ISSN: 2501 - 2568 (2016) Volume 1, Issue 3, 246 - 270

Journal of Food Bioengineering and Nanoprocessing

open access journal

www.nanobiofoods.com

Review

received: 10.12.2015
revised: 15.02.2016
accepted: 20.04.2016
published: 02.06.2016

Nano-technology to safe clean drinking water suitable for food industries: a review

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ABSTRACT

The availability of clean water is necessary for all aspects of food production, preparation, distribution and consumption. Yet the magnitude, intensity and diversity of water pollution and the depletion of some water resources continue to grow, reducing the availability of clean, usable water and raising the potential for a water-related crisis that would have a severe impact on food processes. Nanotechnology providing a unique opportunity for water purification where they have a large specific surface area, high reactivity, size dependent properties, affinity for specific target contaminants, etc. These unique properties improve the potential efficiency of drinking water treatment that contaminated with metal ions, organic and inorganic pollutants, and microorganisms. Accordingly, different nanomaterials either at nano-powder forms include nanosorbents, nanocatalysts, nano-composites and bioactive nano-materials or nanofiltration membranes will be recruitment toward the drinking water purification to safe clean water suitable for food industries.

Keywords: *nanomaterials, water purification, membranes, water pollutants, nano-composite, nano-catalysts, food industry, bioactive nano-materials.*

INTRODUCTION

As a great challenge of this century, the guarantee of authentic clean and affordable water resources represents vital request all over the world. With respect to the extreme increment of the world's population and industrial activities beside the changes at the global climate that intimidates with water scarcity in many areas, all these aspects improve the world's challenge. Accordingly, there is an urgent need for wastewater reuse culture even as portable water resources. However, the wastewater collection systems are not designed to accommodate this new culture. Moreover, at developed countries, the infrastructure of centralized water and wastewater faces growing demands to produce higher quality water using less energy and treatment costs. So, as an attempt to apply and circulate the wastewater reuse culture, there is an urgent need for development of innovative technologies to change the systems of treatment, distribution and reuse of water and wastewater.

There is limited possibility of an increase in the supply of fresh water due to competing demands of increasing populations throughout the world; also, water-related problems are expected to increase further due to climate changes and due to population growth over the next two decades (Metcalf and Eddy, 1991). It is estimated that worldwide population will increase by about 2.9 billion people between now and 2050 (according to UN's average projections). Shortage of fresh water supply is also a result of the exploitation of water resources for domestic, industry, and irrigation purposes in many parts of the world. The pressure on freshwater resources due to the increasing world's demand of food, energy, and so forth is increasing more and more due to population growth and threats of climate change. Polluting surface/ground water sources is another cause of reduced fresh water supplies. Water accumulates different type of compounds during its use becoming wastewater and unsuitable to be reused. Water pollution with toxic compounds is one of major concerns for human health as well as for the environmental quality. Toxic substances can be due to industrial pollution, urban pollution or agricultural pollution through the application of fertilizers and pesticides. Toxic pollution can have an immediate (acute) or a chronic (long-term toxicity) impact on the environment.

The pollutants frequently found are heavy metals (cadmium, chromium, copper, mercury, lead), organic substances (solvents, hydrocarbons, dye) and/or chemical products (pharmaceutical products, personal care product)

Discharging different kinds of wastewater and polluted waters such as domestic, industrial and agricultural wastewaters into environment, especially to surface water, produce effluents which are often contaminated with harmful/poisonous substances. There are various methods for the removal of these substances. These broadly fall into three categories: Physical, Chemical and Biological. Any of these treatment processes have their own advantages and disadvantages.

Nanotechnology is the key to improve costs, efficiency and offer new functionality, products and systems as an emerging technology in water purification. The impacts of nanotechnology are increasingly evident in all areas of science and technology, including the field of food industry in terms of water management. Nanotechnology and its application is one of the rapidly developing sciences. As demand of fresh drinking water is increasing, nanotechnology can contribute noticeable development and improvement to water treatment process. Nanotechnology represents the key to improve costs, efficiency and offer new functionality, products and systems as a promising technology in water and waste water domain. The impacts of nanotechnology was clear at most areas of science and technology especially the fields of environmental and food industries. The remarkable properties of nanomaterials such as their superior surface area and pore size, optical, and magnetic properties that enhance their performance as photosensitive, catalytic and antimicrobial activate materials that provide useful features for water and wastewater applications. Accordingly, nanotechnologies will produce huge environmental and food industry benefits in terms of water management and treatment through enhancing filtering, decontamination, desalination, recycling, analysis and monitoring and sewerage systems. Advances in nano-materials engineering suggest that many of the water sector problems could be resolved or greatly ameliorate using nanosorbents, nanocatalysts, bioactive nanoparticles, and nanostructured membranes (nanofiltration membrane) among other products and processes. This review seeks to provide a more holistic view of the recent advances on the development of novel nanoscale materials and processes for remediation of polluted water contaminated by toxic metal ions, organic and inorganic solutes, bacteria and viruses to be safe for food industries.

WATER POLLUTION AND WATER POLLUTANTS

Water pollution is any undesirable change in the physical, chemical, or biological characteristics of water that can harmfully affect the health, survival, or activities of human or other living organisms. Two types of water pollutants exist: point source and non-point source. Point sources of pollution occur when harmful substances are emitted directly into a body of water. They include factories, wastewater treatment facilities, septic systems, and other sources that are clearly discharging pollutants into water sources. A non-point source delivers pollutants indirectly through environmental changes. An example of this type of water pollution is when fertilizer from a field is carried into a stream by rain, in the form of run-off which in turn affects aquatic life. Non point sources are much more difficult to control. Pollution arising from nonpoint sources accounts for a majority of the contaminants in streams and lake.

The main water pollution resources may be presented as domestic, industrial and agricultural. Domestic water pollution induced from all indoor and outdoor households activities. The characteristics of industrial wastewaters depend on the type of industry and the manufacturing process in question. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their content of specific inorganic compounds.

Generally, the contaminants presence in polluted water may be defined by its physical, chemical, and biological features. Physical consideration includes colour, odour, temperature, and turbidity. Insoluble contents such as solids, oil and grease, also, have been fall into this category. Solids may be further subdivided into suspended and dissolved solids as well as organic (volatile) and inorganic (fixed) fractions. Chemical factors associated with the organic content of waste-water include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and total oxygen demand (TOD). Inorganic chemical parameters include salinity, hardness, pH, acidity and alkalinity, as well as concentrations of ionized metals such as iron and manganese, and anionic entities such as chlorides, sulfates, sulfides, nitrates and phosphates. Bacteriological parameters include coliforms, fecal coliforms, specific pathogens, and viruses. Water pollution may be classified as strong, medium or weak, depending on its contaminant concentration. The effects of water pollutants into the food industry and human health are manifold and depend on the types and concentrations of pollutants (Yung-Tse H. et al., 2011).

Table.1. Important contaminants in polluted water and their impact on human health.

Contaminants	Effect on human
Sediments and suspended solids (SS)	Can interfere with fish spawning because they can cover gravel beds and block light penetration making food harder to find. Can also damage gill structures directly, smothering aquatic insects and fish. Organic sediments can deplete the water of oxygen creating anaerobic conditions and may create unsightly conditions and cause unpleasant odors.
Biodegradable organics	Principally made up of proteins, carbohydrates and fats. They are commonly measured in terms of BOD and COD. If discharged into inland rivers, streams or lakes, their biological stabilization can deplete natural oxygen resources and cause septic conditions that are detrimental to aquatic species.
Pathogens and microbial contaminants	Spreads infectious diseases through contaminated drinking water supplies.
Organic and inorganic compounds such as calcium, sodium and sulfate.	May be highly toxic, carcinogenic, or mutagenic.
Heavy metals	Usually derived from industrial activities, can harm aquatic organisms or bioaccumulate in the food chain, even if the metal concentration in water is relatively low.
Refractory organics	That tend to resist conventional waste-water treatment include surfactants, phenols and agricultural pesticides
Nutrients	Over-stimulates growth of algae (eutrophication) which then decomposes, robbing water of oxygen and harming aquatic life. High levels of nitrate in drinking water lead to illness in humans.

The most common water pollutants that have important impact on the human life through their accumulation in the foods chain are nutrients, organic matter, heavy metals, microbial contaminants, toxic organic compounds (oil, pesticides, some plastics, and other industrial chemicals), salts, acids, sediments and suspended solids. Table 1 presents the important contaminants in wastewater and their reason of importance. These components are either in solution or as particulate matter and can have (bio-) cumulative, persistent and synergetic characteristics affecting ecosystem health and function, food production, human health and wellbeing.

