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TOPICAL REVIEW

A review of the function of using carbon nanomaterials in membrane filtration for contaminant removal from wastewater

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Abstract

Water is a necessity for all living and non-living organisms on this planet. It is understood that clean water sources are decreasing by the day, and the rapid rise of Industries and technology has led to an increase in the release of toxic effluents that are discharged into the environment. Wastewater released from Industries, agricultural waste, and municipalities must be treated before releasing into the environment as they contain harmful pollutants such as organic dyes, pharmaceuticals wastes, inorganic materials, and heavy metal ions. If not controlled, they can cause serious risks to human beings' health and contaminate our environment. Membrane filtration is a proven method for the filtration of various harmful chemicals and microbes from water. Carbon nanomaterials are applied in wastewater treatment due to their high surface area, making them efficient adsorbents. Carbon nanomaterials are being developed and utilized in membrane filtration for the treated wastewater before getting discharged with the rise of nanotechnology. This review studies carbon nanomaterials like fullerenes, graphenes, and CNTs incorporated in the membrane filtration to treat wastewater contaminants. We focus on these CNM based membranes and membrane technology, their properties and applications, and how they can enhance the commonly used membrane filtration performance by considering adsorption rate, selectivity, permeability, antimicrobial disinfectant properties, and compatibility with the environment.

1. Introduction

The earth's surface contains 71% of water, but only less than 1% meet human consumption due to the discharge of heavy metal ions, pathogenic bacteria, radionuclides, and viruses. Heavy metals ions present in wastewater are a serious environmental issue globally. The presence of heavy metals inside the cell and the surface of microorganisms can lead to huge alterations to their biochemical cycles. The common types of heavy metal ions present in water are chromium (Cr), copper (Cu), arsenic (As), cadmium (Cd), lead (Pb), and antimony. Chromium is a toxic metal ion, carcinogenic to humans, and has several negative impacts. They can delay growth and reduce germination of some plants, increasing reproduction rates and mortality in living beings such as earthworms, aquatic beings by affecting gills, human kidneys, and liver cells of fish in freshwater and their possible diatom demises. Conventional water treatment methods are not capable of removing all heavy metal ions. Nanotechnology and membrane technology has become the most prominent methods of treating water. Carbon nanomaterial materials have shown great results in removing metals ions, pathogens, organic contaminants, and nano-pollutants effectively. They have characteristic properties like high surface volume ratio, adsorption, catalytic activities, and reactivity. Based on various studies, it is understood that adsorption is a tenable, feasible, and environmentally friendly process for wastewater treatment. It is considered one of the most flexible operations to detect and extract heavy toxic metal ions. The different parameters studied on the effect of efficiency of the sorption process are time, temperature, pH, speed, sorbent doses, and metal concentration. Since adsorption is a surface phenomenon, the surface area plays a major role and determines how efficiently adsorption occurs.

Carbon nanomaterials include carbon nanotubes (CNTs), graphenes and their derivates, fullerenes, carbon nanoparticles, etc The application of CNMs can be cost-effective, viable, environmentally friendly, and used as a better alternative to the conventional treatment technique. Carbon nanotubes are allotropes of carbon that resemble fullerenes and graphene structures. Carbon nanotubes (CNTs) can either be single-walled or multi-walled. Single-walled carbon nanotubes are one-dimensional sheets of Graphene that are cylindrically shaped, while multi-wall carbon nanotubes are multiple single-wall CNTs. Carbon nanotubes can also be treated with other substances to increase their adsorption efficiency and increase stability. Gases such as ammonia (NH_3), Nitric oxide (NO), Nitrogen dioxide (NO_2), hydrogen (H_2), Sulfur Hexafluoride (SF_6), and Chlorine (Cl_2) can be effectively adsorbed by both single-wall and multi-wall carbon nanotubes. Carbon nanotubes follow a heterogeneous adsorption behavior. High-level energy adsorption sites in CNTs are due to the functional groups, structural defects and groove regions, and morphology.

Nano zero-valent metal iron (NZVI) has strong effects against viruses, bacteria, and fungi due to its high toxicity to microorganisms. NZVI is known as the best remedial material considering its efficiency of recovery and cost of production. The incorporation of nano zero-valent Iron with CNT has been studied for several years. It has outstanding properties like the efficiency of high absorption, large specific area, large surface area, ease of transport, reductive activity making extraction of heavy metals much more rapid. Another main carbon nanomaterial that has shown excellent adsorption efficiency is Graphene. Graphenes yield the thinnest structures with great mechanical stability and thermal conductivity. Modification of graphene-based can be achieved with the same methods as well. Electrophilic addition, nucleophilic substitution, and addition and condensation reactions are achieved for the covalent functionalization of graphenes. In non-covalent functionalization, polymers (Polyaniline, Polysulfone, and polyvinyl), surfactants, and biomolecules can improve capacitance and mechanical strength. In the study of adsorption of gas and vapor by CNMs, it was found that Fullerene was weakly polarizable and behavior similar to alkenes rather than polyaromatic molecules.

Both organic and heavy metals can be effectively extracted and removed using membrane filters like reverse osmosis (RO), ultrafiltration, Nanofiltration, and Microfiltration. Nanofiltration is a quickly advancing technique in wastewater and water treatment, defined as a pressure-driven process. NF membranes have greater water fluxes and operate at medium pressure than Reverse osmosis (RO). RO provides the highest purity of water. Nanofiltration removes heavy metals and salts and has very high effectiveness in removing protozoa (Giardia, cryptosporidium) and removing viruses like enteric viruses, norovirus, rotavirus, etc Membrane filters are also used in the desalination of water. Desalination of water is considered a process requiring high power consumption and operating costs, making them difficult to implement. The use of nanomembranes resolves this issue. Even though nanotechnology and membrane are important and have shown outstanding results in wastewater treatment, it also has limitations and toxicity.

Using CNMs in a huge quantity for wastewater treatment can lead to aquatic toxicity. Aquatic organisms show different responses since each CNMs affect them in different ways. NDs can easily enter into cells and cause metabolic and signal interference. Studies have shown that CNTs can cause reproductive toxicity, carcinogenicity, and persistence in human cell lines. Other modifications of CNTs such as pristine CNT, SWCNT, MWCNT, MWCNT-OH, MWCNT-COOH also affect aquatic life by triggering huge disturbances. Several characteristics such as surface feature lateral and concentrations of graphene nanomaterials trigger toxic effects in the aquatic biosphere. This can be aggregation in zebrafish larvae's heart, blood vessels, and eyes, causing delayed hatching, apoptosis, health risks, and oxidation stress. It was reported that derivatives of Graphene could also have terrible effects. The functionalization of CNMs can easily eliminate these risks and toxicity, briefly explained in the review. The two major challenges faced in the membrane filtration method are membrane fouling and concentration polarization. Fouling of membranes may occur due to the excess growth of species/contaminants accumulating on the surface, colloidal fouling, deposition of organic substances, and accumulation of minerals precipitating from the feeder's membrane surface. Therefore, it is crucial to modify the membrane by the addition of carbon nanomaterials. This paper provides a detailed, comprehensive review of the different approaches to modifying carbon nanomaterials like fullerenes, Graphene and its derivatives, and CNTs to improve the existing membrane performance such as porosity hydrophilicity, morphology, etc and overcome the limitations in wastewater treatment. Particularly, incorporation of carbon nanomaterials in membrane filtration technology to prevent membrane fouling. Different treatment methods for and processes for the functionalization and preparation of CNT membrane and graphenes are also discussed in this review. In addition, fabrication of zero nano valent Iron and activated carbon nanotube hybrid membrane (NZVI/ACNTs) by using CNT as a substrate and NZVI as a dynamic layer.

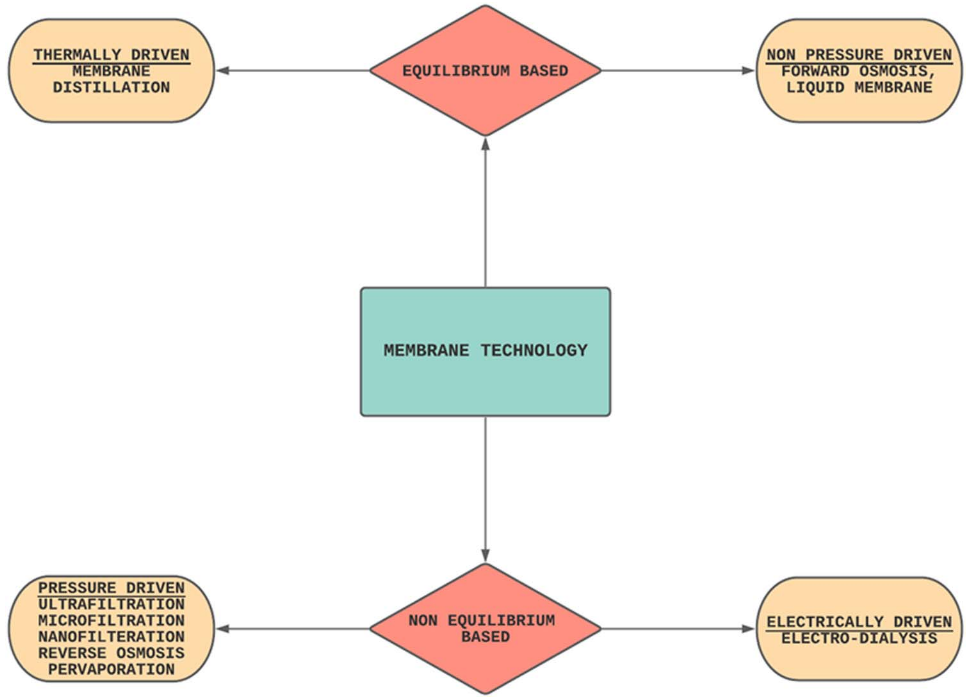

Figure 1. Schematic representation of some membrane processes. Reprinted from [2], Copyright (2016), with permission from Elsevier.

