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REVERSE OSMOSIS PRETREATMENT TECHNOLOGIES AND FUTURE TRENDS: A COMPREHENSIVE REVIEW

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Abstract

Recent progress in reverse osmosis (RO) technology is not limited to RO membrane materials, module designs and RO process optimization. It involves prior feed treatment which directly impacts RO system performance. The ongoing challenges of membrane fouling in RO membranes can be addressed by increasing the operational efficiency through the use of correct pretreatment options which can mitigate organic and inorganic fouling by selectively rejecting contaminants prior to reaching the RO unit.

Highly polluted water resources have put critical stress on the existing conventional pretreatment techniques, whereby membrane pretreatment has emerged as a promising alternative. This paper provides an overview of the development and current trends in conventional and non-conventional RO pretreatment techniques whereby the techniques are critically reviewed to inform readers of potential improvements in such areas. This paper addresses the major drawbacks of conventional pretreatment methods which have necessitated the use of membrane pretreatment techniques. Special attention is given to microfiltration, ultrafiltration and nanofiltration methods and their development in terms of advanced membrane materials based on ceramics and self-cleaning membranes. Studies from laboratory scale standalone systems, pilot scale and large scale integrated systems for performance, cost and ecological analysis have been reviewed to familiarize readers with the many factors which need to be analyzed for selection of the appropriate pretreatment method(s). The critical review in this paper will help researchers focus more on the areas which have room for further development for cost-effective and advanced RO pretreatment techniques.

Keywords: Reverse osmosis; pretreatment; membranes; desalination

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1. Introduction

Water scarcity has become a global, critical issue, whereby many countries of the Middle East, South East Asia and North Africa are now classified as water-stressed regions [1]. Global water consumption has increased considerably, leading to a massive increase in the proportion of the world population living in water stressed areas from 14% in the 1900's to about 58% in the 2000's [2]. According to the World Health Organization (WHO), around 2.1 billion people in the world lack safe drinking water, whereas by 2025, half of the world's population are predicted to be living in water-stressed areas [3]. Moreover, scarcity of fresh water is also causing a dramatic impact on agricultural developments. These alarming facts have called upon extensive efforts to address the lack of safe drinking water by developing alternative means for fresh water resources. One method is to utilize the abundant seawater through desalination. Desalination has come up as an emerging technology to supplement diminishing freshwater sources, and seems a promising source for future fresh water needs. The two main categories of desalination are thermal and membrane processes. Thermal desalination separates salt from water through evaporation and condensation, whereas membrane desalination uses a membrane through which water diffuses while salts are retained on the feed side of the membrane [4]

Large scale desalination units began to be installed first in the Middle East in the 1950's [5]. According to the International Energy Agency (IEA), today, about 58% of the world's total desalination capacity lies in the Middle East and North Africa combined (Figure 1a), while globally, about 90 million m^3 of water is desalinated each day. Thermal desalination plants dominate the desalination industry in the Middle East, constituting about 70% of overall desalination operation in the Gulf region [6]. Nevertheless, thermal desalination is more energy intensive due to large amounts of energy required for heating water and high plant maintenance costs compared to membrane processes such as reverse osmosis (RO), where most energy required is for pumping. Therefore, RO desalination installations have been gradually increasing, comprising about 80% of the total desalination plants today worldwide. This number is increasing as the technology is constantly improving, both in terms of cost and energy efficiency [5, 7]. Figure 1b shows the distribution of desalination production capacity for different processes. Membrane processes such as RO and electrodialysis (ED) constitute almost 50% of the capacity, while the rest is dominated by multi-stage flash (MSF) thermal desalination. Other distillation processes include multiple effect distillation (MED) and vacuum compression (VC). However, in terms of number of installations, the number of global desalination plants is dominated by RO, whereas thermal desalination plants constitute only about 20% of the total production capacity [8]. When deciding to commission a new desalination facility, the first decision to be made is which process to use for desalination. The answer depends on several variables, including the incoming feed water salinity and quality, product requirements, and site-specific factors, such as available energy, labor cost and land area [9]. Nevertheless, RO has stepped up predominantly due to its lower specific investment costs, lower energy consumption (4-5 KWh_{el}/m^3 compared to 13 KWh_{el}/m^3 for MSF) and, most importantly, the potential for improvement in membrane materials, pretreatment technologies and system designs leading to further cost reductions [8]. RO technology is expected to predominate in the coming decades due to it lower unit water production costs in contrast to thermal desalination [10, 11]. Nevertheless, there exists an urgent need to further work towards more sustainable and efficient RO practices with much lower water production costs.

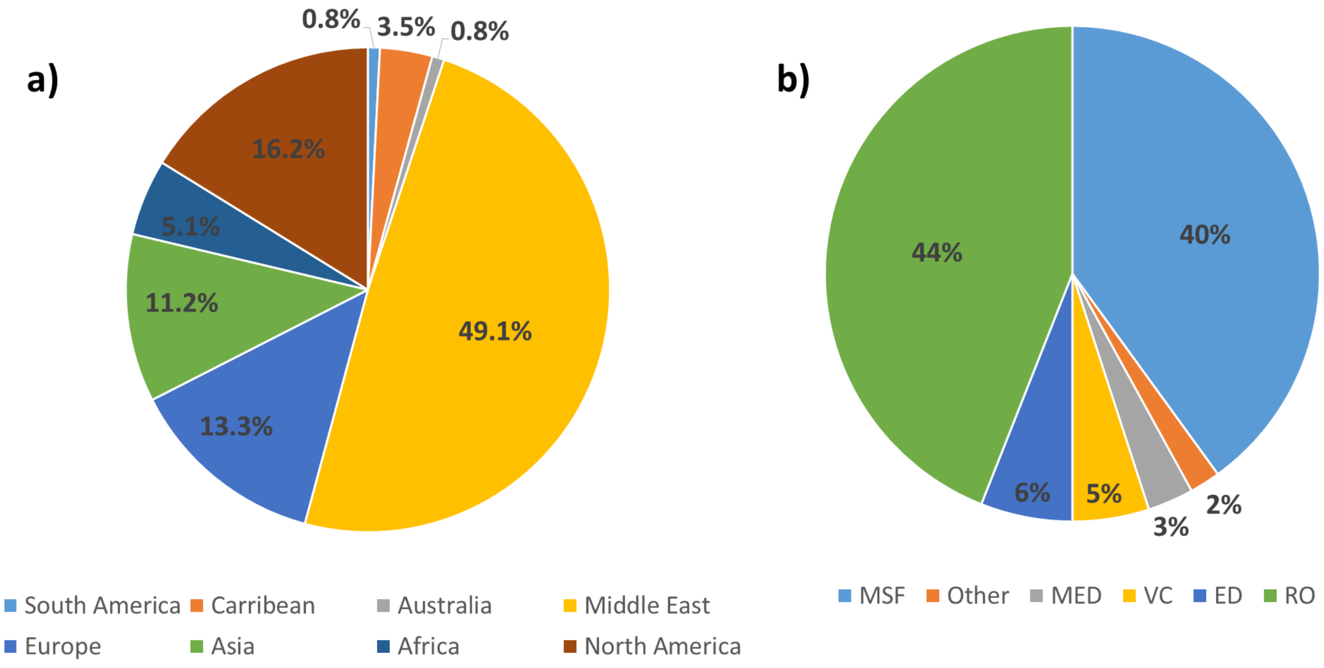

Figure 1: (a) Worldwide desalination capacity by region (Adapted from Ref. [12]) (b) Distribution of global desalination production capacity by process technology, Reproduced with permission from Ref, [5]. Copyright © 2009, Elsevier.

Besides investing in improving existing membrane materials for increased energy efficiency, future research should also focus on improving existing RO pretreatment technologies and new strategies. Pretreatment is critical in RO because it directly effects fouling of the RO membranes. Fouling is the buildup of undesired deposits either at the membrane’s surface or within the membrane structure [13]. Fouled membranes adds to increased operating and maintenance costs due to required cleaning, higher feed pressures needed to maintain water flux and lowered membrane lifetime. Figure 2 depicts a typical sea water RO (SWRO) plant cost consumption [8] for which membrane replacement accounts for around 13% of the total cost. Maintenance includes membrane cleaning which adds to the total energy cost and use of cleaning chemicals is in itself costly and themselves present a potential environmental hazard. Additionally, fouling can result in reduced permeate water quality and decreased selectivity, thereby directly impacting the water production [14, 15]. Nevertheless, one strategy for controlling membrane fouling is the use of correct pretreatment technology/technologies. Following pretreatment, the high-quality feed water containing less foulants can increase membrane lifetime and reduce the affinity of foulants to the membrane's surface.

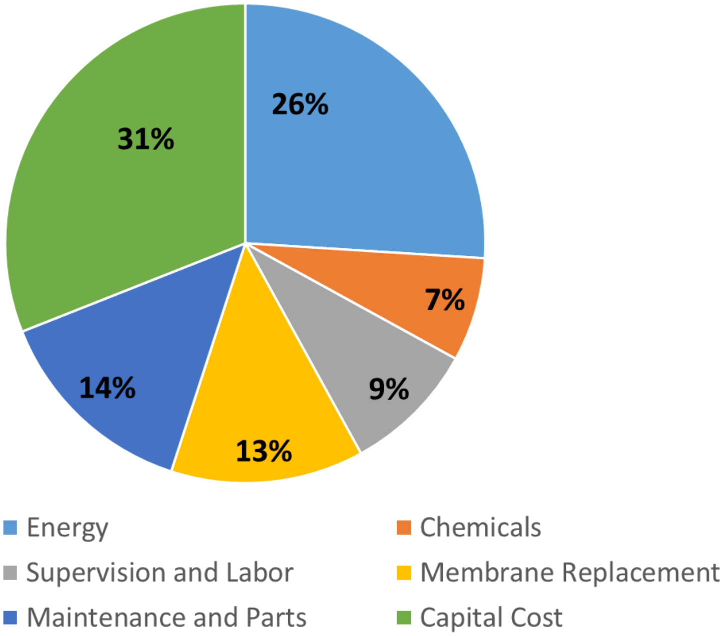

Figure 2: Typical SWRO plant cost consumption (Adapted from [8]).

Seawater characteristics are very complex. Seawater salinity ranges from 30,000 mg/L TDS to even above 40,000 mg/L TDS depending upon the region [16]. Besides dissolved salts, it contains several different foulants ranging from suspended solids, colloids, microorganisms and a variety of organic matter [17], all of which can substantially degrade RO membrane performance and increase costs [18].

It is imperative to understand the feed water quality to successfully implement pre-treatment operations. An in-depth analysis of the feed water will help in identifying the contaminants present which can cause severe RO membrane fouling. Membrane fouling is a major concern which requires special attention through the use of proper pretreatment of feed water. A cake layer may form on the RO membrane's surface by the coagulation of suspended particles causing a drop in permeate flux, while dissolved organics can further intensify fouling by interacting with the membrane [19, 20]. A turbidity value of less than 0.2 nephelometric turbidity unit (NTU) and a silt density index (SDI) of less than 3 is a good indication of low levels of suspended solids, and these values are often required to be monitored and controlled for constant RO membrane performance. SDI is indicative of the amount of submicron particulates present in water while turbidity is a measure of water clarity [21]. However colloidal fouling through the deposition of metal oxides, proteins, and clay, which may create a colloidal slime on the membrane's surface, is beyond the detection through Turbidity and SDI values [22]. Anti-foulants used specifically for colloidal fouling prevent the colloidal particles from aggregating on the membrane's surface [23]. A high total dissolved solids (TDS) can cause natural crystallization of the dissolved salts, thus causing scaling to occur. However, the use of advanced anti-scalants has considerably lowered the scaling problem [24]. Another important type of fouling is biofouling, where a buildup of microbes on the membrane surface results in the formation of a biofilm [15] which severely deteriorates the performance of RO membranes in terms of permeate flow and selectivity. In fact, as microbes are present in most waste or natural water sources, biofouling is known to contribute to more than 45% of all membrane fouling.

To lower the fouling propensity of RO membranes, the necessity for an appropriate pretreatment method is inevitable. This, in turn, will reduce costs related to membrane cleaning and increase the membrane's lifetime. Likewise, lower pressures will be required to sustain the RO process resulting in lowered energy consumption. Menachem et al. [25], in their review "The Future of Seawater Desalination: Energy, Technology, and the Environment", stressed the importance of focusing on pretreatment methodologies in order to improve the energy efficiency of SWRO desalination. Numerous investigations and research studies have established that mainstream inefficiency in RO systems is due to improper feed pretreatment [26]. Therefore, a comprehensive review in this critical area addressing different pretreatment technologies is essential. This review paper focuses on different conventional, as well as non-conventional methods for seawater pretreatment. However, more emphasis will be given to emerging non-conventional membrane pretreatment techniques which have higher separation efficiency. The latest trends pertaining to self-cleaning, fibrous and inorganic membranes in membrane pretreatment will provide further insight into future potential. Moreover, the performance of different hybrid systems, whereby RO is coupled with various pretreatment technologies, will be analyzed in terms of cost, efficiency and carbon footprint. This critical review will help researchers focus more on the RO pretreatment methods which have room for further development.

2. RO Pretreatment Technologies

Pretreatment helps in altering the sea water characteristics and improve SWRO performance by providing the constant feed water quality required for efficient RO plant operation. To date, many conventional and non-conventional RO pretreatment methods have been utilized. The prevalent conventional pretreatment techniques include coagulation/flocculation, acidification, disinfection, dissolved air floatation (DAF), scale inhibition, hardness removal by lime, UV radiation, particulate removal by coarse strainer and media filtration. However, in recent years, non-conventional methods based on membrane technology have been investigated due to their superior separation efficiencies. Hence a very significant trend includes the use of membrane-based pretreatment technologies to improve the performance in SWRO. Different membrane processes are utilized for different particulate separation: microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). Figure 3a highlights the proficiency of different membrane pretreatment processes in removing substances of various sizes. Often a combination of pretreatment methods are utilized, depending upon the incoming feed water quality [27, 28]. Figure 4 is a schematic of such a hybrid system, while Table 1 highlights common seawater quality parameters that are essential to investigate before concluding on the selection of pretreatment required.

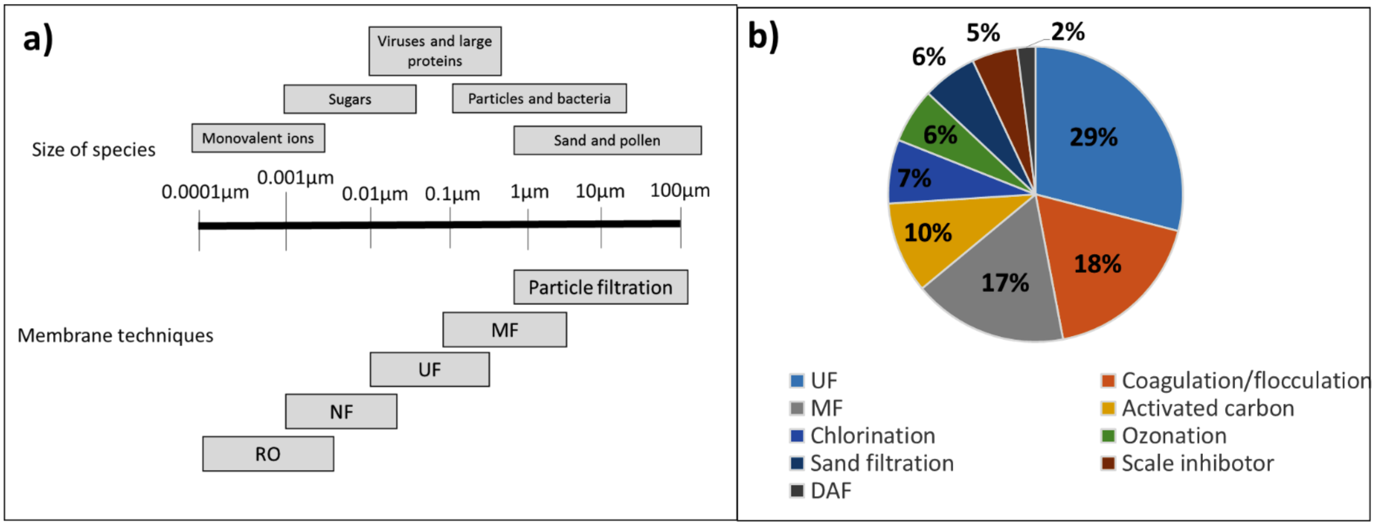

Figure 3 (a) Membrane techniques capable of removing different sizes of contaminants from seawater (b) Commonly studied RO pretreatment technologies in the last decade. Reproduced with permission from [29], Copyright © 2017, Elsevier.

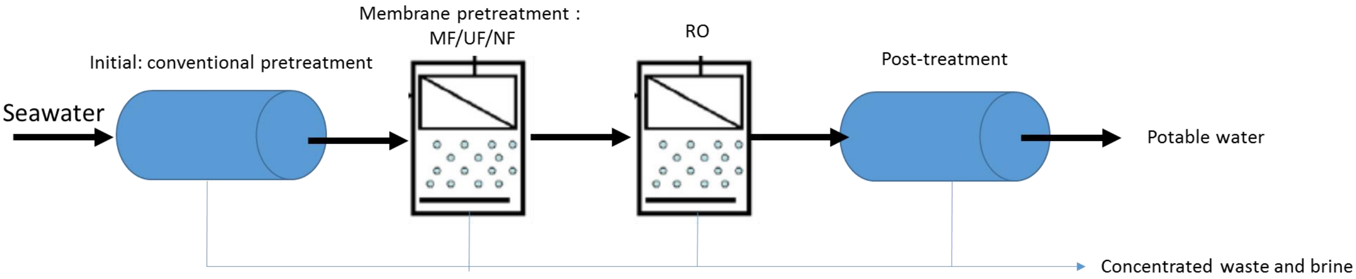

Figure 4: Examples of typical SWRO setup using more than one pretreatment technique. Reproduced with permission from [30], Copyright © 2015, Elsevier.

Table 1: Seawater quality characterization for pretreatment. Reproduced with permission from [31]. Copyright © 2010, Elsevier.

Parameter	Pretreatment consideration
Turbidity (NTU)	High levels > 0.1 mg/L may lead to fouled membranes. Values > 50 NTU usually requires DAF and filtration.
TOC (mg/l)	High contents > 2 mg/L may lead to organic or biofouling.
SDI$_{15}$	Pretreatment is a must for SDI>4.
TSS (mg/l)	The parameter assesses the amount of residuals. It does not correlate well with turbidity > 5 NTU.

Iron (mg/l)	State of iron is important. In reduced forms, ≤ 2mg/l is tolerable for RO membranes while in oxidized forms, > 0.05mg/l is detrimental to performance.
Manganese (mg/l)	State of manganese is important. In reduced forms, ≤ 0.1mg/l is tolerable for RO membranes while in oxidized forms, > 0.02mg/l is detrimental to performance.
Silica (mg/l)	Concentrations > 20 mg/L causes accelerated fouling.
Chlorine (mg/l)	Concentrations > 0.01 mg/L causes RO membrane damage.
Temperature	Intake temperature is critical. T ≤ 12 °C causes increase in unit energy use. T ≥ 35 °C can lead to enhanced mineral scaling and biofouling. T > 45 °C may cause permanent damage to RO membranes.
Oil	Concentrations > 0.02 mg/L causes accelerated organic fouling
pH	For pH < 4 and pH >11, long term exposure will case RO membrane damage.

Pretreatment based on conventional processes are quite popular. However, as can be seen from Figure 3b, membrane based processes, such MF and UF, have been of enormous research interest in the past decade [29]. Nevertheless, there is definitely a pressing need to go for state-of-the-art membrane pretreatment techniques replacing the conventional ones.

2.1 Conventional Pretreatment Techniques

Conventional pre-screening devices, such as coarse and fine meshes in the range of 1-100 mm are usually used to sieve large debris. However, they are not proficient in removing algae, bacteria and other microbes which have a much smaller size than the mesh [32]. Sedimentation is another physical pretreatment method which allows relatively large particles, which are denser than water to settle at the bottom of the sedimentation tank. This process increases the clarity of the feed water by removing large impurities. Often sedimentation is preceded by coagulation/flocculation and followed by media filtration [33]. Microbes and organics require advanced physical and chemical pretreatments, as reviewed below.

2.1.1 Coagulation- flocculation

Suspended particles which are small enough for Brownian forces to overcome gravitational forces cannot be removed through gravity driven sedimentation alone. Therefore, coagulant chemicals are often added to enhance particulate and organic matter removal. Their role is to bring together small particles together which can form heavier, larger particles for easier removal from feed water by either sedimentation or filtration. Coagulant mechanisms of action typically involve reduction or removal of charges from the surface of colloids, lowering repulsive interactions, allowing particles to bind together. Examples of common coagulants include aluminum sulfate (alum), ferric sulfate and ferric chloride [29, 34]. Tabatabai et al. [35] studied the effect of coagulation on algal organic matter (AOM) in seawater using ferric chloride, with an effective dosage of >1 mg Fe/L, in combination with ultrafiltration. They concluded that the fouling potential of the membranes reduced substantially together with an added advantage of reduced compressibility of the cake/gel layer formed at the ultrafiltration membrane surface. The adsorption of biopolymers to iron hydroxide resulted in iron-biopolymer aggregates which rendered a lower flux-dependency of AOM fouling, resulting in linear development of pressure in filtration tests at constant flux. Peiris et al. [36] used polyaluminum as a coagulant to reduce fouling by humic substances (HS), protein-like and colloidal matters, while Duan et al. [37] concluded that the use of activated carbon (AC) shortly before the addition of metal salt coagulant provides better efficiency for humic acid adsorption in saline water. The enhanced adsorption was due to the reduced electrostatic repulsion between the HS and AC at high salinities, as well as chemical bonding between the functional groups. However, the adsorption strongly depended on the coagulant dose, solution pH and the sequence of AC and HS addition.

There are two types of coagulation which have been extensively studied, chemical coagulation and electrocoagulation [38-40]. In chemical coagulation, high energy mixing is used to ensure full mixing of coagulants to take advantage of the formation of microflocs, whilst in in electrocoagulation, water is passed over metallic electrodes. When electricity is applied to these electrodes, the metal goes from its neutral state to its charged state, which causes charged metal coagulants in water to bond with the colloids and particulates. The electrode needs to be replaced periodically as per consumption. Usually flocculation follows coagulation, whereby slower mixing of microflocs form visible particles to be removed later by sedimentation or filtration [29]. Recently, electrocoagulation has attracted much attention It has high potential for mitigating organic and biofouling by removing dissolved organic matter and microorganisms in seawater. Hakizimana et al. [41] studied the effect of electrocoagulation using aluminum electrodes for the removal of organic matter from seawater. In addition, disinfection ability and total hardness were monitored. Their study showed that a high current density and low pH of the solution effectively removed the dissolved organic matter by 70.8% with a complete removal of microorganisms. However, there was practically no real effect on the total hardness and thus the process proved weak for softening of seawater. Sadeddin et al. [42] showed that the electrocoagulation efficiencies can reach up to more than 99% for total suspended solids (TSS) removal. The efficiency was increased by increasing the electric current up to 2.5 A, as well as by increasing the residence time. However, the operating costs associated with electrocoagulation are usually high, limiting its applicability on a large scale.

Coagulation is by far one of the most prevalent methods for the removal of aqueous particulates and colloidal foulants. The Fujairah desalination hybrid plant commissioned in 2003 with a production capacity of 454,000 m^3/d (170,500 m^3/d from RO production) uses 5 mg/L of ferric chloride which is mixed with the incoming seawater in coagulant tanks prior to filtration [43]. The 13.3 million gallons per day (MGD) SWRO plant in Saudia Arabia for Yanbu Industrial city also uses ferric chloride in their inline coagulation and flocculation unit for the inhibition of biological fouling [44]. The addition of this inorganic coagulant also enhances the performance of the following dual media filtration. Usually, an acid such as H_2SO_4 or HCl is added together with the coagulant to reduce the feed water pH, enhancing the coagulation step and preventing the formation of calcium carbonate scaling. Lower pH helps the inhibition of hydrolysis of the RO cellulose acetate membrane [44]. Inorganic coagulant dosage is in the range of 5–30 mg/L, while polymers usually require smaller doses of about 0.2–1 mg/L [7]. However, these synthetic polymers are deemed toxic due to the carcinogenetic potential of their monomers. This raises ecological and occupational safety concerns pertaining to their synthesis [45].

Coagulation is also one of the most employed and documented techniques for arsenic removal from seawater [46]. Many coagulants including ferric chloride [47] and alum [48], have been extensively studied for this purpose. pH plays a critical role here, as it determines the chemical state of arsenic, in which arsenate is more efficiently removed compared to arsenite. $Al_2(SO_4)_3$, and $FeCl_3$ are the most effective for pH below 7.6 [49]. However, at pH values higher than 7.6, $FeCl_3$ outperforms $Al_2(SO_4)_3$. Dedicated case studies for arsenic removal through coagulation are available for further reading, such as the ones written by Ana María Sancha [50] and Wickramasinghe et al. [51]. Coagulation is effective in removing other heavy metals such as manganese. $AlCl_3$ was reported to reduce Mn(II) concentration by 99.83% for an initial manganese concentration of 1085 mg/l. Often the removal is enhanced by K_2MnO_4 oxidation [52].

