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Anti-fouling electrospun organic and inorganic nanofiber membranes for wastewater treatment

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ABSTRACT

Researchers favor polymeric membranes for water treatment because of their excellent separation selectivity, high membrane performance, unique interconnected structure and inexpensive cost. Electrospinning, phase inversion, track-etching, slip casting, and film-stretching are some of the methods for fabricating polymeric membranes. Among them, electrospun nanofiber membranes (ENMs) are the most actively explored which address the fouling issues during wastewater treatment. It has a lot of advantages for wastewater treatment application. ENMs can be classified into inorganic and organic, and it is important to determine the type of membrane or polymer that is the most suitable for the application. The choice of membrane depends on many factors, including the composition of the operation parameters, application area and separation goals. Nevertheless, membrane fouling that results in poor rejection efficiency and membrane flux behavior remain as challenges. Therefore, membrane surface modification has been widely embraced to improve the membrane process. Therefore, this review paper aims to provide a detailed analysis of most common used inorganic and organic ENMs in wastewater treatment applications. It also provided insights into the future perspectives for ENMs in water treatment. We hope that this article can provide some guidance for a wide range of application in the membrane industry. This chapter discusses various kinds of vapor deposition processes used to deposit functional coatings onto various substrates and introduces some industrially important wet processes.

1. Introduction

The level of urbanization and industrialization is continuing to the massive rise due to rapid development of the human population, which posing a threat to worldwide safe water scarcity. The availability of fresh water has dramatically declined in recent years (Dharupaneedi et al., 2019). Many impending water problems brought by urban and industrial pollution are definitely acknowledged as causing not just ecological imbalance, but also having a direct impact on human health. Furthermore, environmental pollution constitutes a significant affect to the water ecosystem, such as the direct sewage discharge from mining, industrial and agricultural operations into the environment, which has resulted in serious water quality deterioration (Khan and Malik, 2019; Sikder et al., 2019). According to reports, about 1.2 billion people will be without safe drinking water, and 2.6 billion people will have insufficient amount of water or no sanitation at all (Homaeigohar and Elbahri, 2014). Therefore, the world faces major challenges to meet the growing demand for clean water, and scientists are required to develop highly skilled and environmentally friendly water treatments to solve this critical problems.

It is fortunate that we can make the wastewater potable and usable by employing wastewater treatment technologies that filter and treat the wastewater by removing contaminants such as sewage and chemicals. Three common ways to treat wastewater include physical water treatment, chemical water treatment and biological water treatment. Table 1 lists the benefits and drawbacks of common wastewater treatment technologies. Many new water purification technologies are being developed in order to improve the cost-effectiveness, efficiency, and stability of the treatment process (Chen et al., 2020). Membrane-based separation methods, which have a smaller carbon footprint and can

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operate successfully with high permeability and good fouling resistance, have dominated in water treatment (Fane et al., 2015; Bilad et al., 2018). Both membrane adsorption and filtration are excellent methods for removing undesirable species from contaminated water and preventing dangerous toxins from entering the environment and the human body. Conventional membranes, on the other hand, have several disadvantages, including low flux and a high tendency for fouling, which is dependent on membrane materials, geometrical pore structure, pore size distribution, and the formation of undesirable macro-voids over the thickness of the whole membrane (Abd Halim et al., 2020). These drawbacks can be partially overcome, as nanofiber-based membranes could be an effective replacement for conventional membranes for water. Nanofibrous membranes are substantially more effective for surface adsorption of pollutants from polluted water than standard porous affinity membranes because of their huge surface-to-volume ratio and tunable functionality. Membranes can alternatively be classified as polymeric membranes, mixed-matrix membranes, or ceramic membranes, depending on the materials and processes used to fabricate them (Ismail et al., 2020). Flexible polymeric nanofibrous membranes exhibit homogeneous nanopores and an interconnective porous morphology, as well as a tunable pore size distribution ranging from micrometres to submicrometers, making them ideal for a variety of filtration applications (Wang and Hsiao, 2016). In comparison to the currently used conventional membranes, highly permeable nanofibrous membranes could reduce pressure drop and increase permeate flux for water filtration (Thavasi et al., 2008; Yoon et al., 2008).

Electrospinning is a one-of-a-kind strategy that uses electrostatic forces to generate thin fibers from polymer melts or solutions (Sun et al., 2014). The electrospinning device mainly consists of: a high-voltage power supply, a pipette tip usually called as spinneret and a grounded collector (Xue et al., 2019). The principle of electrospinning eventually simplifies the fiber formation process. It was stated that the polymer droplets outweigh the surface tension when the devoted electric field reaches a critical magnitude to form a jet, and an unstable and fast whipping of the jet happens in the area between the collector and capillary tube, causes the solvent to evaporate and leave the polymer behind (Hou et al., 2018). The following parameters appears to have an impact on the processes; solution parameters, processing parameters and ambient parameters (Hou et al., 2018). Spinning voltage is the most fundamental processing parameter of electrospinning. During spinning process, the thruster drives the spinning solution from the syringe into a high-voltage electric field, which charges the spinning solution and generates a repulsive force to overcome the surface tension of the solution (Mishra et al., 2019). The electrospinning process begins only once a threshold voltage is achieved, producing the essential changes in the solution with the electric field and initiating the formation of fiber (Collins et al., 2008). The form of initial drop depends on the spinning parameters of voltage, viscosity, and feed rate, according to previous study. However, Reneker et al. have shown that electric field has little effect on the fiber diameter (Reneker and Chun, 1996). Zhang et al. hypothesised that greater voltage causes more polymer ejection, resulting in bigger fiber diameter formation (Tlili and Alkanhal, 2019). In addition, the tip-to-collector distance is related to the duration of the jet until it gets to the collector and thus plays a crucial role in shaping the fiber morphology and fiber diameter (Liao et al., 2018). In the electrospinning process, the ideal tip-to-collector distance (TCD) must be long enough for the solvent to evaporate from the electrospun nozzle before the solidified fiber strands are collected on the metal plate. If the TCD is too short, the solvent molecules will not evaporate sufficiently from the nozzle and the fibers may melt. Because it is dependent on the evaporation rate, deposition duration, and whipping or instability interval, the distance might have a significant impact on nanofiber shape (Ahmed et al., 2015). The spinning jet will have more splitting opportunities as the spinning distance increases, and the diameter will be drastically reduced. To summarize, a fundamental distance must be maintained to produce a smooth and uniform electrospun nanofiber membrane, and any evolution on either side of the basic distance will disturb the morphology of the membrane. The diameter and shape of fibers can be affected by environmental factors such as air humidity and temperature (Han et al., 2019). Recently, it has been reported that the surface morphology of electrospun polymer nanofiber membrane can also be affected by different levels of humidity. Low humidity causes the solvent to dry completely and the solvent evaporates faster. In fact, the high humidity of the air means that the diameter of the thick fibers that can be derived from the charge in the beam is neutralized and the stretching force is small (Ibrahim and Klingner, 2020). In terms of temperature, it has two opposing impacts on the average fiber diameter. The evaporation rate of the solvent will increase as the temperature rises, restricting further stretching of the jet. For example, Mituppatham et al. have shown that increased temperature favors finer fiber diameter of polyamide-6 fibers due to the inverse relationship between solution viscosity and temperature (Mit-Uppatham et al., 2004). Since the concentration of the solution was fixed, increasing the solution temperature caused swelling of the polymer molecules, which decreased the degree

Table 1
Benefits and drawbacks of common wastewater treatment technologies.

