Review article

Desalination and Non-potable Water Remediation Using Nanotechnology Based Membranes - A Review

Poornima Govindharaj, Agnishwar Girigoswami and Koyeli Girigoswami*

Medical Bionanotechnology, Faculty of Allied Health Sciences, Chettinad Hospital and Research Institute, Chettinad Academy of Research and Education, Chettinad Health City, Kelambakkam, 603103, Tamilnadu, India

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Abstract

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water filtration

Potable water plays its role in many fields, including agriculture, energy production, and industries, which increases the demand for potable water in society. In order to meet the need for clean drinking water, desalination and purification play a leading role. When desalination is mentioned, the subject of membrane technology often covers its attention, and in this review, we have discussed membrane-based desalination. Advances in nanotechnology and membrane engineering have provided a new platform for enhanced performance in membrane filtration. The hybrid membranes made from a combination of different nanostructures have yielded high precision and durable membranes which are cost- effective. The membranes that incorporate in nanotechnology cannot only remove very small particles from contaminated water, but also remove sulfate, phosphate, magnesium, and calcium- dissolved compounds with multivalent ions. The nanomembranes are more energy efficient also. The different nano-scale materials used in membrane preparation along with their performance have been discussed. The peaks and valleys of the development of nanomaterials for desalination purpose provide a clear view of the upcoming era of membrane desalination.

1. Introduction

The growing global community, along with the depletion of water resources for household, industrial, and farming reasons, has given rise to a major scarcity of freshwater resources in many regions of the globe. In our world, nearly 1.4 billion cubic kilometers of water is present, out of which only 0.5% is accessible fresh water, and this small fraction is also scattered. In the span of

*Corresponding author: Tel.: (+91) 9600060358 Fax: (+91) 4447411000
E-mail: koyelig@gmail.com

the last 50 years, industrial growth and overspilling of the population have caused an increasing demand for available water resources [1]. With sea or brackish water accounting for the majority of 98% of the world's usable water supply, desalination has been identified as a prominent alternative source of clean water. The sea is not only the source of water for our planet but also contains many types of seaweed and marine organisms that have differential biomedical applications [2-5]. While cost-effective water usage and recycling for human and animal use can help to minimize the problem, other sources of clean water are necessary to meet the rising demand. Nowadays, efficient production and adequate supply of freshwater have become a pressing challenge that confronts the planet for both human utilization as well as industrial use. Water consumption is increasing as the global population is growing, resulting in the depletion of many of the world's main aquifers [6].

As a consequence, whatever water resources are available have to be effectively managed. Water pollution, particularly in undeveloped countries, is another crucial matter that presents major health risks. Furthermore, agriculture requires a significant amount of freshwater; on the other hand, agriculture hugely contributes to the pollution of ground water because of pesticide usage, fertilizer usage, and other chemicals. Water supplies across the world are in crisis with constant growth in demand, which is compounded by increases in population, changes in global climate, and deterioration of the overall quality of water. As a result, scientific innovation in comparison to conventional strategies is required. Because of the profusion of salt water and the relative scarcity of fresh water on the globe, seawater desalination and contaminated water treatment have now become major challenges in order to supply fresh water while also protecting human health and the environment [7].

Nanotechnology is a field of science that has opened its arms to various fields of science and technology. Nanotechnology has been used in biomedical science, environmental applications, biosensors, nanomedicine, targeted drug delivery, imaging, theranostics, etc. [8-13]. Bioremediation of wastewater has been largely exploited using nanotechnology, involving a wide range of nanostructure assisted filter membranes, flocculants, sedimentary agents, etc. [14]. A variety of engineered nanomaterials (ENMs) have been developed over the past three decades that possess unique properties compared to their bulk counterparts, such as tunable surface properties, high reactivity, and tailored structures. Water disinfection, decontamination, and desalination were performed using these ENM properties [15]. A number of mechanisms enable ENM-based microorganism inactivation, including the nanoscale disruption of cell walls [16, 17], electrostatic interaction facilitating surface-active processes [18], and photochemical generation of reactive oxygen species [19, 20]. Besides their unique surface properties, ENMs also possess a reactivity that leads to the inhibition of biofilms. This reactivity represents another untapped method for reducing pathogens in potable water, as microbial regrowth in treated water during storage and delivery is a concern to be addressed. In both developing and industrialized countries, organic and inorganic pollutants contaminate drinking-water sources, including rivers, lakes, and groundwater. Pharmaceutics, pesticides, and flame retardants are among the anthropogenic chemicals of concern, while arsenic, for instance, is a naturally occurring chemical [15]. Decontamination of water can be achieved with ENMs that have exceptional catalytic, adsorptive, and optical properties. It is crucial to optimize adsorption capacity, binding mechanisms, and selectivity of nano adsorbents such as nanoscale metal oxides (such as aluminum and iron oxides) and carbon-based ENMs (such as carbon nanotubes and graphene) if effective contaminant adsorption is to be achieved. It is possible to provide clean water by generating nonselective radicals and oxidizing pollutants using reactive ENMs [15]. An important role is played by reverse osmosis (RO) membranes in desalination. RO membranes are constructed with thin-film composites (TFC) and contain fabric backing, a porous polymer layer for mechanical support, and a highly crosslinked polyamide layer, with molecular size being the primary determinant of the separation of water from dissolved solutes. Performance is hindered by membrane fouling, which can be overcome with nanotechnology. A variety of zeolites and metal-organic frameworks (MOFs) have intrinsic pores that may be appropriate for desalination. Mixed-matrix membranes use ENMs directly incorporated into polyamide selective layers, such as zeolite, MOF, and other ENMs [15]. Thus, it is evident that the versatile properties of nanomaterials can facilitate the purification of contaminated water in many ways.

2. Desalination of Seawater

Pre-treatment is required to execute a high-quality reverse osmosis process since accumulated materials cannot be removed from the membrane surface systems, resulting in membrane fouling (a vital issue in the reverse osmosis process) [21]. This procedure divides saltwater into two separate streams: the first stream contains fresh water with a low percentage of dissolved salts, whereas the second contains concentrated brine. Furthermore, as a result of the seawater desalination process, the disinfection procedure is utilized to eliminate hazardous particles from the sea water. The process of eliminating salts and minerals from saline water is known as saltwater desalination. Pre-treatment, reverse osmosis, and conditioning-disinfection are the three primary procedures involved in saltwater desalination. Indonesia has a vast coastline, which means that seawater desalination is one of the water treatment techniques that has a high likelihood of success. Several pieces of research have been carried out in order to develop practical and usable water treatment methods. Because of their high-water permeability, these methods have demonstrated up to 1000 times higher desalination efficiency than reverse osmosis [22]. Accessible water resources, on the other hand, are frequently polluted with waterborne pathogenic microorganisms such as cryptosporidium, coliform bacteria, and virus, as well as different alkalis and metals (As, Cu, Pb, etc.), materials like- medicines and cosmetics, endocrine disruptors, and contamination from radioactive materials, which arise either naturally or as a result of human activity. Furthermore, because of Indonesia's geographical location (on the equator), its saltwater has a low salinity level, making desalination a more viable option. Reverse osmosis, to be precise, consists of membranes made from aligned-carbon nanotubes, biomimicking protein polymers, and nanocomposite thin-films are among the most promising low-energy alternatives. To supply the huge demand of clean potable water, different countries have adopted different technologies. Seawater desalination has been used in Israel, Iran, and a number of Asian nations, including Indonesia. These high technologies may be commercialized in the forthcoming years, but this will require improvements of the composition, purification efficacy, and long-term stability which are the most essential issues to overcome [22].

