoglobinemia, a disease in which the oxygen-carrying ability of the blood is reduced.[166] For the treatment of chemical contaminants in wastewater effluents various methods such as chemical oxidation, biological methods, combustion, flocculation, adsorption on carbon (granular activated), air stripping and precipitation have been employed so far. These methods have limitations such as high cost and ineffectiveness. The biggest drawback instead is the degrading of the organic chemicals completely, converting them into secondary contaminants.[167–171]

Photocatalysis has emerged as a green technology for the complete mineralization of hazardous organic chemicals to water, carbon dioxide and simple mineral acids[172, 173] and occurs at room temperature. Photocatalysis is a light-induced reaction which is enhanced by the presence of a catalyst. When light radiation falls on the surface of metal, electrons absorb it and get excited. An ideal photocatalyst should be nontoxic, stable, inexpensive, easily available and highly photoactive.[173] Various semiconductor NPs and nanocomposites are reported for the photocatalytic degradation of organic contaminants present in wastewater, which include TiO_2, ZnO, ZnS, Zn–CeO_2, Si–Ti, and CdS-TiO_2.[159, 160, 163, 173, 174] The photocatalytic processes are affected by different parameters such as pH, oxidizing agents, catalyst loading, doping content and the influence of calcinations temperature.[175] Table III represents different parameters that affect photocatalytic degradation of some pollutants.

Nanocrystalline photocatalysts are nanosized semiconductor particles with diameters in the 1 to 10 nm range. The main advantage of nanosized semiconductor particles is the quantum-size effect, which increases the band-gap energy with a decrease in the size. When photons with energies at or above the band gap strike the surface, valence electrons get excited and jump to the conduction band. The excited NPs undergo charge separation and oxidize the organics at the semiconductor surface.[159] Photodegradation have many advantages over other water purification methods and are depicted in Figure 1.

TiO_2 has emerged as the best photocatalyst for degradation of organic chemicals using the UV region, because it is easy to prepare, recyclable, tolerates both acidic and alkaline solutions, is radiation stabile and does not require any strong oxidizing agent.[161, 162] Commonly found three-dimensional structures of TiO_2 are anatase, rutile and brookite. TiO_2-based photodegradation of 2-propanol, *n*-carboxylic acid, phenolic compounds (phenol, 2,4,6-trichlorophenol, 2,3,5-trichlorophenol and 4-chlorophenol have been reported. Generally anatase is considered more efficient over rutile; however, Tsai et al. lab-made rutile TiO_2 phase showed the highest activity compared to the anatase phase and completely oxidized the phenol and chlorophenols to CO_2. This occurred due to the presence of a large number of O–H groups, which stabilizes both holes and electrons from recombination in both the valence and conduction bands respectively.[162] However, a wide band gap of TiO_2 (3.2 eV) limits its use at the UV, region and only a small fraction of UV reaches the earth surface restricting the large scale degradation.[172]

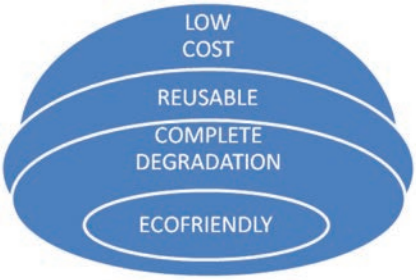

Figure 1. Advantages of photocatalytic degradation over other methods.

Several approaches has been investigated to make use of the visible light region and to increase the photoactivity of TiO_2 including increasing the surface-area-to-volume ratio with the purpose to improve light absorption.[161] Further, sensitization of TiO_2 with organic and organometallic dyes seems to be unsuccessful due to their instability. These sensitizers show visible light absorption and blue shift by altering their size.[173] CdS-sensitized TiO_2 is efficient in photodegradation of phenazopyridine but leaching of cadmium ions in water prevents its use for degradation as cadmium itself is hazardous.[174] Also, doping with nonmetals such as carbon, fluorine, nitrogen and sulfur[176–179] or with metal ions affects the interfacial charge transfer and electron-hole recombination mechanism. With a dopant size of 1–2 nm the highest enhancement in photoreactivity was reported.[180] During the degradation of organic water pollutants by the TiO_2 photocatalyst, hydroxyl radical is the primary oxidant. Based on the OH attack, different mechanisms are suggested.[181]