Technologies	Methods	Benefits	Drawbacks	Reference
Physical methods	Adsorption Air flotation Ion exchange Nanofiltration Ultrafiltration Reverse osmosis membrane Solvent extraction	Easy to use and maintain management, and low environmental and site requirements	Expensive maintenance; typically employed to eliminate undesirable matter, the removal rate need to be enhanced	(Dotto and McKay, 2020; Goh and Ismail, 2018; Heiderscheidt et al., 2020)
Chemical methods	Coagulation Electrolysis Electrodeposition Neutralization precipitation Redox method	Fast and efficient with excellent targeting and removal	Secondary pollutants are resistant to treatment and come at a significant cost	(Miklos et al., 2018; Rodríguez-Chueca et al., 2019; Zhu et al., 2021)
Biological methods	Activated sludge process Anaerobic biological treatment Biofilm method Bioflocculation Biosorption Biotransformation	Organic contaminants are degraded by microorganisms into innocuous compounds at a low cost and with a long-term effect.	Environmental regulations are more stringent; there is a large footprint and a considerable response time.	(Bourgin et al., 2018; Belogolova et al., 2019; Liu et al., 2019)

of chain entanglement and the viscosity of the solution. A decrease in viscosity implies a decrease in viscoelastic force relative to the Coulomb stretching force, ultimately leading to a decrease in the observed fiber diameter. The viscosity of the solution is reduced at low temperatures, leading to the formation of thinner fibers (Acik and Altinkok, 2019). As a result, suitable adjustments to the temperature and humidity of environment are required to achieve optimal electrospinning conditions. Aside from processing and ambient parameters, it has been discovered that solution parameters have an impact on fiber diameter and morphology. The polymer concentration is another important solution parameter since it influences electrospinning fiber production. At low concentrations, chain entanglement renders the jet unstable, and surface tension causes the diameter of the jet to diminish, causing the solution to form beads or beaded fibres (Wang et al., 2019). Electrospinning, on the other hand, is not possible if the solution concentration is too high to generate a liquid jet. As a result, only the optimal concentration range of polymers can be electrospun. In general, uniform fiber diameters can be fabricated by adjusting the concentration of the polymer. Furthermore, several studies have shown that polymer insulator solutions are completely difficult to be electrospun (Zhang et al., 2019). To improve the conductivity of the polymer solution, certain ionic compounds or salt are added (Thomas and Rajiv, 2020). Furthermore, the volatility of the solvent impacts the solidification speed of the jet hence affects the fiber formation (Angel et al., 2020). The jet instantly solidifies due to too much volatile solvent, causing nanofibers to spiral around the needle. The jet will not stretch if the volatility is too low, which is why increasing the electrospinning critical voltage will finally solve these problems. As a result, in some circumstances, mixed solvents are required to get optimum electrospinning materials. Last but not least, the three parameters that affect the morphology of electrospun nanofibers have been summarized in Table 2 and the bead-free nanofibers can be produced by adjusting operation parameters appropriately.

Over the last few years, more and more organic polymers and inorganic materials have been electrospun into nanofibrous membranes as adsorbents for the removal of contaminants from water, thanks to the rapid development and maturation of electrospinning technology (Zhu et al., 2021). Based on their material composition, membranes are classed as organic or inorganic. Synthetic organic or natural polymers are used to produce organic membranes. Synthetic organic polymers are almost solely used in membranes for pressure-driven separation processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis). Polyethylene (PE), polytetrafluorethylene (PTFE), polypropylene, polyamide-imide (PAI), and polyvinylidenedifluoride (PVDF) are examples of synthetic polymers, whereas rubber, wool, and cellulose are examples of natural polymers (Aliyu et al., 2018). Ceramic, carbon, silica, zeolite, different oxides (alumina, titania, zirconia), and metals such as palladium, silver, and their alloys are examples of inorganic membranes (Ezugbe and Rathilal, 2020). The two main types of inorganic membranes are porous inorganic membranes and non-porous inorganic membranes. They are chemically and thermally stable, and they are typically used in industrial applications such as hydrogen separation, ultrafiltration, and microfiltration (Zhang et al., 2012; M. M.-2008 R Mallada 2012).

A new class of nanocomposites materials based on the nanoscale combination of organic and inorganic species has recently gotten increasing attention (Li and Xia, 2004; Shao et al., 2003). These so-called organic–inorganic nanocomposites are mainly organic polymer composites containing inorganic nanoscale building blocks that offer both organic polymer and inorganic material benefits, such as light weight, flexibility, dielectric, ductility, and processability (Wu et al., 2020). Catalytic membranes, ultrafiltration, scratch- and abrasion-resistant hard coatings, nonlinear optical materials, contact lenses, and elastomer and plastic reinforcing are all likely to benefit from these composites (Larsen et al., 2003; Chronakis, 2005). The use of organic-inorganic materials for membranes is appealing because it allows for synergetic effects on permeability and selectivity, as well as new functionalizations and improved mechanical and thermal stability (Nunes, 2008).

One of the most serious issues with membrane-based water treatment systems is fouling. The chemical and physical properties of foulants are discovered to have a substantial impact on fouling behavior (Zularisam et al., 2006). The molecular structure, surface charge, molecule size, and functional groups of the foulant can all be used to classify it. Fouling was generally caused by the adsorption of inorganic precipitates, organic compounds, and biological colloidal particles on the surface of the membrane (Fuwad et al., 2019; Shahid et al., 2017). To be specific, colloidal particles stimulate the production of bio-film on the membrane surface, which is known as biofouling and is a widespread issue in material architecture (Zhao et al., 2010). The fouling process and the features of foulants are directly related to the anaerobic sludge, in addition to the composition and form of waste (Nguyen et al., 2020). According to Eric and his group, a bio-film on the membrane surface can be seen when a thick layer of a brown cake was visible between the membrane leaves (Hoek et al., 2008). This viscous, gel like material can be scraped from the membrane surface using a razor blade. Membrane fouling is a vexing problem that has kept microfiltration from gaining traction (Belfort et al., 1994). Membrane fouling was caused by pore blockage and cake formation (Davis, 2006). A typical microfiltration flux-time curve begins with a rapid initial decline in pure water filtration flux, continues with a long-term progressive flux decrease, and ends with a steady-state flux (Wang and Song, 1999). Membrane fouling caused unwanted flux reduction and increased supererogatory energy consumption, despite the fact that colloids and filter cakes were supposed to be helpful to membrane filtration quality.

Table 2
Parameters affecting the property of ENMs.

Operation parameters	Variable	Effects on ENMs	Reference
Processing parameter	High voltage	Smaller nanofiber diameter	(Zhou et al., 2019; Liu et al., 2019)
	High flow rate	Smaller nanofiber diameter, smaller membrane pores	(Terada et al., 2012)
	Longer tip-to-collector distance (TCD)	Smaller nanofiber diameter, smaller membrane pores	(Jiang et al., 2020; Ahmed et al., 2020)
Solution parameter	High molecular weight of polymer	Uniform nanofiber, excellent membrane performance	(Hou et al., 2020)
	High polymer concentration; high viscosity; high surface tension	Nanofiber diameter increases, larger membrane pores	(Dodero et al., 2020; Amariei et al., 2017)
	High conductivity	Smaller nanofiber diameter, larger membrane pores, membrane fluxdecreases	(Viola et al., 2020)
	Solvent selection	The dielectric constant of the solvent influences the nanofiber diameter and has a good compatibility with polymers	(Lasprilla-Botero et al., 2018)
Ambient parameter	High humidity	Larger nanofiber diameter, larger membrane pores, membrane flux decreases	(Zhang et al., 2020)
	High temperature	Smaller nanofiber diameter, membrane flux increases	(Li and He, 2019)

2. Electrospun nanofiber membrane

Large specific surface area, high porosity, good permeability, adjustable pore shape, and outstanding functional abilities are some of the advantages of electrospun nanofiber membranes (ENMs) (Pereao et al., 2019; Li and Xia, 2003; Cui et al., 2020). ENMs have overcome the drawbacks of high energy consumption and limited separation efficiency, particularly in wastewater treatment (Tian et al., 2017; Ma et al., 2017). In recent years, ENMs has received a lot of attention to act as adsorbents because of its interpenetrating porous structure (70% porosity), adequate specific surface area (approximately 10–20 m^2g^{-1}), and easy scale-up feature (even several meters) (Bhattarai et al., 2004; Li et al., 2001). Furthermore, unlike activated carbon, which has a high internal specific surface, the specific surface of ENMs is almost exclusively generated from the exterior surface, which aids the regeneration process. ENMs were found to be a suitable membrane for obtaining an adsorbent that does not require further shaping and is easy to recycle and replace (Zhao et al., 2016; Fu et al., 2018).

In addition, the application of polymer composite membranes in reactive separation processes has been reported (Kotobuki et al., 2021). Porous polymeric membranes offer many advantages over palladium-based membranes, but their poor thermal and chemical resistance, poor durability, and catalytic deactivation limit their applications (Chee and Ihm, 1986). Organic membranes are also characterized by decomposition at temperatures above 100–300 °C when used as supports for wastewater treatment (Armor, 1989). Due to the limitations associated with organic membranes, inorganic membranes based on zeolitic materials have been developed, making the realization of the catalytic membrane concept increasingly feasible. A general comparison between organic and inorganic membranes is shown in Table 3.

2.1. *Inorganic membrane*

Recently, inorganic membranes have been rapidly developing and innovating in recent years. Chemical resistance, high temperature and wear resistance, high chemical stability, longer lifetime, and autoclavability are all advantages of inorganic membranes (Fard et al., 2018). Inorganic membranes were an excellent contender for water treatment and desalination applications because of all of these outstanding features. Because of its capacity to have both better permeability and selectivity, inorganic membranes, which are classed as metal membranes, ceramic membranes, and carbon membranes, have gotten a lot of interest. Recent progress in inorganic membrane science and technologies have shown great potential in many water treatment applications, such as metallic membrane, ceramic membrane, carbon membrane and zeolite membrane.