2. Understanding membrane filtration for wastewater treatment

A membrane is a porous layer that can allow a certain fluid to flow through them with restriction to specific contaminants or particles based on their physicochemical properties and molecular sites. In laymen's terms, a membrane is a selective barrier that allows some things to pass through and stops others. These membranes act as a selective barrier separating the two phases and lining up those two phases [1]. Working similar to the cell walls in our bodies, scientific membranes are used in the process to filter out impurities, salts, heavy metal ions, viruses, and many other particles from water. In wastewater treatment, the membranes are the selective barriers that allow the passage of water through them while stopping the passage of unwanted substances through it.

Over the past few decades, the use of membranes as a filtration technology has been improving and being implemented for large-scale industries, textiles, and domestic uses. One of the most prominent features of membrane filtration is that it requires less space for usage. The chemicals used in this process are also less, thus making it more preferable and viable than conventional pre-treatment methods. The membrane technology is divided into equilibrium-based and non-equilibrium-based processes, as shown in figure 1.

The membrane Filtration process can be of different sizes depending on the pore size. They are Microfiltration (MF), Nanofiltration (NF), Ultrafiltration (UF), & Reverse Osmosis (RO). These four processes work under the application of pressure (pressure-driven). Discussing these four processes in detail first comes Microfiltration. MF is generally more efficient at a low differential pressure of about 2 bar than the conventional raw filtration process. These MF membranes' pore size diameter varies from 0.1 to 10 microns. Though these MF membranes are being used to suspend particle removal and colloidal dyes, they still cannot prevent leakage of organic pollutants (dissolved) or auxiliary chemicals that remain unconsumed [3]. Ultrafiltration is that stage that has a pore size ranging from 10 A to 1000 A. These membranes can separate to remove divalent ions (mainly responsible for the water hardness in textile industries). Lafi *et al* 2018 [4] concluded that the molecular masses of dyes in such high coloured textile discharge are much lower than the molecular mass cut off of ultrafiltration membranes, limiting its application in the textile industry.

Particles with pore size diameters around 0.5–1.5 nm are removed using the Nanofiltration method. A recently developed new membrane filtration technique, its application ranges from wastewater treatment and purification processes on a domestic and large industrial scale. In this separation process, pressure and concentration gradient play a major role and characterize UF and RO based on their performances. Here, water and the solutes with low RMM (molecular weight) permeate through the membrane and leave the suspended solid particles and solutes with high RMM (molecular weight) on the retentate sides of the membrane. Under the NF process, the fabrication of TFC membranes has been a breakthrough where the membranes can be manipulated and processed to get our required performance characteristics and morphology [5]. The

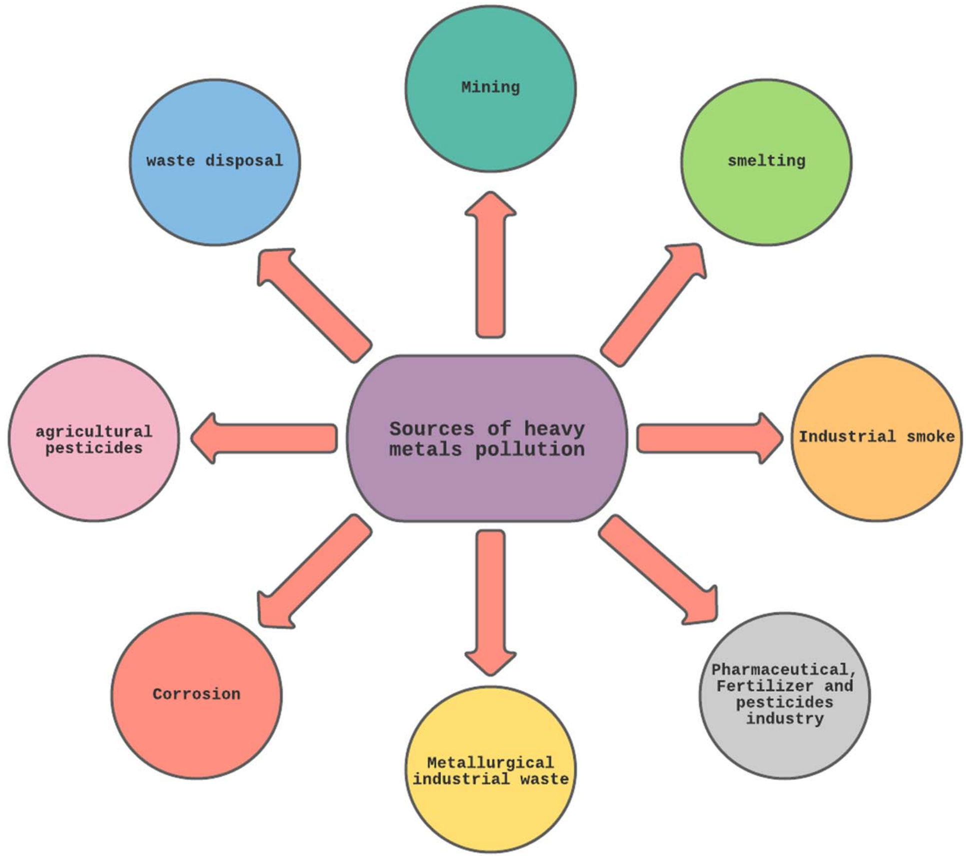

Figure 2. Source of heavy metal ions in wastewater.

performance of Nano-filtration membranes is highly dependent on fouling and concentration polymerization. Fouling occurs when the accumulation of organic compounds blocks the pores, thus decreasing the membrane's permeability.NF membranes with hydrophilic surfaces are preferred for wastewater treatment, especially in the textile industry [6]. While talking about fabrication, under Parma Study on ceramic membrane fabrication (2004), Parma and Chowdhury, with their developed ceramic membrane, figured out that ceramic membranes can remove crude oil from the wastewater. They achieved this ability by fabricating their membrane with aluminum foils over circular discs at sintering temperatures ranging from 500 to 800 °C [7].

Reverse osmosis or RO membrane filtration is efficient and can remove about 99% of contaminants like pathogens and dissolved solids in the wastewater system. Like normal osmosis, RO involves the opposite process where the solvent is passed via a membrane between high solute concentration and lower solute concentration. These membranes are known as semi-permeable or selectively permeable membranes. Salt rejection is one of the features RO membranes are renowned for. These membranes are widely used in chemical and agricultural-related industries to remove water hardness, colours, and other organic contaminants.

Wastewater sources can be classified into two classes: residential sources and non-residential sources. Residential sources include total suspended solids, biodegradable dissolved organic and inorganic compounds, proteins, nutrients, metals, and pathogenic microorganisms. Non-residential wastewater is mainly discharged from industrial plants, agricultural fields, and commercial activities, as shown in figure 2.

A tabulation of different types of wastes rejected by membrane filters and the toxicity is shown in table 1. Wastewater treatment can be done by the conventional preliminary, primary, secondary, and tertiary treatment stages. Preliminary treatment includes screening, which separates a large chunk of materials followed by the Primary and secondary methods. In Primary treatment, the separation of the debris is done by the process of Sedimentation using Clarifier. Secondary treatment includes biofilm process or Activated sludge (Aerobic or Anaerobic) technique, which removes the excess organic matter and reduces BOD level. To ensure the treated sludge does not pollute the environment, it is released to, and Tertiary treatment is done, such as further disinfection of the treated sludge using methods like chlorination or UV treatment. These are mainly the steps that are being used in the conventional Wastewater purification system. The introduction of Membrane filtration techniques has helped in improving the wastewater treatment process. RO and Nanofiltration are often

Table 1. Membrane Filtration of wastewater treatment compared with other alternatives.

Types of waste filtered	Toxicities	Membrane Filtration	Remarks	References
Calcium (Ca)	No toxicity	Nanofiltration	—	[8]
Chromium (Cr)	Headache, nausea, vomiting, carcinogenic	Nanofiltration	76.5%–98.8% Cr removal achieved by NF90 membrane	[9]
Protozoa and Viruses	Respiratory tract infection, diarrhea, vomiting, skin, eye problems, cardio-pulmonary diseases, abdominal pain, asthma, and dyspnoea.	Nanofiltration	Effective in removing Giardia, cryptosporidium enteric viruses, norovirus, rotavirus	[10, 11]
Protozoa	Respiratory tract infection, diarrhea, vomiting, skin, eye problems	Reverse Osmosis	Not designed to remove viruses and bacteria	[12]
Perfluoro octane sulfonate (PFOS)	Neurotoxicity, renal toxicity, thyroid disruption, Weakens immunity, and Reproductive toxicity.	Nanofiltration (NF270)	—	[13]
Cadmium Cd(II), Chromium Cr^{3+}	Renal disorder, kidney failure, carcinogenic	Ultrafiltration	93% Cd^{2+} rejection and 86% Cr^{3+} rejection	[14]
Organics Materials	Carcinogenic, Immune system suppression, other chronic diseases	Dynamic membrane filtration (DMF)	51% organics were retained from wastewater and 50% influent COD were recovered in the concentrate	[15]

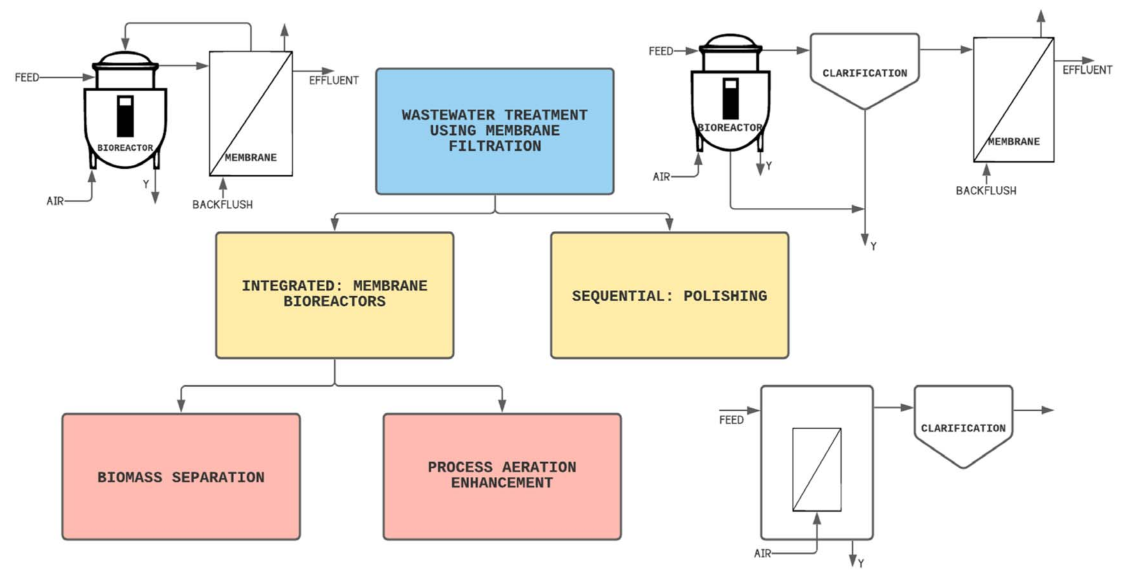

Figure 3. Membrane Filtration in Wastewater Treatment.

used in the pre-treatment method and have proven to be more efficient, safe, easy to operate, and cost-effective. UF is also done to remove pathogens such as viruses.