2.1.2 Media Filtration

Coagulation-flocculation often fails to remove 100% of suspended impurities. Media filtration can be effective in the removal of remaining impurities by infiltrating it downward through a bed of porous, granular material, as in granular media filtration (GMF). As the feed water passes through the filter bed, the suspended particles adsorb onto the surface of the individual media grains and become trapped within the pores of the filter media. Conventional packed-bed filters using different granular media [29], such as gravel, sand, diatomaceous earth, sponge, cotton, AC and anthracite possessing different sizes, have the advantage of being able to be regenerated through hydraulic backwashing [53, 54]. For a constant feed water quality, these granular media filters are effective in removing particles significantly larger than a few micrometers or smaller than 0.1 µm. Key parameters include media type, surface charge, size, and geometry of both the contaminant particles and the media particles [7]. Often, more than one type of medium is used, such as those in dual media filtration (DMF). Dual media filters usually comprise of 1.0-2.0 m sand covered by 0.4 to 0.8 m of anthracite. They are more effective than single medium filtration for the removal of soluble organics. Often, anthracite is replaced by GAC for the removal of high levels of organics [31]. AC is one of the most widely employed media for commercial filtration. It can effectively remove free chlorine, which may be persistent after a chlorination pretreatment step [29]. If the feed water is cold, usually below 15 °C, with a high organic content, then GAC is a viable option instead of anthracite because the biofiltration removal efficiency would otherwise be hindered by the low temperature [31]. Accordingly, tri-media filters may be employed for harsh intakes containing fine silt or algal blooms for improving coarse-to-fine filtration [55].

Bonnelye et al. [53] reported case studies of different SWRO pretreatment options for two open intakes: Gulf of Oman (Indian ocean) and the Persian Gulf. Depending upon the feed water quality, direct media filtration was studied in either one or two stages using anthracite, pumice, sand and garnet media with different sizes, shapes and densities. For the Gulf of Oman, single stage dual filtration rendered an SDI<3.3 for raw water with SDI of <15 while for the Persian Gulf, double filtration was used with two coagulation injections for worst quality water with an average SDI of 21.7 as shown in Figure 5.

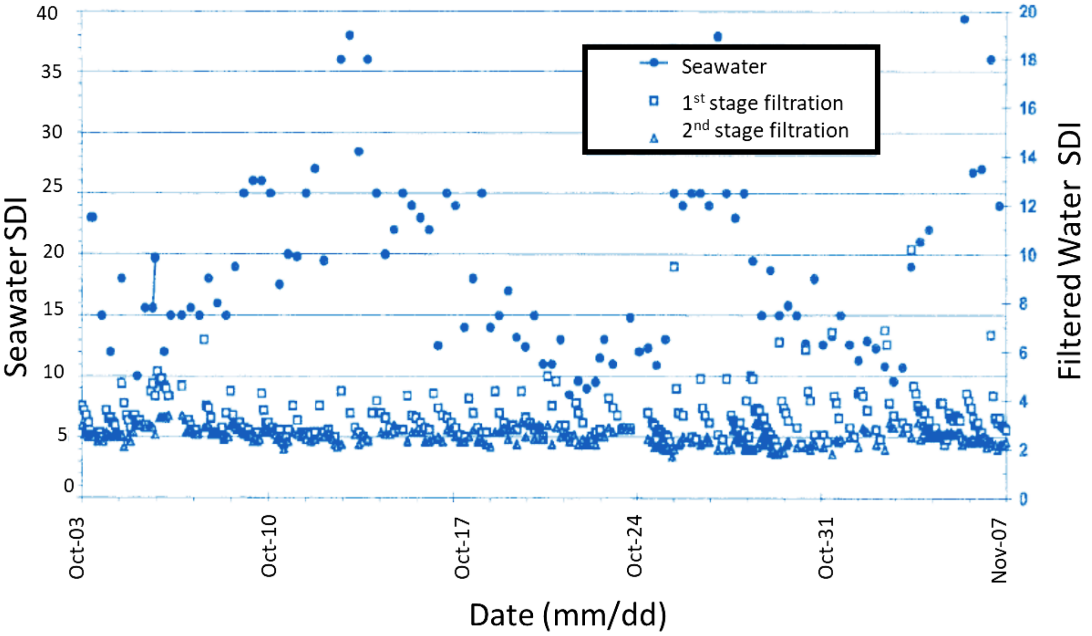

Figure 5: SDI values in raw water after each dual media filtration step. Reproduced with permission from [53], Copyright © 2004, Elsevier.

Gravity driven filtration usually use open configurations with filtration beds open to the atmosphere, while closed configurations usually utilize pressure for driving the water through the beds [56]. Though open atmosphere configurations might sound the most economical option, the pressurized media filtration dominates in RO pretreatment where it can reduce SDI by a factor of 2 and produce permeate water with 0.1 NTU [5, 53]. Jeong et al. [57] reported a parametric study on the monitoring of DMF by using DOC and organic fractions and using DMF in the biofiltration mode for the Perth seawater desalination plant. DMF was used under pressure to ensure longer runs. It consisted of a 0.3mm effective layer of sand and a 1.6mm effective layer of anthracite. The filtered samples were collected at different time intervals of 0 h, 1 h, 4 h, 8 h, 12 h, 18 h, 24 h and 30 h. Low adenosine tri-phosphate (ATP) values of 2.9 -14.7 nmol/L during a stable operational period of 5–24 h was observed, which is indicative of low biomass or biological activity. A detailed study showed that optimization of backwashing was essential in addition to the DMF parameters for the reduction of biological fouling. Their study was a step forward in operating DMF for enhanced biofouling inhibition. The Fujairah SWRO plant [43] also utilizes dual media filters but in the open atmosphere fed by gravity, producing filtrate with an average SDI of 2.7 and a turbidity of 0.08-0.2 after pretreatment. Zouboulis et al. [58] compared a sand filter bed with a dual media filter bed of sand and anthracite. It was concluded that the dual media filter produced similar water quality as the single bed, with an added advantage of operating at greater filtration cycles (around 3 times higher) directly resulting in a 10% increase in water production. Often, cartridge filtration is used as a last pretreatment step using 1-10µm filters for the final removal of suspended solids which had passed through the media filtration unit before [56]. The Pilot plant trials of SWRO in Singapore [59] reported permeate water quality of SDI 6.1-6.5 using a 5 µm cartridge filter and a SDI value of 4.2-6.2 using a 1 µm cartridge filter.

GMF (either single or dual mode) has become of the most popular conventional pretreatment processes used at large scale in SWRO plants due to its economic characteristics [57, 60]. A comparison of three different pretreatment technologies in terms of production capacity for world's 49 largest SWRO plants installed between the years 2001 and 2013 showed that GAF dominates over DAF and UF [61]. Johir et al. [62] evaluated single and dual media filtration processes with in-line coagulation. Figure 6 shows the effect of these for turbidity removal at two different velocities, 5 and 10 m/h. The results showed that sand, being a finer filter media, gave higher turbidity removal efficiency compared to anthracite at both the velocities. Removal efficiency of >60% was achieved with dual media filtration at 5 m/h. Thus, a single media filter can be sufficient for turbidity removal if optimized for effective size and velocity.

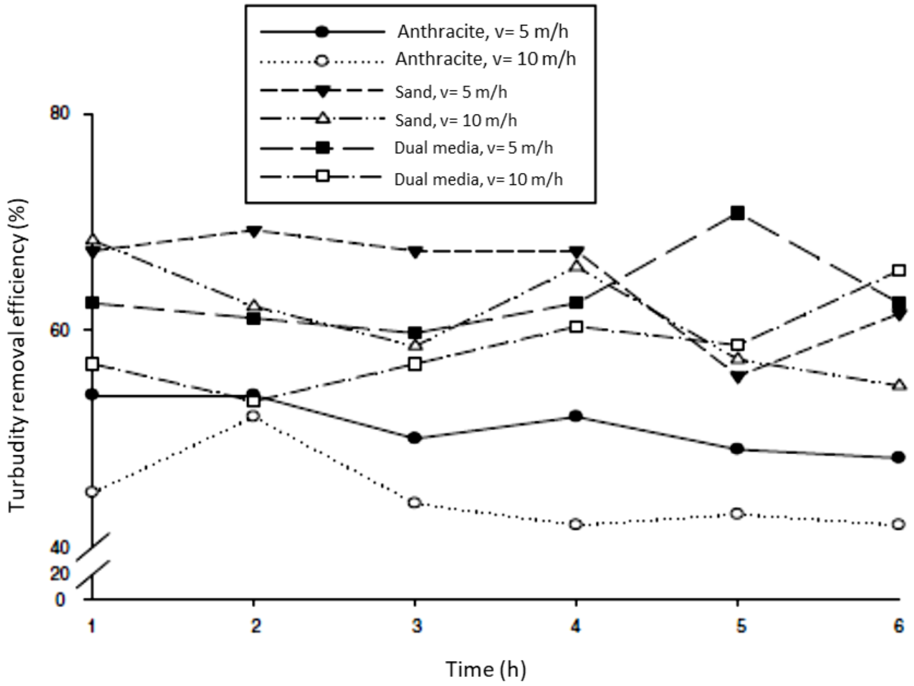

Figure 6: Effect of filter media and filtration velocity on turbidity removal (average seawater turbidity was 0.82 NTU). Reproduced with permission from [62]. Copyright © 2004, Elsevier.

2.1.2 Dissolved air flotation (DAF)

DAF is an alternative to conventional sedimentation where pressurized air is introduced into the feed water air bubbles which in turn assist in the removal of hydrophobic suspended particles [29]. The air to solids ratio is critical in the performance of a DAF unit [61]. DAF has been largely studied as an industrial pretreatment for the removal of poultry by-products and phosphorus and metals from acid mine drainage water [63]. DAF has rapidly gained importance as an RO pretreatment, with many full scale operations reported, with the earliest in Europe and South America [61]. Since 2003, DAF has demonstrated its ability to remove a high percentage of NOM

[64] with about 90–99% of algal cells removal achievable, compared to only 60–90% by sedimentation . This is an important application of DAF as algae are difficult to remove through conventional sedimentation processes and can lead to clogging of granular media filters and short filter runs. In the review by Henderson et al. [65], they reported that algal removal was capable of reaching 99.9% with proper DAF optimization. DAF has also been shown to enhance the robustness of SWRO pretreatment in case of oil spills with about, 90% oil removal [61]. A full scale DAF process has been operated in Korea in the Songjeon drinking water treatment plant [66]. During a service period of 4 years, the plant showed a constant performance for treating high turbidity water (64–430 NTU), achieving 0.15 ~ 1.16 NTU through DAF. However, major problems were encountered during heavy rainfall season and the increase in turbidity due to AC prior to the DAF process. It was concluded that DAF integrated with pre-sedimentation is an attractive method to control the specific raw water characteristics, especially during an unexpected increase in turbidity.

DAF has gained popularity as an effective clarifier of biological solids from aerobic processes over gravity clarifiers because DAF offers a smaller footprint, provides better process control and is capable of handling high suspended solids (>8,000 mg/L) [63]. Cleveland et al. [67] studied DAF as an UF pretreatment for algae removal and found a 70% increase in UF flux while Sanz et al. [68] reported the effectiveness of a 3-stage pretreatment RO plant for a South-Pacific Seawater, El Coloso Plant in Chile which included 3-stage flocculation, DAF and 2-stage filtration. Feed water with an SDI of typically 3 containing high concentrated algae and zoo-planktons was suitable for RO after these pre-treatments steps. A case study on the Persian Gulf for SWRO using

DAF as one of the pretreatment methods [53] showed good removal of turbidity and of suspended solids in this highly variable quality water.

The Tuas Desalination Plant in Singapore utilizes a DAF filtration pretreatment unit (DAFF) for SWRO. The system combines both clarification and filtration processes in one unit thus making the pretreatment a compact one. The system is also integrated with coagulation-flocculation and is efficient in removing color, suspended particles and colloids [69]. When used with the right chemistry, DAF-filtration systems can be effective in producing high quality treated [61]. Chew et al. [70] developed a numerical algorithm, termed as a Dynamical Rapid Filtration Model (DRFM), to optimize the timing for backwashing of clogged filters. They further demonstrated the ability of their model to optimize the filter's energy performance during its effective filtration stage for controlled and uncontrolled parameters. Such novel models and extensive process and operational optimization is necessary for a more enhanced DMF system.

2.1.3 Disinfection

Disinfection is another important pretreatment method which is used for destroying microorganisms responsible for causing water borne diseases and inhibiting biofouling. There are several types of disinfection methods including chemical [71], electrical[72], ultrasonic [73], ultra-violet radiation [74] and thermal [75]. Among them the most popular ones are the chemical means. These comprise chemical agents such as ozone [76] and chlorine species [77] such as hypochlorite, chloroamines and chlorine dioxide. However, other mechanical-chemical-physical methods, such as ultrasound and UV light, are gaining importance due to their superior effectiveness in killing and de-clumping bacteria. Some of the main disinfectant methods are discussed below.

2.1.4.1 Chlorination

Chlorine is one of the most widely used chemical disinfectants. When added to water, it reacts and produces hypochlorous and hydrochloric acids [78]. Hypochlorous acid partly dissociates and oxidizes the microorganisms [79], which is more effective at low pH. Free chlorine has the benefit of having a residual effect that inhibits the re-growth of microorganisms [80]. However, high residual concentrations in the range of 0.5–1.0 mg/L might be required to maintain disinfectant efficacy throughout the pretreatment system [81]. Figure 7 shows a simple schematic of a conventional pre-treatment process where the disinfectant is added at the beginning of the process followed by other pretreatment steps. At the end, the water is dechlorinated and the filtered water is passed to the RO system [82]. Usually, the dechlorination step includes the unreacted chlorine being reduced by the addition of either AC or sodium bisulfite [5].

Chlorine can react with ammonia to form chloroamines which is a preferred disinfectant over free chlorine, due to being less reactive and more stable. However, their pH requirements are quite different, usually requiring more alkaline environments [83]. Chlorine dioxide is another attractive alternative and has been widely researched due to its insignificant corrosive effects and high efficiency in deactivating bacteria and viruses [78]. It is reported to produce negligible amounts of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) when used at dosages <10 mg/L [84, 85]. Besides serving as a disinfectant, addition of chlorine aids in coagulation and alleviates odor problem in water. Usually, intermittent chlorination is more effective than continuous chlorination as it promotes coagulation of colloid polymers while continuous chlorination adds to biofouling of the membranes. Similar is practiced in the Fujairah SWRO plant [43] where variable high doses of up to 14ppm of free chlorine are used depending upon the fluctuations in feed water quality. Two different injection points are used for dose adjustment, one at the bell mouth while other in the coagulation chambers. The RO desalination plant for Yanbu Industrial City [44] also utilizes intermittent chlorination with a chemical dosage of about 1.4ppm/m^3 permeate of NAOCl formed from the initial chlorine gas. Nevertheless, over the past years, prechlorination has become a concern due to the formation of THMs and thus more focus is put into alternative chemical methods such as ozonation.

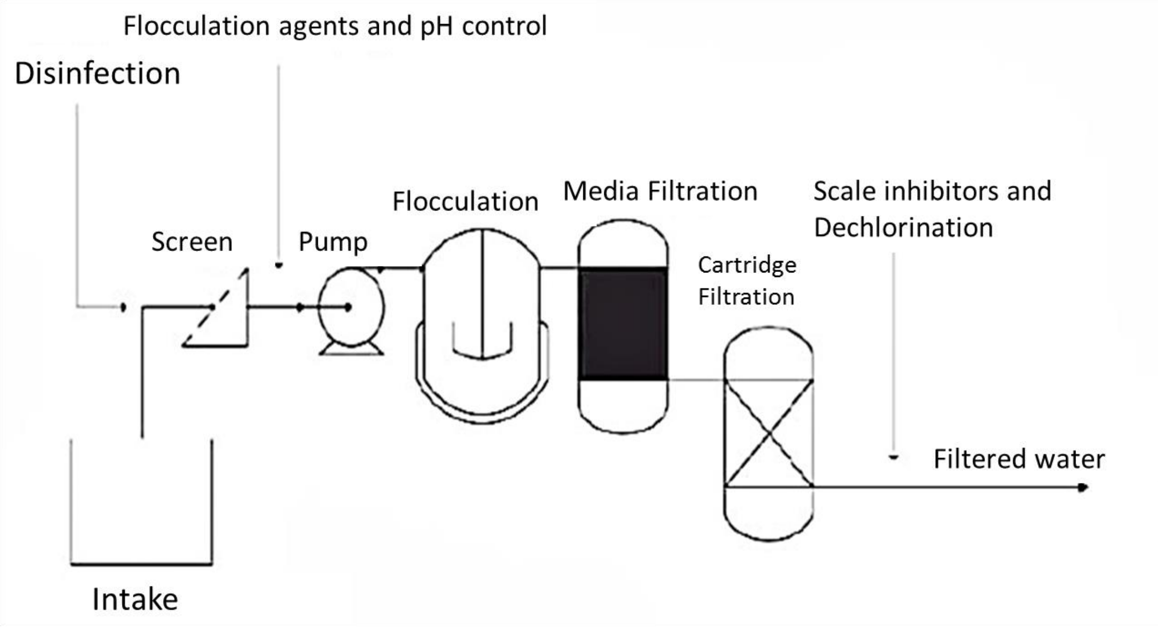

Figure 7: Simplified process scheme of a conventional pre-treatment process. Reproduced with permission from [82]. Copyright © 2007, Elsevier.

2.1.4.2 Ozonation

The DBPs created by chlorination and its other associated disadvantages have led ozone to emerge as another powerful oxidizing chemical, which decomposes into free radicals and OH- ions in solution [86]. These hydroxyl ions are capable of removing bacteria, protozoa, endospores and other microorganisms [87], without leaving any DBPs nor causing any taste and odor problems. Moreover, the OH- ions can combine together to form hydrogen peroxide (H_2O_2) which is another powerful oxidizing chemical, hence improving the cell destruction process [88]. Park et al. [89] reported improved removal efficiency of heterotrophic bacteria through ozonation. They evaluated the effect on foam fractionators with excessive ozonation for the removal of suspended solids, DOC and volatile suspended solids for a period of 44 days. It was observed that the overall mean particle diameter of these solids decreased with a gradual increase in ozonation. Lee et al. [90] reported the combined effect of ozone/biofiltration for the removal of pharmaceutical products with an ozone dose of 4–8 mg/L. Such combinations are more energy efficient and as such more research needs to be put into advanced ozonation methods. Wang et al [91] investigated the elimination of total organic carbon (TOC) from oxalic acid (OA) by the electro-peroxone technique, which is a novel electrocatalytic ozonation process combining ozonation with electrolysis for enhanced contaminant degradation. This technique clearly outperformed the usual ozonation process by eliminating TOC with a superior rate of 10.2-12.5 times compared to ozonation alone. Zhoe et al. [92] reported the superior efficiency of ozonation over UV for the removal of dissolved organic carbon, with the highest efficiency achieved through an integrated process of ozonation-photocatalysis-coagulation pretreatment and coagulation. More feasibility studies are required for such integrated systems and advanced ozonation methods. Improvements to the ozonation method may involve improving contact basin hydraulics and maximizing uniform ozone contact. In addition, efficient ozone gas dispersion is necessary for an effective disinfection [93].

2.1.4.3 Ultrasound

In recent years ultrasound has been gaining research into its effectiveness as a pretreatment method to mitigate fouling in RO membranes [73, 94, 95]. It is an effective alternative to chlorination and UV light [73] for de-agglomerating bacterial clusters through acoustic cavitation, where the cavitation disrupt the bacteria in the feed water by chemical and mechanical means. The process may be combined with pressure (manosonication), temperature (thermosonication) or both (manothermosonication)[96] to enhance its effectiveness and decrease the required energy consumption. Nevertheless, there exists a threshold beyond which any increase in temperature and pressure will have no effect on the process efficiency. Therefore, optimum operational parameters need to be sought when combining ultrasound with either pressure or temperature [96, 97].

Ultrasound efficiency for RO pretreatment may be affected by several factors [78] including the feed water quality, the type of ultrasonic reactor and process parameters. Hulsmans et al. [73] studied ultrasonic treatment on a pilot scale setup. They proposed specific acoustic energy (Es) as a reference parameter for their study where they observed a higher bacterial reduction with higher levels of Es and high electrical power of the ultrasound. The nature of bacteria can have a significant impact on the treatment. R. Davies [98] reported that rod shaped bacteria are more sensitive to ultrasound treatment than coccal forms. Joyce et al. [99] investigated the effect of ultrasound at different powers and frequencies on spherical clusters of *Bacillus subtilis.* A significant increase in microbial reduction was achieved by increasing the duration of exposure and at an ultrasound intensity in the range of 20 to 38 kHz. Higher frequencies of 512–850 kHz registered a significant increase in bacteria count suggesting the de-agglomeration of the bacteria. Dadjour et al. [100] studied the kinetics of disinfection of *E. coli*, in the presence of a TiO_2 photocatalyst, using an ultrasonic irradiation system. The addition of TiO_2 pellets to a suspension of *E. coli* considerably improved the ultrasonic treatment process by a 98% reduction in the bacteria compared to only 13% reduction in the absence of the photocatalyst. Al-Juboori et al. [101] applied ultrasound as a chemical-free disinfection method for biofouling mitigation by selecting an *E. coli* sample with a concentration of 10^6 Colony Forming Units (CFU)/ml. They measured the efficiency of thermosonication as a pretreatment for RO system by measuring the permeate flux and the development of biofilm on the RO membrane. Thermosonication intensity of 21.5 W/cm^2 with a treatment temperature of 48 °C eliminated almost 10^3 CFU/ml of the sample and helped in recovering the permeate flux by more than 0.1 L/m^2.hr during 60 h operation. In addition, the membrane micrographs (Figure 8) revealed a larger biofilm coverage area for the untreated cells compared to the ultrasonically treated ones. Kwang Ng et al. [102] reported an experimental increment of 15%–20% permeate flux when they used ultrasound of 20kHz on a 10 kDa pore size membrane with trans-membrane pressure (TMP) of 100 kPa. However, no significant change in flux was observed for large pore size membranes of 100 kDa at higher TMPs of 140 kPa, and a low frequency of 20 kHz was evaluated to be more efficient in fouling mitigation compared to higher frequencies of 40 kHz. Being a *free-chemical* method, effective in killing and de-clumping several types of bacteria, ultrasound needs more attention for potential large scale application in RO pretreatment. Extensive studies are required for its applicability as a sole pretreatment technique for RO [94]. Nevertheless, combination with other techniques, as stressed by several researchers [73, 103], needs to be explored to a greater extent.

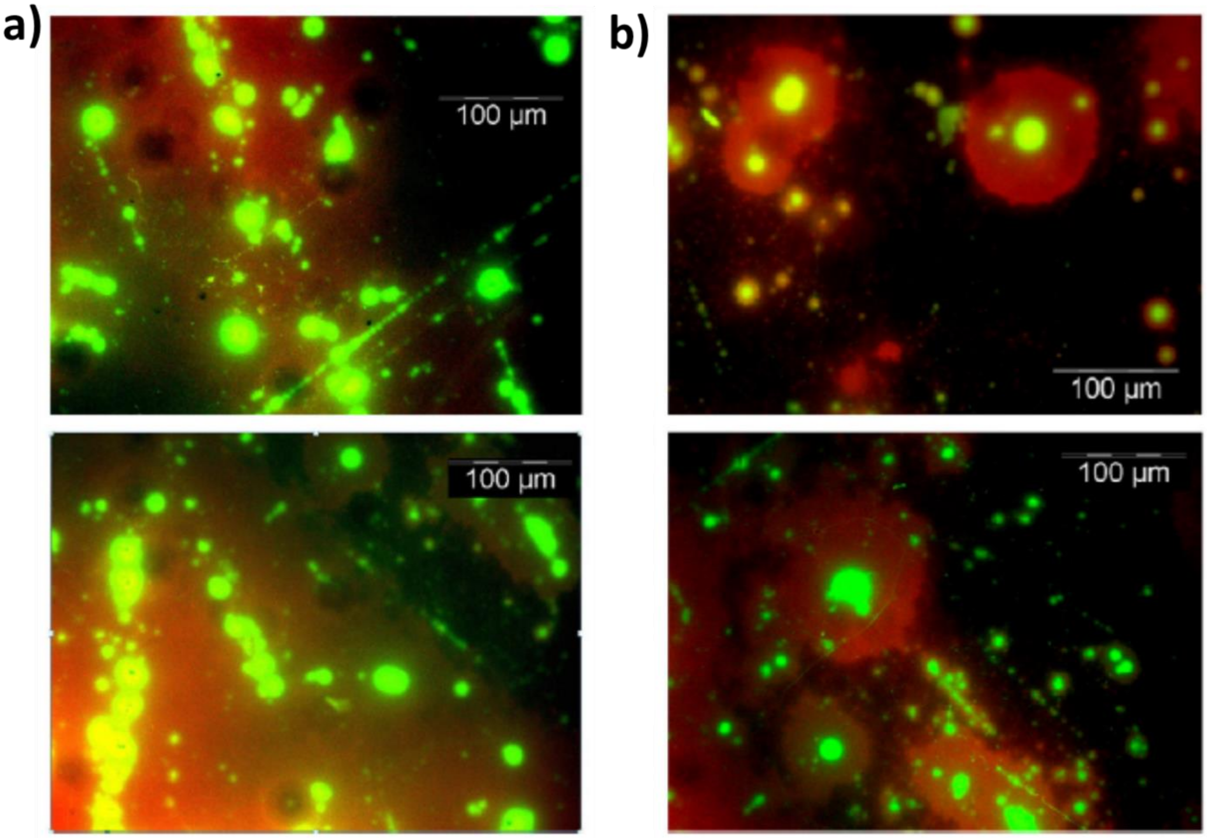

Figure 8: Distribution of biofilm on the center of RO membranes using LIVE/DEAD BacLight, (a) for untreated suspension and (b) treated suspension. Reproduced with permission from [101]. Copyright © 2012, Elsevier.