2.1.1. *Metallic membrane*

Metallic membrane is a type of porous material having a thin layered, smooth surface with pore sizes as small as 0.01 μm. They appear to be suitable to clarify rainwater because of their high treatment efficiency of microorganisms and particulates (Ree-Ho Kim and Lee, 2010).

2.1.1.1. Silver. Chou et al. demonstrated that a silver-loaded asymmetric cellulose acetate (CA) hollow fiber membrane may inhibit the growth of *Escherichia coli* and *Staphylococcus aureus* for water treatment (Chou et al., 2005). The sponge-like nature of these hollow fibres, as well as their dense inner and outer surfaces, make them a good option for water treatment. Alt et al. also found that polymethylmethacrylate bone loaded with 5–50 nm metallic silver particles had no in vitro cytotoxicity and was highly effective against multi-resistant bacteria (Alt et al., 2004). Ag-PA/PES membranes have good antibacterial and antifouling properties, according to Zhu et al., and it can be employed to kill bacteria in ballast water and saltwater (Zhu and Lua, 2021). Electrostatic forces arise between the Ag^+ ions in the bacterial solution and the negatively charged cytoplasm. The cytoplasm is assumed to have enough electrostatic attraction to rip the cell membrane apart, allowing the cytoplasm to squeeze out of the phospholipid bilayer and into the bacterial solution, killing the bacteria. The zwitterionic of silver nanoparticles combined with surface modification of poly(carboxybetaine acrylate-co-dopamine methacryamide) (PCBDA) copolymers significantly inhibited biofilm growth on polyamide membrane surfaces, indicating a possible pathway to achieve long-term biofouling resistance while maintaining water flux for conventional MF membranes (Wang and Song, 1999). Not only that, the water disinfection performance of PCBDA@AgNPs membrane demonstrated that hazardous bacteria in water could be effectively inactivated in contact with the membrane surface during the filtration process, resulting in pure drinking water.

Table 3
Comparison between inorganic and organic membranes.

Inorganic membrane	Organic membrane
Do not swell	Do swell
Possibility of uniform, molecular sized pores allowing for molecular sieving	Do not have uniform molecular sized pores
Chemically resistant to solvents and low pH	Not chemically stable. Denatured at low pH
Thermally stable	Not thermally stable
High cost of production	Lower cost of production
More brittle	Less brittle

2.1.1.2. Zinc. ZnO membranes have received a lot of interest in recent years because of their unique properties (Lee et al., 2016). They are preferred over freely suspended nanoparticles because they are easier to remove from cleaned water. Hong et al. revealed that the performance of PVDF microfiltration membranes was increased by nanosized ZnO (Hong and He, 2012). PVDF-$ZnO_{0.005}$ had the highest pure water flux (452.1 L m^{-2} h^{-1}), maximum porosity (75.16%), largest pore size (0.08 μm) and lowest surface roughness. Clearly, the improved hydrophilicity and reduced roughness of the composite membrane improved anti-fouling performance during recovered water treatment. The composite membrane surpassed the pure PVDF membrane in terms of breaking strength (2.92 MPa) and elongation at break value during mechanical testing (210.6%). Purushothaman et al. demonstrated that adding ZnO to PEES membrane improves hydrophilicity of the membrane (Purushothaman et al., 2022). The fouling-resistant capability of the membranes was tested using a model foulant, humic acid (HA), and the resulting membrane demonstrated an enhanced anti-fouling irreversible feature with a corresponding flux recovery rate of 92.43%. The rejection rate and flux permeability of HA were 98.03% and 166.73 L m^{-2} h^{-1}, respectively, contributed by the hydrophilic properties of ZnO particles. According to the findings of Taherizadeh, ZnO nanoparticles incorporated with ferric chloride are strong suggestions for enhancing municipal wastewater treatment quality, and the treated wastewater is of extremely high quality and may be used for a number of reasons (Taherizadeh et al., 2021).

2.1.2. *Ceramic membrane*

Ceramic membranes have cemented their place in wastewater treatment systems when the environment is hostile due to their durability and chemical stability. Recent studies have demonstrated that wastewater treatment using membrane bioreactor (MBR) systems with ceramic membranes is very effective and produces high yields (Fard et al., 2018). The MBR is a revolutionary wastewater treatment method that combines an effective membrane separation process with a traditional activated sludge process in which the filtering membrane replaces the secondary clarifier (Zhang et al., 2005). As a result, MBR has solved many of the shortcomings of the activated sludge process, such as low solids separation efficiency, minimal mixed liquor suspended solids (MLSS), and a delayed biological response rate. Silica, alumina, titania, and zirconia are commonly used in the development of ceramic membrane materials.

2.1.2.1. Silica. Silica membranes for water treatment were studied by Yang et al. by recovering ammonia from sewage sludge using a molecular sieve silica membrane in pervaporation (PV) (Yang et al., 2014). Under the experimental conditions used, the eco-nanomagnets silica coated dithiocarbamate showed high efficiency for Hg^{2+} uptake (74%) even at contamination levels as low as 50 μg L^{-1} (Guo et al., 2014). As a result, these materials have a lot of promise for magnetic separation to remove heavy metal ions from polluted water. By functionalizing chitosan–silica hybrid materials with (ethylenediaminetetraacetic acid) EDTA ligands, Repo et al. successfully synthesised a new adsorbent (Repo et al., 2011). The synthesised adsorbents were found to benefit from the advantages of both silica gel (high surface area, porosity, rigid structure) and chitosan (surface functionality). The maximal adsorption capacities of the combined materials for metal ions rejections ranged from 0.25 to 0.63 mmol/g under the analysed experimental conditions.

2.1.2.2. Alumina. Alumina membrane is one of the most prevalent used ceramic membranes for water filtration. Alumina can be used as a substrate, intermediate layer, and active layer in the structure of a ceramic membrane because of its intrinsic properties of high strength, chemical and thermal stability, and ease of production (Hofs et al., 2011). Das et al. showed that the maximum flux obtained for clay-alumina membrane for desalination of brine was 98.66 L/m^2 day at a temperature difference of 60 °C. This result came together with water impurities rejection rate up to 99.96% (Das et al., 2016). Another study revealed that the high separation efficient can be attained with oil rejection at 98% and water flux of 21.62 L/m^2.h by using alumina membrane composite contained surfactant sodium perfluorooctanoate (Raji et al., 2020). The fluorosurfactant significantly plays a role in simultaneously acting as interfacial surface material and improving the dispersion of alumina particles on the alumina composite membrane. He et al. developed an alumina double-layered membranes with increased flux, which have a lot of promise in water UF (He et al., 2020). Sol-gel, dip coating, and sintering procedures were used to tighten the pore size of alumina MF membranes, resulting in alumina UF membranes. The resultant UF membranes had higher hydrophilicity and better particle size retention performance in comparison to the MF membrane. The double-layered UF membrane had superior anti-fouling properties in comparison with the single-layered UF membrane. It could be due to the gradient pore sized structure of the bi-layered membrane, which showed 1.7 times higher flux than the single-layered membrane. This suggests that the profile of a double-layered active layer with gradient pore sizes could improve flux compared to a coating single active layer directly over the MF membrane.

2.1.2.3. Titania. The efficiency of the fabricated electrospun Nano-Palm Frond Titania Fiber (Nano-PFTF) membrane was tested with methylene blue (MB) dye and hexavalent chromium (Cr (VI)) under UV-C and visible light irradiation (Zayadi et al., 2021). Within 120 min, 97.82% rejection percentage of 10 ppm MB was achieved by Nano-PFTF membrane (CA/N-TiO_2) while 99% rejection percentage of 10 ppm Cr (VI) was achieved by Nano-PFTF membrane under visible and UV light irradiation respectively. Based on the results, the Nano-PFTF membrane showed remarkable potential in industrial wastewater treatment and increase the potential usefulness of oil palm frond. Chang et al. showed that nano-titania/polyethersulfone composite membrane demonstrated high rejections ($\geq$ 92.3%) on filtration against BSA aqueous solutions (Chang et al., 2020). This membrane also possessed the highest water flux (181 LMH/bar) and antifouling capability among all prepared membranes; specifically, the flux recovery ratio value remained as high as 94% even after three cycles of filtration-cleaning tests.