Heavy metals as an essential pollutant at food industry

Diet is the main route of exposure to trace metals for human, so the assessment risks of these elements to human via dietary intake is important. Numerous scientific studies have been revealed that cereal, sea product, and vegetable were the main sources of heavy metal intake from foodstuff for adults and children. However, fruit, milk, bean, and egg were secondary contributors. Accordingly, heavy metals are considered to be one of the most hazardous water contaminants at the food industry. They are major pollutants in ground, industrial and even treated wastewaters (Metcalf and Eddy, 1991). Unlike organic pollutants, metals are non-biodegradable and have tendency to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic as their enter at the human food chain (Fu & Wang, 2011). The presence of heavy metals in drinking water can be hazardous to consumers; these metals can damage nerves, liver and bones and block functional groups of vital enzymes. Metal ions in water can occur naturally from leaching of ore deposits and from anthropogenic sources, which mainly include industrial effluents and solid waste disposal. Due to rapid development of industrial activities in recent years, the levels of heavy metals in water system have substantially increased over time (Nouri et al., 2006). Certain metals are regulated because they are toxic to operation. Regulated metals include arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver and zinc (Edwards, 1995).

In view of their harmful effects on human health as they enter the food chains, the toxic effect of some heavy metals will be briefly discussed in the following section.

Lead is Chronic lead poisoning is characterized by neurological defects, kidney dysfunction and anemia. Damage to the brain and central nervous system is marked feature in children. Cadmium is toxic to virtually every system in the body. Pathological changes have been observed in the kidneys, liver, gastrointestinal tract, heart, testes, pancreas, bones and blood vessels and anemia is a common feature of chronic cadmium toxicity in all species. Changes in the skin, hair and feathers characteristic of zinc deficiency can also be induced by cadmium. The manifestations of chronic mercury poisoning are mainly neurological, with tremors, irritability, vertigo and depression, when the mercury is ingested it causes progressive in coordination, loss of vision and hearing and mental deterioration. Copper is a very common metal, which is widely used in electroplate, light industry, mechanical manufacturing industry and architecture. Additionally copper is an indispensable micronutrient to humans and other life form. Moreover, exposure to high levels of copper can make disorders associated with abnormal Cu metabolism and neurodegenerative changes. Accordingly, heavy metals water pollution must be faced with more and more strict regulations. Currently, heavy metals pollution represents the most serious environmental contaminates. Accordingly, these toxic pollutants should be separated from polluted water to protect the human life and health (Fu and Wang, 2011).

Microorganisms as a vital pollutant at drinking water

The largest public health impact of unsafe drinking water that affect directly at the food industries and causes diarrheal disease and the majority of water-associated outbreaks of disease can be related back to the microbiological quality of drinking water. These water-associated parasitic diseases include cholera, typhoid, dysentery, hepatitis, giardiasis, guinea worm and schistosomiasis. Specific bacteria of concern at polluted drinking water include Campylobacter, E. coli O157, Salmonella. Most strains of bacteria are harmless such as E. coli which lives in the intestines of healthy animals and humans but one species E. coli O157:H7 is a strain that produces a toxin that can cause severe illness. The most important protozoan pathogens are Cryptosporidium and Giardia with the majority of recent outbreaks of illness associated with drinking water being due to Cryptosporidium.

Organic contaminates at polluted water

Organic pollution is the term used when large quantities of organic compounds presence at water. It originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater. Organic pollutants in water are defined as agents that degrade water quality, and form threats to human health and aquatic life. Organic water contaminants mainly include food processing waste, disinfection by-products (DBPs) found in chemically disinfected drinking water, volatile organic compounds (VOCs), pesticides including insecticides and herbicides, tree and bush debris from logging operations, polyaromatic hydrocarbons (PAHs), dyes, phenols, and detergents. Persistent organic pollutants (POPs) are observed to be spread over long-range. Bioaccumulation of these pollutants at human and animal tissue through food chains has significant impacts on human health and the environment. Many POPs are currently used as pesticides. Others are used in industrial processes and in the production of a range of goods such as solvents, polyvinyl chloride, and pharmaceuticals (Gupta & Ali 2013).

Diuron is a commonly used herbicide in agriculture (Rosas et al. 2014), however the use of it leads to contamination of the aquatic environment through soil leaching, and it is persistent when applied in high dosages to the soil. Diuron is considered a Priority Substance by the European Commission (DIRECTIVE 2008/105/EC) among 33 substances of priority concern at Community level, due to their widespread use and their high concentrations in rivers, lakes and coastal waters. The maximum allowable concentration in surface waters has been set to be 1.8 μg/L. Most of the commercial products containing diuron are classified as harmful chemicals, as they are generally considered dangerous for aquatic life, flora, and for humans. For example, it may damage developing foetuses and congenital malformations have been reported. Diuron is toxic to photosynthetic organisms; therefore, it is important to eliminate diuron from polluted water to be safe for food industries (Pohanish 2012, Wintgens et al. 2008). Among other organic contaminants that have harmful impact on human life are effluents containing colouring agents. The major sources of dyes at the polluted water are various dyestuff manufacturing and the industries which use them, such as textile, leather, printing, petroleum, cosmetics, paints, pesticide and pharmaceutical industries. Usually, the dyes are not entirely used, and it is estimated that approximately 10-60% of reactive dyes are lost during textile dyeing (Alinsafi et al. 2007, Allégre et al. 2006 and Rosa et al. 2015). The polluted water contaminated with dyestuff is toxic/carcinogenic and thus harmful for humans, e.g. methylene blue, used extensively for dying of cotton, wool and silk, causes burning effects on the eyes, nausea, vomiting and diarrhoea, they might inhibit the light penetration and consequently prevent the photosynthesis of aqueous flora (Cardoso et al. 2011a, Cardoso et al. 2011b). This is due to the fact that dyes have complex aromatic molecular structures and thus they are stable and extremely resistant towards biological or chemical processing (Nguyen & Juang 2013).

NANOTECHNOLOGY FOR WATER TREATMENT AND SAFE REUSE

There are rising demands of clean water throughout the world especially at food industries regarding to the depletion at the freshwater sources/resources due to prolonged droughts, increasing population, climate changes threats, and strict water quality standards. Masses in developing countries are using unconventional water sources (e.g., storm water, contaminated fresh water, brackish water) due to limited and depleting freshwater supplies. The existing water treatment systems, distribution systems, and disposable habits coupled with huge centralized schemes are no more sustainable. The current researches do not adequately address the practices that guarantee the availability of water for all users in accordance with the stringent water quality standards (Theron et al., 2008).

Several commercial and non-commercial technological developments are employed on daily basis but nanotechnology has proved to be one of the advanced ways for water purification. Developments in nanoscale research have made it possible to invent economically feasible treatment technologies for effectively treating polluted water that meeting the ever increasing water quality standards. Advances in nanotechnology have provided the opportunities to meet the fresh water demands of the future generations. It is suggested that nanotechnology can adequately address many of the water quality issues by using different types of nanoparticles and/or nanofibers (Li et al., 2012).

Nanotechnology uses materials of sizes smaller than 100nm in at least one dimension meaning at the level of atoms and molecules as compared with other disciplines such as chemistry, engineering, and materials science (Hornyak et al., 2009).

At this scale, materials possess novel and significantly changed physical, chemical, and biological properties mainly due to their structure, higher surface area-to-volume ratio offering treatment and remediation, sensing and detection, and pollution prevention. These unique properties of nanomaterials, for example, high reactivity and strong sorption, are explored for many fields concerned with the human life care such as diet and nutrition, toxicology, food science and water purification based on their functions in unit operations as highlighted in Figure 1.

