Chapter

Nanoparticles in Wastewater Treatment

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Abstract

Water plays a crucial role in every animate life. There are a multitude of problems that can be occurred without water; thereafter, mankind's lives can be extinct. Several solutions should be implemented in order to protect water supplies and to treat water used in industries. Among solutions, wastewater treatment is sounded economical and convenient way to overcome water scarcity. Physical, chemical, biological, and mixed treatment systems provide ample opportunity to use water over and over again. However, by using nanotechnology in these systems wastewater treatment can reach much more quality and overcome their drawbacks. Nanomembranes in MBR technology is one of most appropriate treatment technologies that have such potential to postpone water shortage until several years.

Keywords: water scarcity, wastewater treatment, water reuse, nanoparticles, nano-materials, nanocomposite membranes

1. Introduction

Let us imagine a world without water. When you get up in the morning, the first place you usually go is the lavatory and use water to feel fresh and to get rid of the tiredness of the night. But, what will happen if water is not flowing from the faucet or pipes? Perhaps, on the first day, it would impair your ability to focus on your work besides thinking about water would deter you from doing even your daily chores and errands. Indeed, lack of water can affect all people's life adversely like making them sick or even causing them to pass away in just a few days.

Hence, why water is so important in mankind's life? Why should all people do their best to protect water supplies? The imagination of the world without water is terrible; therefore, what will happen if individuals do not have water in reality? There is an enormous amount of water all over the Earth, so why we have to hear the news of water scarcity every day on news? Is it possible for people to reuse water that was used before? What are the best ways of treating water and wastewater in order to use them over and over again? We are going to discuss all of these questions and answer them whereby our aim is that people try to protect WATER from being polluted.

Every organism, regardless of micro-organisms and macro-organisms, needs water to continue living. Some micro-organisms could live without oxygen, however, there are no animated that could live without water. So, water is absolutely more important than oxygen by which human beings and marine animals are breathing. Indeed, their lives rely on water due to the fact that their bodies comprise a lot of water and they need to consume water to gain energy and to metabolism activity.

Insufficient water causes the human body's systems to change. Almost two billion people do not have access to basic water services in public health care facilities around the world. Hand washing with soap has a proven health benefit, but in reality, one out of six health facilities worldwide lacks functioning hand washing facilities either at clinics or toilets. It is widely believed that training in basic water, sanitation, and hygiene is essential for making a healthy learning environment. Without that, cells of the body shrink. Mankind's brain will tell their bodies to urinate less. A kidney's ability to eliminate waste from the blood depends on adequate water levels. People's kidneys cannot function properly without adequate water. Without enough water, the kidneys have to work harder and wear down tissues. Water is essential to the health of the kidneys and other organs in the body. Without adequate water intake, these organs and others may not function properly. A lack of water will result only in a matter of days before a person dies, so people need more than enough water in their bodies. Keep in mind that exercise, hot temperatures, and illness can increase the need for water for staying healthy. Generally, thirst will guide individuals when it comes to how much water they should drink [1].

It can be inferred from the aforementioned determinants of water that without water humans will be extinct. Even though water is utilized by living organisms and so necessary for them, the main water using pertains to industries and agricultural activities around the world. Living organisms' share of use of water in comparison with factories and agriculture activities is negligible. Various kinds of factories and industries use water as a raw material to produce beverages, to manufacture cars, to separate crude oil, to irrigate their farms, etc. Under such circumstances, water being polluted since it is used in different kinds of processes and related to its process usage, its contaminations could be various. If the world has unlimited water sources, it is not even acceptable to use water in the factories and pour them somewhere else without treatment because its contamination would spread pathogen microbes. Oceans have plenty of water, however, it is salty water and it is needed ridiculously expensive processes to eliminate its salt so that it can be used. Therefore, our world does not have sweet water, so industries have to treat water used in their processes. Treating wastewater is much more convenient than seawater. Treating and reusing wastewater provides people with a water cycle and it postpones water scarcity until several years later. So, not only do governments enact serious laws in order to oblige industries to treat their used water in a very appropriate way, each individual had better do their responsibilities not to use water more than their needs. Eventually, Water scarcity and the increasing demand for clean water make treating and recycling wastewater inevitable in the Twenty-First Century.