2.1. Working of membrane filtration in wastewater treatment

In wastewater treatment, membrane filtration technology has been widely used in the remediation of various impurities such as heavy metal ions, oil-based contaminants, total suspended solids, organic and inorganic materials, and many other waste effluents. When we talk about TDS removal in specific, this removal process is based on Microfiltration or ultrafiltration. To understand the working, the membranes used in the wastewater treatment process can be introduced using a unit operation separately or by integrating the process from the beginning, illustrated schematically in figure 3.

It is important to distinguish between the integrated processes such as the membrane bioreactors where the membrane forms a part of the biological process and the non-integrated processes where the membrane is placed just after the conventional biological processes (here, the process is referred to as a polishing process). We have the conventional activated sludge process within the integrated processes where the membrane retains the biology in the tank and filters the water down to well below 0.1 microns, producing a largely clarified disinfected water. In the case of MABR (Membrane Aerated Biofilm Reactor), the membrane is used as an aerator that effectively enhances the biological process but does not provide any clarification. This means the effluent from the biological process from an MABR requires further clarification. In simpler words, the MABR works the membrane as an efficient diffuser instead of solid-liquid separation as in MBR (Membrane Bioreactor).

3. Involvement of carbon nanomaterials in the membrane filtration process

As time progresses, there have been many advancements and developments in nanotechnology and its applications, and it has been used in the treatment of water and wastewater over the years. We know particles of a particular size and range have their unique surface and physical-chemical properties, which can be useful for many applications, especially for wastewater treatment. These particles can be between a few to hundreds of nanomaterials in diameter. Since traditional methods such as extraction, oxidation, and adsorption are effective but are often very costly, nanotechnology is used to detect and extract these numerous pollutants from wastewater and treat them. Numerous nanotechnology processes include photocatalysis, Nanofiltration, adsorption, electrochemical oxidation using metal or metal oxides like TiO_2, membranes made of ceramics and polymer membranes, nanocomposites, etc [16].

Nanomaterials such as Carbon nanomaterials or CNMs have been used as advanced membrane materials and possess novel size dependant properties which are extremely helpful in removing organic and inorganic contaminants in wastewater treatment. Carbon nanomaterials attracted high interest from science and large-scale textile industries, mainly for water purification due to the excellent range in contaminant removal and outstanding novel features [17]. CNMs offer better features and advantages over the conventional water purification system. Adsorption is one of the major processes that is employed for removing contaminants.

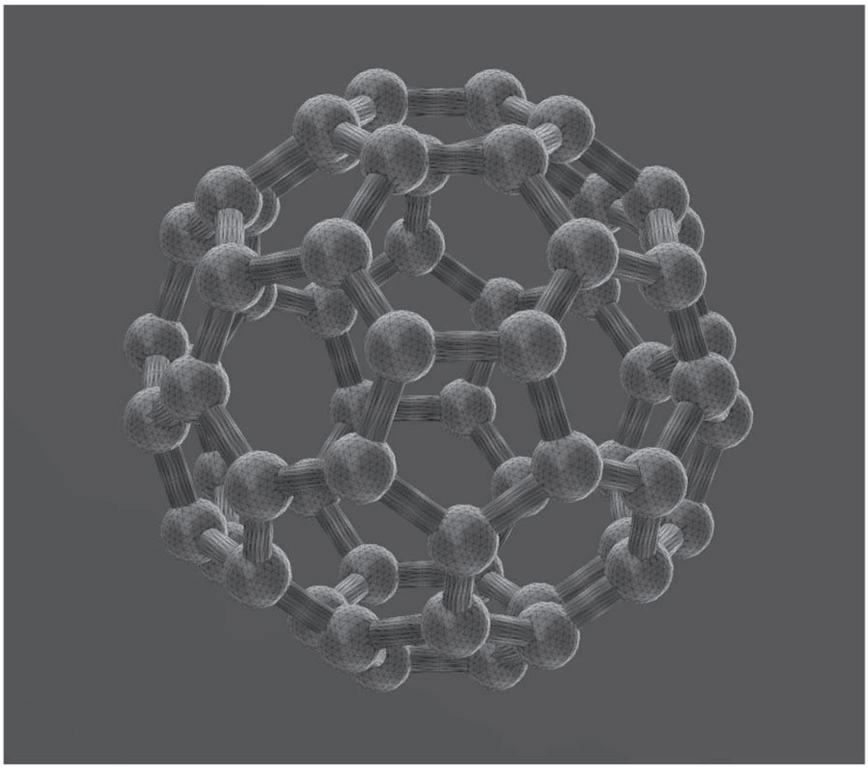

Figure 4. Structural representation of fullerenes.

Introduction of Nanoadsorbents like CNTs and Nanoscale metal or metal oxide can be used as a better and more efficient treatment technique than activated carbon as it possesses high surface area, which is essential for the adsorption of required contaminants. Other properties include high reactivity, fast dissolution, and discontinuous properties that include superparamagnetism, quantum confinement effect [18].

Depending on the type of carbon atoms arranged, carbon nanomaterials could be classified into different types. These CNMs may vary in the surface morphology but possess similar use in removing the organic contaminants such as pathogens and excess concentration of heavy metal ions in the wastewater treatment that can cause serious health hazard cases to humans.

3.1. Different carbon nanomaterials used in membrane filtration process in wastewater treatment

Adsorption is the most flexible operation used to extract and remove heavy metal ions from the wastewater and ensure that the wastewater effluents released from many industries are safe for the environment. Time, temperature, pH, sorbent doses, metal concentration, and speed all affect the efficiency of the sorption process. The rate of sorption for these heavy metal ions is directly proportional to the factors mentioned above [19, 20].

Adsorption is a surface phenomenon. Organic and inorganic contaminants present in the wastewater are accumulated on the surface of the adsorbent. The surface area plays a very important factor in this process and determines how efficient adsorption can occur. Activated carbon (AC), due to its highly porous structure and surface area, activated carbon (AC) is the most known adsorbent used to remove contaminants for wastewater treatment.

Carbon-based adsorbents are emerging as the best alternative to conventionally used adsorbents because of their better features. CNM based adsorbents with normal adsorbents have a higher surface area, contain oxygen-containing functional groups, and have better corrosion resistance [21]. The presence of functional groups helps remove heavy metal ions, which causes toxicity by increasing hydrophobicity that can cause increased interaction towards metal ions.

3.1.1. Fullerenes

Fullerenes are a zero-dimensional allotrope of carbon that forms a hollow spherical or cage-like structure, as shown in figure 4. Their formula is C_{20+n}, where n is an integer. The most commonly studied fullerenes are C_{60}. Fullerenes have a high affinity and surface-volume ratios, thus making them suitable for separating species from aqueous solutions. Fullerenes are often considered adsorbents for industrial wastewater treatment because of the large surface area that helps remove heavy metal ions considered contaminants. They are non-toxic as well as bio-compatible. Pathogens present in the wastewater can be treated with the help of Hydrophilic functionalized fullerenes along with photocatalysts. Water-soluble fullerenes are also known as fullerols which, upon photocatalysis of UV rays or visible rays, produce ROS or reactive oxygen species. ROS produced are used for the removal of organic contaminants present in the wastewater [22]. The defects present in the surface define the sorption capacity of fullerenes [23].

To prevent the issue of high cost, Certain modifications are done to nano adsorbents. Fullerenes are embedded with other nanomaterials such as zeolites and Activated carbon, which act as a low-cost substitute adsorbent. It has also helped improve the sorption capacity because of more porous structures in these adsorbents. This, in turn, increases the hydrophobicity. Fullerenes are embedded with polymer membranes to form nanocomposites, which helps improve the host polymer's mechanical property and adsorption rate. Cu (II) ions in excess concentration in the wastewater can be removed with the help of Fullerene, and it showed better efficiency than nanocomposite polystyrene film [24]. C60 grafted with polyvinylpyrrolidone (PVP) showed great antibacterial property, thus showing great potential in wastewater disinfection. Proteins are one of the organic foulants present in wastewater that can lead to membrane fouling. Membranes that undergo surface modifications by fullerenes and CNTs have shown better values of flux reduced recovery when in contact with protein-containing wastewater. C60 of about 10% was embedded with polyphenylene isophthalamide, or C60-PA membranes examined using SEM images. It has shown an increase in its physical properties, such as intrinsic viscosity and density compared to normal PA membranes, increased flux, and lowered sorption of proteins [25]. It was found that the contact angle of water on the membrane surface increased with the addition of Fullerene. PPO-C60 membranes (where PPO is Poly-2,6-dimethyl-1,4-phenylene oxide) have shown an increase in the pores' size compared to the regular PPO membranes. This type of membrane can be used to remove compounds that are organic present in the wastewater [26]. Fullerenes show a wide range of properties that help treat wastewater contaminants, but one of the major disadvantages of these carbon nanomaterials is expensive.

3.1.2. Buckypaper membrane (BP)

Buckypaper membranes are light in weight, self-supporting having unique structural and surface properties. It has exceptional hydrophobic properties and is thus used for water desalination by membrane distillation. CNTs increase hydrophobicity and the ability to create stable suspensions. It is a paper-like structure of CNTs fabricated from single or multi-walled carbon nanotubes using vacuum filtration. A widely used application includes membrane distillation, where the BP performances are correlated using microscopy and porosimeter. CNT BPs are characterized with the help of techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and nitrogen adsorption [27]. BPs are commonly used for salt removal from the aqueous phase, filter membranes, as actuators, and for the removal of heavy metals and dyes.

