water

Review

Desalination Pretreatment Technologies: Current Status and Future Developments

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Abstract: Pretreatment of raw feed water is an essential step for proper functioning of a reverse osmosis (RO) desalination plant as it minimizes the risk of membrane fouling. Conventional pretreatment methods have drawbacks, such as the potential of biofouling, chemical consumption, and carryover. Non-conventional membrane-based pretreatment technologies have emerged as promising alternatives. The present review focuses on recent advances in MF, UF, and NF membrane pretreatment techniques that have been shown to be effective in preventing fouling as well as having low energy consumption. This review also highlights the advantages and disadvantages of polymeric and ceramic membranes. Hybrid technologies, which combine the benefits of conventional and non-conventional methods or different membranes, are also discussed as a potential solution for effective pretreatment. The literature that has been analyzed reveals the challenges associated with RO pretreatment, including the high cost of conventional pretreatment systems, the difficulty of controlling biofouling, and the production of large volumes of wastewater. To address these challenges, sustainable hybrid strategies for ceramic membrane-based systems in RO pretreatment are proposed. These strategies include a thorough assessment of the source water, removal of a wide range of impurities, and a combination of methods such as adsorption and carbon dioxide with a low amount of antiscalants. Furthermore, the suggestion of incorporating renewable energy sources such as solar or wind power can help reduce the environmental impact of the system. A pilot study is also recommended to overcome the difficulties in scaling ceramic systems from laboratory to industrial scale. The review also emphasizes the importance of conducting an effective assessment to suggest a treatment for the brine if needed before being discharged to the environment. By following this framework, sustainable, energy-efficient, and effective solutions can be recommended for pretreatment in desalination systems, which can have significant implications for water scarcity and environmental sustainability.

Keywords: RO pretreatment; conventional technologies; polymeric membrane; ceramic membrane; hybrid systems

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1. Introduction

Water scarcity is a significant international issue that has been gaining attention for several decades [1]. Population growth, changes in consumption patterns, climate change, uneven distribution of water resources, and the increase in individual water demands are all contributing to the problem [2–7]. Many countries are currently suffering from unavailability, low quality, and inaccessibility of water resources [3]. The World Health Organization (WHO) predicts that by 2025, half of the world's population will suffer from water scarcity [8]. According to the United Nations University—Institute for Water, Environment, and Health (UNU-INWEH), by 2050, global water demand is expected to increase by 400% for manufacturing and 130% for household use [9].

In Europe, many regions are facing water scarcity with a minimum of 11% of the population affected [10]. In India, around 600 million people are suffering from extreme and high water stress, with 70% of available water being contaminated [6,11]. In the Middle East, countries are facing an exacerbated issue where 60% of the population is exposed to high water stress [12]. The availability of water per capita in the affected regions has reduced to 170 m^3 per year, which is significantly lower than the internationally recognized standard of 1000 m^3 per year for water scarcity criteria [13,14].

Among these Middle Eastern countries, the United Arab Emirates (UAE) has a severe water scarcity challenge due to low freshwater supplies and high levels of groundwater depletion and salinity [15,16]. Additionally, the cost of producing drinking water is high, and the country has a high per capita water consumption rate. These factors contribute to the ongoing water challenges faced by the UAE [16–19]. To overcome this water scarcity and high water demand, water desalination was inevitably adopted as one of the best choices worldwide [20]. Desalination is the process of removing dissolved solids from saline water to produce freshwater suitable for human consumption, while the remaining highly saline product is called desalination brine [21,22]. According to the Food and Agricultural Organization (FAO), saline water is classified into six categories, as summarized in Table 1 [23], where seawater has the highest concentration of salts, ranging from 35,000 to more than 45,000 parts per million (ppm), and brackish groundwater has a lower concentration, ranging from 15,000 ppm to 35,000 ppm in very saline aquifers [20,23,24]. Desalination of seawater and brackish water is considered highly viable to meet the world's needs; the desalination of seawater is the dominant method, accounting for around 60% of water desalination globally, followed by brackish water at around 20% [25]. As seawater desalination is the dominant method, Table 2 presents the salinity and other general characteristics of the UAE's seawater based on the analysis of the Ministry of Climate Change and Environment [26].

Table 1. Classification of saline waters according to FAO, "Reprinted/adapted with permission from Ref. [23], The use of saline waters for crop production, 1992, FAO".

Water Classes	Salt Concentration (mg/L)	Type of Water
Non-Saline	<500	Drinking and irrigation water
Slightly Saline	500–1500	Irrigation water
Moderately Saline	1500–7000	Primary drainage water and groundwater
Highly Saline	7000–15,000	Secondary drainage water and groundwater
Very Highly Saline	15,000–35,000	Highly saline groundwater and seawater
Brine	>45,000	Seawater

Table 2. General characterization of seawater in the UAE [26].

Parameter	Value
Turbidity (NTU)	<75
Temperature (°C)	19–35
Salinity (mg/L)	>45,000
pH	6.5–9.0

Desalination is being rapidly adopted as a solution to global water scarcity and high water demand, as conventional water sources are insufficient to meet the world's needs [27]. The desalination market is growing exponentially, with 15,906 desalination plants currently in use worldwide [25], producing around 90 million m^3 per day of desalinated water [27–31]. More than half of the world's desalination plants (58%) are concentrated in the Middle East and North Africa [31,32]. The UAE is ranked as the second-highest desalinated water producer in the world after Saudi Arabia [18,33], accounting for 10.1% of the world's desalinated water [27]. In the UAE, over 40% of the freshwater supply is obtained from desalination plants, with 1452 million imperial gallons per day of desalinated water being produced [33,34].

Thermal desalination is the first technology used for desalination and is based on evaporation and condensation processes [35]. Multi-stage flash (MSF) and multi-effect distillation (MED) are common methods within thermal desalination [21,22,36]. Membrane-based technologies, such as reverse osmosis (RO), have also emerged and developed significantly in recent years [35]. RO technology is a pressure-driven membrane that removes dissolved salts and ionic solids [32,37,38]. It has become the most widely used technology in the desalination field due to its improvements in membrane technology and energy consumption [39–41]. About 70% of the total number of desalination plants worldwide are using RO technology, as depicted in Figure 1 [27,42].

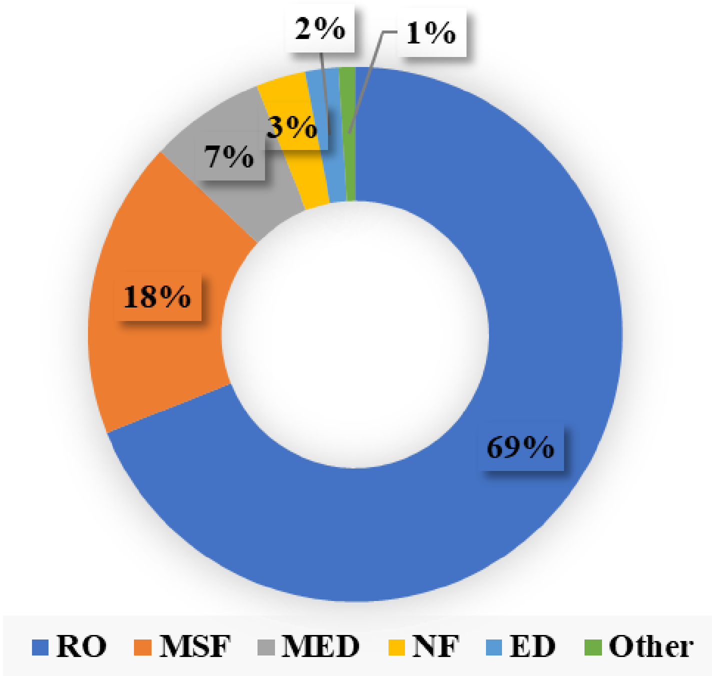

Figure 1. Percentage of desalination facilities worldwide categorized based on different technologies: reverse osmosis (RO); multi-stage flash (MSF); multi-effect distillation (MED); nanofiltration (NF); and electrodialysis (ED) [27,42].

Even though RO membranes have high water permeability and salt rejection compared with other technologies [43], they still have shortcomings, i.e., membrane fouling sensitivity [43]. Fouling occurs when particles cover and block the pores of the membrane, leading to higher resistance and pressure [44–47]. This is particularly problematic in seawater desalination due to the variation in water quality and the presence of microorganisms and suspended and dissolved matter, including sand and oil [48], which accumulate on the RO membrane and affect its performance efficiency [45,49]. To prevent and mitigate damage to RO membranes, comprehensive and integrated pretreatment technologies are needed to maintain successful and long-term membrane performance [45,50,51].

Pretreatment of feed water has shown a dramatical impact on the efficiency and performance of RO membranes [52]. It helps in providing high-quality feed water with lower levels of total dissolved solids (TDS) and organic and inorganic matter, which extends the lifespan of the membranes [53–55]. According to the US-EPA, feed-water quality parameters must be within specific standard limits that suit the RO membranes for a longer lifespan. These standard limits depend on the origin and quality of the produced desalinated water and the membrane type that will be installed in the desalination plants [56]. In general, the recommended RO feed-water parameters must not exceed 3, 0.5 NTU, 2 mg/L, 0.1 mg/L, and 0.1 mg/L of silt density index (SDI15), turbidity, total organic carbon (TOC), free chlorine, and oil and grease, respectively [57–59]. Therefore, pretreatment technologies are often coupled with RO desalination plants on a large scale to support the operation of the membranes and adjust the feed-water quality within the standard limits [55].

Due to the importance of pretreatment technologies for RO desalination plants, extensive research has been conducted, resulting in a dramatic increase in publications from 1997 until the present, as illustrated in Figure 2. The main goal of these studies is to better understand and improve these technologies, as well as to identify the best design for implementation in the desalination industry. The Figure demonstrates the large number of publications that have focused on this topic where a dramatical increase has been noticed, reaching approximately 1029 articles in 2022 and continuing to increase in the current year.

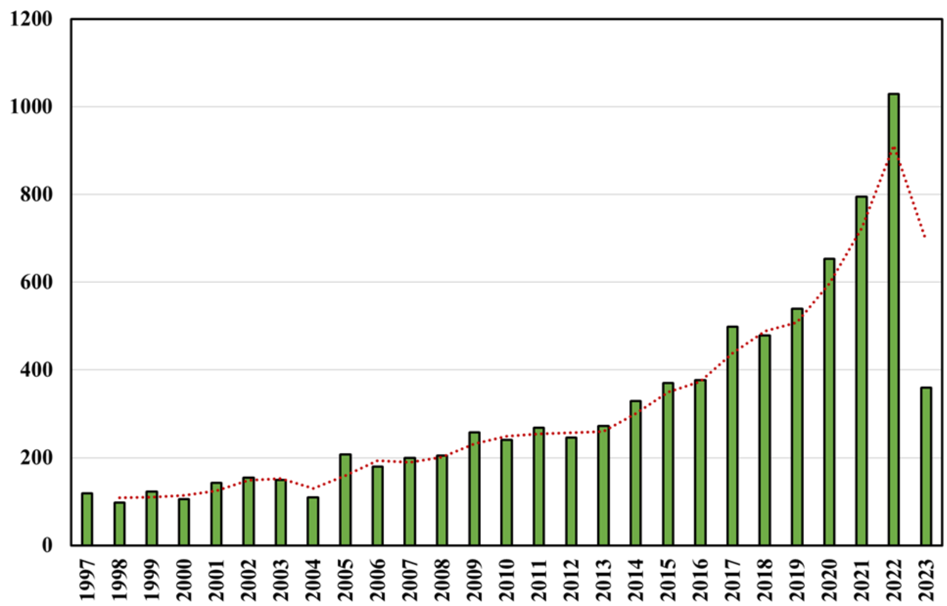

Figure 2. Academic literature database from 1997 to March 2023 extracted from Science Direct with the keyword "Pretreatment for Desalination".

Therefore, due to the significance of this topic, a comprehensive review has been conducted on the current and future state of pretreatment technologies in the RO desalination field. This review paper aims to provide an in-depth examination of the various aspects of membrane fouling in RO systems, including the different fouling indices used to measure and understand the phenomenon. Additionally, the various RO pretreatment technologies available, including conventional technologies, non-conventional technologies, as well as hybrid technologies that combine the strengths of multiple processes for effective pretreatment, are elaborated. The goal is to present a thorough overview of the current state of research in this field, highlighting the latest developments and identifying areas for future research. More emphasis is placed on developing a sustainable and cost-effective hybrid pretreatment technology, which is an aspect that has been identified as crucial in previous research. Specifically, a sustainable framework for ceramic membrane-based hybrid systems in RO pretreatment is suggested, considering the specific water quality and treatment goals.

2. Membrane Fouling

Membrane fouling is the buildup of material that is unwanted onto the surface of a membrane, which can reduce its efficiency and effectiveness. There are several types of fouling, including biological, colloidal, organic, mineral, and oxidant fouling. Physical and chemical cleaning methods can remove reversible fouling, but frequent cleaning can damage the membrane and shorten its lifespan. Some types of organic and biological fouling can cause severe irreversible fouling and are not easily removed by physical or chemical cleaning methods [60]. Table 3 lists the major foulants that can impact the performance of SWRO systems, along with their causes and the damages they can inflict.

Table 3. Major foulants impacting the performance of SWRO systems [60,61].