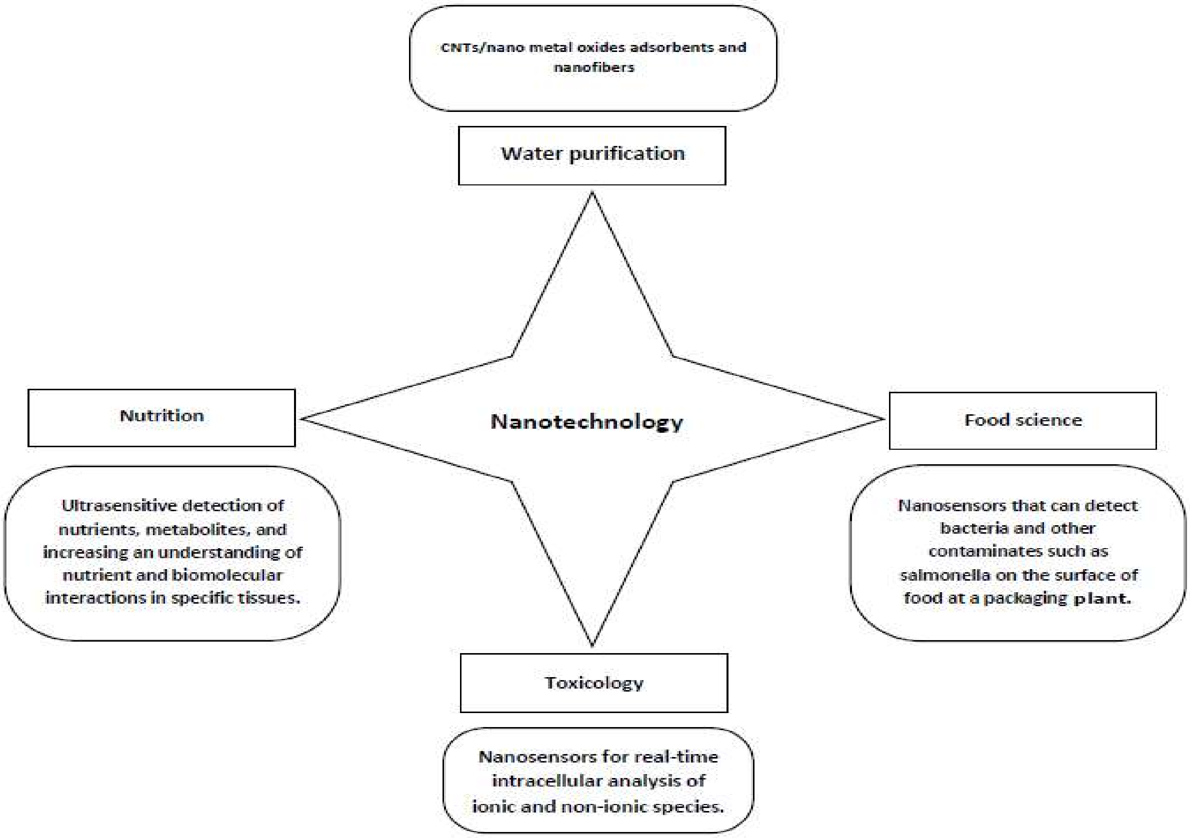

Figure 1. Potential impact of nanotechnology on human life.

Nanotechnology is actively pursued to both enhance the performance of existing treatment processes and develop new processes. The innovation of new technologies to increase the availability of clean water commenced 40 years ago with the establishment of three membrane separation processes (Table 2): reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) (Sutherland, 2008). During the 1970s and 1980s, nanofiltration membranes were developed as an intermediate filtration material between ultrafiltration and reverse osmosis (Eriksson, 1988).

Table 2. Characteristics of membrane separation processes for water purification.

Membrane type	Pore size (nm)	Pressure (bar)	Product water
Reverse osmosis	<0.6	30-70	Pure water (PW)
Nanofiltration	0.6-5	10-40	(PW) and low molecular solutes
Ultrafiltration	5-50	0.5-10	All above and macromolecules
Microfiltration	50-500	0.5-2	All above and colloids

The impact of nanotechnology on the development of tools and techniques for water treatment will be more pronounced in the near future. As scarcity of natural water threatens the advancement and the social security of many communities around the world (Figure 2), it is expected that the solution will emerge from the exploitation of nanoparticles to make water purification, water recycling, seawater desalination and water remediation more efficient and cost effective. The advantages of using nanofiltration relied in the direct humanitarian benefit from using nanotechnology and in the promotion of economical viabilities in rural communities. Therefore, the production of nanostructures, nanocomposites and modified nanostructures for water remediation will increase because of the need for producing clean water in fast and low energy consumption ways. Nanotechnology should be regarded as the tool to ensure the sustainability of social communities in different places. This is possible through the use of advanced filtration nanomaterials that enable desalination of seawater, recycling of contaminated water and reuse of wastewater (Theron et al., 2008).

Figure 2. Nanotechnology for safe clean water for human sustainability.

Recently, nanoremediation has become the main focus of research and development. There is great potential to use this technology to clean up the contaminated sites and save clean water resources. This eco-friendly technology is considered to be an effective alternative to the current practices of site remediation. Nanoremediation techniques involve application of reactive materials for the detoxification and transformation of pollutants (Cheremisinoff, 2002). These materials initiate both chemical reduction and catalysis of the pollutants of concern. The unique properties of nanomaterials make them best suited for in situ applications. Their small size and novel surface coatings enable them to achieve farther and wider distribution when compared to large-sized particles (Trarnyek and Johnson, 2006). The use of nanotechnology for water remediation could potentially provide a solution for faster and more cost-effective site remediation. Innovations in the development of novel technologies for water remediation are among the most exciting and promising. This section gives an overview of the use of nanomaterials in water purification. We highlight recent advances on the development of novel nanoscale materials and processes for treatment of water contaminated by toxic metal ions, organic and inorganic solutes, bacteria and viruses. Utilization of nanotechnology in the cleanup of contaminated water could be summarized as

1. Nanopowder materials utilized as potent sorbents; in some cases combined with magnetic particles to ease particle separation.
2. Nanopowder materials utilized as catalysts for chemical or photochemical destruction of contaminants
3. Nanostructure filtration membranes (nanofiltration membrane)

4. Bioactive nanomaterials for bacteria and viruses removal

Nanopowder materials as sorbent agents for water purification

Sorption process is commonly represented as polishing step for organic and inorganic contaminants remediation at water treatment processes. Conventional sorbent materials are lack at their selectivity and reactivity regarding to their surface area and active sites limitations. Material surface area is key parameter that responsible for its high sorption capacity. Thus, Nano-sorbent materials offer significant performance improvements over the conventional adsorbent materials respecting to their higher surface area and and tunable pore size. Moreover, the selectivity of nano-materials may be enhanced through surface functionalization of material to be selective toward specific pollutants rather than the others. Nano-sorbent materials may be utilized at various water purification processes either as slurry reactants or filter media.

Nano-sorbent materials should satisfy the following criterions: 1) the nanosorbents themselves should be nontoxic. 2) The sorbents present relatively high sorption capacities and selectivity to the low concentration of pollutants. 3) The adsorbed pollutant could be removed from the surface of the nano adsorbent easily. 4) The sorbents could be infinitely recycled. So far, a variety of nanomaterials (Figure 3) such as carbon based materials such as carbon nano-tubes and graphite, inorganic materials such as nano zeolite, polymeric sorbents and composite materials have been investigated for decontamination various pollutant types from aqueous solutions with high purification capacity. Nano-sorbents can be readily applied in the powder form at the slurry reactors effectively since all material surfaces are utilized that improves the mass transfer rate. However, in order to separate the nano-sorbent material from the treatment media, an additional separation unit is required that improve the overall process cost. Instead, nao-adsorbent materials may be formulated into pellets/beads or porous granules loaded with nano-adsorbent materials to facilitate their separation process (Dotzauer et al., 2006). Fixed bed treatment columns are usually suffering from mass transfer and pressure drops limitations. These limitations may be overcome using nano-magnetic sorbent materials that may be controlled using external magnetic fields to avoid clogging of fixed bed reactors and decrease the pressure drop inside the water purification treatment column.

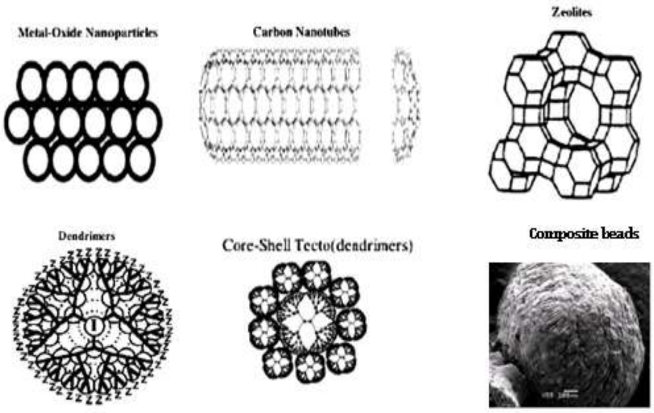

Figure 3. Nanomaterials evaluated as functional materials for water remediation.

Carbon based nanomaterials as sorbent agents

As one of the most important inorganic sorbent materials, carbon based nanomaterials are used widely in the field of removal heavy metals in recent decades, due to its nontoxicity and high sorption capacities. Activated carbon is used firstly as sorbents, but it is difficult to remove heavy metals at ppb levels. Then, with the development of nanotechnology, carbon nanotubes, fullerene, and graphite are synthesized and utilized as advanced nanosorbent materials (Lee et al., 2010).