3. Desalination Methods

To extract fresh water from the saltwater, membrane distillation (MD), multi-stage flash distillation (MSF), multiple-effect distillation (MED), and reverse osmosis (RO) are typical desalination techniques. As previously stated, desalination has become a significant alternative source of clean water since sea or brackish water makes up about 98% of the world's accessible water supply. Membrane technologies, distillation procedures (thermal technologies), and chemical methods are the three major categories of water purification technologies utilized for desalination [23]. The most widely used desalination process is pressure-driven reverse osmosis, which presently consumes the least amount of energy among the desalination techniques listed. There are sub-categories (processes) that use diverse approaches within those three major kinds, namely, membrane technology, distillation, and chemical treatments.

The primary impediments to the global expansion of desalination technology are energy and infrastructural expenses, which prevent the cost-effective production and delivery of clean water. The different types of desalination techniques are shown in Figure 1.

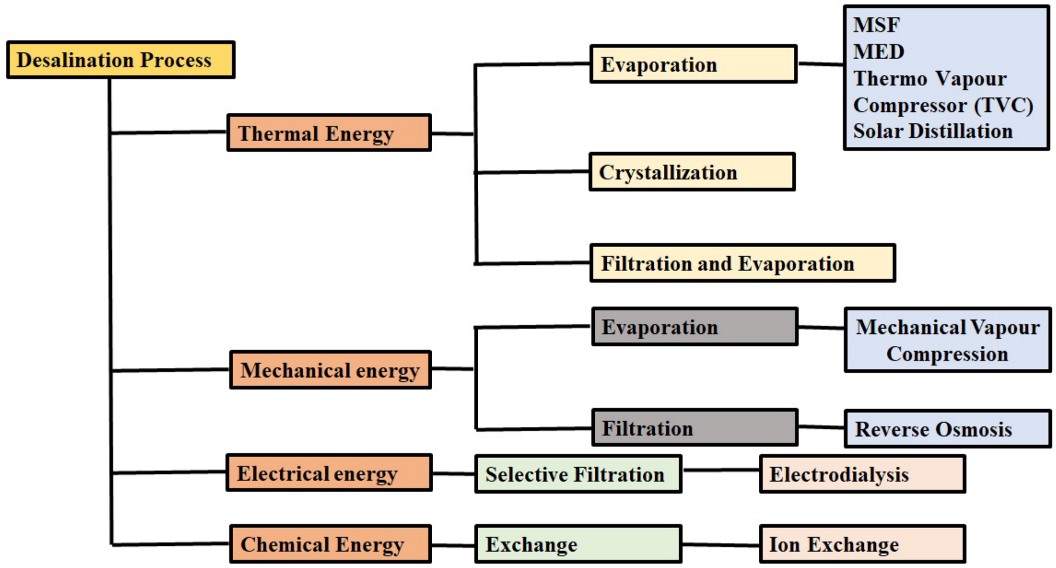

Figure 1. Types of desalination techniques [23]

3.1 Thermal technology

In thermal technology, seawater is heated to its boiling point, and the steam is collected and condensed to yield pure water. There are three sub-groups of thermal technology: multi-stage flash distillation (MSF), multiple-effect distillation (MED), and vapor compression distillation (VCD). The thermal or electrical energy required for running these desalination units is provided majorly by solar energy (photovoltaic (PV) systems and concentrated solar thermal collectors) because it is a renewable and green energy source. Solar desalination can be direct or indirect, and for the generation of heat, solar collectors are combined with traditional desalination equipment, like vapor compression (VC), multi-stage flash desalination (MSF), membrane distillation (MD), reverse osmosis (RO), and electrodialysis [24]. Reverse osmosis (RO), electrodialysis, and electrodialysis reversal (ED/EDR) utilize membrane technology to remove salts from saltwater, leaving seawater on one side and drinkable water on the other. There also exist alternative processes of water purification, such as freezing and ion exchange. Solar thermal collectors come in a variety of shapes and sizes, including evacuated tube collectors, flat plate collectors, and parabolic trough collectors, which possess significantly greater efficiency than the PV systems. Solar cells collect incident solar energy and convert it to electricity in a solar PV system. PV panels include semiconductor thin films and crystalline silicon thin films, which act as solar thermal collectors by absorbing sunlight and collecting heat. One of the most promising uses of renewable energies is utilizing solar energy for effective thermal desalination. The focus is on technology that can be used in distant locations, particularly desalination technology that can be incorporated in solar thermal energy systems. Sun desalination requires a large area of land, and its yield is low compared to indirect methods.

3.1.1 Multi-stage flash distillation (MSF)

Saline water heating happens under high pressure before flowing the water inside the initial 'flash chamber' to relieve the pressure, allowing a quick boiling of water and causing 'flashing'. Saltwater is passed through a heater and flash chambers only once before being discarded into the membrane, whereas seawater for cooling is recycled [25]. The unevaporated water leaves the system containing a higher amount of salt than when it arrived; this water is dumped as trash. On the other hand, the purified water gets released as potable water into the municipal water supply. The primary elements impacting the cost of drinking water are the solar portion of the system and performance ratio (PR). Similarly, García-Rodríguez and Gómez-Camacho [26] examined the economics of solar-MSF versus fossil fuel-powered MSF in comparison. The capital cost components of a freestanding solar powered MSF plant include solar collectors, batteries, PV arrays, thermal storage and fossil fuel energized generators, desalination units, and steam generators. Erosion is induced by turbulence in the feed water as it travels from one stage to the next in the flash chamber. The solar percentage depicts the plant's energy requirements as provided by the collector field, whereas the performance ratio (PR) depicts the ratio of the quantity of distilled water generated to the quantity of steam required in kilograms. It is possible to design each of these processes as a 'long tube' or a 'cross tube'. Since each step's pressure is lower than the previous, the 'flashing' of a piece of feed continues.

3.1.2 Multiple-effect distillation (MED)

The multiple-effect distillation (MED) method runs at lesser temperatures, around 70°C. This helps to prevent tube erosion and the creation of probable scales along the tube surfaces. In MED, the feed water quantity is low compared to the RO process. There are lower pretreatment and operational expenses for the MFD, therefore the MED procedure consumes less energy than the MSF method. Moreover, the fundamental process employs the heat released after condensation to deliver that heat to the next saltwater batch. It results in the parting of condensed water vapor (distilled water) and subsequently produces more water vapor as the steps continue. To improve the efficiency of the system, all subsequent chambers repeat this sequence. On the other hand, in this procedure, the high-pressure water vapor from each cell is utilized to heat the water in the next cell, which is under lower pressure than the previous cell. MED units can be characterized as vertical tubes, horizontal tubes, or vertically stacked tube bundles depending on how the heat exchanger tubing is arranged. The MED method is a kind of thermal desalination. It entails boiling seawater under pressure and forcing it through a number of chambers (or stages). One high efficiency MED desalination system unit is a solar collector with a 14 effect-MED unit established at the Solar Research Tact Plataforma Solar de Almera (PSA-CIEMAT) which has a capacity of 72 m^3/day [27].