Fouling	Causes	Damages
Biological fouling (Biofouling)	Microorganisms, bacteria (Pseudomonas, Bacillus), viruses	Growth of biological creatures on the membrane's surface, causing: – Irreversible fouling, – Inactivation of catalytic surfaces of the membrane, – Flux decline, – Increase in normalized pressure drops (during RO operation).
Organic fouling	Humic and fulvic acids, biopolymers, natural organic matter	– Deposition of organic particles on the membrane's surface, causing a decrease in the membrane performance, – When oxidized with oxidants (such as chlorine), some dissolved organic compounds in the raw water could serve as a nutrient to bacteria and microorganisms.
Particle fouling	Clay, sand: suspended solids, turbidity	Decline of membrane productivity over time.
Colloidal fouling	Inorganic and organic compounds, micro-algae	Loss of membrane permeate flux.
Inorganic fouling/Scaling	– Multivalent cations: iron, manganese, calcium, magnesium, barium, strontium, copper, zinc, and aluminum. – Multivalent anions: sulfate, carbonate, and phosphate.	Accumulation of inorganic precipitates from the feed stream on the surface of the membrane or within the pore structure, resulting in: – Membrane pore blockage. – Increase in chemical cost of the RO plant. – Increases the risks of physical damage of the membrane. – Flux decline (it could be more significant than organic or colloidal fouling).
Oxidant fouling	Pretreatment chemicals: Chlorine, Ozone …	– They might aggravate fouling problems in the RO membrane. – Membrane damage.

3. RO Membrane Fouling Indices

In this section, the different fouling indices that are commonly used to assess RO membrane systems' performance will be discussed. Specifically, the Silt Density Index

(SDI), the Biofouling Index, and the Modified Fouling Index (MFI) will be covered. Each of these indices provides a unique insight into different aspects of fouling and can be used to identify and troubleshoot issues in RO systems.

3.1. Silt Density Index (SDI)

SDI is a parameter used to measure the quality and the fouling capacity of an RO system and its test is applied worldwide as a routine step for operators due to its cheapness and simplicity [46,62]. Its measurement is based on testing the flow rate of a specific volume of feed water by filtering it through a 0.45 µm microfiltration (MF) membrane at 206.8 kPa (30 psi) water pressure [63]. SDI_5, SDI_{10}, and SDI_{15} are the most measured parameters in which the difference is in the flow time. The equation below represents the way to measure this parameter, which illustrates the percentage drop in the feed-water flow rate through the membrane over a period of time [64]:

$$SDI_T = \frac{1 - (t_1/t_2)}{T} \times 100 \quad (1)$$

where t_1 and t_2 represent the filtration time in seconds to collect a fixed volume of permeate while T demonstrates the total flow time in minutes [65]. The SDI value can illustrate the efficiency of the MF pretreatment process and predict the fouling of the RO membrane. For instance, when SDI_{15} is >5, this will not be accepted, and additional feed-water pretreatment is required; between 3 and 5, this indicates that fouling is susceptible and frequent cleaning is needed for the membrane; from 1 to 3, the membrane requires cleaning after several months; while <1 means that the membrane will operate for many years without fouling [66,67]. However, this index can only illustrate and measure the potential of fouling of the feed water caused by particulates and colloids without measuring organic and biological fouling [68].

3.2. Biofouling Index

Microorganisms are present in and colonize all water systems, and their presence can lead to a permeate flux reduction and increase in the operational costs of desalination plants since they cause biological fouling of the RO membranes [69]. It was estimated that 70% of the seawater desalination plants in the Middle East suffer from biofouling issues [70]. Biological fouling in the desalination process occurs due to the production of extracellular polymeric substances (EPS) by microorganisms [71]. These EPS tend to accumulate and adhere on the membranes' surfaces, leading to the formation of biofilms [68,72]. As a result, a serious problem will occur in the operation of desalination plants, including an increase in pressure, called transmembrane pressure (TMP) [73].

Therefore, monitoring the biological fouling potential of the RO membrane through pretreatments is crucial. Consequently, to measure this biological fouling, various methods were developed, such as bacterial regrowth potential (BRP) [74], membrane biofilm formation rate (mBFR) [75], and bacterial growth potential (BGP) for seawater RO (SWRO) systems [76]. For instance, mBFR was developed to examine the formation rate of the biofilm on the membrane surface by measuring the increase in the adenosine triphosphate (ATP) rate. In this way, biofouling potential can be monitored and mitigated [44].

3.3. Modified Fouling Index (MFI)

The MFI0.45 index test, as with the SDI index, was developed based on the filtration of feed water using an MF membrane with 0.45 µm pore size at a constant pressure of 30 psi [77,78]. Due to the low accuracy of the SDI and its deficiency in reflecting fouling mechanisms, the MFI0.45 index test was developed and adopted in the American Standard Testing and Methods (ASTM) [79,80]. MFI addresses the cake formation theory (retaining of substances) and takes into consideration the operating conditions, including the membrane area, pressure, and viscosity [79]. In addition, it has the capability to measure the fouling of the RO membrane in high and low-turbidity waters [81]. However, recent studies have addressed the MFI index using tighter membranes, such as ultrafiltration (UF) and nanofiltration (NF) to mitigate the fouling from small-sized colloids with a constant pressure of 40 psi [78,82,83]. In all types of filtration, measurement is achieved by measuring the rate at which the cake will be formed on the membrane surface at three stages; pore blocking, cake filtration, and cake compression [79]. This index is measured using the following equations:

$$\frac{t}{V} = \frac{\mu \cdot R_m}{\Delta p \cdot A} + \frac{\mu \cdot \alpha \cdot C_b}{2 \cdot \Delta P \cdot A^2} \cdot V \tag{2}$$

$$I = \alpha \cdot C_b \tag{3}$$

$$MFI_{0.45} = \frac{\mu \cdot I}{2 \cdot \Delta P \cdot A^2} \tag{4}$$

where 0.45 is the membrane pore size (μm), V is the volume (L), t is the filtration time (s), Δp is the applied pressure (Pa), μ is the water viscosity (Pa·s), R_m is the resistance of the membrane (m^{-1}), α is the specific deposited cake's resistance ($m \cdot kg^{-1}$), C_b is the particles' concentration in the feed water ($kg \cdot m^3$), A is the area of the membrane (m^2), and I is the resistivity (m^{-2}) [84]. When the MFI is <1, this can indicate that the colloids are sufficiently controlled in the feed water [85].

4. RO Pretreatment Technologies

Feed-water pretreatment is a crucial factor for RO systems. It helps to modify the raw water characteristics and thus improves the overall operational performance, for example, by minimizing chemical cleaning and membrane replacement and increasing plant lifetime. Various conventional and non-conventional pretreatment strategies have been suggested. This section provides an overview of these technologies.

4.1. Conventional Pretreatment Technologies

Classic conventional pretreatment processes might consist of all the following treatment strategies or just some of them, including pre-screening, chlorination, coagulation and flocculation, sedimentation/dissolved air flotation (DAF), granular media filtration, ozonation, and scale inhibitors. An illustration of conventional pretreatment technologies illustrations is presented in Figure 3, including screening, chlorination, coagulation–flocculation, sedimentation, multimedia filtration (MMF), cartridge filtration, anti-scaling addition, and dichlorination using sodium bisulfite (SMBS).

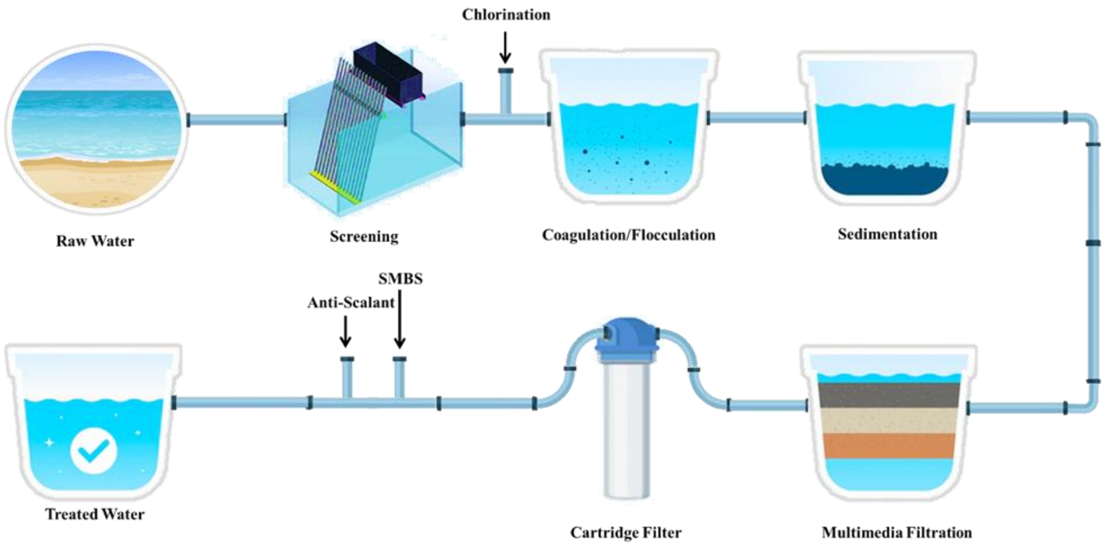

Figure 3. Simplified illustration of a conventional pretreatment system.

4.1.1. Pre-Screening

The pre-screening process is the first and most basic important step in the RO water treatment process. The purpose of this pretreatment is to remove large and non-soluble solids to reduce the pollutant load and protect all the subsequent treatment steps. Large particles in the raw water of the treatment plant, including plants, fish, seashells, and microorganisms, could be attached to and grow in the water intake pipelines. Therefore, prior to further processing, the raw water should be screened to remove these materials. A simple mesh inclined at a specific angle serves as a screening process to block the intrusion of marine creatures at the intake grids. Then, a mechanical rake attached to the screens removes them from the mesh [63]. Although different types of screens have been suggested in the literature, the appropriate screen should be selected based on the characteristics of the feed water, site requirements, and hydraulic calculations [86]. Factors such as the size of the screening openings and mechanical properties are commonly used to classify the screens. The screening process in desalination treatment plants often employs screens with openings between 120 and 500 μm. Previous studies have shown that screens with openings between 400 to 500 μm perform well in treating fresh surface source water and provide an effective screening solution prior to membrane filtration [57]. However other studies have reported that screens with openings larger than 120 μm may not be effective for the seawater source. Seawater contains barnacle larvae, which can pass through larger openings and damage the pretreatment process as they can withstand chlorination. Therefore, Murkute et al. have revealed that the use of a finer screen filter (100 μm) is necessary for removing barnacle larvae if MF or UF pretreatment is selected for open seawater intakes [87]. It is worth mentioning that granular media filtration pretreatment systems do not require micro-screens since they can remove barnacles at all stages of development. Therefore, they are adequately protected by traveling screens of 3 to 10 mm. When comparing conventional granular media filtration and membrane filtration pretreatment, it is important to consider the cost of micro-screening systems [57].

4.1.2. Chlorination

Conventional water disinfection is often achieved through chlorination to inhibit biological growth that leads to filter and membrane biofouling. Pre-chlorination consists of adding chlorine to the raw water after it has been screened [49]. Chlorine is a commonly used disinfectant in water desalination because it is readily available, easy to apply, and can effectively deactivate many microorganisms. As an oxidant, it destroys cellular, microbiological, and internal components of microorganisms [88]. Three specific mechanisms have been proposed for chlorine-based bacterial inactivation [89]. For example, Fiedler et al. found that chlorinated effluents significantly reduced membrane fouling due to the partial oxidation and the change in the organic matter's properties, which affects its reactivity with membranes [90]. There are several chemicals that can be used in pre-chlorination. Chlorine gas and sodium hypochlorite are perhaps the most commonly used forms of chlorine that form hypochlorous acids in water. Gaseous chlorine is more cost-effective than hypochlorite. However, since it is more dangerous than hypochlorite, it needs careful handling [91]. Shock chlorination and continuous chlorination could be used in water pretreatment. It has been shown that shock chlorination was better than continuous chlorination since long-term exposure to chlorine could destabilize natural organic matter such as natural colloidal polymers, which further promotes more coagulation of these compounds [92]. In addition, continuous chlorination increased the concentration of some foulants such as polysaccharides and irritated sea organisms [49]. However, it is worth noting that the application mode (continuous or shock), as well as the optimal chlorine dosage, are mainly site-specific, depending on different factors such as environmental conditions, local regulations, permeate quality, and the existence of other interfering substances such as transition metals [89]. Although chlorination is the most effective method for disinfection and odor control, chlorination has some serious drawbacks. Carcinogenic by-products such as trihalomethanes and haloacetic acids could be formed from its reaction with organics in water [60]. In addition, polyamide membranes' sensitivity to chlorine oxidation has led the membrane to be susceptible to biofouling after dechlorination using sodium metabisulfite, as the residual chlorine has to be eliminated prior to the RO membranes to prevent their damage [89]. These have intensified the search for chemical alternatives. Chloramine, peroxide, and chlorine dioxide have been proposed as oxidizing chemicals, while isothiazolones and 2,2-di-bromo-3-nitrioproprionamide have been suggested as non-oxidizing chemical alternatives [93]. Nevertheless, these chemicals are not as effective as chlorine and lack many characteristics of the ideal disinfectant given by Bates [89]. Membrane modification and the development of anti-fouling membranes are promising techniques to mitigate biofouling post-dichlorination and/or increase chlorine resistance [94–96]. Consistent with this idea, a lab. scale study conducted by Hong et al. [96] showed promising chlorine-resistant polyamide membrane production to overcome the severe issue of biofouling. However, there are challenges that require further research to scale up these alternative techniques [69].

