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Enhanced Membrane Pre-Treatment Processes using Macromolecular Adsorption and Coagulation in Desalination Plants: A Review

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Enhanced Membrane Pre-Treatment Processes using Macromolecular Adsorption and Coagulation in Desalination Plants: A Review

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Abstract: Recent advances in membrane technology have prompted the rapid growth of the Reverse Osmosis (RO) desalination in comparison to other water desalination technologies. One of the major problems of RO is fouling which leads to major reduction in the efficiency of this process. RO membranes are usually fouled with colloids, humic substances, micro-organisms, and heavy metals. This is why it is critical to treat the feed water prior to RO filtration. Conventional pre-treatment methods include processes such as coagulation, adsorption, sedimentation, flotation, sand filtration, disinfection, and the addition of anti-scalants. Recently, membrane pre-treatment processes including micro-filtration (MF), ultrafiltration (UF) and nano-filtration have been introduced prior to RO, with or as a replacement for conventional pre-treatment. These processes are useful in providing feed water superior in quality to conventional pre-treatment, but they are limited in the range of pollutant removal and operating conditions. Full description of water composition and the interactions and aggregations between the contaminants found in feed water for RO desalination is shown in this review. The review includes introduction to membranes, including

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retention and fouling mechanisms, conventional and membrane pre-treatment, and membrane backwashing. It also highlights the role of coagulation and adsorption in the pre-treatment process and the impact of integration of coagulation and/or adsorption with membrane pre-treatment.

Keywords: Membranes, pre-treatment, desalination, fouling, macromolecular adsorption, coagulation

INTRODUCTION

Desalination is the process of removing contaminants and reducing the dissolved salts content in a water source to produce water suitable for a particular application. Several technologies were developed to achieve this and these can be categorized as thermal or membrane processes. The multi-stage flash is the most common thermal process in which the feed water is heated to a temperature few degrees higher than the condenser temperature causing the water vapor to flash and condense on the condenser tubes bundle. The feed water then flows to consecutive chambers (stages) where the condenser temperature is a few degrees lower than the pervious stage causing more vapor to flash and condense. There are 18 to 24 stages in a typical multi-stage flash plant and the last three stages are used for heat rejection to maintain steady-state operation. It is an energy intensive process, requiring 5–7 kWh of mechanical energy and 12–19 kWh of thermal energy per m^3 of produced water (1) and thus multi-stage flash desalination plants are often integrated with steam power plants. Multi-stage flash plants are also capital intensive and mainly used for large capacity applications.

Reverse osmosis (RO) is the most commonly used membrane technology for water desalination. Due to its modular nature, this process is the first choice for small and medium-sized desalination plants. It is also the first choice for brackish water desalination. During RO desalination process, the saline feed water is pumped at high pressure to special membranes, forcing fresh water to flow through the membranes. No heating or phase change is necessary for this separation. The major energy required for desalting is for pressurizing the feed water. The concentrate (brine) remains on the upstream side of the membranes, which is passed through an energy recovery device before being discharged back to the sea (2). The energy consumption of modern RO desalination plants is in the range of 4–7 kWh/m^3 of produced water, making it the least energy intensive desalination process.

In the market place, when judged by installed capacity, the RO process leads with 44 percent of total capacity, closely followed by the multi-stage flash with 40 percent of total capacity. The remaining 16 percent are divided between other processes (3). The estimated water cost for the multi-stage flash process is \$0.52/ m^3, whilst the RO cost is \$0.45/m^3 of desalinated seawater (4). The expected costs for the RO desalination of brackish water are between \$0.20–\$0.35 per m^3 of produced water (5). The cost figures indicate that RO will be the dominating desalination technology in the near future.

Fouling is the biggest obstacle facing the operation of RO desalination plants. Ideal reverse osmosis (RO) membranes should be resistant to chemical and microbial attack and the separation and mechanical characteristics should not change after long-term operation. Unfortunately, seawater contains many foulants that foul RO membranes such as suspended particles, natural organic matter (NOM), micro-organisms and heavy metals. RO process is restricted to certain operating conditions. The typical reverse osmosis elements have limitations with respect to temperature (45°C); pH value (2–10), silt density index (less than 3 SDI), chlorine (dechlorination mandatory), and several other parameters (6). Seawater and brackish water contain different composition of pollutants depending on the source of collection. These pollutants cause different deteriorating effects on the RO desalination process, thus; many pre-treatment methods had been proposed to obtain the desired results. Extensive pre-treatment is also required to increase the water recovery ratio of 30–50% for RO seawater desalination (7, 8).

Different processes such as coagulation, flocculation, acid treatment, pH adjustment, and addition of anti-sealant and media filtration, have been used as conventional pre-treatment for years (9). Nowadays, the trend is moving in the direction of Integrated Membrane Systems pre-treatment. Reasons are mainly feasibility, process reliability, plant availability, modularity, relative insensitivity in case of raw water, and lower operating costs. Integrated Membrane Systems are expected to offer 14% reduction in RO treatment plant compared to conventional pre-treatment (10). This is due to the substantial drop in membrane prices in the last few years and further reduction is expected in the coming years (5).

This review contains a description of water composition and the interactions and aggregations between the contaminants found in feed water for RO desalination. It also includes introduction to membranes, including retention and fouling mechanisms, conventional and membrane pre-treatment, and membrane backwashing. The review then highlights the role of coagulation and adsorption in the pre-treatment process and the impact of integration of coagulation and/or adsorption with membrane pre-treatment.

WATER COMPOSITION

Typical natural water contains natural organic matter (NOM), mono- and multivalent ions, micro-organisms and organic and inorganic colloids (11). These contaminants are divided into soluble (<1 nm), colloidal (1 nm–1 μm) and particulate fractions (>1 μm) (12). With respect to dissolved ions, the ions of Na, Cl, Mg and SO_4 together constitute about 97% of all ions in seawater of the international mean ocean water standard of 35,000 mg/L (13). The silt density index (SDI) is the test most commonly used to measure the feed quality in terms of non-dissolved substances. The lower the SDI, the longer the RO running cycle will be between chemical cleaning (14). According to Teng et al. (15), particles having sizes varying from 1 μm to 5 μm have a higher impact on SDI than particles' having sizes greater than 5 μm in seawater. Membrane manufacturers recommend that SDI should not exceed 4 or 5 and set limits of membrane productivity depending on the SDI. However, despite the wide acceptance of the SDI in the RO industry, cases of poor correlation with fouling propensity are not rare (16). Other indices are the MFI (Modified Fouling Index) and the MPFI (Mini Plugging Factor Index). All three are based on batch filtration of feed waters through a 0.45 μm Millipore microfilter. Recently, the MFI-UF has been introduced which employs ultrafiltration membranes instead of the Millipore microfilter. Other measurements, such as turbidity, particle counts, and particle electrophoretic mobility are also employed, but are not accepted as reliable tools for fouling prediction (16, 17).

Humic Substances

Natural organic matter (NOM) is present in all water sources and is a complex mixture of compounds formed from the breakdown of plant and animal material in the environment. Natural organic matter consists of small, low molecular weight species such as carboxylic, amino acids, and proteins, through to larger and high molecular weight (from 0.5–30 kDa) humic and fulvic acids. Natural organic matter is one of the major fouling agents during membrane filtration of surface water (18). They bind particles to each other and to membrane surfaces (19).

Dissolved organic matter (DOM) in natural environments consists of a large variety of molecules. Most of these have no readily identifiable structure. This heterogeneous group of organic macromolecules is often referred to as humic substances (HS). Humic substances constitute a major part of the NOM present in ground water (20). They occur as long linear chains at high pH and low ionic strength due to charge repulsion of functional groups, and as coiled, spherical molecules at low pH and high ionic strength, hence they are more soluble at high pH (11). It is well established that HS are amphiphiiic molecules, containing at the same time hydrophilic and hydrophobic groups. Representing the hydrophilic groups in HS are those containing oxygen, nitrogen, phosphorous and sulphur, while hydrophobic groups are aliphatic, aromatic, and cyclic hydrocarbons (21).

Humic substances are toxic to aquatic organisms in high concentrations. They induce a high risk to humans because of the direct exposure and/or bioaccumulation through food chains (22). Humic substances are known as trihalomethane formation potential, being precursors of trihalomethanes formed during chlorinating (particularly pre-chlorinating) (23, 24). They are refractory anionic macromolecules of low to moderate molecular weight. They contain both aromatic and aliphatic components with primarily carboxylic and phenolic functional groups. Carboxylic functional groups account for 60–90% of all functional groups (25). As a result, humic substances are negatively charged at the pH range of natural waters (24, 25). Bjelopavlic et al. (26) showed that at pH 4 the NOM is negatively charged (−0.008 mmol/mg) and at pH 7 and 9 the magnitude of the negative charge (−0.016 and −0.017 mmol/ng, respectively) is twice that at pH 4.

Humic substances are usually defined as substances containing humic acids (HA) and fulvic acids (FA) plus other components. HA are the acidic components which are soluble in bases, but precipitate in acids. Fulvic acids are the acidic components that are soluble in both bases and acids (27). To understand better the different behavior of humic and fulvic acids, it is necessary to consider their different molecular weight as well. Fulvic acids have a lower molecular weight and a higher percentage of carboxylic groups than humic acids, and that increases their hydrophilicity. That is why fulvic acids are soluble also at low pH values (pH 2), where humic acids precipitate. Thus, fulvic acids have less affinity for binding hydrophobic compounds, while they often show a high metal complexion capacity; otherwise, the high molecular weight and basic hydrophobicity of the humic acids favour the formation of micelle like structures (28).

HS molecular weight and molecular weight distribution differs from site to site. The average molecular weight varies from 0.5–10 kDa for aquatic fulvic acids (29) to a value as high as 40–300 kDa for Aldrich humic acids (30). These values are far greater than the values reported previously by other authors, typically, 0.5–2 kDa for aquatic fulvic acids, 1.5–5 kDa for aquatic humic acids and 4–6 kDa for soil humic and fulvic acids (31–33). Groundwater containing lower molecular weight distributions less than 1 kDa has the highest concentration level of dissolved organic carbon (DOC), while samples from surface water have more smaller molecules (<1 kDa) and larger ones (>30 kDa) (34).

Heavy Metals

Many metals exist in seawater and ground water. Their concentration varies significantly with water source (35). Among the various contaminants, trace metals are of particular concern due to their environmental persistence, biogeochemical recycling and ecological risks. Metals are introduced into the marine environment through river runoff, atmospheric deposition, hydrothermal venting, digenetic remobilization, and anthropogenic activities (36). Heavy metals are known to exist as free ions in a strong acidic medium and have molecular sizes less than the pore sizes of ultrafiltration membranes (23). Heavy metals like Co, Ni, Zn, Cu, and Cd were grouped as elements of 1 – 10 kDa fraction that have a tendency to form inorganic or organic complexes (35).

River and anthropogenic inputs, and biological and geochemical cycling may influence the concentration of metals in estuarine and coastal seawater to a much greater extent than that occurring in open-ocean water. Transport of metals from rivers and estuaries is dependent on the partitioning of metals between dissolved and particulate phases. The partitioning of trace metals between dissolved and particulate phases is modified by several factors including: specific metal ion, metal concentration, nature of particles, particle concentration, pH, salinity, and dissolved oxygen (37).