2.1.2.4. Zirconia. Because zirconia has been found to be used in ceramic membranes alongside other ceramic membranes made of silica, alumina, and titania, zirconia has been identified as a favoured option in microfiltration for wastewater compared to polymeric membranes due to its chemical stability and ability to endure high temperatures and pressures (Hubadillah et al., 2018). Yang et al. stated that zirconia membranes are one of the most well-known ceramic membranes because of their high chemical resistance, that promotes steam sterilization and cleaning procedures at extremely high and low pH, outstanding pure water permeability, and excellent permeation flux due to their unique surface properties, as well as their high thermal stability (Hubadillah et al., 2018). Nishiyama et al. added zirconia to the silica-based membrane to increase the dissolution of the silica-based membrane in alkaline condition (Nishiyama et al., 2003). Similar procedure used by Kumar et al. which also added zirconia-based materials to the surface of kaolin-based membrane in order to use it in alkaline condition (Kumar et al., 2013). Furthermore, Pauzan et al. conducted another study to attach zirconia to kaolin suspension to overcome the dissolution of kaolin in high alkali solution (Pauzan et al., 2021). Zirconia was used in these studies because zirconia is reported to be resistant in high alkali condition and the results showed that zirconia-kaolin hollow fiber membrane (ZKHFM) had the best mechanical strength (21 MPa) and outstanding membrane flux (~1600 Lm^2/h), indicating that ZKHFM can be used in alkaline solution. Separation of whey components was also done using zirconia-based ceramic composite membranes (Erdem et al., 2006). The obtained membrane improved remarkably high protein content (80%) and low lactose retention (7%), with a permeate flux value of 40 L/m^2h.

2.1.3. Carbon membranes

2.1.3.1. Carbon nanotube. Carbon Nanotube (CNT) has been identified as a potentially transformative technology for addressing existing water scarcity and pollution issues (Goh and Ismail, 2018). CNTs, as members of the fullerene family, are made up of cylindrical graphite sheets that are rolled up into a seamless tube-like structure with a nanometer-scale diameter and a lattice-like appearance. CNTs are categorised as single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), or multiwalled carbon nanotubes (MWCNs) based on the layers of graphene shells (MWCNTs). The atomic arrangement (chirality), morphology (defect development), and nanotube diameter and length all play a role in the properties of nanotubes. CNT has the potential to be a useful absorbent in the removal of heavy metal ions from aqueous solutions (Srivastava, 2013). It was reported that oxidation of CNTs with HNO_3, NaOCl, and $KMnO_4$ can considerably improve the sorption capacity of metal ions. The sorption mechanism appears mainly attributable to chemical interaction between the metal ions and the surface functional groups. Researchers have investigated the adsorption of aqueous cadmium (II) onto customised MWCNT. Yu and colleagues have also investigated about lead sorption and discovered that smaller and rich oxygen content enhance adsorption performance (Yu et al., 2013). Pb(II), Cd(II) and Cr(VI) exhibited superior sorption capacity on oxidized CNTs from water (Robati, 2013). Wei et al. have developed another study to improve the antifouling and separation performance of CNT by coupling CNTs/ceramic flat sheet ultrafiltration membrane with electro-assistance via crosslinking technique (Wei et al., 2021). The resulting membrane features a good permeability 1.8 times higher than that of the membrane without electro-assistance. Furthermore, the electro-assisted membrane filtration process showed 70% reduction in energy consumption compared with the filtration process of the commercial membrane. CNTs have also been shown to have successful desorption of divalent metal ions while simultaneously having better sorption ability, which helps to reduce pollution in the environment (Thomas and Rajiv, 2020; Rao et al., 2007).

2.1.3.2. Graphene. Graphene is a two-dimensional material that contains carbon atoms in the sp^2 hybrid orbitals, has high heat conductivity and stiffness, and can reconcile the brittleness and ductility qualities (Jiang et al., 2016). Due to its extraordinarily large specific surface area and ease of broad functionalization, graphene has been incorporated into a number of composite materials, providing ample 'anchoring' sites for various functional nanoparticles (Geim and Novoselov, 2009). Membrane strength and desalination performance can be improved with graphene-containing polymer composites. GO membranes with weak and stable interactions (hydrophobic or π–π interactions) may not be sturdy enough to endure actual water filtration process (Dong et al., 2020). As a result, changing the membrane spacing and surface functional groups can improve the performance of GO-based membranes. In addition, Liu et al. developed a novel composite chitosan-graphene oxide (CS-GO) membrane with tunable characteristics with a simple cross-linking process at ambient temperature, which shows great promise for water treatment applications (Liu et al., 2021). The permeability and separation performance of the CS-GO composite membranes were found to be influenced by increased interlayer spacing. This is due to the fact that CS molecules increased the binding force between GO nanosheets by providing hydrogen bonds, electrostatic interactions, and chemical bonds such as C—OH and C—N. The results show that CS-GO membranes have excellent separation performance for bovine serum albumin (BSA), sodium alginate (SA), and humic acid (HA) was very good (>95% rejection). Because porous reduced graphene oxide (PRGO), which is generated by perforating graphene following reduction, may overcome the problem of GO aggregation while preserving flow and retention, PRGO has been applied to dye removal, desalination, and other disciplines (Sheath and Majumder, 2016; a K et al., 2016). To develop a composite membrane with significantly enhanced flow, Zhu et al. employed poly (sodium-p-styrenesulfonate) (PSS) and modified halloysite nanotubes (HNTs) intercalated PRGO (Zhu et al., 2017). The interlayer spacing of PRGO rises after intercalation, and the dye removal rate exceeds 97%. Monovalent and divalent ions are removed at a rate of less than 10%. As a result, the composite membranes can be used to ease the color separation from salt in mixed solutions.

2.1.3.3. Zeolite membranes. Zeolites are aluminosilicates that are porous and have a well-defined molecular channel structure. They can tolerate a variety of monovalent and divalent cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and so interchange easily in a contact solution (Goh and Ismail, 2018). Both gas and liquid processes have shown interest in zeolites as potential membrane materials. Because of their unique molecular sieving properties, which allow them to precisely segregate molecules based on the size exclusion ability offered by controlled pore channel sizes. Zeolite membranes have various distinguishing characteristics that typical polymeric membranes lack. Thermal and chemical stability, adjustable pore sizes, and reduced fouling are just a few of the benefits (Goh and Ismail, 2018). The addition of inorganic materials to the active layer has been shown to be capable of breaking the trade-off phenomenon during the separation process based on their excellent hydrophilicity and the sieving effect (Zhao and Liu, 2019). As a result, zeolite is the optimum membrane material for using the FO method to remove heavy metals. This inorganic substance has the ability to adsorb heavy metals and can be shaped into a thin layer membrane. The inclusion of porous and hydrophilic zeolite might significantly improve the support qualities, resulting in increased water permeability (Ding et al., 2017). By adding NaY zeolite nanoparticles in the polyamide rejection layer, Ma and colleagues investigated the effect of zeolite on FO performance. The addition of zeolite to the polyamide layer enhanced the water permeability of the membrane (Ma et al., 2012). Table 4 summarizes the advantages and disadvantages of inorganic membranes as discussed earlier.

2.2. *Organic membrane*

2.2.1. *Chitosan*

Chitosan is an example of natural and biodegradable polysaccharides. Physical and chemical properties of chitosan include hydrophilic, bioadhesive, high crystallinity, antimicrobial, biocompatibility, good chelating and complexing agent, and good ionic conductivity (Silva et al., 2021). However, the use of chitosan directly (as raw materials itself) to prepare electrospun membranes is still a challenge as chitosan particles have small surface area and weak mechanical strength thus limited chitosan application especially in metal adsorption (Cui et al., 2020; Tu et al., 2017). Shi et al. reported the fabrication of antibacterial hydrogel coating from alkynyl chitosan using electrophoretic co-deposition method. The alkynyl chitosan was prepared by reacting chitosan with 3-bromopropyne. The hydrogel was shown to have better antibacterial activity against E. coli and S. aureus than pure chitosan assessed (Ding et al., 2013). Deng et al. reported the fabrication of chitosan-rectorite nanospheres immobilized on polystyrene (PS) fibrous mats for copper ions adsorption. The incorporation of rectorite increased the surface area of the composite mats thus increased the uptake capacity of the PS mats for copper ions up to 134 mg/g (Tu et al., 2017). Bumgardner et al. added elastin to chitosan electrospun membranes to improve the mechanical strength and bioactivity of the membranes. The fiber diameters increased as the amount of elastin increased, while the water contact angle decreased upon addition of more elastin showing greater hydrophilicity (Su et al., 2021). Meanwhile, Li et al. prepared chitosan stacking membranes for adsorption of copper ions. The stacking membranes were stabilised by sodium carbonate and the proposed adsorption mechanisms of copper

Table 4
The advantages and disadvantages of inorganic membrane.