2. Wastewater treatment methods

Wastewater treatment methods can be categorized into three main areas: (1) physical, (2) chemical, and (3) biological. Wastewater treatment using physical processes is primarily dealing with solid–liquid separations, in which filtration plays a major role. Conventional and nonconventional filtration techniques are divided into two general categories. Water treatment applications rely on this technology. The treatment process is only one unit of a conventional water treatment scheme, in which there is a wide range of equipment and technology options to choose from depending on the ultimate goal of treatment. It is important to understand the role of filtration in water purification in comparison to other technologies as well as the objective of different unit processes. This economic process can remove suspended solids of the wastewater and also in some cases like using membranes it can eliminate micro-organisms of wastewater. Nevertheless, it is not able to decrease organic contaminations and heavy metals of the wastewater alone which are so harmful either in reusing at industries or domestics. Membrane filtration is one of the dominant examples of this process whose structure not only can be modified by using some novel technology like nanoparticles but can be exploited with other methods of treatment easily.

Chemical methods of treatment rely on chemical interactions between the contaminants and the operator of the chemical apply and provide assistance in either removing contaminants entirely from water or neutralizing harmful effects associated with contaminants. It is possible to apply chemical treatment methods standalone and also as a part of a treatment process that involves physical processes. Organics of the wastewater will be removed by utilizing this expensive method; however, it will enter some new compounds into the wastewater some of which might be harmful. For instance, adsorption by activated carbon is commonly used in industries and domestic treatments in order to remove turbidity and the scent of water without any side effects.

The biological treatment of wastewater has an apparent simplicity because it relies on natural processes to help with the decomposition of organic compounds, but it is actually complex, not fully understood, and taking place at the intersection of biology and biochemistry. Wastewater contains organic matter, including garbage, organic wastes, partially digested foods, heavy metals, and toxins. Biological treatments tend to rely on bacteria, nematodes, and other small organisms to break down organic matter. Biological treatment can be used worldwide because it is flexible, economic, and environmentally friendly. Many mechanical or chemical processes cannot match the effectiveness or efficiency of biological treatments. The conventional activated sludge (CAS) process is a good illustration of this. These systems typically include an aeration tank that acts as a biological degradation agent and a secondary clarifier for separating sludge from treated wastewater [2].

Wastewater treatment methods can incorporate any combination of these three technology groups, or select ones, depending on the treatment objectives. According to the reusing standards, these methods can be combined with one another and it is quite obvious that if anyone wants to reach high quality of treated water, they should combine all three methods in order to reach the water which even can be drunk. Totally, the main factors affecting the way of treatment methods choosing are the characteristics of the wastewater and the quality needed for reusing. Depending on the manufacturing process, industrial wastewater can contain specific organic constituents, high salinity, heavy metals, acids with high pH, and inorganic particles with high turbidity. In this regard, a wastewater treatment plant, either industrial, municipal, or drilling water treatment, is not much different from, say, a rubber factory or an oil refinery. In most industrial and agricultural activities, high-quality clean water is crucial; however, treating water to high standards is expensive; and droughts, contamination of water resources, and competing demands inevitably limit the availability of water for agriculture and oil and gas extraction, complicating food production and energy production. The successful treatment of poor quality water must not only produce water of desirable quality but also protect downstream processes. In industrial wastewater treatment, multiple sequential treatment steps are often needed. This is called a "treatment train." The cost of distilling contaminated water is prohibitive and not all industrial waters require this level of treatment. While distillation can remove all contaminants, it may not always be feasible. Moreover, certain technologies have inherent limitations, particularly at high water recovery and salinity. Membranes are limited by osmotic and hydraulic pressures, as well as mineral precipitation. Adsorbers are limited to certain compounds having specific functional groups. Specifically, unit processes for removing contaminants from a range of chemical groups are needed, as is the ability to convert a variety of industrial waste streams into high-value materials and energy. Dedicated wastewater treatment plants often pre-treat industrial wastewater on-site. In terms of sustainable economic development and the environment, new technologies for the treatment of impaired and unconventional water are crucial. By using nanotechnology, waste streams can be treated, allowing water to be reused and energy to be recovered, as well as highly valuable materials [3–5].