Copper (Cu) and its compounds are ubiquitous in the environment and are thus found frequently in surface water (38). Although. the toxicity of Cu to humans is fairly low, bioaccumulations of even small amounts of Cu (on the order of tens of mg) are lethal to a host of uni- and multicellular aquatic organisms (39). Local Jordanian standards of industrial wastewater discharges suggests that the concentration in discharged water should not exceed 1 ppm of Cu^{2+} and 0.41 ppm of Cd^{2+} (40). Chemical precipitation is the most commonly used method for the treatment of industrial wastewater containing heavy metals. This process requires a large amount of treatment chemicals to decrease the heavy metals to levels imposed by the regulations. In addition, the sludge produced from the precipitation process has to be subjected to dewatering and disposal into landfills, which adds an additional cost to the treatment process. Membrane processes give high rejection of heavy metals such as Cu^{2+} and Cd^{2+} from wastewater streams. Reverse osmosis and nanofiltration studies on synthetic water resembling wastewater containing Cu^{2+} and Cd^{2+} resulted in a total rejection of 99.4% (3 ppm) for RO and 97.4% (13 ppm) for NF. Another RO study reduced the concentration of Cu^{2+} and Cd^{2+} in discharged water to a value lower than 1 and 0.01 ppm, respective (40).

Cobalt is another heavy metal which effects humans, this has been shown in (41). Permissible limits of cobalt in the irrigation water and livestock watering have been outlined in guidelines by Environmental Bureau of Investigation, Canadian Water Quality Guidelines (41).

Colloids

Although the term "colloids" is still subject to an operational definition, there is a general consensus that colloids fall largely in the nanometer to submicrometer size range and occur in relatively large concentrations (more than 10^9 colloids per litre). Colloids are ubiquitous; they occur in natural waters; seawater, groundwater, and interstitial soil water. Colloids may include clay minerals, oxides, or hydroxides of iron and aluminium, colloidal silica, organic matter, and biocolloids including viruses and bacteria (23). In suspensions, colloids interact with each other via different types of mechanism (42);

- Electrostatic double-layer repulsion and/or
- Van der WaaIs attraction and/or
- Short range repulsion (Born or hydration forces).

Colloids have a large specific surface area and a large number of reactive surface functional groups per unit mass because of their small size. Therefore, they are efficient sorbents for contaminants, such as heavy metals, nonpolar organic compounds, and radionuclides and can potentially enhance contaminant mobility (43).

Under environmentally relevant conditions, fulvic acids are likely to be responsible for coating and imparting a negative charge to colloids. Colloidal organic carbons, especially chain-like structures were involved in the aggregation of inorganic colloids through the formation of bridges (12).

A full understanding of metal chemistry in natural waters needs to take into account the competitive reactions of metals with humic matter. The binding ability of HS towards heavy metals is known to depend on ion size (44) as well as HS-Metal ratio i.e. the presence of HS increases the rejection of heavy metals (23). Heavy metal (23) rejection in the presence of humic acids (HA) occurs due to HA-metal complex formation (45). According to Alpatova et al. (23); the metal removal efficiency gradually increases with increasing weight HS-Metal ratio up to 2. Further increase of HS concentration did not influence the Cu rejection in case of both HA and FA. High metal content results in a transition of intra-molecular complexes into inter-molecular ones that leads to an aggregation of HA-Metal complexes and the ultrafiltration productivity decreases. The FA form mostly intra-molecular complexes with divalent metal ions that led to constant volume flux. The effectiveness of metal removal is concordant with stability constant of HS-Metal complexes and higher affinity of metals with larger ion size to HS.

Eyrolle and Benaim (46) studied Amazonian surface water using sequential UF. Several fractions, defined by the nominal molecular weight cut-off (MWCO) of the UF membranes were obtained: $<5\,\mathrm{kDa}$, $5\,\mathrm{kDa}<<20\,\mathrm{kDa}$, $20\,\mathrm{kDa}<<100\,\mathrm{kDa}$, $100\,\mathrm{kDa}<<0.2\,\mu\mathrm{m}$ and $0.2\,\mu\mathrm{m}<<0.45\,\mu\mathrm{m}$. The first fraction was defined as "true solution," while the others were defined as colloidal classes. The metal binding capacity of these fractionated samples revealed that the $20\,\mathrm{kDa}<<100\,\mathrm{kDa}$ fraction was the most efficient fraction for copper binding. Fokrovsky and Schott (35) UF experiments showed that several transition metals including Cu, Zn, Ni, Co, and Cd can be partially transported by low-molecular weight ($<1-10\,\mathrm{kDa}$) organic acids.

Figure 1 provides the results of Cu aggregation with HA study, deducing that as Cu increases, the percentage of higher molecular weight species

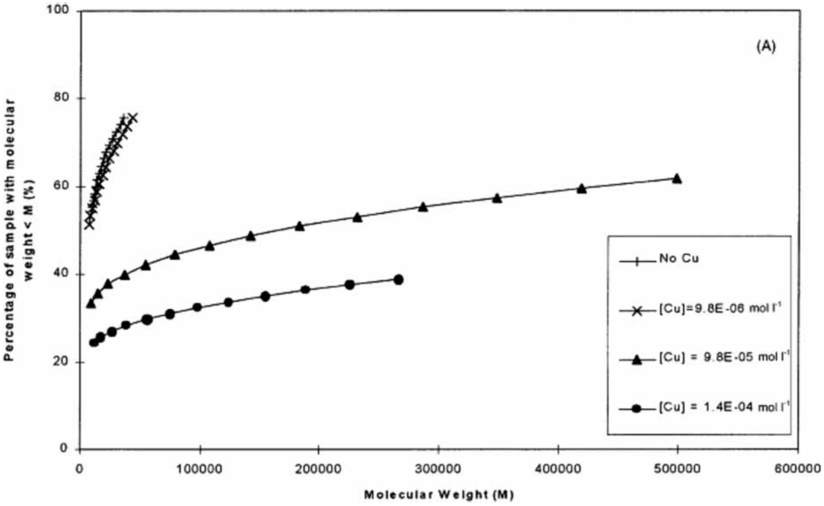

Figure 1. Cumulative molecular weight distribution during the aggregation of Whitray Beck aquatic humic acid (WBHA2) by copper(II) ions (47).

increases. Hamilton-Taylor et al. (48) used equilibrium dialysis to measure Co and Cu binding by an isolated peat humic acid (PHA). The presence of seawater concentrations of Ca and Mg had a relatively small effect on Co-humic binding and no measurable effect on that of Cu.

MEMBRANE TECHNOLOGY

This section provides an introduction on the different types of membranes. It also gives an overview of the different retention mechanisms and fouling models of the membranes.

Types of Membranes and Filtration Modes

Microfiltration (MF) is a pressure driven separation technique used to separate micron-sized particles from fluids. The suspended particles are in the approximate range size of 0.02–10 μm. The transmembrane pressure (TMP), which drives the process, is relatively small. According to Van Houtte et al. (49), the MF system is capable of treating many types of waters, including water with high iron content and water with high organic load or bio-fouling potential. Microfiltration membranes are used for the removal of small suspended particles, large colloids and microbial cells (12, 14).

Ultrafiltration membranes (UF) typically have pore sizes in the range of 10–500 nm and are capable of retaining species of molecular weight higher than 1000 Da. Typical rejected species include sugars, biomolecules, polymers, and colloidal particles. Most UF membranes are described by their nominal molecular weight cut-off (MWCO), which is usually defined as the smallest molecular weight species for which the membrane has more than 90% rejection. Ultrafltration can provide high quality feed water with low SDI and free from all suspended solids and microorganisms (50). UF process is strongly dependent on membrane material, operating conditions and raw water quality. It is not sensitive to the high salinity of sea water (51).

In the seventies, RO membranes with a reasonable water flux operating at relatively low pressures were developed. Operating such membranes at high pressures resulted in inefficient power consumption. These "low-pressure RO membranes" became known as NF membranes (52). NF membranes first applications were reported in the second half of the eighties (53). NF membranes are usually made of polymeric films with a molecular weight cut-off between 0.3 and 1 kDa. They operate at relatively low pressure, usually in the range of 50–150 psi (3.4–10.3 bar) (20). NF combines removal of uncharged components on nanoscale and ionic species due to charge effects between charged solutes and the membrane. The removal of uncharged components may be a result of size exclusion, as known from ultrafiltration, or may be a result from differences in diffusion rates in a non-porous structure, which depend also on molecular size. According to the Stokes-Einstein law, expressing an inverse proportionality between the diffusion constant and the size of a component, the diffusion rate will be smaller for a larger component, resulting in an effect similar to size exclusion. The charge effect, on the other hand, results in removal of (mainly multivalent) ions, the former effect results in the removal of uncharged organic species (54).

Two main types of filtrations are usually carried out in membrane separation processes; these are dead-end and cross flow filtrations. The dead end filtration is normally used in laboratories on small scales while cross flow filtration is the main process used on large scales in many industries including desalination (55).

There are many materials used for the manufacturing of membranes i.e. polyethersulfone, polysulfone, regenerated cellulose, cellulose acetate, aromatic polyamide, Polyvinylidenefluoride and polypropylene (23, 56, 57). Care has to be taken when choosing membrane material. Membrane retention and fouling is dependent on membrane material i.e. MWCO and hydrophobicity (56). During the last two decades new membranes had been developed. These polyamide thin-film membranes can be used at low TMP (7 bar) and still offer better membrane flux and rejection compared to the original cellulose acetate membrane operating at 28 bar (6).

Retention Mechanisms

Single solute retention is defined as (58, 59):

$$R = 1 - \frac{c_p}{c_b} \tag{1}$$

where R is the percentage solute rejection, c_p is permeate concentration and c_b is bulk (feed) concentration.

Mixture solute retention is defined as (60):

$$R_{Mi} = \frac{W_{Mi}(feed) - W_{Mi}(permeate)(1 - R_{overall})}{W_{Mi}(feed)} \tag{2}$$

where R_{Mi} is fractional rejection for a certain relative molecular mass (RMM) of component (i), W_{Mi} is the mass fraction of that RMM in the specific stream and $R_{overall}$ is overall NOM rejection by the membrane.

There are different retention models that have been developed to approximate the real rejection instead of the observed rejection. The real rejection differs with different membrane fouling phenomena.

Concentration polarization model is used when higher solute concentration in present at the membrane surface. This higher concentration forms a thin boundary layer of thickness (δ). The real rejection is calculated using (58):

$$J = k_s \ln \frac{(c_m - c_p)}{(c_b - c_p)} \tag{3}$$

which can also be defined as:

$$\frac{c_m}{c_b} = R.e^{(J_v/k)} + 1 - R \tag{4}$$

where c_p, c_{m} and c_b are permeate, membrane surface and bulk concentrations, respectively, J_v, is flux, k is mass transfer coefficient and R is solute rejection.

The effect of osmotic pressure on membrane flux is defined as (58):

$$J_v = \frac{\Delta P - \Delta \Pi}{\mu R_m} \tag{5}$$

ΔP is the transmernbrane pressure, $\Delta \Pi$ is the osmotic pressure difference, R_m is the membrane resistance, and μ is solution viscosity. A recent review (61) introduced modified equation (5) using the cake filtration model:

$$J_v = \frac{\Delta P - \Delta \pi_m^*}{\mu(R_m + R_c)} \tag{6}$$

$\Delta \pi_m^*$ is the transient osmotic pressure drop and R_c is the transient hydraulic resistance imparted by the colloid cake layer.

Cake (gel) layer model for dead end operation is defined as (62):

$$J_p = \frac{\Delta P}{\mu R}\left(1 + 2R'_C \frac{\Delta P}{(\mu R_m)^2} \frac{C_0}{C_g - C_0} t\right)^{1/2} \tag{7}$$

where R'_C is specific resistance of the cake layer, m^{-2}, C_0 is feed concentration, C_g is gel concentration and t is time.

Assuming the gel layer is incompressible, the specific resistance can be defined as (62):

$$R'_C = 45 \frac{(1-\varepsilon)^2}{\varepsilon^3 - a_p^2} \varepsilon \tag{8}$$

where ε is porosity and a_p is solute radius.