Inorganic membrane	Advantages	Disadvantages
Metallic Membrane	• Resistant to high temperature and corrosive environments (van der Bruggen) • High removal rate of microorganisms and particulates (Kim et al., 2005) • Long term durability (Li et al., 2020) • Chemical stability in wide pH (Lee et al., 2008)	• Higher porosity (Li et al., 2020) • Expensive
Ceramic membrane	Thermally stable and resistant to chemicals with long lifespan (Asif and Zhang, 2021) Pore size can be more easily controlled (Mouratib et al., 2020)	• High capital cost (Samaei et al., 2018) • Complicated fabrication and manufacturing processes in forming and sintering (Dong et al., 2022)
Carbon membrane	• Good resistance to high temperature and chemical solvent erosion (Li et al., 2021) • Easy preparation and high degree of cleanliness (Ahmed et al., 2022)	• Only feasible in non-oxidizing condition (Ji and Zhao, 2017) • High capital cost (Lee et al., 2015)
Zeolite membrane	• Extremely uniform pore sizes and unique surface properties (Kazemimoghadam, 2010) • Resist harsh chemical cleaning, high temperature and wear resistance (Fard et al., 2018)	• Has the smallest chemical and thermal resistances (Lin and Duke, 2013) • Not used as substrate generally (He et al., 2019)

ions is due to the presence of large number of amino and hydroxyl groups which can interact with the metal through chelation (Zhang et al., 2019).

2.2.2. Polyacrylonitrile (PAN)

It has been shown that adjusting the pH of the solution can easily influence the adsorption/desorption process based on non-specific electrostatic interaction (Qiu et al., 2014; He et al., 2016). As a result, adding protonable groups to the ENFM scaffold surface, such as nitrogen-containing groups, is thought to be a smart strategy to improve the membrane's adsorption ability for negatively charged Cr(VI) ions. Wang et al. developed a polyacrylonitirile/hyperbranched polyethylenimine (PAN/HPEI) aminated electrospun nanofiber membrane that was used as a permeable reactive barrier material for in-situ Cr(VI) polluted soil remediation (Wang et al., 2021). Because of its amine group-rich membrane surface and interpenetrating porous structure, the as-prepared PAN/HPEI electrospun nanofiber membrane has a remarkable Cr(VI) adsorption capacity (206 mg g^{-1}) and outstanding reusability (>9 cycles).

2.2.3. Poly(vinyl alcohol) (PVA)

Poly(vinyl alcohol) (PVA) is widely reported as heavy metals adsorbent due to the presence of large number of hydroxyl groups in the polymer backbone. The chemical composition also gives the hydrophilic properties to PVA. Tian et al. fabricated crosslinked PVA nanofibers by treating electrospun PVA nanofibers with glutaraldehyde solution to adsorb $Cu^{2+}$and Pb^{2+} ions. The crosslinked PVA nanofibers show enhanced water resistance, mechanical properties and fibers morphology compared to the non-crosslinked nanofibers with decreased adsorption equilibrium time for both metals (Tian et al., 2019). Tian et al. later prepared grafted PVA by incorporating octaamino-silicon sesquisiloxane (octaamino-POSS) to further improved the adsorption efficiency of PVA nanofibers towards metals. The presence of large number of amino groups increased the adsorption capacity of the fibers with significantly improved for adsorption of Cu^{2+}ions. (He et al., 2021) Karim et al. reported the fabrication of composites nanofibers membranes consisting of PVA and chitosan for $Pb^{2+}$and Cd^{2+} ion removal in wastewater. At the optimum conditions, the reported maximum adsorption capacity was 266.12 mg/g (Pb^{2+} ions) and148.79 mg/g (Cd^{2+} ions) (Karim et al., 2019). Other application of PVA-based nanofibers reported include methylene blue dyes removal (Moradi et al., 2019), (Liu et al., 2018) and oily wastewater treatment (for antimicrobial activity) (Kwon et al., 2020).

2.2.4. Polyethersulfone (PES)

The properties of polyethersulfone (PES) include hydrophobic and robust in term of mechanical and thermal properties, thus PES is among the raw material to fabricate ultrafiltration membranes (Gangemi et al., 2019; Pendergast and Hoek, 2011). Several functionalised PES fibers have been reported for removal of common pollutants in wastewater. These include porphyrins functionalised PES mats for removal of toxic compound, para-nitroaniline (Gangemi et al., 2019); positively-charged PES nanofibrous membranes prepared through electrospinning and in-situ cross-linked polymerization of poly ([2-(methacryloyloxy)-ethyl] trimethyl ammonium chloride) in PES solution for removal of bacteria and cationic dyes (Lv et al., 2019); and PES nanofibrous membrane prepared by electrospinning of blended mixture of poly(acrylic acid-co-methyl methacrylate) and PES for removal of methylene blue (Xu et al., 2019).

2.2.5. Poly (vinylidene fluoride) (PVDF)

Poly (vinylidene fluoride) (PVDF) has been reported to produce superhydrophobic membranes due to excellent properties. This include the low surface energy, sound chemical inertness, and robust in term of thermal stability and mechanical strength. Thus, Zhou and Wu reported the fabrication of ultrathin fibrous PVDF-based superhydrophobic membrane by electrospinning for low-cost, high-efficiency oil/water separation. Herein, the properties of the membranes (superhydrophobicity and superoleophility) could be controlled by adjusting the PVDF added in the electrospinning solution (Zhou and Wu, 2015). Alvarez et al. reported the fabrication of porous fibers consisting of polyvinylpyrrolidone (PVP) and poly(vinylidene fluoride) (PVDF). TiO_2 was embedded and immobilised in the fibers to produce photocatalytic mat and have shown to degrade common water pollutants (Lee et al., 2018). Due to the membrane's high surface hydrophobicity and adequate pore diameters, Feng et al. explored chloroform, a VOC that could be eliminated by membrane gas stripping utilizing electro-spun PVDF nanofiber membrane (Feng et al., 2012). Chloroform mass transfer coefficient over the nanofiber membrane was reported to be 2.40×10^{-5} m/s. This value is higher than that found for a hollow fiber module-based membrane air-stripping system. It could be because the nanofiber membrane performs better than the hollow fiber membrane in terms of chloroform mass transfer. It could possibly be attributable to the flat sheet module's lower boundary layer resistances than the hollow fiber module employed in this study.

2.2.6. Polyaniline (PANI)

Polyaniline (PANI) is well known as material for conducting polymer, thus only few has been reported for PANI to be used in wastewater treatment. Advantages of PANI include easy to synthesize, inexpensive starting materials (monomers), properties that are tunable, and robust in term of environmental and thermal stability. (Deshmukh et al., 2017; Arunachalam, 2018) In most fabrication of nanofibrous membranes, PANI was used as coating materials. Dognani et al. reported the fabrication of PANI-coated polyvinylidenefluoride-co-hexafluoropropilene (PVDF-HFP) nanofibrous membranes for removal of toxic chromium (VI) ions. (Dognani et al., 2019;Dognani et al., 2021) PANI coating enhanced the adsorption intake of the membranes up to 15.08 mg/g at pH 4.5 with good reusability (efficiency >70% even after five cycles). (Dognani et al., 2019) Ali et al. fabricated electrospun membranes combining PANI-β-cyclodextrin and cellulose acetate for removal of cationic dyes in water. The PANI-modified cellulose acetate membranes showed good methylene blue removal which was reusable up to 3 cycles with adsorption efficiency >80%. (Ali et al., 2019) In another study of methylene blue removal, Mohammad and Atassi reported the fabrication of PANI-coated electrospun nanofibrous membranes of polylactic acid (PLLA) and polyacrylonitrile (PAN). Herein, the PANI membranes (PLLA-PANI and PAN-PANI) were prepared and their performance were compared with the pure PLLA and PAN membranes. The PANI-coated membranes were found to have higher methylene blue adsorption capacity compared to the pure polymer membranes. (Mohammad and Atassi, 2020) For removal of heavy metals, Mohammad and Atassi fabricated PANI-coated nonofibrous polyacrylonitrile membranes to adsorb lead and chromium (VI) ions. The membranes showed higher lead ions removal (99%) compared to chromium (VI) ions (90%) at 5 mg/L (Mohammad and Atassi, 2021).

2.2.7. Polyvinylpyrrolidone (PVP)

Polyvinylpyrrolidone (PVP) is the most common hydrophilic additive used to improve membrane hydrophilicity among the hydrophilic additives available. It can serve as a pore-forming agent and an antibiofouling agent (Al-Husaini et al., 2021). According to multiple studies, any increase in PVP molecular weight tends to increase membrane pore diameter, resulting in increased water permeability (Chakrabarty et al., 2008; Zhang et al., 2010). Table 5 listed the advantages and disadvantages of organic membrane.