Carbon nanotubes (CNTs): are being explored as substitutes for activated carbon, as they effectively remove both organic and metal contaminants. CNTs have shown higher efficiency than activated carbon on adsorption of various organic chemicals (Pan and Xing, 2008). Carbon nanotubes (CNTs) a new form of carbon, are attracting great research interest due to their exceptional adsorption and mechanical properties and unique electrical property, highly chemical stability, and large specific surface area mainly because of their extremely small sizes, uniform pore distribution, and large specific surface area. The high characteristics adsorption capacity of the material was generated from its large external surface area as investigated from Figure 3 (Yang and Xing, 2010). Carbon nanotubes attain hydrophobic properties for their surfaces, so, they have tendency to form aggregates at the aqueous solutions that decline their effective surface area. On the other hand, these aggregates have interstitial spaces and grooves that are suitable for adsorption organic molecules (Pan et al., 2008). Moreover, CNTs have high adsorption capacity for some bulky organic molecules such as many antibiotics and pharmaceuticals because of their larger pores in bundles and more accessible sorption sites (Ji et al., 2009). The high adsorption affinity of CNTs materials for low molecular weight polar organic compounds may be owed to the diverse contaminate CNT interactions including hydrophobic effect, π-π interactions, hydrogen bonding, covalent bonding, and electrostatic interactions (Yang and Xing, 2010). The π electron rich at CNT surface allows π-π interactions with organic molecules with C=C bonds or benzene rings such as polycyclic aromatic hydrocarbons (PAHs) (Chen et al., 2007; Lin and Xing, 2008). Moreover, the functionalized organic pollutants with -COOH, -OH, -NH2 groups may be adsorbed onto CNT materials through their surface hydrogen bonding which donates electrons (Yang et al., 2008). The adsorption of positively charged organic contaminates such antibiotics onto CNT materials may be occurred through electrostatic attraction (Ji et al., 2009). The affinity of CNT materials for metal ions adsorption may be enhanced through their surface functionalization such as the addition of carboxyl or hydroxyl groups or by their surface oxidation (Lu et al., 2006). Generally, CNT materials may be utilized as selective sorbent agents to be targeted toward specific pollutants regarding to their superior surface chemistry.

On the other hand, regeneration is an important factor to determine the cost-effectiveness of the adsorbent materials. The desorption process of metal ions from CNT materials may be takes through the reduction of solution pH. The percentage metal ions recovery rate from carbon nanotubes materials are ranged between 90 to 100% at pH < 2 with relatively stable material adsorption capacity (Li et al., 2005; Lu et al., 2006). Based on the best-fit regression of Zn^{2+} adsorption capacity onto carbon nano-tubes, Lu et al investigated that CNT nano-materials can be regenerated to be reused as adsorbent material up to several hundred times for zinc ions decontamination with reasonable high adsorption capacity (Lu et al., 2007).

Nano-graphene

It is another type of carbon based material as nanosorbent, which is a kind of one or several atomic layered graphites, possesses special two-dimensional structure and good mechanical, thermal properties. Graphene sheets perforated by small holes have been firstly investigated as potential candidates for water filtration. Their holes with average diameter equivalent to 1 nanometer are big enough to pass water and small enough to reject the pollutant molecules. Accordingly, with graphene sheet nanopores a reality, a graphene water filter comes within reach. Recently, new shout emerged known as graphene devices such as that utilized as DNA detectors.

Recently announced that it has obtained a patent for graphene nanopore-based water filters. The technology, called Perforene (David and Jeffrey, 2012). In spite of the promising performance of graphene due to its small weight and size that could significantly reduce the costs and energy footprint of portable water filters and desalinators, however, the technology for mass production has not yet been developed.

Inorganic nanomaterials as sorbent agents

Nano-zeolite

One of the oldest and commercially famous inorganic sorbent materials is zeolite materials. Nano- zeolites are hydrated aluminosilicate materials with special ion-exchange and sorption properties. Their superior physical-chemical properties depend up on the unique tree-dimensional porous structure that gives the material various application possibilities. Nano-zeolites are classified as cationic exchange materials because of the negative excess on their surfaces that results from isomorphic replacement of silicon by aluminium in the primary structural units. Their excellent performance on the removal of metal cations from polluted water was established from various researches. However, zeolites can be utilized as anionic exchanger after chemical modification by inorganic salts or organic surfactants, which are adsorbed on the surface and lead to the generation of positively charged oxi-hydroxides or surfactant micelles that binding with anions, like arsenates or chromates. Nano-zeolites have advantages over other cation exchange nano-materials since they are cheap and exhibit excellent selectivity for different cations at low temperatures that combined with release of non-toxic exchangeable cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) to the environment. The efficiency of water treatment by using nano and chemically modified zeolites depends on the type and quantity of the used zeolite and its particle size distribution. On the other hand, the treatment process parameters such as the size distribution of zeolite particles, the initial concentration of contaminants (cation/anion), pH value of solution, ionic strength of solution, temperature, pressure, contact time of system zeolite/solution and the presence of other organic compounds and anions have important impact on the water purification process. Nano-zeolites may be utilized for water purification using either batch or column techniques (Karmen et al., 2013).

Nano-inorganic ion exchange materials

The last forty years or so have seen a great upsurge in the researches on synthetic inorganic ion exchangers. The main emphasis has been given to the development of new materials possessing chemical stability, reproducibility in ion exchange behaviour and selectivity for certain metal ions important from analytical and environmental point of view.

Synthetic inorganic ion exchangers are generally produced as gelatinous precipitates by mixing rapidly the elements of groups 3, 4, 5 and 6 of the periodic table, usually at room temperature. Sometimes refluxing is also recommended to improve their reproducibility and ion exchange characteristics. The precipitate thus formed is filtered, washed and dried before putting in demineralized water to obtain granules suitable for column operations. A large number of such materials have been prepared by mixing phosphoric, arsenic, molybdic, antimonic and vanadic acids with tin, titanium, thorium, zirconium, cerium, iron, antimony, niobium, bismuth, tantalum etc. So a large number of synthetic inorganic substances have been described which exhibit ion-exchanging properties. These materials may be divided into the following main groups (Auffan et al., 2008; Yang et al., 2008):

1. Acidic salts of multivalent metals are large group of ion exchangers, amongst which tetravalent cations Zr, Th, Ti, Sn are most studied, followed by some trivalent cations such as Al and Cr. The anions most extensively employed include phosphate, arsenate, antimonate, vanadate and molybdate.
2. Insoluble ferrocyanides (HCF) are super inorganic materials for the removal of cesium from high concentrations of alkali metals and they have been used for that purpose for decades. HFC complexes may be synthesized in either Fe(II) or Fe(III) form, and mixing them with a solution of a transition metal salt usually precipitates small particles or a colloidal product .
3. Hydrous oxides are solids with an oxide-water system, where the water molecules are fairly strongly bound to the metal hydroxide groups at the surface of the material. However there is no evidence of definite hydrates and hydrous oxides of stoichiometric composition are scarce. Hydrous oxides exhibit both cationic and anionic exchange properties depending on the surrounding medium.
4. Salts of heteropolyacids are a much smaller group of ion exchangers than the groups discussed above. A good example of their structure is provided by ammonium molybdophosphate ($(NH_4)_3PMo_{12}O_{40}$, AMP), where phosphorus is surrounded tetrahedrally by four groups of three MoO_6 octahedra (Hu et al., 2005).
5. Certain other substances, e.g., synthetic apatites, sulphides, alkaline earth sulphates

Many inorganic solids are ionic and exhibit ion exchange properties (broadly speaking) and these are usually referred to as other ionic compounds in the ion exchange literature. This group is extensive, including all forms of insoluble materials (halides, sulphides, carbonates and perchlorates).

Polymeric nanomaterials as sorbent agents

An efficient sorbent with both high capacity and fast rate adsorption should have the following two main characteristics: functional groups and large surface area. Unfortunately, most current inorganic sorbents rarely have both at the same time, carbon nanomaterials has high surface area, but without adsorbing functional group. On the contrary, organic polymer, polyphenylene diamine nano-powder, holds a large amount of polyfunctional groups (amino and imino groups) can effectively adsorb heavy metal ions, whereas their small specific area and low adsorption rate limit their application. Therefore, new types of polymers called dendritic polymers have been developed. These types include random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers, are relatively monodispersed and highly branched macromolecules with controlled composition and architecture consisting of three components: a core, interior branch cells and terminal branch cell (Arkas et al., 2006). Dendritic polymers exhibit many features that make them particularly attractive as functional materials for water purification. These 'soft' nanoparticles, with sizes in the range of 1–20 nm, can be used as high capacity and recyclable watersoluble ligands for toxic metal ions, radionuclides and inorganic anions. Dendritic polymers can also be used as (i) recyclable unimolecular micelles for recovering organic solutes from water and (ii) scaffolds and templates for the preparation of redox and catalytically active nanoparticles (Scott et al., 2005). Dendritic polymers have also been successfully used as delivery vehicles or scaffolds for antimicrobial agents such as Ag (I) and quaternary ammonium chlorides (Chen and Cooper, 2002). In spite of the good properties of the polymeric nanomaterials as sorbent agents, however, they are suffering from some limitations such as

—Their low sorbent capacity compared with other materials especially inorganic nano-materials,

—Their excessive swelling and tendency to peptize,

—The very limited radiation stability of cellulosic and protein materials,

—Their weak physical structures,

—Their non-uniform physical properties,

—That they are non-selective,

—That they are unstable outside a moderately neutral pH range.