According to the model, the initial value of permeate flux corresponds to that of a clean membrane. Afterwards permeate flux decreases linearly with time for a short period, due to the build up of a cake layer. As permeate flux decreases, the cake layer formation velocity also decreases. For a long period of operation, permeate flux decline is conversely proportional to the square root of time. The validity of the model is restricted to the case when cake layer formation is the fouling mechanism (62).

Temperature affects the viscosity of solution leading to changes in flux. Poland equation correlates between temperature and flux as such (63):

$$J_T = J_{25} 1.03^{(T-25)} \tag{9}$$

where J_T is a permeation flux at an arbitrary temperature (T) and J_{25} is the permeate flux at a reference temperature of 25°C.

Another viscosity correction may be used (64):

$$J(40) = \frac{\mu(\mathrm{T})}{\mu(40)} J(T) \tag{10}$$

where $J(40)$ is the recalculated flux to 40°C, $1/(\mathrm{m}^2\mathrm{h})$, $J(T)$ is the measured flux at temperature T, $1/(\mathrm{m}^2\mathrm{h})$, $\mu(\mathrm{T})$ is the viscosity at temperature T and $\mu(40)$ is the viscosity at 40°C.

FOULING MODELS

Fouling, often associated with accumulation of substances on the membrane surface or within the membrane pore structure, worsens membrane performance and ultimately shortens membrane life. These include dissolved and macromolecular organic substances, sparingly soluble inorganic compounds, colloidal and suspended particles, and micro-organisms. Dissolved naturally occurring organic substances are considered a major cause of fouling in membrane filtration of natural waters (6, 65). To prevent reverse osmosis

(RO) membrane fouling, the organic, colloidal and biological matter needs to be removed from the feed water to the RO system (66). The following fouling mechanisms may play a role: colloidal or particulate fouling, organic fouling, biological fouling (or biofouling) and scaling. Different fouling mechanisms require different pre-treatment strategies. Biological fouling may. be reduced by a biological process in the pre-treatment (such as slow sand filtration) or by soil passage or using membrane filtration. Scaling cannot be avoided by pre-treatment but can be dealt with by reducing the recovery and by adding chemicals e.g. acid and anti-scalants.

Two kinds of fouling can be distinguished; reversible and irreversible fouling. Reversible fouling is caused by the physical separation mechanisms that induce concentration polarization phenomena, deposit formation, and plugging of the pores. The phenomena induce important variations of the system permeability. These variations can be regulated by enhancing the hydrodynamic shear stresses close to the membrane; such as cross-flow circulation, back flushing and momentary filtration stopping. Irreversible fouling is linked to interactions between compounds in solution and membrane material. Chemical cleaning is necessary to detach these compounds from the membrane surface. However in water treatment this kind of fouling does not cause very important variation of membrane permeability (67). Polysaccharides usually foul the membranes irreversibly (68) and Cho et al. (69) indicated that polysaccharide or polysaccharide-like substances reduced contact angle and reduced negative charge leading to fouling.

The most critical particle sizes for fouling are in the range 0.1–1.5 μm and some membrane types do not show significant fouling because of their low affinity to the membrane material (70). Shaalan (71) developed a generalized equation enabling predictions of membrane performance in terms of time (*T*), ionic strength (*I*), total organic carbon (*TOC*), operating pressure (*P*) and membrane MWCO (*D*).

Verification of the generalized correlation using external data sets indicates deviation range from 0 to 19%. This correlation is applicable for the following conditions: $T = 10\text{–}80\,\text{h}$, $I = 1.6\text{–}75\,\text{mM}$, $TOC = 0\text{–}20\,\text{mg/l}$, $P = 80\text{–}147\,\text{psi}$ and $D = 3000\text{–}1000$ Daiton. This correlation enables reasonable prediction of flux decline changes with respect to initial set of conditions:

$$\frac{J}{J_o} = 0.65e^{(-0.13T-0.031I+0.896TOC+1.23P-0.34)}, \quad R^2 = 97\% \tag{11}$$

There are different causes of flux decline. In general, the flux decline is caused by a decreased driving force and/or an increased resistance (72). The fouling process may be attributed to a number of mechanisms including pore blocking by solutes that are of similar diameter to the pares, formation of a cake from excluded solutes (i.e. solutes unable to pass through the membrane pores), precipitation or gelation of inorganic and organic particulates at the membrane surface as a result of the localized high concentrations that occur at the membrane/solution interface and reversible and irreversible physical changes to the membrane (for example, compression). A number of research papers have dealt with fouling mechanisms (73, 74) with a recent review showing up-to-date detailed studies of fouling and its mechanisms (75). A schematic diagram of membrane fouling mechanisms is found in Fig. 2 (60, 72, 76). These mechanisms can be defined using a resistance in series model (76):

$$J_v = \frac{\Delta P}{\mu(r_m + r_c + r_g + r_a)} \tag{12}$$

where J_v is flux through the membrane (cm/s), ΔP is transmembrane pressure (Pa), μ is dynamic viscosity (Pa · s or g · s · cm^{-1}), r_m is membrane hydraulic resistance, r_c is concentration polarization resistance, r_g is gel layer resistance, r_a is adsorption resistance (all resistances are in cm^{-1}).

The difference between concentration polarization and gel layer resistances is that the former is a thermodynamic modification of the pressure driving force, and the latter is the viscous resistance for flow through highly concentrated (precipitated or gelled) solutes. They can be removed by water cleaning, hence, it's a reversible fouling.

A five-parameter membrane resistance-in-series model may also be used (77):

$$J_v = \frac{\Delta P}{\mu(r_m + r_c + r_g + r_{a1} + r_{a2})} \tag{13}$$

where r_{a1} is weak adsorption resistance and r_{a2} is strong adsorption resistance. The weak adsorption can be defined as the adsorption that can be removed by chemical cleaning with 0.1 M NaOH. Strong adsorption is attributed to the NOM that cannot be desorbed even with this chemical cleaning.

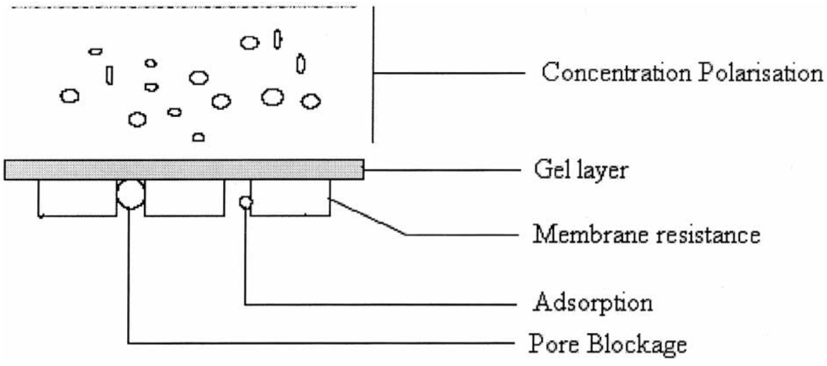

Figure 2. Schematic diagram of membrane fouling mechanisms (72).

The blocking fouling mechanisms can be pore plugging (complete blocking), direct adsorption on the pore walls (standard blocking), or boundary layer resistance (cake filtration). The volume flow ($m^3/m^2 \cdot s$) versus time dependency for the complete blocking model is defined as (78):

$$J_v(t) = J_{v0} e^{-K_{CB} t} \tag{14}$$

where:

$$K_{CB} = C_{CB} A \frac{\Delta P \pi r_0^4}{8 \eta \ell_0} \tag{15}$$

C_{CB} is the number of pores per unit surface blocked per unit of filtered volume (m^{-5}), A is the membrane area (m^2), η the solution viscosity ($kg/m \cdot s$), ΔP is the applied pressure (Pa), ℓ_0 is the membrane thickness (m) and r_0 the initial mean pore size (m). Hagen Poiseuille equation has been assumed. The rest of the models can be summarized as follows (78):

$$J_v(t) = \frac{1}{A}\frac{dV}{dt} = J_{v0}(1 + Kt)^{-n} \tag{16}$$

where for standard blocking: $n = 2$

$$K = \frac{1}{2} K_s J_{v0} \tag{17}$$

and

$$K_s = C_s \frac{A}{2} \left(\frac{J_{v0} \Delta P N_0}{2 \eta \pi \ell_0^3} \right)^{1/2} \tag{18}$$

C_s is the volume deposited on the pore walls per unit of permeated volume (s/m) and N_0 is the initial number of pores per surface unit (m^{-2}). By integrating equation 16 (78):

$$\frac{t}{V^*} = K_s t + \frac{1}{J_{v0}} \tag{19}$$

with $V^* = V/A$.
For cake model:

$$n = 1/2$$

$$K = 2 K_{CF} J_{v0}^2 \tag{20}$$

and

$$K_{CF} = C_{CF} \frac{\rho_C \eta}{\Delta P} \tag{21}$$

where ρ_C is the cake mass per unit of permeated volume (kg/m^3) and C_{CF} is the apparent specific resistance of the cake (m/kg). By integrating equation 16 (78):

$$\frac{t}{V^*} = K_{CF} V^* + \frac{1}{J_{v0}} \tag{22}$$

PRE-TREATMENT PRIOR TO DESALINATION

An introduction to conventional pre-treatment is provided in this section. The uses of different types of membranes are listed, followed by membrane fouling and retention during filtration. Backwashing and chemical cleaning are briefly highlighted as well as pre-treatment prior to membrane filtration.

Conventional Pre-Treatment

A conventional water treatment plant. consists of a multi-step process applying screen filtration, ozonisation, coagulation and flocculation, sedimentation, sand filtration and usually disinfection as a last step. The use of ozone, flocculants, hydrogen peroxide, lime and chlorine requires special precautions for safety purposes. Each step of this process has to be controlled to get an optimal performance of the overall process, which results in a complex control system (79, 80). Pre-treatment chemicals may include chlorine, ferric chloride bisulfate coagulant, sulphuric acid, sodium meta bisulfate and anti-scalant (81).

A conventional seawater reverse osmosis (SWRO) pre-treatment is an extremely complicated chemical process. Due to its complexity and inefficiency compared to membrane pre-treatment, it frequently fails in providing the required seawater quality (Figs. 3 and 4) (82). In the past, clarification and media filtration (conventional filtration) have been used as pre-treatment to RO systems. These systems typically require large footprints and large amounts of chemicals to aid in filtration. Conventional filtration is

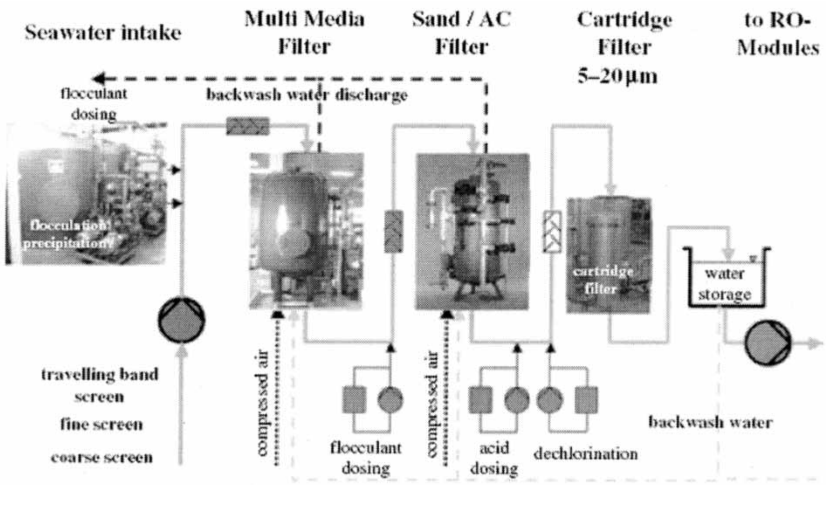

Figure 3. Conventional pre-treatment prior to RO desalination (82).