4.1.3. Coagulation–Flocculation

Coagulation–flocculation processes are utilized to enhance the elimination of suspended solids and colloidal particles from water [97]. They can also be used to remediate some bacteria and dissolved organic matter [98]. It is used in the first stage of solids–liquids separation. The process typically encompasses the addition of coagulant chemicals to destabilize colloidal particles and form larger, heavier particles that can be separated easily using sedimentation, flotation, or filtration. Common coagulants used include ferric salts, such as ferric sulfate and ferric chloride, and aluminum salts, including aluminum and polyaluminum chloride [63]. The usual dose for inorganic coagulants is between 5 and 30 mg/L, while polymers often require only 0.2–1 mg/L [99]. The pH of the water plays a crucial role in coagulation. Iron salts are typically preferred to aluminum salts due to difficulties in controlling the pH and potential scaling problems in RO membranes [49,100]. Ferric-based coagulants, particularly ferric chlorides, are commonly used in desalination plants. For example, Fujairah II, the largest hybrid desalination plant in the world, uses ferric chloride in coagulant tanks before filtration [101]. This same coagulant is also used in a desalination plant in Saudi Arabia to enhance the performance of the subsequent dual-media filtration and to mitigate biofouling. To improve the coagulation stage and prevent calcium carbonate scaling formation, an acid solution is added alongside the coagulant to lower the pH of the feed water [102]. Coagulation using ferric chloride has been demonstrated to be effective in eliminating suspended solids, colloidal particles, and natural organic matter such as humic and fulvic acids and algal organic matter [103,104]. Studies have also found that using a ferric-based coagulant can reduce the concentration of algal organic matter in seawater when combined with UF. Low dosages of coagulant are sufficient to decrease the fouling potential of the membranes, but iron-biopolymer aggregates, produced by the adsorption of biopolymers to iron hydroxide, can reduce the flux-dependency of algal organic matter fouling [103]. Additionally, it has been shown that residual iron can have negative effects on both RO membranes [100] and thermoelectric plants by causing corrosion [105]. To prevent this, polyaluminum coagulants have been tested as an alternative to conventional inorganic coagulants. One such coagulant, polyaluminum chloride, has been shown to not consume excessive amounts of alkalinity, resulting in little variation in pH when added to water [106,107]. However, it is crucial to note that these synthetic polymers are toxic, and their monomers are carcinogenic [99]. Therefore, researchers are testing different alternative coagulants to mineral coagulants. Cationic organic compounds may be able to replace inorganic coagulants in some cases as they can directly neutralize negative colloids [60]. Alshahri et al. [108] have proposed the use of clays combined with low doses of liquid ferrate as an alternative coagulant that can effectively remove turbidity, dissolved organic carbon, algal organic matter, and also reduce chemical consumption and sludge production. However, more research is needed to investigate the application of this strategy on a large scale. Duan et al. [109] found that the use of powdered activated carbon, before the addition of the metal salt coagulant, is recommended to significantly reduce the concentration of humic acid. It is worth noting that coagulation has been proven to be an effective technique for enhancing water quality in both conventional and membrane filtration pretreatment technologies, which could surpass conventional pretreatment in terms of performance [110]. Therefore, the focus of current and future research should be on integrating conventional technologies, particularly coagulation–flocculation, with low-pressure membrane pretreatment technologies. A summary of common coagulants and their targeted foulant particles is provided in Table 4. Additionally, when the size of the micro-flocs produced by the coagulation process is insufficient for settling, adding flocculants may be necessary to form larger floccules that can settle. The main flocculants used in water pretreatment include inorganic polymers such as activated silica, natural polymers such as starches and alginate, and synthetic organic flocculants. Synthetic organic flocculants are particularly efficient and require low dosages, resulting in less sludge production [60]. Combining coagulation–flocculation with modern separation techniques may allow that production of dense sludge that can be treated in a dewatering unit.

Table 4. Main coagulants and targeted pollutants.

Coagulants	Fouling Treatment
Ferric-based coagulants: ferric chloride and ferric sulfate (6.0–7.4: optimum pH)	Biofouling Organic fouling: humic and fulvic acids and algal organic matter
Aluminum-based coagulants: aluminum sulfate, aluminum chloride, and polyaluminum chloride	Organic fouling: humic substances Colloidal fouling: colloidal particles Biofouling: protein-like
Activated carbon + metal salt coagulant	Organic fouling: humic acid
Organic coagulant	Colloidal Fouling: colloidal particles
Clays	Colloidal fouling: algal bloom Organic fouling: natural organic matter
Clays combined with coagulants	Colloidal fouling: algal bloom Organic fouling: natural organic matter

4.1.4. Clarification Technologies

Sedimentation and DAF are common water pretreatment technologies utilized to separate liquid and solid phases based on density and buoyancy, respectively, after coagulation–flocculation and upstream of a granular media filter. These two clarification methods are used to produce clarified water upstream of the granular media filter.

Sedimentation

Sedimentation is the process of allowing the flocculate particles, formed after coagulation and flocculation, to settle at the bottom of a sedimentation tank under the influence of gravity following an optimal detention period. The settled particles are then pumped out of the system through a sludge pipeline [111]. The main purpose of sedimentation is to reduce the total suspended solids (TSS) concentration to improve the efficiency of subsequent filtration while avoiding the need for continuous backwashing. The efficiency of the sedimentation system is influenced not only by TSS concentration but also by the volume/area of the tank, the flow rate through the tank, and the settling velocity of the suspended particles [112,113]. Sedimentation can effectively remove suspended solids when source water has a daily average turbidity of higher than 30 NTU (TSS concentration higher than 10 mg/L) and produce clarified water with a turbidity of less than 2 NTU, suitable for pretreatment filters. However, in the case of highly turbid sea water, a conventional sedimentation system may not produce water with the desired turbidity level. To overcome this limitation, conventional sedimentation systems are often coupled with lamella plates [63]. These inclined plates increase the effective surface area for settlement, which allows for a smaller system footprint compared to conventional tanks. Studies have shown that the addition of lamella plates can increase sedimentation efficiency by up to 20% [114]. Lamella sedimentation tanks are often used to treat open ocean intake source water that is heavily influenced by river water or wastewater discharges with high turbidity [57]. A life cycle analysis (LCA) was performed to compare the energy consumption of two RO pretreatment methods, one using sedimentation-based pretreatment at the Fujeira 1 Desalination plant in the UAE, and the other using simulated membrane pretreatment [111]. The results showed a significant difference in energy consumption between the two systems, with the membrane-based pretreatment system being less energy-intensive. However, it is worth noting that cleaning the membrane-based system still requires more energy than sedimentation-based pretreatment. Additionally, it is important to note that the study compared a real sedimentation system to an idealized membrane pretreatment system and thus, simulated results should be followed by pilot studies as real systems may have higher energy consumption. It is critical to note that the sedimentation process has the drawback of not being able to remove all suspended solids, such as algae, which can lead to short filter runs, clogging of the subsequent granular media filters, and cause biological fouling on the RO membrane [99].

Dissolved Air Flotation (DAF)

DAF is a water treatment method that is an alternative to conventional sedimentation. It is frequently used to treat water when suspended particles cannot easily settle. DAF can remove high concentrations of suspended solids, up to 8000 mg/L, and is particularly effective at removing low-density particles such as algae and natural organic matter that cannot be eliminated by conventional sedimentation [115,116]. The process involves creating fine air bubbles that attach to flocs and suspended matter, causing them to float to the surface. The floating flocs are then skimmed off, and clarified water with low turbidity is collected from the bottom of the tank [63]. The performance of a DAF unit depends on the air-to-solids ratio. DAF has mostly been examined as a pretreatment method for industrial waste waters [117], and more recently for seawater applications. Coagulation combined with DAF and in situ-generated liquid ferrate or ferric chloride has been proposed as a strategy for removing algal cells and organic matter from seawater [118]. However, this should be followed by pilot and cost studies, and the removal of residual iron, which can cause corrosion, must also be considered. A full-scale DAF process was investigated in a drinking water treatment plant [99]. It was found that the integration of DAF with the pre-sedimentation stage could be an effective method to produce stable water quality, as the pre-sedimentation process is crucial in removing heavy particles that may damage the DAF process. Alayande et al. [116] have recently conducted a comprehensive review of the current methods for controlling fouling in SWRO desalination plants and found that DAF pretreatment processes were employed in 16 out of 22 plants in the Arabian Gulf and Gulf of Oman. For example, the Fujairah II seawater RO desalination plant in the UAE incorporated the DAF system in combination with granular media filtration as a successful pretreatment technology for harmful algal blooms. However, the DAF process is still limited in its ability to remove nano- and pico-algae, as well as extracellular toxins, which are prevalent in some seawater [119,120].

4.1.5. Media Filtration

Granular media filtration is a common pretreatment technology in existing full-scale SWRO plants [86]. Suspended or colloidal particles in water, remaining after the clarification process, may be effectively removed through media filtration. When water passes through a bed of porous and granular material, contaminants in the water are captured by the medium, leaving only clear water [121]. The filtration process involves the mechanisms of diffusion, interception, inertial compaction, adsorption, staining, and sedimentation. The performance of seawater pretreatment filters is influenced by the type, uniformity, and size of the filter medium, as well as the geometry of the contaminant particles, as highlighted in reviews by Anis et al. [99] and Jacangelo et al. [86]. It has been shown that granular media filters can reduce turbidity and improve water clarity by removing particles as small as 10 µm [99]. These filters use materials such as sand, gravel, garnet [122], magnetite, anthracite, and activated carbon [123], and often employ a combination of two or more materials in layers, such as in dual-media filtration (DMF). The main benefits of DMF are a high filtration rate, long runs, and a low RO feed-water silt index [99]. Studies have also found that using anthracite and sand together in filtration provides all the benefits of single-media filtration but requires less backwash water and allows for higher filter rates than using either one alone [124]. Research has shown that using a layer of granular activated carbon in dual-media filters is effective in removing high levels of organics. This method has the benefit of organics removal by adsorption, resulting in cost savings while reducing chlorine demand and producing safer water [125,126]. It can even remove remaining free chlorine from the chlorination pretreatment step [57]. Recent studies [127] have also examined the use of calcite ooids, a novel filter bed created through the seawater softening process, as a pretreatment stage in seawater desalination plants. The use of this new adsorbent media was found to remove 89.4% of turbidity and 66% of total organic carbons, with the potential to reach 95.7% removal after a granular activated carbon filter. Conventional seawater pretreatment filters can be either gravity or pressure-driven. These filters are used in desalination plants and operate in a down-flow manner. Gravity-driven filtration, which uses open-atmosphere filtration beds, is a cost-effective option for large desalination plants. However, pressurized media filtration is also widely used in small desalination plants, as it requires less space and can be installed faster. For example, the pretreatment in the Fujairah II SWRO plant is based mainly on coagulation and dual-media gravity filters, producing a water quality of SDI 2.7 [101]. Pressurized media filtration has also been widely used in small desalination plants since they require less space and can be installed faster [99]. However, additional studies are needed to reduce the energy cost of these pressure filters. Cartridge filters, which use 1–10 µm filters, are often used as a last pretreatment stage to remove remaining suspended solids [128]. However, they are mainly used as a protection device and do not perform significant silt removal. A well-designed granular media filtration system can improve the performance of an RO membrane, but organic and biofouling are still limiting factors [129]. Modifications to the design and operational parameters of media filtration are needed to alleviate the organic and biofouling of the RO membrane.

4.1.6. Scale Inhibitors

Scaling occurs on the surface of the RO membranes because of salt and mineral precipitation from seawater. This precipitation, which often occurs in the final stage of installation, is caused by supersaturation. Scaling reduces permeate flow and shortens the lifetime of membranes. Scale inhibitors, also known as antiscalants, can be used as a conventional pretreatment technique to control scaling by introducing them at concentrations typically below 10 mg/L [130]. These inhibitors work by adsorbing or reacting with the active growth sites of the scale matrix [131]. The use of antiscalants depends on the water quality, concentrate discharge limits, and targeted recovery. It has been shown that scale inhibitors are recommended when desalination plants operate at a recovery rate of 35% or higher [86]. Various chemicals, such as sodium hexametaphosphate, organophosphates, polyphosphates, and polyacrylates, can act as antiscalants [92]. However, the correct dosage of these chemicals can be difficult to calculate and may require the use of a simulation tool. Overdosing can lead to biofouling of the RO membrane [44,132]. In fact, these chemicals can act as a nutrient for bacteria, leading to their attachment to the membrane. Additionally, the presence of phosphorus-based scale inhibitors in brine discharge may result in algal blooms around the discharge area [49]. Another issue is that residual cationic flocculants from the pretreatment process may react with some antiscalants to create sticky foulants [99]. Some desalination plants control scaling by adding acid, such as sulfuric or hydrochloric acid [44]. For economic and safety reasons, sulfuric acid is the most used. However, research has shown that it may increase the risk of sulfate scaling, such as barium sulfate scaling [99]. It should also be noted that the use of acid can cause corrosion of equipment and shorten the lifetime of membranes [60]. Anis et al. [99] have analyzed the toughest challenges to overcoming the drawbacks of conventional scale inhibitors, such as the utilization of environmentally friendly and non-phosphorus-based scale inhibitors with the optimization of operating procedures. As a result, various alternative green inhibitors against scale formation have recently been suggested [130,133]. However, most of the research is limited to laboratory-scale testing.

Table 5 shows a summary of the reviewed conventional RO pretreatment technologies, which includes their targeted fouling, advantages, disadvantages, challenges, and estimated cost. This section has reviewed the most commonly used conventional pretreatment technologies. These techniques are widely utilized for their cost-effectiveness and ability to reduce foulants. However, they also have significant drawbacks, including the risk of biofouling, chemical consumption, and carryover, which can lead to the formation of additional foulants and corrosion problems. As a result, in recent years, there has been a push to develop more advanced technologies, such as membrane processes and hybrid systems as alternatives for RO pretreatment. These technologies will be discussed in more detail in the following section.

Table 5. Summary of common conventional RO pretreatment technologies.

Pretreatment	Targeted Fouling	Advantages	Disadvantages	Challenges	Estimated Cost or Energy Consumption
Chlorination	Biological fouling	Effective for disinfection and odor control.	– Carcinogenic by-products. – Residual chlorine toxicity. – Sensitivity of polyamide membranes to chlorine oxidation. – Sodium bisulfite used for dichlorination can act as a bacterial nutrient.	– Chemical alternatives. – Membrane modification and development of anti-fouling membranes. – Development of alternative disinfectant methods: UV or thermal disinfection [49].	Cost USD 1000: 2160 [134]. (Raw Water Feed Flowrate 300,000 m^3/day, TDS: 2700 mg/L, Chlorine dose: 2.4 ton/day)
Coagulation–flocculation	– Colloidal fouling. – Organic fouling,	– Effective for removal of colloidal and suspended solids. – It can be used for mitigating some bacteria and dissolved organic matter.	– Synthetic polymers are toxic, and their monomers are carcinogenic – Sludge production. – Excess dosage of coagulants and flocculants might turn into a foulant on RO membrane and media filters.	– Alternative green coagulant and flocculants. – Use of activated carbon in combination with coagulation. – Optimization of operating procedures. – Integration of coagulation–flocculation with low-pressure membrane pretreatment technologies [103,104].	Cost USD 1000: 6933 [134]: Chemical treatment/flocculation clarification and sludge dewatering (Raw Water Feed Flowrate 300,000 m^3/d, TDS: 2700 mg/L, NaOH dose: 120 ton/day, flocculant dose: 3 ton/day.