3. Surface modified nanofiber membrane

Electrospun nanofiber membranes made from a single polymer, on the other hand, often exhibited poor separability. To increase membrane separation behavior, raw materials and the electrospun membrane

Table 5
The advantages and disadvantages of organic membrane.

Organic membrane	Advantages	Disadvantages
Chitosan	Biodegradable, hydrophilic, high crystallinity, antimicrobial, biocompatibility, good chelating and complexing agent, and good ionic conductivity.	Small surface area and weak mechanical strength.
Polyacrylonitrile (PAN)	hydrolysis, acids, alkalis, oxidation and organic solvents (Adegbola et al., 2020)	
Poly(vinyl alcohol) (PVA)	Hydrophilic and biocompatible polymers.	High water uptake thus swelling of polymers (depends on the application) (Sonker et al., 2016)
Polyethersulfone (PES)	Thermal and mechanical robust.	Hydrophobic and poor UV light stability (Ran, 2015)
Poly (vinylidene fluoride) (PVDF)	Low surface energy, chemical inertness, durable and robust.	The nanoparticles and PVDF nanofibers have a low bonding strength.
Polyaniline (PANI)	Simple to synthesize, low-cost monomers, tuneable properties, and robust.	Low processing capacity, rigidity, solubility and biodegradability (Chlanda et al., 2018)
Polyvinylpyrrolidone (PVP)	Hydrophilic	

surface are commonly modified (Wang and Hsiao, 2016). This paper provides a review of surface modification of ENMs in water treatment, since current membrane technology research focuses on the modification of membrane materials to achieve the goal of eliminating various pollutants (Bose et al., 2018). Many surface modification approaches have been investigated, with the goal of changing unwanted surface features without compromising the bulk qualities that make polymers appealing for membrane production. Surface modification of membranes is thought to be just as important to the membrane industry as membrane material and process development; surface functionalization has already established itself as a key technology, with the main goals being improved performance (flux and selectivity) through the reduction of unwanted protein fouling (often considered the first step for biofouling).

There are two types of surface modification: chemical and physical. Etching, grit-blasting, and milling are examples of physical modifications that change the surface topography or morphology with little to no chemical change (Qin et al., 2018). The goal of membrane surface modification is to produce a certain chemical and physical environment that gives the membrane advantageous active sites. Chemical adsorption, in contrast to physical adsorption, is built on the foundations of a stable chemical connection between adsorption materials and metal ions or an oxidation–reduction reaction to treat water. As a result, the surface chemical properties of adsorbents are the primary determinants of chemical adsorption processes. By changing the surface of an ENM, effective adsorption materials can be obtained, as for this principle.

To improve overall effectiveness, different modification technologies, including physical and chemical modifications, might be combined (Cheah et al., 2013). Physical surface modification uses physical methods such as physical adsorption or physical coating to impart a roughness or pattern to the surface of materials (Suwaileh et al., 2018). Physical surface modification such as coating, deposition, and electrostatic attraction are commonly used to introduce functional groups or chemicals onto the surface of ENMs. (Xie et al., 2020). For example, Xie et al. coated cellulose hydrogel on stainless mesh to separate oil/water mixtures by gravity (Zhang et al., 2020). Underwater superoleophobicity was shown by the hydrogel covering the mesh uniformly. When separating combinations of water and different oils, the coated mesh demonstrated separation efficiency of over 98.9%, high permeate flux of up to 38,064 Lm^{-2}h^{-1}, and great reusability. A simple polyol-assisted hydrothermal approach can also be used to make a multifunctional hydrophilic nanofiber membrane, which is subsequently coated with a polydopamine (PDA) layer and carbonised in a N_2 atmosphere (Mollahosseini and Rahimpour, 2014). By covering a polysulfone membrane with a TiO2 layer, Mollahosseini and Rahimpour improved its anti-fouling properties (De Villiers et al., 2011). The resultant membrane was smoother and thicker, with a lower fouling tendency when exposed to Bovine serum albumin solution.

Furthermore, researchers are increasingly favouring layer-by-layer (LbL) multilayer assembly of ENMs through electrostatic attraction between materials with opposite charges. Several polyelectrolytes and nanoparticles can be used in LbL assembly to create an ultra-thin multilayer structure with simple processes as well as a very stable coating layer (Saetia et al., 2014). This method uses electrostatic interactions through the surface charge of a polyelectrolyte to adhere photocatalysts to a surface, in which the negatively charged PVDF membrane surface is modified with a cationic polyelectrolyte called PDDA. In addition, it was reported that MWCNTs multilayer porous network with opposite charges were built through vacuum assisted spray to form a highly porous (Guo et al., 2020). In addition to LbL technology, $(TA/JA)_n$/PAN membranes showed good stability throughout a long-term separation process, which might be attributable to hydrogen bonding interactions and covalent reactions between TA and JA in the selective layer (Xu et al., 2017). The interactions and reactions have both been shown to be the driving force behind the LbL process.

Chemical surface modification, in other words, employs specialised chemical reactions. The exposed groups on the surface of the material can react with the target functional groups so that the grafted brushes are attached to the surface of the material (Venault et al., 2014). Unlike the physical method, the chemical method employs chemical processes to chemically attach the polymer brush to the substrate surface. Because chemical bonds are far stronger than intermolecular interactions, a chemically produced grafted layer can adhere to the surface of the membrane more securely. Chemical grafting involves using chemical reactions to join the target functional group with the functional group in the nanofiber. The adsorption or separation capacity of composite ENMs can be greatly boosted due to the dual benefits of the target functional group and the large specific surface area (Venault et al., 2014). The primary goal of surface modification is to increase membrane hydrophilicity, which boosts membrane performance. Hydrophilic polymers including poly(ethylene glycol) methyl ether methacrylate, poly(ethylene glycol) hydroxyethyl methacrylate, poly(2hydroxyethyl methacrylate), poly(acrylic acid), and zwitterionic polyelectrolytes were chemically modified onto membrane surfaces by forming covalent bonds. The findings revealed that hydrophilic membranes generate compact hydrated layers to prevent oil droplets from fouling membrane surfaces and facilitate oil removal during the cleaning process (Cheng et al., 2017; He et al., 2015; Gu et al., 2020). In response to the membrane hydrophility, the graphene oxide quantum dots (GOQDs) were chemically grafted through the dehydration process between carboxyl groups (-COOH) in GOQDs and amino groups ($-NH_2$) in hydrolyzed (3-aminopropyl) triethoxysilane (Wu et al., 2021). As a result, the GOQDs modified ceramic membranes exhibit better water permeability, with the PWF increasing from 1434 to 1827 LMH and the membrane resistance decreasing from $27.15 \times 10^{10}\, m^{-1}$ to $23.20 \times 10^{10}\, m^{-1}$. The surface modified ceramic membranes exhibit outstanding anti-organic fouling qualities, with a significant reduction in irreversible fouling, thanks to the negatively charged and hydrophilic characteristics of GOQDs, as well as the smooth surface. Aside from that, modified sludge-based activated carbon (MSBC) considerably increased its adsorption capacity on humic acids and aromatic proteins, and both NaOH-MSBC and HCl-MSBC were agreeably effective for removing a variety of dissolved organic matter from sewage (Yu et al., 2013). Yu et al. developed a novel hydrophilic PES membrane by grafting SiO_2 nanoparticles modified with N-halamine onto a PES membrane. The hybrid membrane showed good antifouling and antibacterial properties, which could expand the use of PES in water treatment while also making some potential contributions to membrane antifouling (Zhu et al., 2021).

4. Adsorption mechanism of inorganic and organic nanofiber membrane

ENMs are widely used to remove organic and inorganic contaminants such as oil, heavy metal ions, and dyes because of their variable surface morphology, huge specific surface area, and changeable wettability. Adsorption and filtration are the most common approaches for ENMs to remove contaminants from aqueous solutions. In terms of filtration, the surface of ENMs has an interconnected porous structure that effectively promotes separation flow. Meanwhile, by developing unique wettability on the surface of membranes, the anti-fouling and separation effectiveness of the membrane may be effectively increased. The filtering membrane is depicted schematically in Fig. 1A. ENMs are a potential material for adsorbing contaminants from aqueous solutions because of their high specific surface area, porosity, and ease of regeneration. In addition, the layered structure on the fibers offers more adsorption sites for nanoparticles with specific charges and functional groups, improving adsorption speed and capacity. A schematic diagram of an adsorption membrane is shown in Fig. 1B. The adsorption of contaminants on ENMs, whether on functionalized organic ENMs or inorganic ENMs, mainly depends on the interactions between functional groups and the contaminants (ie. heavy metal ions, oil, organic dyes etc.) including electrostatic interaction, coordination chelation and ion exchange (Sun et al., 2012). That is to say, the functional sites inherent or anchored on the fiber surface are the leading characteristics that determine the removal capability of the electrospun membrane. According to the different types of interaction between heavy metal ions and functional groups on the surface of nanofibers, it can be divided into physical adsorption and chemical adsorption.