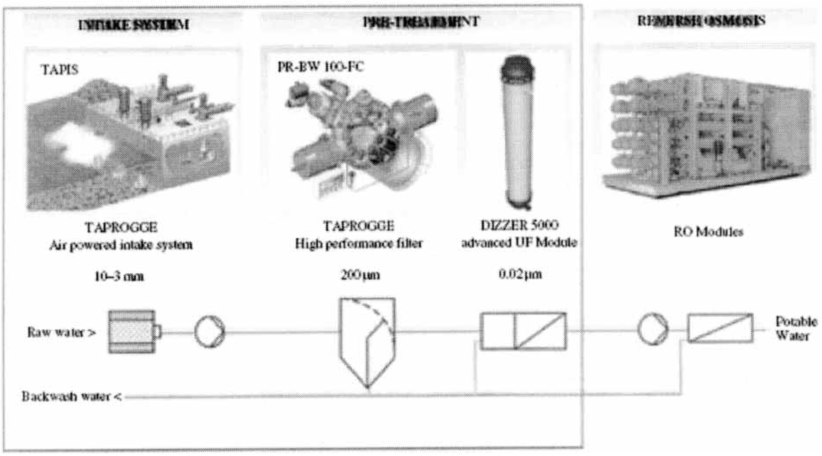

Figure 4. UF as pre-treatment to RO desalination (82).

also susceptible to inconsistent filtrate water quality when the feed water quality varies. Chemical addition and changing water conditions can lead to an operator intensive plant (83).

Membrane Pre-Treatment

The failure of conventional methods to produce treated seawater capable of reducing the fouling tendencies of the reverse osmosis plants and the high cost of specific operations of such conventional methods are the main factors, which lead to the use of membrane filtration as a pre-treatment to RO (6).

Membrane technology is widely accepted as a means of producing various qualities of water from surface water, brackish water and seawater. Over the past years, such processes have been widely adopted by different industries. The advantages of membrane processes as compared to conventional process include (79, 84):

- Little conditioning or ripening time after backwashing
- Limited or no chemical requirement. No chemicals are used apart from those for cleaning the membranes, i.e. substantially reduced residues and by-products
- Ease of operation and minimal operator involvement. The membrane plant is easier to automate owing to its simple design and greater flexibility owing to its modular construction (e.g. later extension of capacity)
- Low spatial requirement
- The permeate is free from viruses and other micro organisms reducing biofouling and recontamination; in later stages (e.g. RO), due to the physical barrier of the UF membrane

- Reduction of sludge and water volume
- Higher water quality.

Desirable membranes, when applied in liquid separation processes must have the following characteristics (85):

- A suitable porosity to keep a large volume flux
- Appropriate pore sizes and a narrow pore size distribution to meet the separation requirements
- Essential mechanical strength to withstand the pressure operation
- Chemical and biological resistance.

Microfiltration

Using microfiltration (MF) membrane technology as a pre-treatment reduces capital and operating costs on reverse osmosis (RO) plants. It can reduce the chemical usage and a consistent filtrate flow rate and quality are continuously sustained with an automatic process, irrespective of the quality of the feed water (86). Many researchers studied the role of MF as a pre-treatment to desalination (12, 14, 40, 87–90). Teng et al. (51) stated that moderate removal of colloidal silica and suspended solids are possible through MF pre-treatment. There was no rejection of reactive silica and a rejection of approximately 40% was achieved for organics. Pianta et al. (90) studied MF and UF membranes as a possible process to overcome the irregular and unpredictable increases of turbidity and NOM in karstic spring water. The study showed stable performance at low turbidity levels, but at higher turbidity peaks the MF performance is mainly influenced by submicron particles contained in the raw water suspension.

Hagen (88) concluded after 2 years operation on four pilot plants with five modules of MF and UF that at correct operation, in spite of fluctuations in raw water quality, the complete and safe removal of bacteria, parasites and particles can be achieved. Bacterial disinfection was ensured despite raw water quality fluctuations and the removal of MS2 viruses reached 2.5–3 log (90). Microfltration membranes provided significant rejection of viruses under appropriate condition, however, ultrafiltration membranes gave complete rejection of viruses (91). UF and MF membranes showed similar performances in removing micro-organisms and turbidity from water according to Bodzek and Konieczny (87) and Mavrov et al. (89). At high microbial concentration membrane fouling occurs. The addition of chlorine and pH adjustment will reduce membrane fouling (92).

According to Abu Qdais and Moussa (40) the procedures of coagulation and sedimentation could remove most of Giardia and Cryptosporidium parasites from raw water, where as pre-ozonation would destroy both parasites effectively, but complete removal will be expected using MF and

NF membranes. Hsu and Yeh (93) studied the removal of Giardia and Cryptosporidium using three processes. These processes include; conventional process without pre-chlorination (Process 1), conventional process plus ozonation and pellet softening (Process 2), and integrated membrane process (MF plus NF) followed the conventional process (Process 3). Process 1 and 2 removed most of the parasites, but all of the parasites were removed using Process 3.

Microfiltration has been evaluated as an alternative treatment to conventional treatment of groundwater for the City of Oviedo, Florida, that contains gaseous hydrogen sulphide (H_2S). The conventional treatment has normally utilized air stripping as a mean to remove this undesirable contaminant (94) Membrane filtration of lake water through porous ceramic membranes was proven very useful for drinking water production. Suspended solids were completely removed along with micro organisms and algae and this led to a noticeable reduction in the chlorine demand needed to render hygienically safe the transport and the distribution network of the water (80).

Ultrafiltration

Ultrafiltration for seawater desalination has the benefits of a better/safer pre-treatment compared to conventional pre-treatment. It has the potential to reduce the cost of seawater desalination (95). Ultrafiltration systems require significantly less space and often have less power and chemical consumption than conventional pre-treatment systems. As a result, UF membrane systems are a practical solution to SWRO pre-treatment needs, especially for locations with limited space or variable seawater quality (83). Ultrafiltration pre-treatment also allows the economical utilization of RO membranes in areas where membrane desalination has not been considered as the appropriate technology due to difficult raw water conditions. Furthermore, using UF membrane technology to produce high quality pre-treated feed water allows troublesome RO installations to be brought to design productivity levels. UF, unlike conventional pre-treatment technologies, provides a physical barrier to particulate and colloidal material and ensures that RO plants can operate on a continuous basis, at high and stable fluxes, at higher recovery rates, and also allow a better control of contaminants limit values. With the cost of membrane pre-treatment constantly declining and quality of feed water deteriorating, an increasing number of plant owners are nowadays considering the use of membrane based pre-treatments to replace less efficient, conventional pre-treatment systems, which do not represent a positive barrier to colloids and suspended solids and produce unsteady quality of RO feed water (96).

Water Supply Company of North Holland and Kiwa combined ultrafiltration/ultra low-pressure reverse osmosis for the treatment of surface water. Measurements showed $>95\%$ removal of haloaeefic acids (HAAFP) (97).

According to Teng et al. (15) the removal of colloidal silica and coliform group of bacteria could be significant with 0.1 μm nominal pore size UF membrane treatment. However, a small percentage removal of organics was encountered. The removal of fouling constituents of seawater was more efficient with UF pre-treatment than with conventional pre-treatment (68). A study by Van Hoof et al. (13) showed a reduction of turbidity from 3–4 NTU to around 0.3 NTU using UF as a pre-treatment to seawater RO. Ultrafiltration could be used to reduce the high turbidity of the source water to protect the NF/RO membranes. The turbidity of the UF permeate was consistently below detection limit (98).

UF membrane pre-treatment is a reliable technology capable of providing consistently good quality feed water for RO seawater system independently of the raw water quality fluctuation (99). The performance of UF prior to RO membrane was studied by Murrer and Rosberg (100). In their study, the UF-treated water had <0.16 NTU turbidity, 0.7 mg/L TOC, 36,200 mg/L TDS and <15 mg/L suspended solids. The SDI of the beach well water was typically 5.5–6.2, while the UF treated water was in the range of 2.8–3.3. The installation of UF increased the output of RO by >25%. Hofman et al. (101) used UF for phosphate removal, removal of suspended solids and colloidal matter to improve the hygienic water quality of surface water. The results showed that stable operation of the membranes was feasible and an excellent water quality could be produced, Phosphate was removed from an average of 60 to 20 μg/L P in the ultrafiltrate. Iron and turbidity were almost completely removed.

Nanofiltration

Saline Water Conversion Corporation (SWCC), R&D Center located in Al-Jubail, Kingdom of Saudi Arabia, introduced NF for the first time as a pre-treatment to SWRO and multi-stage flash in 1997. In this new approach to membrane and thermal seawater desalination processes, the nanofiltration (NF) membrane unit was placed ahead of the SWRO and the multi-stage flash pilot plant units to form integrated desalination systems of an NF-SWRO, NF-MSF and NF-SWROreject-MSF. Preliminary results enabled both the SWRO and multi-stage flash pilot plants to operate at high water recovery: 70% and 80%, respectively (7). The integration of NF with conventional desalination processes lead to a significant improvement in the seawater desalination processes, for example by doubling the seawater reverse osmosis (SWRO) product water output and recovery ratio and the production of high purity permeate (TDS <200 ppm) from one single stage SWRO. NF used as a pre-treatment to SWRO removed turbidity, micro-organisms, provided a significant rejection of scale forming hardness ions and reduced TDS, producing a partially desalinated seawater superior to seawater in quality, (20, 102).

Van Der Bruggen and Vandecasteele, (52) studied the removal of pollutants from surface water and ground water. Results indicate the possibility of the removal of NOM, micropollutants, micro-organisms, metals and for partial desalination using NF. Table 1 (52, 103) Provides typical pollutants removed using NF from ground and surface water sources.

The physical and chemical characteristics of NOM and the membrane surface markedly influence the interaction of NOM with polymeric NF membranes (20, 104) Divalent ions are rejected better than monovalent ions (20, 54) Mohsen et al. (105) studied the efficiency of NF and RO in brackish water desalination proving the high efficiency of reducing the organic and inorganic contents present in the raw waters. The removal of dissolved organic matter (as total organic carbon) was found to be about

Table 1. Average (min.-max.) values of measurements and analyses during pilot plant operation with nanofiltration (52,103). A: The trial period August 17–December 18, 1995 using DOW NF45 NF membrane and B: The trial period January 4–30, 1996 using DESAL DL5 NF membrane

Analysis and measurements	Raw water		NF permeate		NF concentrate	
	A	B	A	B	A	B
Turbiclity, FNU	4.2	3.2	0.02	0.09	9.7	5.7
Color, mg Pt/L	51	50	<1	<1	294	230
DOC, mg/L	8.5	9.1	<1	<1	62	49
COD-Mn, mg/L	10.2	—	<1	—	64	—
Soluble COD-Mn, mg/L	10.2	—	<1	—	—	—
Conductivity, mS/m	14.4	15.8	9.6	9.3	43	46
Alkalinity, mg/L HCO_3^-	35	39	31	—	59	—
Iron, mg/L	0.40	0.38	<0.05	<0.05	0.86	0.91
Manganese, mg/L	0.06	0.04	<0.01	<0.01	0.13	0.08
Calcium, mg/1	14	16.3	8	7.5	51	57
Magnesium, mg/L	3.3	3.7	1.7	1.7	14	13
Chloride, mg/L	11	12.3	12	11	11	—
Fluoride, mg/L	0.14	0.15	0.11	<0.10	0.3	—
Sulphate, mg/L	15	16	<1	<2	98	—
Nitrate-N, mg/L	0.37	0.60	0.36	<0.6	0.44	—
Ammonia-N, mg/L	0.04	<0.02	0.04	<0.02	0.06	—
Phosphate-P, mg/L	0.02	0.02	0.03	<0.02	0.06	—
Heterotrophs, 2d/ml	208	79	2	5	1700	—
Heterotrophs, 7d/ml	583	625	91	61	3100	—
E.Coli/100 ml	<2–5	4	<2	<2	2	—
Coliforms/100 ml	8	9	<2	<2	33	—
Smell	Lake	Weak	None	None	Lake	Lake
Chlorophyll a, μg/L	2	<0.80	—	—	—	—

80% for both NF and RO membranes (106). Linde and Jonsson (54) studied the retention of salts salt solutions and landfill leachate using NF membranes. The retention of NaCl was found to be strongly related to the concentration. The retention decreased when the concentration was increased. The retention of cadmium, zinc, lead, and chromium was found to be higher than 70%, while the retention of potassium and sodium was less than 10%. The NF membranes are less prone to fouling than are polyamide RO membranes, and this probably caused by a combination of membrane chemistries and the lower salt rejection of NF membranes. The low fouling tendency and high rejection of divalent ions make NF suitable for removal of sulfate and hardness from seawater. At least one seawater RO plant uses NF as pre-treatment for RO, and the low fouling tendency of the NF membrane is the key to the success in that case (107).