An alkyl-modified silica-titania composite material was introduced that shows a high affinity to hydrophobic contaminants in water and have good photodegradation stability under visible and UV radiation.[182] In comparison to commercial Degussa P-25 TiO_2, the combustion-synthesized nano-TiO_2 is more efficient for photocatalytic degradation because of its crystallinity, more surface hydroxyl groups, higher surface area and optical absorption at higher wavelength.[183]

ZnO is also a large band-gap semiconductor. ZnO has an advantage over TiO_2; i.e., its strong emission in the visible region that mostly occurred from anionic vacancies. ZnO emission is very sensitive to organic compounds, such as chlorinated phenols, present in its immediate vicinity. ZnO film-based sensors are used to monitor the decontamination

Table III. Parameters affecting photocatalytic degradation of some pollutants.

Pollutant type	Photocatalyst	Light source	Tested pH range	optimum pH	Range of catalyst weight	Optimum catalyst weight (g/l)	Percent degradation
Fast green FCF	TiO_2	UV	3–11	4.4	0.5–4.0	Continuous increase	Not indicated
Methyl orange	Pt–TiO_2	UV	2.5–11	2.5	0.5–6.0	3	90.5
Methyl orange	SiO_2–TiO_2	Visible	2–11	2.5	0.4–5.0	Increase	Not indicated

Source: Reprinted with permission from [175], U. G. Akpan and B. H. Hameed, *J. Hazard. Mater.* 170, 520 (**2009**). © 2009, Elsevier.

Table IV. Types of heavy metals and their effect on human health.

Pollutants	Major sources	Toxicity	Permissible level (ppm)
Arsenic	Pesticides, fungicides, metal smelters	Cancer in liver, kidneys, lungs, bladder; skin lesion and dermatitis	0.02
Mercury	Pesticides, batteries, paper industry, mining	Damage to nervous system, protoplasm poisoning	0.01
Fluoride	Pesticides, batteries, mining	Fluorosis, liver, thyroid, bone disease, lesion of endocrine glands	15
Lead	Paint, pesticide, smoking, automobile emission, burning of coal	Liver, kidney, gastrointestinal damage, mental retardation in children	0.1
Zinc	Refineries, brass manufacturing, metal plating, plumbing	Zinc fumes have a corrosive effect on skin, cause damage to nervous system membrane	15
Manganese	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system	0.26
Cadmium	Welding, electroplating, pesticide fertilizer Cd–Ni batteries, nuclear fission plants	Kidney damage, bronchitis, gastrointestinal disorders, bone marrow, cancer	0.06
Chromium	Welding	Allergic dermatitis	0.5

Sources: Reprinted with permission from [5], T. A. Kurniawan, et al., *Crit. Rev. Environ. Sci. Technol.* 42, 1233 (**2012**). © 2012, Taylor and Francis Group; From [60], H. K. Alluri, et al., *Afr. J. Biotechnol.* 6, 2924 (**2007**). © 2007, Academic Journals.

process for determining the quality of water.[159] ZnO-CeO_2 nanostructures are quite easy to synthesize, are low cost, have high sensitivity to ethanol and show high photocatalytic degradation for organic compounds such as methylene blue and acridine orange.[160]

A novel $CaBi_2O_4$ semiconductor is a visible-light-driven new green heterogeneous photocatalyst for the degradation of various organic contaminants such as acetaldehyde and methylene blue dye. Within 20 min of visible light irradiation, $CaBi_2O_4$ oxidized 65 percent of acetaldehyde into CO_2. Oxidation gradually increased and after 2 hrs, the concentration of acetaldehyde decreased from the initial value to 0 ppm.[172] Table IV represents various sources and the bad effects of heavy metals on human health beyond their permissible levels.