3. Nanotechnology in wastewater treatment

Conventional water treatment is not always very effective at removing contaminants such as metals and micro-organisms. The formation of disinfection byproducts (DPBs), which can harm human health, is another problem. The DPBs are formed when chemical disinfectants react with organic matter and inorganic ions in the water. The removal of metals, microbes, and oil from contaminated water has been studied using nanomaterials in some studies. Nanomaterials have been used as an alternative to remove contaminants. In nanoscience, phenomena are studied at the nanometer scale. Nanotechnology involves materials with at least one component whose dimension is less than 100 nm [6]. These materials differ greatly from conventional materials, in terms of mechanical, electrical, optical, and magnetic properties, due to their nanoscale size. The nanomaterials' small size and large surface area make them highly adsorbent and reactive. In addition, nanomaterials have been reported to be highly mobile in solution. Heavy metals, organic pollutants, inorganic anions, and bacteria have all been reported to be removed using various types of nanomaterials. Many nanomaterials have been extensively investigated for their potential applications in water and wastewater treatment, including zero-valent metal nanoparticles, metal oxide nanoparticles, carbon nanotubes, and nanocomposites.

3.1 Zero-valent metal nanoparticles

3.1.1 Silver nanoparticles

Antibacterial properties of silver nanoparticles have been attributed to their high toxicity to microorganisms, including bacteria, viruses, and fungi. Since silver nanoparticles are good antimicrobial agents, they are widely used to disinfect water. There is no clear understanding of how Ag NPs have antimicrobial effects, and the mechanisms remain unclear. The adherence of Ag nanoparticles to bacterial cell walls and subsequent penetration, which caused structural changes within the membrane and thus increased its permeability, has been hypothesized. Moreover, when Ag NPs contact bacteria, free radicals are produced. These free radicals damage cell membranes, causing the death of cells. DNA contains abundant sulfur and phosphorus elements, which also cause the death of cells. More importantly, the NPs when broken down will release Ag^+ ions, which will interact with enzyme thiol groups, inactivate them, and hinder normal functions of the cell [7–9].

3.1.2 Iron nanoparticles

Recently, zero-valent metal nanoparticles, such as Fe, Zn, Al, and Ni, have been gaining wide research interest in water treatment. Nanozero-valent aluminum is thermodynamically unstable in water due to its high reductive abilities, which leads to formation of oxides/hydroxides on the surface, interfering entirely with electron transfer from the metal surface to contaminants. The standard reduction potential of Ni is less negative than that of Fe, indicating lower reduction ability, while nano-zero-valent Fe or Zn has a moderate standard reduction potential and are ideal reducing agents relative to most redox-labile contaminants. While Fe has weaker reduction abilities, it has many effects on water pollution and is an excellent adsorbent, precipitates and oxidizes (if oxygen is present), and is relatively inexpensive. So far, zerovalent iron nanoparticles have been subjected to the most extensive study among zerovalent metal nanoparticles [10].

3.2 Metal oxides nanoparticles

3.2.1 TiO_2 nanoparticles

It has been proven that photocatalytic degradation technology can successfully be used in the treatment of water and wastewater by oxidizing contaminants into low molecular weight intermediate products, which eventually turn into CO_2, H_2O, and anions such as NO_3^-, PO_3^-, and Cl^- for reuse. Metal oxides and sulfide semiconductors are the most common photocatalysts. Of them, TiO_2 has been investigated most intensively in recent decades due to its high photocatalytic activity, reasonable price, photostability, and chemical and biological stability [11]. Besides, Due to its low cost, toxic free property, chemical stability, and easy availability on earth, titanium dioxide (TiO_2) is one of the best photocatalysts existed on the earth. Anatase, rutile, and brookite are among the three natural states of TiO_2. Until today, Anatase is considered a good material for nanophotocatalysis [12]. In short, its running process described as below: a semiconductor like TiO_2 absorbs light that is greater or equal to its band gap width, carrying electron–hole pairs (e^--h^+). By separating the charge further, the electrons and holes may travel to the catalyst surface, where they are combined with the sorbed species to produce the redox reactions. The hydroxyl radicals are generated when h^+_{vb} react with water (surface-bound) and the radical anion (superoxide radicals) when e^-_{cb} selected by oxygen, as shown below in figure [13]:

3.2.2 ZnO nanoparticles

Apart from TiO_2 nanoparticles, ZnO nanoparticles have emerged as a valuable photocatalytic candidate in water and wastewater treatment due to their unique properties, including high oxidation capacity and good photocatalytic property. In addition to being environment-friendly, ZnO NPs are also compatible with organisms, which make them ideal for sewage treatment. Their photocatalytic capacity is similar to that of TiO_2 NPs because their band gap energies are similar. In contrast to TiO2 NPs, ZnO NPs are more affordable [14]. ZnO nanoparticles can

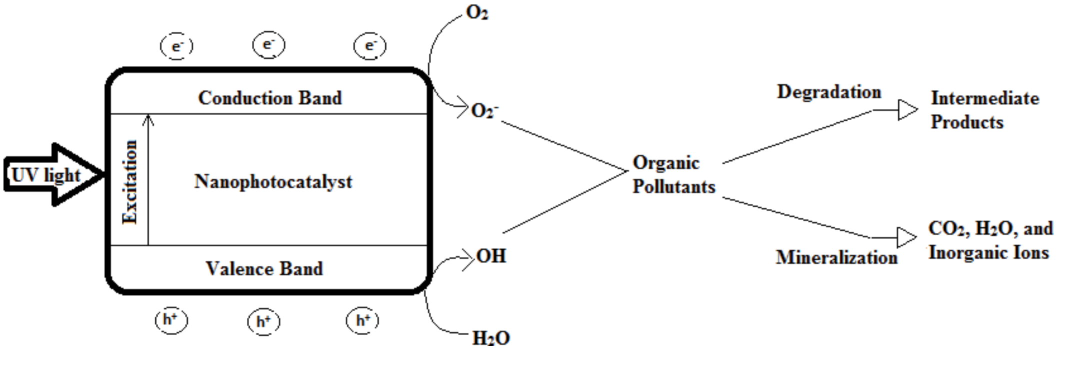

Figure 1.
Nanophotocatalytic degradation of organic toxic compounds: A general mechanism.

also adsorb a larger range of solar spectra and a greater number of light quanta than several semiconducting metal oxides [15]. However, the light absorption of ZnO NPs is also limited in the ultraviolet wavelength region, similar to that of TiO2 NPs. Additionally, ZnO NPs are susceptible to photocorrosion, resulting in fast recombination of photogenerated charges and resulting in low photocatalytic efficiency [16]. Metallic doping of ZnO nanoparticles is a common method of improving their photodegradation. Researchers have evaluated a wide range of metal dopants, including anionic, cationic, rare-earth, and codopants [17]. The coupling of ZnO with other semiconductors, including Cadmium oxide (CdO) [18], Cerium dioxide (CeO_2) [19], Stannic dioxide (SnO_2) [20], TiO_2 [21], Graphene oxide (GO) [22], and Reduced graphene oxide (RGO) [23], has also been shown to enhance photodegradation efficiency of ZnO particles.

3.2.3 Iron oxides nanoparticles

There has been a growing interest in iron oxide nanoparticles as adsorbents for heavy metal removal due to their simplicity and availability. The nonmagnetic hematite (Fe_2O_3) has also been used in recent years for the removal of heavy metals. In general, nanosorbent materials can be difficult to separate and recover from contaminated water due to their small size. It is possible to separate and recover both magnetic magnetite (Fe_3O_4) and magnetic maghemite (-Fe_2O_4) easily by implementing of an external magnetic field. These materials were successfully used as sorbent materials to remove various heavy metals from water systems. Several ligands like ethylenediamine tetraacetic acid (EDTA), L-glutathione (GSH), mercaptobutyric acid (MBA), α-thio-ω-(propionic acid) hepta(ethylene glycol) (PEG-SH), and meso-2,3-dimercaptosuccinic acid (DMSA) or polymers like copolymers of acrylic acid and crotonic acid have been used to enhance the adsorption efficiency of iron oxide nanoparticles by mixing them with various metal ions [24–26]. It has been reported that a flexible ligand shell facilitates the incorporation of a wide array of functional groups into the shell as well as enabling Fe_3O_4 nanoparticles to retain their properties. Moreover, polymer shells have been shown to enhance the dispersibility of nanostructures and prevent particles from aggregating. Metal ions found in treated water could be "carried" by polymer molecules as binders [27].