CNT BPs are seen as a better adsorbent since it has fewer negative surface charges present. BP is found to have high porosity, and contact angle since BPs are non-woven of entangled CNTs. It has a low thermal conductivity which makes it a better option than polymeric membranes, which are widely found in membrane distillation. When coated with a thin layer of poly(tetra-fluoro-ethylene) (PTFE), the hydrophobicity gets enhanced, and the mechanical stability improves. This also increases the contact angle and the bubble point pressure [28]. Since BPs have a high surface area and strong self-interaction, they tend to agglomerate when dispersed in a polymer solvent which results in difficulty while preparing uniform dispersions [29].

Chitosan and carrageenan, two common biopolymers, are used to facilitate the formation of aqueous dispersions of MWCNTs. Biopolymers are exceptional for use as binders in CNTs in BP membranes since the long biopolymer molecules consist of flexible bridges between the short CNTs. It also enhances the membrane properties and makes it useful for experiments related to water permeability, salt, and rejection of other contaminants [30].

Filtration is avoided due to low solute selectivity, limited lifetime, and fouling. Thus, BPs are preferred for water purification. Energy consumption of BPs in desalination is low as compared to reverse osmosis. The prepared membranes are used for salt rejection from synthetic water, having a removal rate of around 99%, making it a suitable candidate for desalination [31].

3.1.3. Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are mono-layered carbon atom sheets rolled up to form a cylindrical molecule. CNTs can occur as more than one concentric cylinder known as multi-walled carbon nanotubes (MWCNTs) or just a cylinder/tube called single-walled carbon nanotubes (SWCNTs) shown in figure 5. They have outstanding properties such as great aspect ratio, high surface area, great thermal conductivity, optical, vibrational, mechanical properties (high tensile strength and young's modulus), etc which makes them unique from other materials [32].

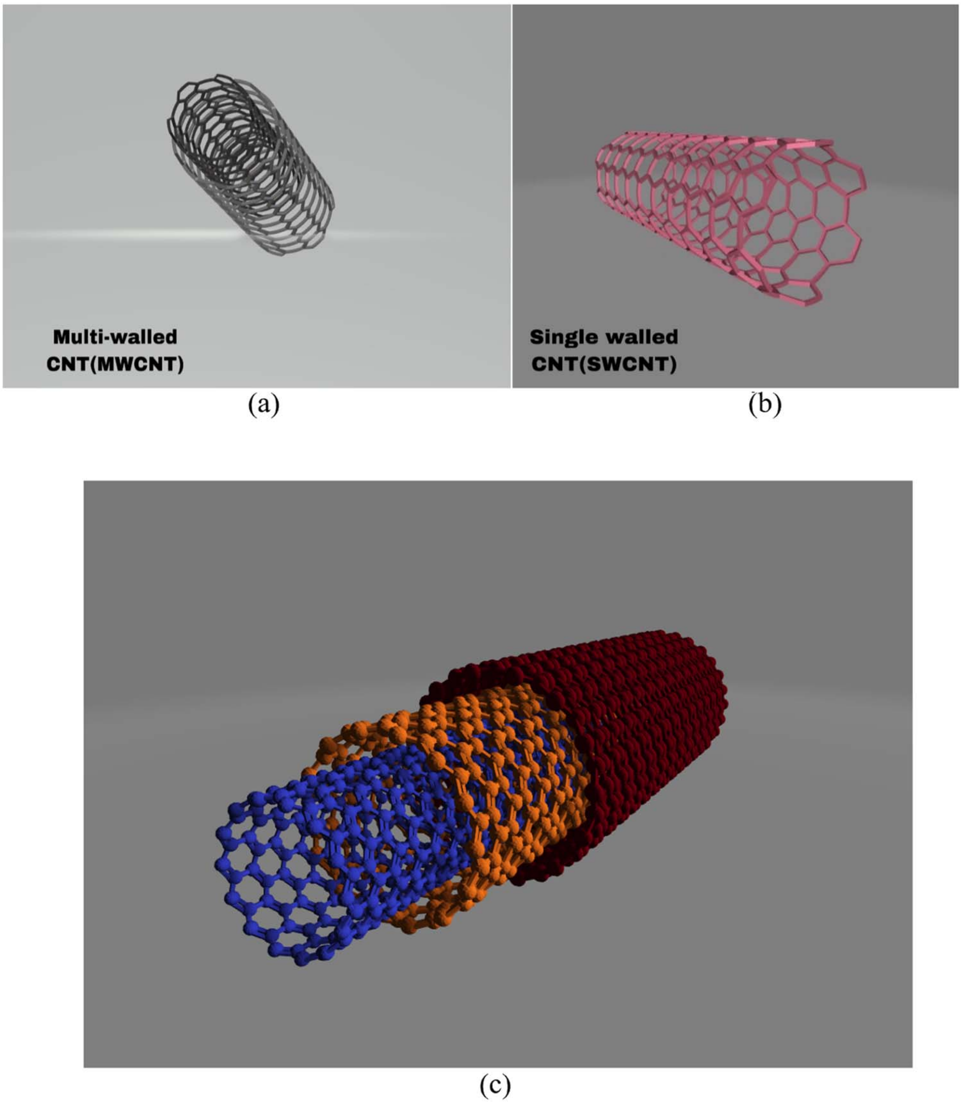

Figure 5. (a) and (c) shows the structural representation of MWCNT and (b) shows the structure of SWCNT.

CNTs have shown great advancement potential in nanotechnology by gaining significant consideration in the innovation of membranes. Limitations of membrane filtration such as fouling and the issue between permeability and selectivity are believed to solve by CNTs.

3.1.3.1. Preparation of functionalized and modified CNTs by nano-zero valent iron incorporation
The preparation methods of CNT functionalization are separated into chemical and physical methods. Functionalization by physical method consists of wrapping the modifier and storing it in the cavity of the CNT or absorbing it onto CNT. They are also chemically bonded with the functional groups, known as chemical functionalization. Different functional groups are carboxylic, amine, polymer, hydroxyl, and inorganic compounds. Acid treatment, plasma oxidation, chemical grafting and wrapping, hydrothermal treatment, *in situ,* precipitation, surface-initiated polymerization, precipitation, etc, are the methods to prepare functionalized CNTs. Some of the methods and procedures followed by the use modifier are represented in table 2.

One of the most studied ways of introducing carboxylic groups onto CNT is acid treatment. This will improve CNT dispersity in a polar organic solvent because of the hydrophilic properties of the carboxylic group. In this treatment method, CNT is dispersed in a concentrated acid mixture (1/3 v/v HNO_3/H_2SO_4) such as nitric and sulfuric acid and refluxed for some time in high temperature [33, 37–39]. CNT is then washed, filtered, and dried. This method can be used to make CNT membranes. Other functionalization techniques include situ polymerizations, electrochemical polymerization, using zwitterionic functional groups, etc.

Nano-zero valent iron (NZVI) nanomaterials are arising as a solution for removing both organic and inorganic pollutants, i.e., heavy metal ions present in wastewater, shown in table 3. They are highly reactive and

Table 2. Different methods of functionalization of CNT.

Modifier	Method	Procedure	References
Carboxylic	Treated with Acid	$HNO_3/H_2SO_4 = 3/1$	[33]
Carboxylic	Plasma oxidation	Vertically aligned CNT (VACNT) undergoes plasma treatment in H_2O plasma oxidation	[34]
Poly (allylamine hydro-chloride) PAH	Chemical wrapping	Multi-walled CNT (MWCNT) dispersed in PAH solution (0.5 M NaCl) treated with heat and ultrasonication	[35]
1,3-Phenylenediamine (mPDA)	Amination, Acid treatment	$HNO_3/H_2SO_4 = 1/3$ Amine functionalized Multi-walled CNT: MWCNT-COOH +mPDA in DMF resulted in powder drying at 70 °C for 96 h	[36]

Table 3. Removal of heavy metal ions from wastewater by Zero valent Iron (Summary).

Zero Valent Iron	Heavy metal ions removed from the water	Summary	References
Pumice Supported Nanoscale Zero-valent iron (P-NZVI)	Cr (VI) and Hg (II)	Pumice prevents agglomeration of NZVI. With the increase in pH, the removal rate of Hg (II) increases while the removal rate of Cr (VI) decreases slightly	[40]
Nanoscale Zerovalent Iron (nZVI)	Cd (II)	Removal of nitrate and Cadmium simultaneously by nZVI doped with Au	[41]
Nanoscale Zerovalent Iron (nZVI)	Cd (II)	nZVI is an effective adsorbent for Cadmium. The pseudo-second-order kinetic model well describes adsorption kinetics, and the Langmuir isotherm was a better fit	[42]
Zeolite and nanoscale Zerovalent Iron Z-nZVI	Pb (II)	Experiments showed that Z-nZVI is better in the adsorption of Pb in an aqueous solution than zeolite. Zeolite also increased the surface area and reduced aggregation in the composite	[43]
Nano zero-valent iron particles reduced by borohydride (Ferragels)	Cr (VI) and Pb (II)	Cr (VI) was reduced to Cr (II), and Pb (II) to Pb (0) by nZVI from XPS and XRD analysis. The overall removal of Cr (VI) and PB(II) quickly used the reduced nZVI	[44]
nanoscale Zerovalent Iron loaded onto kaolinite (K-nZVI)	Pb (II)	K-nZVI has high removal efficiency of Pb (II). High removal of Pb (II) was possible due to enhanced reactivity of K-nZVI and reduced aggregation of nZVI	[45]

have a high surface area making them suitable for water contaminant removal. They possess good mechanical properties, contaminant removal efficiency, and are non-toxic, making them suitable for the environment. Elemental Iron present in NZVI is a strong reducing agent that helps in the faster adsorption rate of heavy metal ion contamination. The increased amount of Cr, Co, and Se metal ions in water can cause negative effects on human health. Chromium ions present in the wastewater occur in different forms (Cr (III) or Cr (VI) ions). They are considered carcinogens and can cause major health diseases and must be effectively removed [46].