4. DISINFECTION

From years, disinfection has been an affordable and robust method for obtaining safe water against infectious pathogens. Waterborne pathogens such as helminthes, protozoa, rickettsia, viruses, fungi, bacteria, and prion have a devastating effect on human health, particularly in developing countries.[184, 185] Four hundred thousand cases of acute gastroenteritis were reported in Milwaukee in 1993 caused by Cryptosporidiosis infection due to contamination of the public water supply.[186] Disinfection provides a ray of hope for fighting against the water-borne infectious agents in drinking water. Commonly used disinfectants for treating drinking water are chlorine, ozone, chloramines and chlorine dioxide. Several waterborne pathogens have been decimated and uprooted by disinfectants but still the use of disinfectants is not working as new pathogens take hold in water, and disinfection byproducts (DBPs) formed during treatment are harmful. Several byproducts were reported with various adverse effects; some are even carcinogenic. New strategies are needed to balance the microbial control and DBPs risks. Nanomaterials are currently being investigated for water disinfection.[187]

Over the last few decades, viruses together with prions have become a major concern because they cause the majority of fatal diseases. Enteric viruses are not easy to detect, and free chlorine is ineffective over viruses. Hence, these are given less attention in comparison to bacteria and protozoan parasites.[2] Silver NPs are effective against viruses and bacteria.[188–190] Zero-valent silver are found effective in inactivation of HIV-1 virions.[188] Biogenic silver (zero-valent silver NPs with lactobacillus fermentum) has been found to be very effective against enterobacter aerogenes-infecting bacteriophage and is used for disinfection in drinking water supply.[191]

Chlorine is the most universal disinfectant used by almost 100 percent of small water systems and about 80 percent of large water systems. Large water systems use about 20 percent chloramines, 5 percent chlorine dioxide and 2 percent ozone.[186] Chlorine is ineffective in treating pathogens such as Cryptosporidium parvum and Mycobacterium avium. M. avium is omnipresent in biofilms.[2] Recent research reports that ozone is much more effective in treating Cryptosporidium than chlorine.[186] Current U.S. disinfection regulations demands for alternative technologies other than chlorine, needed to control C. parvumoocysts with minimal DBPs formation.[192, 193] For the persuasive treatment of waterborne pathogens, new disinfection strategies are now available. A multiple-barrier approach based on the physico-chemical removal in addition to effective photon-based or chemical inactivation is available. Instead of free chlorine, a combination of chlorine with UV/ozone is being used in many drinking-water systems as both UV and ozone are very persuasive in controlling C. parvumoocysts. The combination even helps to regulate DBP formation.[2]

Disinfection byproducts produced by disinfectants:

(1) Chlorine reacts with organic contaminants and humic acid, forming a chlorinated product. This product, with

other halogens, produces halogenated DBPs such as haloacetonitriles and iodoacetic acid, which are toxic and carcinogenic.[186, 194, 195]

(2) Ozone and chlorine dioxide produces the oxygenated species of DBPs.[186]

(3) Chloramine introduces nitrogen species such as cyanogen chloride as by-products.[186]

The present demand for developing new, robust and safe alternatives to chlorine (free and combined) and UV disinfection for the treatment of viruses in water supplies is possible through the proper understanding of virus inactivation. Free chlorine and UV light reacts with amino acids present in capsid as well as nucleic acid, but the exact mechanism of inactivation is not known.[196, 197]

A carbon-based nanomaterial, buckminsterfullerene (C_{60}) is relatively insoluble in water but can find its way in water through hydrophilic molecules encapsulation or forming nanoscale, stable water-soluble aggregates; i.e., nC_{60}. This nC_{60} was reported to have antimicrobial activity against various bacteria.[198–200] The antibacterial activity of fullerenes is not influenced by its photosensitive nature, because the ability of nC_{60} to kill bacteria remains the same under light or dark conditions, even under anaerobic/fermentative conditions. Table V lists some examples of bacteria that show antibacterial activity.

In developing countries, non-governmental organizations promote centers of disease control and prevention systems in rural areas using sodium hypochlorite as a disinfectant. They also came out with the use of visible light irradiation for destroying the waterborne pathogens present in polyethylene terephthalate bottles.[201]

Silver shows an antibacterial mechanism due to its interaction with phosphorus and sulfur, which are the thiol groups (S–H) present especially in cysteine and various other biochemical compounds.[202] Damage to bacterial proteins, dimerization of DNA and interruption in electron transport chain occurred by the interaction of ionic silver with thiol groups forming S–Ag or disulfide bonds.[203–205] Even without releasing silver ions, silver NPs may kill some bacteria and viruses. From total silver, silver ion dissociation accounts for approximately 1 percent, which concludes that toxicity cannot be explained only by the release of silver ions; in fact some mechanism exist in NPs that results in toxicity.[206]

Table V. MIC of fresh nC_{60} with different bacteria.