Table 5. *Cont.*

Pretreatment	Targeted Fouling	Advantages	Disadvantages	Challenges	Estimated Cost or Energy Consumption
Sedimentation	Colloidal fouling: organic/inorganic complexes and colloidal particles	– It enhances the filtration process – Low operating and maintenance costs (compared to the DAF system). – It can minimize the need for coagulation and flocculation	– Not effective for removing algae. – It can cause biological fouling. – High footprint.	– Improving the design of settling tanks to decrease the volume of the dead zones and improve the performance of sedimentation [57].	– Operational cost: 0.005 to 0.01 USD/m^3 permeate. – Energy consumption: – 5×10^{-4} to 1×10^{-3} kW h/m^3 [135].
DAF	– Organic fouling – Colloidal fouling	– Effective for removing algae. – Small footprint (compared to sedimentation system). – Ease of operation. – Reduced sludge volume.	– Not effective for removing extracellular toxins and nano- and pico-algae. – Scraper problem: lack of feed water for the DAF unit	– Ensuring uniform air distribution. – Reducing the operation and maintenance costs (compared to sedimentation) [115,116].	– Operational cost: 0.005–0.025 USD/m^3 permeate. – Energy consumption: 9.5×10^{-3} to 35.5×10^{-3} kW h/m^3 [135].
Media filtration	– Particle fouling – Organic fouling – Colloidal fouling	– Ability to be used with waters with high turbidity and suspended solids. – Ability to produce low RO feed-water silt index. – DMF provides high filtration rates and long filtration runs. – Pressurized filters fit well with small RO plants	– Not effective for biofouling inhibition. – Sensitive to seawater with high algae and oil contents. – Non-optimized media filters could lead to frequent cartridge filter replacement and RO membrane cleaning. – High chemical demand for seawater conditioning.	– Energy cost optimization of the pressure filters. – Modification in the design and operational parameters of media filtration [99].	– Operational cost: 0.005 to 0.01 USD/m^3 permeate [135]. – Investment cost for the 90,000 m^3/day SWRO plants.: USD 64,400 K (716 USD/m^3-day) [136]. – Energy consumption: <0.05 kWh/m^3 [49].
Scale inhibitors	– Mineral fouling.	– Effective scale control. – Cost-effective.	– Antiscalants can increase biofouling potential.	– Optimization of antiscalant dosing. – Utilization of environmentally friendly and non-phosphorus-based scale inhibitors [99].	– Estimated bulk cost: 25.61 USD/52 m^3 [137]. (Operational costs including power consumption, pipelines and distribution system, labor, and overheads were not included in the cost estimation)

4.2. Membrane Pretreatment Technologies

Membrane pretreatment technologies have become widely and increasingly applied instead of conventional technologies, especially after the decline of membrane costs [138]. As formerly mentioned, the application of conventional pretreatment does not lead to desirable feed-water quality. Consequently, membrane technologies gained immense importance when MF, UF, and NF membranes were introduced with tighter pore sizes [53], as illustrated in Figure 4 [139]. Table 6 represents a summary of these membranes with their specifications and the materials that they are capable of retaining [140,141]. Many comparisons have been conducted and have shown that these membrane technologies have advantages over conventional technologies [92]. Membrane pretreatment technologies have a 30–60% lower carbon footprint to conventional methods; lower chemical cost; reject various pollutants simultaneously; and lower operating cost due to their long membrane life [92,99]. Membranes are made up of a variety of materials that were extensively studied to optimize their cost and their flux [142]. However, polymeric and ceramic membranes are the dominant materials due to their relatively low cost and their smooth processing [99].

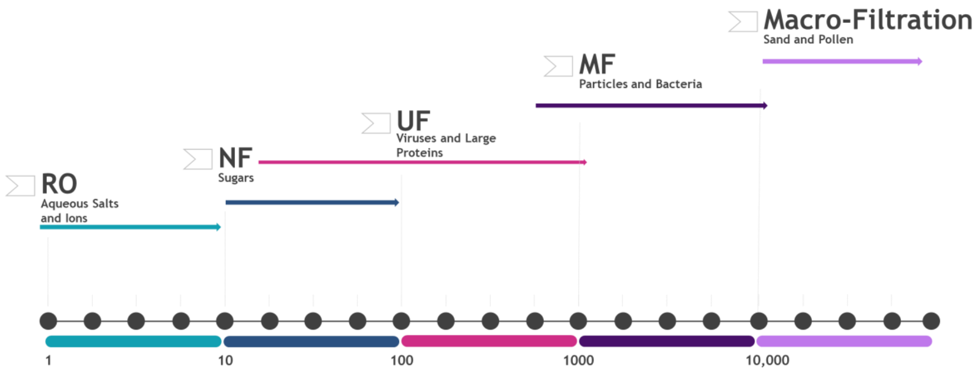

Figure 4. Filtration spectrum of commercial membranes based on the pore diameter and material retained [139].

Table 6. Membrane specifications based on the pore size and their separation process including RO (Adapted from [63,140,141]).

Process	MF	UF	NF	RO
Pore size	0.1 to 5 µm	0.01 to 0.1 µm	0.001 to 0.01 µm	0.0001 to 0.001 µm
Separation mechanism	Molecular sieve	Molecular sieve	Solution diffusion	Solution diffusion
Material held	Suspended particles and bacteria	Viruses and large proteins	Micropollutants, sugars, and divalent ions	Dissolved salts
Material passed	Water and dissolved solutes	Water and dissolved salts	Water and monovalent salts	Water

4.2.1. Polymeric Membranes

Membranes synthesized from polymeric materials are generally organic in nature. These membranes are comparably more cost-effective than those manufactured from inorganic materials or ceramics [143]. They are easily handled during the fabrication process and can be made into a variety of different configurations for optimum performance, typically with a high water production capacity [143–145]. The permeate quality and the operating cost of water production are greatly influenced by the type of polymer material used during the fabrication process. Therefore, it is crucial that the most appropriate polymer and pore size are properly selected for any filtration process to avoid long-term problems such as frequent membrane replacement and high energy consumption.

MF, UF, and NF Polymeric Membranes

MF membranes are large pore-sized membranes that range from 5 μm to 0.1 μm with the ability to filter out emulsions of latex, blood particles, cells, and bacteria [92,139]. In the last 15 years, extensive research has been conducted to establish these MF membranes and determine their validity as an alternative pretreatment method to conventional techniques. Based on this research, it was found that MF membranes were able to increase the water flux and reduce the SDI [146] without requiring changes in the feed water pH, and were effective in microbial elimination [63,147]. Nevertheless, one of the major disadvantages of MF is membrane fouling. Foulants including proteins, organic algae, and oil particles are the main contributors to MF membrane fouling [140]. Although membrane fouling is the most significant disadvantage of MF membranes, low thermal stability and resistivity toward free chlorine are other limitations [148–150]. Many studies have emphasized the importance of modifying these membranes for better performance and utilizing hybrid pretreatment techniques to overcome this issue, which are going to be discussed later [151].

UF membranes, based on multiple studies, were found to be more efficient than MF membranes and the conventional pretreatment methods. UF membranes are cost-effective with a better removal capability of silt, suspended organics, and microbes, resulting in a high and consistent filtrate quality with low RO fouling potential [57,152,153]. SWRO systems designed with UF membrane pretreatment are often termed "dual-membrane systems" [154]. In Wang Tan Power Plant, a dual-membrane system was installed and operated with low flux and low chemical treatments and resulted in a high filtrate quality with SDI < 2.5 and a reduction in turbidity of 98–99.5% [155]. In Singapore, experimental studies showed that using sand filtration, MF membrane, and UF membrane resulted in a filtrate quality with SDI between 2.8 and 6.3, 2.0 and 3.0, and 1.0 and 2.0, respectively, showing the superior efficiency of UF membrane technology compared with MF and conventional methods [156]. However, as in MF membranes, UF suffers from membrane fouling that affects its performance. The primary foulants are referred to as natural and effluent organic matter (NOM and EfOM) [157–159]. Modifying the UF membrane, using for example graphene oxide nanosheets [160] and/or integrating it with other conventional pretreatment methods, such as coagulation, has been identified by Yang et al. [161] as a viable solution to solve the UF fouling problem. The hybrid system showed good permeate quality compared to stand-alone pretreatment units.

While NF, a pressure-driven membrane process, is considered a promising membrane pretreatment method and represents a major milestone in the membrane technology field as it has a high retention capability of divalent ions and salts [162–164]. NF membranes, with a typical pore size of 1 nm, operate as porous and non-porous membranes as they transport in sieving and diffusion mechanisms [165,166]. These membranes are typically capable of achieving the elimination of divalent and monovalent ions in the range of 75–99% and 30–50%, respectively [167]. They are capable of eliminating microorganisms, turbidity, and a part of the dissolved salts [168]. Furthermore, they can significantly and efficaciously reduce the scaling of the RO membrane by eliminating Ca^{2+}, Mg^{2+}, and $SO4^{2-}$ ions [169] with a reduction in total hardness of 86.5% [168]. In the Umm Lujj SWRO plant, Saudi Arabia, NF combined with their system resulted in a noticeable growth in the permeate flow rate from 91.8 to 130 m^3/h [170]. Therefore, extensive research studies have been carried out on NF membrane and considered it as a confirmatory step to be applied in RO pretreatment systems [168,169]. However, as in MF and UF membranes, NF membranes encounter the same fouling issue that results in an energy consumption increase and a reduction in the lifetime of the membranes [167,171]. Inorganic foulants including metal hydroxides, carbonate, and sulfate-based salts are among the common NF foulants that cause membrane scaling [172]. Therefore, fabricating modified NF membranes with anti-scaling properties is of great value to maintain the performance of the NF technology [173].

Common Polymers for MF, UF, and NF Fabrication

Table 7 displays some of the most frequently used polymers in polymeric membrane fabrication, typically in MF, UF, and NF membrane filtration processes. As seen in the table below, a widespread range of polymers are used for the formulation of both MF/UF membranes. Recently, much focus has been laid on the use of polysulfone (PSF), polyethersulfone (PES), and polyvinylidene fluoride (PVDF) materials due to their vast range of benefits over other polymeric substances [148–150]. Despite their low operating pressure limits and fair hydrophilicity, these materials are broadly known for their flexibility in membrane fabrication, high thermal stability, wide pH tolerance, good resistance to chlorine and chemicals, and good mechanical strength and durability. For NF fabrication, polyamide (PA), PSF, polyacrylonitrile (PAN), and cellulose acetate (CA) are among the most common materials for NF membranes, where some are considered the active layer component of the NF membranes and others are known to be the support layer [174]. Most of these polymeric materials have a high hydrophilic nature and free chlorine resistance except PA NF membranes, which are susceptible to chlorine ion attack [150,175].

Table 7. Advantages, disadvantages, and features of commonly used polymers for MF, UF, and NF membrane fabrication.

Filtration Process	Polymers	Advantages	Disadvantages	Properties	Ref.
MF/UF	Polyacrylonitrile (PAN)	- Oxidant tolerant - Resistant to chlorine	Broad pore-size distribution	- Fair mechanical strength and durability - Good hydrophilicity	[148–150,176,177]
	Polysulfone (PSF)	- Good mechanical properties - Chemically resistant - Good resistance to chlorine	- Bulk structure - Low binding force between fibers - Lack of solvent resistance - Hydrophobicity	- Good mechanical strength and durability - Fair hydrophilicity	
	Polyethylene (PE)	- Highly resistant to organic solvents - Cost-effective - Oxidant tolerant	- Poor thermal stability - Weak anti-fouling ability - Poor chlorine resistance	- Fair mechanical strength and durability - Poor hydrophilicity	
	Polyvinylidene fluoride (PVDF)	- Very oxidant tolerant - Resistant to chlorine - Good anti-fouling ability	- Vulnerable to contamination and water flux decline - Broad pore-size distribution	- High thermal stability - Good chemical resistance - Good mechanical strength and durability - Poor hydrophilicity	
	Polyethersulfone (PES)	- Compaction resistant - High permeability - Oxidant tolerant - Narrow pore size distribution - Good chlorine resistance	- Dense structure - Rough surface - Hydrophobic - Fair anti-fouling ability	- Good mechanical strength and durability - Fair hydrophilicity	
	Polypropylene (PP)	- Highly resistant to organic solvents - Fair mechanical strength	- Low resistance to fouling - Not oxidant tolerant Poor chlorine resistance	- Fair mechanical strength and durability - Fair hydrophilicity	

Table 7. *Cont.*

Filtration Process	Polymers	Advantages	Disadvantages	Properties	Ref.
NF	Polyamide (PA)	- Highly hydrophilic - Resist fatigue and abrasions - High selectivity - High salt rejection	- Intolerant to extreme pH conditions - Low porosity - Susceptible to chlorine attack - Low permeability	- Negatively charged - Thermally, chemically, and physically compatible with various solvents	[150,175]
	Polyacrylonitrile (PAN)	- Highly porous - Hydrophilic nature - Highly oxidant tolerant - Chlorine ions resistant - High mechanical strength - Narrow pore size distribution - Resist a wide range of pH	- Poor solubility in various solvents - Low chemical stability	Improves membranes' anti-fouling capability	[150,178–180]
	Cellulose acetate (CA)	- Rich in functional groups - Renewable source - High tensile strength - High chlorine resistance	- Low permeability - Prone to compaction - Low mechanical strength	Easy to be chemically or physically modified	[150,178]

Advances in Membrane Material: Synthesis and Modification

For decades, numerous fabrication techniques have been employed in the preparation of polymeric membranes for a wide range of applications. The choice of fabrication technique depends on the polymer and the desired membrane structure. Non-solvent-induced phase separation (NIPS), evaporation-induced phase separation (EIPS), thermally induced phase separation (TIPS) and vapor-induced phase separation (VIPS), and other fabrication methods including interfacial polymerization, stretching, track-etching and electrospinning are among the commonly used techniques for the preparation of polymeric membranes [181]. These techniques aid in tailoring the membranes' morphology, mechanical properties, pore-size distribution, hydrophilicity, selectivity, fouling mitigation, and flux [182].