3.3 Carbon nanotubes

These materials are unique in their structures and electronic properties, making them a fascinating class of materials that have attracted scientists for fundamental research and diverse applications, including sorption processes. They have a great capacity for adsorbing a wide range of contaminants, fast kinetics, large specific surfaces, and selectivity towards aromatics, making them very effective for the treatment of water and wastewater. Carbon nanotubes (CNTs) are one type of carbon nanomaterials (CNMs), but there are several others, including carbon beads, fibers, and nanoporous carbon. Among these, CNTs have gained the most attention and have progressed rapidly in recent years. Carbon nanotubes are graphene sheets rolled up in cylinders with a diameter as small as 1 nm. The remarkable properties of CNTs have made them a very attractive adsorbent. CNTs show extremely high specific surface areas and adsorption efficiencies for a wide variety of contaminants, due to their abundant porous structures. Many carbon nanotubes are combined with metals or other supports in order to improve their surface area, mechanical properties, optical properties, and electrical properties [28, 29].

The inhibitory mechanism of nanoparticles against different bacteria and fungi includes release of metal ions that interacts with cellular components through various pathways including reactive oxygen species (ROS) generation, pore formation in cell membranes, cell wall damage, DNA damage, and cell cycle arrest and ultimately inhibits the growth of cells. Therefore, they can be used to treat water and wastewater to gain usable besides drinkable water without any pathogens. However, Nanotechnology raises concerns in the public and activist groups regarding several fundamental aspects. In view of the much greater surface area to volume ratio of nanoparticles, researchers acknowledge the risk associated with nanomaterials may be different from the risk associated with bulk versions of the same material. This could lead to undeveloped and untested interactions with biological surfaces compared to bulk materials [30].

3.4 Nanocomposite

Recent years have seen a surge in the production of various nanocomposites. A huge amount of research has been carried out all over the world on the basis of numerous studies. According to the results, the adsorbent has good potential in removing nitrate from water quickly and effectively. Furthermore, due to its unique magnetic property, the adsorbent can be easily removed from the solution using a magnet. Real composite materials should be smooth, bulky, immobile materials that achieve nano reactivity by anchoring or impregnating a parent material structure with nanomaterials. Furthermore, treatment of water and wastewater needs nontoxic, long-term stable, low-cost materials. Further research is still necessary to obtain desired nanocomposites [31].

4. Type of nanomaterials in wastewater treatment

The obvious way of using nanotechnology in water and wastewater treatment is that this technology cannot be used itself, and, as a result, it has been found that nanomaterials had better be incorporated into industrial water treatment processes. A large amount of research has been carried out into the application of nanotechnology for wastewater treatment. Nanotechnology can be classified into three main groups based on the kinds of materials they use: Nano-adsorbents, Nano-catalysts, and Nano-membranes [6].

4.1 Nano-adsorbents

Adsorbent nanoparticles are nano-sized particles made from organic or inorganic materials that have a strong affinity for adsorbing substances. This means that they are able to remove a lot of pollutants. It is possible to use these nanoparticles in the removal of different kinds of pollutants due to their important characteristics, such as their catalytic potential, small size, high reactivity, and their higher surface energy. Adsorption processes can be distinguished among metallic nanoparticles, mixed oxide nanostructures, magnetic nanoparticles, and metal oxide nanoparticles [6].

4.2 Nano-catalyst

In nano-catalysis, light energy interacts with metallic nanoparticles, leading to high and wide photocatalytic activities. This treatment is gaining popularity due to its high and wide photocatalytic activity. In a photocatalytic reaction, bacteria and organic matter are destroyed by hydroxyl radicals. Materials used in nano-catalysts usually contain inorganic components like semiconductors and metal oxides. A nano photocatalyst must meet certain criteria to be considered a nanocatalytic; these include: being harmless and their concentration in water and air below the maximum permissible level; making agglomerates, precipitating, and forming ordinary particles [6].