Bacteria	Description	MIC (mg/l)
Bacillus subtilis	Gram +, soil	0.01–0.05
Burkholderia cepacia	Gram −, pathogen	0.0125–0.025
Desulfovibrio desulfuricans	Gram −, anaerobe	0.1–0.2
Escherichia coli	Gram −, potential pathogen	0.01–0.05
Pseudomonas aeruginosa	Gram −, ubiquitous pathogen	0.05–0.066
Ralstonia pickettii	Gram −, pathogens	0.025–0.0375
Streptomyces albus	Gram +, soil	< 0.05

Source: Reprinted with permission from [200], D. Y. Lyon, et al., *Water Sci. Technol.* 57, 10 (**2008**), © 2008, IWA Publishing.

A new innovative disinfection method introduces the combined use of light energy; i.e., photons and engineered nanostructures. Nanophotocatalysts are a good candidate for disinfection. They utilize both UV and visible light and destroy the microorganisms, including viruses, by a simple catalysis process.[207] TiO_2, ZnO, TiO_2 doped with nitrogen (TiON) or a transition metal such as palladium are the most commonly used photocatalysts. For better and faster removal of pathogens from water, improved knowledge about the interaction of pathogens and photocatalyst surface is necessary. Immobilization of antiviral photocatalysts is possible on various materials fibers and foams.[208–210] The visible-light photocatalysts may also be incorporated into membranes and reactors using sunlight as the main source of photons.[211–213] The best part of using photocatalysts in membranes and reactors is that they destroy all microorganisms including bacteria, viruses, protozoans and their oocyts without forming any type of harmful product, such as DBPs, and provides an ecofriendly alternative.[214] List of waterborne pathogens categorized by their relative infectivity, persistence in water, and resistance to common disinfection methods[215] is shown in Table VI.

5. FATE, TRANSPORT AND RISKS ASSOCIATED WITH ENGINEERED NANOMATERIALS

With the rapid advancement in nanotechnology, large numbers of engineered nanomaterials (ENMs) may inevitably enter the environment. Fate and transport of ENMs is determined by the processes involved in these transformations. The processes involved are photochemical transformation, dissolution and precipitation, adsorption and desorption, oxidation and reduction, combustion, biotransformation, agglomeration and abrasion.[216–220] A good knowledge of the bioavailability, mobility and ecotoxicity of ENMs is required to assess the environmental risks.[221] The surface properties of ENMs are crucial for their aggregation behavior, mobility in aquatic and terrestrial systems and for their interactions with algae, plants and fungi.[222] Nanomaterials (NMs) are formed by natural sources, anthropogenic activities and engineered nanomaterial production.[221] Natural sources such as volcanos, fire, weathering, and mineralization by microorganisms produce NMs. Fullerenes and CNTs were found in geological deposits and in 10,000-year-old ice cores from Greenland, which is evidence that even before the use of fires by humans NMs were present in ambient air.[223–225] Anthropogenic activities such as emissions from vehicles, factories, cooking, wood burning and daily-used products have more than doubled the flux of NMs into the atmosphere.[226] Engineered nanomaterials are man-made and synthesized by various biological, chemical

Table VI. Characteristics of waterborne pathogens.