Liikanena et al. (108) studied the performance of different NF membranes in treating raw water collected from a small humus-rich lake. Results showed that judged by the criterion of bacterial growth, none of the tested NF membranes produced a biologically stable permeate and a minor post-chlorination was required to suppress microbial growth in distribution system. Different NF membranes showed remarkably different removals of organic and inorganic matter. With tight membranes higher than 95% removal of TOC content might be achieved. In an investigation comparing the performance of rapid sand filtration inter-chlorination system was compared with nanofiltration (NF) to reduce Arsenic: It was found that rapid sand filtration with inter-chlorination is not effective in removing arsenic, while NF membrane technology can remove over 95% of pentavalent arsenic As (V) and more than 75% of trivalent arsenic As (III), which is the toxic form of arsenic (109).

Van Der Bruggen et al. (110) compared capillary NF membrane with commercial flat sheet NF membranes for surface water treatment from the river Dijle (Flanders, Belgium). The rejection of organic matter, measured as chemical oxygen demand COD, was satisfactory for all membranes used. The rejection of ions, measured as conductivity, was lower for the capillary membrane than for most flat sheet membranes. In Khalilk and Praptowidodo (111) study, NF was used for the treatment of deep well water because of the effect of excess chlorine used for microbiological disinfection reacting with organic matter (THMFP) to produce trihalomethane (THM). The treatment proved to be less costly and with a better quality compared to the previous conventional treatment.

According to Agenson et al. (112) the retention of organic carbon by NF membranes was dependent on solute size and branching of functional groups. The molecular weight of the solutes was useful, but the molecular width was shown to be the more appropriate parameter for describing the sieving retention by the membranes. Anne et al. (113) studied the capabilities of six nanofiltration membranes to selectively demineralise salt water containing the same cations as seawater (monovalent: Na^+, K^+; divalent: Ca^{2+}, Mg^{2+}).

Al-Sofi et al. (114) studied different NF membranes as a pre-treatment to seawater desalination. Good results were achieved and the authors recommended the use of UF prior to NF for further improvement in production and cost reduction of the plant. A cost comparison of chemical addition and energy consumption revealed that the additional energy required to operate an NF process is cheaper than the chemicals required to achieve a comparable organics removal with MF However, it is appreciated that for an application only requiring removal of turbidity (including microorganisms) MF or loose UF have a clear cost advantage (115).

Fouling and Retention During Membrane Filtration

There are many factors affecting membrane filtration performance. These include alkalinity (pH), operating pressure, feed flow, temperature and concentration. The method of filtration, ionic strength of the solution, initial concentration of the sample and the type of membrane used will also affect the quality of the separation of contaminants (116). Membrane fouling is attributed largely to the chemical composition of feed and membrane process chemistry (15, 20). The loss of membrane flux due to fouling is a major impediment to the development of membrane processes for use in drinking water treatment (117). The general mechanistic view of NOM interactions with membranes which plays a major role in the filtration process are (60):

1. The NOM mixture has an intrinsic chemical nature (aromaticity, polarity, ionizable groups, etc.) and molecular size. The actual charge, configuration, and chemical potential of the NOM in solution depend on the current solution environment (pH, ionic strength, ion compositions, temperature, pressure, etc.), which varies throughout the filtration process.
2. The combination of (i) the operating conditions of the filtration process (transmembrane pressure and hydrodynamic mass transfer at the membrane/feed interface); (ii) the membrane geometry (porosity and pore size distribution) and (iii) the membrane's rejection characteristics toward the NOM controls the NOM's concentration at the membrane surface and in the pores.
3. The chemical nature of the NOM; its concentration at the membrane fluid-solid interfaces and the chemical and geometrical nature of the membrane (under the given solution conditions) control the amount (and degree) of gel or precipitate formation and reversible and irreversible adsorption that occurs.
4. The NOM's interfacial concentration; the interfacial solution's viscosity and the mass and porosity of the adsorbed layer influence the hydrodynamic aspects of flux decline and the change in the filtration process's apparent rejection of the NOM through both porous media and physical property aspects.

Alkalinity plays a major role in a membrane process. Hong and Elimelech (20) observed that NOM was removed better at pH 8 than pH 4 for NF membranes and Yiantsios and Karabelas (118) showed an increase in humic acid rejection when the pH was in the range of 6–8. The flux of five different cellulose acetate (CA) membranes was found to be lower at pH 7 than at pH 5.3 (18). The more extensive flux decline at pH 9 could be ascribed to increases in molecular sizes and to charge repulsion forces. At pH 7 NOM molecules contained approximately equal amounts of COO^- and COOH groups resulting in a very stable conformation of NOM which lowered the interactive forces between the membrane surface and foulant molecules (119). Pure water flux decreases with increase in pH (increase in alkalinity) indicating the charge of the membrane pores have a significant effect on membrane flux and rejection. As the pH increases, the membrane pores become more negatively charged due to preferential anion adsorption. This reduces the pore size of the membrane, which causes a flux decrease and a rejection increase. The pH effect for raw water (high turbidity) is different from pure water. When turbid water is used the flux at pH 4.13 is lower than the flux at 8.33 and higher than 7, indicating the effect of pH on membrane and type of water. At pH 4.13 the polysulfone membrane becomes less negatively charged and more carboxylic groups of NOM become protonated. This decreases the hydrodynamic radii of humic substances while increasing their hydrophobicity and their tendency to adsorb. Therefore, a dense fouling layer develops and flux is lower at pH 4.13 than at pH 8.33 (120).

Costa and De Pinho (18) addressed the evaluation of the influence of the membrane pore size on the permeation characteristics of humic acid solutions. Five cellulose acetate UF laboratory made membranes were prepared covering a wide range of MWCO (5, 7, 25, 60, and 150 kDa). The membrane performance was investigated at TMP from 1 to 4 bar and at the values of pH of 5.3 and 7.0. For the tighter membranes MWCO of 5, 7 and 25 kDa, respectively, there was a linear variation of the fluxes in the range of pressures up to 4 bar and for both values of pH. A non-linear behavior of fluxes vs. pressure is displayed at pH 7 by the membrane with a MWCO of 60 kDa. The same non-linear behavior was displayed at pH 5.3 and 7 for the membrane with the highest MWCO. Concentration polarization is more pronounced in membranes with higher pore diameters. Likewise, the influence of pH is more pronounced for the more permeable membrane. The rejection mechanism is also not only dependent on the steric hindrance.

Humic substances readily adsorb to the membrane surface (NF & RO) and markedly influence the membrane surface charge and the negatively-charged functional groups of the HS dominate the membrane surface charge. As the pH increases, the effect of HA an the membrane surface charge diminishes, and eventually, in the high pH range, the effect is very small. This pH-dependent behavior can be explained by changes in humic-membrane interactions. Below the isoelectric point of the membranes, where the membranes and HA are oppositely charged, adsorption of HA is favorable because of both electrostatic and hydrophobic interactions. Just above the isoelectric point, where the HA and the membrane are similarly charged, adsorption is likely to be dominated by hydrophobic interactions. At higher pH values, only minimal adsorption occurs because of the electrostatic repulsion between the HA and the membrane surface and the increased hydrophilicity of the HA. Humic acid cause the membrane to be more negatively charged. The magnitude of this effect differs with different sources of HA. The difference in the effect of these HA on the membrane surface charge is attributed to the difference in their adsorption behavior Humic acid with the largest molecular weight adsorbs to the greatest extent, whereas HA with the smallest molecular weight adsorbs to the least extent (121).

Schafer et al. (11) studied the effect of natural organic matter (NOM) and humic substances on the deposition and rejection of inorganic colloids (hematite) by hydrophilic and hydrophobic membranes. Parameters of interest were solution pH, ionic strength, calcium concentration, primary colloid size (75, 250 and 500 nm), organic-type, and concentration. Membrane type and hydrophobicity, aggregate structure and colloid stability were also studied. The systems studied were grouped into

a. Organics in the absence of inorganic colloids
b. Stable primary particles
c. Primary particles at pH extremes with organics
d. Particles pre-aggregated in electrolyte solution prior to adsorption of organics (SPO), and
e. Particles stabilised with organics (OPS) (Fig. 5).

The results showed that the particles of size closest to the membrane pore size (250 nm) caused largest flux decline. At pH conditions closer to surface waters and in the presence of an electrolyte solution, the colloid aggregates are fully rejected and flux decline depends on the deposition on the membrane rather than primary colloid size. This corresponds more or less to a surface water of high turbidity, but no organic content. Once the organics were added there are two cases to be distinguished. In the first case the colloids are first aggregated in the electrolyte solution before mixing with the organics (SPO order). The organics adsorb on the aggregate surface and fouling increases compared to aggregates in the absence of organics. In the second case colloids are first mixed with the organics and then with electrolyte solution (OPS order). Charge steric or charge stabilization of the colloids occurs due to adsorption of organics on the colloid surface. Rejection drops to almost zero and fouling depends fully on primary colloid size. Rejection could be increased in this case by destabilization of the colloids using calcium. Comparing OPS and SPO showed important differences between the two systems. The organic-type has no effect for SPO, whereas for OPS

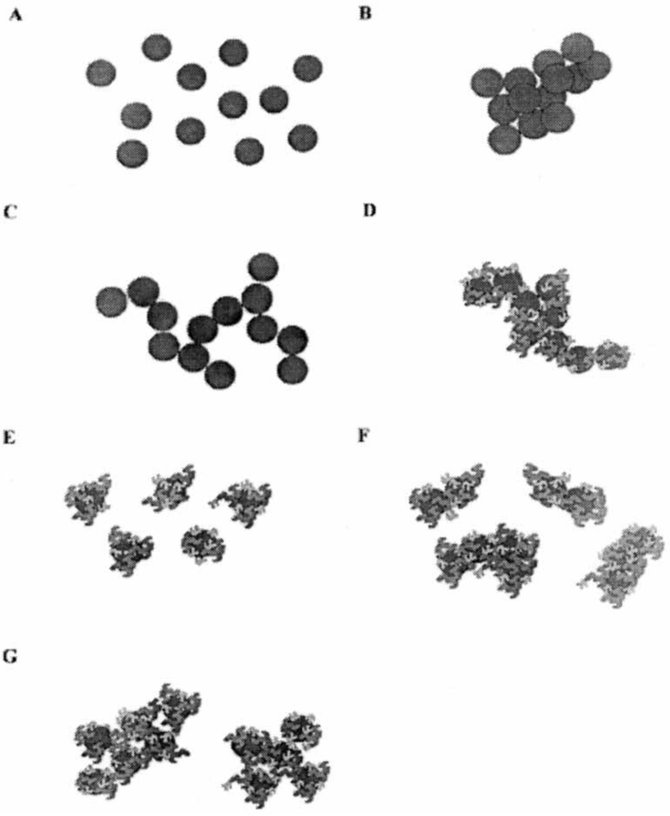

Figure 5. Postulated aggregate structures (A) stable hematite colloids in absence of organics, (B) aggregates formed by reaction limited aggregation (RLA), (C) aggregates formed by diffusion limited aggregation, (D) SPO: aggregates with organics, (E) OPS: colloids stabilised with organics, (F) OPS: colloids stabilized with NOM, (G) OPS: colloids stabilised with organics and destabilised with calcium (11).

flux decline is low for FA and HA and very high for NOM. Calcium has opposite effects on both systems. For OPS calcium increases flux decline due to destabilization effects, whereas for SPO the flux decline is lower at higher calcium concentrations. This is presumably due to a different structure of the initial aggregates. There are also differences due to pH. While for SPO pH would affect aggregate structure, in the OPS case it affects colloid stability and thus the highest flux decline occurs when colloids partly aggregate. Most severe fouling was observed when the smallest (75 nm) colloids were mixed with NOM, which contains salt and organics. In this case aggregation and stabilization effects occur at the same time producing very small aggregates, which are detrimental to flux. This is the condition closest to 'real' surface water, where detrimental flux decline is often observed. Overall the largest difference with the strongest implications on water treatment is the low rejection of the stabilised colloids. Due to their low settlability these systems will be most abundant in most streams and chemically pre-treated feed water. The characterization of the colloid—organic associates in natural water is clearly critical in predicting likely MF behavior.