Many studies have reported improvements in the morphology, properties, and performance of the prepared membranes simply through the addition of inorganic and high molecular weight organic materials such as polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG), Arabic Gum, or lithium chloride (LiCl) as additives to the polymer solution [183,184]. The addition of LiCl increases the viscosity of the casting solution due to its strong interactions with the polymer and solvent, thus improving the membrane's permeability and rejection [185–187]. Similarly, the incorporation of PVP enhances the membranes' performance owing to the increased hydrophilicity and pore density. PVP causes a decrease in the effective thickness of the dense layer due to the formation of macro-voids in the support layer [188]. Other filler materials including metal/metal oxide or carbonaceous nanoparticles have also been reported to enhance the anti-fouling characteristics and permeate flux of membranes. For instance, a recent study reported the fabrication of oxidized carbide-derived carbon-incorporated polyether sulfone UF membranes prepared via NIPS [189]. The prepared membranes demonstrated improved porosity, pore size, and surface free energy with a noticeable reduction in the water contact angle. The membranes revealed a humic acid (HA) rejection of 96.8% and a maximum flux recovery ratio (FRR) higher than 86.7% over three cycles of pure water/HA filtration over a period of 140 min, suggesting excellent stability and reusability of the membranes. Table 8 gives an overview of recently prepared membranes using various fabrication techniques. The table highlights key features and performances of the membranes towards the rejection of different pollutants.

Table 8. Key features and performance of recent membranes prepared using different fabrication techniques for water treatment applications.

Membrane	Fabrication Technique	Key Features	Flux (LMH)	Rejection (%)	Ref.
PVDF membrane	VIPS	Symmetric microporous membrane Bi-continuous bulk structure with interlinked crystallites in 3D porous networks High hydrophobicity, large porosity, and submicron pore size	17.2 at 1 bar	N/A	[190]
2D TiO_2@GO/PEN fibrous composite membrane (without PMMA core)	Electrospinning and spraying	High hydrophilicity and underwater hydrophobic properties, low oil adhesion, and efficient water channels High permeability while maintaining a stable rejection. Enhanced photocatalytic degradation performance. Fast separation of multi-component pollutant—oil–water emulsion	2146 (SFE *) at 4 bar 1671 (SSE *) at 4 bar	99.47% 99.21%	[191]
3D TiO_2@GO/PEN fibrous composite membrane			4830–5160 (SFE) at 4 bar 3062–3514 (SSE) at 4 bar	>99.4% >99.03%	
PET track-etched membrane	Track-etching	Regular pore geometry and narrow pore size distribution Highly hydrophobic Exhibit stable fluxes and high separation efficiency during filtration cycles. Good oil–water separation abilities	1098 at 700 mbar	99.9–99.5% towards Water/Chloroform	[192]
			270 at 700 mbar	99.9–99.5% towards Water/Cetane	
PIP-GO NF composite membrane	In situ interfacial polymerization	Highly wrinkled and sandwiched structure Rough and hydrophilic surface with a 2D capillary network formed by the stacked GO nanosheet. High surface area Enhanced hydrophilicity, water permeation, and high salt rejection	242 at 10 bar	~90% towards $MgSO_4$	[193]
PEI-SiO_2/PSF membranes	NIPS	Asymmetric, finger-like, and porous structures Excellent compatibility between PEI-SO_2 nanoparticles and polymer matrix. Thus, improved membrane mechanical properties Improved membrane porosity, permeability, and flux recovery ratio Excellent hydrophilicity due to the presence of amino groups. Hence, improved anti-fouling properties	70 at 3 bar	99.6% towards Reactive Green 19 dye	[194]
PES/sPDA-TEOS-APTES	NIPS-VIPS/coating	Symmetrical and porous membrane with a sponge-like structure Highly hydrophilic with enhanced permeability Robust membranes with superior anti-fouling properties	1836 at 0.5 bar	~99.1% toward diesel fuel	[195]

Notes: * SFE: surfactant-free emulsions; * SSE: surfactant-stabilized emulsions.

Properties Affecting Membrane Performance

Although the fabrication technique has a significant effect on the performance of the polymeric membranes' separation, there are other factors that highly influence the membrane performance including the membrane's hydrophobic/hydrophilic nature, surface charge, porous structure, and surface roughness [196]. Materials used for fabricating hydrophobic membranes include polypropylene (PP), PES, polytetrafluoroethylene (PTFE), and PVDF [178]. However, hydrophobic membranes were reported to be more prone to membrane scaling compared to hydrophilic membranes, which significantly affects their performance. Hence, various attempts were conducted to improve the hydrophilic nature of the membranes through modification using, e.g., polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), guar gum, and cellulose in the membrane casting solution [197]. For instance, Cheng et al. [198] used tunicate cellulose nanocrystals (TCNCs) in membrane fabrication, which resulted in a super-hydrophilic membrane surface [198]. The surface charge of the membrane is another parameter that is considered while modifying and fabricating polymeric membranes. Chen et al. [199] prepared Iron (II) phthalocyanine (FePc)/PVDF membrane for oil treatment, which resulted in 96.7% oil rejection with 158.94 L/m^2h water flux, where Fe played a great role in increasing the negative charge of the membrane surface. Liu et al.'s [200] study revealed that among various carbon-nanotube (CNT)-modified polymeric membranes for oil filtration, the PVA/CNT membrane presented a superior anti-fouling property owing to its hydrophilicity and the carboxyl functional groups that increased the surface negative charge where the flux recovery ratio (FRR) was 100%. A negatively charged membrane is less susceptible to membrane fouling due to electrostatic repulsion towards oil droplets and other foulants such as bacteria cells [201,202]. Therefore, most of the recent research has been directed towards modifying the membrane surface by increasing its surface negative charge [203].

Membrane pore structure is one of the most crucial morphological criteria of polymeric membranes that influences their efficiency [204]. The larger the pore size of the membrane (>100 nm), the faster the irreversible fouling of the membrane compared with narrow pore membranes (30 nm) [205]. Surface roughness is a further membrane characteristic that has an influence on the membrane performance. Increasing surface roughness has been reported to increase permeability and diffusion due to the increase in the cross-sectional area [178]. However, high surface roughness is known to be a key factor that leads to membrane fouling. This is ascribed to the accumulation and absorption of the foulants onto the membrane surface, which consequently causes a reduction in water flux [206]. To avoid this, efforts have been concentrated on fabricating membranes with low surface roughness. An oil separation study conducted by Panda et al. [207] demonstrated that by varying PAN concentration in a PAN/PEG membrane, a higher concentration demonstrated a higher surface roughness (35 nm), which resulted in a higher fouling tendency compared with the low surface roughness membranes (10 nm). By reducing surface roughness, a dramatic reduction in the flux decline ratio (FDR) was reported from 55% to 25%. Modifying the membrane is a way to reduce membrane roughness. For example, Wan Ikhsan et al. [208] revealed a reduction in PES membrane surface roughness after the employment of halloysite nanotube-hydrous ferric dioxide nanocomposite (HNT-HFO), which induced a significant improvement in oil rejection of about 99.7%.

Membrane Configurations

Despite the contribution of the aforementioned factors in the performance and application of polymeric membranes, the configuration of the membranes is an essential aspect that is to be considered during membrane fabrication and selection [178]. The most commonly developed module configurations are tubular, spiral wound, hollow fiber, and plate types [209], as depicted in Figure 5. Plate and tubular modules are among the highest-cost and lowest-industrially practical configurations. This is because plate membranes are more prone to fouling [210] while tubular membranes are energy-intensive [211]. Hence, due to the problems generated by the plate and tabular membrane configurations, most water treatment plants have replaced them with spiral wound and capillary fiber membranes, as presented in Figure 5b,d [178]. Although spiral wound membranes are energy-intensive, various features have been reported compared with other membrane configurations, presenting their high packing density, high salt rejection, simple construction and operation, less cleaning frequency, and effective flow mixing [212]. Capillary fiber membranes are selective membranes with great packing density and strong resistance to filtration pressure [213]. This makes both configurations the selected types of membrane in large water treatment plants.

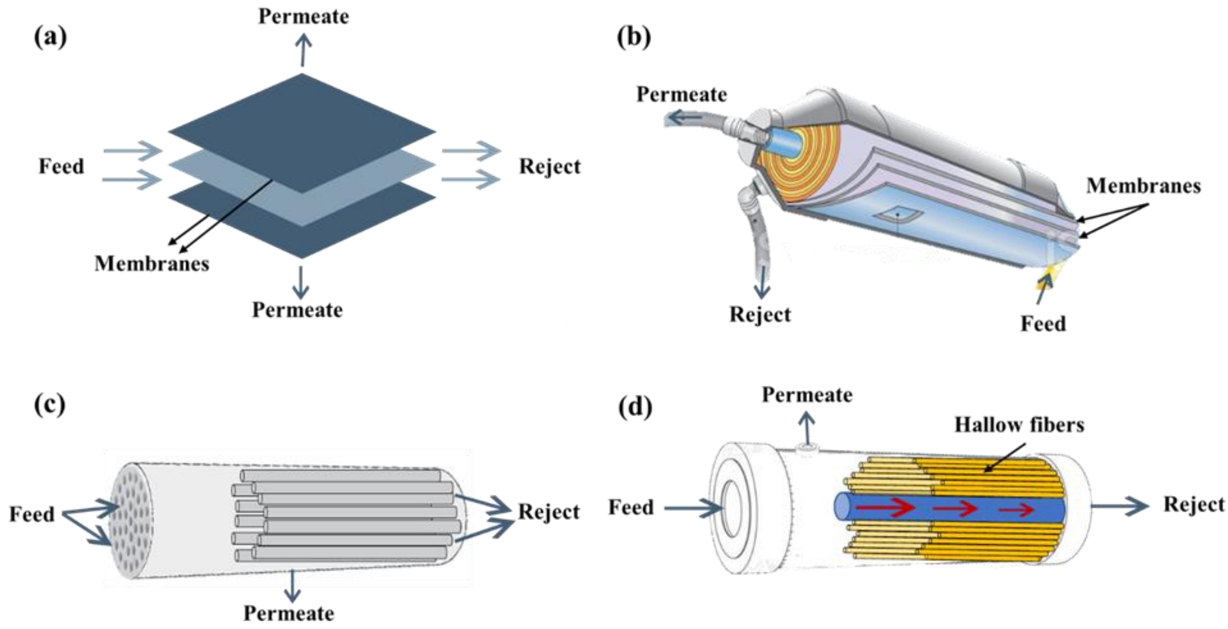

Figure 5. Membrane configurations: (**a**) plate and frame, (**b**) spiral wound, (**c**) tabular, and (**d**) capillary fiber.

4.2.2. Comparisons of Polymeric and Ceramic Membranes

As mentioned above, polymeric and ceramic membranes are the most used materials for filtration and separation processes due to their high performance. However, the main drawbacks of using polymeric membranes are fouling, biofouling [214], and sensitivity to pH and temperature [215], which can decrease flux and selectivity. As a result, many efforts have been made to improve these properties in polymeric membranes or find alternatives. Accordingly, a recent increase in research on ceramic membranes for UF, MF, and NF processes as alternatives to polymeric membranes was observed. Therefore, a comprehensive literature search was carried out for all studies related to performance factors on both ceramic and polymeric membranes, as presented in Table 9. While ceramic and polymeric membranes are used in various water pretreatment applications, ceramic membranes present competitive advantages over polymeric membranes. The excellent chemical resistance achieved by ceramic membranes make them strongly competitive against other commercial membranes as they are able to withstand a wide range of chemicals, including strong acids and bases [216], contrary to the polymeric membranes that might be sensitive to certain strong acids and bases [217]. Ceramic membranes also have a higher temperature tolerance and can operate at high temperatures of up to 500 °C without degrading. This can be beneficial in removing irreversible foulants from the ceramic membrane surface. In comparison, fouling and biofouling are among the biggest challenges in applying polymeric membranes. In this respect, Sarkar et al. have recently presented a comprehensive review of polymeric membranes and highlighted that this type of membrane has some limitations, including poor thermal and mechanical stability, sensitivity to salinity, and lower lifetime [218]. While ceramic membranes have a higher initial cost due to the use of expensive materials and manufacturing processes, they also have a longer lifetime and can operate for several years before needing replacement [216]. This can reduce the frequency and cost of maintenance and membrane replacement, resulting in lower overall costs over the membrane's lifespan. On the other hand, it should be noted that some ceramic membranes use unrefined raw materials such as clays, zeolites, apatite, fly ash, and rice husk ash [219]. These low-cost raw materials could offer a promising approach to reducing the capital cost of ceramic membranes. Li et al. and Kommineni et al. have reviewed the advantages of ceramic membranes, including fouling resistance, high permeability, good recoverability, chemical stability, higher mechanical robustness, ability to handle higher loading of particulates, and long lifetime [216,220]. It seems that ceramic membrane pretreatment can be a cost-competitive option and a critical player in water technology [221]. Additionally, hybrid membranes, which combine ceramic and polymer materials, can also be used to improve membrane performance. In the following section, these types of membranes are discussed in more detail.