2.1.5 Scale Inhibitors

Scaling is another major problem encountered with RO membranes. Thus, proper seawater treatment is necessary to avoid the concentration of salts exceeding their solubility limit leading to scaling at membrane surface. Commonly encountered scalants include barium sulfate, silicates and calcium carbonate. Among the many scale mitigating techniques available, addition of antiscalants is the most popular, utilizing phosphates, phosphonates and polycarboxylates [30]. Scale inhibitors reduce inorganic fouling in membranes by modifying the physical and chemical characteristics of the ions [29]. Antiscalants are primarily used after granular media filtration [104]. Some of their functionalities include crystal modifiers, which work by distorting the salt crystallites at the submicroscopic level, adsorption of these antiscalants to the crystal surface forming constituents that repel ions keeping them in solution, and inhibiting the clustering of charged ions and crystal structure [105].

Pramanik et al. [106] compared the performance of polyaspartic acid (PASP) and its derivative PASP-SEA-ASP with a commercially available RO antiscalant. PASP-SEA-ASP gave a water recovery of 90% compared to 85% for the commercial antiscalant. This was attributed to the reduced deposition of the scale forming ions on the membrane’s surface. The choice of antiscalant is governed by the feed water characteristics. As much as optimization of antiscalants is important, a heavy dose might not be a solution for decreased salt precipitation. Antiscalants should be avoided in cases where certain precipitates are too high in quantity [5].

Shammiri et al. [107] reported the performance evaluation of two different antiscalants used at a Doha research plant for a total operational time of 6000 hours. Commercial antiscalants, Permatreat 191 and Flocon 100, were used for this purpose, whereby both showed similar effectiveness as an antiscalant. However, Flocon 100 was more cost effective. The salt rejection for Floccon 100 was more stable at 98.8% while the salt rejection for Permatreat 191 declined from 99.4% to 99.0% due to compaction issues. Rashed et al. [108] investigated the efficiency of Ammonium Biflouride (ABF) as an antiscalant for silica in improving the RO membrane performance. Figure 9 depicts the seriousness of silica scaling on the membrane's surface. ABF is a promising antiscalant which is currently being used in several countries for its mitigation. Addition of ABF increased the solubility product of silicate before ionization, thus preventing the formation of silica layer. An increase in ABF dosage from 2mg/l to 6 mg/l led to the increase fluoride scaling hinting towards the use of an optimum antiscalant dosage. Each year, new types of scale inhibitors claim the desalination market. Therefore, scale inhibitors are continually evaluated at the laboratory scale before being introduced as a pretreatment for RO [109]. As new improved inhibitors come into the market, old ones are gradually becoming obsolete. Sodium hexametaphosphate (SHMP) was commonly used as an antiscalant, but has now been widely replaced by polymeric compounds due to disposal problems associated with SHMP.

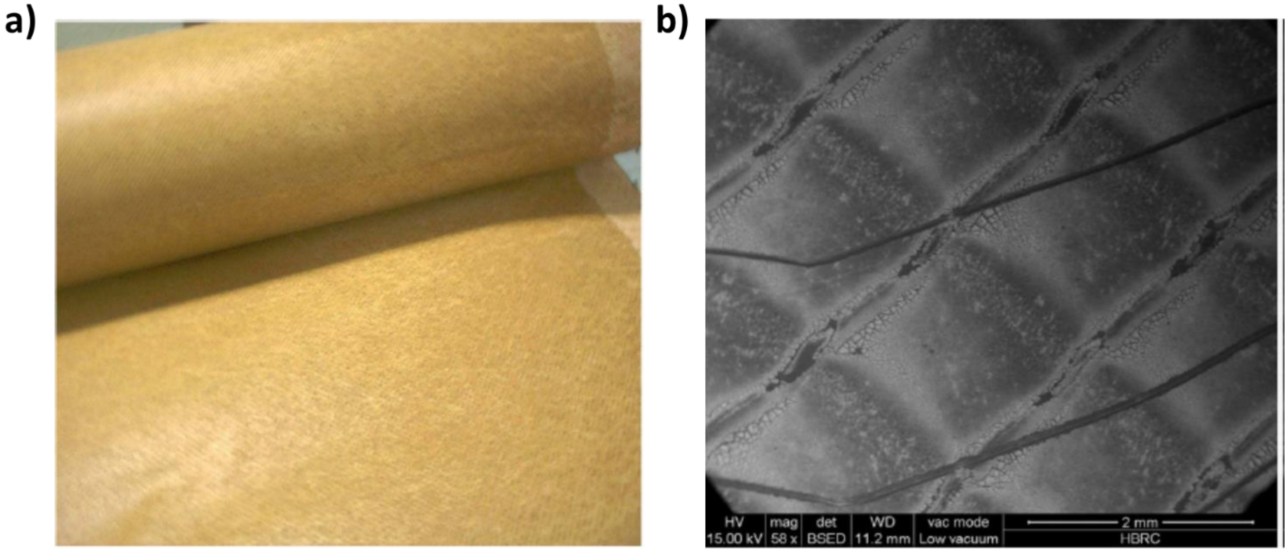

Figure 9: (a) Sodium metasilicates detected on RO membrane's surface and (b) SEM image of the membrane's surface fully covered with sodiummetasilicates (Reproduced with permission from Rashed et al. [108], HBRC Journal, 12 (2016) 205-211)

2.1.7 Common problems encountered with conventional RO pretreatment techniques and suggested improvements.

Today, conventional RO pretreatment techniques widely prevail in numerous RO plants worldwide [4, 43, 44, 59]. These techniques may produce feed water for an RO system with acceptable water quality under normal operational conditions, such as when the incoming water quality is almost constant. However, often this is not the case and fluctuations in incoming seawater quality can greatly hamper the treatment and pretreatment processes. Seawater intakes may be of poor water quality, especially in the season of storms and during algae blooms [18]. Therefore, conventional pretreatment units might in return produce fluctuations in feed water quality to the RO membrane, with difficulties in supplying water with SDI < 3.0 and causing a large carbon footprint due to sluggish filtration velocities [82]. Table 2 highlights the advantages and disadvantages of the commonly used RO conventional pretreatment techniques with their suggested improvements.

Fluctuations in performance were noticed in a Doha research plant where the conventional pretreatment procedures produced instability in SDI value and required a high rate of coagulant and acid consumption together with clogging of media filters [110]. Similar observations were made in the SWRO plant at Jeddah [111]. One possible solution is to modify the pretreatment to adjust to the seasonal variations. This can be done in terms of coagulant and acid dosages, and fine tuning the backwash procedure [112]. Nevertheless, it is a challenge to control and predict the optimal coagulant dosage, which is highly dependent on feed water temperature, pH, and turbidity, alkalinity, and algae concentrations. This effort often results in overdosing of the coagulant. Care has to be taken to avoid such overdosing which can be detrimental to the performance of SWRO membranes. The use of polymer coagulants above 1 mg/L should be avoided as it might plug the filters and, in the worst scenarios, be carried to the RO unit downstream [113]. During a case study on the intake water off the Gulf of Oman for SWRO, it was found that $FeCl_3$ coagulant gave poor results by clogging the filtering bed of the DMF. However, an optimum dosage of 3 g/m^3 together with the best media configuration improved the results substantially [53]. Although pretreatment by coagulation significantly improves colloidal and particulate removal, many studies suggest that coagulant residuals from inorganic salts such as aluminum and iron salts can be detrimental for RO performance [7]. Permeate flux and salt rejection were seen to significantly decline when aluminum sulfate (alum) coagulant was used in the range of 6–8 mg/L. Microscopic analysis revealed the presence of the fouled membranes with aluminum hydroxide and aluminum silicate being the primary foulants [114].

There are other major disadvantages associated with conventional pretreatment techniques, such as the possibility of failure during filter backwash and a low removal frequency of small particles less than 10µm [30]. Pesticide removal through AC may cause problems due to AC saturation and formation of toxic by-products [115]. Biofouling is yet another serious problem and the failure of conventional pretreatment techniques to supply water with lower SDI values may cause the existence of nutrients in the water promoting biofouling. In the Alberto Pasqualini oil refinery RO plant in Southern Brazil, conventional pretreatment techniques failed to remove major biofouling constituents. Granular AC (GAC) was found to be the main source of microorganisms with fouling films of bacteria being revealed in the matrix through microscopy analysis [116]. Acidification such as by sulfuric or hydrochloric acid when used to mitigate scaling, may promote the formation of sulfate scales [105]. The pilot plant studies by Amsterdam Water Supply concluded that the addition of sulfuric acid increased the risk of barium sulfate scaling [117]. Therefore, other alternatives have to be sought which involves the optimization of operating procedures. Nevertheless, the use of antiscalants also lead to enhanced biofouling in RO membranes by accelerating the biological growth of organisms by up to 10-fold. It has been shown that polyacrylate- and phosphate based anti-scalants can enhance biofouling by modifying the physico-chemical properties of the membranes [22, 118] and acting as a source of nutrients. Similar to the coagulant doses, the correct dosage of antiscalants is very important, as excess might turn into a foulant at a later stage [119]. Another associated problem is the carryover of pretreatment chemicals which may react with antiscalants decreasing the efficiency of the scale inhibitors. Cationic flocculants may react with some antiscalants to form sticky foulants [105].

Though chlorine is widely used as a disinfectant, chlorine residuals can be detrimental to RO membrane performance if not removed before subsequent membrane treatment. The amide linkage in polyamide membranes is susceptible to attack by chlorine, which can gradually reduce flux and salt selectivity [25]. Hong et al. [120] fabricated chlorine resistant polyamide membranes to overcome this limitation, with RO membranes prepared from m-phenylene diamine (MPD), 1,2,4,5-benzene tetracarbonyl chloride (BTC) and trimesoyl chloride (TMC). These membranes eliminated the chlorine-sensitive sites by replacing the amide linkages with imide linkages. Other drawbacks of chlorine are related to the lower deactivation capability towards endospores and protozoa, and its capability of forming carcinogenic DBPs such as trihalomethanes [78, 121]. Susan D.Richardson [122] reported that one of the major risks of DBPs on public health lies due to unidentifiable DBPs formed in chlorinated water. Free chlorine might be replaced by chloramines or chlorine dioxide. As an alternative, however, monochloroamines are less efficient in deactivating bacteria, while chlorine dioxide produces chlorite by-product, which is toxic for animals [123]. Also, there is less experience in using chlorine dioxide in commercial SWRO plants, thus requiring more extensive research for this purpose. Moreover, lab-scale experiments confirm that the chlorite ion is not easily removed by common reducing agents, such as sodium bisulfate, and can also be a cause of regeneration of chlorine dioxide and free chlorine concentration in the presence of certain metal ions such as copper (II) [124]. Ozone is not a very effective sterile agent and can cause bromate formation. Bromate is a well known carcinogen and thus again needs to be regulated for this purpose [5]. Moreover, ozone is unstable and cannot be stored, necessitating it to be produced on-site. Disinfection through ultrasonic treatment may be used to achieve a complete destruction of bacteria. However, high ultrasonic intensities may be required for this purpose leading to the process becoming cost-inefficient [94]. This technique is faced with some key challenges when used for membrane cleaning, but has the potential to be commercialized if used as a pretreatment method for flux enhancement. A combination of ultrasound with other conventional and non-conventional techniques can be a promising alternative. Owing to its limitations associated with large-scale application and suitable reactors, this technique is still in its infancy, and thus requires special attention and extensive research for potential improvement. Other alternatives might be used such as the use of solar disinfection techniques utilizing sunlight to treat water [125]. Their first reported use came in 1878 when Downing et al.[126] discovered the effect of sunlight on bacteria. Solar disinfection is a promising solution to control biofouling in RO membranes which occur due to the addition of chemicals, coagulants and other disinfectants. In addition, it leaves no residuals for the regrowth of microorganisms. However, it suffers from basic limitations [75] such as solar radiation intensity varying with latitude, altitude and the requirement of cooling processes.

Though conventional pretreatment techniques are prevalent in commercial SWRO plants, they encounter harder real-time challenges today due to their various shortcomings. For example, in 2008–09, these techniques were not able to maintain production capacity in RO plants due to the severity of red tide bloom in the Gulf of Oman and Persian Gulf. GMF demonstrated high clogging rates, which deteriorated the treated water quality significantly. This called for severe backwashing, increasing downtime and causing failure to maintain pretreatment production capacity [127]. Similarly, at the Fujairah SWRO plant, filter runs were reduced from 24 to 2 h and increased coagulant dosages led to higher clogging rates in the media filters[61]. These limitations have led to the use of membrane technology for RO pretreatment and today, many SWRO plants worldwide make use of membrane pretreatment processes [22].

Table 2: Common conventional RO pretreatment techniques and their advantages, disadvantages and suggested improvements

Pretreatment technique	Advantages	Disadvantages	Suggested Improvements
Coagulation-flocculation	• Significantly enhances the removal of colloidal and particulate matters.	• Overdosing of the coagulants and flocculants can cause detrimental effects on the SWRO membranes.	• Use of environmental friendly, natural coagulants to reduce the detrimental ecological

	- Controls organic, colloidal and biofouling.	- Carcinogenic potential of the monomers used for the synthesis of synthetic organic coagulants. - Not effective in inhibiting organic scaling.	impact of synthetic polymers. - Improvements in automated modelling and incorporation of advanced tests for a prompt prediction in fluctuations of incoming seawater.
Chlorination	- Effective disinfectant for destructing microorganisms and other bacteria. - Reduces odor.	- The effectiveness of chlorine in deactivating protozoa and endospores is poor. - Polyamide RO membranes susceptible to attack by chlorine. - The use of chlorination is accompanied by the formation of carcinogenic DBPs	- Use of chlorine dioxide instead of free chlorine to decrease the DBPs. - New developments are necessary for chlorine resistant RO membranes. - Research and improvements required in alternative disinfectant methods such as thermal and UV.
Media filtration	- Ability to filter water with high turbidity and suspended solids. - DMF offer long filtration runs and high filtration rates - Pressure filters for small SWRO plants are space efficient and easier and faster to install.	- Sensitive to feed water changes. - Permeate SDI can vary several units during algal blooms and oil contamination. - Not effective for inhibiting organic and biofouling. - DMF filtered seawater may have high fouling potential for cartridge filters which might need replacement every 2-8 weeks. - Non-optimized DMF may lead to frequent chemical cleaning of RO membranes.	- Optimization of DMF which can reduce operational and energy costs and increase the cartridge filter lifetime. - A proper design and operational parameters should be established for DMF in relation to organic and biofouling.
Acidification HCl or H_2SO_4	- Reduces pH for inhibition of scaling and improved coagulation - Effective in Boron rejection at low alkalinity.	- High alkalinity can cause salt precipitation and hence scaling.	Careful modelling of the RO system to adjust alkalinity levels in the feed water due to sudden water quality fluctuations.

		Low alkalinity in finished water causes corrosion.	
Ozonation	Does not cause taste or odour problems	Formation of bromate, a known carcinogen, in waters containing bromide. Needs to be produced on-site due to its storage problems. Difficult to monitor.	Extensive research in the areas of advanced ozonation methods such as electro-peroxone and their selection of cathode materials for maximal TOC removal.
DAF	Cost-effective Up to 99.9% removal of algae cells possible if optimized	Scraper problem due to the shortage of feed water to the DAF unit. Increase of turbidity due to the use of AC prior to the DAF process can decrease the effectiveness of the treatment if used as a sole technique.	Ensure uniform distribution of process influent and effluent for equal opportunity for particle bubble attachment and flotation. Ensure uniform air distribution.
Scale Inhibitors	Effective for scale inhibition on RO membranes caused by salt crystallization.	Overdosing of antiscalants causes biofouling of RO membranes.	Use of environmentally friendly and non-phosphorus based scale inhibitors. Optimization of antiscalant type and dosage.
Ultrasound techniques	Free- chemical technique. Ability to be used with high suspended solid solutions.	High cost Cooling requirements.	Extensive research on pilot scale are required for studying the potential of this technique. Combination of ultrasound with other techniques to increase process efficiency and lowering energy demands.
Ultraviolet light radiation	Effective in deactivating spores. Low cost Easy to implement.	Mutagenic activity. Low performance in light scattering water. Breaks down large natural organic matter into organic acids for subsequent biofilm formation.	Sensitivity of microorganisms to UV needs special attention. Combining UV with other conventional techniques prior to RO needs more pilot scale feasibility studies.

2.2 Membrane Pretreatment Techniques

Membrane pretreatment processes have gained immense importance over the past decade. This increasing trend in research and real time installations in RO plants is due to the various shortcomings associated with conventional pretreatment techniques, as discussed in section 2.1.7. More often, colloids and suspended particles pass through the conventional filters and contribute to RO membrane damage [128]. Therefore, the use of large pore size membranes in MF (0.1-0.35μm), UF (0.01-0.05μm) and NF (1-2nm) to pretreat RO water becomes essential [4]. Among these, UF remains the most popular choice in pilot tests and large scale desalination plants [59, 129, 130]. This is due to its greater operational flexibility and an optimum balance between permeate production and contaminant removal [30]. All three RO membrane pretreatment processes provide numerous advantages over conventional pretreatment techniques (see Table 3), however, with a compromise on higher energy requirements and capital costs. Nevertheless, costs can be substantially reduced with the growing progress in advanced membrane materials as discussed in sections 2.2.4-2.2.5. Membrane pretreatment can provide permeate waters with SDI<2, and can reduce the turbidity to less than 0.05 NTU [5]. This in turn provides higher RO flux and recovery, longer RO membrane lifetimes, lowered chemical consumption and reduced membrane cleaning frequency leading to reduced downtime [4]. In addition, an added benefit of membrane pretreatment lies in its ability to reject multiple contaminants simultaneously. For example, NF is efficient in removing colloids, particulates, dissolved contaminants, and in reducing hardness, color and pesticides in the feed water [5, 30]. Nevertheless, in case of highly turbid feed waters, such as in Kuwait from the Tigris-Euphrates basin, conventional pretreatment using coagulation is still preferred due to intense membrane fouling issues. When a combination of DAF and UF was used for Doosan built facility in Shuwaikh in Kuwait, the intense algal blooms caused extracellular polymeric substances (EPS) to deposit on the membrane's surface [131]. Numerous research studies, pilot plant studies and full-scale installations of membrane pretreatment have been conducted covering different membrane materials and their advancements, optimization in operational parameters and integration of membrane pretreatment [30] with other unit processes for a hybrid membrane process. Integrated/hybrid systems are prevalent in commercial SWRO plants due to the harsh seawater quality which increases the propensity of membrane fouling. Coagulation, chlorination, DAF and other conventional pretreatment methods can provide an additional contaminant barrier before the water reaches UF/MF/NF units [132, 133]. Subsequent sections review the recent advances in these three membrane pretreatment processes with respect to membrane materials and discusses pilot-scale and large-scale RO plants where membrane pretreatment has been in operation. In addition, special attention is given to advanced fibrous, ceramic and self-cleaning membranes which are gaining popularity and hold immense potential to be scaled up commercially for a more efficient and cost competitive RO pretreatment system.

Table 3: Comparison of conventional and membrane pretreatment techniques. Reproduced with permission from [22, 82, 134]. Copyright © 2007, 2014, Elsevier.

	Conventional Pretreatment	**Membrane Pretreatment**
Capital cost	Competitive with membrane pretreatment	Higher than conventional practices. However, more potential for development leading to further cost reductions.
Carbon footprint	High	Low (about 30-60% of conventional)
Energy requirements	Low	High
Chemical costs	High	Low
RO capital cost	High since RO operates at lower flux	Higher flux is possible resulting in lower cost

RO operating cost	High, more fouling potential.	Low, longer membrane life is expected
Average RO flux	~14 L/m^2h	~18 L/m^2h
Treated water quality	SDI <4, 90% of the time. Fluctuating quality Turbidity: <1.0 NTU	SDI <2.5, 100% of the time. Constant reliable quality. Turbidity < 0.1 NTU

2.2.1 Microfiltration (MF)

MF can effectively remove suspended solids and bacteria ≥ 0.1 µm. One of the early studies on the feasibility of MF as a SWRO membrane pretreatment method was carried out in 1997 when it was realized that MF can be an alternative to conventional pretreatment techniques for supplying good quality water to the RO unit. However, these early studies also remarked upon the need to combine MF with other techniques, such as chlorination and strainers, to reduce the biofouling propensity [135]. Since then, many studies have reported hybrid configurations. Chinu et al. [136] reported a study on coagulation–DMF–MF as a pretreatment for SWRO. They concluded that any prior pretreatment to MF reduced the MF flux by 45%, which further reduced to 42% with coagulation, 24% with coagulation-sand filtration and finally to 22% with DMF. Soo Oh et al. [137] evaluated a combined ozone and (MF) pretreatment process whereby the ozonation step significantly reduced the fouling in MF membranes. Similar studies on ozone-MF hybrid systems have been reported in the literature [138, 139]. Lee et al. [140] investigated the effect of chlorination and microfiltration pretreatment processes on biological organisms. The combination was successful in removing the bacteria initially. However, their regrowth occurred at a later stage due to the chlorination by-products. Jeong et al. [141] studied three different submerged MF membrane hybrid systems (SMHSs) for SWRO which they abbreviated as SMCHS, SMAHS and SMCAHS for submerged membrane coagulation hybrid system, submerged membrane adsorption hybrid system, and submerged membrane coagulation–adsorption hybrid system respectively. In a submerged system, the membranes are placed in an open tank where the filtrate is drawn through the membranes via vacuum. SMCAHS gave the best results in terms of flux and organic removal, whereby enabling around 72% of DOC removal with low coagulation dosages. An increase in RO salt rejection from 97% to 98.8% was observed with MF pretreatment [142]. Corral et al. [143] reported the pilot study of Central Arizona Project water from 2007 to 2010. The RO pretreatment utilized MF and slow sand filtration (SSF) in standalone modes. It was reported that MF consistently produced water with SDI < 3, improving the long term RO performance. Ebrahim et al. [144] compared MF with other conventional techniques during their R&D at Doha Research Plant to conclude that the feed water was markedly improved after MF step giving only slight SDI variations of about 0.24-3%, with an average SDI of 2.42. In addition, the biological oxygen demand (BOD) for the water produced by MF was estimated to be 3 compared to the high BOD of 10 from conventional pretreatment for similar intake

At the heart of the MF system lies the MF membrane. MF membrane materials have been extensively researched to optimize flux, selectivity and cost. Figure 10 shows a variety of membrane modules and membrane material types. Selection of membrane modules is driven by the size of installation and the quality of incoming feed water. This paper does not review research studies and progress on membrane modules. However, readers are encouraged to read case studies and articles pertaining to the design and feasibility of membrane modules as it holds an important place in membrane pretreatment performance [145, 146]. Usually, polymeric membranes dominate the MF market owing to their ease of processing and low cost (Table 4).

The common polymeric membranes used for MF include polyvinylidiene fluoride (PVDF), polyether sulfone (PES), polyacrylonitrile (PAN) and polyethylene (PE). Commercially available MF membranes are predominantly formed by the phase inversion method. A variation of the process, non-solvent induced phase separation involves a polymer film dissolved in a solvent immersed in a water bath causing controlled precipitation of the polymer. Other variations include controlled solvent evaporation and thermally induced phase separation. Membrane morphology is governed by the polymer type, polymer concentration and the solvent. Figure 11a shows a SEM image of a 0.22µm pore size polyvinylidene fluoride commercial MF membrane formed through phase inversion [147].

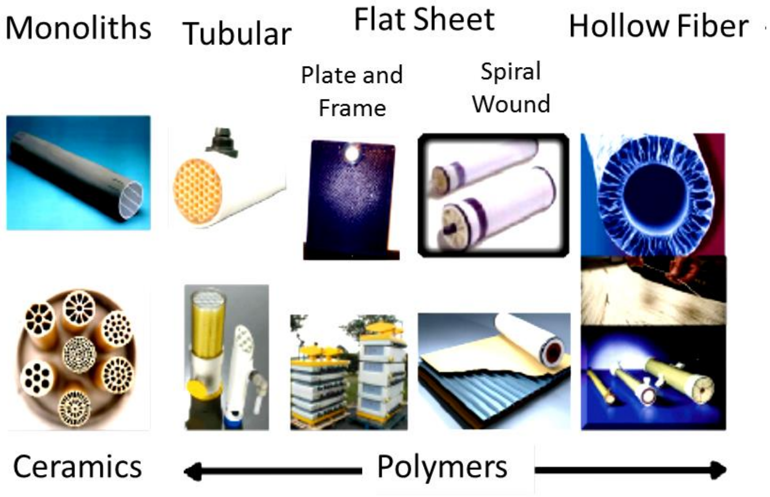

Figure 10: Different membrane module types for polymeric & ceramic materials. Adapted from [148]

In general, hydrophilic materials are more resistant to fouling as they attract water and limits the foulants adhering on the membrane's surface. This in turn provides higher flux and recovery. However, hydrophobic polymeric membranes are more robust and long lasting if cleaned with harsh chemicals periodically, but their hydrophobicity leads to more rapid flux losses and lower recoveries [148]. A polypropylene membrane with a 0.2 µm pore diameter was reported to produce a 40% increase in RO flux compared to other conventional pretreatment techniques [26].