Activated CNTs along with NZVIs make an effective nanocomposite for the removal of Cr (VI), Co (Cobalt), Se (Selenium) ions present in the wastewater. Usually, Multi-walled CNTs are chosen for these nanocomposites. To synthesize Activated CNTs (ACNTs), MWCNTs are mixed with 72% and 68% of H_2SO_4 and $HN0_{3,}$ respectively, to form sites for NZVI loading and etch the MWCNT surface. Using vacuum filtration, the ACNTs are removed as filter cakes, then washed with a huge volume of di-mineralized water to remove residual acid contents and get a neutral filtrate. A quantity of 0.1 g was taken from the pre-prepared sample, dissolved in a solution of ethyl alcohol of 20 ml, and kept under ultrasonic for three h until all the CNTs were completely dispersed. Ethylene glycol is later removed, causing deposition of ACNTs and combined by re-weaving to form a membrane. This membrane was dried in an oven at 50 °C for further process. The next step, to attach the Fe2+ ions to the surface of the membrane, the ACNTs membrane was first immersed in 75 ml of FeSO4 solution of concentration 0.1 mol l^{-1}, after which the same volume NaBH4 of 3 mol l^{-1} concentration is added to the solution at the rate of 2 drops per second. The entire procedure took place in a nitrogen environment to prevent NZVI from oxidation [47].

3.1.3.2. Preparation of CNT membrane

Based on the fabrication method, CNT membranes can be divided into vertically aligned carbon nanotube membranes (VA-CNT) and mixed matrix membranes. In VA-CNT, fluid is forced by the straight aligned CNT

Table 4. VA-CNT versus Mixed matrix membrane [49].

Vertically aligned CNT membrane	Mixed matrix membrane
Carbon nanotubes are vertically aligned.	Polymeric materials are mixed with carbon nanotubes.
The fabrication process is difficult.	Easy process of fabrication.
A high-performance operating system may be required.	Works with a simple operating system.
Water flux is very fast.	Water flux is moderately fast.

Table 5. Preparation of VA-CNT.

Method	Matrix/Support	Structure	CNT layer thickness (μm)	Tortuosity	References
CVD	Polystyrene matrix	MWCNT	5	1.1	[50]
CVD	Silicon nitride	MWCNT	10	—	[51]
CVD + functionalization	Polystyrene matrix	MWCNT	5	—	[34]
CVD	Porous alumina	MWCNT	Less than 10	1.26	[52]
CVD	epoxy	MWCNT	Less than 4000	—	[53]
CVD	Silicon nitride	Double-walled -CNT	5	—	[54]
CVD	Polyethersulfone	MWCNT	130	—	[55]

to pass through the hollow CNT interior or between the CNTs bundles. The mixed matrix membrane contains a top layer mixed with a polymer and CNT, making a structure similar to the thin-film composite reverse osmosis membranes [48]. A short comparison of VA-CNT and mixed matrix membrane is shown in table 4.

The method of preparation of vertically aligned CNT membranes is done by chemical vapor deposition. A tabulation of various studies on the preparation of VA-CNT membranes is shown in table 5.

Incorporating functionalized CNT has affected chemical properties and rheological/physical properties such as porosity, roughness/smoothness of the modified membrane, and pore size. Hydrophilicity is one of the chemical properties recognized due to incorporating hydrophilic/functionalized CNT with a membrane. This property is described by using the water contact angle as the indicator. This is done by comparing the base membrane with the water contact angle of a modified membrane, which proves that the decrease in water contact angle increases the hydrophilicity of the membrane. The challenge of overcoming membrane fouling can be attained by making the membrane hydrophilic. The parameters used to quantify the antifouling performance of membranes are total fouling resistance (R_t) and Flux recovery ratio (FRR). The total fouling number that occurs on the membrane's surface is defined by total fouling resistance, while the membrane's recovery ability from membrane fouling is defined by flux recovery ratio. On the contrary, the hydrophilicity resulted in the high permeability of the fouled membrane. This permeability can still be greatly recovered. A decrease in R_t and increase in the FRR number is observed after backwash is due to the high permeability of the fouled membrane, and higher FRR and lower Rt indicates antifouling property improvement of modified CNT membranes than base membrane [56].

3.1.3.3. Graphene

The 2D Allotrope of Carbon is called Graphene. Nonporous Graphene/Graphene Oxide is being developed for advanced and modern membrane separation processes due to its molecular sieving feature. Graphene undergoes surface modifications in order to get desirable properties that were initially not present in pristine Graphene. Chemical oxidation is done by Hummer's method in order to obtain Graphene Oxide sheets. This method introduces functional groups such as hydroxyl group (–OH) and carboxylic acid (–COOH) in the lattices of Graphene. In the presence of a highly porous structure and surface area, Graphene/Graphene Oxide sheets are being used for wastewater treatment. GO sheets are very compatible with polymer membranes; hence polymer embedded with GOs are being manufactured. This can boost certain properties, such as the mechanical properties of the polymer host. The hydrophilicity of the polymer host is boosted because of the presence of the –OH group in the GO lattice. GO/APAN (Aminated Polyacrylonitrile) membranes developed showed high porosity attributed to their exceptional antifouling performance in oil and water emulsion. These showed a very high flux rate. GO was coated on the polyamide surface or PA membrane, enhancing antifouling property and maintaining stability [57]. Surface roughness plays a huge role in determining the antifouling property. GO/OMWCNTs were embedded into membranes that showed a reduction in the roughness of the surface. A reduction in surface roughness showed an increase in the antifouling property. Graphene and CNTs have similar structures, thus exhibiting similar mechanical and electrochemical behaviors [58]. Phase inversion method was conducted in order to fabricate an asymmetric PES-GO membrane. The results showed a significant enhancement of rejection of organic dyes and water flux with the addition of GO into the polymer matrix [59].

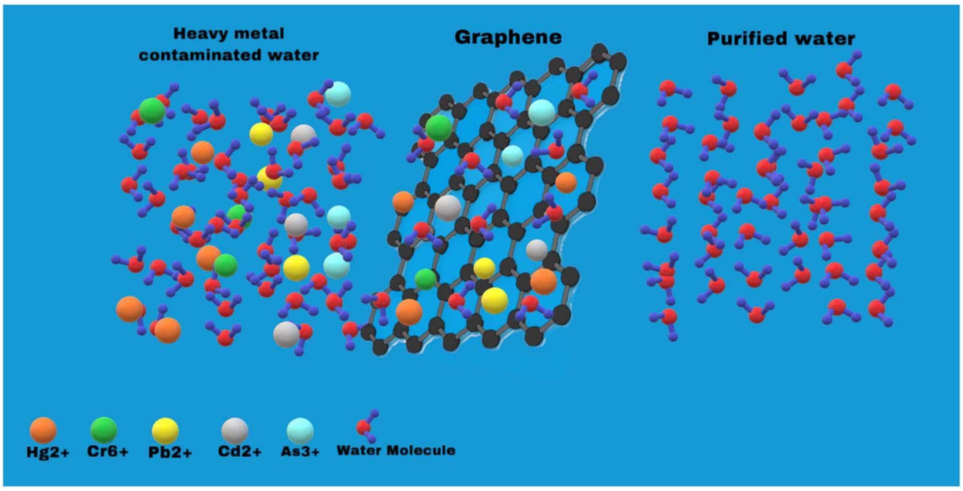

Figure 6. Rejection of heavy metal ions by Graphene sheets that are present as contaminants in the wastewater.

Table 6. Advantages and disadvantages of Graphene-based nano adsorbents and their specific interaction mechanisms [60].

Graphene-based adsorbent	Interaction mechanism	Advantages	Disadvantages
Graphene functionalized by organic molecules	Electrostatic interaction	The greater area of the surface	Based on the strategy of modification, the loaded molecule stability is varied.
	Complex formation with organic molecules	Colloidal stability	
		Increased functional groups	
Reduced Graphene oxide (Pristine Graphene)	Electrostatic interaction	sp^2 domains are re-established	Low colloidal stability
	Lewis's acid-base mechanism	Electron transport property was improved	Oxygen-containing functional groups are found to be of low density
Magnetic Graphene nanocomposite	Electrostatic interaction	Greater surface area	Reduced colloidal stability
	Interaction with surface particles	Ease of recovery	Co-reduction of Graphene
	Magnetic properties of nanoparticles	Increase in binding sites	
Graphene oxide	Electrostatic interaction.	Colloidal stability	Limited sorption sites
	Ion exchange	Higher dispersibility in water	
		The abundance of oxygenated groups	

Graphene-based nanomaterials do not contain any catalytic residues; thus, it does not require additional purification steps.

Graphene can be used as a substitute to CNTs for removing the concentration of heavy metals that are available in excess quantities in the wastewater. In figure 6, the rejection of various types of heavy metals like such as mercury (Hg_2+), Cadmium (Cd_2+), arsenic (As_3+), chromium (Cr_6+), lead (Pb_2+), and so on by graphene sheet is illustrated. Pb (II) ions in excess quantities in the wastewater can be treated using chemically oxidized graphenes. In addition to heavy metal ion treatment, Graphene can eradicate the issue of organic impurities present in wastewater, such as phenols and dyes. Graphene-based nanomaterials used for effective wastewater treatment undergo different interaction mechanisms for each material, such as electrostatic interactions, ion exchange, magnetic, etc Their mechanism of interactions, merits, and demerits are discussed in the table 6.

Further, rGO or reduced Graphene oxide are also obtained by these modifications, which can be used for efficient organic dye removal. The introduction of functional groups improves the adsorption of the contaminants. There are two types of functionalization involved in GOs. This includes Covalent and non-covalent functionalization. Among these two functionalizations, non-covalent is more preferable because of more alterations. Different polymer-GO nanocomposites that undergo non-covalent functionalization have strong pi-pi bond interaction, making them better in performance than the initial GO sheets. GO are very dispersible in water, thus making them very hard to reuse for the sorption of the metal ion. Magnetic-GO nanomaterial composites are being developed to counter this issue. Magnetic materials include $Fe3O_4$ $MnFe_2O_4$, and the advantages of using these magnetic materials are that their toxicity levels are low and hence compatible in the separation of pollutants effectively [61–64]. Graphene-based membranes for wastewater treatment are still in development, and their potential is immense. GO incorporated membrane technology can be utilized to manufacture less expensive and non-toxic membranes used in wastewater treatment. However, further research and studies must be conducted in order to reach their maximum potential.