Table 9. Comparison table of ceramic and polymeric membranes, showcasing their main advantages and drawbacks.

	Ceramic Membranes	**Polymeric Membranes**
Chemical resistance	Excellent resistance to various chemicals, including strong acids and bases.	Good resistance to a wide range of chemicals but may be less resistant to some strong acids and bases.
Temperature tolerance	Can operate at high temperatures up to 500 °C without degrading.	Limited temperature tolerance, with some polymers only operating at <30 °C [222].
Mechanical strength	High resistance to mechanical stress and high pressure.	Low resistance to mechanical stress and high pressure.
Fouling resistance	Excellent fouling resistance, with a low likelihood of becoming clogged or blocked.	Poor fouling resistance, with a higher likelihood of becoming clogged or blocked.
Average Silt Density Index (SDI)	SDI < 3 Example [223]: SDI = 2.1 (Raw water: Sea seawater of 6.1)	Average 0.5 < SDI < 3 Example [153]: Standalone UF: SDI > 1
Average Turbidity	Turbidity levels: <0.1 NTU [223]	turbidity levels: <0.1 NTU [57]
Footprint	Large footprint	Low footprint
Cost	High cost due to the use of expensive materials and manufacturing processes.	Low cost due to the use of inexpensive materials and manufacturing processes.
	Average total operational cost USD 1,106,000 (Ceramic MF membrane) [224]	Average total operating cost USD 1,141,000 (Polymeric UF membrane) [224]
Lifespan	Several years Example [224]: Lifespan = 20 years	Few months-10 years Example [224]: Lifespan = 10 years

It is important to note that these provided values are just approximate averages, and actual results may vary depending on the specific operating conditions, type of feed water, and type and size of the ceramic or polymeric membrane.

4.2.3. Ceramic Membranes

In the last two decades, the use of ceramic membranes (CM) for water desalination has attracted significant attention because of their excellent properties such as high flux rates; reliability; thermal, mechanical, and chemical stability; ability to withstand harsh environments such as acidic conditions; and ease of cleaning [225,226]. Despite the fact that the investment cost of CM is higher than polymeric membranes, the overall cost can be compensated by longer lifetimes and higher permeate fluxes [226]. Moreover, the pore size of CM can be tuned during the manufacturing process toward specific applications. According to the application of CM, different fabrication techniques including pressing, slip casting, and extrusion were utilized to produce micro, ultra, and nanofiltration CMs [99]. Moreover, the geometry and configuration of CM (flat sheet, hollow fiber, or tubular) can be produced based on the support and the required application [225].

Alumina, zirconia, zeolite, natural clays, silica, and titania are the most widely used materials for CM manufacturing. Similar to polymeric membranes, the quality of the feed water and the desired quality of the permeate flux inform the selection of the pore size of CM [226,227]. Moreover, the active surface of CM can be altered based on the quality of the feed water and toward a specific pore size of the membranes. For instance, Nogochi et al. [228] investigated seawater treatment by a commercial flat sheet CM with a pore size of 0.1 µm. The results demonstrated that the permeate flux from the CM has a turbidity of 0.04–0.1 NTU and SDI of 1.6–2.2, indicating that the system can provide high-quality water for RO treatment.

Cui et al. [229] utilized the ZrO_2/Al_2O_3 CM in a seawater desalination pilot plant in Tianjin Bohai, China. The raw seawater was pretreated by different methods, and it was concluded that flocculation and natural sedimentation was the optimum method for pre-CM filtration. The filtration system is shown in Figure 6. The CM was used in two configurations, honeycomb and multichannel. The study concluded that, for the seawater obtained in Tianjin, China, coagulation is required before CM filtration. The filtration results demonstrated a high removal of turbidity, and the permeate SDI was 0.18–1.1. The membrane maintained a stable permeability for a long time even at low temperatures (3–6 °C). Achiou et al. [230] fabricated a tubular CM from natural pozzolan for the treatment of raw seawater. The CM was prepared by the extrusion and sintering method at 950 °C.

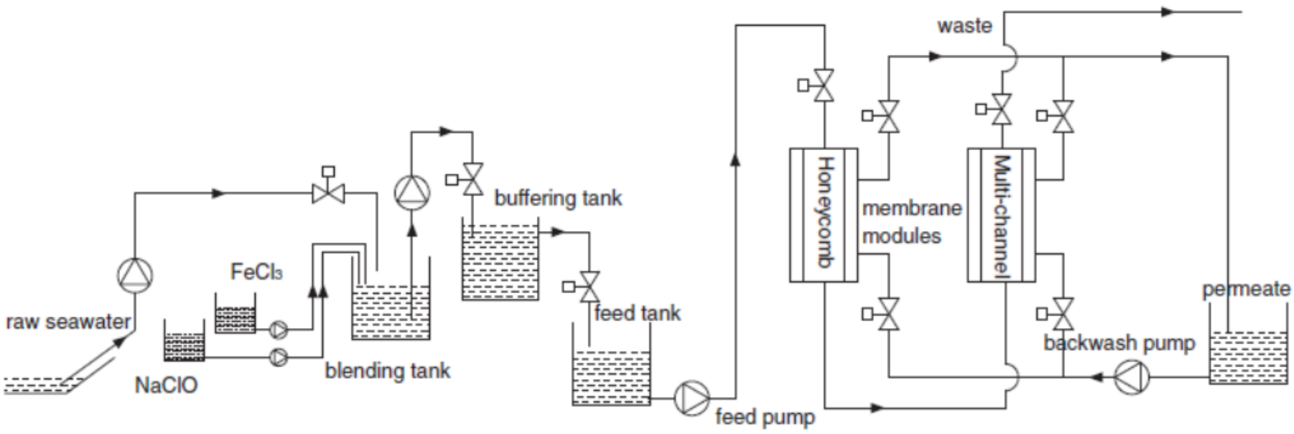

Figure 6. Representation diagram of CM filtration system [229]. Reprinted with permission.

Two-layer CM was obtained by mixing natural clay and pozzolan for the support layer, and pozzolan powder was deposed on the inner surface of the tube by the crossflow filtration technique as a filtration layer. The fabricated membrane demonstrated an average pore size of 0.37 microns and a porosity of 41.2%. Filtration tests showed rejection of 98.3% and 70.8% for turbidity and COD for an initial concentration of 6.29 NTU and 5.69 ppm, respectively.

In another study, seawater pretreatment was conducted by a zirconium-based ceramic membrane with 0.05 µm pore diameter, and the obtained results demonstrated that the sea water flux and COD rejection rate were significantly enhanced due to the disruption of the adsorption layer and membrane surface fouling layers with heavy flow rates [231]. Wang et al. [232] synthesized a hallow fiber γ-aluminum coated on α-aluminum ceramic by changing the aluminum nanoparticle solution soaking time to investigate the influence of layer thickness on flux rate. The obtained results revealed that pure water permeate flux significantly increased with the mean pore size of 1.61 nm. In addition, the high multi-valent cation rejection rate was increased compared to monovalent cations since the aluminum-coated ceramic membrane demonstrated a positive surface change nature.

De Friend et al. [232] modified the aluminum-based ceramic membrane with different metals including Fe, Mn, and La. The filtration results showed that the water permeate flux was 50% higher compared to Mn-modified and bare aluminum ceramic membranes, which might be due to the chemical properties of modified aluminum ceramic membranes.

In another study, Belgada et al. [233] studied the effect of sintering temperature on the characteristics of raw phosphate CM. At the optimized sintering temperature (1000 °C), the membrane showed an enhanced permeability flux of 697 L/(h·m^2·bar) and porosity of 25.6%. The CM tested for raw seawater treatment, and the results revealed a promising rejection of turbidity and TOC of 98% and 73%, respectively. The membrane has shown a 40%

reduction in the SDI, in which the authors concluded that the seawater permeate product has sufficient quality for RO treatment. According to the flux recovery and fouling analysis results, both intermediate pore blocking and cake layer formation fouling mechanisms were identified; however, the membrane revealed 74.3% of seawater flux recovery after cleaning. Cui et al. [234] reported the influence of crossflow velocity on the flux of commercial CM with a pore size of 50 nm. It was found that the crossflow velocity has a great effect on the water permeate flux in laminar and turbulent regions. The permeate coming out from the CM has a turbidity of less than 0.1 NTU. Bottino et al. [235] treated lake water from Genoa, Italy by alumina CM with an average pore size of 200 nm. A complete removal of algae and microorganisms was achieved by the CM. Moreover, rejection rates of 56% and 64% were obtained for chloroform and TOC, respectively.

Cui et al. [236] examined the effect of membrane pore size, NaOCl addition, coagulation method, and transmembrane pressure on the permeate flux and quality of commercial multichannel alumina CM. It was found that the membrane pore size does not affect the permeate flux, which was attributed to the formation of a gel layer onto the ceramic membrane surface, which in turn makes the total resistance the same at the end. However, coagulation was unavoidable and significantly affected the permeate flux. The addition of NaOCl does not affect the turbidity, while increasing the concentration of NaOCl was found to increase the SDI. The extra addition of NaOCl leads to oxidizing some of the organic matter and damaging the filtered cake on the membrane surface, which increases the permeate flux ratio of organic matter, and hence SDI increases. Finally, the study concluded that CM seawater filtration can provide suitable turbidity and SDI values for RO treatment.

Kang et al. [237] tested alumina commercial CM (pore size 100 nm) for synthetic seawater treatment. The study concluded that the best removal of turbidity (0.076 NTU) and lowest value of SDI (0.9) were achieved utilizing 6 mg/L of $FeCl_3$ as a coagulant. Moreover, the permeate flux and DOC removal were significantly improved by coupling coagulation and CM filtration. Islam et al. [238] synthesized porous supported YSZ (Yttria Stabilized Zirconia) CM using an atmospheric plasma spraying technology, and the preparation procedure for the YSZ membrane is shown in Figure 7. This technique yields a high porosity with a lower pore size of YSZ membrane, and the YSZ membranes are homogenous and defect-free in nature. The YSZ CM exhibited remarkable filtration results for permeate flux, rejection rate, and permeability for three different contaminated water sources including waste and salt water up to 400 Lm^{-2} h^{-1}, ~95%, and 380 Lm^{-2} h^{-1} bar^{-1}, respectively. In addition, the YSZ membrane also presented excellent cycling stability. Based on the filtration results, the authors concluded that YSZ-coated ceramic membranes showed better performance than commercial ceramic membranes.

Xavier et al. [239] prepared a slag-modified pozzolanic clay ceramic MF membrane by a hydrothermal process for seawater pretreatment. In this study, the effect of clay particle size and slag concentrations (10%, 20%, and 30%) for seawater pretreatment was investigated. The authors reported that the CM with 20% slag concentration performed 97.4% removal of turbidity, and it was concluded that the utilization of stainless-steel slag was a good choice to prepare CM for pretreatment of seawater for RO and to reduce the solid residues generated from industries being discharged into the environment.

Dong et al. [240] developed a novel technique to synthesize thin-film nanocomposite nanofiltration membrane. The TFC was coated with zeolite nanoparticles, and then a polyamide layer was formed on the zeolite surface layer using interfacial polymerization. The characterization results revealed that zeolite nanoparticles enhanced the membrane surface roughness and resulted in high permeability compared to bare TFC. CM membranes have great potential for the RO pretreatment process; however, further research is needed to fully understand their impact on RO pretreatment processes.

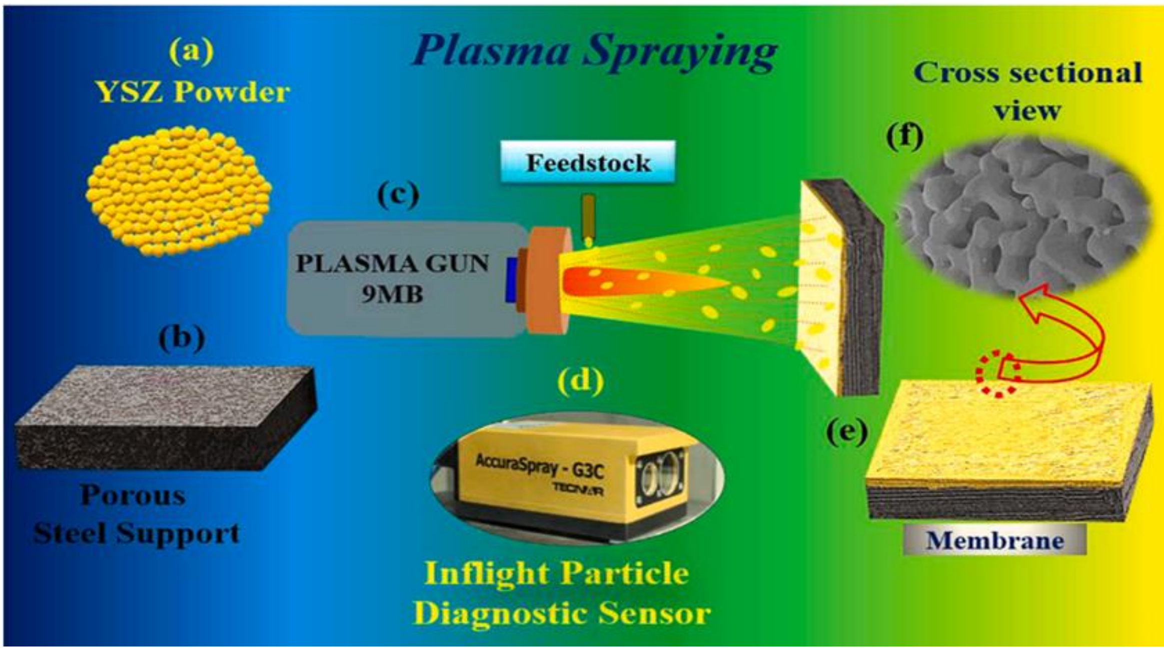

Figure 7. Schematic illustration of YSZ CM preparation process. (**a**) YSZ powder feedstock, (**b**) porous steel support, (**c**) plasma gun (9 MB) sprays the molten YSZ powder, (**d**) diagnostic sensor for temperature and velocity measurement, (**e**) YSZ membrane after its deposition onto porous steel support, (**f**) YSZ membrane cross-sectional image [238]. Reprinted with permission.