Vial and Doussau [149] reported pilot plant testing on Mediterranean seawater using a 0.1 µm, 37m^2 PVDF MF membranes. PVDF membranes have intrinsic hydrophobic properties, with good chemical and oxidant resistance [150]. The isotropic membrane structure, with PVDF's good elastic performance was reported to reduce abrasion and increase resistance to mechanical shocks during backwashing. Under optimized operating conditions, with $FeCl_3$ coagulant addition, good quality permeate water was achieved with SDI<2 [149]. Nevertheless, many studies have reported modification of PVDF to enhance its hydrophilicity for a more fouling resistant membrane. Recently, Fontananova et al. [151] reported a versatile method to synthesize hydrophilic PVDF membranes through solution casting and phase separation techniques. They prepared novel composite membranes displaying tailored physicochemical and microstructural features by combining PVDF with oxidized multi-walled carbon nanotubes (MWCNTs) with different loadings. A loading of 1wt. % MWCNTs showed superior performance compared to lower and higher loadings due to better dispersion. The presence of these MWCNTs increased the more hydrophilic β-phase of PVDF polymer, increasing the flux and reducing the fouling propensity of the membranes. The MWCNTs formed a bridge through the pores in the membrane influencing the transport of water through the asymmetric composite membranes. Yang et al. [152] synthesized MF membranes through isothermal immersion precipitation from grafted PVDF-PDMAA powder in 1-methyl-2-pyrrolidone (NMP) solution from a water bath. The presence PDMAA graft chains was reported to improve the hydrophilicity of PVDF with improved fouling resistance to proteins.

Besides solution casting and phase inversion techniques, other MF membrane fabrication methods have been studied. Han et al. [153] used an ion beam aperture array lithography process to develop MF membranes with highly ordered and uniform cylindrical pores. Castro et al. [154] reported a vacuum assisted UV micro-molding (VAUM) process for the fabrication of freestanding methacrylate polymeric MF membranes. The fabricated membranes showed great flexibility, high mechanical robustness and superior particle capture efficiencies of about 98% for an 8µm pore size membrane. Although these membranes were tested for cancer cell separation, they hold future potential for SWRO pretreatment if produced with controlled porosity. Fan et al. [155] fabricated a cost-effective MF membrane from linear low-density polyethylene (LLDPE) through a combination of hot imprint and thermal field induction. The membrane was reported to have an ordered 'wine bottle' shaped pores of about 2µm after imprint and about 1µm after the thermal treatment. Pure water flux of the fabricated membranes was found to be 1.4–1.6 times higher compared to the commercial MF membranes over the applied pressure range of 20-160kPa. These membranes also showed excellent performance for the rejection of *E. coli* bacteria. Gopal et al. [156] reported nanofibrous PSf membranes developed through the electrospinning technique (Figure 12a). Electrospinning has emerged as a promising method for organic and inorganic fiber production [157-160]. The fibrous membrane was reported to have a high porosity resulting in high flux of 1964 kg/h at the end of separation for particles ≈10µm while 672 kg/h for particles ≈0.1µm in size. The membrane could successfully remove >99% of particles without any noticeable fouling for particle sizes >7µm [156]. Wang et al. [161] reported a novel two-layered MF membrane based on PAN and PET containing infused cellulose nanofibers (5nm diameter), as shown in Figure 12b. They were reported to remove a variety of contaminants such as bacteria, viruses and toxic heavy metal ions simultaneously, yet maintaining a high permeation rate of 1300 L/m^{2}h/psi.

Recently, Wu et al. [162] reported a detailed real-time case study on a pilot gravity-driven microfiltration (GDM) reactor used as a pretreatment for a SWRO plant in Singapore. A flat sheet MF membrane module, made of PVDF with pore size 0.08 µm was submerged into the reactor. The GDM pretreatment showed significantly lower RO fouling potential when compared to the UF system. This was because the permeate produced from GDM contained less assimilable organic carbon (AOC) and biopolymers. Though MF membranes make an ideal choice for particle rejection down to 0.1µm, it may fail in circumstances where silt particles of a size comparable to MF pores is brought into the intake. These may clog the membrane pores rendering irreversible membrane fouling [31]. Thus, before any mainstream operation, comparative pilot plant studies become essential for understanding the suitability of the type of membrane pretreatment. Unlike MF membranes, UF membranes do not suffer from such problems, owing to their smaller pore sizes. Table 6 lists some common advantages and disadvantages of MF as a pretreatment to RO while Table 7 summarizes some recent advancements in MF membrane materials over the last five years.

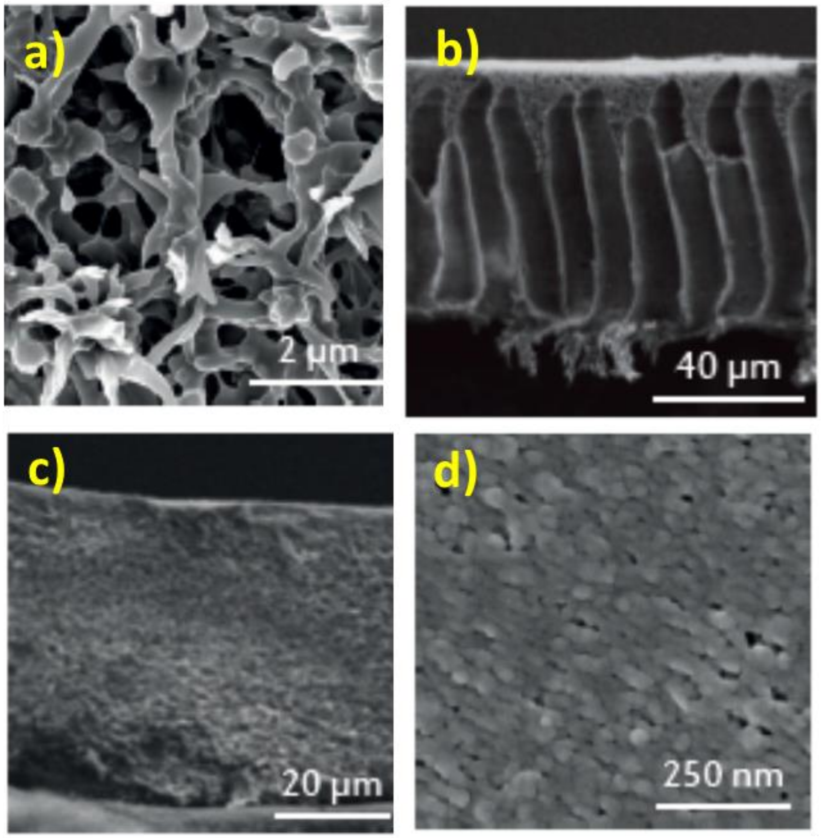

Figure 11: SEM images of MF/UF membranes formed from phase inversion. (a) Top view of a commercial 0.22-µm pore size polyvinylidene fluoride MF membrane (b) Cross-section of an asymmetric PSf UF membrane with finger like macro voids (c) Cross-section of an asymmetric PSf UF membrane with a sponge-like structure (d) Top view of a hand-cast PSf UF membrane. (EMD Millipore, Billerica, Massachusetts, USA). Figures b and c are reproduced with permission from [163] , Copyright © 2011, Elsevier.

Table 4: Comparison of polymeric and ceramic membranes. Adapted from [148].

Parameter	Polymer	Ceramic	Polymer-Ceramic
Cost	L	H	M
Packing density	H	L	M
Ease to Manufacture	H	L	M
Robustness	L	H	M
Fouling tolerance	L	H	M
Cleaning ease	L	M	M

Comparisons: H=high, M=medium, L=low

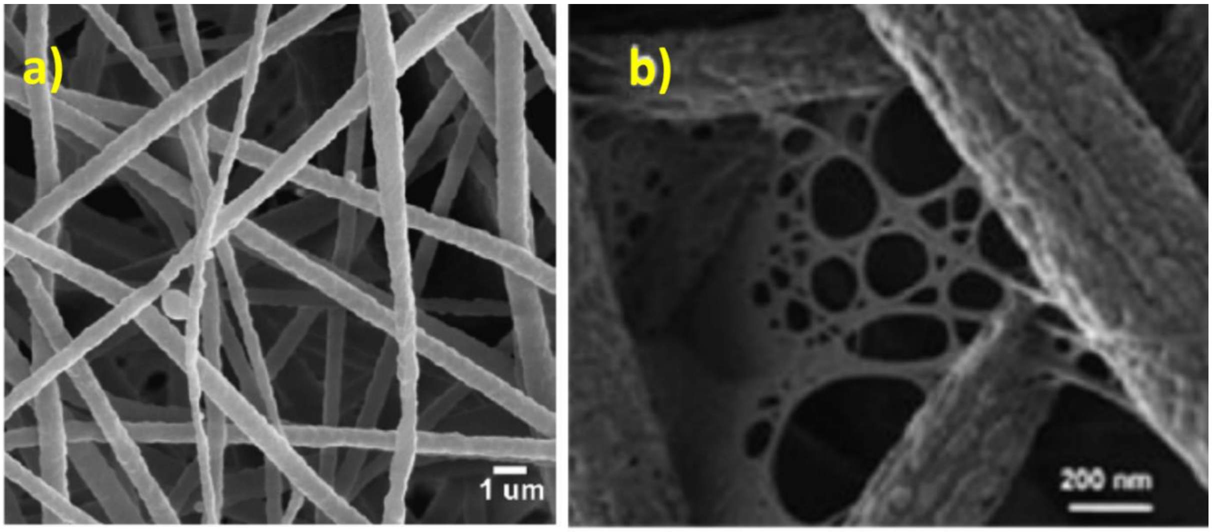

Figure 12: SEM images of (a) electrospun PSf membrane 12,000× magnification [156] and (b) top view of PAN/PET membrane infused with cellulose nanofibers. Reproduced with permission from [161]. Copyright © 2013, Elsevier.

2.2.2 Ultrafiltration (UF)

Compared to MF pretreatment, UF has found broader applications for SWRO pretreatment due to its ability to reject a wide variety of contaminants ranging from viruses, suspended organics, silt and bacteria. Comparative studies have proven that UF can produce permeate waters with lower fouling potential for RO units [31]. The Wangtan Datang power plant uses UF pretreatment for SWRO which is capable of producing water with SDI<2.5 and removing turbidity by 98–99.5% [164]. When UF and MF pretreatment methods were compared at pilot trials in Singapore [59], permeate waters after UF gave SDI between 1.0 and 2.0 while for MF, SDI values fluctuated between 2.0 and 3.0. Nevertheless, just as in the case of MF, hybrid systems integrating UF with other conventional pretreatment techniques have proven to be more efficient in giving permeate waters with lower SDI compared to stand-alone units [165]. Recently, Monnot, et al. [166]

reported the feasibility of using GAC before UF. GAC strongly reduced SDI and turbidity and removed around 70% of DOC and 90% of colloids. A pilot plant operating on Gibraltar surface seawater used a combined UF-coagulation system prior to RO. This integrated system effectively reduced the SDI from an initial value of 13-25 to 0.8 [167]. Kim et al. [168] reported a comparison of UF and DMF for low turbidity seawaters. UF coupled with coagulation could produce high quality feed waters with low SDI, while DMF failed to remove particles several microns in size leading to increased SDI values. Guastalli et al. [169] reported comparative studies on DAF-DMF and DAF-UF pretreatment techniques for the removal of dissolved organic matter. Both treatments exhibited a high microbial elimination rate and maintained the turbidity <0.1 and SDI<2. However, UF was able to remove algal content by almost 100%, while DMF could only achieve about 60% algal removal. The Heemskerk water treatment plant in the Netherlands also utilizes a UF/RO system. Initially, a coagulation-sedimentation-filtration method was adopted prior to RO. However, on integration with UF, superior particle removal led to the mitigation of colloidal fouling. The hybrid pretreatment system coupled with RO achieved several objectives including removal of organic pollutants, inorganics and biological stability [130]. Field evaluation on the Mediterranean water at Ashdod showed that during periods of severe storms, a hybrid coagulation-UF system gave consistent water quality compared to conventional pretreatment. Similar results were observed at the Kindasa SWRO plant where conventional pretreatment severely affected the RO unit during algal blooms. However, a hybrid system of coagulation-UF produced consistent permeate waters of SDI<3 [170]. Pilot plant testing at the U.S Naval Facilities clearly showed a vast difference when UF was used as a standalone process before SWRO. Figure 13 shows the SDI_{15} variation with time. Without coagulation addition, the average SDI values are greater than 1, while a hybrid system lowered the average SDI to 0.5 [171]. Laboratory scale studies on the impact of coagulation on UF revealed that coagulation can postpone membrane fouling and retard membrane cleaning frequency by the removal of large sized hydrophobic compounds and reducing humic acids [172]. One of the largest UF pretreatment units, at Addur, Bahrain, has a SWRO production capacity of 140,000 m^3/day and uses a media filtration-UF hybrid system. UF membrane performance gave a flux of around 40 l/m^2h [173]. Similar large scale and pilot tests have been reported, confirming the superior efficiency of UF hybrid systems [174-176]. Table 5 lists some large scale SWRO plants utilizing UF as a pretreatment to RO. In contrast to the above studies, Riaza et al. [177] reported their study on the Qingdao Pilot plant where coagulation using 0.1–0.5 mg/L Fe could not improve the UF operation in terms of permeate flux. Similarly, numerous other studies such as those based on the Wang Tan plant (2005), Moni desalination plant in Cyrus (2008), Magong plant (2008) and Barcelona pilot plant (2009) [178] showed that a well-designed UF unit can be based on minimum primary treatment, requiring only screens. Today, around 3.4 M m^3/d of SWRO capacity uses UF pretreatment. Figure 14 shows the relative importance of key drivers for UF pretreatment emergence in the SWRO industry. It is evident that its superior capability to cope with difficult waters and its simple design and operation has been a primary reason for its emergence. Nevertheless, present and future drivers include lower carbon footprint and pretreatment costs [178], which will be discussed in more detail in sections 4 and 5

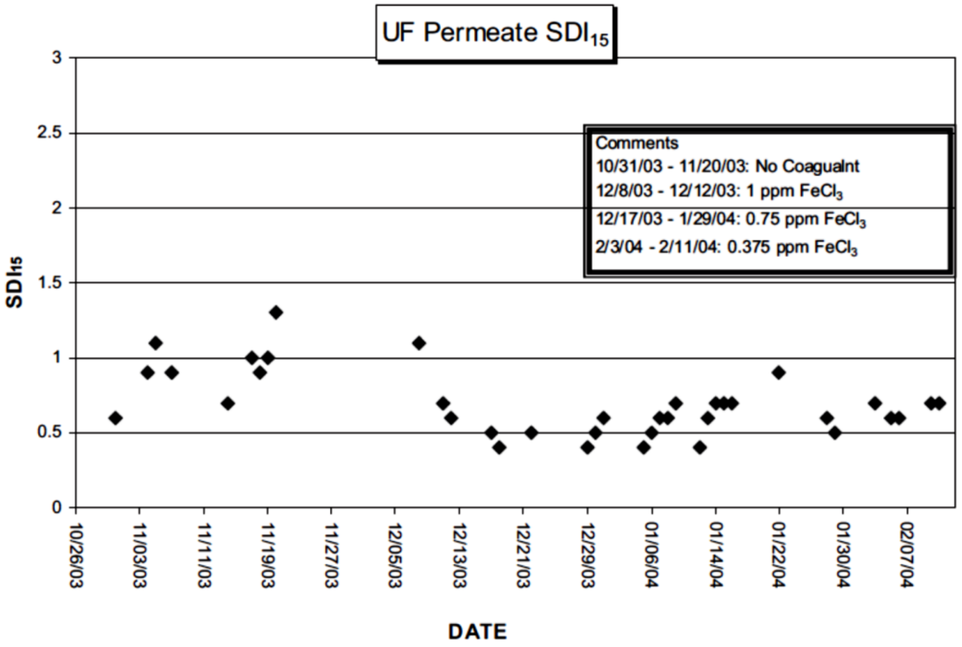

Figure 13: Variation in SDI with and without coagulation addition before UF. Reproduced with permission from [171], Copyright © 2005, Elsevier.

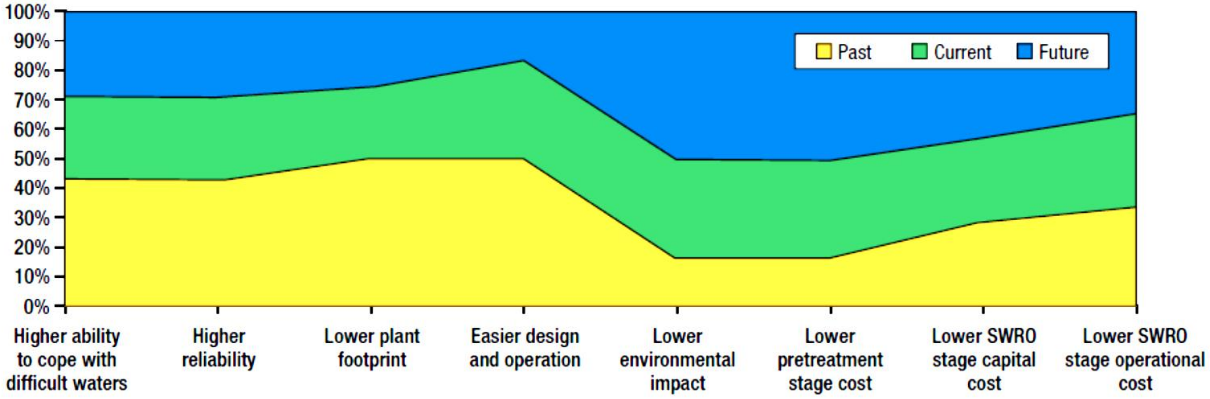

Figure 14: Relative importance of key drivers (in terms of %) for the emergence of UF pretreatment for SWRO. Reproduced with permission from [178]. Copyright © 2010, Taylor and Francis.

Usually, MF and UF are fabricated from similar types of polymeric membranes based on second generation membrane materials such as PVDF, PSf and PAN, produced through the phase inversion process. These polymers are mechanically robust and thermally stable. DOW™ produces commercial hollow fiber PVDF UF modules with 0.03 µm nominal pore diameter for the rejection of bacteria, viruses, and particulates [179]. Cellulose-acetate (CA) based membranes are also an exciting option because they possess a more hydrophilic character, but are less thermally stable and their application is limited to a narrow pH range of 2–8 and an operating temperature of less than 30 °C [147]. Soyekwo et al. [180] reported CA nanofibers made initially though freeze-extraction, which were later developed into UF membranes by filtering the dispersions onto a CA MF support layer. High porosity of 71% was obtained within the membranes which gave ferritin rejections of about 90.7% with a 3540 l m^{-2} h^{-1} bar^{-1} water flux. Such high fluxes, which were 10 times greater than the commercial ones, were the key result of their study.

Different types of membrane morphologies might result depending upon different process parameters. Figures 11 (b-d) show SEM images of various asymmetric PSf UF membranes consisting of a dense active layer on a support layer [147]. Gómez and Lin [181] prepared acrylonitrile-vinyl acetate /acrylonitrile-vinyl acetate-sodium p-sulfophenyl methallyl ether UF membranes through the phase inversion process. Membrane characteristics were found to vary with cast solution compositions with the membrane's charge density increasing with the percentage of acrylonitrile-vinyl acetate-sodium p-sulfophenyl methallyl ether. Recently, Akhondi et al. [162] reported a study on gravity-driven membrane ultrafiltration pretreatment utilizing PSf as the membrane material. A cake layer was observed on the PSf membrane which required a higher hydrostatic pressure and temperature to improve the water flux. However, most of the particles in the feed seawater were removed leading to lower RO membrane fouling, with the exception of DOC due to the conversion of CO_2 into organics by algae. Conidi et al. [182]

experimented an initial UF step (prior to NF) using PSf hollow fiber membrane modules for the removal of suspended solids from an artichoke extract. An initial permeate flux of about 19 kg/m^2 h was gradually seen to decrease due to concentration polarization. The step was unable to remove sugars (glucose, fructose and sucrose), chlorogenic acid and cynarin. However, suspended solids were completely rejected. In another study, Giacobbo et al. [183] demonstrated the recovery of polysaccharides and polyphenols using a PES flat-sheet UF membrane. Around 56.6% reduction in TOC was obtained by optimizing the transmembrane pressure from 0.5 to 4.0 bars.

Poly (ether sulfone) (PES) has shown good potential as an UF membrane material. Pieracci et al. [184] reported the modification of poly(ether sulfone) (PES) UF membranes by photolysis using UV light. They used graft polymerization of hydrophilic monomers which created more hydrophilic sites on the membrane's surface leading to their lower fouling propensity. These membranes were compared with the unmodified PES membrane, a commercial low protein adsorbing (LPA) PES membrane and a commercial regenerated cellulose (RC) membrane using 1 wt. % bovine serum albumin (BSA). Bare PES membrane had the highest contact angle of 56 ± 3^{o}. Compared with the unmodified membrane, *N*-vinyl-2-pyrrolidinone modified membrane gave a 49% decrease in BSA fouling due to its 25% increased hydrophilicity, and a 4% increase in BSA retention. The RC membrane showed the lowest fouling, but had a low flux due to its low porosity, while LPA gave the highest flux but with the lowest selectivity. The modified membrane showed an optimum performance with respect to the best combination of fouling mitigation, selectivity and flux. Marchese et al. [185] prepared several PES UF membranes with the addition of small quantities of different molecular weights of polyvinyl-pyrrolidone (PVP). Pore volume and pore size could be controlled by the polymer concentration in the casting solution whereby an increased concentration led to a high polymer concentration at the membrane interface. Addition of PVP increased the membrane’s permeability without sacrificing its selectivity towards BSA and DL-histidine (DLH). BSA caused external fouling of the membranes while the smaller size of DLG caused internal fouling. The addition of PVP was reported to prevent pore blockage due to its hydrophilic character. The plant at the Palavas les Flots , France treating the Mediterranean Sea water utilizes polysulfone hollow fibers, a proprietary design from Polymem to achieve permeate waters with SDI in the rage of 1.2-2 [186].

Besides membrane material, another important factor is the pore size distribution of the membranes. Polydisperse pore sizes can lead to increased fouling. Large sized pores will foul faster due to more local permeation and foulant penetration in the membrane’s pores, causing irreversible fouling [147]. Narrow pore sizes of about 30 nm can achieve good water quality with small coagulant doses compared to large pores > 100 nm with greater coagulant doses. Different UF configurations may behave differently. For example, at the Addur plant in Bahrain, the spiral-wound module caused fouling problems while hollow fiber modules were reported to operate well. Though pressured modules are more energy intensive, they can tolerate more difficult operations compared to gravity driven modules. This leads to lower cleaning frequencies and reduced chemical usage [178]. Moreover, during an algal bloom, if the driving pressures of UF are high enough, it could rupture the algal cells and contribute to biofouling on RO membranes. Lower energy based membrane processes and advanced materials have been suggested to address the shortcomings of the UF process [162]. Table 6 highlights advantages and disadvantages of the process while Table 7 highlights important advances in UF membrane materials.

Table 5: Large scale SWRO plants utilizing UF membrane pretreatment methods [21, 31, 178].

Plant/ Country	**Plant capacity** (m³/day)
Adelaide, Australia*	300,000
Red Sea coast, Saudia Arabia	30,000
Fukuoka, Japan	96,000
Kindasa, Saudi Arabia	90,000
Teshin, Ghana	60,000
Ashdod, Israel	275,000
Tuas, Singapore	318,000
Palm Jumeirah, UAE	64,000
Yu-Huan, China*	34,500
Ajman, UAE	115,000
Tangshan, China	110,000
Accra, Ghana	60,000
Addur, Bahrain	140,000
Chennai, India	100,000
Perth II, Australia	153,000
Honaine Tlemcen, Algeria	200,000
Piura SWRO (Biwater), Peru	100,000
Kalba, UAE	13,640
Honaine Tlemcen, Algeria	200,000

*Submersible UF membranes.

2.2.3 Nanofiltration (NF)

MF and UF membrane technologies have emerged prominently for RO pretreatment, where they have been successfully tested and installed on pilot as well as commercial scale. However, these technologies usually provide a great challenge for low quality feed water polluted with low molecular weight organic matter and pesticides [187]. Furthermore, scaling is somewhat difficult to control through the use of MF and UF as these processes fail to remove mineral salts. NF has emerged as a promising membrane pretreatment technique to overcome the shortcomings of MF and UF technologies, where it can provide high retention of multivalent anion salts and low molecular weight organic molecules, together with relatively low investment and operating pressure than RO membranes. Sofi et al. [188] reported the NF technique for water softening as a feed pretreatment step prior to SWRO. Total hardness was reduced by 86.5%, together with slight rejections of Cl^-, Na^+ and K^+ ions. During the 1970's, RO membranes operating at relatively low pressures were developed, which eventually emerged as NF membranes at a later stage, with the current RO membranes operating at high pressures with high fluxes and higher rejection of dissolved components [189]. In 1990, the NF process was tested as a pretreatment for seawater desalination by the Saline Water Conversion Corporation. The NF unit received non-coagulated filtered seawater feed, after which the NF permeate was passed as RO feed to SWRO unit. It was found that NF, operating at 22 bars, could reduce the turbidity and microorganisms, as well as reduced the content of Ca^{++}, Mg^{++}, $SO_4^{=}$, HCO_3^- ions. The NF process proved capable of supplying high quality permeate without scaling problems associated with scale forming ions. Thus, the SWRO plant was able to operate at high water recoveries of up to 70% with no requirement of a second-stage RO treatment due to the low TDS<200ppm obtained [190]. This preliminary pilot study was an important milestone for further adaption of NF as a membrane pretreatment process prior to RO. A demonstration plant built in Umm Lujj, Saudi Arabia, consisting of NF-SWRO confirmed these initial pilot studies [191]. Al-Amoudi and Farooque [192] reported a dual NF–SWRO desalination process in Umm Lujj plant increased permeate flow significantly from

91.8 to 130 m^3/h compared to a single SWRO desalination process. Since then, many studies have reported NF-SWRO operational improvements. For example, a NF process was operated at a flux of 12 gdf with occasional flushing of pretreated seawater to avoid chemical cleaning for up to 2 years. In another report, 42% increase in production rate was achieved when NF was operated at 25 bars and a feed pH of 6 [193]. Xia et al. [194] showed that NF could be useful for the removal of arsenic. They tested PA membranes in a pilot plant for fresh salt water mixed with arsenic species. Their results showed that there was a difference in the removal of arsenic depending upon the arsenic ion. The membrane was able to fully remove As(V), while only 5% rejection was obtained for As (III). Further, the presence of salt mixtures and pH was shown to have an impact on arsenic removal as well with the percentage removal increasing with increasing pH. Recently, He et al. [195] studied novel TFC NF membranes for the same. They incorporated a zwitterionic copolymer P[MPC-co-AEMA] during the interfacial polymerization reaction with TMC. Superior Arsenic rejections reaching about 99.8% were achieved, much higher than the commercial membranes. The enhanced performance was attributed to the small pore size of the membrane together with its hydrophilic character owing to the PA selective layer consisting of the copolymer P[MPC-co-AEMA].