Pathogen	Associated disease	Relative infectivity	Persistence in water	Resistance to disinfection
	Bacteria			
Burkholderia pseudomallei	Melioidosis	Low	May multiply	Low
Campylobacter jejuni, C. coli	Gastroenteritis	Moderate	Moderate	Low
Escherichia coli—pathogenic	Gastroenteritis	Low	Moderate	Low
E. coli O157:H7 (entero haemorrhagic)	Gastroenteritis, hemolytic-uremia	High	Moderate	Low
Legionella pneumophila	Legionnaires' disease	Moderate	May multiply	Low
Non-tuberculous mycobacteria	Pulmonary disease, skin infection	Low	May multiply	High
Pseudomonas aeruginosa	Pulmonary disease, skin infection	Low	May multiply	Moderate
Salmonella Typhi	Typhoid Fever	Low	Moderate	Low
Salmonella enterica	Salmonellosis	Low	May multiply	Low
Shigella spp.	Shigellosis	High	Short	Low
Vibrio cholerae	Cholera	Low	Bioaccumulates	Low
Yersinia enterocolitica	Gastroenteritis	Low	Long	Low
Clostridium botulinum	Botulism	High	Moderate	Low
Mycobacterium marinum	M. marinum infection	High	May multiply	High
Leptospira spp	Leptospirosis	High	Moderate	Low
	Viruses			
Adenoviridae virus	Gastroenteritis, respiratory infection	High	Long	Moderate
Enteroviruses	Gastroenteritis	High	Long	Moderate
Poliovirus	Poliomyelitis	High	Long	Moderate
Coxsackievirus	Meningitis	High	Long	Moderate
Astroviruses	Gastroenteritis	High	Long	Moderate
Hepatitis viruses A, E	Hepatitis	High	Long	Moderate
Noroviruses	Gastroenteritis	High	Long	Moderate
Sapoviruses	Gastroenteritis	High	Long	Moderate
Rotavirus	Gastroenteritis	High	Long	Moderate
Coronavirus	SARS (Severe Acute Respiratory Syndrome)	High	Long	Moderate
	Protozoa			
Acanthamoeba spp.	Keratitis, Encephalitis	High	May multiply	Low
Cryptosporidium spp.	Cryptosporidiosis	High	Long	High
Cyclospora cayetanensi	Gastroenteritis	High	Long	High
Entamoeba histolytica	Amoebiasis	High	Moderate	High
Giardia lamblia	Giardiasis (Beaver fever)	High	Moderate	High
Naegleria fowleri	Primary amoebic meningoencephalits	Moderate	May multiple	Low
Toxoplasma gondii	Toxoplasmosis	High	Long	High
	Helminths			
Dracunculus medinensis	Dracunculiasis (Guinea worm disease)	High	Moderate	Moderate
Schistosoma spp.	Schistosomiasis	High	Short	Moderate
Tapeworms of genus Taenia	Taeniasis	High	Short	Moderate
Ascaris lumbricoides	Ascariasis	High	Short	Moderate
Enterobius vermicularis	Enterobiasis	High	Short	Moderate
Fasciolopsis buski	Fasciolopsiasis	High	Short	Moderate

and mechanical methods for use in various fields of food packaging, agriculture, medicine, vehicles, sports, oil and paints, cosmetics, coatings etc. ENMs include metal and alkaline earth metals (such as Ag, Fe, Pt, Sn, Al, Cu, Zr, Se, Ca, Mg), metal oxides (such as TiO_2, ZnO, CeO_2, SiO_2, Al_2O_2), carbon materials (such as carbon black, fullerenes, CNTs, graphene) and miscellaneous compounds (such as nanoclay, ceramic, quantum dots and organic NPs).[227] ENMs are characterized by various techniques such as scanning emission microscopy, transmission electron microscopy, atomic force microscopy, elemental analysis electron loss spectroscopy, energy dispersive X-ray spectroscopy, X-ray diffraction, Fourier transmission infrared spectroscopy, size-exclusion chromatography, capillary electrophoresis, nuclear magnetic resonance, dynamic light scattering, multi-angle laser light scattering, etc.