Although significant membrane enhancement has been achieved, the industrial application of ceramic membrane is still hindered due to the fouling problems, which results in high operating costs and huge capital investment because of the periodic membrane cleaning and replacement. Several approaches have been devoted to mitigating the fouling phenomenon, including membrane cleaning, membrane module design, and modification of membrane surfaces [241,242]. For instance, Xu et al. [243] applied different membrane cleaning processes including chemical cleaning, backwash, and ferric coagulation to improve the applicability of commercial UF membranes as a pretreatment of RO seawater desalination. In this study, α-$A_{12}O_3$-based tubular UF CM with a surface layer of ZrO_2 was used. The results demonstrated that ferric coagulation with optimal $FeCl_3$ dosage played a significant role in enhancing the ceramic UF membrane for seawater. Furthermore, chemical cleaning results indicate that NaClO showed much better performance than HNO_3. In addition, cleaning efficiency increased while increasing the NaClO concentration. Anti-fouling grafting methods on ceramic membranes have been recently developed [244].

Moyo et al. [245] investigated the anti-fouling improvement of the ceramic membrane via surface modification by atomic layer deposition (ALD) of TiO_2. The results indicated that the ALD coating significantly enhanced the water permeability and anti-fouling resistance due to increased membrane surface roughness and hydrophilicity. Rabiee et al. [246] noticed enhanced hydrophilicity in PVC/TiO_2 nanocomposite UF membranes synthesized via the phase inversion technique with different TiO_2 percentages. The hydrophilicity was increased on PVC/TiO_2, resulting in improved water flux, and upon increasing TiO_2 to more than 2 wt%, the flux rate started to decrease, which was due to the agglomeration of nanoparticles. However, improved BSA rejections of up to 98% were observed with improved anti-fouling capacity for PVC-2 wt% TiO_2 membranes. The development of anti-fouling or self-cleaning membranes is of great interest for the RO pretreatment process. However, it is worth mentioning that the parent membrane should not decrease the permeate flux and rejection while modifying the ceramic membrane surface.

In general, CM is considered a promising solution for RO pretreatment. New research should focus on new methods for CM fabrication for scaled up production in all CM configurations. Cost estimation analysis and comparison studies between CM and current

RO pretreatment technologies keep the room open for future research. The selectivity of CM can be improved by modifying the filtration layer of CM, which requires further investigations. Moreover, improving the flux and mechanical properties of CM can also be investigated using different kinds of additives. CM cleaning and regeneration procedures require detailed investigations and special studies. Due to the variety of manufacturing procedures, experimental parameters, membrane characteristics, and membrane performance, it is not easy to provide a proper comparison between CM-based materials for desalination purposes. However, to date, only alumina CM is available commercially due to its abundance, low price, and high thermal stability compared to some other ceramic materials such as zirconium oxide, silicon carbide, and titanium oxide. Table 10 summarizes the performance of selected studies on water desalination by CM.

Table 10. Summary of selected studies on water desalination by CM.

Raw Material	Fabrication Method, Modification	CM Shape	Pore Size (µm), Porosity (%)	Mechanical Strength (MPa), Contact Angle (°)	Conclusion	Ref.
Natural pozzolan	Extrusion followed by sintering at low temperature of 950 °C. Filtration layer by crossflow filtration of pozzolan powder.	Tubular	0.37 µm, 41.2%	15.36 MPa	For raw seawater filtration, turbidity rejection 98.25%, COD retention 70.77%.	[230]
Rice husk ash, amorphous membrane	Burned at 600 °C, then phase inversion (extrusion) and sintering at 1200 °C, followed by grafting with a FAS agent	Hollow fiber	1.21 µm, 54.1%	71 MPa, 157°	Tested in DCMD, water flux of 52.4 kg/m^2h and salt rejection up to 97.5%.	[247]
Rice husk ash, crystalline membrane	Burned at 1000 °C, then phase inversion (extrusion) and sintering at 1200 °C, Followed by grafting with a FAS agent	Hollow fiber	0.54 µm, 35.9%	66 MPa, 161°	Tested in DCMD, water flux of 38.2 kg/m^2h and salt rejection up to 99.9%.	[247]
Mullite–kaolinite (Clay)	Phase inversion and sintering At 1500 °C followed by FAS grafting	Hollow fiber	0.31 µm, 43%	139°	Tested in DCMD, salt rejection 99.99% and water flux 22.51 kg/m^2h.	[248]
Raw phosphate	Pressing and sintering at 1000 °C	Flat	0.26 µm, 25.6%	19.74 MPa	Water flux 697 $L/(h{\cdot}m^2{\cdot}bar)$. Tested for raw seawater, 40% reduction in SDI, 98% reduction in turbidity, 73% reduction in TOC	[233]

4.3. Hybrid Pretreatment Systems

Hybrid pretreatment systems can be defined as the combination of one or more conventional pretreatment units with one or more of membrane pretreatment (MF, UF, and NF), as depicted in Figure 8. These systems are a viable and efficient option as they utilize the strength of different units. Additionally, due to severe saltwater conditions, which increase the risk of membrane fouling, these systems are often used in commercial SWRO plants. Conventional pretreatment methods such as DAF, coagulation, and chlorination are used to provide a contaminant barrier before the water reaches membrane units [99].

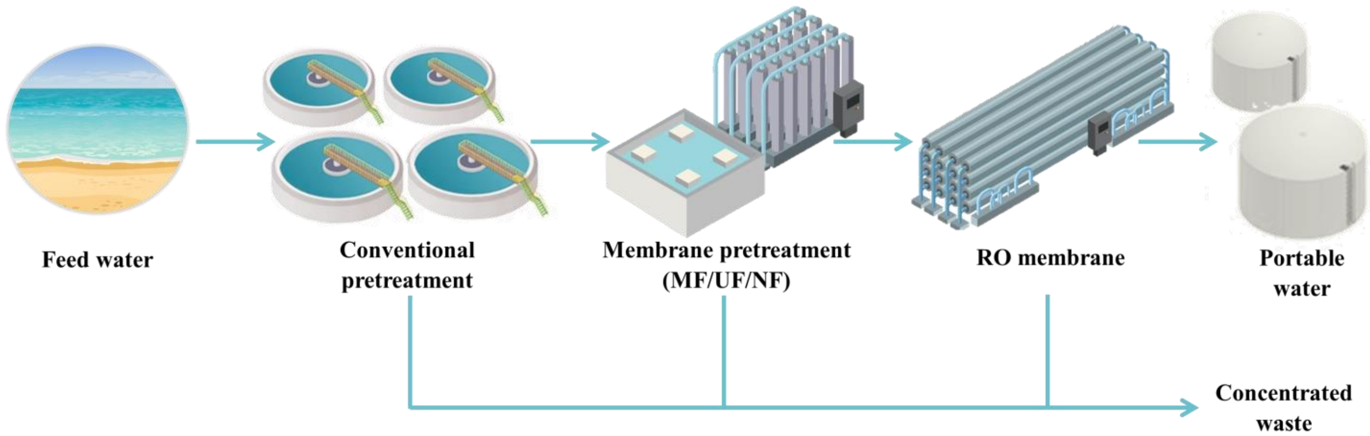

Figure 8. Typical SWRO setup using hybrid pretreatment systems.

Starting with MF membranes, Ebrahim et al. [249] conducted a study in Kuwait that demonstrated RO pretreatment design where the feed water is chemically treated with chlorine and filtered by a coarse strainer before being fed to the MF membrane. With this design, an excellent SDI value of the filtrate was observed (2.22% average value). As biofouling is considered a major industrial problem, a hybrid chlorination–MF system was evaluated by Lee et al. [250]. In their research, they reported that this hybrid system can remove several bacteria in the permeate of the MF membrane while Soo Oh et al. [251] reported a significant reduction in MF membrane fouling after the application of the ozonation pretreatment method.

UF is considered the most used membrane pretreatment in hybrid systems. Glueckstern et al. [252] tested the UF membrane performance in an SWRO system with a hybrid pretreatment method. Screen filtration, coagulation, and chlorination were applied prior to the UF membrane. This resulted in a good filtrate quality where SDI and turbidity ranged from 0.8 to 3.8 and 0.1 to 0.2 NTU, respectively. Villacorte et al. [129] reported that combining coagulation with UF membrane technology can reduce the fouling potential that is caused by harmful algal blooms. These results support the experimental study conducted by Kim et al. [253], who applied coagulation/flocculation before the DMF and UF membrane. The results showed the SDI value was 6.0 and 2.0, respectively. The Heemskerk water treatment plant, which is located in the Netherlands, utilizes integration between coagulation-sedimentation filtration and a UF system prior to RO [254]. The results showed that this integration results in superior particle elimination, which resulted in the mitigation of colloidal fouling. In addition, a recent study carried out by Monnot et al. [255] demonstrated the feasibility of utilizing granular activated carbon (GAC) pretreatment before UF to reduce its fouling potential and increase efficiency in the removal of dissolved organic carbon (DOC). In addition to GAC, powdered activated carbon (PAC) with UF were combined as a pretreatment to SWRO by Tansakul et al. [256]. The addition of PAC in the UF process enhanced the performance of UF; the UF fouling rate was reduced, and the NOM retention rate increased from 10% to 45% without and with PAC, respectively. In the same study, Tansakul et al. [256] studied the effect of utilizing a low-cost and widely available bentonite adsorbent as a conventional pretreatment to UF. However, this addition has no significant effect on UF performance. Park et al. [257] studied the combination of DAF technology with a membrane-based filtration system. The Al-Shuwaikh desalination plant in Kuwait equipped with DAF/UF systems presented SDI < 2.5 for good quality feed water and <3.5 [257]. Yang and Kim [161] studied the effect of coagulation on the performance of MF and UF for the removal of particles with two types of membranes. The results showed that the SDI_{15} of permeate from coagulation–MF and coagulation–UF were 0.75 and 1.88, respectively. While SDI_{15} for only MF membrane permeate was 3.17 and 2.76 for UF only. According to this study, MF was more efficient than UF in the enhancement of the filtration flux and turbidity removal by applying coagulation as a pretreatment method [161].

Numerous research studies have been conducted to assess the feasibility and efficiency of hybrid systems that couple NF membranes with conventional pretreatment [258]. Using NF as a pretreatment in SWRO not only improves the feed-water quality, for example, through the removal of hardness, turbidity, or microorganisms but also improves the entire desalination process [259]. NF membrane reduces the ionic salts content present in seawater, resulting in significantly reducing the osmotic pressure, and hence the RO unit can be operated at a lower pressure and subsequently with less energy along with a higher recovery rate [260]. For example, at 40 bars, the permeate flow and recovery from the conventional SWRO is only 1 l/m and 16.7%, respectively, as compared to a much higher flow of 4.8 l/m and recovery ratio of 48% using the new NF-SWRO process [260]. Park et al. [174] conducted a study aimed to minimize scale formation potential in RO membranes. They used a UF/NF/RO hybrid pilot system as a pretreatment unit to remove divalent ions from seawater. The results showed that the UF did not reject any ions because of pore size. The rejection of divalent ions by NF was in order of sulfate (>95%), magnesium (>60%), and calcium (>30%) in every rejection experiment based on a water recovery rate of (40, 50, 60, 70, and 80%). In the UF/NF/RO hybrid system, most of the divalent (>99%) and the monovalent (>97%) ions were effectively rejected with slightly increased divalent ion rejection compared to the UF/RO system [174]. In Saudi Arabia, fine and thick sand filtration media were utilized prior to NF and highly improved the feed-water quality [170]. In addition, the utilization of NF as a pretreatment in the SWRO desalination pilot plant enhanced the production of water by more than 60%, which led to a cost reduction of 30% [261]. Table 11 summarizes the research studies on hybrid systems used for RO pretreatment.

Table 11. Summary of research studies on hybrid systems used for RO pretreatment using membrane technologies coupled with conventional technologies.