These limitations of polymeric nano-materials forced the scientific research to establish new materials that combine in their properties between the advantages of both the inorganic and polymeric nano-materials, which called as composite or hybrid nano-materials.

Composite nanomaterials as sorbent agents

Composite nano-materials consist of one or more material combined with another material, which can be inorganic or organic. Nano-composite can be fabricated with enhanced physical, chemical, optical, thermal and other unique properties. They can be synthesized using simple and inexpensive techniques to have superior properties compared with the conventional microscale composite materials. In order to assess the potential value of nanocomposites at the different water purification processes, the determination of the integrated nanomaterials that will effectively improve the composite properties and how they will affect the structure of the polymer is very essential. The main reason for manufacturing a composite material is to produce a granular material from the nano-materials. This granular materials were fabricated through injection the fine nano-powder materials into either polymeric or inorganic matrices to attain new composite nano-materials with sufficient strength for column use, from nano-powder materials that do not form, or only form weak, granules themselves. Synthetic nano-zeolites are manufactured in a granular form using inorganic binders such as aluminium oxide. Different organic binders have also been tested at the laboratory scale. A composite ion exchange nano-material has been developed by coating cupric ferric hexacyanoferrate nano-powder material on to polyacrylic fibers. This was done with a view to improving the column characteristics of the nano-hexacyanoferrate (Anish et al., 2012). A granulation process based on the incorporation of various kinds of inorganic ion exchange materials in a polyacrylonitrile gel has been developed; these materials have been tested for water purification processes (Anish et al., 2012).

Therefore, new sorbents with both polyfunctional groups and high surface area are still expected. More recently, the development of hybrid sorbents has opened up the new opportunities of their application in deep removal of different pollutants from water (Auffan et al., 2008). Polymer-layered silicate nanocomposites have attracted both academic and industrial attention because they exhibit dramatic improvement in properties at very low filler contents (Pavlidou and Papaspyrides, 2008).

In summary, nanomaterials including traditional inorganic nanoadsorbents and novel polymer supported composites are used to remove various pollutants from water, due to their novel size- and shape-dependent properties, and gain the good to excellent removal efficiency.

Magnetic nanomaterials as sorbent agents

Nano-magnetite possesses unique super paramagnetic properties that facilitate the separation process from aqueous media using magnetic field as indicated at Figure 4. A new class of core shell structure nanoparticles was fabricated through the magnetic core materials that attain shell matrix provides specific function (Dai et al., 2011). With respect to the water purification process, nano- magnetic adsorbentmaterials can be designed using amphiphilic dendrimers with specific binding sites (Theron et al., 2008).

Figure 4. Magnetic nanoparticles.

Recently, several studies have focused on the removal of inorganic and organic contaminants from polluted water, using nano-sized iron oxide particles. Iron oxide magnetic nanoparticles have been chosen as promising adsorbents because: (1) they can be produced in large quantities using physicochemical methods, (2) it is expected that their adsorption capacity and affinity for pollutants is higher considering the larger surface area and possibly highly active surface sites, (3) the separation of metal-loaded magnetic nano-adsorbent from treated water can be achieved via an external magnetic field, and (4) nanoparticles might be regenerated and reused (Ngomsik et al., 2005). Also, iron oxide nanoparticles can be surface-coated with organic compounds to increase their sorption efficiency and specificity for pollutants. Magnetic nano-materials represented as an appealing solution for water treatment, where they have large ability to combine with water pollutants such as arsenic or oil due to their large surface areas relative to their mass then easily removed using a magnet.

Magnetic field separation technique allows one to design processes where the particles not only remove compounds from water but also can easily be removed again and then be recycled or regenerated. This approach has been proposed with magnetite (Fe_3O_4), maghemite (g-Fe_2O_3) and jacobsite ($MnFe_2O_4$) nanoparticles for chromium (VI) removal from wastewater (Hu et al., 2005). Water-soluble CNTs have been functionalized with magnetic iron nanoparticles for removal of aromatic compounds from water and easy separation from water for re-use.

Catalytic nano-powder materials for water purification

Catalysis is an acceleration or retardation of the rate of a chemical reaction, brought about by the addition of a substance (the catalyst) to the reaction medium. The catalyst, usually present in small amounts, is not consumed in the reaction. Catalysts are a class of materials that enhance the rate of a reaction and the process of catalysis is that of a catalyst involved in a reaction. The main role of a catalyst is to enhance the rate of reaction. The rate for any chemical reaction is the step at which the reactants transform to products. This step is the slowest step and often determines the rate of reaction. The reactant must form an activated complex where there are no reactants but are not yet transformed to products. This is a transitional state and the energy needed to reach this state is named the activation energy. The reactants must reach and pass the energy barriers to transform to products. The catalyst provides another path that is more complex but has an activation energy that is remarkably lower than that of the uncatalysed reaction so the rate is much larger for the catalysed one (Figure 5). As the catalyst is not consumed in the reaction, it does not exist in the final chemical equation and it accelerates the reactions that are kinetically possible. This suggests that if the reaction is thermodynamically impossible, catalysts cannot make it possible. In the field of water purification there are two types of catalytic processes that have significant roles in the water treatment, which are chemical and photo-catalytic processes.

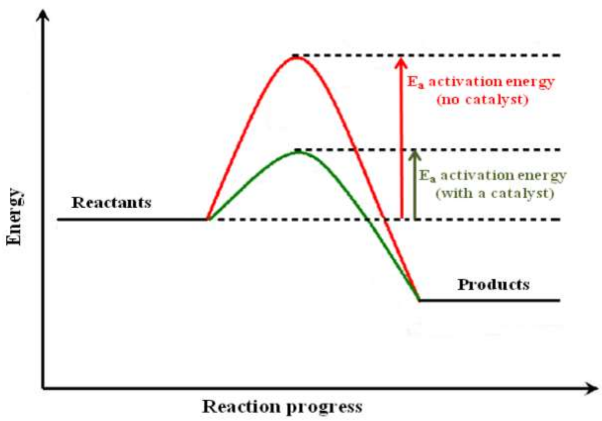

Figure 5. Activation energy for catalysed reaction and uncatalysed reaction.

Chemical catalysis using nano-materials for water purification

Chemical catalysis has significant role at water purification using solid nano-materials that act as catalytic agents and the process is known as heterogeneous chemical catalysis (Rothenberg, 2008). A key feature of this type of catalysis is that the reactants must adsorb to the catalyst's surface. Large catalyst surfaces, then, ensure that the desired reaction occurs rapidly. A heterogeneous catalyst has active sites, which are the atoms or crystal faces where the reaction actually occurs. Depending on the mechanism, the active site may be either a planar exposed metal surface, a crystal edge with imperfect metal valence or a complicated combination of the two. Thus, not only most of the volume, but also most of the surface of a heterogeneous catalyst may be catalytically inactive. Finding out the nature of the active site requires technically challenging (Bond, 1987). The use of solid catalysts in water treatment technologies requires also adapting the solid characteristics with respect to those typically used in conventional catalytic applications. Heterogeneous catalysts are typically "supported," which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Supports prevent or reduce agglomeration and sintering of the small catalyst particles, exposing more surface area, thus catalysts have a higher specific activity (per gram) on a support. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly alumina, zeolites or various kinds of activated carbon. Specialized supports include silicon dioxide, titanium dioxide, calcium carbonate, and barium sulfate. Titanium-based nano-materials and nano-iron-oxide coated sand are the most common chemical catalysis for the removal of arsenic reduction from polluted water (Palmisano et al., 2010).

Nano- metal and metal oxides as catalytic agents for water purification

Nanocatalysts are materials characteristics with catalytic properties that can chemically break down pollutants. These catalytic materials have potential for treating contaminants at very low levels with cost effective manner. As the nano-catalytic materials having high surface activity through enhancing the reactivity and degradation of contaminants, so, they are widely used in water treatment processes. Semiconductor materials, zero-valence metal and bimetallic nanoparticles represent the most common utilized Nanocatalysts for contaminated degradation such asazo dyes, halogenated aliphatic, organochlorine pesticides, halogenated herbicides, and nitro aromatics (Xu et al., 2005). For microbial decontamination from polluted water, silver (Ag) nanocatalyst, N-doped TiO_2 and ZrO_2 nanoparticles catalysts act as effective degradation matrices. Polluted water with halogenated organic compounds (HOCs) can be selectively biodegraded using advanced nanocatalytic activities. They are firstly transformed into organic compounds using plladium nano-catalysts followed by its biodegradation in suitable treatment plant (Macak et al., 2007).