5.1. Transformation of Nanomaterials in Water

The fate of nanomaterials in water is governed by dispersability/solubility, mode of interaction between biotic–abiotic factors and nanomaterials. Generally NPs settle down more slowly compared to other larger particles but due to their high surface-area-to-mass ratio, they sorb to soil and sediment particles.[228] These can easily be removed from the water column. CNTs and underivatized fullerenes are extremely insoluble in water.[229] Until a physical mixing occurs within the water body, they exist on the water surface or at the water sediment interface. Carbon nanomaterials usually interact with dissolved organic materials

(DOM) in the water, which definitely affects their presence in the water column. The as-manufactured form of ENMs is termed pristine ENM (P-ENM).[220] Various transformation occurs in the P-ENM and results in other forms of ENMs; i.e., product-modified ENM (PM-ENM), product-weathered ENM (PW-ENM) and environmentally-transferred ENM (ET-ENM).[220] The processes responsible for transformation are the following:

The incident light of sufficient frequency falls on the ENMs and induces the excitation of ENMs, creating photoreactive species and the product-modified ENMs are produced. This process is called "photochemical transformation." This may alter the interaction between ENM and environment. For example, when photoactivation of TiO_2 occurs, its binding to the dissolved organic matter is altered.[220, 230] Oxidation/Reduction is favored by thermodynamics.[220, 231] Both dissolution (release of ions that are soluble in water) and precipitation (deposition of dissolved species) also modify the ENM species causing alteration in their interaction.[220, 232–237] Adsorption (attachment of substances to the solid surface) occurs by Van der Waals interaction,[238] chemical bonding[239] and electrostatic interaction.[240] This process play a vital role in water system as the particle may act as a vector if it adsorbs some small microorganism or contaminants on its surface.[230, 241–245] Sometimes desorption of the sorbed species may occur if the concentration of adsorbent in lower in media. Combustion (burning in presence of air) results in oxidation of the components of ENM and may alter the PW-ENM interaction due to adsorption of foreign compounds on it.[220]

5.2. Ecotoxicity of Engineered Nanomaterials (ENMs)

5.2.1. ENMs Leach Into Treated Water

While ENMs are expected to have several benefits, it is crucial that potential risks are identified and cured to ensure proper use of them. NPs are likely to enter surface water during the production, usage, and disposal of NP-containing products. However, only a few studies have investigated the leached NPs from treated water. although this is an important measure in the healthy development of nanotechnology-related products.[246] It has been reported that the leached NPs can be removed by conventional treatment, but that the removal efficiencies depend on water characteristics such as pH or impurities as well as NPs characteristics.[247, 248] These factors complicate the ENM removal process, specifically if conventional techniques are employed.

The estimated NP production rate[249, 250] is 500 tons/year for silver and 50,000 tons/year for titanium dioxide (TiO_2). Concentration of NPs in some natural surface waters is estimated to be in the nano-micro g/l scale.[250, 251] Since 1990, the number of patents for NP products has doubled every two years.[252] So the concentrations may increase with an increase in production rate. It has been reported that surface drinking water contains NPs (253), but it has not yet been determined whether this occurred naturally or originated from engineered NPs. It is expected that with an increase in research laboratories' capabilities, the contamination sources will be identified and removed in the process.

NPs such as silver, TiO_2, and zinc oxide (ZnO) are used for water purification, especially in the developing world. The findings of laboratories suggest that these antibacterial particles are very efficient in treating drinking water[254, 255] and could replace chemical disinfectants that can produce harmful byproducts.[255] Silver NPs are being embedded into paper and ceramic filters for their antimicrobial properties during water treatment.[256, 257] Already, many groups are using ceramic filters impregnated with silver NPs to remove pathogens from drinking water in the rural areas of developing countries.[258]

Water treated using filter paper coated with nanosilver showed a detectable level of silver NPs, but it was below the U.S. Environmental Protection Agency and World Health Organization guideline of 100 ppb.[256] Ceramic filters coated with silver NPs showed that the level of NPs in treated water is higher than the recommended guidelines.[257] As has been highlighted earlier, while the NPs are effective at removing the microbial contaminants, it is important to attain the end product free from any harm to human health.

It has been reported that rats after ingesting TiO_2 NPs contaminated water for 5 days showed DNA damage.[259] Similar data on organs damage of rats were also reported by some other laboratories.[260–262] The authors[260–262] observed damage in the liver, kidneys and brain of rats that ingested TiO_2 NPs.

Some of the properties that make ENMs a unique material have given rise to concern that they may harm human health. Exposure to ENMs has been reported that initiate some health concerns, including pulmonary inflammation,[263–266] genotoxicity,[267, 268] carcinogenicity,[269, 270] and circulatory effects.[271, 272] Several types of ENMs, including titanium dioxide and CNTs, are known to produce pulmonary inflammation and fibrosis in animals.[264, 265] These and other observations have emphasized the importance of assessment of exposure and delineating health effects possibly induced by exposure to ENMs.