Physical and chemical adsorption are the key mechanisms for removing metal ions using electrospun membrane technology. Electrostatic or intermolecular forces between the adsorbent and metal ions are the main causes of physical adsorption. The physical adsorption performance is mostly determined by the specific surface area of adsorbent. As a result, numerous studies have loaded physical adsorption materials onto the surface of the electrospun membrane to successfully improve the specific surface area of the adsorption materials. As a result, effective adsorption can be attained.

4.1. Inorganic contaminants

In the last decade, many researchers have focused their work on removing the inorganic pollutants from wastewater using nanofibers fabricated via the electrospinning technique, as shown in Table 6. Guo et al., studies revealed that the ionic state of the hydroxyl and carboxyl function groups on the surface of EDTA-mGO, altered the adsorption process in the electrostatic attraction between metal ions (M^{2+}) and EDTA-mGO. The protonation of functional groups occured at low pH, thus electropositivity of the EDTA-mGO surface would prevent the adsorption of M^{2+} and result in decreased removal effectiveness (Guo et al., 2014; Liu et al., 2017). The functional groups, on the other hand, might be deprotonated as pH increased, resulting in heavy metal ions being drawn to these negatively charged groups due to electrostatic attraction. Furthermore, the π-π electron donor-acceptor (EDA) interaction can influence the adsorption mechanism (Yang et al., 2011). Sulfamethazine adsorption onto modified activated carbon was the focus of a study proposed by Liu et al. The amidogen on sulfamethazine is protonated, and the pH of sulfamethazine is typically 5.0–7.0. The amidogen and sulfonyl of neutral sulfamethazine can attract the electron of the benzene ring, making it a π–π electron acceptor (Ji et al., 2009; Tahvili et al., 2019). The level of graphitization of modified activated carbon was higher, indicating that the graphitic structure of the modified activated carbon can establish more π–π EDA connections between the two materials, according to Raman spectra.

The most typical way for membrane surface modification is to either functionalize the membrane with particular functional groups adsorption materials or to reduce the membrane surface using reducing chemicals. Although those approaches can enhance the specific surface area and the active sites of the membrane, they can cause the adsorption materials to come off and even compromise adsorption effectiveness in some extreme situations or after repeated use. Matter of fact, the problem can be efficiently handled by directly grafting functional groups on the surface of spinning polymers, resulting in high-stability and high-performance adsorption materials. Tahvili et al., presented an iminic modified nanofibrous film (PTSNFM) in aqueous media using a nano Schiff base (S) as ultrasensitive Hg (II) (Hu et al., 2021). The Hg ions were chemically bonded to the PTSNFM surface by chelation with the donor atoms of S immobilised on the surface of the electrospun nanoafibers network, as shown by FTIR and FESEM measurements. Furthermore, Hu et al. found that grafting dialdehyde carboxymethyl cellulose

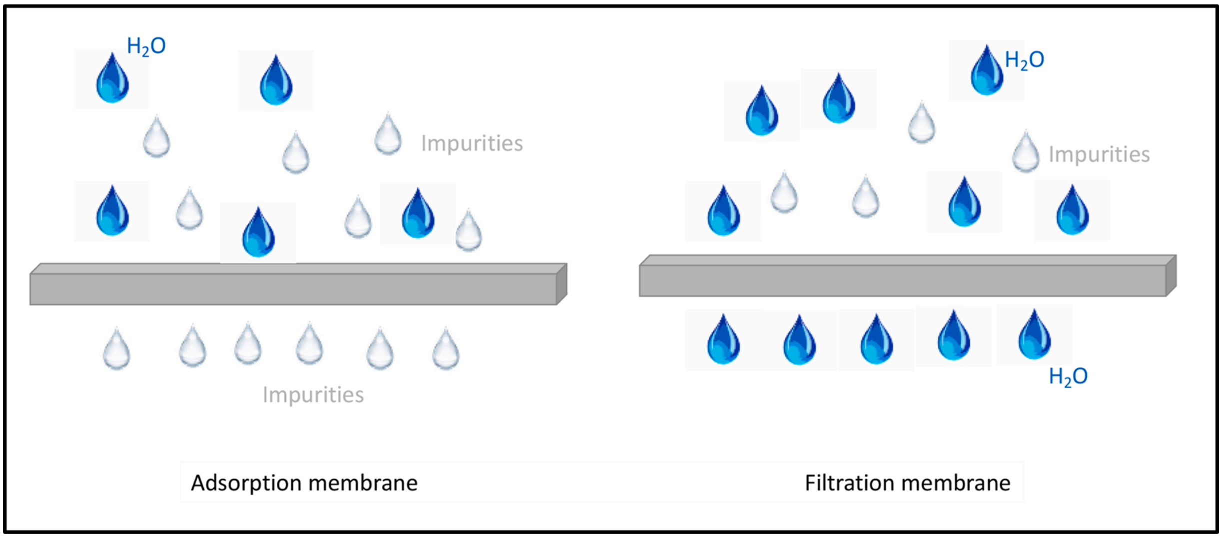

Fig. 1. Schematic diagram of adsorption membrane and filtration membrane (Cui et al., 2020).

(DACMC) on a polyamide membrane increased hydrophilicity and surface smoothness while retaining substantial NaCl (Ren et al., 2021). Aside from that, an anti-biofouling nanofiltration membrane made by in-situ photo-grafting bactericidal and hydrophilic polymers, polyhexamethylene biguanide (PHMB), and polyethylene glycol (PEG), demonstrated high water permeability of 18.6 L m^{-2} h^{-1}bar^{-1}, and even an outstanding divalent ions rejection ability of 91.7% and long-term operation stability (Guo et al., 2014).

4.2. Organic contaminants

Various novel and promising nanofibers and their potential modifications have been assessed for their use in removing different organic contaminants from wastewater, as shown in Table 7. In the removal of dyes from water, common materials such as GO, polydopamine (PDA), β-cyclodextrin (β-CD), and magnetic nanoparticles have been frequently employed (Zhang et al., 2014; Yu et al., 2014; Lee et al., 2014). These adsorbent materials, on the other hand, usually clump together, resulting in less adsorption than desired. Fortunately, as the carrier of these adsorbent materials, ENMs increase the specific surface area of the adsrobent, speeding up and enhancing the efficiency of adsorption. Finally, we believe that electrospinning technique has significant future applications in wastewater filtration and adsorption.

Natural polymers, particularly β-cyclodextrin (β-CD) (Sikder et al., 2019; Wu et al., 2018) and chitosan (CS) (Li et al., 2017; Koushkbaghi et al., 2018; Fan et al., 2019), gotten a lot of interest as electrospinning materials because of their great availability, large scale production, and environmental friendliness (Wu et al., 2018). β-CD is a cyclic oligosaccharide with seven glucose units linked by α -(1,4)-glycosidic linkages that is harmless and stable. It may form noncovalent host–guest inclusion complexes with organic contaminants due to its unique toroid-shaped molecular structure (hydrophobic internal cavity and hydrophilic external surface). Fan et al. studied the adsorption behavior of bisphenol A (BPA) onto electrospun β-CD/CS/PVA nanofiber membrane (Xu et al., 2020). The hydrophobic effect, hydrogen bonding, and host–guest inclusion interaction were shown to be the most important factors in the interaction between BPA and the β -CD/CS/PVA nanofiber membrane. As the temperature rises, the hydrophobic effect becomes stronger, increasing the equilibrium adsorption capacity.

Furthermore, Yin et al. have created a flexible Pd adorned polydopamine-SiO2/PVA electrospun nanofiber membrane for much more effective oil, organic chemical, and dye removal from water (Celebioglu et al., 2017). The Pd nanoparticles were found to be equally dispersed on the surface of the nanofiber membrane, substantially preventing nanoparticle (NP) aggregation and thereby greatly enhancing catalytic activity. In addition, the hydrophilicity of the membrane, together with the micro-nano hierarchical structure generated by Pd NPs and nanofibres, ensures its superior underwater superoleophobic and anti-oil-fouling characteristics, which are particularly favourable to the subsequent oil-water separation.

Table 6
Comparison of maximum adsorption capacity of different functional electrospun nanofibrous membranes on various inorganic contaminants.