3.1.3 Vapor compression distillation (VCD)

Solar energy is used to produce steam from saltwater, which is then allowed to flash before being compressed with a mechanical vapor compressor or a thermo-vapor compressor. Because a rise in vapor pressure causes an enhanced temperature of condensation, the same vapor can serve as the medium of heating for the concentrated solution from where the vapor was created. Depending on the plant's architecture, pressure can reach up to 2000 kPa. The apparatus utilized in this technique is smaller than MSF and MED, which is one of the benefits. In comparison to MSF and MED systems, the operational costs are lower. VCD has several drawbacks, including high energy consumption. The cost of capital is considerable. Compressors and heat exchangers have higher maintenance expenses than other systems. The heat used to evaporate the water originates through vapor compression rather than direct heat exchange from the steam produced in a boiler. The entering seawater cools the compressed steam, resulting in distilled water precipitation while simultaneously heating the seawater to create additional steam [27].

3.2 Membrane technology

Membranes can be composed of a number of materials including polymeric materials like nylon and cellulose acetate, as well as non-polymeric materials like metals, ceramics, and composites. A membrane is a permeable sheet that permits water molecules to flow through while blocking bigger and unwanted microorganisms (viruses, bacteria), and metals from passing through [28]. Reverse osmosis (RO), nano filtration (NF), ultrafiltration (UF), and microfiltration (MF) are all pressure-driven membrane technologies. Pressure-driven or electrical-driven technologies are used in most membrane treatment procedures.

3.2.1 Reverse osmosis (RO)

A Reverse Osmosis (RO) set up usually involves four main sub-systems:

a) Pre-treatment system
b) High-pressure pumps
c) Membrane systems
d) Post-treatment

By the use of pressure in the RO process, saline water is driven through a semi-permeable membrane and converted into a product water stream and a concentrated brine stream. As part of the membrane assembly, there is a pressure vessel in addition to a semi-permeable membrane that permits the feed water to pass through the membrane [29]. The reverse osmosis set up is shown in Figure 2.

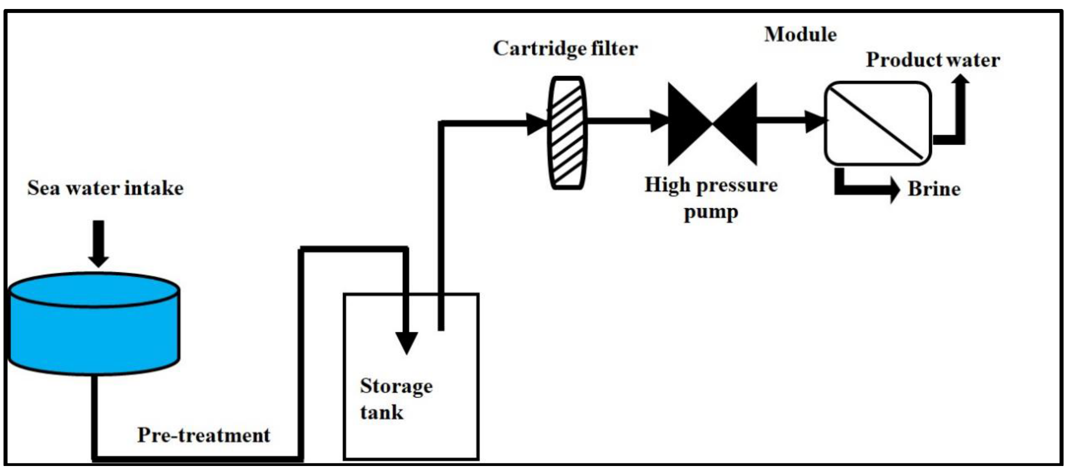

Figure 2. Reverse osmosis apparatus [23]

In the presence of a higher salt content solution, pressure is applied, and the water flows through the semi-permeable membrane in the opposite direction, leaving the salt behind. As a part of the water goes through the membrane, the salt level of the remaining supply water rises. Within the membrane envelope, pressured feed water travels in a spiral route, collecting pure (desalinated) water in the central tube [30]. It is known that osmosis is a natural process in which a low salt-concentration flows across a semi-permeable membrane towards a solution of higher salt concentration. The selection of procedure for pretreatment is dependent on a variety of criteria including quality of feed water, availability of space, RO membrane needs, and so on. High-pressure pumps provide the necessary pressure for the water to flow across the membrane and subsequently reject the salt. The percentage of feed water released as concentrate varies between 20% for brackish water and around 50% for saltwater. Pretreatment can take the form of traditional techniques such as chemical feed followed by coagulation/flocculation/sedimentation as well as sand filtration or membrane processes like ultrafiltration (UF), and microfiltration (MF). Without passing through the membrane, a portion of the supply water is ejected. As a result, all the suspended particles should be removed first, and then the water must be pre-treated to prevent the precipitation of salt or microbiological development on the membranes.

3.2.2 Electrodialysis reversal (EDR)

Since electrolysis is used in ED units, brackish water (rather than saltwater) is usually desalinated due to its high salinity. The following broad ideas underpin ED: salts contain ions that are positively charged (cations) or negatively charged (anions) and get dissociated in water. All of the cells are constantly supplied with desalinated water as well as a steady flow of concentrate (brine). An electrical potential moves salts across a membrane, leaving behind the fresh water as an output [31]. Once the lines have been cleaned out and the required water quality has been restored, the water is withdrawn immediately after reversal. Ions in the solution, such as sodium (+) and chloride (-), pass through membranes that allow cations or anions to pass through (but not both) as they move to the opposite electrodes in a saline solution. Despite the fact that ED was designed for saltwater desalination, it is most commonly utilized for brackish water desalination [32]. There is dilution of salt content in the channel of water during this process, whereas concentrated solutions develop on the electrodes. The ions move toward the electrodes of opposite electric charges because of the attraction of like charges and repulsion of opposite charges exerted to or from the electrodes. In the gaps between the alternating membranes, concentrated and diluted solutions are produced, and these areas bound by two membranes are referred to as cells. The polarity of the electrodes is switched many times each hour, that causes the ions to flow in the opposite way through the membranes [32].

3.3 Membrane filtration

Membrane processes have a wide range of industrial applications, including water and milk product purification, non-potable water desalination, purification of wastewater, production of food and beverage, separation of gas and vapor, air pollution control, energy conversion and storage, and treatment of hazardous industrial waste. There is a rapid development of these desalination technologies that have provided the outstanding economic, operational expenditures of the desalination plants in the past 50 years. Although, a much greater level of attention is necessary for the environmental and resource depletion impacts of membrane-based desalination which requires pretreatment and recovery [33]. In addition, desalination plant model, advice, and assess the performance of traditional membrane desalination, notably for saline water reverse osmosis (SWRO), has been established for decades to adhere to a wide variety of industrial standards [34].