5.3. Water Pollution

Different laboratories are working on aquatic pollution that may be caused by ENMs. Toxicity was reported in Daphnia magnato when exposed to CNTs.[273] Oberdorster et al. reported toxicity of C_{60} (fullerenes) on freshwater crustaceans D. magna, fish (Pimephales promelas and Oryzias latipes) and the marine copepod Hyalella azteca.[274, 275] A few studies have been performed with fish, e.g., zebrafish embryos (Daniorerio) when these were exposed to CNTs.[276] Exposure of the estuarine copepod (Amphiascus tenuiremis) to CNTs was studied by Templeton et al.[277] Ecotoxicological studies of carbon nanomaterials present a major difficulty because carbon nanomaterials have poor aqueous solubility and require some combination of chemical dispersants, stirring or sonication to maintain them in an aqueous solution. The choice of dispersant is problematic, since some of the best dispersants from a chemistry point of view are also likely to be toxic to organisms. For example, tetrahydrofuran (THF) is a good dispersant of C_{60} fullerenes and CNTs, but there are concerns about its toxic effects. Table VII represents ecotoxicological effects of engineered nanomaterials.

5.4. Human Health Risk Assessment

Risk assessment is defined as risk quantitatively determining the probability that a contaminant will cause harm given particular use scenarios. A major difficulty scientists have encountered in explaining the risk associated with ENMs is that the toxic effects are complex in nature and are not only a function of ENM mass. The toxicity relates to particle size, aggregation, solubility, surface chemistry, etc.[293–298] In addition, the physico-chemical characteristics of ENMs and the correlation of ENM characteristics and biological effects is not fully understood.[299] ENMs are also not a uniform group of substances.[300, 301] They are produced from many different raw materials, in many different forms and sizes, and coated with many different formulations. The health assessment of such diverse materials requires validated analytical methods, both for their characterization in bulk samples and for the detection and measurement of ENMs in the workplace. Thus, the development of human health risk assessment tools lags way behind the growth of nanotechnology products, and the gap will continue to increase as shown in Figure 2.[302,303]

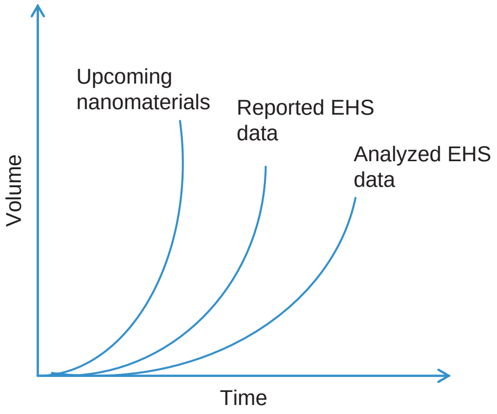

Figure 2. Upcoming nanomaterials, reported, and analyzed environment, health and safety (EHS) data.

Nanotechnology presents enormous challenges to risk management, and existing risk models are not up to the challenge. Nanotechnology demands a more incremental, multi-actor, and multi-component oversight model. Marchant et al. (2008) have suggested an incremental regulatory pyramid for ENMs and nanotechnology regulatory activities, which start with information gathering and move forward with a goal of being registered as hard regulatory actions and legislation.[303]

The unique physical and chemical properties of engineered nanomaterials deepen the challenge regulators and industry face in managing and understanding the potential risk from nanomaterials. Human health and environmental effects are intimately linked and their functions call for including both in assessing risk.[304] Assessing the risks of nanotech advancements is way behind in terms of developing those advancements. Klaine et al. suggest few reasons for this gap: The scientific research does not yield adequate data for risk assessments, and less than 5 percent of the funds spent on development of new

Table VII. Ecotoxicity of ENMs.