4.3 Nano-membrane

A nano-membrane is responsible for separating particles from wastewater. These filters are very effective in removing dyes, heavy metals, and other contaminants. Nanotubes, nanoribbons, and nanofibers are nanomaterials used as nano-membranes.

Among nano-adsorbents, nano-catalysts, and nano-membranes, nanoparticles integrated into membranes are more convenient and useful because of the fact that not only does this process include a powerful physical treatment in it, but it also has nanoparticles to improve the quality of the treatment. Therefore, the upcoming discussion is about nano-membranes.

As nanotechnology has grown rapidly, the fabrication of nanocomposite membranes has become increasingly significant and efficient. As a result, a wide range of nanoparticles (NPs) has been examined for their implications on polymeric nanocomposite membrane engineering properties; in many cases, these NPs have improved mechanical, thermal, and antifouling properties significantly [32]. **Table 1**. shows some of the membranes prepared with nanotechnology in order to prepare modified membranes. NPs are widely known to increase the mechanical and thermal properties of polymeric membranes when they are dispersed uniformly into the polymeric matrix and formed strong interfacial bonds with the matrix. Membranes are broadly used in membrane bioreactor (MBR) systems for treating various types of wastewater. As compared to conventional processes, the MBR process, which combines activated sludge with membrane filtration,

Membrane type	Material of membrane	Nanoparticle	Main result	Reference
Ceramic	α-Al_2O_3 filters	TiO_2	Rejection improved	[33]
Ceramic	Alumina	Fe_2O_3	Rejection improved	[34]
Polymeric	Polypropylene (PP)	SiO_2	Modified membrane fouling decreased	[35]
Polymeric	Cellulose acetate (CA)	Nanodiamond (ND) and ND-COOH	Mechanical, thermal, and antibacterial properties improved	[36]
Polymeric	Polyvinyl chloride (PVC)	Ag and Ag@SiO_2	Fouling improved and flux increased	[37]
Polymeric	PVDF	ND and PVP-ND	Fouling and flux improved	[38]
Polymeric	PVDF	Ag@SiO_2	Fouling and flux improved	[39]
Polymeric	PVDF	Ag@TiO2	Fouling resistance and antibacterial performance enhanced	[40]

Table 1.
Uses of diverse nanoparticles in several membranes and results.

produces a much higher effluent quality, a smaller footprint, a higher organic loading rate, and less sludge. In this process, membranes are fouled by not only organic matters but also by micro-organisms and their productions. Even though the operating conditions have a great effect on membrane fouling in MBRs, membranes' characteristics plays a key role in this regard [41].

In order to boost the hydrophobicity of polymer membranes and their antifouling properties, different techniques can be used by embedding organic nanoparticles in polymer matrices, for example. In a broad sense, as mentioned in **Table 1**., incorporating nanoparticle in membrane matrix have these three obvious effects:

1. (NOT IN ALL CASES) Triggers to smaller and more pores on the surface of the membrane that leads to more flux and better rejection.

2. By using anti-bacterial nanoparticles and modifying operating conditions the fouling of the membrane can considerably be decreased.

3. Prevent micro-organisms and their bodies' production, which are mainly composed of proteins and carbohydrates, from attaching membrane surface and pores and causes severe fouling.

4. Decreasing frequent cleaning needs for recovery.

It should be noted that a lot of studies have been done by using one nanoparticle in a membrane matrix and found that under these circumstances releasing of the nanoparticle is regarded as a downside. Therefore, researchers try to use more than one nanoparticle in order to make them bigger and to trap them in the membrane matrix with the least releasing.

5. Conclusions

Nanotechnology should be utilized as a supplementary technology beside other means for wastewater treatment. The best form of using nanomaterials in this process is incorporating them with or coating them on membranes and composites. When comparing nanofilters to conventional systems, nanofilters have the following key advantages: Less pressure is required to pass water across the filter that means it dramatically decreases the operational costs, they are more efficient, and they have enormous surface areas which can be easily cleaned by back-flushing compared to conventional methods. Briefly, nanotechnology is highly improved the downside of the treatment technologies; however, it is not eliminated all problems of them. Thus, there is a long way to study and comprehend the suitable ways of the combination of the diverse treatment systems in order to reach several best treatment processes whereby human beings can save the water on Earth for more years to the next generations.

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