Carbon and graphene quantum dot (CQD) refers to the carbon-based nanoparticles which consist of sp3 and/or sp2 hybridized atoms. The strong electrochemical, electronic and quantum size effects, easy surface functionalization, adjustable composition have this unique ability to harness the light of larger wavelength and easy proficiency towards the photodegradation of numerous organic contaminants. Such adsorbed reductants/oxidants interactions with the electron-hole pairs produce an improved quantity of activated oxygen radicals with a strong oxidation prowess for removing toxic gases.

GQDs are intact aryl-basal flat structures, and unlike the micro-sized GO layers, they are of rich periphery carboxylic groups. The doping of nitrogen is mainly used to modify and modulate the structural functionalities, chemical and electronic properties/features of graphene and GQDs. Mainly used in remediation by elimination of organic pollutants such as azo dyes and VOCs. They are also mainly used in eliminating highly toxic pollutants, namely dyes and heavy metals. QDs-based photocatalysts via hydrothermal-, solvothermal-, ultrasonic treatment and microwave-assisted routes are discovered in the paper [60].

4. Discussions

Our study focuses on the different carbon nanomaterials and their applications that benefit membrane filtration for wastewater treatment. Membrane filtration has been used as a major step for organic and inorganic wastes removal present in the wastewater released by industries. However, membrane fouling is one of the most common barriers that concerns the membrane filtration processes. The accumulation of foulants in the membrane pores can decrease the adsorption rate of the membrane. Carbon nanomaterials are either used as substitutes or nanocomposites through surface modifications with these membranes to boost its antifouling property that reduces or permanently stops the membrane's fouling for efficient wastewater treatment. It is also noted that these carbon nanomaterials used as a counter for the prevention of membrane fouling also have major advantages such as low cost, increased physical properties. Summary of different carbon nanomaterials-based membranes and their performances are shown in table 7.

In developing countries like India, the application of CNM based technology in wastewater treatment is not so well-practiced, and if undertaken in many places, it will benefit a lot for the country's welfare. Many water treatment plants in the country use the conventional old method treatment of wastewater treatment. As previously mentioned CNM based membrane technology has provided a huge advantage over normal treatment methods. It may take some amount of time as there are many factors. In the case of India, CNM based membranes are not easy to get in most parts because being very diverse, and population size economic balance varies from state to state. There must be a strong connection with other countries that have already employed these methods and huge investment in the foreign market.

The problems of water pollution in the northern parts of India, which is caused by the release of wastes into the rivers, could be minimized. Textile and agricultural industries will not use RO membrane processes in some regions due to insufficient fundings. Using screening and traditional separation methods will not exactly remove the harmful contents present in the water. Graphene-embedded with zeolites or other nano adsorbents or GO sheets would be much more efficient as it can remove the inorganic dyes and heavy metals that the normal methods cannot remove. These are of low cost, and operation is made much simpler.

By understanding and analyzing the parameters more carefully, we could improve efficiency. This will be a time-consuming process, but as the technology develops, the parameters that are hard to improve or study will be made easier. One example is working on a parameter such as a contact time to a maximum extent to increase the membranes' efficiency and self-cleaning property greatly. More improved methods for incorporating carbon-based nanomaterials into the desired polymer or other matrices that could improve its adsorption capacity, mechanical strength, resistance to a higher temperature, and pH can be undertaken. Further research must be done to determine the compatibility of CNM based polymer matrices or membranes. Polymer-based membrane matrices are in development, and there is much potential if an ideal Matrice is developed so we could make effective CNM nanomembranes.

In the study conducted by Fatemeh *et al* (2019) [5] with the help of FTIR spectra, it can be concluded that the surface of the carbon-based nanocomposite membrane has more polar functional groups than the surface of the

Table 7. Application of Carbon nanomaterials for removal of contaminants from wastewater (Summary).

Adsorbent materials	Specific application	Observation	Remarks	Efficiency	Cost-effectiveness & reusability	References
Polypyrrole(PPy) coating over oxidized multi-wall carbon nanotubes	Removal of chromium Cr (VI) from water.	Positively charged nitrogen atoms in polypyrrole (PPy) promote its application in adsorption. The main mechanism of adsorption is ion exchange.	The highest efficiency of Cr (VI) removal was achieved at pH 2, and adsorption efficiency is strongly pH dependant.	High	Cost-Effective & Reusable	[1]
PVP-C60	Disinfection Of microbial activities in Wastewater	Increases porous size and hydrophobicity of the membrane.	Organic matter contamination, which causes membrane fouling, can be controlled with Fullerene on the membrane surface.	Moderate	Moderate costs & reusable	[22–24]
NZVI embedded with CNTs	Removal of Cu (II), Se (II), and Co (II) ions	Increases Surface area and reactivity	Great contaminant removal efficiency, enhanced mechanical property, and non-toxic. Usually done with MWCNTs	High	Low cost & reusable	[46]
Fe3O4 MnFe2O4(Magnetic nanoparticle embedded with GO)	Effective separation of organic and inorganic waste in aqueous solution	Helps in the separation of water-soluble GOs Those are hard to be removed in wastewater treatment. Increases the efficiency of adsorption	They are cost-efficient and non-toxic hence can be used as a substitute for another Graphene-based membrane	Moderate	Low cost & Low reusability	[61–64]
Amino functionalized magnetic graphene oxide (AMGO)	Radioactive metal ions, in specific Uranium (VI)	The adsorption process depends highly on pH. Magnetic separation is used to separate AMGO from the medium.	AMGO is an environmentally friendly, cost-effective, and simple method for the removal of uranium.	Moderate	Costly & Moderate to low reusability	[65]
Reduced graphene oxide with tunable magnetic nanoparticles	Bisphenol A(BPA)	It is a great adsorbent for BPA due to the high specific area of Graphene oxide and the magnetic properties of MNPs. It is also proven that the adsorption process is well-fitted by a pseudo-second-order model.	The overall process is favorable at ambient temperatures, and the reduced graphene oxide composite has great reusability.	Low	Low cost & Reusable	[66]
CNT-PAC composite	Cadmium (II)	Carbon nanotubes are grown on powdered activated charcoal oxidized be HNO_3 or $KMnO_4$ altered the surface activity of powdered activated charcoal significantly to adsorb heavy metal ions.	Chemical oxidation alters the surface properties of CNT-PAC.	High	Low cost & Reusable	[67]
Multi-walled Carbon nanotubes	Bismuth (III)	It is also proven that the adsorption process is well-fitted by a pseudo-second-order model. The adsorption process is exothermic and is spontaneous when the solution temperature is decreased.	The adsorption process depends highly on the pH and temperature of the aqueous phase.	High	Low to moderate cost & Reusable	[68]
Multi-walled Carbon nanotubes coated with Fe_3O_4	Sudan dyes		MWCNT can be reused multiple times due to its magnetic property and easy desorption.	High	Cost-effective & reusable	[69]

Table 7. (Continued.)

Adsorbent materials	Specific application	Observation	Remarks	Efficiency	Cost-effectiveness & reusability	References
		High reusability up to ten times without noticeably decreased efficiency. Dyes can be separated with a magnetic separation technique.				
The nanocomposite of multi-walled carbon nanotubes and cobalt ferrite	Rhodamine B (dye)	The adsorption increased with increasing MWCN-COOH content. MWCNT-COOH has the highest adsorption capacity among CNT-based composites and CoFe2O4 nanoparticles. At pH 7, maximum adsorption occurred.	The Langmuir isotherm best describes the equilibrium data, and the pseudo-second-order model was best suited for the data.	High	Low cost & Reusable	[70]
Single and multi-walled carbon nanotubes	Oxytetracycline (OXY) and Ciprofloxacin (CIP)	The adsorption capacity of all tested CNTs remained the same in cold and warm conditions. Single wall carbon nanotubes had the highest adsorption capacity for both antibiotics.	To enhance the adsorption of Oxytetracycline, ultrasound was applied.	Moderate	Low cost & reusable as MWCNTs	[71]
Short multi-walled carbon nanotube functionalized by Carboxyl (MWCNT)	Sulfamethazine (SMT)	The carbon nanocomposites were prepared by the dip-coating procedure of rice straw and pyrolysis.	Ultrasonication methods were found to be more effective than the ones without ultrasonication	Low	Low cost & Highly reusable	[72]
Magnetic Calcium Silicate Graphene Oxide composite adsorbent (MGSi)	Acridine Orange (dye)	Greater adsorption capacity towards alkaline dyes. The adsorption of acridine orange on MGSi followed pseudo-second-order and Freundlich, isotherm models.	Calcium silicate-coated over Fe_3O_4 nanoparticles immobilized on the graphene oxide surface did not fall off easily during adsorption than normal magnetic graphene oxide.	Moderate	Cost-effective & Technique specific usage	[73]
Graphene Oxide (GO) and activated Graphene oxide (GO_{KOH})	Anionic orange dye IV	High surface area and rigid structure of pores	The Langmuir isotherm best described the equilibrium data, and the pseudo-second-order model was best suited for the adsorption process.	High	Low cost & Reusable	[74]
Magnetic nanoparticle graphene oxide (MGO)	Se (IV) and Se (VI) ions	The nanomaterial composite has an efficient high binding capacity for Se (IV) and Se (VI). The adsorption increases with acidic pH. The removal percentage for selenite is >99.9%, and selenate is ~80% with the dosage of MGO $1\ g\ l^{-1}$.	They are known for their superparamagnetic properties and are efficient in immobilizing enzymes.	High	Low cost and reusable	[75]
Magnetic Polyaniline based graphene oxide composite MPANI/GO	Cu (II)	Magnetic separation easily separates the adsorbent, and MPANI/GO composites can effectively remove Cu (II) from large volumes of aqueous solutions.	The pseudo-second-order model well describes the sorption kinetics, and the Langmuir model can well describe the sorption isotherms.	Moderate	Low cost & Reusable	[76]
Multilayer graphene	Phenanthrene	Exfoliation and fragmentation possibly increase the adsorption sites created by sonication.	It can be used for controlling thickness.	High	Moderate cost & Reusable	[77]

Table 7. (Continued.)