Feed Water	Conventional Pretreatment	Membrane Process Pretreatment	Performance	Ref.
Chowder Bay, Sydney, Australia. Seawater Conductivity = 51.8–55.5 mS/cm	Flocculation ferric chloride ($FeCl_3$)	MF cellulose acetate 0.45 µm	Flux decline (without conventional pretreatment) = 45%	[262]
	Deep bed filtration (sand filtration and DMF)		Flux decline (after pretreatment of $FeCl_3$ flocculation) = 42% Flux decline (after pretreatment of sand filtration with in-line coagulation) = 24% Flux decline (after pretreatment of DMF (sand and anthracite) = 22%	
Kijang, Busan, South Korea Seawater Turbidity = 0.99 NTU DOC = 2.38 mg/L hydrophilic matter = 5773.2%	Coagulation $FeCl_3$	MF hollow fiber membrane (Polysulfone, polyethersulfone, polyvinylidene fluoride (PVDF)) 0.1 mm	Humic-like material was reduced from 12.7 to 1.41–2.31. Aromaticity of humic material increased by 70% of DOC	[263]
	Coagulation-adsorption $FeCl_3$ powder activated carbon (PAC) wood-based.			
Artificial seawater Na_2SO_4 = 4000 mg/L NaCl = 23,500 mg/L	Coagulation $FeCl_3$	MF 0.1 µm PVDF	Fouling index (J/J_0) = 61% for MF SDI_{15} (MF with coagulation) = 0.75 SDI_{15} (MF alone) = 3.17	[161]
		UF 0.05 µm PVDF	J/J_0 = 94% for UF SDI_{15} (UF with coagulation) = 1.84 SDI_{15} (UF alone) = 2.76	
Red Sea water (Saudi Arabia) and isolated BOM Conductivity = 59.0–60.1 mS/cm	Coagulation $FeCl_3$	UF PESM MWCO = 100 kDa and 50 kDa.	Transform transparent exopolymer particles (TEP) from (0.1–0.4) into TEP (>0.4)	[264]

Table 11. *Cont.*

Feed Water	Conventional Pretreatment	Membrane Process Pretreatment	Performance	Ref.
Raw seawater close to the SEAHERO desalination plant	Coagulation $FeCl_3 \cdot 6H_2O$	UF Regenerated cellulose MWCO =100 kDa.	Turbidity removal efficiencies (UF) > 99% Turbidity (UF permeate) = 0.05 NTU UV_{254} removal efficiency (UF) increased from 16% to 32%	[253]
Seawater southern shore of Barcelona (Spain), Conductivity = 1 56 ± 1 mS/cm SDI75% 20 ± 10% min^{-1}	DAF coagulation ($FeCl_3$) flocculation by axial mechanical mixing flotation	UF Hollow fiber PVDF 0.02 µm pore size	Biopolymers were partially removed in raw seawater by both pretreatments tested (41%) removal in UF permeate Low molecular weight (LMW) removal (UF) = 6% Humics removal (UF) = 8%	[265]
Seawater of Gibraltar conductivity of 48.7 mS/cm at 20 °C and a Silt Density Index (SDI) = 13–15	Coagulation $FeCl_3$	UF Hollow fiber Cellulosic derivative 100 kDa	Steady-state was maintained over 80 days Maximum flux = 150 L/h·m^2 at 20 °C.	[45]
Jeddah Port on the Red Sea in Saudi Arabia seawater TDS = 42,000 ppm Turbidity 0.2–1.1 NTU	Coagulation $FeCl_3$	UF	SDI = 2.2, which was 2 units better than the conventional pretreatment	[266]
Gulf seawater TDS = 44,046 ppm Conductivity = 60,000 µs/cm	Dual-media filtered Fine sand filter 5-micron cartridge filter	NF	Reduced the levels of Cl^-, Na^+, and K^+ by 40.3% each and overall seawater TDS by 57.7%	[260]

In addition to the polymeric membranes (MF, UF, and NF) discussed in the previous section, ceramic membranes have been recently employed in many applications [267,268], to replace conventional methods [269], as previously discussed. Hybrid ceramic technologies have gained attention in recent years as a potential solution for various applications. These technologies combine the advantages of ceramics with those of other technologies such as conventional methods. As mentioned in the previous section, in the study by Cui et al. [229], a hybrid ceramic membrane was tested in a seawater desalination pilot plant using different configurations, as pretreatment to SWRO. Additionally, the effectiveness of using a hybrid ceramic adsorption filter (CAF) and UF pretreatment in reducing RO fouling was studied by Nakano et al. [270]. The results showed that the CAF could eliminate a fraction of the dissolved organic matter that escaped from the UF membrane, thus reducing RO membrane fouling. In addition, the results showed that the use of CAF pretreatment reduces the amount of biofilm formed on the RO membrane, which delays the reduction in RO membrane permeability and the membrane cleaning frequency. These two factors could reduce the operating costs of seawater desalination plants and enhance capacity utilization, leading to lower costs of water production [270].

The water cost is considered one of the important factors in the selection of water desalination and pretreatment technologies. The pretreatment technology's economic analysis based on total water cost indicates that the membrane pretreatment system is less expensive than the conventional pretreatment system by 3–4% [63]. The total water cost for facilities using a conventional system is USD 0.59/m^3 and for facilities using membrane systems, it is USD 0.55/m^3. However, when considering capital costs, membrane systems prove to be more expensive than conventional systems by 2%. The RO membrane requires two cleanings per year whereas the conventional systems require nine cleanings per year, which dramatically contribute to the costs of the plant operation [63]. Hybrid technologies have the potential to reduce costs as they can combine the advantages of different systems while minimizing their drawbacks. However, it is important to note that the cost of hybrid pretreatment depends on the technologies employed and other factors such as local regulations. Unfortunately, the water cost using a hybrid pretreatment system has not been well studied, and further investigation on this aspect is a must to understand the cost-effectiveness of the hybrid approach.

In conclusion, hybrid pretreatment processes, combining conventional and membrane methods, could improve the performance of the SWRO plants. However, further research including the performance, environmental impact, and economic feasibility of these new systems is required. In addition, the total water production cost should consider the waste discharge cost and should not be neglected. A hybrid ceramic membrane and UF may be a viable option for RO pretreatment. However, further research is needed to investigate the potential integration of other technologies, such as adsorption and advanced oxidation, to improve the performance of these hybrid systems. From the previous reviewed studies, to make a clear choice of pretreatment techniques, it is important to extensively investigate the potential of hybrid pretreatment systems as opposed to standalone processes. However, such systems still need more pilot studies to commercialize a novel combination for specific feed quality, and intense study on the cost of the suggested system.

5. Future Recommendations

Despite the importance of RO pretreatment technologies in improving the efficiency and lifespan of RO systems by reducing the risk of membrane fouling, scaling, and chemical degradation, they still have some shortcomings that require further development. The challenges associated with RO pretreatment include the high cost of conventional pretreatment systems, the difficulty of controlling biofouling, and the production of large volumes of wastewater.

One potential solution for effective RO pretreatment is the use of hybrid systems that combine multiple pretreatment technologies to achieve higher water recovery rates and reduce the amount of wastewater produced. The use of ceramic membranes in hybrid systems could be a valuable solution to address fouling concerns, particularly when sustainability is considered. Ceramic membranes have high thermal and chemical stability, making them more resistant to fouling than polymeric membranes.

In regions such as Gulf countries where biofouling is a significant concern due to warm waters, high nutrient levels, and oil and gas operations, a sustainable framework for ceramic membrane-based hybrid systems in RO pretreatment could be developed as ceramic membranes are less susceptible to microbial growth (Figure 9). This framework should consider the economic, environmental, and social impacts of the system.

A combination of methods such as adsorption and carbon dioxide (CO_2) with a low amount of antiscalants could be an effective strategy for the implementation of a sustainable approach for RO pretreatment. After conducting a thorough assessment of the source water to identify potential contaminants and fouling, the removal of a wide range of impurities, such as dissolved organic matter, colloids, and microorganisms could be initially conducted using a natural process such as adsorption [271–274]. The challenges in this step should focus on modifying the adsorbent surfaces to increase the adsorption capacity, which might also reduce chemical consumption. Careful consideration of the regeneration of adsorbents using sustainable techniques such as electrochemical treatment while recovering valuable products, such as metals or other compounds, would contribute to economic and environmental benefits [275,276]. Other sustainable technologies, such as biofiltration, membrane bioreactors, or advanced oxidation processes, can be integrated if further purification is needed.

Next, the use of CO_2 as a sustainable approach to replace or reduce the amount of antiscalants [137], which can also act as a nutrient for bacteria, could be effective, not only for ceramic membranes but also for the overall RO system, as it reduces the risk of acid corrosion, which can damage equipment and shorten the lifetime of membranes. The idea of using CO_2 as a waste while reducing greenhouse emissions and treatment costs to potentially reduce environmental pollutants could be studied and considered.

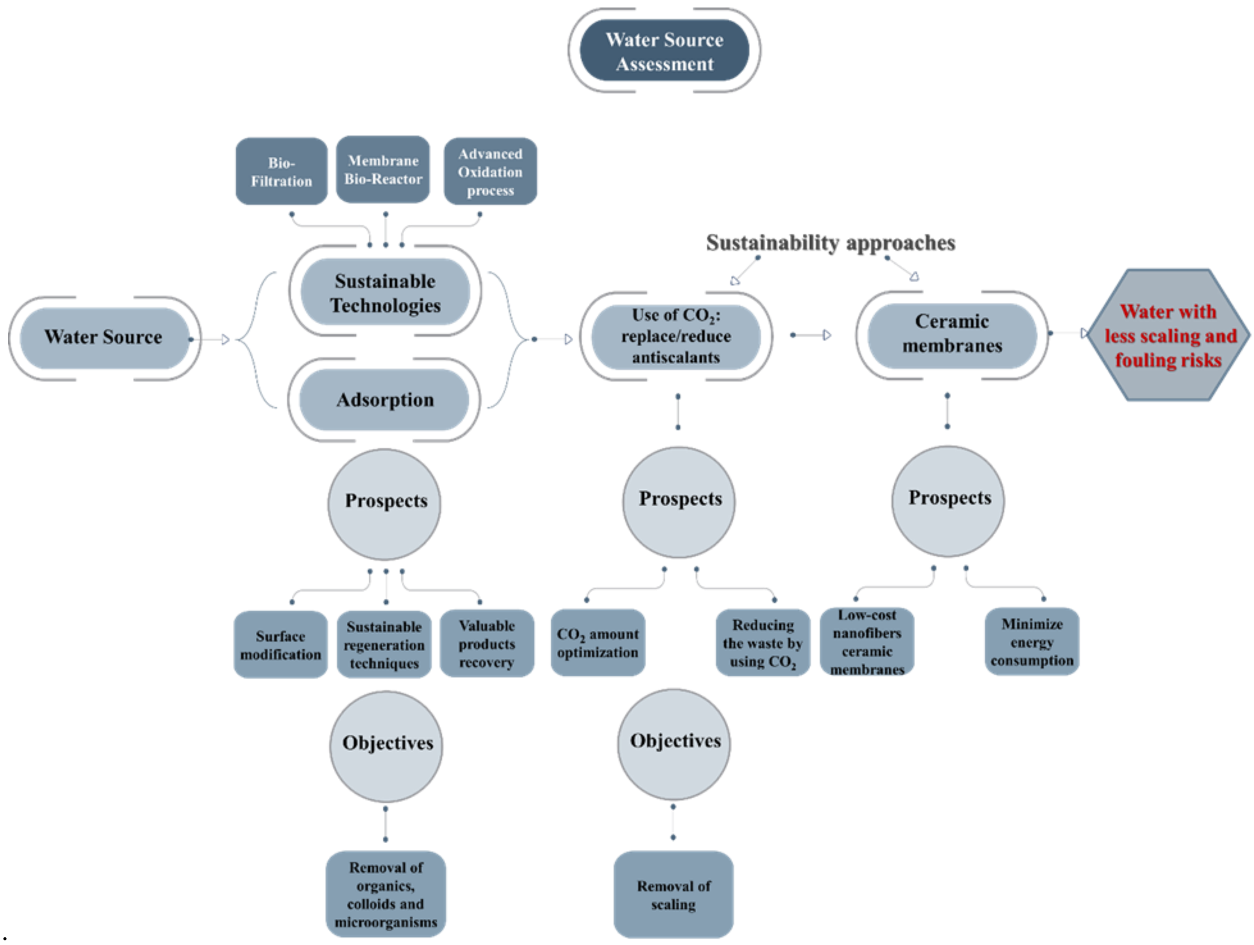

Figure 9. A suggested framework for effective hybrid RO pretreatment with a focus on Gulf countries.

The selection of ceramic membrane types, such as nanofibers or hybrid configuration ceramic membranes, as well as the optimization of the system design to minimize energy consumption and waste generation, should be considered. Additionally, regular cleaning and maintenance of the membranes can help prevent biofouling and extend their lifetime. Furthermore, incorporating renewable energy sources such as solar or wind power can help reduce the environmental impact of the system.

A pilot study is recommended to overcome the difficulties in scaling ceramic systems from laboratory to industrial scale.

Although the brine generation from the ceramic membrane is less than with other membranes, it can be a concern in terms of sustainability. Therefore, it is important to conduct an effective assessment to suggest a treatment for the brine if needed before being discharged to the environment. By following this framework, sustainable, energy-efficient, and effective solutions can be recommended for pretreatment in desalination systems.

6. Conclusions

RO pretreatment is crucial for the proper operation of an RO plant. It helps reduce the risk of fouling on the RO membrane, resulting in less frequent cleaning and lower costs for membrane replacement. This review has highlighted that conventional pretreatment technologies are effective in preventing fouling and are widely utilized for their cost-effectiveness. However, the current technologies also have significant drawbacks, including the risk of biofouling, chemical consumption, and carryover. Non-conventional technologies, specifically membrane-based technologies, have emerged as promising alternatives. MF, UF, and NF membrane pretreatment techniques have been shown to be effective in preventing RO fouling while having low energy consumption, compared to traditional pretreatment methods.

Although polymeric membranes can offer benefits such as low cost and protection for the RO membrane from fouling, thus extending its lifespan, there are some drawbacks to consider such as susceptibility to biofouling, chemical attack, and physical deterioration, which can require costly repairs or replacement. In this study, it is shown that ceramic membranes have certain advantages over polymeric membranes, such as higher mechanical strength, chemical and thermal stability, and long lifespan, which makes them resistant to biofouling. However, ceramic membranes are also more expensive and involve a relatively more complex fabrication process. The findings of this study suggest that the major challenges to enhance the pretreatment system using ceramic membranes are ensuring proper pretreatment and the development of low-cost and efficient membranes. To address these challenges, surface modification of ceramic materials, development of hybrid configurations, and optimization of ceramic-based pretreatment processes are necessary to achieve the highest possible efficiency and cost-effectiveness.

Integrated hybrid systems that incorporate conventional pretreatment with membrane processes have been found to be effective in reducing fouling and improving the overall performance of the RO system. Combining different types of membranes can achieve higher levels of purification and water recovery, thus reducing the amount of generated brine. Ceramic membrane-based integrated systems can effectively address fouling concerns but may be relatively costly when scaling up. Despite these challenges, ceramic membrane-based hybrid systems can still be an effective solution for addressing fouling concerns in RO pretreatment, particularly when sustainability is considered. The findings suggest that a case-by-case evaluation of the potential advantages/disadvantages of these systems is necessary, considering the specific water quality and treatment goals. A possible future direction for membrane pretreatment is the development of a sustainable framework for ceramic membrane-based hybrid systems in RO pretreatment (Figure 9). This is especially important in regions such as Gulf countries where biofouling arises due to warm waters, high nutrient levels, and oil and gas operations.

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