Photo- catalysis using nano-materials for water purification

Advanced oxidation processes (AOPs) based on ozonation, UV irradiation; Fenton reaction, catalytic peroxide oxidation etc. have been suggested as potential treatment alternatives for water purification containing organic pollutants by oxidizing and mineralizing them into less harmful inorganic substances preferably into carbon dioxide and water. These processes are of particular interest for the treatment of effluents for which biological processes might not be applicable e.g. for highly toxic organic compounds. The main objective of most AOPs is the generation of powerful oxidizing agents, such as the highly reactive hydroxyl radical, ($OH^{\bullet}$ with the oxidation potential 2.8V), that reacts rapidly (the rate depends on the contaminant molecules) (Saien & Nejati 2007) and relatively nonselectively with practically any organic compounds by hydrogen abstraction, by addition to unsaturated bonds and aromatic rings, or by electron transfer (Daneshvar et al. 2005). Heterogeneous photocatalysis is one of the AOPs, and it uses titanium dioxide or other semiconductor nano-materials as a catalysts activated by UV irradiation. Photocatalysis has been studied widely in the degradation of organic compounds in both liquid and gas phase processes (Lazar et al. 2012, Malato et al. 2009, Zhao et al. 2011). It has the potential to reduce the toxicity of the contaminants and even mineralize target compounds (Kirchnerova et al. 2005). Due to the non-selective nature of the photocatalytic processes, photocatalysis can be used for the simultaneous abatement of several different organic pollutants via converting them into less harmful compounds. The process is typically operated at ambient temperatures and pressures, and can be applied to environmental remediation by following the principles of green chemistry (Herrmann et al. 2007, Richter & Caillol 2011).

The energy needed to produce the reactive radicals in photocatalysis is provided, when a semiconductor is irradiated with the energy (hv) equal or superior to the band gap energy of the semiconductor (e.g. for TiO_2: hv ≥ 3.2 eV). Electrons (e^-) of the valence band are excited to the conduction band forming an electron-hole pair (Figure 6) (Herrmann 1999).

The photo-generated holes (h^+) in the valence band diffuse to the surface of the photocatalyst and react with adsorbed water molecules, creating hydroxyl radicals. The nearby organic molecules can be oxidized by these radicals and the holes on the surface of the semiconductor. The electrons in the conduction band participate in reduction processes e.g. in the formation of superoxide radical anions ($O_2^{\bullet-}$) with the molecular oxygen of the environment. (Nakata & Fujishima 2012, Carp et al. 2004).

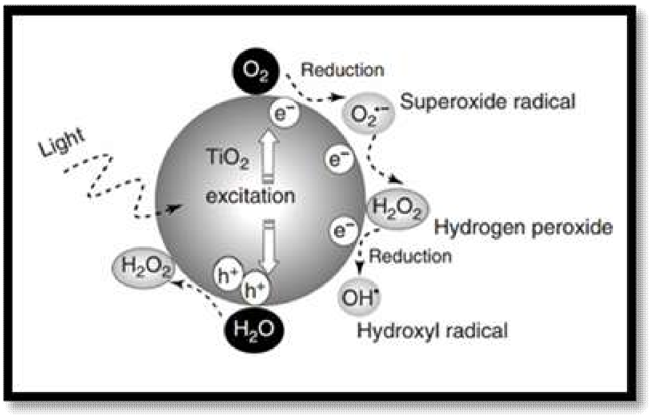

Figure 6. Principle mechanisms of photocatalysis.

Nano- metal oxides as photo catalytic agents for water purification

The ideal photocatalyst should process the following properties (i) photoactivity, (ii) biological and chemical inertness, (iii) stability toward photocorrosion, (v) suitability towards visible or near UV light, (vi) low cost, and (vi) lack of toxicity (Bhatkhande et al., 2001). A wide range of semiconductor nanomaterials may be used for photocatalysis, such as TiO_2, ZnO, MgO, WO_3, Fe_2O_3, CdS. TiO_2 nano-material is known to have excellent pigmentary properties, high ultraviolet absorption and high stability which allow it to be used in different applications, such as electroceramics, glass and in the photocatalytic degradation of chemicals in water and air. It has been used in the form of a suspension, or a thin film in water treatment Titanium dioxide, also known as titanium (IV) oxide or titania, is the most commonly used catalyst material in photocatalysis. It can have sizes ranging from clusters to colloids to powders and large single crystals, and it is close to being an ideal photocatalyst, displaying almost all the properties mentioned above (Han et al., 2009). The advantages of TiO_2 are its good activity (the photo generated holes are highly oxidizing), high physical and chemical stability both in acidic and basic conditions, nontoxicity, resistance to corrosion, commercial availability and inexpensiveness (Fujishima et al. 2008, Carp et al. 2004, and Hung et al. 2006). Further, it can be utilized as a photocatalyst itself or it can be combined e.g. with noble metals (Pd, Pt) or carbon nanotubes to achieve higher activity in certain reactions (Rosseler et al. 2010, Ye et al. 2012). TiO_2 exists in different allotropic forms including natural anatase, rutile and brookite, and an artificial form (TiO_2–B, TiO_2–H), for example the commercially available Aeroxide (former Degussa) is a mixture of anatase and rutile. Anatase shows a greater photocatalytic activity for most reactions. The energy band-gaps of anatase and rutile are 3.23 and 3.02 eV, respectively. Anatase is thermodynamically less stable than rutile, but it has a higher surface area, and a higher surface density of active sites for adsorption and for catalysis (Herrmann 1999).

The nanoscale form of zinc oxide (ZnO) can be considered as one of the most important semiconductor oxides at present (Ischenco et al. 2005). ZnO is a widegap semiconductor with a direct band gap around 3.4 eV (i.e. in the near-UV) (Klingshirn 2007). The potential use of ZnO in photocatalysis has particularly arise great interest, as there have been several examples of ZnO displaying more impressive photocatalytic activity in solar light than widely studied titanium dioxide due to the higher quantum efficiency (Sakthivel et al. 2003). Also it has been shown that ZnO is more efficient in the degradation of industrial effluents at neutral pH than TiO_2. Zinc oxide (ZnO) exists with three types of crystal structure; hexagonal wurtzite, cubic zinc blende, and cubic rock salt. Wurtzite is the most stable structure and is abundantly available, unlike the other two structures.

Other metal oxide photocatalysts, such as iron, vanadium, tungsten, and copper oxides, have been used to treat wastewaters based on their photocatalytic properties. For example, tungsten oxide (WO_3) has a narrower band gap (2.5 eV) than TiO_2, allowing it to be activated by visible light (<500 nm) (Kominami et al. 2001). Iron (III) (hydr) oxides can absorb light up to 600 nm, and most of them have semiconductor properties, thus electron/hole recombination generally takes place efficiently (Paola et al. 2012). For example, Fe_2O_3 is an n-type semiconducting material and can be used for photodegradation under visible light conditions. Iron oxide nanomaterials can even achieve better photocatalytic performance when compared to TiO_2 due to significant generation of electron–hole pairs through a narrow band-gap illumination (Xu et al. 2012).

Nanostructure filtration membranes (nanofiltration membrane) for water purification

As modern water purification technologies, membrane and filter based processes well considered. However, their major drawback are organic and bio fouling problems. The incorporation of various inorganic nano-materials such as carbon nanotubes and zeolites contribute in developing cost-effective and more efficient water filtration processes (Stanton et al., 2003). These incorporated nano-matrices act as selective reject substances smaller than the membrane pores, in addition to their performance as physical barrier that facilitate the separation of harmful contaminates rather than nutrients present in water as indicated in Figure 7. The filters and membranes may be fabricated from a variety of nanomaterials such as carbon nanotubes, nanoporous ceramics (clays), dendrimers, zeolites, nanofibres and nanosponges (Meyer, 2004). It is anticipated in future that most membranes and filters will become commonplace in detecting and removing viruses from water. Where, they may develop to act as multi–tasking filtration systems to detect, separate out, and/or detoxify contaminants (DeFriend et al., 2003).