Choi et al. [196] reported that among various pretreatment technologies NF produced the highest flux for RO. NF not only removed inorganic scalants, but also colloidal particles. An integrated MF–NF–RO-MD system was reported by Drioli et al. [197] which showed an increase in water recovery of up to 92.8% due to removal of hardness and lower osmotic pressure of the pre-treated feed water at the RO stage. Besides NF, MF prior to NF was found to play a critical role in reducing membrane fouling at later stages. Furthermore, a hybrid UF–NF membrane system for desalination pretreatment was reported by Song et al.[198] which produced better effluent with 96.3% TOC removal for long term operations. However, more operational improvements were required due to membrane fouling. For example, scaling of a hybrid UF-NF-SWRO unit was investigated [199], which showed a different scaling potential of NF compared to SWRO and thermal desalination. Such directed studies are necessary for effectively tackling the fouling problems in membranes. One solution to improved fouling resistance, as well as lower operational burden lies in the type of membrane material utilized. Today, an advanced understanding of molecular level mechanisms and well-defined fabrication processes have enabled control over NF nanostructured membrane materials. Selectivity can be improved by tailoring the pore size of the membranes, whereby the water can be allowed to pass through the membrane keeping solvated ions behind.

Interfacial polymerization has emerged as a promising method for thin film NF membrane fabrication, where an active thin layer of ≤ 50nm is formed on a support through the copolymerization reaction of two reactive monomers. This active layer determines the overall permeability, selectivity and overall efficiency of the membrane. Various types of monomers have been studied for interfacial polymerization including BPA, MPD and TMC [200]. Abu Seman et al. [201] studied BPA and Tetramethyl Bisphenol A (TMBPA) aqueous solutions at different concentrations and reaction times together with TMC in order to modify PES membranes. Fouling tests were performed using humic acid as a model organic foulant. Lower irreversible fouling tendency was observed for the membranes modified with BPA-polyester when compared with unmodified TMBPA-polyester membranes, predominantly due to the repulsion between the negatively charged humic acid and the negatively charged BPA-polyester layer. Li et al. [202] reported a novel enhanced fouling resistant, NF membrane prepared by the interfacial polymerization of an antibacterials monomer called polyhexamethylene guanidine hydrochloride (PHGH) and TMC on a PSf UF membrane support. Salt rejections followed the order of $MgCl_2$>$MgSO_4$>Na_2SO_4>NaCl, while dye rejection results showed promising feasibility of the novel membranes to reject organic molecules with a MWCO of around 700 Da. Recently, Abdikheibari et al. [203] reported thin film composite NF membranes using polypiperazine amide (PPA) active layer incorporating amine functionalized-boron nitride, $BN(NH_2)$, nanosheets. Membranes with $BN(NH_2) \geq 0.004$ wt. % showed greater hydrophilicity with contact angles of about 30^o and less compared to the bare PPA membrane ($\approx 40^o$), resulting in higher water permeability with superior fouling resistance. Apart from interfacial polymerization, Malaisamy and Bruening [204] reported the layer-by-layer deposition of poly(styrenesulfonate) (PSS)/protonated poly(allylamine) (PAH) and PSS/poly(diallyldimethylammonium chloride) (PDADMAC) to form NF membranes on an UF support layer. Fluxes through PSS/PAH and PSS/PDADMAC thin films on 50 kDa UF supports were reported to be twice those of commercial membranes, with high rejections of sucrose and raffinose of around >95%. In addition to the above mentioned polymers, much other research has focused on polymer membranes fabricated using TMC and MPD monomers. Tsuru et al. [205] reported a spray-assisted, 2-step interfacial polymerization of TMA and MPD for PA membrane preparation. TMC/hexane solution was first sprayed onto MPD-PSf support, which was then put into contact with the TMC/hexane solution. Water permeability was seen to increase with this 2-step process due to the increased interfacial surface area of the PA membranes through the formation of small and large ridge-valley structures consisting of globular projections of about 100-200nm, as shown in Figure 16. The surface (Figures 15 (a-b)) and cross section (Figures 15(c-d)) images also confirmed the presence of a multilayered structure.

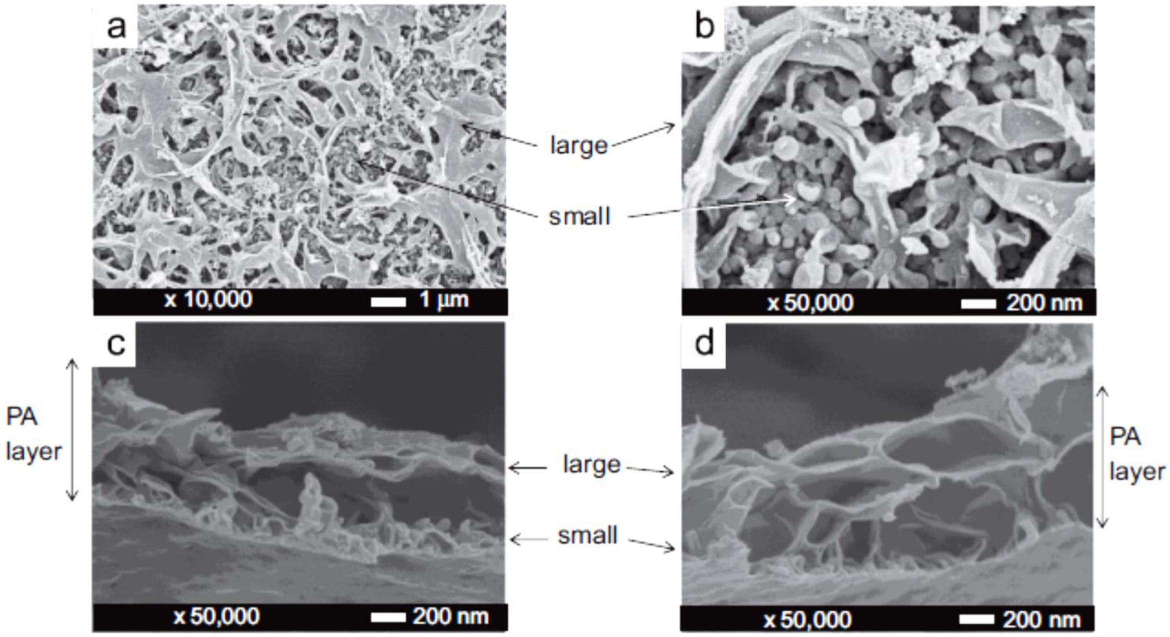

Figure 15: SEM images of (a-b) surface and (c-d) cross-section of membrane and different magnifications. Reproduced with permission from [205], Copyright © 2013, Elsevier.

Table 6 lists NF advantages and disadvantages. A major disadvantage of NF is related to membrane fouling predominantly caused by hydrocarbons and extracellular materials [5]. Bruggen et al. [206] identified several challenges for using NF. Apart from membrane fouling, these include lifetime of membranes, improving the separation between solutes, insufficient rejection of pollutants and the need for new and improved modelling and simulation tools. Limited work has been reported on the modelling of fouling in NF. The Hagen–Poiseuille and the Jonsson and Boesen models, which are commonly used for MF and UF membranes, does not account for the interaction parameters. Usually, membrane manufacturers develop their own simulation software, however these are often limited to standard configurations and membranes [206]. NF offers several advantages when used prior to RO treatment. It can provide operational and maintenance cost reductions by reduced RO membrane replacement and lower RO membrane cleaning requirements. However, higher capital cost requirements and membrane fouling propensities need to be considered when designing pretreatment operations based on NF [22]. In most cases, a hybrid system consisting of conventional-membrane pretreatment processes is the most viable option, depending upon feed water quality. Table 7 lists recent advances in the NF membrane materials field.

Table 6: Advantages and Limitations of RO membrane pretreatment technologies

Membrane pretreatment method	Advantages	Limitations
MF	• Reduction in chemical dosages. • Reduction/elimination of fine filters in the RO system • Lower RO membrane replacement cost. • Lower operational costs. • Less RO system downtime • Elimination of cartridge filters cost.	• Sensitive to oxidizing agents. • Not able to reject viruses. • Membrane damage may be caused by hard and sharp particles > 0.1 mm. • Economic concerns: highly concentrated concentrate containing bacteria and suspended matter.
UF	• Ability to reject a wide range of contaminants ranging from suspended organics, silt, pathogens and viruses. • Eliminates pH increase before SWRO stage. • Reduce continuous chlorine additions or intermittent dosing. • Tolerable to unfavorable variations in feed water • Lower sludge production.	• UF alone cannot isolate individual phenolic fractions. • Polydisperse pore size distribution may cause irreversible fouling; challenging to control porosity and pore sizes. • Can contribute to biofouling in RO membranes during periods of high algal blooms. • Critical to module designs; hollow fiber, flat sheets, tubular, etc.
	• High retention of multivalent anion salts	• Subject to salt precipitation causing membrane scaling in NF

NF	• High retention of low molecular weight organic materials. • Reduces scaling in RO membranes by removal of hardness. • Lower required pressures to operate SWRO plants by reducing seawater feed TDS by 30- 60%. • Higher RO design flux and recovery may be possible • RO membrane replacement reduced significantly • Reduced requirement for RO disinfection and cleaning	membranes, due to smaller pore sizes. • Chemical resistance and limited lifetime of membranes. • Limited simulations and modelling tools availability.

Table 7: Recent advances in MF/UF/NF membrane materials in the last 5 years

MF			
Reference	**Materials**	**Fabrication Method**	**Key Features**
Nasreen et al. [207], 2014	PVDF-poly hydroxyethylmethacrylate (HEMA)	Electrospinning	Enhanced hydrophilicity and improved flux
Fontananova et al. [151], 2015	PVDF-MWCNTs	Solution casting and phase separation technique	Increased hydrophilicity leading to increase in flux and reduced fouling propensity.
Ghandashtani et al. [208] , 2015	SiO_2/ PES	Combination of vapor induced phase separation and non-solvent induced phase separation	Improved Hydrophilicity
Huang et al. [209], 2015	PVDF-SS mesh	Immersion precipitation in non-solvent bath.	Conductive MF membrane providing fouling mitigation
Fan et al. [155], 2016	Thermoplastic linear low-density polyethylene (LLDPE)	Imprint and thermal field induction	An innovative well-ordered ‘wine bottle’ Shaped through-pore channels. Pure water flux was found to be is 1.4–1.6 times higher compared to the commercial MF membranes.
Yu et al. [210], 2017	N-isopropylacrylamide (NIPAM) and methacrylic acid (MAA)	Polymerization inside three dimensional (3D) inverse colloidal (silica) crystals (ICC) templates.	A smart thermo- and pH-responsive, conductive MF membrane.

Castro et al. [154], 2017	PMMA	A vacuum assisted UV micro-molding (VAUM) process	Cost effective, robust, high aspect ratio, and porosity. High particle capture efficiencies (≈98%).
Zielińska and Galik [211], 2017	TiO_2 and ZrO_2 (commercial membranes from Tami industry, France)	-	MF prior to UF gave the best results. >87% of COD removal, and almost complete removal of TSS and turbidity.
UF			
Rabiee et al. [212], 2014	TiO_2/PVC	Non-solvent induced phase separation method	Improved hydrophilicity
Soyekwo et al. [180] 2014	CA nanofibers	Direct filtering technique	10 times higher flux than commercial membranes
Liu et al. [213], 2014	Zeolite 4A/PSf	Casting	Improved hydrophilicity and selectivity.
He et al. [214], 2014	MCM-41/PVDF	Electrospinning	Improved mechanical properties and water permeability.
Li et al. [215]	MWCNTs/PES	Simple drop-casting and phase inversion	Pre-aligned vertical CNTs enabled high flux compared to randomly oriented CNTs in PES matrix
Lalia et al. [216], 2015	CNS/PVDF	Vacuum filtration	High electrical conductivity membranes for period electrolysis cleaning of foulants.
Xu et al. [217], 2016	Graphene oxide/TiO_2-PVDF	Solution casting and phase inversion	Photocatalytic antifouling function
Li et al. [218], 2016	SiO_2 /GO PVDF	Thermally induced phase separation	Improved hydrophilicity
Rakhshan et al. [219], 2016	SiO_2/cellulose acetate	Phase inversion	Improved hydrophilicity
Ghaemi et al. [220], 2016	polypyrrole@ Al_2O_3/PES	Phase inversion	Improved metal removal and higher flux compared to pristine PES.
Xu et al. [221], 2016.	Ag–Cu2O/PSf	Phase inversion	Enhanced antibacterial properties
Omi et al. [222], 2017	Carboxylic-functionalized MWNTs/PSf	Vacuum filtration assisted layer-by-layer deposition	Almost complete inactivation of E-coli at low applied DC potential (1–3 V)
Wang et al. [223], 2018	Sodium lignosulfonate functionalized CNTs- PES	Phase inversion	Antibacterial properties on application of a small electric field.
NF			
Gholami et al. [224], 2014	Fe_3O_4/PVC-cellulose acetate	Casting	Superior performance in lead removal compared to other modified pristine membranes.
Rashid et al. [225], 2014	Self-standing MWCNTs-bucky paper	Vacuum filtration	Highly hydrophilic

Mehwish et al. [226]	PVDF-SBS- SCN/silver-modified MWCNTs	Solution blending/Casting	Superior porosity and high permeate flux, selectivity and recoveries.
Dong et al. [227], 2016	PA/Zeolite LTL-PSf support	Casting and interfacial polymerization	Increased surface roughness and water permeability.
Wang et al. [228], 2017	Diamine and acyl chloride on cellulose nanocrystal / support	Interfacial polymerization	Ultra-high permeation flux up to 204 L.m^{-2}h^{-1}, Na_2SO_4 rejection > 97%.
Lv et al. [229], 2017	polyydopamine (PDA)/polyethyleneimine (PEI) / UF support	Co-deposition method	Efficient photocatalytic activity and self-cleaning capability.
Yang et al. [230], 2017	ZIF-8/ polyethyleneimine (PEI)	self-assembly and interfacial reaction method	Easier synthesis routes for uniformly dispersed zeolite particles in a polymer matrix.
Wang et al. [231], 2018	PA layer via on a single-walled CNT /PES support	Interfacial polymerization	High water permeance up to 53.5 l m^{-2}h^{-1} bar^{-1} with a rejection above 95% for Na_2SO_4.
Abdikheibari et al. [203], 2018	Polypiperazine amide (PPA) active layer incorporating amine functionalized-boron nitride,$BN(NH_2)$ nanosheets.	Interfacial polymerization	Improved fouling resistance

2.2.4 Ceramic Membranes

The third generation of membranes, based on ceramic materials, appeared in 1980 when France introduced the CARBOSEP® mineral membrane. These membranes had a tubular configuration with carbon covered by a thin microporous layer of zirconia (ZrO_2). Ceramic membranes offer an ideal combination of hydrophilicity and robustness. However, their cost is usually higher than their polymeric counterpart. Nevertheless, the high capital investment in this membrane material can be compensated by their higher fluxes and longer lifetimes (up to 10 years). These membranes offer excellent thermal properties, chemical stability and can bear high operating pressures. Their superior thermal stability can be advantageous, allowing them to be subjected to high temperatures >500^{o}C during membrane cleaning. An added advantage is easy control of process parameters during manufacture, leading to controlled pore sizes and thus more foulant resistance [148, 232]. Table 4 highlights some basic differences between polymeric and ceramic membranes. Symmetric or isotropic ceramic membranes are typically fabricated through either extrusion [233], slip casting [234] or pressing [235], while asymmetric membranes can be prepared by coating symmetric ceramic membranes using dip-coating [236], sol-gel [237] and chemical and electrochemical vapor deposition techniques [238]. Isotropic membranes comprise a homogeneous composition usually consisting of a single material while asymmetric membranes usually consist of a macro- or/and mesoporous support layer with a thin active layer of about 1µm or less on the upper surface. Ceramic membranes for UF, MF and NF has seen a rapid increase in research during the past years [239]. Alumina (Al_2O_3) [240], silica (SiO2) [241], titania (TiO2) [242], zirconia (ZrO_2) [243] and/or their combinations are among the widely used ceramic membrane materials for RO pretreatment. For example, Ahmad and Mariadas [244] reported a study of tubular single channel δ-alumina ceramic membranes for MF, possessing nominal pore size of 0.2 µm. They inserted helical baffles to promote turbulence and the flux was increased to up to 104.9% during the MF process. Jiang et al. [241] reported mesoporous silica membranes prepared using H_3PO_4 as the pore forming agent. They reported its potential for UF whereby the pores of the membrane could be easily controlled by adjusting the H_3PO_4 concentration. Shang et al. [245] reported their study on two commercial TiO_2 UF membranes possessing different molecular weight cut-offs, obtained from TAMI Industry, France for phosphate rejection. Rejection of phosphate prior to RO can be an effective means for controlling RO membrane biofouling. It was observed that a higher negative surface charge of the membrane provided greater electrostatic repulsion against phosphate, while a pH of 8.5 registered the highest phosphate rejection of 86%. These ceramic membranes come in various configurations (Figure 10) and structures.

Dey et al. [246] studied a hollow fiber MF 0.1 µm Microza® ceramic module for Arabian coastal sea water. A flux of 370 LMH was achieved with an SDI < 2.0 for raw water SDI of 6 and above. Hamad et al. [247] reported a pilot plant study using a flat sheet, hydrophilic alumina monolithic membranes obtained from METAWATER having pore size of about 0.1µm. Ceramic membranes successfully reduced the SDI_{15} of Red Sea seawater from 6.1 to 2.1, while turbidity values improved to 0.05 from 0.6. However, it was observed that a significant increase in TMP was needed after backwashing which was attributed to biofouling due to the presence of sticky transparent exo-polymers particles (TEP), which are usually abundant in seawater. Typically, the choice of material strongly depends on the water quality to be treated. Certain biological contaminants such as bacteria, virus, algae and protozoans, can cause serious water borne illnesses. Zhang et al. [248] synthesized hierarchical TiO_2 nanowire (TNW) UF membranes through a hydrothermal and hot-press approach. 10nm TiO_2 nanowires (TNW_{10}) (Figure 16a) were used as an active membrane layer while those having 20nm diameter (TNW_{20}) (Figure 16b) were used as a support layer. The membrane was successfully tested for the removal of polymeric and bacterial derivatives, with an added advantage of completely destroying organic and biological pollutants under UV irradiation. Figures 16 (c-d) show the schematic and the digital image of the TNW membranes.

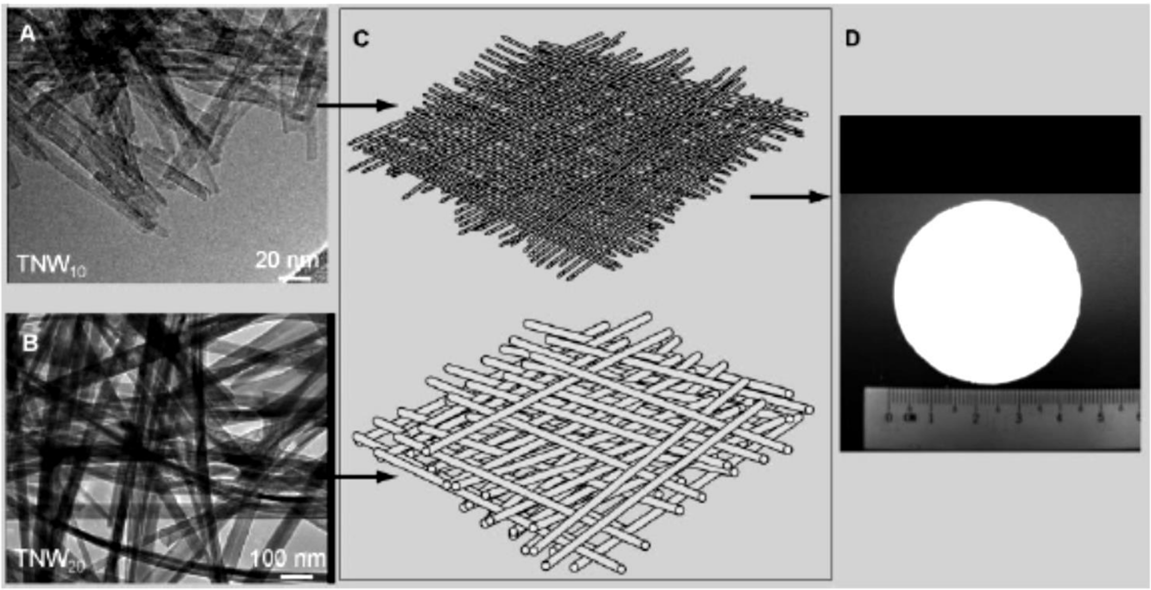

Figure 16: a) TEM image of TNW_{10}, b) TEM image of TNW_{20}, C) Schematic profiles of the TNW UF Membrane and d) a digital photo of the TNW membrane. Reproduced with permission from [248], Copyright © 2009 WILEY-VCH VerlagnGmbH & Co. KGaA, Weinheim.

Figure 17 compares the selectivity-permeability trade-off for different UF membranes fabricated from different materials for BSA rejection including PSf, PES, acrylic, acrylonitrile cellulosic, ceramics and polycarbonate track-etched materials [249]. Apart from some outliers, most of the materials cluster along the same curve. The polycarbonate track-etched materials are usually confined to laboratory studies, while the E-series membranes are produced by Desalination Systems available in spiral wound modules. An ideal membrane usually displays a high separation and a high permeability, something which is non-existent in Figure 17. Therefore, a lot of room for improvement is present to achieve highly selective and permeable membranes to be utilized prior to RO. One solution is hybrid membranes where a combination of materials is utilized for improved membrane performances.

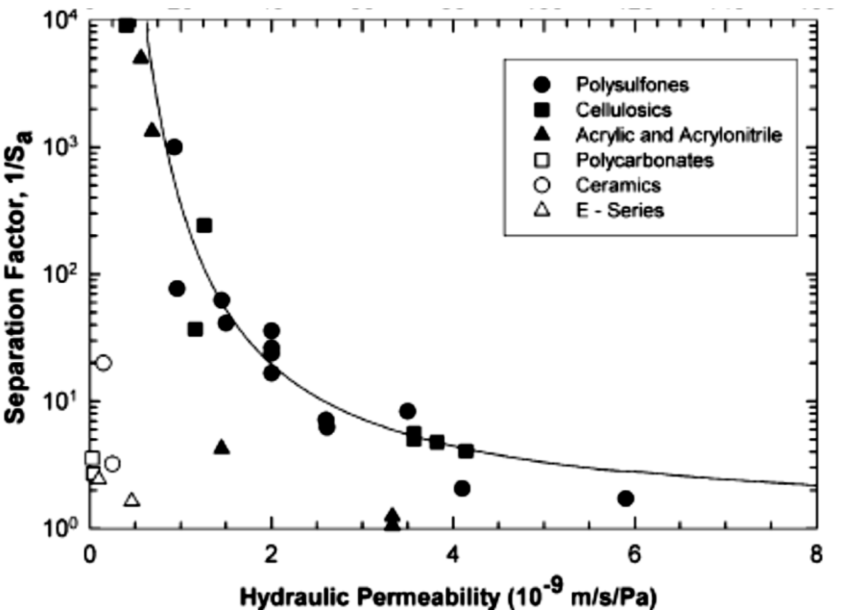

Figure 17: Selectivity–permeability trade-off for UF membranes using BSA as the model protein. Reproduced with permission from [249], Copyright © 2005, Elsevier.