Increasing the feed flow increases both permeate flow and recovery up until an optimum feed flow is reached, then the recovery starts to decline (102). According to Teng et al. (15) low flux-high recovery operation is more suitable than high flux-low recovery approach for direct application on seawater UF. High flux-high recovery operation is not suitable, due to the increment of TMP trend. Intending to increase the production capacity with higher flux has to be weighed carefully against the increase in chemical cost of backwashing. Brehant et al. (68) showed combined MF/UF cannot operate at high flux rates when treating highly fouling surface water because of severe membrane fouling and plugging of fibres. In general the NF membranes with high permeate flow rate and high recovery tend to have low rejection of Ca^{2+}, Mg^{2+} and TDS, while the reverse is true for membranes with low flux. This might be explained in terms of membrane physical structure. Membranes with tight structure, thus small size pores have high salt rejection but low permeate flow, resembling RO membranes in behavior, while membranes with less of a tight structure and larger size pores resembling UF membranes in behaviour. A mixture of both membranes may improve the unit flow and recovery as well as ions rejection.

The ratio of the initial sample volume to the final retentate volume is called the concentration factor (CF) (122). For feed waters containing only salt (NaCl), permeate flux declined linearly as CF was increased, but salt rejection was nearly constant for both RO and NF membranes. On the other hand, a sharp decrease in permeate flux and significant decline in salt rejection with increasing CF were observed under conditions where colloidal fouling took place (123). Guo et al. (122) studied the effect of concentration factor an the permeation of colloids (size fraction of 1–200 nm) through UF membrane having a MWCO of 1kDa. Results show that significant amounts of low molecular weight molecules are retained during ultrafiltration, resulting in an increasing permeate concentration with increasing CF. Membranes may be fouled by relatively hydrophilic and/or hydrophobic NOM components, depending on NOM characteristics, membrane properties and operating conditions (124). The major contribution to fouling was attributed by the NOM fraction comprising small, neutral, hydrophilic compounds. The NOM fractions comprising humic and fulvic acids made only a minor contribution to fouling (125). Jucker and Clark (104) and Nilson and DiGiano (126) studies concluded that the hydrophobic fraction of NOM was mostly responsible for permeate flux decline, whereas the hydrophilic fraction caused much less fouling. They also concluded that only the large molecular weight fraction of NOM contributed to the formation of a fouling layer. Foulants larger than the pore size will only cause surface fouling and for this reason the surface fouling becomes more important as the pore size is reduced. Observations showed the presence of magnesium, aluminium, silica, potassium, calcium and iron on UF membrane surface (68).

Yiantsios and Karabelas (127) studied the effect of colloid stability on membrane fouling. Fouling was caused by colloidal material when the raw water was filtered untreated and by NOM when the raw water was coagulated before filtration. The rate of fouling is relatively low for strong and weak hydrophobic fractions of NOM and for the charged hydrophilic fraction. However in the case of the neutral hydrophilic fraction, the rate of fouling was considerably faster. Colloidal material may cause fouling by forming a cake on the membrane surface, while dissolved material may cause fouling by precipitating at the membrane surface or adsorbing within the membrane pore space (125). Cho et al. (69) compared contact angles, zeta potentials, and IR spectra of clean and NOM-fouled membranes to demonstrate differences in hydrophobicity, surface charge, and functional groups, respectively. Contact angle increased and decreased for membranes fouled with hydrophobic and hydrophilic NOM, respectively. The zeta potential decreased negatively (less negative) for membranes fouled with both hydrophobic and hydrophilic NOM.

In Jarusutthirak et al. (128) study, colloidal fractions showed high flux decline and fouling on NF and UF membranes was primarily due to the effects of pore blockage. The hydrophobic and transphilic fractions exhibited less fouling and flux decline than the colloids due to their molecular size as well as electrostatic repulsion between organic acids and the membrane surface. However, hydrophobic interactions play a significant role with hydrophobic membranes, causing a reduction of permeate flux.

In a study by Schafer et al. (76) based on experiments with MF membranes, six UF membranes and four organic NF membranes. Results showed that in MF, pore plugging and cake formation was found responsible for fouling. This reduced the pore size and increased rejection. In UF, internal pore adsorption of calcium-organic flocs reduces the internal pore diameter and subsequently increases rejection. In NF, the key factor appears to be the charge of the deposit. In essence, the rejection characteristics of membranes depend more on the fouling state of the membranes and the nature of the foulants than on the initial membrane characteristics. For feed water containing colloidal particles, the salt rejection of both the RO and NF membranes decreased continuously as fouling progressed. The deterioration in salt rejection is attributed to the substantial increase in salt concentration at the membrane surface due to enhanced concentration polarization within the colloidal cake layer as well as the vast permeate flux decline resulting from the enhanced salt build-up near the membrane surface. The NF membrane suffered a much greater decline in salt rejection than RO, most likely due to a substantial decrease in charge (Donnan) exclusion as salt concentration at the membrane surface increases (123). The increasing ionic strength (neutral salts-KCl) deteriorates membrane fouling (129). This is attributable to the fact that the pore size of the membrane was reduced due to the decreased double layer of the membrane surface by the increased ionic strength (63).

Khulbe et al. (130) stated that the fouling of UF membrane was dependent on the size and shape of the macromolecular solute and the operating feed pressure. Apart from particle size and concentration, colloid stability plays a significant role in membrane fouling. As colloid stability is decreased, fouling becomes more severe and thicker deposits form. Bian et al. (131) used Chitose River water with relatively high concentration of HS and small colloids to determine the effect of shear rate on controlling the fouling of MF and NF membranes. Concentration polarization of humic substances in NF and MF membranes can be reduced by increasing the shear rate. This has been proved by the increase in mass transfer coefficient and the decrease in the concentration on the membrane surface with increasing shear rate.

Backwashing and Chemical Cleaning

During prolong membrane performance, the product flow constantly decreases as different foulants adhere to the membrane's surface, which increases hydraulic resistance of the membrane module and diminishes the active surface of the membrane. To restore the initial flux, chemical regeneration procedures could be performed to remove accumulated foulants (50). Hillis et al. (132) explored a variety of parameters associated with the backwash operation, such as backwash pressure, interval, duration, volume, chemical assistance, fiber integrity and the use of water pulsing. The efficiency of the applied backwash procedure depends on backwash duration τ, rate (also depends on backwash pressure) and filtration duration t. Backwashing cycle varies depending on the quality of the feed stream. e.g. 20–60 min (50) and 30–90 min (15). To backwash the membrane, clean water is pumped into the product line. During the backwash cycle clean water destroys the foulants layer and sweeps accumulated foulants out of the membrane surface (50). Kampa et al., (133) concluded that colloidal fouling can be controlled by standard backwashing procedures. The reversibility of fouling (effectiveness of cleanings) plays a major part in the success of the pretreatment process (134). The purpose of water flushing is to wash away all loosely attached deposit from the membrane. The remaining deposit, thus, corresponds by definition to the so called irreversible fouling (129).

The addition of chemicals during the backwash cycle can enhance performance. The nature of the fouling material will determine the choice of chemical and a good knowledge of the raw water characteristics will enable this judgement to be made (132). Free chlorine had been used as a backwashing agent by Brehant et al. (68) and the process may involve air scouring to loosen solids followed by an air/liquid backwash to remove solids from the membrane fibre bundle (10). In periods of algae bloom enhanced backwash with hydrogen peroxide was insufficient and had to be replaced by sodium hypochlorite backwash (133). To prevent biofouling of ultrafiltration modules, biocide and disinfectant chemicals are added to clean water during the backwash. Several cleaning agents are used, some researchers recommended the use of a single agent, Sodium hypochlorite (NaOCl) and hydrogen peroxide (H_2O_2) (14, 50), others recommended a mixture of agents, citric acid, and sodium hypochlorite (13, 15). H_2O_2 is definitively less effective than NaOCl for oxidizing organic matter that adheres to the surface of the membrane during filtration and the reagents used during backwashing, alongside the seawater pre-treatment have an effect on the rate of permeability and on filtrate quality (14). Acid cleaning; sulphuric acid (pH of 1–1.5) was conducted to remove the inorganic foulants on the surface of the membrane followed by alkaline cleaning; sodium hydroxide (pH of 11.5–12 at 40°C) to dissolve the organic foulants (135).

Visual inspection done by Yiantsios and Karabelas (118) showed that backwashing was progressively less effective and increasing amounts of deposits remained attached on the less hydrophilic UF membrane. Lipp and Baladauf (136) studied air-water-mixtures backwash of MF and UF systems. The investigation showed that regular backwash with filtrate supported by air flush on the feed side was a very effective method to keep TMP low and minimize its increase. The investigations also showed that there still is the need for chemical cleaning, because some irreversible fouling always remains. The frequency of chemical cleaning however is very much dependent on the raw water quality. According to Nakatsuka et al. (137), backwashing pressure should be more than twice as high as filtration pressure in order to maintain a high and stable flux for river water treatment.

Pre-Treatment Prior to Membrane Filtration

Operating on seawater directly, instead of sand-filtered filtrate put more strain on membrane systems. Indication of strain established by Teng et al. (15) include a 10% drop in filtrate flux and a slowly increasing TMP trend. Brehant et al. (68) pumped the seawater through a 1 mm screening, then a prefilter (200 μm) in order to eliminate the particles that could block the UF fibres. Redondo (10) used an improved multimedia filter upstream of the UF pre-treatment, which was efficient in reducing the total suspended solids and turbidity by 90%.

Hassan et al. (102) pre-treated the seawater feed prior to NF using dual media filter followed by fine sand filter and 10 μm cartridge filter. This was then replaced with a new media having the media thickness and particle size shown in Table 2. The new media was found to improve the efficiency

Table 2. Thickness and particle size of filter media (102)

Filter	Media	Thickness (mm)	Particle size (mm)
1-Dual media	Anthracite	400	0.8
	Fine sand	400	0.55
2- Fine sand	Fine sand	800	0.25–0.425

of the filtration system. One of the reasons might be due to the fact that more suspended solids were rejected using the new media.