3.3.1 Mode of operation

There are two modes of operation: crossflow mode and dead-end model. However, the crossflow mode necessitates more sophisticated equipment than the dead- end method, and the expenses to run the crossflow mode are greater due to the energy necessary to circulate the feed flow. Under driving pressure, only a portion of the feed stream travels directly through the membrane surface in crossflow operations [35]. In the dead- end mode, the entire feed flow travels perpendicularly in the direction of the membrane, accumulating and depositing retained particles and other components on the membrane surface. The stream constantly eliminates trapped material, and the penetration flux can be significantly higher when the feed flow is tangentially applied to the membrane surface. In the water/wastewater sector, the dead-end mode is commonly employed for diluting inputs such as surface waters or secondary effluents.

3.3.2 Membrane fouling

Membrane fouling is a complicated phenomenon influenced by seawater properties, the physicochemical properties of the membrane, and the conditions of operation (temperature, crossflow velocity, and transmembrane pressure (TMP)). As a result of membrane fouling, membrane permeability decreases (there is a decrease in flux at constant pressure, or there is a rise in pressure at a constant flux), and solute retention changes (MF and UF tend to increase, NF and RO tend to decrease). The primary issues in membrane filtering applications are the performance loss due to the fouling of the membrane and the increased expenses associated with membrane cleaning. Depending on the process, several fouling processes may occur including pore blockage, pore narrowing or adsorption, irreversible cake layer development, and so on. Membrane fouling becomes a buildup of material on or inside the membrane structure that cannot be easily removed by merely releasing the pressure or back washing.

3.3.3 Membrane filtration types

Separation membranes are used to alter the combination of mixtures, such as binding membranes are used to prevent penetration; ion-exchange and bio-functional film are used to alter the saturating components physically/chemically; usage of proton conducting sheets for conducting electric current; and usage of non-selective membranes for controlling the rate of permeation [36]. Synthetic membranes, for example, can be solid or liquid, organic or inorganic, homogeneous, or heterogeneous in structure, electrically charged or can be neutral in nature, and symmetric or asymmetric in form. Synthetic membranes are classified as flat, tubular, or hollow fiber membranes based on their geometric forms.

1) Microfiltration

MF membranes are unable to extract smaller chemicals since the microfiltration process employs low pressures and high porosity. Impurities ranging in size between 0.1-10 mm are separated from a solvent or additional components of low molecular weight using MF membranes. MF membranes can be primarily utilized in the pharmaceutical sector for sterile filtration (removal of microorganisms), and in the semiconductor industry for final filtration (removal of particles) of rinse water [37]. After World War II (WWII), membrane filter technology was used for the bacteriological inspection of water supply systems, which sparked considerable research into membrane filter technology. Goetz discovered a novel technology for manufacturing membranes with enhanced performance in 1950, and Millipore Co. was founded in 1954. In the 1960s, the first application of MF membranes commercially was in the biological and pharmaceutical industries. Bechhold [38], who created membranes using various casting solution compositions and discovered that the size of the pore could be altered, began systematic investigations on MF membranes around the turn of the twentieth century. Microfiltration is the part-by-part removal of impurities from a fluid using a microporous membrane under pressure. Stricter pathogen elimination regulations for supplying water have resulted in a significant shift to membrane technologies involving low pressure. With the introduction of extremely durable membranes like polyamide, polypropylene, and polysulfone, the MF method is now utilized on a wide scale. In addition, researchers have utilized the measurement of bubble point to approximate the extreme opening size of the membrane filters, which is still used today. Around 1918, Zsigmondy and Bachmann created the initial commercially viable process for producing nitro-cellulose membranes [37].

2) Ultrafiltration

Due to the dual benefits of treating water pollution and recovering valuable products, ultrafiltration (UF) membranes have been a valuable market area for the dairy industry. With the use of horizontal cellulose acetate (CA) membranes, there was a considerable reduction in emulsion and water consumption without the requirements of current or organic stability; therefore, no electrophoretic paint industry would have been able to survive without UF membrane [37]. It has been thirty years since UF membranes were introduced, and the market for these membranes has grown to include a wide range of applications. A difference between UF membranes and RO membranes is that UF membranes do not create substantial retentive pressure because the membrane structure (pore size 1-100 nm) allows micron-sized particles (MWs 300) to pass through the pores. In tandem with RO membranes, UF membranes evolved from commercial cellulose acetate RO membranes. UF membranes are occasionally utilized as a pretreatment alternative for feed solutions that are to be treated by NF or RO. UF membranes were researched in the laboratory or on a limited scale as early as 1907, although they were first constructed with the objective of generating high-flux RO membranes during 1960s [39]. Millipore and Amicon created the first commercial UF membranes in the mid-1960s as a byproduct of the invention of asymmetric RO membranes. It is a very common practice to use UF membranes to separate macromolecules, colloids, and solutes with molecular weights more than 10,000 from those with low molecular weights. Solvents and salts with low molecular weight flow through ultrafiltration membranes, while big molecules are rejected. These asymmetric materials provide UF membranes with a wide range of pH and temperature resistance, as well as chlorine resistance, which considerably broadens UF membrane applicability. There are several factors that contribute to the selectivity of UF membranes, including the differences in sizes and surface charges of the components to be separated as well as the characteristics of the membrane and hydrodynamic conditions. A variety of polymers and polymer blends have been used in making UF membranes, including aromatic polyamides, polyacrylonitrile, polysulfone, polyvinylchloride, polyethersulfone, and polyvinylidene fluoride. In most cases, UF membranes possess an asymmetric porous structure and are often prepared through phase inversion techniques.

3) Nanofiltration

As opposed to RO membranes that have a nonporous structure and function via a solution-diffusion transport mechanism, nanofiltration membranes (NF) work at the interface between porous and nonporous membranes. A major advantage of NF membranes over RO membranes is that they possess better water recovery functions (water fluxes) at much lower pressures than RO membranes because of their 'loose' feature [40]. According to the size and shape of the compounds, this process can remove multivalent ions and dissolved compounds containing sulphate, phosphate, magnesium, and calcium. NF was coined in the 1980s by FilmTec to describe a 'RO process' in which ionic solutes can flow through membranes. Originally, membranes with selectivity between RO and UF were present as early as the 1960s and were classified in three categories: open, loose, low-pressure RO membranes, intermediate RO/UF membranes or tight UF membranes. Furthermore, because most NF membranes are surface-charged, electric interactions play a role in NF membrane transit and selective rejection. The fluxes over the membrane surfaces are greater in nanofiltration systems than in RO systems, and the quality of the permeation is poorer than in RO systems. The difficulty of controlling the repeatability of membrane pore size and pore size distribution is the most significant disadvantage of NF membranes. Although NF membranes possess an increased absorptivity for monovalent salts, such as NaCl, KCl, etc., they may also reject multivalent salts and comparatively tiny organic molecules. The membrane rejects NaCl 30-40%, $MgSO_4$ 85-90%, sucrose 99%, and raffinose 99%. An RO membrane operating under UF membrane pressures was first demonstrated in the NF-50 membrane, which showed that NF membranes had an intermediate capability between "loose" RO (nonporous, diffusion) and "tight" UF (porous, sieving). Prior to 1990, NF membranes were used in the seawater softening, food, textile, and mining industries. Cellulose acetate's (CA's) first- generation, NF (loose RO) membranes, on the other hand, had poor biological and chemical stability. In terms of salt retention, Bhattacharyya [41] discovered that charged UF membranes behaved similarly to NF membranes. Furthermore, NF membranes are prone to fouling, which can result in significant flux loss. Figure 3 shows the different stages of purification and desalination of sea water to yield clean water.