Nanomaterial	Test species	Effect	Measurement	Refs.
Ag NPs	Zebra fish embryos	Development and embrogenesis	Decreased	[278, 279]
Fullerenes	P.putida and B. subtilis	Bacterial membrane lipid	Growth inhibits	[280]
TiO_2	Oncorhynchus mykiss	Oxidative stress and physiological effects		[281]
Au NPs	D. magna	Intake	Retention in gut	[282]
Au NPs	Human cells	Cell death		[283]
CNTs	D. magna	Biomodification of CNTs	CNTs with natural lipid layers can be ingested	[273]
Fullerenes	D. magna	Acute toxicity		[282, 284]
Fullerenes	D. magna	Accumulation of different pollutants	Increases toxicity	[285]
Fullerenes	Zebrafish	Embryo development	Malformations	[286]
SWCNTs	Rainbrow trout	Respiratory toxicity	Toxicity increases	[287]
TiO_2 NPs	D. magna	Acute toxicity	Increase of immobilization	[288]
TiO_2 NPS	D. magna	Acute toxicity	40-percent mortality	[289]
ZnO NPs	D. magna	Acute toxicity		[290]
Uncoated alumina particles	Corn, cucumber, soyabean, carrot	Inhibited root elongation	Negative effect	[291, 292]

nanomaterials is available for research on the environmental health and safety of nanomaterials.[304] There is a need to train and recruit a new generation of interdisciplinary scientists, who not only have a background in biology, chemistry, and engineering, but also have a technical backgrounds in physics and material science. Interdisciplinary collaboration will play a crucial role in understanding and developing every aspect of nanotechnology, from synthesis to application, hazard and risk assessment.[304] An increased rate of dissolution and degradability and the presence of strongly bound aggregates indicate loss of nanoproperties.[305] Some test strategies have been developed for risk assessment of ENMs.

The risk assessment posed by nanomaterials to humans requires accurate measurements and modeling of human exposure. Measurements for nano-exposure faces many challenges. Factors such as breathing patterns and lung anatomy are well known for affecting the actual dose deposited in the lungs and air pathways. For describing exposure of nanomaterials no benchmark or standard exist. However, there is consensus that for a comprehensive health-relevant exposure assessment, a multimetric approach is needed, including mass concentration in nano, total and size resolved surface area concentration and particle number concentration, bioactivity, inhalable/respirable ranges as well as particle shape and agglomerate structure and composition. Until now, no single device met all required measuring features, so a suite of devices was needed. Presently, a new range of devices is being developed that can assess breathing zone concentrations more accurately than previous ones. New exposure models may hand over the appropriate concentrations in the breathing zone. However, much more information is needed for a dose estimate.[306–309] On the potential ecotoxic impact of ENMs on human health, further studies and extrapolation of the present data are needed to be able to clearly state the degree of ENM influence on human health and environment. In this context, more mechanistic and environmental investigations are needed to understand the potential risk of any given type of ENMs on the ecosystem and finally to help policy makers with recommendations to develop methods for an appropriate regulation.

6. CONCLUDING REMARKS

All over the world, clean and safe water demand is rapidly rising with the increased concern and awareness about the health and environment. Nanotechnology has a great potential to overcome the cost and technical capacity barriers for providing the clean water to current and future generations. With the advancement in science and technology, more techniques for water purification will be available in the coming future. Green manufacturing by using natural materials to develop nanomaterials will resolve the environmental and cost problems related to nanomaterial synthesis. It is essential to invest in the leapfrogging opportunities provided by nanotechnology to save both water quantity and quality. Many issues have been raised by different researchers related to some of the applications and properties of nanomaterials. Being very small in size, they may transfer to human body and other aquatic organisms. They may or may not be toxic depending upon the interaction, concentration, pH etc. Thus, a great effort is needed to explore every side of this new technology to have more benefits and reduce the side effects. The future of nanomaterials for wastewater treatment looks very promising and requires dedicated and sincere efforts from the scientific community, industrial enterprises and government machinery. Nanomaterials can help to a great extent for providing fast, economical, energy efficient and feasible water purification technologies.

Acknowledgment: The authors thank the Department of Science and Technology (DST) and the government of India for financial support within the framework under the international research grant DST/INT/THAIP-06/2012 dated 31-01-2013.

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Received: 25 July 2013. Accepted: 3 September 2013.