Van Hoof et al. (131) used sand filtration due to the relatively high suspended solids content (20–60 mg/L). This pre-treatment produced feed water containing 0.6–7.9 mg/L of suspended solids. It also increased the flux and reduced the operating cost of the whole plant. Isaias (66) used a dual media anthracite/sand filter, stating that the ratio between the maximum and minimum particle sizes in a filter medium is conventionally 2 : 1. Commercial granular materials normally conform to this requirement. The uniformity coefficient defined as the ratio between the 60 percentile and 10 percentile sizes for the sand should be less than 1.3, and for anthracite, which is more friable, to be less than 1.5. Wider size ranges can cause marked stratification with fine media migrating to the top during backwash. This will shorten filter runs because most of the filtration is taking place in a finer grade than intended, thus causing the surface of each layer to be clogged with impurities.

INTEGRATION OF COAGULATION AND ADSORPTION WITH MEMBRANE FILTRATION

This section provides an overview of coagulation and adsorption use to enhance membrane filtration. It provides a description of coagulation and adsorption before listing different outcomes of combining coagulation and adsorption prior to membrane pre-treatment.

Coagulation

In general, very small particles are difficult to remove from water using conventional separation methods such as sedimentation and filtration. Those separation techniques work very effectively for larger particles and it is the goal of coagulation and flocculation to coalesce the smaller particles into larger and more easily removed particles (flocs). Removal of dissolved organic matter (DOM) by chemical coagulation requires physical/chemical incorporation into flocs which are subsequently removed by a solid-liquid separation process (138). Coagulation pre-treatment is known to reduce the rate of fouling of membranes, possibly by aggregating particles to increase cake permeability or prevent pore blockage. Conditioning of the cake is achieved by incorporation of particles into highly porous flocs or precipitation or adsorption of dissolved material into flocs (125). Choksuchart et al. (67) results reckon the necessity of coagulation as a pre-treatment to remove microparticles in aqueous suspension before conventional sedimentation or membrane filtration of surface water. Coagulation enhances the flocs settling velocity. Figures 6 and 7 show the particles size before and after coagulation using ferric chloride $FeCl_3$.

Coagulation/flocculation processes were mainly used for the removal of colloidal material, which caused color and turbidity in wastewater treatment (139). Humic substances interact strongly with cationic additives, especially hydrolyzing metal coagulants and cationic polyelectrolytes (24). Kuo and Amy (138) study highlighted the importance of initial water quality and treatment conditions (Initial pH, initial turbidity, coagulant dose, pre-ozonation dose, and flocculation time) affecting the removal of dissolved organic matter (DOM) during alum coagulation. It provided a detailed study of how important characteristics of the DOM affect its removal; namely, molecular weight distribution, humic substances content, and the carboxylic acidity of the humic substances fraction. The methodology for coagulant addition is determined by the rate at which the reaction occurs between the coagulant and the soluble constituent. Kinetics of coagulant reactions is very fast and is normally complete within the first few seconds after coagulant addition (140).

The effect of different coagulants (aluminium sulphate, polyaluminium chloride, ferric chloride, and ferric sulphate) on cake formation and hydraulic resistance in membrane filtration of upland surface water had been investigated by Pikkarainen et al. (141). The optimization of a pre-coagulation-membrane filtration process revealed that ferric chloride was slightly

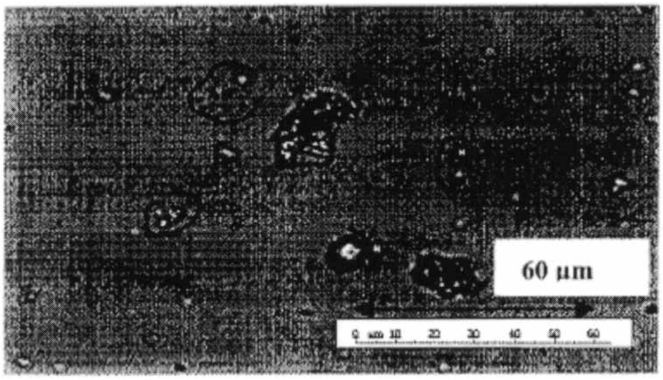

Figure 6. Microscope analysis of 0.1–0.5 g/L clay particles without $FeCl_3$ (67).

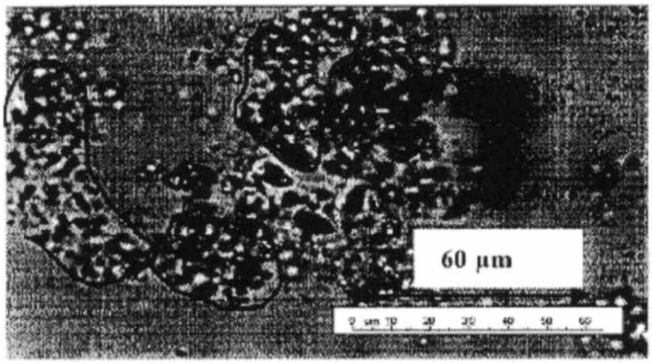

Figure 7. Microscope analysis of 0.1–0.5 g/L clay particles with 0.01 g/L $FeCl_3$ (67).

superior to ferric sulphate (142). Coagulation improves the permeate flux in a very significant way. The coupling makes it possible to modify the structure of the deposit on the surface of the membrane by the formation of larger particles of flocs. It also permits the reduction of the cost of membrane regeneration (143).

Due to the sensitivity of coagulation processes, different optimal doses were obtained for different water and NOM qualities. Variations in the daily and seasonal raw water quality and chemistry issues such as pH, alkalinity, total organic carbon (TOC), and temperature determine the optimum coagulant dose (140). Coagulation has an optimum dosage since a higher dose may result in an increase of the residual turbidity of the settled water and at low dosages a substantial reduction of residual turbidity maybe observed (144). The data shown in Fig. 8 indicate that there exists a threshold coagulant concentration value below which there is deleterious effect on plant operation. This implies that floc growth needs to proceed to a certain critical floc size prior to challenging membrane filtration, which otherwise is apparently partially irreversibly clogged by the flocculants solids (145).

Alum coagulation has an optimum alum dosage at 70 mg/L for surface water treatment (144). For Colorado River water treatment, alum was dosed at 6–8 mg/L with 1.0–1.5 mg/L polydimethyldiallylammonium chloride (PDADMAC) cationic polymer and ferric chloride was dosed at 4–5 mg/L with 1.5–2.0 mg/L of the cationic polymer (146). The amount of ferric chloride used at a desalination plant was 0.8 to 1.0 mg/L as Fe (66). An optimum coagulant dose of 0.055 mM (3.1 mg/L) Fe^{3+} was identified on the basis of operational cost based on coagulant cost and cake resistance, all other aspects of the system being substantially unchanged for an upland-reservoir water treatment plant (145). The chemical type and the dose of coagulants were the most influential parameters for the optimized treatment results followed by the pH and the test solution (139). The effect of

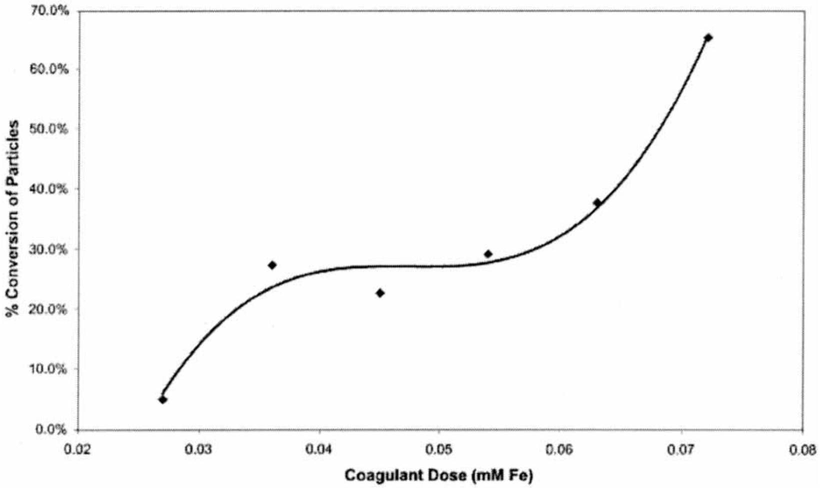

Figure 8. "Percentage conversion of particles" for increasing coagulant dose after 20 s of floc growth (145).

coagulant dose between 18 and 71 μM Fe^{3+} is much more significant than a change in pH between 5 and 9 for the alum coagulation system: a 53-fold increase in specific flux compared with a 7-fold increase (145).

Different coagulants have different optimum pH value. A pH of 5.5 is the optimum value to coagulate humic substances molecules present in river water in Hokkaido Island located in northern Japan (142). The optimum pH for an alum-based system appears to be between 7.5 and 8 on the basis of cake resistance (145).

Humic substances with higher apparent molecular weight and lower carboxylic acidities are preferentially removed by alum coagulation (138). The enhancement of the coagulation was more obvious when the organic content in water was relatively high (144) and the multi-valency of the coagulant i.e. Ca and Al ions could conceivably lead to large molecular aggregate (119). Experimental results indicate that the removal of organics by coagulation is directly related to the molecular weight. The interaction of alum with humic acid involves complexation, charge neutralization, precipitation, and adsorption. As the dosage is increased, the major mechanism of humic acid removal by alum coagulation can be expected to shift from complexation-charge neutralization-precipitation to adsorption, Fig. 9 (147). Molecular weights less than 500 Da are difficult to coagulate and cannot be rejected by an ultrafiltration membrane, while most natural organic matters having larger molecular weight are caught by a floc (142).

Results obtained by Maartens et al. (119) indicated that a reduction in NOM concentration, by coagulation with metal-ions before filtration, could not reduce or prevent membrane fouling. In fact, irreversible membrane

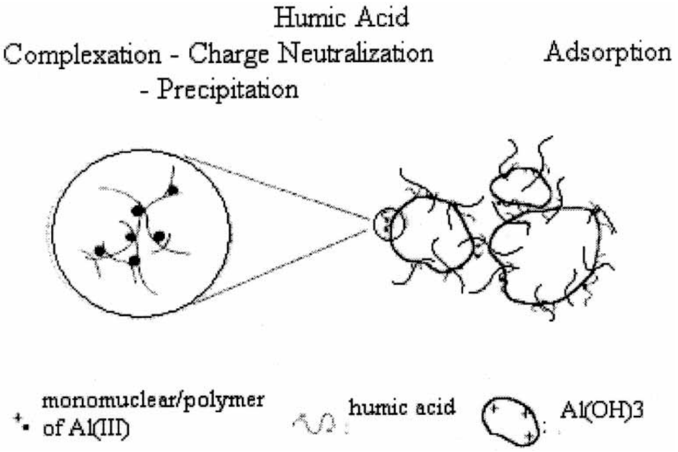

Figure 9. Schematic diagram of mechanisms of alum coagulation (147).

fouling was much worse, indicating that more substances were adsorbed onto the membranes from the pre-treated water, probably because metal-ions that remained in solution formed complexes with the NOM in the feed solution. A conventional membrane separation system was decided to be unsuitable to treat the river water coagulated by poly aluminium chloride (PACl) because of the risk of plugging in the flow path and fouling on the surface of the membrane (142). In contrary; Low et al. (148) indicated that it is possible to protect polypropylene membranes from fouling occurring inside the membrane pores as well as the formation of the cake layer using two step coagulation using $FeCl_3$ with anionic polyelectrolyte in the first step and aluminium coagulant in the second one.