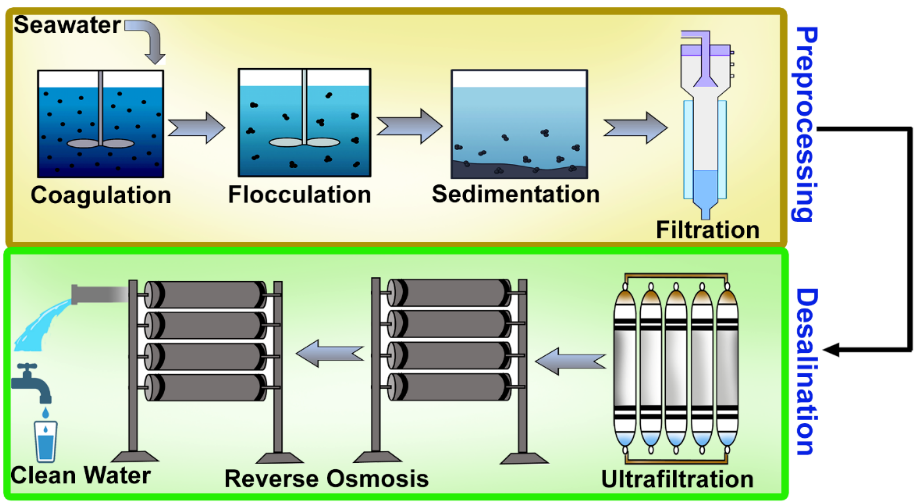

Figure 3. The step-by-step process of removal of debris and salt from sea water by the method of coagulation, flocculation, sedimentation, filtration, ultrafiltration and reverse osmosis to produce clean water

4. Nano-composite Thin Film

The present status of nanoparticle-modified membranes for reverse osmosis desalination usually involves carbon-based nano-fillers, metal oxide-based nano-fillers, metals, and a range of various nano-sized fillers. In addition to these membrane types, the desalination performance of these thin-film nanofibrous composite (TFNC) reverse osmosis membranes needs to be discussed. Polymer nanocomposite membranes can be classified into two categories: blended nanocomposite membranes and TFNC membranes. Polymer nanocomposite membranes are modified polymeric membranes with nanoparticles dispersed throughout the lattices of the polymer. The nanocomposite membranes that have been developed are known as nanoparticles entrapped membranes or nanoparticles combination films. By dispersing nanoparticles in the polymer solution prior to the phase inversion operation, the phase inversion method can be utilized to produce polymer nanocomposite membranes in hollow fibers or in flat-sheet topologies [42]. TFNC membranes have previously been employed in a wide range of zeolites, carbon nano tubes, metal and metal oxide nanoparticles, graphene oxides, and other materials with varying functions and properties. Polymer nanocomposite membranes were applied in a range of applications such as organic solvent nanofiltration, water treatment, gas separation, per-vaporization, applications as sensors, and so on.

Polymers as well as nanoparticles were dispersed in the casting fluid at the time of the casting process for blended nanocomposite membranes. Surface chemical modification of hydrophilic carbonaceous nanoparticles such as carbon nanotubes (CNTs) and graphene oxide, metallic oxide, and metal-based nanomaterials such as silver, silica, zeolite, ZnO, $CaCO_3$, Mg $(OH)_2$, Al_2O_3, TiO_2 were used to generate the hybrid materials [43].

The use of nanoparticles is considered to have contributed to the improvement of TFNC membrane properties and separation characteristics. Nanoparticles have facilitated improved hydrophilicity and capacity of water penetration without any reduction of selectivity for salt, resistance to chlorination, or fouling. Numerous recent research has concentrated on the fabrication of TFNC membranes using numerous nanoparticles, as well as their procedures for preparation and evaluation of membrane separation performance. Inorganic material, organic material, biomaterial, and hybrid material are the nanomaterials used in nanocomposite membranes. When the TFNC membrane is present, a thin layer of the nanoparticles on the outside of the membrane surface can be created with a dip-coating method or pressure deposition. During the deposition of the residue, all the following properties improve as a result: mechanical stability, water flow, film hydrophilicity, permeability, thermal stability, salt rejection, selectivity, and chemical stability. A polymeric system is frequently used to synthesize nanoparticles due to the presence of specific functional groups on the backbone of polymer chains that make it possible to synthesize nanoparticles. The pressure of vessels and film modules must be lowered in order to maintain the same desalination capacity, as a lower feed pressure will suffice for the initial flux to be generated. The substantial contributions of nano-enabling synthesis and manufacturing processes can effectively improve water recovery and fouling resistance, allowing a longer membrane life lifetime with the same number of membrane modules. Carbon based materials such as graphene-family nanomaterials (GFNs), carbon nanotubes (CNTs), and nano-diamonds are different nanomaterial types that hold great ability in solving the ongoing issues associated with conventional membrane-based purification processes. It is important to note that when it comes to membrane desalination technology, achieving sustainability means engaging in an exciting transformation with the fewest harmful effects on the environment, which means less wastage of energy, using fewer materials, and in turn, fewer chemicals. As soon as new membrane components are developed, they may be incorporated into retrofitted desalination systems to maximize sustainability benefits and minimize the cost of construction. Exciting discoveries and advances have been made by employing conventional nanomaterials in desalination membrane design, such as silica, metal oxides, and zeolites, to add new degrees of freedom [42]. The different applications of nanostructures in polluted water remediation are schematically represented in Figure 4.

4.1 Polymeric RO membranes

It was found that the evolution of membrane materials can be categorized into two phases based on the research activity of membrane materials. The first was the search for suitable compounds and membrane preparation processes, and the second was the creation of more regulated membrane formulation conditions to increase the performance of the membrane. From the inception of composite RO membranes until 1985, operations covered composite RO membranes. There have been few improvements in conventional polymeric RO membranes, such as improvement in membrane permeability, since the late 1990s [44]. Although advanced polymer synthesis capabilities that allow molecular control over the placement of functional groups on the polymer backbone can be helpful in designing advanced purification membranes, little is known about how this affects water and salt transport. Carbon-derived nano porous and biomimetic membranes are all discussed previously. On the other hand, polymeric membranes can also be produced using new techniques. Table 1 describes the different polymers used for desalination membrane preparation.