Many studies report the incorporation of ceramic particles embedded in a polymer film. These mixed matrix membranes (MMM) generally have inorganic particles incorporated into a macroscopic polymeric matrix. This provides a combination of properties from both classes of materials achieving higher mechanical strength with superior processability and low cost of polymeric materials. MMM can be prepared using several of the conventional and non-conventional ceramic materials such as AL_2O_3, Fe_3O_4, SiO_2, TiO_2, ZrO_2 and CNTs into various polymeric materials through phase inversion and, surface coating techniques [239]. Liang et al. [150] reported a novel approach for fabricating PVDF UF membranes through post-fabrication grafting of surface-tailored silica nanoparticles. This improved the hydrophilicity of PVDF which otherwise is prone to fouling. Pure PVDF membrane was grafted with PMMA by plasma induced graft copolymerization. This provided carboxyl sites to which the silica nanoparticles could bond to. Positively charged amine functional groups were used to tailor the surface of these nanoparticles producing a high surface energy, hydrophilic membrane (Figure 18). Strong antifouling performance was observed using BSA filtration tests suggesting a promising material for membrane filtration. In an another study, Rabiee et al. [212] reported improved hydrophilicity using PVC/TiO_2 nanocomposite UF membranes prepared through the phase inversion method with varying metal oxide concentrations. An increase in flux was observed owing to increased hydrophilicity with increasing TiO_2 concentration, which however started to show an opposite trend after 2 wt. % TiO_2 content because of nanoparticle agglomeration. Enhanced BSA rejections of up to 98% were reported with high antifouling performances for PVC-2 wt. % TiO_2 membranes. Arsuaga et al. [250] reported improved hydrophilicity of TiO_2/PES, Al_2O_3/PES and ZrO_2/PES UF membranes produced through the phase inversion method leading to improved fouling resistance. Similar improved hydrophilicity has been reported by Ghandashtani et al. [208] and Rakhshan et al. [219] for SiO_2/PES and SiO_2/CA membranes respectively. Table 7 further highlights some important recent research into improving the hydrophilicity of MF and UF membranes through metal oxide nanoparticles embedded in polymer matrix.

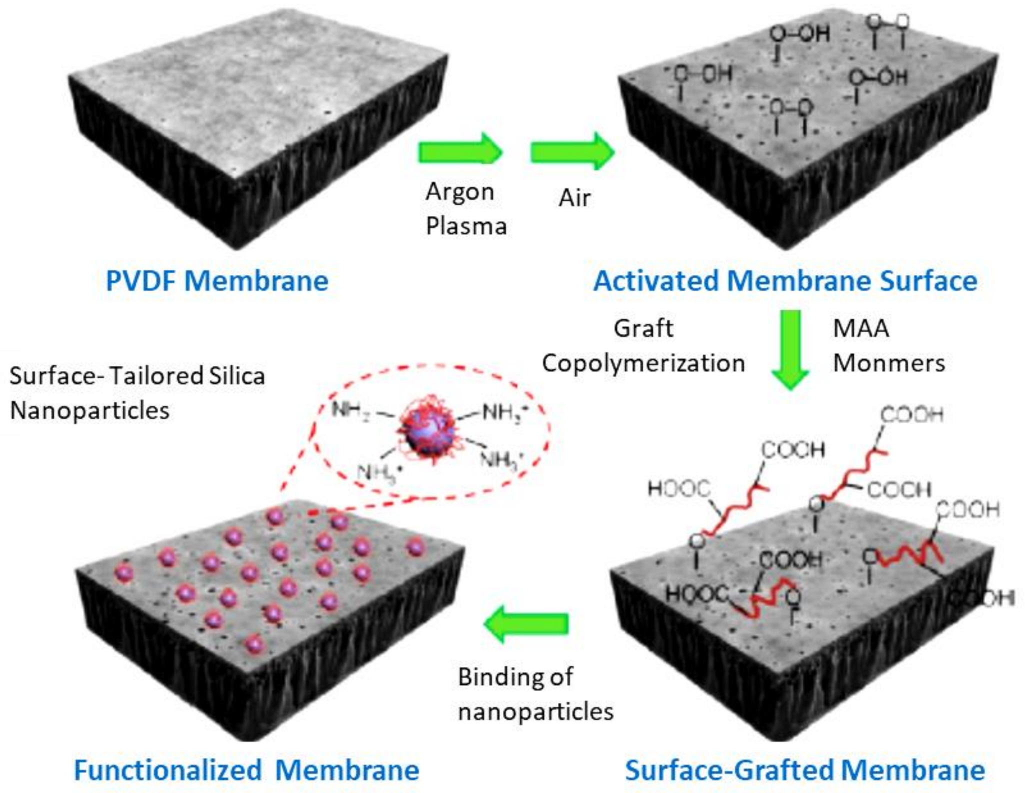

Figure 18: PVDF membrane activated with plasma and introduced to MMA monomers leading to the attachment of carboxyl groups on the membrane surface. These acted as binding sites for the silica nanoparticles. Positively charged ligands, terminated with amine functional groups, were then used to tailor the surface of the nanoparticles rendering a highly hydrophilic PDVF membrane (Reproduced with permission from Liang et al. [150], Copyright © 2013, American Chemical Society.

Besides SiO_2 and Al_2O_3, their combination as crystalline aluminosilicates called zeolites have been of great research interest whereby zeolite membranes, zeolite supports and MMM of zeolite-polymeric membranes have gained considerable attention in membrane filtration. Several methods have been reported for zeolite membrane fabrication [251, 252]. Zeolite membranes on porous inorganic supports offer many advantages compared to polymeric membranes, such as uniform porosity, high selectivity, high thermal and chemical stability and molecular-sized pores [239]. Zeolites can put a break on the apparent tradeoff which exists in UF and NF membranes based on selectivity and permeability. Due to its unique, well ordered pore structures, zeolite membranes can offer both high selectivity and high water permeation. Among the various types of zeolites reported till date [253, 254], hydrophilic zeolites, type-X with a low SiO_2/Al_2O_3 are the more prominent ones for membrane filtration. Liu et al. [213] reported the performance of Zeolite 4A/PSf UF membranes. Morphological analysis confirmed the presence of zeolite 4A embedded in the active membrane layer within the depth of less than 1 µm whereby an increase in hydrophilicity was observed, together with a more negatively charged membrane with an increase in zeolite content. The membranes registered a pure water flux of 500 $l/(m^2.h)$ with 97.0% BSA and 88.6% pepsin rejections. Han et al. [213] reported NaA/ poly(phthalazinone ether sulfone ketone) (PPESK) UF membranes. NaA zeolite with 3 wt. % imparted hydrophilicity to the much hydrophobic PPESK membranes with improved PEG 6000 rejection from 77.9% without zeolite addition to about 96.8% with zeolite addition. However, a slight decrease in membrane flux was observed together with microscopic evaluation revealing agglomeration of the zeolite particles above 3 wt. % zeolite concentration. He et al. [214] reported electrospun nano MCM-41/PVDF UF membranes (Figure 19a) where a 3 wt. % addition of zeolite improved the membrane's permeability and mechanical properties considerably. Pure water permeability of 118.9×10^3 L/m^2h bar was achieved compared to 91.2×10^3 for pure membranes, while a tensile strength of 71.75 MPa was obtained compared to 22.5 MPa for pristine PVDF UF membranes. Figure 19b shows a TEM image of the hybrid fiber highlighting the zeolite nanoparticles within the fiber. Yang et al. [230] reported the fabrication of metal organic framework (MOF)-polymer NF membrane produced through the combination of self-assembly and interfacial reaction method. Polyethyleneimine (PEI) molecules were first deposited on hydrolyzed polyacrylonitrile(HPAN) substrate via self-assembly, after which ZIF-8 particles were formed in-situ in a PEI layer through an interfacial reaction. These NF were tested for methyl blue model compound which gave high rejections up to 99.6% with a permeance of 33.0 L m^{-2} h^{-1} bar^{-1}. Wang et al. [231] reported the fabrication of PA/CNT NF membranes with ultrahigh permeability and high rejection. The active layer was formed through interfacial polymerization on an UF support embedded with ZIF-8 nanoparticles. These nanoparticles were later removed by water dissolution after interfacial polymerization to facilitate the formation of a rough, crumpled PA active layer. High water permeability of 53.5 l $m^{-2}h^{-1}$ bar^{-1} was obtained with Na_2SO_4 rejection > 95%. Dong et al. [227] reported a novel approach for synthesizing thin-film nanocomposite (TFN) NF membranes which involved a PSf support layer embedded with zeolite LTL nanoparticles. A PA layer was then formed on top of this support layer through interfacial polymerization. Zeolite nanoparticles brought about an increase in surface roughness of the membrane with an improved water permeability over conventionally fabricated TFC NF membranes (1.57 vs. 0.64 10^{-6} m/s/ bar). This was attributed to the well-ordered zeolite pores and the microdefects present between the zeolite nanoparticles and the PA matrix. Therefore, zeolites offer an exciting class of membrane materials for increasing hydrophilicity and improving fouling resistance of existing polymeric membranes. Nevertheless, more research is required in this area for improved novel materials incorporating various zeolite types-polymer combinations. For example, zeolite particles have already proven to enhance water flux, and hence, recent trends of utilizing nano-sized zeolites should be exploited for extensive research to study other aspects pertaining to leaching and cost feasibility. Recently progress has been made by the development of highly crystalline nano-zeolites through ball-milling of micron sized particles in the presence of a damping material [255], for zeolites which are not possible to be produced directly for specific zeolite types and SiO_2/Al_2O_3 ratios. Hence, highly crystalline nano-zeolites produced through ball milling can now be explored and studied in conjunction with well-established polymeric materials for UF, MF and NF membranes.

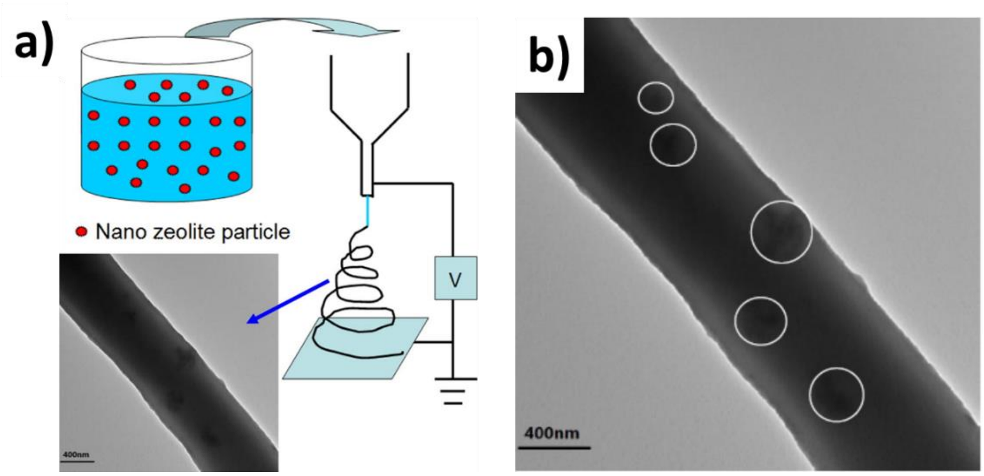

Figure 19: (a) Schematic of electrospinning of nano-zeolite/PVDF UF membranes and (b) TEM image of 3 wt. % zeolite-PVDF nanofibers with nano zeolite particles marked with the circles. Reproduced with permission from [214], Copyright © 2014, Elsevier.

2.2.6 Electrically Conductive Membranes

The ongoing efforts to minimize problems related to fouling have led to the development of many new advanced polymeric and ceramic membrane materials. Despite the rapid rise in the development of these novel membrane materials, fouling still persists as a serious threat for MF, UF and NF membrane performance when used prior to RO pretreatment. Recently, attention has shifted to electrically conductive membranes to prevent fouling and to remove foulants from the used membranes [256]. The mechanism lies in simple electrostatic interactions and/or electrochemical redox reactions on the membrane's surface. Wu et al. [257] demonstrated nanobubbles as an effective cleaning agent for fouling prevention and defouling fouled membranes. The bubbles were electrochemically produced on pyrolytic graphite surfaces, and were observed to decrease BSA coverage by 26–34%. As a defoulant, the nanobubbles were reported to remove absorbed proteins on the membrane's surface due to the air–water interface of the bubble. Firstly, the foulant gets adsorbed on the membrane's surface, electrochemical treatment follows which produces nanobubbles on the surface with the substrate as the working electrode and the foulant molecules are forced to migrate from the solid-liquid interface to the liquid-vapour interface. The protein molecules adsorbed at the vapour-liquid interface are then readily washed away. Other mechanisms by which lead to anti-biofouling effects include the direct oxidation of viruses [258], cathodic current causing bacteria detachment [259] and prevention of biofilm growth via small electrical pulses [260].

Intrinsically conductive polymers have not been widely adopted as membrane materials due to their relatively low selectivity and flux [261]. Besides performance drawbacks, conductive polymers are not readily soluble in common solvents and are therefore difficult to process [256]. CNTs have emerged as a promising candidate for this purpose. CNT membranes possess high electrical conductivity, fast water transport facilitated through CNTs leading to higher flux, and improved mechanical properties. Self-standing CNT membranes can be fabricated, called bucky-paper which usually have a paper like structure [225]. Rashid et al. [225] fabricated free-standing through vacuum filtration, by first dispersing functionalized and non-functionalized MWCNTs with different surfactants. Hydrophilic membranes were reported with contact angles as low as 28°. Electrical conductivities for the membranes ranged from 24 to 58 S/cm. BPA rejections of about 90% were achieved, and bucky-paper synthesized using Triton X-100 gave trace organic rejections greater 80%. However, these self-supporting membranes offer limited control over pore size [262].

Following the drawbacks of pristine CNT membranes, the need arises for potential alternatives for forming conductive membranes. Therefore, incorporating CNTs in intrinsically insulating polymers through coating or deposition is a viable option for fabricating electrically conductive membranes. De Lannoy et al. [263] fabricated electrically conductive UF membranes prepared from poly(vinylalcohol) (PVA)-cross-linked with carboxylated CNTs-succinic acid through pressure filtering method. Cellulose nitrate was used as a support. The active layer exhibited electrical conductivity greater than 20 orders of magnitude compared to pristine PVA membranes. Pure water flux of 1440 L/m^2 h was achieved with PEO rejection >90% for low wt. % CNT additions of 2 and 5wt. %. Functionalized MWCNT/PSf membranes were prepared through vacuum filtration assisted layer-by-layer deposition. PSf membranes were functionalized through oxygen plasma treatment with oxygen-containing negatively charged groups while the MWCNTs were functionalized with amine- and carboxylic- functional groups. These membranes showed almost complete inactivation of *E-coli* at an applied voltage of 1–3 V. [106]. Majeed et al. [264] fabricated MWCNT–PAN UF membranes through the phase inversion method. Water flux was reported to increase by 63% at 0.5 wt. % CNT loading, while an increase in tensile strength by over 97% at a CNT loading of 2 wt. % was reported. Lannoy et al. [265] reported PA-CNT NF membranes prepared through interfacial polymerization exhibiting conductivity of 400 S/m with NaCl rejection >95%. Microscopy analysis revealed CNTs embedded within PA. Li et al. [215] reported a novel concept for the preparation of high-flux UF membranes based on MWCNTs and PES. The membrane consisted of vertically aligned CNTs uniformly distributed within a PES matrix. This provided well-oriented water transportation pathways along the unique CNT structure. Water transportation may be achieved through one or several mechanisms as highlighted in Figure 20. A drastic increase of permeability of over 3 times was achieved with these membranes, compared with the randomly oriented MWCNT membranes. CNT-polymer membranes have also been reported to be used in conjunction with ceramics. Teow et al. [266] fabricated TiO_2 coated MWCNTs/PES NF membranes through phase inversion induced by immersion precipitation. Addition of 1 wt. % TiO_2 was enough to increase the pure water flux of PES membranes from ~3.71 to 5.66 $kg/m^2 \cdot h$ at 5 bar feed pressure. NF membranes fabricated from PVDF and poly (styrene–butadiene–styrene) (SBS) blend were also reported with thiocyanate-modified and silver-modified MWCNTs used as a filler. A smooth, homogeneous surface in a spongy matrix was identified, with tensile strength values ranging from 12.6–20.1 MPa. Salt rejection increased to 95.5% from 83.3%, compared to when no Ag was used. These novel membranes showed potential for further improvement by using a combination of polymer-metal blends for advance water treatment which can be utilized prior to RO operations [226].

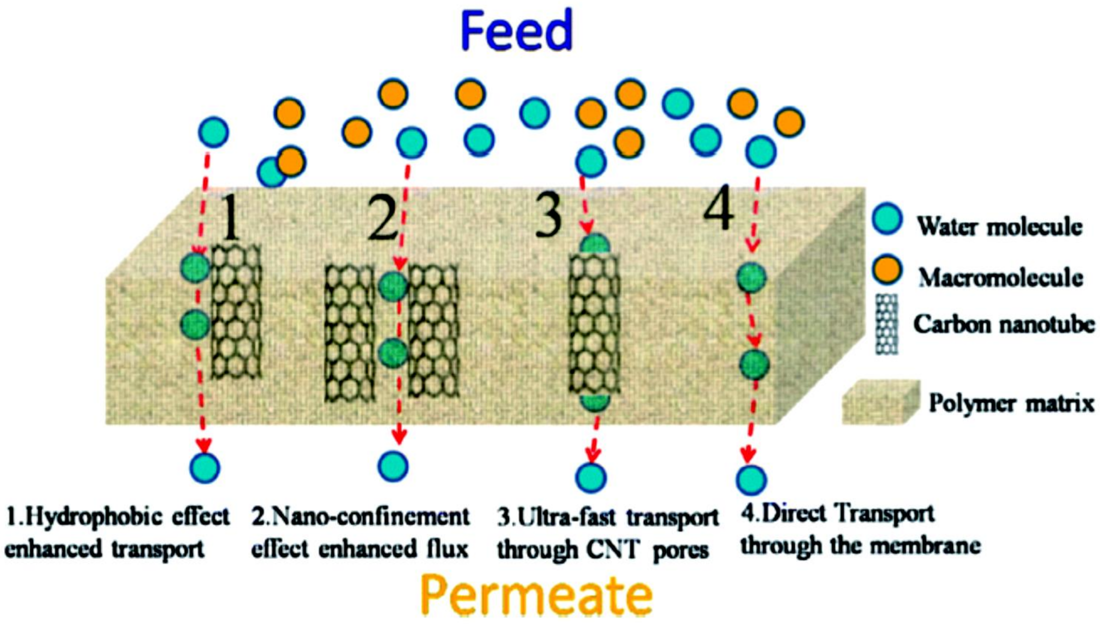

Figure 20: Schematic of possible pathways for water transportation in CNT-polymeric membranes: due to (1) hydrophobic effect enhanced transport, (2) Nano-confinement enhanced flux, (3) ultrafast transport through the CNT pores, and (4) direct transport through the membrane matrix. Reproduced with permission from [215], Copyright © 2014, Royal Society of Chemistry.

Hashaikeh et al. [267] reported a fast and efficient in-situ cleaning method for CNT-based membranes through periodic electrolysis. MWCNTs were coated on a commercial membrane support by vacuum filtration, which acted as a cathode, with a separate stainless steel anode and salt water as the electrolyte. The membranes registered a conductivity of 10 S/cm. Again, formation of bubbles was responsible in sweeping away the foulant layer improving the flux. Following this study, Lalia et al. [216] synthesized self-standing carbon nanostructure (CNS) membranes, where PVDF was used as a binder inside the networked CNS structure. Figure 21a shows an SEM image of PVDF-CNS membrane while Figure 21b shows the schematic depicting the binding of CNS microbundles with PVDF binder. CNS membranes registered a conductivity of 41 S cm^{-1}, while addition of PVDF slightly increased the conductivity due to CNS structure compaction. High mechanical stability was observed where the CNS/PVDF membranes showed high tensile strength both in the wet and dry state (6.4MPa and 9.8 MPa respectively) as shown in Figure 21c, compared to bare CNS membrane possessing tensile strengths of 2.5MPa and 3.6 MPa in the wet and dry states respectively (not shown in the figure). This improvement in tensile strength is seen as a promising step for sustaining pressures during filtration. Yeast filtration was studied where a 70% increase in flux was observed when periodic electrolysis was applied. Without periodic electrolysis, flux values were observed to steadily decline reaching 40% of their initial values after less than 5 hours, as shown in Figure 21d.

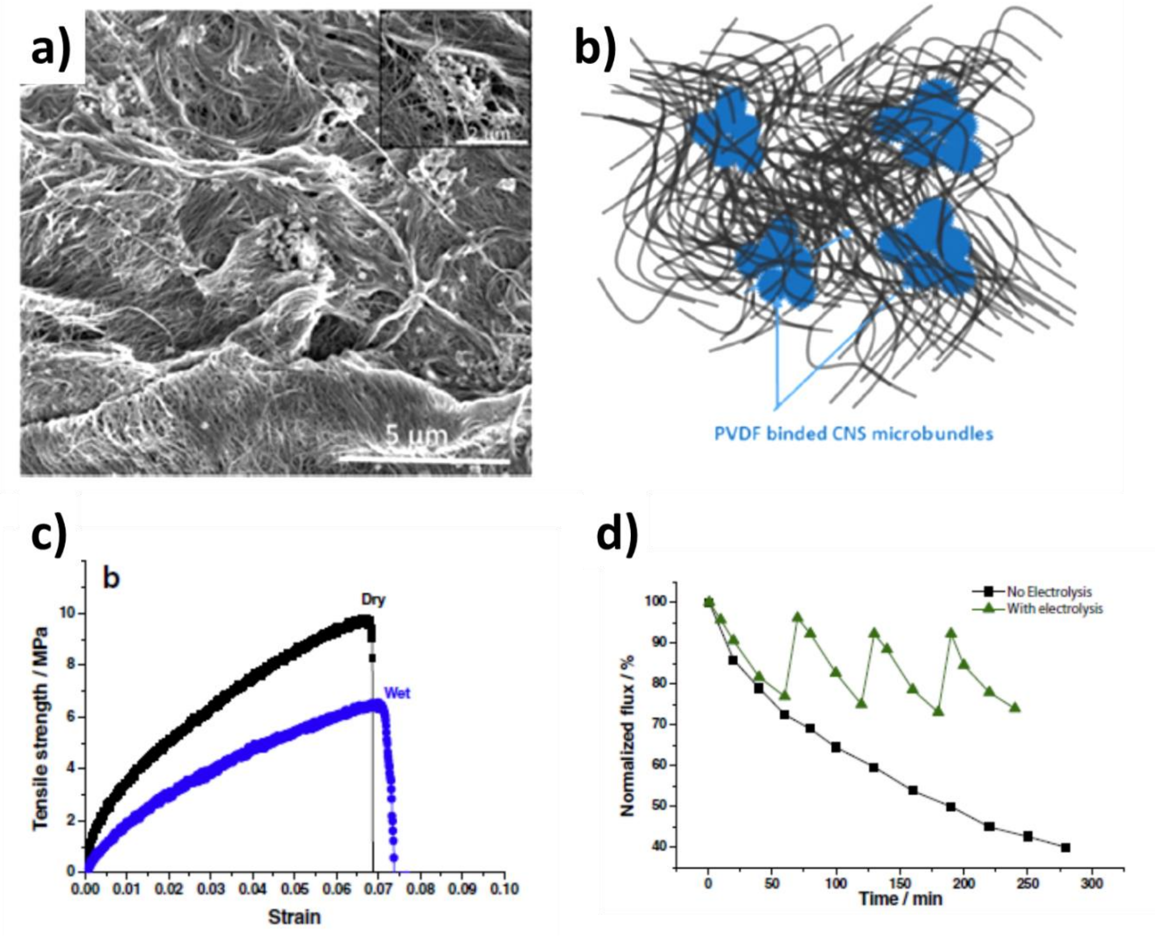

Figure 21: (a) SEM image of CNS-PVDF membrane (b) schematic showing binding of CNS microbundles with PVDF binder (c) Stress–strain graph of CNS-PVDF membranes in dry and wet

states and (d) variation of normalized flux with time for CNS-PVDF membrane with and without in-situ periodic cleaning. Reproduced with permission from [216]. Copyright © 2015, Elsevier.

Conductive polymer-CNT membranes are also capable of bacterial inactivation, leading to enhanced bio-fouling prevention when an electrical bias is applied. Wang et al. [223] reported sodium lignosulfonate functionalized CNTs-PES UF membranes prepared through the phase inversion method. Antibacterial tests confirmed that hybrid membranes showed good antibacterial properties when biased with low electric fields (direct current (DC), about 1.5 V cm^{-1}). Lee et al. [268] reported the fabrication of UF membranes based on vertical CNTs using water-assisted chemical vapor deposition (CVD). The membranes gave water permeability values of 30,000 $l\ m^{-2}\ h^{-1}\ bar^{-1}$, compared with to 2,400 $l\ m^{-2}\ h^{-1}\ bar^{-1}$ reported for CNT membranes. The membranes were also reported to impede bacterial adhesion, leading to enhanced biofouling resistance. Apart from CNTs, other materials have also been reported for fabricating conductive membranes. For example, Huang et al. [209] reported a composite conductive membrane made from a stainless steel mesh incorporated into a polymeric MF membrane. Electrochemical tests studied through linear sweep voltammetry and electrochemical impedance spectroscopy showed promising electrochemical properties for the membrane. Though the membrane was tested in a membrane bio-reactor (MBR) for treating wastewater, it can also be applied as a MF membrane prior to RO pretreatment where low electric fields of 2 V/cm can be used for in-situ membrane cleaning by H_2O_2 generated from oxygen reduction. The use of impedance spectroscopy for early fouling detection is gaining importance whereby filtration units combined with electrochemical systems show promising aspects for efficient membrane cleaning. However, most of the reported conductive membranes are limited to laboratory scale testing, while their prospect can only be better predicted when studied at pilot and commercial scales. This should include filtration systems built in conjunction with electrochemical setups which can assess membrane material feasibility and economics. Extensive membrane 'tailoring' is further required to produce long-lasting reliable membranes, which makes the field of conductive membranes an open research area for further development.