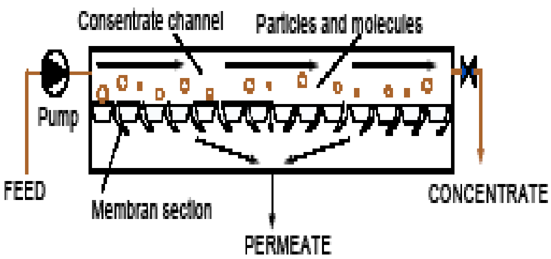

Figure 7. Nanofiltration operation.

A major challenge of the membrane fabrication is to combine in its properties between selectivity and permeability. The most important difficulties for membrane technology application at pressure driven membrane processes is the energy consumption. The fouling properties of the membranes improve the energy consumed beside the reduction at the membranes lifetime at pressure driven membrane processes. In order to improve the membrane properties such as its permeability, fouling resistance, mechanical and thermal stability, as well as to render new functions for contaminant degradation and self-cleaning, functional nanomaterials may be incorporated into the membrane matrices (Allabashi et al., 2007).

Nanoreactive filters and membranes are the main two categories of membranes nanotechnology, where these categories particularly functionalized nanoparticles better the filtration process by selectively binding with the target contaminants; and nanostructured filters. Carbon nanotubes or nanocapillary arrays provide the basis for physical separation via nanofilteration (Bhattacharyy et al., 1998). In order to fabricate reactive membranes instead of simple physical barrier membranes, membranes may be impregnated with photoactive nanomaterials to achieve multiple treatment goals in one reactor and minimizing fouling. Inorganic prepared membranes and polymer nanocomposite membranes represent the most common types of nanoreactive membranes (Li and Xia, 2004). There is a continuous search for innovative materials to enhance the water purification membrane technologies. Carbon nanotubes, nanoparticles, and dendrimers are considered to develop membrane filtration process.

Carbon Nano-tubes (CNT) enhanced Membranes for water purification

With respect to the very small diameters of Carbon nanotubes, they are considered as useful material for physical separation processes. The CNTs reinforced membranes provide easy and fast pathways for water molecules to pass through and reject almost all contaminants due to their nanoscale pores. CNTs reinforced membranes can be prepared through various techniques; the most proper one involve growing an aligned array of CNTs on a substrate and infiltrating them with a matrix material (Aleksandr Noya, et al., 2007). For example, β-Cyclodextrin and CNTs were linked by a bifunctional linker and tested by passing trichloroethylene (TCE) through the membranes (Krause et al., 2008). This fabricated membrane posses 98% rejection affinity of TCE after recycling the nanocomposite membrane 25 times.

Nanofiber membranes for water purification

In order to fabricate ultrafine fibers from various materials (e.g., polymers, ceramics and metals) using simple, efficient and inexpensive way, electrospinning represents the most proper technique (Cloete et al., 2010). The electrospun nanofibers can be easily manipulated for water purification as nano-filters respecting to their high specific surface area and porosity and their ability to form nanofiber mats with complex pore structures (Li and Xia, 2004). The nanofiber membranes have been widely employed for air filtration applications compared with water treatment processes. Nanofiber membranes can be utilized as pretreatment process prior to ultrafiltration or reverse osmosis where they have ability to remove micron-sized particles from aqueous phase at a high rejection rate without significant fouling (Ramakrishna et al., 2006). Nanoparticle impregnated nanofibers represent an advanced designated functional nanomaterials that can be easily fabricated through doping any functional nano-material into the spinning solutions (Li and Xia, 2004). Eectrospun nanofibers represent an ideal platform for constructing multifunctional membrane filters by either directly using multifunctional materials such as titanium dioxide or by introducing functional materials on the nanofibers. The incorporation of ceramic nanomaterials onto the nanofiber scaffold enhance its affinity to remove heavy metals and organic pollutants during filtration process.

Nano-composite membranes for water purification

Membrane nanotechnology has been focused by various studies for the implementation of multifunction nanomaterials into polymeric or inorganic membranes. These incorporated nanomaterials may be have catalytic, antimicrobial or other activities such as the incorporation of the hydrophilic metal oxide nanoparticles (e.g., Al_2O_3 and TiO_2). These hydrophilic metal oxide nanoparticles are added mainly to reduce the membrane fouling properties through improving the membrane hydrophilicity. Many researches were succeeded to increase membrane surface hydrophilicity, water permeability and fouling resistance through incorporation the polymeric ultrafiltration membrane with different nano-particles such as alumina, silica, titanium dioxide and zeolite to accomplish novel composite polymeric membranes (Maximous et al., 2010; Bottino et al., 2001; Pendergast et al., 2010; Bae and Tak, 2005). Furthermore, these incorporated nanoparticles enhance the mechanical and thermal stabilities of the fabricated composite polymeric membranes (Ebert et al., 2004; Pendergast et al., 2010).

Thin film nanocomposite (TFN) membranes for water purification

The incorporation of active and function nano-materials into the active thin film composite layer (TFC) membranes via doping in the casting solutions or surface modification responsible for developing of thin film nanocomposite (TFN). The most frequently used dopant materials that have shown potential in enhancing membrane permeability include nano-zeolites, nano- Ag, nano-TiO_2, and CNTs. The addition of these dopants has significant impact on different membrane properties such as its permeability and selectivity that depends on the type, size and amount of nanoparticles added. The research results evident that addition of nano-zeolites into polyamide membrane improves its permeable, negatively charged, and thicker polyamide active layer (Lind et al., 2009a). Other research investigate that TFN membranes doped with 0.2 wt% nano-zeolites achieved moderately higher permeability and better salt rejection (> 99.4%) compared with the commercial RO membranes (Lind et al., 2010). The small, hydrophilic pores of nano-zeolites assumed to create special water paths. On the other hand, the membrane water permeability increased even with pore-filled zeolites, although less than the pore-open ones, that may be regarded to defects at the zeolite polymer interface. Nano-zeolites may be utilized as immobilized matrix for antimicrobial agents such as silver ions that improve the membrane anti-fouling property (Lind et al., 2009b). While, doping of TFC active layer with nano-TiO_2 slightly increases the membrane rejection and maintaining the membrane permeability (Lee et al., 2008). As the doping concentration of nano-TiO_2 increased above 5 wt % the water flux increased in the cost of reducing rejection, suggesting defect formation in the membrane active layer. Furthermore, TiO_2 can reduce organic and biological fouling through degrade organic contaminants and inactivate microorganisms in presence of UV irradiation (Kanakaraju et al., 2014).

Bioactive nano-materials for water purification

The presence of pathogenic contaminates at polluted water causes many of infectious diseases. Most of these pathogenic strains are antibiotic resistance that hindering their removal from polluted water. The concept of bioactive nano-materials has been known as the alternative of new chlorine –free biocides.

Antimicrobial nanomaterials for water purification

Recently, nanotechnology represents a new route to take advantage of the antimicrobial behaviour of active metal nanoparticles. The immobilization of Biocidal metal nanoparticles has various applications in medical instruments and devices, water treatment and food processing. However, the formation of metal active nanoparticles polymeric composite represents the favour utilization of the antimicrobial active nanomaterials. Nanoparticles characterized by their stronger antimicrobial effects compared with microparticles or metal surfaces respecting to their rate of release in a given solution is faster than the larger particles. However, the cellular characteristic at the nano-scale is responsible for the new toxic mechanisms taking into account the role of the particle size itself. Thereafter the cell uptakes of particles increments as ionic species are in this manner discharged inside of the cells by nanoparticle disintegration; this process is known as "the Trojan horse mechanism". Massive oxidative stress has been resulted as action of high intracellular concentration gained after nanoparticle dissolution within the cell. The active antibacterial nano-materials are categorized as naturally antibacterial agents, metal and metal oxides andinnovative engineered nanomaterials. These antibacterial nano-materials interact with microbial cells through different mechanisms such as directly interact with the microbial cells, disrupting or penetrating the cell envelope, or oxidizing cell components and produce secondary products that damage the cell. Strong oxidants such as free chlorine, chloramines and ozone are recently used effectively in drinking water purification. These chemical disinfectants react with various constituents in natural water to form harmful and carcinogens disinfection by-products (DBPs) (e.g. trihalomethanes, haloacetic acids and aldehydes). Accordingly, an innovative alternative disinfection technique that enhances dependability and healthiness and avoiding DBP formation are required for replacement the current methods. The antimicrobial nanomaterials such as silver and most of metal oxides haven't any oxidation properties and they are relatively inert in water. So, they haven't any tendency to produce harmful DBPs with the drinking water. Accordingly, the incorporation of theses antimicrobial nanomaterials into the treatment processes instead of the conventional disinfection methods will be safe manner for drinking water purification (Qilin et al., 2008).

Figure 8 shows the major suggested antimicrobial mechanisms using different nano-materials. The various suggested disinfecting mechanisms using different antimicrobial nanomaterials will be discussed.