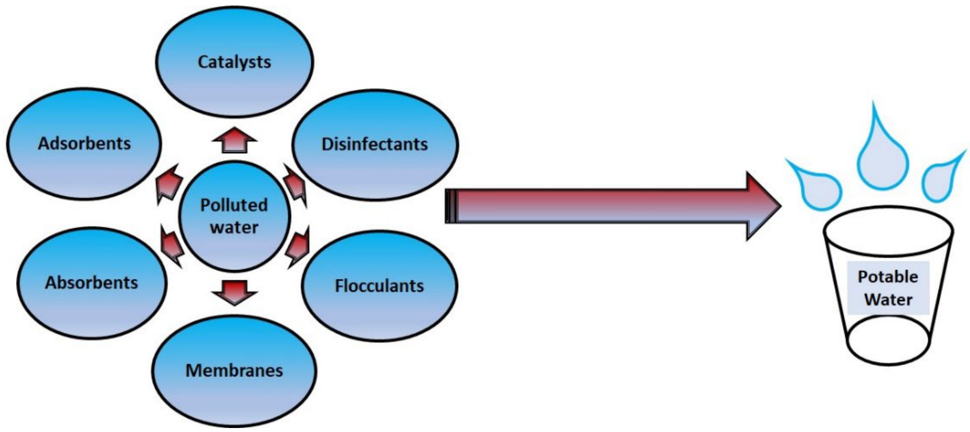

Figure 4. Nanostructure mediated remediation methods for polluted water purification

Table1. Membrane flux and salt rejection for different polymers used in membrane technology [36]

S. No.	Polymer	Flux ($m^3m^{-2}day^{-1}$)	Salt Rejection (%)	References
1	Polyfurane	0.8	99.8	[45]
2	Polyether- Polyfurane	0.5	99.9	[46]
3	Sulfonated Polysulfone	1.06	98	[47]
4	Polyimide via polyethylenimine	0.7	99	[48]
5	Polyimide via polyepiamine	1.0	99.4	[49]
6	Polyvinylamine	2.0	98.7	[50]
7	Polypyrrolidine	0.8	99.7	[51]
8	Polypiperazine- amide	3.3	68	[52]
9	Cross linked Fully Aromatic Polyamide -1- (FT-30)	1.0	99	[53]
10	Cross linked Fully Aromatic Polyamide - (UTC Series)	0.8	98.5	[54]
11	Cross linked Aralkyl Polyamide (A-15)	0.26	~ 98	[55]
12	Cross linked Fully Aromatic Polyamide -3- (X-20)	1.0	99	[56]

Desalination membranes that are advanced and highly selective are needed to filter increasingly dirty and saline water effectively and efficiently in order to meet the expanding demand [57, 58]. Nanotechnology has lately resulted in the development of nano-structured materials that might be utilized to develop new RO membranes. Despite this, significant Donnan effects were seen, suggesting that the divalent cation shielding effect can significantly diminish monovalent ion rejection. With enough flux, RO membranes were susceptible despite its very strong salt and organic compound rejection.

4.2 Carbon based membranes

4.2.1 Carbon nitride

Graphene-based nanomaterials and metal oxide frameworks have recently gained attention since they are known to give excellent permeability and specificity to the resulting carbon nitrate thin film, which lowers energy consumption for filtering while retaining high recovery. Because of their unique optical properties, carbon nanomaterials (CN) were utilized as metal-free photocatalysts for degrading organic pollutants because they possess high thermal stability and chemical stability. The first attempt at such an endeavor was in 2007, when zeolite nanoparticles and carbon nanotube (CNT) impregnated membranes were developed to improve the membrane chemical, thermal, mechanical, and separation behavior [59]. Because of their high salt rejection and water flow, the thin film composite (TFC) membrane has been widely utilized for forward osmosis (FO) desalination. Graphene-like nanosheets are formed from CNs [60]. TFCs are typically made up of a layer of polyamide (PA) that is fabricated over a polymeric substrate using the interfacial polymerization (IP) method. Graphitic carbon nitride has recently gained popularity in a variety of applications. Nitrogen-doped graphitic carbon nitride (g-C_3N_4) exhibits excellent separation capabilities in two dimensions. Using non-equilibrium molecular dynamics simulations, researchers investigated the mechanisms of water and ion permeation through nanoporous g-C_3N_4 membranes. Upon introducing a nanoporous g-C3N4 membrane with the desired opening, they found that it could reject completely calcium and chloride ions and sieve out monovalent cations with over 70% rejection rates [61]. According to the membrane unit structure, another study designed three different g-C_3N_4 nanopores and saline water permeation through nanoporous g-C3N4 membranes using non-equilibrium molecular dynamics simulations was investigated. Despite retaining a considerable water permeability of 14.9 L/cm^2/day/MPa, the designed g-C_3N_4 nanoporous membrane antirely rejected the ions [62].

Gu *et al*. [63] have shown that carbon nitride nanoslits perform efficiently in desalination by analyzing the performance in silico. Permeation of water across slits is dependent on the spacing between the slits. A spacing of 6 Å allows water permeability to reach an ideal value of 15 L/cm^2/day/MPa along with the complete rejection of salts. Water permeability is increased by enlarging the spacings. With two orders of magnitude improvement over conventional commercial membranes, the C_3N nanoslits are superior to conventional membranes for desalination. Aluminium polycations have been used as pillars to activate chemically robust 2D carbon nitride to modulate the spacing of conjugated framework interlayers. In addition to providing a well-interlinked lamellar structure, the noncovalent interaction can also be used to distinguish conventional carbon nitride membranes from random stacking patterns. Structure integrity and adaptive subnanochannels are characteristics of conformally packed membranes. Consequently, swelling resistance was excellent, and a permeability-selectivity trade-off limit was broken in forward osmosis due to the progressively regulated passage of the ions. With tunable permeation behavior, water gating in acidic and alkaline environments was also achieved, along with high salt rejection and water flux (>99.5%). The results of this study position carbon nitride as a promising building block for the functional expansion of 2D membrane libraries for water desalination and purification applications [64].

4.2.2 Carbon nanotubes

In reality, CNT membrane separation performance is determined not only by the capacity of rejection of salt (or ions) and water flux but also in terms of its ability to provide antimicrobial properties synergistically to prevent biofouling of membrane, chemical resistance to hold on the rigid filtration environments, and forcing mechanical properties. Large surface area, antibacterial property, rapid liquid flow related to additional porous materials possessing similar size, along with their appealing adjustable porous property, surface chemistry, and electrical conductivity are some of the major qualities that make CNTs suitable for water purification [65]. Given that the hydrophilic composition of CNT membranes may produce a change in the nanoscale atmosphere, the mechanical as well as electrical smoothness of these nanotubes must be maintained carefully to prevent disruption of the extraordinary fluid flow characteristics. Consequently, CNT membrane applications were limited by unrestricted energy of adsorption and a decrease in pressure was required to facilitate water flow and salt convection [66]. Based on their tunable characteristics, CNTs may be rationally designed and manipulated to be used as adsorbents, catalysts, or membranes, opening new possibilities in wastewater treatment [67]. The findings shown previously preferred that molecule ordering may be controlled by using an axial electric field, which uses a spatially patterned electric field for decreasing the tube entry effects and enhancing flow velocity. Plasma-treated CNT membranes exhibited significantly improved surface hydrophilicity and ion binding capabilities due to the presence of eCOOH and eOH functional groups. A CNT membrane must ideally be made with well-graphitized CNTs having homogeneous nano holes that are uniformly dispersed on the surface of the membrane. CNT membranes are frequently manufactured by aligning CNTs inside perpendicular supporting fillers that are impervious to water, such as epoxy and silicon nitride.