3. New Emerging Trends

Due to harsh seawater quality and the need to achieve good quality permeate from RO pretreatment units to avoid RO membrane fouling, progressive research is active in the field of new, advanced membrane and non-membrane pretreatment technologies. Many different operational improvements have been employed to study different outcomes with respect to final permeate water quality, cost and ecological impacts. For example, for poor feed quality, full flocculation and sedimentation units might not seem an appropriate choice. Instead, inline coagulation has been introduced prior to media filtration through which the coagulated water is directly introduced to the membrane filtration system. This in turn can reduce the carbon footprint of the entire membrane filtration facility [269]. In addition, hybrid systems where membrane pretreatment is coupled with conventional units have emerged as a more efficient and viable option where the strength of one unit is combined with the other. Nevertheless, such systems still require further pilot tests to commercialize any new combination for a particular feed quality.

On the whole, the efforts are directed towards an economical, low energy system providing the desired permeate water for further RO desalination treatment. For example, bio-pretreatment was suggested whereby gravity driven membranes were used. Peter-Varbanets et al. [270] reported gravity driven ultrafiltration in a dead-end mode which did not require any backwash or chemical cleaning. Stabilized flux values were obtained after a week, which remained constant over a period of several months owing to a beneficial biofilm formed on the UF membrane surface. The water treated in the study were mostly surface water and diluted wastewater. However, similar results were reported later for seawater feeds which gave low UF fouling potential with low energy demand of the order of 0.01 kWh/m^3 [162].

Other pilot studies confirmed stabilized gravity driven membranes flux of about 20 L/m^2 h with a driving force of only 40 mBar, achieving lower fouling compared to commercial UF membranes [271]. Such advances are necessary to develop power efficient systems. However, limitations of any system should not be overlooked. For example, gravity driven membrane pretreatment is said to contribute to a larger footprint. However, more studies are required to understand the full potential of this bio-pretreatment system taking into account ecological, economical and performance aspects. SWRO bio-pretreatment has also been suggested using bio-filtration [272, 273] where energy savings of about 0.3 kWh/m^3 in the overall desalination process were achieved. Naidu et al. [273] reported bio-filtration as an efficient means for reduction of biofoulants through adsorption and biodegradation. They studied the performance of a GAC biofilter with various filtration velocities for DOC removal. After a certain time, GAC biofilters showed high DOC removal of more than 60%. Thus, GAC biofilters offer an attractive means for

RO pretreatment, inhibiting the biofouling propensity. Another bio-pretreatment, biologically active ion exchange resin (BIEX) pretreatment has gained considerable attention for organic fouling reduction. Recently, Schulz et al. [274] investigated BIEX pretreatment for organic fouling reduction of UF membranes. The process showed successful improvement in flux with increased rejection of humic substances and low molecular weight acids. Nevertheless, the efficiency of biological processes for organic rejection is largely dependent upon operating conditions. However, only a few studies exist on operational optimization for reduction of membrane fouling limited to temperature and time. Other factors such as concentration of DOC, organic composition need further attention [275].

MBRs are gaining importance as an effective RO pretreatment where experimental results have showed less RO membrane fouling compared to other methods [276]. Lerner et al. [277] compared a full scale activated sludge (AS) plant to a pilot MBR setup. MBR was reported to produce an effluent of much superior quality containing <1 mg/L suspended solids in contrast to 12 mg/L obtained from AS. Dukes and Gottberg [278] reported successful control over calcium phosphate scaling in RO systems through the use of MBRs by decreasing phosphate concentrations (0.1 ppm) obtained in the effluent. In addition, the filtration mechanism within the MBR can be an important factor in determining the permeate quality obtained from RO systems. For example, submerged hollow fiber MF and UF membranes have emerged as a better choice for producing good quality permeate water. Ye et al. [279] reported that these submerged UF membranes were able to remove 60% of the of biopolymers in the influent. Although MBRs can be an attractive alternative for RO pretreatment, the operating conditions of MBRs usually have a significant impact on RO membrane fouling and cleaning frequency. For example, Grelier et al. [280] compared three MBRs with different sludge retention times of 8, 15 and 40 d. Efficient biodegradation was achieved at sludge retention times of 15 and 40 d. MBRs when optimized for operational condition, can save the necessity of any further pretreatment by filtration. However, again, the decision about which pretreatment process is preferred lies in several factors including energy, ecological considerations and the desired permeate quality. For example, during one study, MBR and AC treated water showed similar COD, BOD, phosphorus and ammonia levels. However, membrane blockage due to scaling caused severe flux deterioration compared to AC. Therefore, in many cases, replacement of a well-established pretreatment method is not a viable option and extensive pilot studies are required to justify the replacement [277]. Therefore, on-going efforts have to be directed for pilot tests to address critical issues pertaining to the feasibility of using MBRs prior to RO and using MBRs coupled with other conventional treatment processes.

Apart from advances in pretreatment techniques and exploring the feasibility of existing water treatment technologies for RO pretreatment application, new trends in membrane materials have also been explored. For example, Gorey et al. [281] reported microbial sensing membranes which were developed from a stimulus-responsive polymer film on a CA membrane. The membrane became hydrophilic and expanded at low temperatures, while it collapsed when the temperature was increased. Membrane fouling was controlled by this phase transition trigger response, as well as biofouling detection being enabled by covalently bonding antibodies to the polymer film. Such advances advance the development of membranes for biofouling detection. Nevertheless, research in this area needs much further research in terms of long term feasibility.

The potential of CNTs incorporated into a polymer matrix for fabricating conductive membranes has already been discussed in section 2.2.6. Besides CNTs, graphene has appeared as a new, advanced membrane material due to its superior electronic properties, impermeability to small molecules and high breaking strength. Therefore, with tuned porosity and controlled fabrication techniques, graphene has great potential as UF/NF membrane material which can be used prior to RO [22]. Graphene oxide (GO) has gained enormous interest as a membrane material during the last five years [282], and is thus projected as a new emerging membrane material after Nair et al. [283] reported their study on low-friction flow of a monolayer of water though 2D graphene sheets, while blocking other unwanted molecules. Xu et al. [217] reported graphene oxide/TiO_2-PVDF UF membranes which showed superior photocatalytic antifouling properties, higher permeate fluxes, greater flux recovery and self-cleaning property under UV irradiation compared to bare PVDF membranes. Similarly, Li et al. [218] used SiO_2@GO to develop PVDF/SiO_2@GO hybrid membranes through thermally induced phase separation method. A 0.9 wt. % SiO_2@GO registered the highest BSA rejection of 91.7% with the lowest permeate flux of 182.6 L m^{-2} h^{-1} bar^{-1}. However, a higher SiO_2@GO addition of 1.2 wt. % led to an increased flux of 679.1 L m^{-2} h^{-1} bar^{-1}, but with a lower BSA rejection. Figure 22 shows TEM images of GO nanosheets and SiO_2@GO nanosheets. Their study demonstrated a clear positive effect of using graphene for improved hydrophilicity and antifouling resistance. Han et al. [284] developed ultrathin graphene films for NF through vacuum assisted assembly strategy. The GO sheets formed sub-1-nm sized 2D nano-capillaries. The reported ultrathin NF membranes gave excellent organic dye retention based on physical sieving and electrostatic interactions. Compared to aligned CNT membranes, these membranes are cost efficient and relatively simpler to fabricate which opens new doors for next generation membrane materials based on graphene. Further developments pertaining to control of graphene sheet density, space adjustments between sheets and graphene functionalization is necessary for subsequent advancements. Table 8 summarizes these new emerging pretreatment methods and membrane materials.

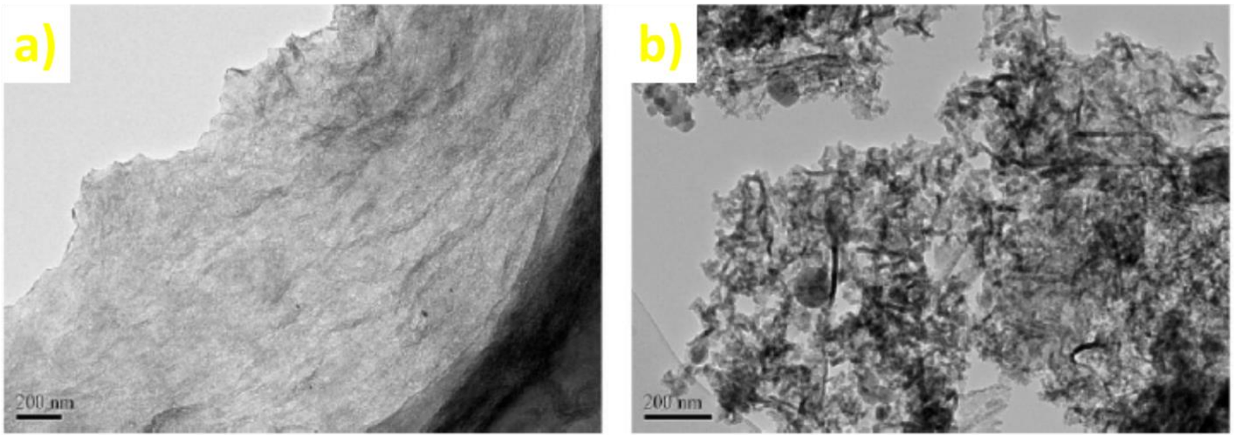

Figure 22: TEM images of (a) graphene oxide nanosheets and (b) SiO_2-GO nanosheets. Reproduced with permission from [218]. Copyright © 2016, Elsevier.

Table 8: New Emerging trends in pretreatment methods and novel membrane materials.

Reference	Pretreatment technique / Novel membranes
Peter-Varbanets et al. [270]	Gravity Driven UF; no backwash or chemical cleaning required with stable fluxes over several periods of months.
Naidu et al. [273]	Bio-filtration; GAC was used an efficient means for reduction of biofoulants through adsorption and biodegradation.
Schulz et al. [274]	Bio-pretreatment; BIEX was used for organic fouling reduction. Improvement in flux and increased rejection of humic substances was achieved.

Lerner et al. [277]	MBRs; much superior effluent was produced compared to activated sludge.
Dukes and Gottberg [278]	MBRs; reduced phosphate concentrations were obtained leading to successful control over calcium phosphate scaling in RO systems.
Gorey et al. [281]	Microbial sensing membranes; hydrophilic membranes which expand at low temperatures and collapse at higher temperatures. This phase transition can provide control over membrane fouling.
Xu et al. [217]	GO based membranes; GO/TiO_2-PVDF UF membranes showed superior photocatalytic antifouling properties, with higher flux compared to bare PVDF membranes.
Li et al. [218]	GO based membranes; PVDF/SiO_2@GO hybrid membranes showed a positive effect of using graphene for improved hydrophilicity and antifouling resistance.
Han et al. [284]	GO based membranes; ultra-thin graphene sheets giving superior organic dye retention.

4. Ecological Impacts of RO Pretreatment

SWRO has become an integral part of the infrastructure for supplying desalinated water in many parts of the world [285]. Therefore, the ecological impacts of RO pretreatment processes cannot be overlooked. Besides the desired permeate quality and cost analysis, environmental impact for various pretreatment technologies have to be assessed prior to selecting the pretreatment method. For this, scientific data has become essential. There is limited research data available on the long term effects of RO pretreatment on marine eco systems and the environment, and thus substantial uncertainty exists regarding the environmental impacts of RO pretreatment methods. Moreover, waste discharge from integrated pretreatment systems has not been well studied. Conventional pretreatment methods consume large amounts of chemicals, such as in coagulation, flocculation and sedimentation processes as well as biocides. Therefore, large amounts of sludge have to be treated before it is discharged to the environment. In contrast to conventional methods, membrane processes have lower chemical consumption. However, the use of chemicals still becomes unavoidable during chemical cleaning of the membranes for foulant removal [286]. Approximately, 76 million tons of CO_2 is emitted annually due to desalination processes and by 2040, this number is predicted to rise to 218 million tons of CO_2 a year [6] . Elimetech and Phillip [25] reported that the current state-of-the-art SWRO plants emit between 1.4-1.8 kg of CO_2 per cubic meter of produced water while consuming more than $3kWh/m^3$ of energy. The use of robust membrane-based pre-treatment systems can largely help in reducing the environmental footprint of RO membranes through lowered fouling and higher fluxes. Willy Yeo, the vice president of Hyflux, highlighted the importance of using membrane based pretreatment technologies which can allow RO membranes to produce the same capacity of permeate compared to conventional techniques, at lower pressures. This in turn can lead to lower energy consumption, longer RO membrane lifetime, less chemical cleaning, hence reducing its carbon footprint. Less chemical cleaning results in reduced chemical waste and discharges into the environment [287]. The footprint for membrane pretreatment is reported to be 30-60% smaller than conventional ones [286, 288]. On the contrary, Beery et al. [289] showed that membrane pre-treatment methods were considerably less environmental friendly due to their higher energy demand, which dominated over the requirement for less chemical cleaning for subsequent RO operation. For example, UF requires frequent backwash of the membranes contributing to significant energy usage ~0.3 kWh/m^3 [290]. Therefore, Beery et al. [289] suggested gravity media filtration as an environmentally feasible sustainable technological solution. However, other conventional pretreatment methods, such as flocculation and DAF, were reported to decrease the eco-efficiency when used in conjunction with gravity media filtration. In this case, membrane pretreatment was sought as the more viable option. Nevertheless, further optimization of membrane based pretreatment design and operation focusing on the environmental aspect is necessary. In many cases, renewable energy technologies can provide an alternative where greenhouse gases are a concern. This is because, even with a lower specific energy consumption below 3kWh/m^3, the carbon footprint can be considerable for large SWRO plants.

Ruan et al. [291] reported a pilot plant study on Qingdao Jiaozhou Bay, the Yellow Sea in China for UF RO pretreatment. The design of a hybrid UF-RO plant was optimized to produce maximum product with filtration and backwash duration adjusted to avoid any use of chemicals. Their study concluded that an optimum UF performance is achieved with a backwash duration of 30 s and a filtration duration of 40 min. Moreover, they recommended the UF operation at a high recovery of 80% and a low flux mode ≈60 L/m^2 h. The permeate quality obtained under these optimized conditions resulted in a turbidity value of below 0.01 NTU and 95% of the SDI_{15} below 3.0.

Usually, UF systems when installed prior to RO do not require additional coagulant or flocculating aids reducing the sludge significantly. Moreover, elimination of continuous chlorine dosing significantly reduces chemicals such as NaOCl in the SWRO plants [178]. Sarkal et al. [33] presented a comparative study on the environmental impact of UF versus sedimentation-based pretreatment for the Fujairah-1 RO plant. They applied a life cycle analysis (LCA) methodology which was based on real data from the Fujairah-1 plant for both sedimentation-based and UF systems. Their study revealed that membrane-based pretreatment has a lower environmental impact compared to the sedimentation-based pretreatment method. They combined all impacts into a single number by using weighing factors to generate a single score impact chart, as shown in Figure 26. Major impact categories for both methods were fossil fuel consumption, respiratory inorganics and climate change, the major contributor being energy consumption forming 80% of the total share. Around 66% and 82% of the environmental impact due to energy consumption comes from pumping the feed water through the system in sedimentation and UF methods respectively. Energy consumption is the major contributor due to the fact that this factor has a continuous contribution whereas other factors have a one-time contribution. Hence, as Figure 23 shows clearly, UF system has much lower points for energy consumption, exhibiting a lower environmental impact compared to its counterpart [33].

With the growing emphasis on sustainable materials and technologies positively impacting the environment, new, sustainable materials are needed for RO pretreatment processes. Natural coagulants (bio-polymers) provide an attractive alternative to synthetic or chemical coagulants because of their low-cost and environmental-friendly behavior. Considerable attention has been put into natural coagulants produced from animal and plant tissues. These produce 20% - 30% less sludge compared to treatment with alum [292]. Environment-friendly coagulants include nirmali seed and maize [293], cactus latifaria [294] and many others [295]. Mukheled Al-Sameraiy [296] reported a novel approach to pretreatment for turbidity removal utilizing date seeds and pollen sheathes. The method consisted of two approaches: coagulation/flocculation and sedimentation processes at a certain mixing speed, mixing time and settling time. Natural coagulants using date seeds and pollen sheath were used in the coagulation process, while alum was used during sedimentation. Their results showed superior performance when using date seeds with a dosage of 30mg/L and alum dose of 10mg/L which gave turbidity of less than 0.1 NTU. Reduced alum dosages of less than 60% than previously used were required, lowering the cost of the overall process. Recently, Katalo et al. [297] demonstrated the effectiveness of using *Moringa oleifera* (MO) as a natural coagulant for coagulation prior to MF. MO showed similar results to alum in terms of membrane fouling mitigation and permeate water quality, thus offering a potentially cost-effective, environmental friendly alternative to harsh coagulants. It has been suggested to use biodegradable polymeric materials for membrane based pretreatment methods such as those based on PVA [298]. Focusing the attention towards sustainable, biodegradable, and natural materials is recommended for lower environmental impacts.

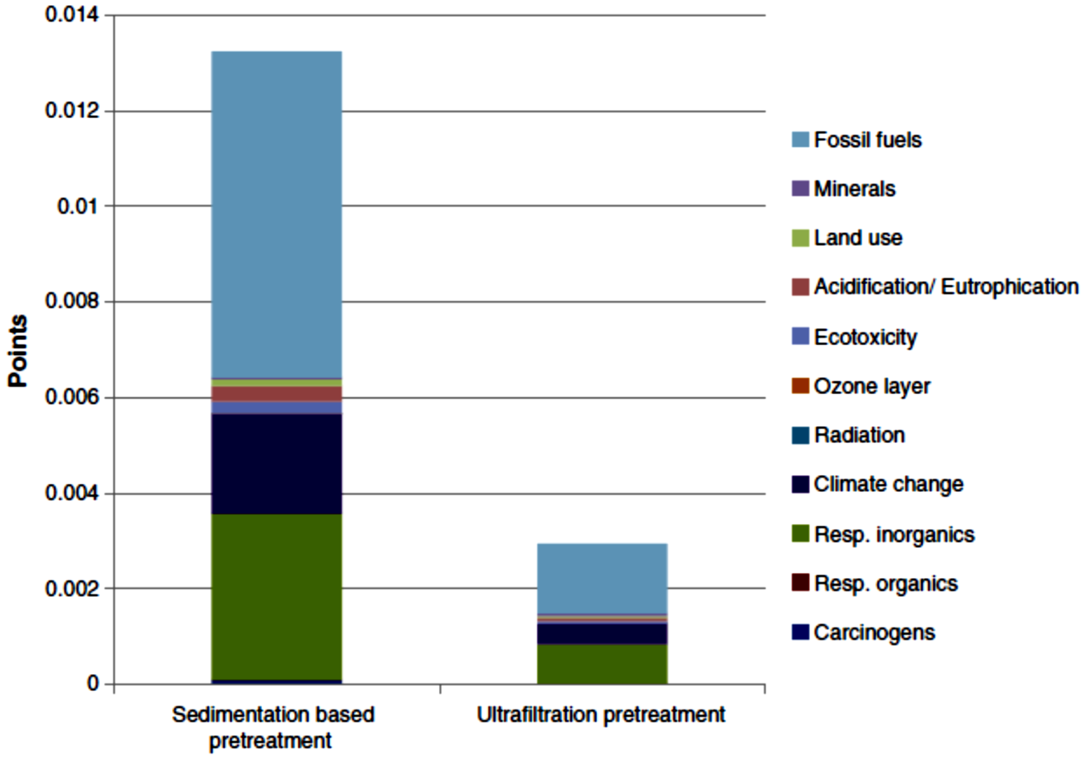

Figure 23: Comparison of environmental impact based on single score method using base line options. Reproduced with permission from [33]. Copyright © 2013, Elsevier.

5. Performance and Economical Aspects of RO Pretreatment

As well as water scarcity, the growing energy crisis is yet another global concern which needs to be urgently addressed. As shown in Figure 2, energy consumes 26% of the total RO plant cost, closely followed by membrane replacement, with the majority of energy needed for high pressure pumping. Water and energy are usually viewed in close relation to each other with desalination plants commonly utilizing renewable energy sources or recovering energy from waste streams in order to reduce energy requirements and drive down the overall costs of desalinated water. Because the majority of SWRO plants are integrated membrane systems, the cost related to such systems is crucial for determining the end economics of the produced water. However, such studies are rare, instead many report only on cost comparisons of standalone systems rather than integrated ones. Also, for standalone systems, one has to keep in mind the end benefits rather than just the overall cost. For example, it is prevalent that membrane pretreatment systems have a higher capital cost than conventional ones, however, the cost should also take into account the end water quality, productivity and system [30]. The energy usage of a pretreatment system for a second stage SWRO plant might contribute to about 2.6%. Thus, effective pretreatment setup need to be considered depending upon incoming feed quality and thus lowering the overall energy cost for an RO plant [30]. Ineffective pretreatment may lead to increased feed pressures, cleaning frequencies and lower membrane lifetimes leading to higher operating costs.

Table 3 provides a qualitative comparison between conventional and membrane pretreatment methods in terms of capital costs, energy requirements, chemical costs and required RO costs. Glueckstern and Priel [299] presented a comparative quantitative study on conventional and UF membrane pretreatment systems for SWRO plant based on the performance of the Ashdod seawater pilot plant tests and other available economic data. The total investment in the 90,000m^3/d SWRO plant was estimated to be 64.4 M$ and 67.3 M$ 67 for media filtration and UF respectively (Table 9), while the unit water cost was calculated to be 51.35 and 52.02 US cent/m^3 for media filtration and UF pretreatment respectively. From Table 9, it is evident that the investment costs for UF pretreatment is much higher than for conventional treatment. Usually, the labor and maintenance costs for both pretreatment methods are similar, but UF membrane cleaning and replacement add extra cost for UF systems. However, the higher cost for membrane based pretreatment is balanced by the reduced cost for RO systems through high membrane flux operations. Though the capital cost of UF/MF is around 25% higher than conventional ones, their life cycle cost is comparable [4]. Further, based on comparative economic analysis, the energy consumption for a conventional media filtration pretreatment unit was found to be about 3.57 kWh/m^3 compared to 3.56 kWh/m^3 for an UF pretreatment setup [299].Cardona et al. [300] reported a similar study whereby the capital cost for conventional pretreatment was lower compared to UF. They used a two-stage RO system coupled with UF and a single-stage RO system coupled with conventional pretreatment method. Figure 24 compares the pretreatment capital cost versus recovery rate for a 10,000 m^3/day permeate. Though the cost for the UF system is higher, the higher cost is usually compensated by the advantages of the membrane based pretreatment method such as flexibility in capacity and chemical cost reductions. It should be noted that pretreatment methods usually account for only 6–9% of product water cost and often UF method causes a decrease in the RO membrane replacement and labor costs bringing down the total cost of the plant by 6-7%. Moreover, an UF system with minimal prior pretreatment can reduce cost of the overall process, competing closely with coagulation and DMF processes. Nevertheless, with increased research on novel membrane materials, the overall cost of membrane technology is expected to decrease due to higher membrane lifetime, increased selectivity and increased flux. Pearce [301] presented a case study which considered many factors favoring membrane pretreatment over the conventional CMF for an open intake of Eastern Mediterranean feed with a feed salinity of 38,000 ppm TDS. He reported that the performance advantage of UF and MF resulted in reduced RO costs outweighing the investment costs in pretreatment. Again, the added capex is offset by a reduced use of chemicals and other consumables. The RO system was based on a flux of 13.6 L / m^2 h and a recovery of 45%. Table 10 highlights the basic cleaning frequency usually required for conventional pretreatment which results in higher chemical costs. The cleaning frequency is reduced with membrane pretreatment to 1-2 times per year. This in turn decreases the chemical costs and subsequent RO membrane cleaning costs by 0.5 US cents/m^3. With a single RO clean per year, membrane pretreatment becomes cheaper than conventional pre-treatment by 0.7 cents/m^3. The additional capex and membrane replacement cost in UF was reported to be about 2.9 cents/m^3. However, UF caused reduction in RO replacement, saving about 1.2 cents/m^3. In addition, the added benefits include 33% space savings and an opportunity to increase RO flux and recovery. Figure 25a shows the effect of pretreatment on the cost of consumables, which includes cartridge costs, chemicals and membranes. The lowest cost is achieved by UF/MF-RO with 1 clean/y while the highest cost is endured by the conventional pretreatment process. Figure 25b shows the total water cost for the study which is again the lowest, 89.31 cents/m^3 for UF/MF with 1 RO clean/y. The added advantage of membrane pretreatment is that it provides a more stable and reliable system which is robust enough to handle major changes in feed water quality. Chua et al. [59] compared MF (PVDF, nominal pore size of 0.1 µm) and UF (PES, nominal pore size of 0.01 µm) pretreatment techniques for a seawater intake in Singapore which had an SDI of 6.1-6.5. Two UF pilot systems were tested, pilot 1 having a production capacity of 0.75m^3/h and pilot 2 having a production capacity of 1.2 m^3/h. The MF system had a capacity of 5.2 m^3/h. Table 11 compares the performance and chemical cost analysis. The comparison serves as an indication for the selection of the appropriate membrane pretreatment method. In certain cases, prior treatment of seawater was required instead of direct seawater intake. For example, the feed for UF pilot 1 was sand filtered to allow for acceptable operating conditions. However, the requirement of a sand filter increases space consumption and maintenance costs. There is a trade-off in certain situations. For example, the operating flux of UF pilot 1 was lower compared to UF pilot 2. However, the SDI of UF pilot 1was inferior to that of UF pilot 2 and equal to that of the MF system. With the same membrane pore size, it is difficult to conclude on the reason for this difference in SDI. Chemical consumption of UF pilot 1 was reported to be more intensive compared to the other two pilot systems, whereby strong adherent films on the membrane's surface necessitated the use of chemicals. Sodium hypochlorite and citric acid chemicals were used for disinfection and antiscaling respectively. In terms of economics, the membrane has to be operated at a higher flux with fewer membrane modules.