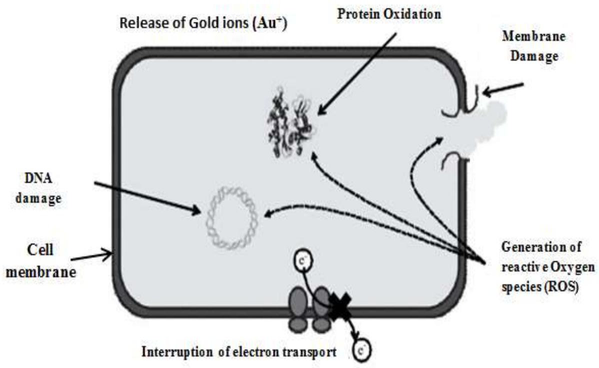

Figure 8. Various antimicrobial mechanisms using nanomaterials.

Chitosan and Peptides as Antimicrobial agents

The fabricated chitosan and peptide based nano-materials from the naturally occurring resources act as potential low cost disinfection materials for water purification. The antibacterial mechanism of peptide based nano-materials is depends mainly upon the osmotic collapse by formation nanoscale channels in the bacterial cell membranes. However, there are various mechanisms belongs to the disinfection using chitosan based nano-materials. One mechanism suggested that the positively charged chitosan particles react with negatively charged cell membranes that rupture and leakage of intracellular components. This suggested mechanism known as the chief antimicrobial mechanism. Another proposed disinfection mechanism using chitosan based nano-materials is the penetration of these anti-microbial materials through cell membrane walls and binding with its DNA and inhibits RNA synthesis within cells. Utilization of chitosan and peptide based nano-materials for water purification may be through linking the water storage tanks with these materials or incorporation of these materials as an antimicrobial agent in membranes utilized for water purification processes (Hollman and Bhattacharyya, 2004).

Silver Nanoparticles as Antimicrobial agents

Silver is the most widely used material due to its low toxicity and microbial inactivation in water with well-reported antibacterial mechanism. Silver nanoparticles are derived from its salts like silver nitrate and silver chloride. The antibacterial effect is size dependent, smaller Ag nanoparticles (8 nm) were most effective, while larger particle size (11–23 nm) results in lower bactericidal activity. Also, truncated triangular silver nanoplates exhibited better antibacterial effects than the spherical and rod-shaped nanoparticles indicating their shape dependence. The mechanisms involved during the bactericidal effects of Ag nanoparticles include, for example, the formation of free radicals damaging the bacterial membranes, interactions with DNA, adhesion to cell surface altering the membrane properties, and enzyme damage (Sahar et al., 2012).

As silver nanoparticles interact with the cells of bacteria, large quantities of silver ions (Ag^+) have been released. These realised ions react with thiol groups in the enzymes and form reactive oxygen species (ROS) within the cells. These reactive spices reduce the respiratory enzymes leading to cell death. Moreover, the released silver ions damages cell's DNA and RNA and prevent DNA replication causing cell death. Furthermore, silver nanoparticles characterized by its photo-catalytic activity, so, it may be utilized as disinfection agent for microbes in presence of UV radiation. Recently, the membranes utilized for water purification and disinfection were immobilized with silver nanoparticles.

TiO_2 Nanoparticles as Antimicrobial agents

Similar to silver nanoparticles, TiO_2 was characterized by its photo-catalytic activity in presence of UV radiation or even in presence of visible sunlight. This photo-catalytic activity can be enhanced through metals doping (Liu and Jaroniec, 2011). Its antibacterial activity is mainly due to ROS production by oxidative and reductive sequence of chemical reactions taking place within a cell producing hydroxyl free radicals and peroxide under UV irradiation or sunlight. Recently, the nanoscale TiO_2 is widely used in water disinfection applications from gram positive and gram negative microorganisms regarding to its stability in water, low cost and non-toxicity (Brunet et al., 2009).

ZnO Nanoparticles as Antimicrobial agents

Similar to both silver nanoparticles and TiO_2, nano-ZnO accomplishes high UV irradiation photo-catalytic activity and absorption efficiency. The photocatalytic degradation mechanism using ZnO is mainly regarded to generation of hydrogen peroxide within the microorganism cells that oxidizes the cell components. Another antimicrobial suggested mechanism using ZnO is bacteria growth inhibition through diffusion of the cell envelope and disorganization of bacterial membrane upon contact with ZnO nanoparticles. The water dissolving rate of nano-zinc oxide is comparatively high compared with nano-TiO_2, so, its applications in drinking water purification are limited and TiO_2 is more promising (Elsayed et al., 2014).

Copper Nanoparticles and its oxide as Antimicrobial agents

As the microbial cells exposed to the high surface of biocidal copper nanoparticles, their membranes were damage causing cells death. The proposed mechanism of the antimicrobial action of copper nanoparticles is mainly owed to the facile oxidization of Cu nanoparticles when interacting with cell membranes containing higher O_2 concentration compared with the cell media. Accordingly, the cell membrane damage using copper nanoparticles related directly to the metal release process at the particle-cell surface interface. On the other hand, copper oxide (CuO) nanoparticles were presented by some researches as antimicrobial agent. The cytotoxicity of the CuO nanoparticles was related to the released soluble ions from nanoparticles that form copper-peptide complexes in amino acid-rich medium which interact with either cellular membrane or intracellularly. Finally, it was concluded that the behaviour of ions released from CuO nanoparticles is different from that released from copper salts at the same concentrations. Where, it was investigated from the antimicrobial mechanism of metal nanoparticles that both the particle itself and their ions can participate in the biocide mechanisms rather than the metal oxide nanoparticles.

Carbon Nanotubes (CNTs) as Antimicrobial agents

The antimicrobial activity of CNTs was proofed to take place through destroying or degradation of bacteria cells using two different techniques. The suggested antimicrobial techniques are the chemical reaction of CNTs with the pathogens or the physical inhibition of their passage through filters. The first antimicrobial mechanism of chemical reaction requires immediate contact between CNTs and the target pathogens which is difficult to achieve stable and homogeneous CNT suspensions in aqueous media. However, CNTs material is effectively utilized in filtering microbes such as bacteria and even viruses by physically inhibiting their passage across membranes. Especially, the single walled carbon nanotubes that have small diameters (2 to 5 nm) can be act as efficient filter for almost all known pathogens (Srivastava et al., 2004).

CONCLUSIONS

Nutrients, organic matter, heavy metals, microbial contaminants, toxic organic compounds, salts, acids, sediments and suspended solids are considered as the most common water pollutants that have important impact on the human life through their accumulation in the foods chain either by the environmental pollution or food process contamination. These contaminates are either in solution or as particulate matter and can have (bio-) cumulative, persistent and synergetic characteristics affecting ecosystem health and function, food production, human health and wellbeing. Several commercial and non-commercial technological developments are employed on daily basis but nanotechnology has proved to be one of the advanced ways for water purification. Advances in nanotechnology have provided the opportunities to meet the fresh water demands of the future generations. It is suggested that nanotechnology can adequately address many of the water quality issues by using different types of nanoparticles and/or nanofibers. Nanotechnology is actively pursued to both enhance the performance of existing treatment processes and develop new processes. The innovation of new technologies to increase the availability of clean water commenced 40 years ago with the establishment of three membrane separation processes that include reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF). The impact of nanotechnology on the development of tools and techniques for water treatment will be more pronounced in the near future, as scarcity of natural water threatens the advancement and the social security of many communities around the world. Therefore, the production of nanostructures, nanocomposites and modified nanostructures for water remediation will increase because of the need for producing clean water in fast and low energy consumption ways. Nanotechnology should be regarded as the tool to ensure the sustainability of social communities in different places. Accordingly, nano-remediation as eco-friendly technology that involves application of reactive materials for the detoxification and transformation of pollutants is considered to be an effective alternative to the current practices of site remediation. These reactive materials initiate both chemical reduction and catalysis of the pollutants of concern. The unique properties of nanomaterials make them best suited for in situ applications. Their small size and novel surface coatings enable them to achieve farther and wider distribution when compared to large-sized particles. Innovations in the development of novel technologies for water remediation are among the most exciting and promising. The recent advances on the development of novel nanoscale materials and processes for water purification have been considered. These include nanopowder materials utilized as potent sorbents; in some cases combined with magnetic particles to ease particle separation. Furthermore, the nanopowder materials utilized as catalysts for chemical or photochemical destruction of contaminants were explored. Additionally, the nanostructure filtration membranes include nanofiltration membrane were discussed. Finally, the antimicrobial mechanisms of bioactive nanomaterials utilization for bacteria and viruses removal were investigated.

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Conflicts of Interest

The authors declare no conflict of interest.