4.2.3 Graphene membranes

Graphene oxides have many applications due to their excellent electrical properties [68, 69]. A single layer of graphene sheet with a regulated pore size of 10 nm can provide water permeability up to 35±5 $L\ m^{-2}\ h^{-1}\ bar^{-1}$ [70]. It has also been hypothesized that, in addition to size exclusion methods, the oxygen-containing functional groups on the surfaces and edges of GO sheets might impart electrostatic attraction with and chemical interaction with hydrated ions, thus enabling salts to pass across GO membranes with the selective passage of molecules. In summary, bottom-up synthesis relies on chemical interactions between organic and tiny molecules on a variety of substrates in order to produce graphene, in contrast to top-down synthesis, which employs techniques such as chemical reduction and electrochemical synthesis to generate high-yield graphene. Graphene nanosheet membranes with mono-atomic thickness and two-dimensional structure have tremendous potential for high flux separation and energy efficiency due to the impermeability of all atoms and molecules across a densely packed two-dimensional array [71]. Only by accurate pore size creation can a nanoporous graphene (NPG) membrane with high flux and excellent molecular sieving characteristics be obtained. Previous research showed that NPG imprinted by oxygen plasma has a salt rejection rate of nearly 100% and therefore is a suitable choice for membrane distillation and RO, based on the higher flow rate than predicted by molecular dynamics simulations [72].

4.3 Ceramic/inorganic membrane

A research team from New Mexico Institute of Mining and Technology published preliminary results on the use of ceramic membranes for purification (RO desalination) as a possible method of desalination. In their study, they described the potential for desalting oil field water, in addition to demonstrating 100% ion rejection by perfect all-Si-ZK-4 zeolite membranes, based on molecular dynamic modelling findings [73]. The group conducted experiments to study the RO separation mechanism and the viability of using ceramic membranes. The major goal of the use of inorganic membranes is to improve the characteristics of each material such as packing density and perm selectivity, and extend the operation idea of polymeric membranes, giving them superior biological, chemical, and thermal stabilities. The original RO test using a zeolite membrane proved to be unsuccessful, i.e., both salt rejection and water flow were too low for the RO to be useful. However, subsequent research has improved the performance of the membrane by altering the structure of the zeolite. In the present day, ceramic membranes are widely used for microfiltration and ultrafiltration. In addition, nanofiltration ceramic membranes are increasingly being developed for microfiltration. The first experimental effort on RO improvisation was a solution of NaCl employing an MFI silicalite-1 zeolite film that yielded a salt rejection of 77% and a liquid flow as low as 0.003 m^3/m^2 day 1 at 21 bars [74]. Although the industrial usage of ceramic membranes for the production of household water is uncommon, its process resilience has attracted researchers for resolving the issues of membrane distillation as well as per-vaporation. Ions are entirely excluded by the zeolite membranes, which possess pore diameters smaller than the dimensions of the hydrated ion, according to theoretical simulations. Because of high production costs, zeolite membranes are presently confined to situations where polymer-based membranes cannot be utilized, such as extreme working temperatures, radioactive/heavily contaminated feeds, and extremely reactive conditions. Inorganic membranes are typically composed of a macroporous layer of support and a meso- or microporous active layer. The promising separation performance of inorganic membranes suggests they can be applied in a range of desalination and wastewater treatment processes [72]. It has been possible to tune and modify membranes based on their varied physical and chemical composition. This is largely due to the dominance of polymeric membranes in commercial-scale RO processes that inorganic membranes were relatively limitedly adopted in the past. It is also possible to produce high-output potable water by preparing ceramic membranes with decreased viscosity, such as interlayer-free inorganic membranes and free-upended CNTs and graphene nanoplatelets (GNP) membranes. The expense of developing these ceramic membranes, predominantly those produced using nanomaterials, remains a significant impediment to their commercialization. For example, in spite of the fast expansion and CNT research development at the laboratory scale, commercial CNT membrane applications for water purification and desalination are still at the development stage and progress is relatively slow.

4.4 Nanoparticle based membrane

4.4.1 Titanium oxide

Titanium oxide (TiO_2) is a well-known photocatalytic material that is frequently utilized for organic compound disinfection and breakdown, and these qualities make it appealing as a photocatalytic material. For desalination, the TiO_2 nanoparticles were dip-coated onto a cross-linked polyamide TFC membrane with carboxylate-functionalized surface layers [75]. Titanium oxide membranes were reported to have anti-biofouling characteristics. After a continuous 7-day RO experiment, no significant loss of TiO_2 nanoparticles from the membrane was detected. The controlled hydrolysis of titanium tetra-isopropoxide yielded anatase TiO_2 nanoparticles (10 nm). Testing with feed water containing *E. coli* revealed excellent anti-bio fouling characteristics, particularly with the help of ultraviolet (UV) stimulation, without affecting the original membrane's flow and salt rejection performance [75].

4.4.2 Zeolite nanoparticles

The application of zeolite nanoparticles in membrane technology creates a new platform for materials with high efficiency, high water flow, and salt rejection. Mesoporous membranes have also been produced using zeolite nanoparticles. Before the interfacial polycondensation process occurs, the zeolite nanoparticles are dissolved in a solution of cross-linking agent (trimesoyl chloride dissolved in hexane). Ultrasonication is utilized before doing conventional interfacial polymerization to create a homogeneous dispersion of zeolite particles. These particles were claimed to be extremely hydrophilic, possessing negatively charged holes of diameter 0.4 nm that resist anions strongly. This is not the same as immersing the previously produced membrane in a nanoparticle-containing solution, as done with the TiO_2 nano composite membrane. A templated hydrothermal process is used to create zeolite nanoparticles-based membranes [76].

4.5 Biometric membrane

Biometric membranes show two alternative membrane orientations: (i) a phospholipid bilayer containing aquaporins that are packed in between two hydrophilic porous layers of support such as mica, polysulfone, or cellulose; and (ii) a lipid bilayer integrating aquaporins that are constructed over a porous polytetrafluoroethylene (PTFE) film. The amazing water transport capabilities of biological membranes have prompted research into membranes containing aquaporins, which are nothing but proteins that function as water-selective channels in biological cell membranes. Many practical issues must be addressed, such as choosing appropriate support materials and determining membrane fouling resistance [36, 77]. To develop this membrane for practical use, a suitable range of operating conditions must first be determined. Aquaporins are anticipated to have extremely strong salt rejection, despite the fact that a salt separation test has yet to be done, their functional performance in the biological field is to specifically allow the water molecules to pass through them. Water transport efficiency was shown to be greater in membranes containing bacterial Aquaporin Z proteins than in normal RO membranes. The aquaporins were incorporated into the walls of self-assembled tri-block co-polymer vesicles, poly(2-methyl-2-oxazoline)-blockpoly(dimethylsiloxane)- lockpoly(dimethylsiloxane)blockpoly(dimethylsiloxane)blockpoly (dimethylsiloxane)-blockpoly(dimethylsiloxan(2-methyl-2-oxazoline). For practical use in water filtration, aquaporins can be incorporated into the phospholipid bilayer. The characteristics of water permeability through a barrier layer made up of aquaporins and triblock polymers have been the focus of previous studies so far [78].