Adsorbent materials	Specific application	Observation	Remarks	Efficiency	Cost-effectiveness & reusability	References
		Adsorption of Phenanthrene was higher on Graphene compared to MWCNTs and graphite.				
Activated Graphene (G-KOH)	Ciprofloxacin	The specific area of Graphene greatly increased after activation.	The adsorption was most efficient between pH 6–8.	Moderate	Low cost & Reusable	[78]
Magnetic reduced graphene oxide composite (MRGO)	Chlorophenols	The isothermal adsorption followed the Freundlich model. MRGO can be easily separated from an aqueous solution and can be regenerated by a dilute NaOH solution.	The adsorption is most efficient in neutral and acidic pH.	Moderate	Low cost & Reusable	[79]
Multi-Wall Carbon Nanotube (MWCNT) and Powdered Activated Carbon (PAC)	Nitrofurazone	The adsorption process is well fitted with pseudo-second-order kinetic. The removal efficiency was close to 94%.	The adsorption capacity decreased with increasing temperature and was not influenced by pH.	Moderate	Low cost & reusable	[80].
Functionalized magnetic multi-walled carbon nanotube nanocomposite.	Toluene, Ethylbenzene and Xylene	The adsorption of Toluene, Ethylbenzene and Xylene are highly pH, temperature and ion strength dependent. The adsorption decreased in the order ethylbenzene $>$ m-xylene $>$ o-xylene $>$ p-xylene $>$ toluene	It is useful in increasing the Tensile strength of the nanocomposite membranes.	High	Low to moderate cost & Reusable	[81]
Kaolin and sodium carbonate	Treatment of oily wastewater	Pore size increases with an increase in temperature due to pore overlapping.	In the batch permeation test, initially, the flux was high but decreased with an increase in pressure. 52% oil rejection rate with oily water.	Low	Low cost & Reusable	[82]
Cellulose nanomaterials (as scaffolds)	Arsenic	CNs are biocompatible and have low toxicity, electrically non-conductive, not photocatalytic, with high tensile strength.	They are highly stable under exposure to organic solvents, with antifouling and biocompatibility properties in the membrane filtration process.	Moderate	High cost & rarely or not reusable	[83]

neat PES membrane. The addition of GO and O-MWCNTs with large oxygen-containing functional groups increases the hydrophilicity of the casting solution, which accelerates the rate of solvent and non-solvent exchange. Deposition of the PVA layer on the substrate surface, the pores of the substrate surface area covered and plugged, and hence a uniform smoother surface is formed.

Zhang *et al* (2013) and Alekseeva *et al* (2016) [23, 24] experimented with the study of Fullerene, C60, and polymer membrane nanocomposite, which has shown an increase in the antibacterial performance of the polymer membrane because of the addition of C60. It has been found that hydrophobicity is increased with surface area, thus providing easy removal of heavy metal ions and self-cleaning ability, which disinfects the foulants like pathogens and organic dye accumulation on the pores.

It was found that the contact angle of water on the membrane's surface helped determine the fouling efficiency on the surface of PA membranes by embedding them with fullerenes. The contact angle was found to increase as the C60 was increased.

It has been observed that the surface area and pore size of the membrane decide the adsorption rate of contaminants. CNMs such as CNTs are found to increase the pore size when used with NF and UF membranes. CNMs were also found to increase the physical properties. Tiraferri *et al* 2011 study showed that around 60% of the bacteria were deactivated when attached to the surface of the membrane in an hour of contact time [84]. Since it involved the usage of nanomaterials on a small scale, it also reduced the perturbation of the active TFN layer. The incorporation of MWCNTs into TFCs enhances membrane antifouling property and also resistance to chlorine. The former is due to electron-rich MWCNTS, which has a higher negative charge and hydrophilicity on the surface. The latter property (i.e., Chlorine resistance) is due to the evaluation of membrane in immersion/dynamic mode, including the protection of amide linkage by MWCNTs [85].

The GOs produced by chemical oxidation were embedded with membranes to increase the antifouling behavior in oily wastewater. From the experiment conducted by Lau *et al* (2018) [58] on GO/MWCNT based membranes, it has been concluded that surface roughness plays a role in increasing the antifouling properties. GO/CNT-based nanomembranes must be studied and researched to reach their full potential in CNM based membrane filtration in wastewater.

It was found that cellulose nanomaterials (CNs) can also be used in nano-remediation standards in wastewater treatment technologies as contaminant adsorbents and as scaffolds (which uses nano iron oxide particles to remove arsenic contaminants, due to their high area-to-volume ratio and it enhances the affinity of the material for hydrophobic compounds/elements). They are used in the membrane filtration process, where they are incorporated in the polymer matrices distinctively. The CNs incorporated even at low weight percentages alter the properties of the membrane to a great extent. Surface hydrophilicity, greater permeability, greater selectivity, and greater resistance to biofouling are some of the alterations. Due to increased viscosity by the cellulose nanomaterials at high concentrations, the electrospun fiber diameters tend to increase, resulting in narrower pore size distributions and smaller overall pore sizes. It is assumed that these interconnected pores in the membrane layer are so small that it improves the contaminant rejection percentage and increase the water flux. Complementary activation products are used to enhance the biocompatibility and anti-biofouling properties.

Under Burakov *et al* (2019) [83] study, it was observed that the efficiency and of the sorbents depended on so many parameters such as pH medium, temperature, contact time, stirring speed, initial and final concentration. These parameters predicted whether the process was reversible or irreversible. When the adsorption process case is such that if the sorption is reversible, the sorbents can be regenerated via the desorption process and vice versa.

Under Ong *et al* (2018) [86] study, it was found that the incorporation of carbon-based nanomaterials (CNMs) into the polymeric membrane matrix had enhanced properties such as chemical, thermal, and mechanical stability of the prepared membranes, antibacterial and conductive properties along with improved surface hydrophilicity, water flux, rejection percentage, and photocatalytic properties. The incorporation of CNMs could be done in various ways, each method having its unique properties and advantages about the needs. For example, the freestanding CNM membranes were used for high specific surface area and large porous surface networks. Carbon nanomaterials with Surface-modified composite membranes are used when properties such as resistance to fouling, chemical stability, and membrane separation properties are enhanced. For effective separation of surfactant-stabilized oil/water emulsions, the surface of the polymeric membranes is attached covalently with hollow carbon nanotubes, which produces hybrid CNT-polymeric membranes. The hollow CNT structure allows smooth, efficient, frictionless water transportation through the membranes, enhancing the water permeability. Under this specific method, the oil droplets are demulsified due to the strong interaction between f-MWCNTs and asphaltenes or resins via π-π and/or nπ interactions.

It has also been studied that a dynamic hybrid CNT membrane can be synthesized and processed to extract tellurium efficiently from wastewater. It was studied that embedding nano-zero valent iron (NZVI) into activated carbon nanotubes (ACNTs) membranes enhanced the chemical stability of the NZVI. However, it also increased the mechanical strength of the ACNT incorporated membrane due to the force of interaction between the ACNT membrane and NZVI particles. The sorption capacity of the membrane was increased to a higher reach of around 800 mg g^{-1} with an extract rate percentage of more than 99. Even though the incorporation of interfering NZVI ions hinders adsorption performance, the slow kinematics maintain equilibrium concerning internal particle diffusion and adsorption. After the adsorption process, NZVI and tellurium can be separated and removed from the CNT membranes utilizing acid treatment, and the CNT membranes are recycled and used again for membrane separation processes. Thus, this unique property allows them to be used in the membrane filtration process to recover and separate some rare elements from the wastewater.

From the above information gathered, it is observed that the ultra-thin composite membrane of SWNT/TiO_2 showed excellent performance for separating oil in water and good antifouling and self-cleaning performance due to the photocatalytic degradation of TiO_2 nanoparticles. First polymer1-g-CNT-g-polymer2 Janus membrane with hydrophilic and hydrophobic polymers grafted on different sides of the membranes can separate both surfactants stabilized oil-in-water and water-in-oil. The second type is vertically aligned CNT membrane, and the third type is polymer-CNT nanocomposite membrane which causes high flux, improves perm selectivity, and better mechanical properties [90].

Checking the toxicity of CNM based nanomembranes is one of the major steps for an eco-friendly approach which is sometimes ignored because the focus is mostly on improving the performance such as porosity, surface roughness, etc One such technique can be the bioluminescent enzyme inhibition-based assay was applied to predict the potential toxicity of CNM presented by single- and multi-walled nanotubes (SWCNT and MWCNT) and aqueous solutions of hydrated fullerenes. Because of its technical simplicity, very quick response time, and high sensitivity, this method has the potential to be developed as a general enzyme inhibition-based assay for a wide variety of nanomaterials.

5. Process parameters

The process parameters motioned and discussed are based on the collective evidence gathered from numerous research work done to date. These process parameters will help and direct the fellow researchers to understand and grasp the ideas, which will give them an ideal result irrespective of the cost, be it cumbersome or not. The empirical findings of the literature from the survey are mentioned below to help you understand why these parameters are viable and optimum.

1. Incorporating carbon nanomaterials (CNMs) into membranes during membrane filtration in wastewater treatment enhances the properties of the membranes in numerous ways. These properties can be chemical, mechanical, the thermal stability of the prepared membranes, hydrophilicity, water permeability, flux rate, rejection percentage, antifouling, photocatalytic, and conductive properties.

2. The incorporation of CNMs can be done in various ways, each method having its unique properties and advantages about the needs. For example, the freestanding CNM membranes were used for high specific surface area and large porous surface networks. Carbon nanomaterials with Surface-modified composite membranes are used when properties such as resistance to fouling, chemical stability, and membrane separation properties are enhanced.

3. For effective separation of surfactant-stabilized oil/water emulsions, the surface of the polymeric membranes is attached covalently with hollow carbon nanotubes, which produces hybrid CNT-polymeric membranes. The hollow CNT structure allows smooth, efficient, frictionless transportation of water through the membranes, enhancing the water permeability characteristic. Under this specific method, the oil droplets are demulsified due to the strong interaction between f-MWCNTs and asphaltenes or resins via π-π and/or nπ interactions.