Functional ENMs	Inorganic contaminant	Maximum adsorption capacity (mg/g)	Reference
EDTA-mGO	Hg^{2+}	167.8	(Brandes et al., 2019)
	Pb^{2+}	157.9	
	Cd^{2+}	163.6	
	Ni^{2+}	158.5	
CS-PNC	Cd^{2+}	232.55	(Karim et al., 2019)
PVA-Chi	Pb^{2+}	266.1	(Khosravi et al., 2021)
SSC/TiO_2/ZnO	Ni^{2+}	282.3	(Abdel-Mottaleb et al., 2019)
	Cu^{2+}	298.1	
PAN-GO-ZnO	Cr^{6+}	690	(Saeed et al., 2011)
Hydrazine modified PAN	Cu^{2+}	114	(Wu et al., 2010)
	Pb^{2+}	217	
PVA/SiO2-SH	Cu^{2+}	489.12	(Qi et al., 2017)

5. Current challenges and future potentials

The pollution to our water resources by industrial pollutants such as wastewater discharges and oil spills, have caused a substantial damage which affects the balance of the ecological environment and human health. These problems have urged the research in developing a sustainable, effective purification technology. Previously adsorption, filtration, centrifugation and biological treatment were used (Cui et al., 2020). These aforementioned techniques in wastewater treatments did suffer from high energy usage, production of by-products and non-recyclability. Nonetheless, the usage of nanofibers in wastewater treatment have attract a great attention due to its high porosity, large surface area, and uniformity (Zhou and Wu, 2015). The uniformity and interconnectivity of the electrospun nanofiber pores pose an added advantage due to its larger surface area, hence increasing the flux as compared to the traditional membranes, which is favourable to drive the pressure separation. Zhou et al. (Wu et al., 2020), have prepared a superhydrophobic PVDF in separating oil and water. The preparation of the superhydrophobic PVDF has been achieved at a low cost with high efficiency in separating those compounds. With nanotechnology, nanofibers pose a great potential in replacing the conventional purification and filtration process.

A new low carbon footprint technology in wastewater treatment is membrane-bioreactor (Liao et al., 2018). A simple technology of membrane separation combines with biodegradation technology leads to a high capacity of water purification (Gede Wenten et al., 2020; Moradi et al., 2018). Nonetheless, the membrane bioreactor did suffer from some drawbacks where there is a decrease in flux as the filtration time increases due to the interaction of fouling and the surface of the membrane. This drawback was being rectified by the formation of a better performing nanofiber membrane.

Moradi et al. (Bjorge et al., 2009), was working on the fabrication of a composite membrane where fumarate-alumoxane particles were added to the PAN precursor. A simple technology of membrane separation combines with biodegradation technology leads to a high capacity of water purification Bjorge et al. (Fane, 2018) have assessed the performance of commercial membrane and the electrospun nanofiber membrane in membrane-bioreactor. It was suggested that the electrospun membrane have the same performance as the commercial membrane in terms of antifouling ability. Based on these studies, it is crucial to improve the electrospinning technology by modifying the surface of the nanofiber membrane in having a better performance membrane (high stability, specificity and high selectivity) for the membrane-bioreactor. This improvements and further exploration are pivotal to increase competitiveness of electrospun membrane as compared to conventional membranes.

Another application of nanofiber membrane is desalination of seawater. In a nutshell, seawater can be desalinated in producing a fresh water, hence minimizing water shortage (Woo et al., 2017; Zhang et al., 2019) where MD technology is paired with membrane where distillation occurs. The steam pressure in a separation process refers to the difference of the two sides of the membranes. This differences are beneficial in reducing the energy usage as compared to the traditional distillation processes and reverse osmosis technology. It acts as a driving force to transfer the water vapor (at atmospheric pressure and low temperature) from the hydrophobic side of the membrane. The electrospun nanofiber pose a potential in replacing those traditional distillation process in MD application, due to its high porosity and interconnected pores. These structures enhance vapor permeability and increase separation flux. Woo et al. (Zhang et al., 2019) have explored the potential of electrospun nanofiber membranes by introducing GO, CNTs, tetrafluoromethane (CF4) plasma and heat treatment in their distillation performance. It was reported that the fabricated membranes have been able to achieve high separation efficiency, flux and antifouling. These positive outcome is pivotal in seawater desalination.

The high production cost has remained the bottleneck in the commercialization of nanofiber membranes. The complicated pathway in increasing the performance parameters attributed to its low adoption in industrial scale. For example, the unsustainable high price of PAN accounts for about 90% of the CNF market which pose a drawback for its potential in various industrial applications (Scholes, 2020). Moreover, the process of recyclability of hazardous toxic solvent such as dimethylformate is still at its infancy, hence, increasing the total cost of production. This problem needs to be addressed and rectified in producing a large volume of nanofiber membranes with sustainable cost incurred.

Membrane technology, as mentioned by Colin Scholes in 2020 (Scholes et al., 2012), has the potential to be fully utilised in a variety of applications such as gas separation for carbon dioxide in industrial processes. It has also been highlighted that the research in membrane technology must be carried out in pilot plants to ensure the feasibility of the technology for industrial processes. Failure to be implemented in pilot plants will ensure a delay in the development of the technology. There are a few examples of pilot plants that explore the potential of membranes in gas separation technology, such as the Mulgrave, H3, and Valves Point projects.

Interestingly, the CO2CRC Mulgrave capture project based in Australia, was obsessed with separating carbon dioxide from an unshifted air-blown syngas. The objective of this project is to expose several membranes to the syngas in which their performance is being determined. Several membrane contactors have also been used to maximize carbon capture from the modules and solvents via the provided syngas. Several membranes were used for gas separation, including polydimethylsiloxane, polyethylene glycol, and polysulfone, while polypropylene and polydimethylsiloxane were the main membranes used for the contactor (Scholes et al., 2012).

One of the downsides of the three pilot plant projects is that the captured carbon dioxide was not stored because there was no storage facility available. For example, the captured CO_2 from the H3 and Valves Point projects and the Mulgrave project was returned to the flue gas and vented back to the atmosphere, respectively. Looking back at the objectives of the pilot plants, they did manage to capture the carbon dioxide from the gas effluent, which makes the objectives successfully achieved. However, from a wider perspective, it may look like a wasted effort as the CO_2 was captured and then released back into the environment (Scholes et al., 2012). This issue is not only applicable to membrane-operated pilot plants, but it is also a drawback for most of the carbon capture pilot plants. Moving forward, there is a crucial need for the technology to be trialed with the objective of a complete carbon capture and storage process.

6. Conclusions

In this review, we provided an explicit summary about several organic and inorganic membranes that has a plethora of uses in wastewater treatment. Researchers have been drawn to the study and development of ENMs due to their versatility. The electrospinning approach for producing ENMs has emerged as a critical procedure in membrane technology for environmental applications. The electrospinning technology may produce membranes with a high surface area to volume ratio, homogeneous pore size, and high pore interconnectivity, which improves the performance of the nanofibrous membrane. Furthermore, the electrospinning procedure is a dependable method for optimizing membrane structure. The properties of ENMs, such as pore size, hydrophobicity, tensile strength, and mechanical behavior, can also be changed. Properties like as pore size and thickness can be adjusted to increase penetration and water flux. Despite all the benefits, there are still drawbacks, such as fouling phenomenon which is caused by the interaction between the membrane surface and the foulants. To address this issue, significant emphasis has been placed on the surface of the membrane by chemical and physical adsorption to enhance the durability and stability of the membrane. The electrospinning technique has recently emerged as one of the critical processes influencing research and development on water treatment applications. As a result, the electrospinning approach is the most attractive candidate for future membrane fabrication because ENMs, as the next generation of filtration media, have promising qualities for enhanced filtration. Additionally, the advantages and disadvantages of the studied membranes had been analysed carefully to better evaluate the environmental applications of those membranes. Hopefully, the information in this paper will be valuable in further research into membrane technology applications in wastewater treatment. Table 7

Ethics approval and consent to participate

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Author contributions

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Data availability statement

Not Applicable.

Consent for publication

The corresponding authors has read the Springer journal policies on

Table 7
Comparison of maximum adsorption capacity of different functional electrospun nanofibrous membranes on various organic contaminants.

Functional ENMs	Organic contaminant	Maximum adsorption capacity (mg/g)	Reference
Inu-GO	Methylene blue	786	(Zhang et al., 2014)
Fe_3O_4-PDA	Methylene blue Tartrazine	204.1 100	(Yu et al., 2014)
HP–CD/PEG400-modified Fe_3O_4 nanoparticles	Congo red	1895	(Lee et al., 2014)
β-CD/CS/PVA	Bisphenol A	352	(Xu et al., 2020)
Poly-CD	Methylene blue	124	(Mahmoodi et al., 2020)
ZIF-8@Chi/PVA	Malachite green	1000	(Zhao et al., 2021)
Chi/sodium alginate	Acid black-172 Methylene blue	817 1488	(Xiao et al., 2018)

author responsibilities and submits this manuscript in accordance with those policies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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