5. Nanomaterials and Water Purification Challenges

In the next decade, most materials will be in the nanoscale forms of existing goods such as titanium dioxide, silica, clays, polymers, metal powders, and chemicals. There has been a limited amount of research on the toxicity of CNTs and fullerenes [79-81]. To the best of our knowledge, there has been no methodical study of the hydrolytic, oxidative, photochemical, and biological stability of nanomaterials in natural and engineered environmental systems that have been published in peer-reviewed literature. Because of their unknown toxicity and environmental impact, one of the most difficult challenges will be gaining regulatory and public acceptability for the employment of nanoparticles in water purification.

The development of profitable and ecologically suitable separation techniques as well as reactive forms that can be used in composite packed-bed reactors to purify water polluted by combinations of (i) alkenes, (ii) organic solutes, and (iii) microorganisms will be a big problem. Furthermore, finding suppliers that can deliver significant quantities of nanomaterials at economically feasible costs will be a major obstacle in the use of nanotechnology for water purification. Nanomaterial environmental destiny, transport, and toxicity are poorly understood [82]. To incorporate new nanostructures and reactive membranes into current water purification systems, further laboratory research and pilot scale testing will be required. As the nanomaterials are becoming essential components of electrical goods, drug delivery systems, and other applications, larger amounts of carbon nanotubes, fullerenes, and dendrimers will be accessible.

Once an appropriate and cost-effective membrane has been identified or synthesized, it may be easily incorporated into existing water purification systems or processes. Another major problem is integrating nanomaterials into current water purification systems. The environmental destiny and toxicity of a substance are essential considerations in the selection as well as the design of materials for purification of water. Membrane water purification systems such as Reverse Osmosis, Nano Filtration, and Ultrafiltration are becoming the 'standard' for communal utilities and industries due to their versatility, scalable properties, modular nature, and comparatively simple maintenance. A study of the nanomaterials industry was conducted by the Freedonia organization [83]. The research examined the demand for nanomaterials in the United States during the years 2000 and 2003. Nanosorbents, redox active nanoparticles, and bioactive nanoparticles can yield toxic outputs. The scale-up of TiO_2-based photocatalytic reactors remains poorly understood, even as significant progress is being made toward producing visible light-activated TiO_2 nanoparticles [84]. Underivatized CNTs and fullerenes are water insoluble and poisonous, according to this research. In some situations, however, fullerenes and CNTs can be functionalized with different functional groups to improve their water solubility and biocompatibility. These findings show that by carefully selecting membrane material building components, non-toxic and biodegradable membranes may be created [83]. Nanomaterials in desalination, therefore, have a major disadvantage since their toxicity and environmental impact are unknown.

6. Future Aspects

The use of nanomaterials in desalination as adsorbents, supercapacitors, and capacitive deionization (CDI) has been reported. Research into the use of membranes for desalination will continue, and improvements in performance should be documented. In order to improve the chances of applications in the desalination process, the following elements should be addressed in future work: Design of scale-up procedures — the majority of the published work is still based on laboratory findings [85]. It is critical that the researchers should figure out how to construct nanomaterials and desalination modules for large-scale manufacturing. Only a few studies on nanomaterials manufacturing scaling-up have been published. Essentially, the manufacturing processes will be identical to those used in the lab, but at a bigger size, they should be more cost-effective and efficient with enduring performance.

The majority of the research done has not taken into account long-term performance, which involves operation decline, maintenance, and cleaning, which are just some of the major drawbacks. Future research should focus on long-term performance data from real-world feed solutions. This would require careful maintenance and cleaning protocols. In order for the technology to be successful, the whole process must be both cost-effective and safe for humans. More research is needed to analyze the process's economic and environmental effects, particularly in light of the uncertain destiny of these nanomaterials in the environment.

7. Conclusions

Water is a vital element for humans; on the other hand, it acts as a feedstock in a diversity of significant industries such as pharmaceutical, electronic, and food industries. The world is fronting difficult challenges in fulfilling the increasing demands for clean water as the availability of potable supplies is diminishing due to (i) prolonged famines, (ii) inhabitation and climate change (iii) stricter health-based protocols and (iv) challenging demands from a wide range of users. Physicochemical properties of nanomaterials make them particularly attractive as separation media for water purification. In terms of mass, they have a much larger surface area than bulk particles. It is also possible to functionalize nanomaterials with different chemical groups to enhance their affinity for a particular molecule. In addition, they can be used as selective and recyclable ligands in aqueous solutions for toxic metal ions, radionuclides, organic and inorganic solutes, as well as anions that are high in concentration. A nanomaterial has the potential to provide unprecedented benefits for the development of water-purification catalysts and redox-active media because of their enormous surface areas as well as their size and shape-dependent optical, electronic, and catalytic characteristics. Through functionalization with chemical groups that specifically target critically, nanomaterials are also being utilized to produce chlorine-free biocides to combat waterborne bacteria and viruses. With progress in the synthesis of cost-effective and ecologically acceptable functional nanomaterials, we anticipate that nanoparticles will become essential components of industrial and municipal water filtration systems. A key longstanding goal of the Desalination and Water Purification Roadmap prepared by the US Bureau of Reclamation and Sandia National Laboratories is the development of smart membranes with biofilm resistant surfaces and embedded sensors/actuators that can automatically adjust membrane performance selectivity by 2020 [86]. We predict that nanoparticles will be important components of those manufactured films. The creation of visible light activated TiO_2 nanoparticles has the potential to significantly influence water supply.

Membrane-based separation and desalination technologies will most certainly remain important instruments in water treatment for the foreseeable future, and nanotechnology will aid in overcoming operational challenges such as fouling and low selectivity to separate explicit ions or molecules. For example, nanoscale grafting, or doping, can improve membrane performance and dependability by avoiding fouling, and nanochannels can be used to construct extremely selective desalination membranes. In the upcoming era, desalination membranes will be resistant to fouling, highly sensitive, and chemically stable to oxidizing chemicals such as chlorine. To achieve this stage, breakthrough advances in new membrane nanomaterials and defect-free manufacturing techniques are needed. Overall, more dependable, and cheaper access to cleaner water will necessitate technical innovation. Nanotechnology is anticipated to play a significant role in improving some water treatment systems by providing a wide variety of new options, such as flexible treatment methods and nanomaterials tailored to achieve specific goals. In the near future, nanotechnology-assisted water treatment will most likely be deployed only in niche applications (such as point-of-use devices) rather than in big municipal treatment facilities, which are risk-averse to innovation and face a number of restrictions against system replacement. Nonetheless, this rising innovation wave may ultimately enable next-generation modular water treatment systems, which can greatly increase water supply safety and reliability while lowering the costs and energy consumption.

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