Table 9: Comparative investment costs in UF filtration vs. conventional MEDIA filtration for the 90,000 m^3/day SWRO plants (Adapted from P. Glueckstern et al. [299], International Desalination and Water Reuse Quarterly, 2003)

Filtration method	**Media Filtration**		**UF**		**UF versus Media Filtration**	
	M $	$/m3-day	M $	$/m3-day	M $	%
Infrastructure	15.5	172	15	167	-0.5	-3.2%
Pretreatment	9.0	100	16.6	184	7.6	+84.4%
RO system	39.9	443	35.7	397	-4.2	-10.5%
Total Investment	64.4	716	67.3	748	4.1	+4.5%

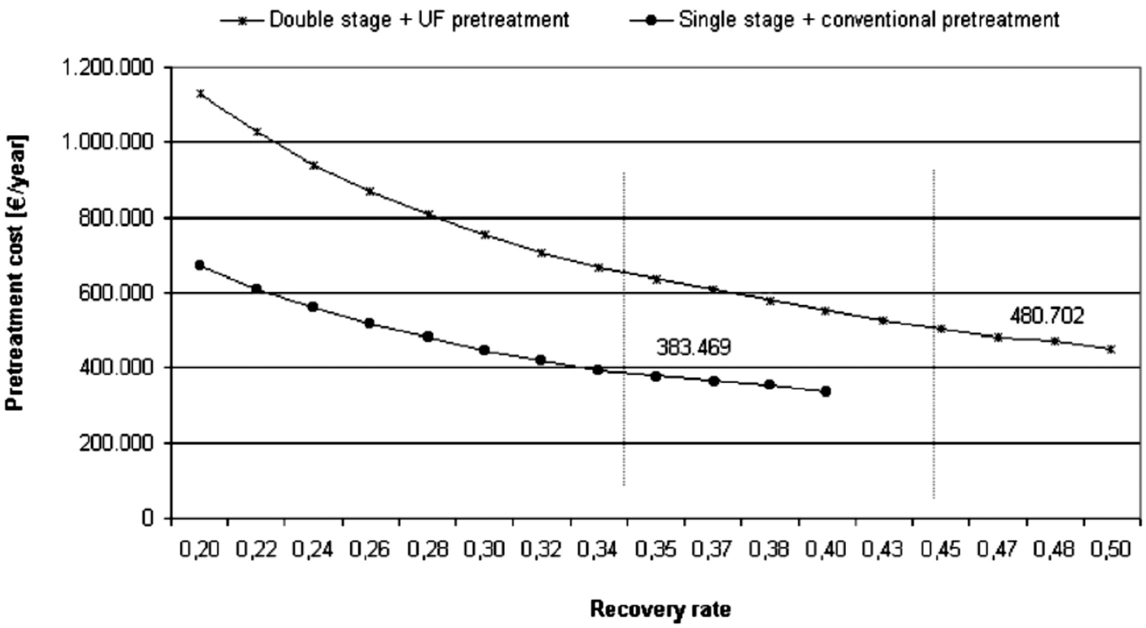

Figure 24: Comparison between UF and conventional pretreatment sections in two-stage/two-pass and single-stage RO systems. Reproduced with permission from [300]. Copyright © 2005, Elsevier.

Table 10: Chemical cost comparison for different pre-treatment options. Reproduced with permission from [301], Copyright © 2007, Elsevier.

Pretreatment process	Conventional	UF/MF	UF/MF
Ro cleaning/year	3	2	1
Dosing and UF/MF cleaning (k, $)	61.4	24.1	24.1
RO cleaning (k, $)	83.5	55.7	27.8
Total (k, $)	144.9	79.8	51.9

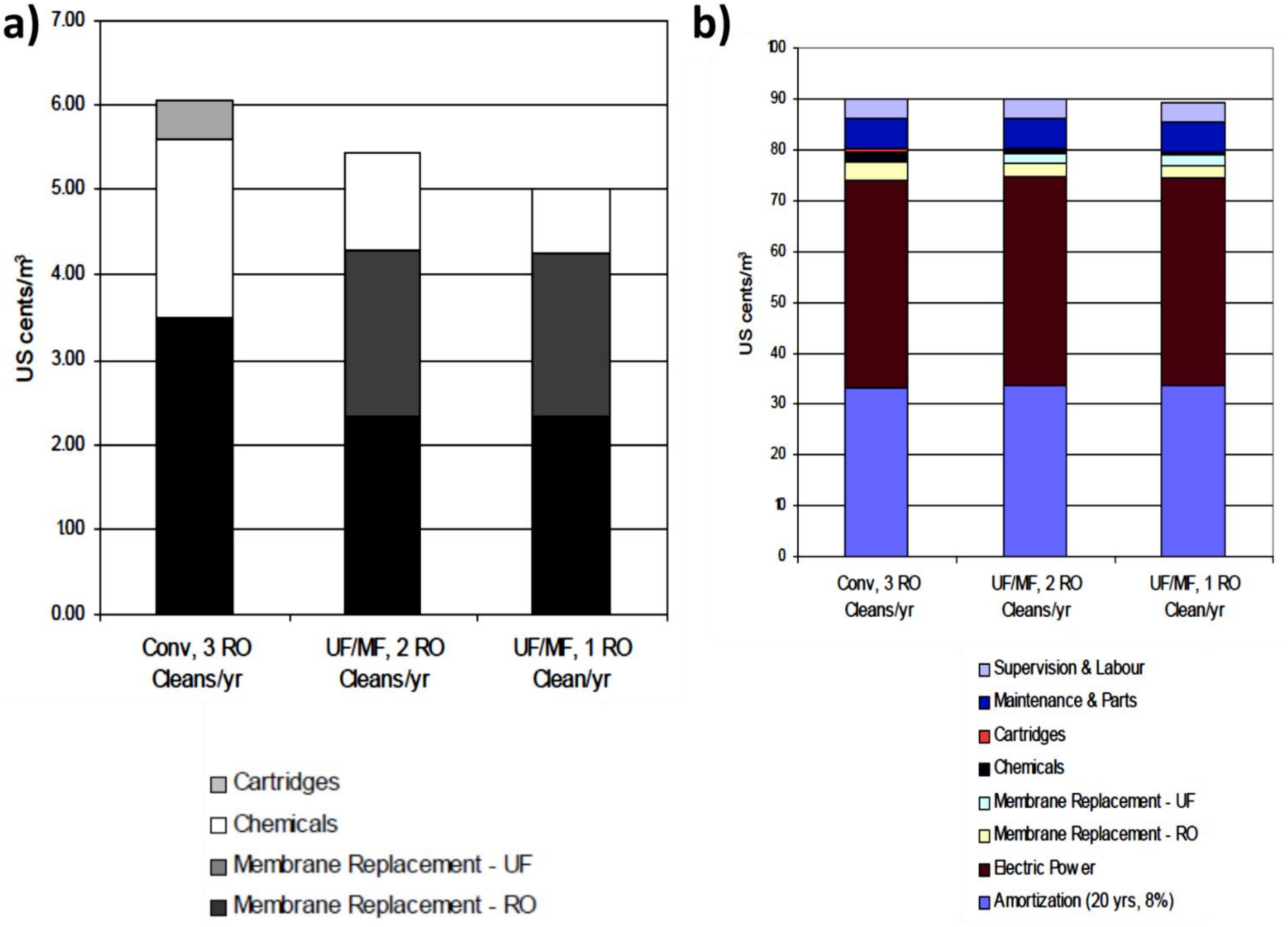

Figure 25: (a) Consumables cost comparison and (b) Total water cost comparison for conventional and membrane pretreatment techniques based on different RO cleaning frequencies. Reproduced with permission from [301]. Copyright © 2007, Elsevier.

Table 11: Performance and chemical cost analysis for UF and MF pilot systems. Reproduced with permission from [59]. Copyright © 2003, Elsevier.

Description	UF pilot system 1	UF pilot system 2	MF pilot system
Feed source	Sand filtered filtrate	Seawater	Seawater
Membrane process	Direct-flow	Cross-flow with recovery of 80%	Direct-flow
Filtrate flux ($l/m^2.h$)	47	57.6	100
SDI	2.5-3.0	0.9-l .2	2.5-3.0
Chemical costs ($US\$/m^3$)	0.01390	0.00027	0.00218

NF has emerged as an exciting pretreatment method, as highlighted in section 2.2.3. However, full scale benefits including cost evaluations of this technique when used prior to RO are scarce. Usually, NF pretreatment is reported to enhance the production of water by more than 60% leading to a significant cost reduction of about 30% [302]. In one study, NF was combined with RO and MD where the introduction of NF increased the performance of the plant and simultaneously decreased the energy requirement. The water production cost of the integrated system was estimated to be 0.92 $\$/m^3$with a recovery factor of 76.2% [303, 304]. In addition, an added benefit of membrane pretreatment lies in its ability to reject multiple contaminants simultaneously. For example, NF is efficient in removing colloids, particulates, dissolved contaminants, and in reducing hardness, color and pesticides in the feed water. Subsequently, many conventional pretreatment techniques can be replaced by a single membrane treatment [5, 30].

New, advanced integrated pretreatment systems are necessary for efficient, cost effective RO desalination plants. For example, Drioli et al. [197] reported an MF–NF–RO integrated system where the MF unit acted on the feed seawater with a recovery factor of 94.7%, while the NF feed was fed from the MF permeate with a water recovery of 75.3%. This approach led to a better control over membrane bio-fouling, thus cutting the membrane replacement and cleaning costs. The integrated system was characterized by a global water recovery factor of up to 50%, with an energy saving of 25–30%, and a lower consumption of chemicals leading to reduced amounts of discharged waste. The unit cost of water production was calculated to be 0.46 $\$/m^3$. Bonnélye et al. [305] reported an enhanced UF/MF pretreatment process to reduce membrane fouling by introducing DAF (AquaDAFTM) prior to immerged membrane filtration, which improved the cost of the UF pre-treatment. The UF membrane flux was expected to increase by 60%. Overall, improvements in performance provided by integrated/hybrid membrane or conventional-membrane pretreatment processes can be achieved with further research taking into account the economics, performance and environmental feasibility for such systems. In addition, costs pertaining to waste discharge need to be added to the total water production cost. From the few studies reported in the literature, the potential of such hybrid systems as opposed to standalone processes should be studied more thoroughly so a clear choice of pretreatment methods can be made.

5.1 *Advanced Membrane Materials*- a solution for cost-effective membrane based RO pretreatment?

The choice of the pretreatment technique will directly impact the overall RO plant performance and related costs. The core of membrane pretreatment techniques lies in the permeablesemipermeable membrane capable of rejecting contaminants from the feed water. Currently, RO plants are already operating near their thermodynamic limit. Novel membranes might provide a possibility for membrane area reduction, however that will require reconfiguration of the membrane modules. Development of novel membrane materials based on carbon nanotubes and graphene are most likely to play a role in terms of energy efficiency. However, the amount of energy saved by these is predicted to be very small, as high water fluxes by such membranes might exacerbate membrane fouling. Nevertheless, development of self-cleaning, electrically conductive membranes and membranes with high fouling resistance for MF, UF and NF pre-treatment are largely expected to improve the energy usage, reliability, and environmental impact of SWRO.

Between polymeric and ceramic membrane materials, several deciding factors need to be assessed to determine the final cost of the system. A techno-economic model has been presented [306] comparing the design and 20 year net present worth of a polymeric and ceramic membrane system. (Table 12). The intake in this case was ground water, instead of seawater. The capital cost was slightly higher for ceramic membranes, with about 50% reduction in costs for membrane replacement achieved due to the longer lifetime of ceramic membranes. Higher labor costs of 2% for polymeric membranes was attributed to the fiber repairs in the polymeric system. These savings with the use of ceramic membranes outweighs the initial investment and allows for a 3% lower cost in the total 20-year present worth. Therefore, even though polymeric materials may be cheaply produced, the net cost of the total filtration system based on polymeric membranes might be quite high due to frequent cleaning and membrane replacement requirements. Fly ash is a commonly researched ceramic material due to its low cost. Jedidi et al.

[234] reported a porous tubular membranes developed from mineral coal fly ash through a slip casting technique. Defect-free membranes were obtained after sintering at high temperatures of 800 °C with an average pore size of about 0.25 µm. When compared to commercial alumina membranes, similar stabilized permeate flux (100 l/h m^2) was obtained, with similar permeate quality; COD and color removal was 75% and 90%, respectively. Singh et al. [307] also reported the use of fly ash ceramic MF membranes with an average pore size of 1.2-2.3 µm, and a porosity of about 35-40%. Disk type membranes were post treated at different temperatures to study the effect of sintering temperature on membrane properties, achieving pure water permeability of about 1,234 to 5,566 $L.m^{-2}.h^{-1}.bar^{-1}$. Table 13 compared the cost of the membranes fabricated from fly ash with the other ceramic membranes reported in the literature. The cost of raw materials was reported to be only about 5-12% of the other membranes [308, 309]. Knops et al. [310] assessed typical operating conditions to quantify amortization of investment in UF membranes and equipment, operating costs for conventional and UF pretreatment and increased output of the SWRO desalination plant. Conventional pretreatment was compared against a novel UF membrane called *X-Flow Seaguard*, made from hydrophilic PES which was specifically designed to cater large scale SWRO plants. They concluded that the total cost of ownership (TCO), the cost being calculated over the life cycle of a desalination plant) of an UF-SWRO plant was 2–7% lower than the total cost of ownership of a SWRO plant based on conventional pretreatment. Usually, the TCO of a large scale RO plants with conventional pretreatment is about 85–90 US cents/m^3 of produced water, while 79-88 cents/m^3 when UF (*X-Flow Seaguard* membrane) was used. Pretreatment occupied ±17% of the total cost. For conventional pretreatment methods, the TCO split was calculated to be approximately 14–15 US

cents/m^3, while for UF, it was approximately 12–16 US cents/m^3. Moreover, UF allowed the RO cleaning frequency to be reduced as also highlighted in the study by Pearce [301] earlier. Thus, with UF, the TCO split for RO membrane replacement and cleaning was only 3–4 US cents/m^3. Figures 26a and 26b compare the components for TCO for both conventional and membrane pretreatment options. Besides RO cleaning and pretreatment, other costs include fixed costs such as amortization of equipment and variable costs such as for energy. It is interesting to note that with UF, shorter construction times are expected, increasing the net production by 1–2%. Extensive cost analysis and studies are required for the new emerging materials based on ceramic and electrically conductive membranes for comparison with the already existing MF, UF and NF membranes available in the market. This can be applied for pilot scale studies for more realistic quantifications. In addition, software analysis can play a key role for cost deductions and extrapolation of membrane replacement and cleaning costs for various membrane materials.

Table 12: 20 year present worth comparing polymeric UF to and ceramic MF membranes. Adapted from Wise et al. [306], Nanostone Water Inc.)

	Polymeric UF Membrane	**Segmented Monolith Ceramic MF Membrane**
Plant Daily Capacity	1 MGD (3.8 MLD)	1 MGD (3.8 MLD)
Active Surface Area Per Module	775 square feet 72 square meters	209 square feet 19.4 square meters
Peak Flux	49 GFD (83 LMH)	249 GFD (422 LMH)
System Recovery Rate	97%	98%
Initial Capital Cost	$400,000 USD	$410,000 USD
Membrane Life	10 years	20 years
Membrane 20 Year Present Worth	$85,000 USD	$41,500 USD
Chemical Consumption 20 Year Present Worth	$26,000 USD	$26,000 USD
Electrical Consumption 20 Year Present Worth @ $0.10/kwh	$117,000 USD	$124,000 USD
Labor 20 Year Present Worth @ $50/hr.	$513,000 USD	$504,000 USD

Total 20 Year Present Worth	$1,141,000 USD	$1,106,000 USD

Table 13: Cost comparison of ceramic membranes from different studies with different pore sizes.

	Bulasara et al. [308]	**Bulasara et al. [309]**	**Singh et al. [307]**
Average pore size (µm)	0.3	0.7	1.2
Material Type	Nickel-ceramic composite membranes	Nickel-ceramic composite membranes	Fly ash
Cost of membrane material ($/kg)	34.5	14.7	1.7
Cost of membrane material ($/m^2)	351.6	149.8	17.3

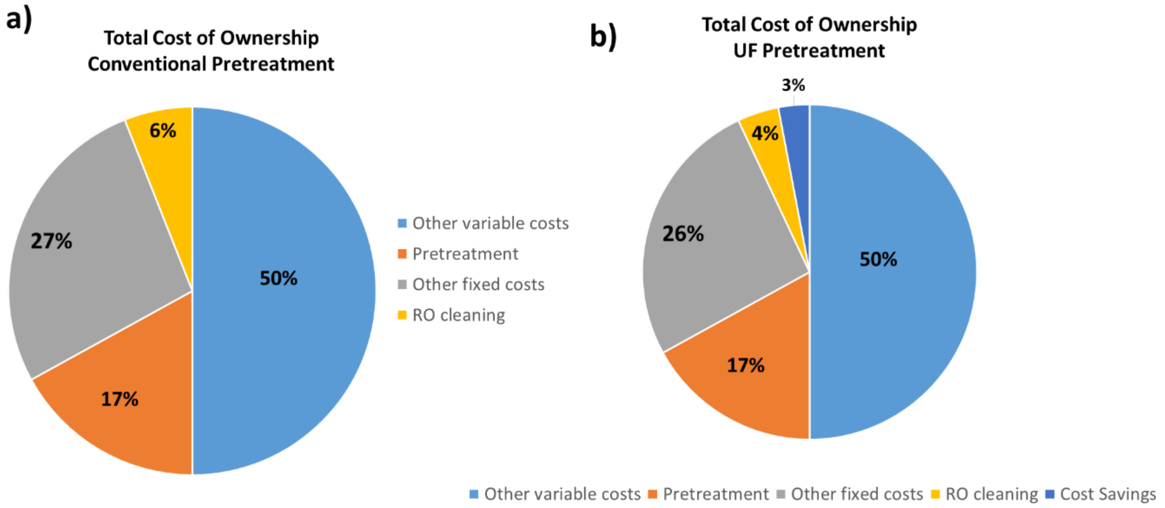

Figure 26: Split of total cost of ownership for various pretreatment options. The UF pretreatment uses the X-flow Seaguard membrane. Reproduced with permission from [310]. Copyright © 2007, Elsevier.

6. Conclusion and Future Recommendations

RO pretreatment techniques form an integral part of any RO plant. It reduces RO membrane fouling propensity which in turn reduces the burden on cleaning frequency and membrane replacement costs. It continues to be one of the most challenging aspects of RO plants due to variations in feed characteristics, regional differences, ecological impacts and economic factors. This paper has reviewed several of the conventional pretreatment techniques including coagulation- flocculation, media filtration, dissolved air flotation, disinfection and scale inhibition. Existing studies, drawbacks and potential improvements were highlighted. Despite the prevalence of these techniques, they offer several limitations for highly polluted feed waters and thus often an integrated, hybrid system comprising of conventional-membrane pretreatment system is necessary. This paper has reviewed MF, UF and NF membrane pretreatment techniques and highlighted case studies on standalone and integrated systems for their performance, cost and ecological impacts. Moreover, membrane materials were given special attention because this is where improvements can most readily be made to further reduce the cost of existing pretreatment and RO systems. Apart from polymeric membranes, ceramic and self-cleaning membranes were reviewed with an overview of existing and future trends presented to equip readers with recent progress and future prospects in this field. New emerging trends include bio-pretreatment and membrane bioreactors. They can effectively be used for reducing biofouling in RO systems in low saline waters, and when integrated with other conventional or non-conventional systems, they can be applied for high saline feed waters as well.

Cost analysis reviewed in this paper clearly marked the distinction between assessing only investment or material costs and end product cost. Though membrane pretreatment options suffer from high capital costs, water production costs are smaller than conventional ones due to improved permeate quality and thus lesser burden on the RO system. Conventional pretreatment capital costs are lower but their chemical consumption costs are higher, putting a stress on RO membrane cleaning and replacement costs. The quality of the produced water from RO systems utilizing conventional pretreatment techniques is also lower. Nevertheless, a major contribution to cost for RO pretreatment is expended as infrastructure and energy. Similarly, the type of membrane material might directly impact the membrane pretreatment cost, for which low cost materials need ongoing research with existing materials requiring improvement for improved selectivity and permeability. Novel membrane materials show rapid progress in utilizing materials incorporating CNTs and graphene. However, limited research exists on the ecological and economic aspects for such materials, together with potential improvement in tailoring membrane properties by controlling their fabrication.

Based on the review in this paper, further recommendations which may answer several questions pertaining to their existing limitations on conventional, non-conventional and emerging RO pretreatment techniques are highlighted below:

- Coagulation is one of the most common conventional techniques for RO pretreatment. Greener coagulants are required to lower the ecological impact of the method. One solution is to use natural coagulants such as maize, *cactus latifaria* and *m*oringa oleifera. More studies are required to develop the feasibility of utilizing such environmentally-friendly, low cost coagulants in terms of end water quality for feeds with various characteristics.

- Antiscalant studies should involve modelling and molecular level understanding for studying their efficiency during pretreatment. Future studies for using various antiscalant mixtures are recommended for a more synergistic effect. However, such studies should include the role of each antiscalant and their reaction with coagulants which might form more foulants leading to RO membrane fouling.
- Ultrasound disinfection is not fully understood and is mostly limited to laboratory scale studies and thus requires further input in terms of understanding the permeate water quality after treatment for various feed water characteristics.
- Advances in membrane technology can play a key role in improving RO membrane pretreatment. These can reduce the burden on pretreatment demands in terms of environment, energy and cost. However, new methods for membrane fabrication for scale-up and membrane modification are required for new generation membranes to meet the demand of higher permeability, selectivity and utility in large scale plants.
- CNTs are an exciting membrane material. However, intensive studies pertaining to the adhesion of CNTs to the membrane surface is essential in preventing loss of the nanotubes. Further, their ecological impact is still a big question and more efforts are needed to understand the environmental impacts of utilizing CNT based membranes for a longer run. Fabrication and testing of electrically conductive membranes based on CNTs should focus on scale-up and testing at pilot-scale levels dealing with harsh feed water conditions.
- Integrated pretreatment systems require more analysis through extensive pilot tests, whereby different combinations of conventional and membrane based pretreatments

should be studied on open intakes for fully understanding the system's combined effects on energy consumption, end water quality and RO membrane fouling.

- For environmental friendly systems, the use of sustainable energy is recommended. Renewable energy sources such as solar energy is suggested to drive the energy for pretreatment as well as RO system. In addition, for cost effective systems, one solution is to recover the energy from concentrated brine to avoid energy wastage. New devices need to be developed for such purposes to lower the burden on water-energy crisis.
- For polymer-ceramic (mostly metal oxides) composite membranes, several studies report the problem of agglomeration of ceramic nanoparticles within the polymer matrix during fabrication. This is due to the high energy of the nanoparticles. Agglomeration causes a decline in flux, adversely affecting membrane performance. One possibility is to improvise material morphology by using ceramic nanofibers instead of nanoparticles. Such studies are rare and thus require more research input to study the impact of polymer-fibrous ceramic composites for RO membrane pretreatments.
- Hydrophilic nanoparticles have a high risk of leak-out from the membrane matrix during fabrication and testing procedures. Hence, such issues have to be addressed with comprehensive, robust life-cycle analyses for utilizing such membranes.

Abbreviations

RO	Reverse Osmosis
SWRO	Seawater reverse osmosis
MF	Microfiltration

NF	Nanofiltration
UF	Ultrafiltration
TDS	Total dissolved solids
TSS	Total suspended solids
NTU	Nephelometric turbidity unit
SDI	Silt density index
DAF	Dissolved air flotation
DMF	Dual media filtration
NOM	Natural organic matter
AOM	Algal organic matter
HS	Humic substances
AC	Activated carbon
BIEX	Biologically active ion exchange resin
GAC	Granular activated carbon
OA	Oxalic acid
ABF	Ammonium Biflouride
THMs	Trihalomethanes
HAAs	Haloacetic acids
TOC	Total organic carbon
DOC	Dissolved organic carbon
DBPs	Disinfection by-products
SEM	Scanning electron microscopy
VAUM	Vacuum assisted UV micro-molding
MPD	m-phenylene diamine
BTC	1,2,4,5-benzene tetracarbonyl chloride
TMC	Trimesoyl chloride
TMP	Trans-membrane pressure
Es	Specific acoustic energy
ATP	Adenosine tri-phosphate
PVDF	Polyvinylidene fluoride
PVC	poly (vinyl chloride)
DRFM	Dynamical Rapid Filtration Model
SMHSs	Submerged membrane hybrid systems
SSF	Slow sand filtration
MWCNTs	Multi-walled carbon nanotubes
PDMAA	poly di-methylacrylamide
PMMA	Poly (methyl methacrylate)
PES	Polyether sulfone
PAN	Polyacrilonitrile
PE	Polyethylene
BSA	Bovine serum albumin
PVP	polyvinyl-pyrrolidone
PEI	polyethyleneimine
PAN	polyacrylonitrile
PA	polyamide
MD	Membrane distillation
MPD	m-phenylenediamine
TMC	Trimesoyl chloride

BPA	Bisphenol A
PHGH	Polyhexamethylene guanidine hydrochloride
PPA	Polypiperazine amide
CNTs	Carbon nanotubes
PVDF	Polyvinylidene fluoride
SBS	poly(styrene–butadiene–styrene)
SCN	thiocyanate
TCO	Total cost of ownership
GDM	Gravity driven microfiltration
TMBPA	Tetramethyl Bisphenol A

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