4. Carboxylic acid, hydroxyl, and epoxide groups are present in Graphene Oxide (GO) and are incorporated at the basal plane and the border edges of the nanosheets. These fillings at even low concentrations provide enhanced mechanical properties and good consistency with the polymeric membranes. The graphene oxide nanosheet membranes act as a barrier and hinder the diffusion of permeable molecules across the membranes allowing only the water to flow pass through it.

5. Chitosan-based adsorbents and GO are non-toxic, biodegradable adsorbents that are highly biocompatible and feasible because of their easy availability (low cost). These adsorbents have hydroxyl and amino functional groups in excess contents, which are efficient in removing dyes and toxic heavy metal contaminants from wastewater because of their readiness for chemical modification. More study and research are currently needed in qualitative and quantitative stages to work on adsorption processes and systems.

6. It was also studied that the optimum property to treat oily wastewater efficiently was observed when the carbon nanomaterial incorporated membranes have a pore size of 1.0 μm at an operating pressure of 0.1 Mpa along with 0.1 m s^{-1} of crossflow velocity. Increasing the crossflow velocity is generally recommended to maximize the antifouling property because of the high shear stress produced on the surface of the membrane, which in turn reduces the height of the sedimentation layer. Also, the enhanced hydrophilic surface due to the carbon nanomaterial incorporation forms an extra layer to prevent the oil droplet depositions and easily lets these droplets be washed and cleaned during the cleaning process and prevents fouling in a way.

7. The incorporation of CNMs showed an increased rate of convectional mass transfer amongst the solvent and non-solvent due to its enhanced hydrophilicity. This tends to form bigger cavities, and it suppresses the formation of the spongy-like structure resulting in bigger cavities and enhanced porosity. It also had a positive impact on the salt rejection percentage and water permeability via CNM incorporated membranes.

8. By the addition of more CNMs on the membrane surface, the oxygen functional groups present in the membrane matrices are greatly increased. This is the root cause of the increase in surface hydrophilicity.

9. CNMs have properties ranging from large surface-to-area ratio, superior chemical and thermal stability, reduced cost, and fewer negative impacts on the environment. Carbon nanotubes are considered one of the best adsorbents because of their flexible modifying, high sorption capacity, and hydrophobic properties. They exhibit the capacity for dye adsorption from aqueous systems using multi-walled nanotubes (MWCNTs) and single-walled nanotubes (SWCNTs), which have modifiable surfaces. This provided significantly much measurable adsorption sites located on the surfaces of the membranes in which they are generally fabricated.

10. Despite their advantageous properties, CNTs have a considerably lower adsorption rate for toxic heavy metal contaminants. This drawback can be rectified, and their adsorption rate can be increased up by oxidizing the CNTs with potassium permanganate ($KMnO_4$), Nitric acid (HNO_3), and Sodium Hypochlorite (NaOCl). CNTs adsorb the toxic metal ions either through electrostatic attraction or via chemical bonding by the addition and oxidation process. Their incorporation in filtration membranes showed antimicrobial characteristics triggered by oxidative stress in bacteria and degrades them. However, CNTs may not be a viable alternative for activated carbons as wide-spectrum adsorbents.

11. Thin Film Nanocomposite membranes (TFNs) are membranes that focus on fabricating the nanomaterials as mentioned above (from point 10) utilizing doping processes and modification of surfaces into the active layers of the TFC (Thin film-composite) membranes. Unaligned Carbon Nanotubes also found their way in incorporation on Thin Film Composite membranes because of their ability to deteriorate microbial activities. When SWNTs were covalently bonded on the surface of a TFN membrane, it portrayed considerable antimicrobial properties that contributed to anti-biofouling properties.

12. Ultra-long Carbon Nanotubes (CNTs), which are plasma-altered, have been observed to produce an adsorption capacity of more than 400% by weight which is phenomenally high and finds huge application in membrane filtration processes specifically for salt-related and have huge potential to compete against conventional carbon-based wastewater treatment systems.

13. CNMs also face some challenges like some forms of CNM based membranes are fragile and face poor dispersion and distribution and weak interfacial interaction between the different surfaces of the CNM matrix. Therefore, it is important to take these parameters into considerations.

6. Summary

Various industries have been utilizing the membrane filtration separation technique for wastewater treatment over the past decades. The different types of membrane filtration methods such as ultrafiltration (UF), Nanofiltration (NF), reverse osmosis (RO), and so on are considered as a better alternative for the removal of organic as well as inorganic wastes present in the wastewater when compared to the conventional methods. Because of their micro-mesoporous structure and hydrophilicity, the RO membranes have immense potential in increasing the salt rejection percentage and flux rate of water. The heavy metal ions present in wastewater are considered carcinogens which causes toxicity to the environment it is released. These include human health. The studied papers show that the sorption capacity of the conventional membrane filtration techniques had limited effects during the wastewater treatment regarding activation energy bonds, water flux, permeability via membranes, slow kinematics. The rise of nanotechnology and Carbon nanomaterials in modern science has helped enhance the application of membrane filtration for the treatment of wastewater. Carbonaceous nanomaterials combine with the distinctive properties of sp2 hybridization, where carbon molecules bond with the unusual characteristics of physical and chemical parameters at the nanoscale. This surface adsorption of oxidized carbon nanomaterials was highly effective in removing heavy metal ions, radionuclides, and organic components from the liquid wastewater. The accumulation of foulants on the membrane's pores causes membrane fouling which is considered to be a major challenge in this field. CNMs such as CNTs, Graphenes, and fullerenes are embedded in membrane filtration to improve antimicrobial behavior and hence eradicate the effects of membrane fouling. These CNMs based membranes usually undergo surface modifications or functionalization to boost their physical and mechanical properties. Many studies have shown that incorporating CNMs with these membranes has increased factors such as the pore size and hence the surface area that defines how well the contaminants are removed. These results were drawn to a conclusion with the help of SEM images and Raman Spectroscopy. Many researchers have experimented on the Hydrophilicity/hydrophobicity behavior of membranes in order to control membrane fouling. The study shows how incorporating these CNMs has improved the pollutant removal efficiency and antifouling behavior, especially in polymer-host matrices. Fullerenes C60 were embedded with membranes used in wastewater treatment were found to increase reduced flux recovery of organic contaminants. The development of the membranes was responsible due to the addition of fullerene content.

The addition of Fullerenes into PPO membranes has increased the adsorption rate of the contaminants and increased antifouling behavior. Fullerenes are found to be expensive Carbon nanomaterials, and in order to discover their use in this field, they are often embedded with polymer membranes to make them cost-efficient. CNTs are major carbon nanomaterials that can be used as a nanocomposite for effective pollutant removal in wastewater. CNTs can be divided into single or multi, and each has its uses and properties in this field. Characteristics of CNTs and effects of different parameters such as pH of the solution and MWCNT contents were observed. Studies have also shown that along with benefits, CNT has risks in terms of side effects that should be aware of and used in a reduced manner. In the future, the functionalization of CNT will be more constructed based on polymerization and coating/attachment concepts [56]. After years of research, functionalization of CNMs was focused on acid treatment, acid treatment along with hydrophilic groups and *in situ* polymerization; direct functionalization *in situ* polymerization in CNT walls; covalent and non-covalent methods for graphenes. Graphene undergoes surface modification such as chemical oxidation to produce Graphene oxide sheets. These GO sheets are found to perform better when compared to the pristine Graphenes for membrane filtration. Different experiments were done in order to prove the non-toxicity and biocompatibility of CNM based matrices.

However, in the long-run efficiency, it was observed that carbon nanoparticles agglomerates and causes severe problems in the membrane filtration treatment industries in terms of maintenance and smooth functioning. In such a scenario, the respective carbon nanomaterial/membrane needs to be improved and made functional to maintain the degree of dispersion. It is equally important to know the risks of these materials as well. Excessive usage can have adverse effects on both humans and aquatic life. It is essential to communicate both the merits and demerits of these materials. The potential of CNMs in wastewater treatment is immense, and further research and experiments must be done to exploit them to their full potential [87–89].

Membrane separation technology plays a vital role in wastewater treatment where carbon nanomaterials such as multi-walled CNTs/single-walled CNTs, graphene oxides, fullerenes are essential candidates to prevent fouling of membranes due to their unique anti-biofouling properties. They have shown promising results in these carbon nanomaterials being used in wastewater membrane filtration processes because of their marginal toxicity, low cost, and excellent hydrophilicity. Reuse, recycling, and effects in the stability during wastewater treatment of these carbon nanoparticles in membrane filtration are still major affairs faced by the industries and need to be tackled for long-term functionality and efficacy.

7. Conclusion and future directions

One of the main challenges the world is facing is the demand for clean water. Even though the estimated quantity of water on earth is 333 million cubic miles, only 2.5% is considered freshwater, and the rest is salty and polluted. It is crucial to treat wastewater with advanced technologies since conventional methods are infective in removing heavy metals and certain microbes. Owing to the many outstanding properties and characteristics of carbon nanomaterials, it is considered the ideal technology required for wastewater treatment in future membrane separation techniques. Carbon nanomaterials have shown a great development opportunity for more efficient wastewater treatment due to their unique properties like optical, electronic, catalytic properties, large surface areas, and size. However, there are still different challenges associated with toxicity, fouling, etc, which explains the necessity of modification/functionalization of nanomaterials, mainly CNTs. The functionalization of CNTs and GO sheets also generate functionalized groups that help in good dispersion in solvents and polymer matrices. This has led to the improvement of membrane properties and membrane performances. The outstanding performance and progressive development of modified/functionalized carbon nanomaterials-based membranes will arise as the best technology in wastewater treatment and many other fields.

Carbon Nanomaterials (CNMs) production requires precision and more knowledge regarding its surface morphology and properties while functionalizing them. Even though these carbon nanomaterials are considered cost-efficient, developing an efficient carbon nanomembrane is a time-consuming process and requires skilled laborers and staff who have better experience in this field. Scientists and researchers must be aware of the toxicity of certain CNMs and how their concentration can affect the environment in the long term. This also adds up to the cost competition. Thus, further study is necessary for effectively synthesizing these nanomaterials and applying them in membrane separation technology. There is no doubt that the utilization of CNMs in membrane filtration of wastewater treatment has proven to be advantageous and not be cost-competitive, but still, they are not applied to mass processes and are carried out on a smaller scale. Further research is necessary for testing their efficiency for large-scale applications.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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