The ability of a polymer to act as a flocculant can depend upon its ability to bond to the surface of the colloidal particles. As a result, in many cases these materials are quite specific (149). These polymers may produce lower rejection, 96% compared with 99% using alum, but they produce a less compacted sludge (139). Comparing the removal efficiency of alum ($Al_2(SO_4)_3$; MW of 342.15) and ferric chloride ($FeCl_2 \cdot 6H_2O$; MW of 270.3) with low molecular weight anionic polyacrylamide flocculant, very high molecular weight anionic polyacrylamide flocculant and high molecular weight cationic polyacrylamide flocculant. It appears that cationic and low molecular weight anionic polymers were not effective. The reason might be related to the supernatant's zeta potential, which was most probably negative or zero when the anionic polymer was used. In addition, increasing the molecular weight of the polymer improved flocculation due to promoting bridge formation. At low polymer concentrations, the number of polymer molecules adsorbed per particle is small. Since the polymer and the supernatant are oppositely charged, the polymer adsorbs with a flat configuration, thus limiting the possibility of bridging. As the polymer concentration increases, the number of polymer molecules adsorbed onto single particles also increase (149).

Jar tests done by Bolto et al. (150) on reconstituted water with alum and/or cationic polyelectrolyte showed synergistic benefits from combinations of the two. The more hydrophobic NOM fractions were the most easily removed by the polymer. The performance of cationic polymers improved significantly with increasing charge density and molecular weight. Kam and Gregory (24) study disagreed in that there was no systematic effect of molecular weight in removing dissolved organic matter, but agreed in that the most highly charged polyelectrolyte showed good removal of humic acid (up to around 90%) over a fairly narrow range of dosages. As the charge density of the polyelectrolyte decreases, the zone of good removal becomes broader and the removal becomes progressively worse (to about 75%). For cationic polymers with a charge density of around 3 meq/g or greater, there seems to be a simple one-to-one charge interaction, so that charge neutralization occurs with a certain amount of added polymer charge, irrespective of charge density or molecular weight. Studying the interaction of humic substances with cationic polyelectrolytes, a fairly steep increase in charge density of the humic acid as the pH is increased from 3 to about 5, followed by a more gradual increase at higher pH values. No definite plateau is reached at high pH, which is a typical behaviour for polyelectrolytes. In practice, it is well known that the filtration of mineral particles at the isoelectric point may give flow rates that are 10 times faster than the filtration at pH values where the particles resist aggregation (151).

Adsorption

Natural organic matter adsorption is influenced by the solution chemistry of natural water, in particular divalent cations, pH, molecular weight and hydrophobicity (152–154). Bjelopavlic et al. (26) studied the adsorption of natural organic matter (NOM) onto activated carbons. While Mavrov et al. (155) studied the adsorption of heavy metals with synthetic zeolite P. The synthetic zeolite P (also referred to as "MAP"–maximum aluminium P) displayed very fast bonding kinetics for copper and zinc with metal reduction of more than 97%, while the results obtained for nickel showed only a reduction of 84%. Ha et al. (156) studied the effect of pre-chlorination on the adsorption/UF treatment for the removal of NOM from drinking water. Pre-chlorination reduce the colloidal particles size. The reduction in size results in large UF flux decline largely due to the formation of a denser cake layer on top of the membrane. Kanungo et al. (157) studied the adsorption of heavy metals including Co, Ni, Cu and Zn on hydrous manganese dioxide. At pH ~ 7.25 Co and Zn showed higher adsorption than Ni. Ni showed higher competition for high-energy sites than Cu and Co and Zn showed an intermediate competition. Illés and Tombacz (158) investigated the adsorption of HA on magnetite (Fe_3O_4). The adsorption studies revealed that HA had high affinity to magnetite surface especially at lower pH, where interacting partners had opposite charges.

Bjelopavlic et al. (26) studied the adsorption of natural organic matter (NOM) onto seven activated carbons with a wide range of surface properties (surface area of $714-2183\,m^2/g$ and pore volume for primary micropores $w < 0.8\,nm$ of $0.23-0.57\,cm^3/g$, secondary micropores $0.8 < w < 2\,nm$ of $0.12-0.54\,cm^3/g$ and mesopores $2 < w < 50\,nm$ of $0.03-0.51\,cm^3/g$) at high and low ionic strength over a range of pH values. From adsorption isotherm studies it was found that, for six of seven carbons, at low surface concentrations, increased ionic strength decreased NOM adsorption. As the surface concentration increased, the adsorption isotherms converged and intersected, after, which the addition of salt resulted in increased adsorption. This "crossover point" marked a change in the adsorption mechanism from the "screening reduced" to the "screening enhanced" adsorption regimes. The adsorption mechanisms are extremely complicated and appear attributable to various factors, including electrostatic forces, pore volume distribution, and chemical interactions between the NOM and the surface functionalities on the carbon surfaces. At pH 7, NOM adsorption increased with available pore volume. When the pH is reduced to 4, NOM adsorption increased, due to high electrostatic interactions (repulsive) between the negative charge of the NOM and the negative surface charge of most of the carbons. Analyzing the non-adsorbed fractions of humic substances in Specht et al. (159) study revealed that the pH value only controls the amount of NOM adsorbed but not the quality. Substances with large apparent molecular size show the greatest affinity towards the clay minerals, whereas apparently smaller molecules with aromatic structure and high content in carboxylic functional groups show no adsorption.

According to Duan et al. (160) the HA adsorption for undiluted seawater was equivalent to that for tap water. The study showed that adsorption of HA by powdered activated carbon (PAC) can be significantly greater in diluted (12.5–50% diluted) saline water compared to freshwater and low conductivity water. This indicates that high organic adsorption removal efficiency by PAC might be expected when treating brackish water. The interaction of HA with the metal ions present in seawater causes some degree of aggregation of the HA molecules. The effects of adding a metal salt coagulant, either aluminium sulphate or ferric chloride, on overall HA removal were found to depend strongly on the coagulant dose, solution pH and the sequence of addition of the PAC and metal salt coagulant. Addition of the PAC shortly before the coagulant was found to give the greatest removal of HA. When metal salts are added to the HA and PAC adsorption system, several processes may occur and there may be competition between these processes. HA in solution may first react with the metal ion hydrolysis species to form either soluble complexes, which may be then adsorbed on to the PAC surfaces, or insoluble precipitates that remain suspended in the bulk solution. Alternatively, HA may be directly adsorbed onto the surface of PAC before interacting with the coagulant hydrolysis species. The overall effect will depend on the order of addition of PAC and coagulant, and the relative kinetics of the interactions between the HA, the PAC and the coagulant. Kozar et al. (161) investigated the adsorption of Pb^{2+} and of Cd^{2+} ions from Krka river water of various salinities on calcite ($CaCO_3$). The results suggest that the two ions are adsorbed at different calcite surface sites; Pb^{2+} remained firmly bound to calcite at all salinities, whereas Cd^{2+} was firmly bound at low salinities and released at high salinities. The adsorption of cobalt, chromium, and nickel from aqueous solutions on IRN77 cation-exchange resin has been studied comparatively. The results showed that the IRN77 cation-exchange resin can be used as an adsorbent for the effective removal of Co^{2+}, Cr^{3+} and Ni^{2+} from aqueous solution (41, 162). The percentage of copper ion removal from 10 ppm solution by these aminated and protonated mesoporous aluminas is more than 95% (38).

A full-scale treatment sequence, studied at the Rusko water treatment plant in Tampere, Finland, consisted of coagulation, flocculation, clarification by sedimentation or flotation, activated carbon (AC) filtration, and disinfection. Results showed after dividing the NOM into five fractions that coagulation with aluminium sulphate decreased the NOM content effectively and led to the total disappearance of the first fraction, i.e. of the high molecular weight NOM. After sedimentation, the concentrations of the second and third fractions (intermediate molecular weight) were reduced by 90% and 48% and after flotation by 93% and 55%. Activated carbon was instrumental in reducing the amount of intermediate molecular weight and low molecular weight matter (163).

Integration of Coagulation and Adsorption with Membrane Filtration

Pre-treatment may constitute up to one-fourth of the total costs of a membrane desalting facility (146). The largest desalination plant currently in operation in Morocco (Laayoune Seawater Reverse Osmosis Plant) uses a combination of processes. The pre-treatment consists of chlorination, coagulation, sand filtration, acidification, antiscalant, microfiltration, and dechlorination (164). Different researchers used different combination of water treatment processes depending on the feedwater quality, feedwater composition and product requirements, Table 3.

Recently, a double membrane barrier concept has emerged as a possible alternative. By installing microfiltration (MF)/ultrafiltration (UF) membrane upstream of the RO membrane in an Integrated Membrane System to filter off bigger suspended solids, the feed water quality to RO may improve (15). An integration of UF with NF process studied by Karakulski et al. (166) resulted in increasing the effectiveness of removal of organic

Table 3. Combination of processes for water pre-treatments

Combined pre-treatment	Raw water	Benefits (Outcome)
Coagulation, filtration and acid and antiscalant injections (50)	Caspian seawater	Supply and sustain good product quality
UF with pre-coagulation at low dose (68)	Surface seawater	Controlling UF membrane fouling Providing water at steady state conditions
Minor coagulation $FeCl_3$ prior to NF (102)	Seawater	Improve the efficiency of membrane
Coagulation with UF and MF (10)	Seawater	Removal of the upset of membranes
	Brackish water	Improving the quality of feed water to RO
Adsorption prior to MF (165)	Synthetic de-ionized water	Removal of humic substances
Adsorption and UF (90)	Spring water	Substantially improving UF performance Stabilising membrane flux
Flocculation and UF (149)	Well water	Improving bacteria removal compared with using flocculation alone

compounds. Siddiqui et al. (167) study concluded that NF alone was not appropriate for potable surface water treatment and could incur serious operational problems such as rapid fouling, increased pressure requirements, and reduced recoveries: The incorporation of MF can lengthen the NF membrane life.

The use of membrane separation as opposed to conventional clarification techniques permits a much reduced flocculation time in the order of 15–60 s and thus a more compact plant (145). A MF study of Lake Michigan water for the production of drinking water concluded that direct filtration of an alum pre-treated feed water was found to greatly increase time of operation between cleanings (84) During Kampa et al. (133) study, coagulation, sedimentation, and filtration (CSF) pre-treatment led to unacceptable colloidal fouling, which could not be improved by an additional (in line) filtration step. Additional pre-treatment by ultrafiltration showed a superior particle removal thereby avoiding colloidal fouling. In addition combined use of CSF/UF reduced biological parameters significantly thereby reducing the risks of a severe biofouling. Therefore the treatment scheme CSF-UF-RO was pursued for a practical application.

According to Nederlof et al. (134) when local circumstances are such that a soil passage is feasible for ground water treatment, bank filtration followed by anaerobic NF/RO treatment is to be preferred based on performance and costs. When soil passage is not possible and enough space is available coagulation-sedimentation-rapid filtration combined with slow sand filtration is a robust and well proven treatment, but will be more expensive. When only little space is available a coagulation-sedimentation with UF pre-treatment may be considered. Costs are relatively high compared to the other integrated membrane systems, however in future, the coagulation-sedimentation combined with UF and RO scheme will compete with the coagulation-sedimentation- rapid filtration combined with slow sand filtration scheme.

During conventional coagulation treatment of river water using polyaluminum chloride (PACl), if the raw water arsenic (As) concentration exceeds the limit, more coagulant dosage or enhanced coagulation is needed. Arsenic (III) cannot be removed by coagulation without oxidation of As^{3+} to As^{5+}. To adopt an optimum coagulant dosage for arsenic removal, monitoring of raw water arsenic concentration is required, but it is difficult because arsenic measurement is time consuming. NF membranes are not affected by source water composition, suggesting that NF membrane can be used in any types of water (109).

Mavrov et al. (89) evaluated the performance of several different MF and UF membranes for the filtration of reservoir water for drinking water production combined with powdered activated carbon. Tests showed that the dosing of powdered activated carbon into the feed water had no significant effect on the hydraulic behavior of the membranes. The dosage of PAC had no influence on the flux of UF pre-treatment of dam water (88). Smith et al. (168) investigated the possibility of using poor quality brackish water as a potential alternative to potable water for toilet flushing at the Millennium Dome in London, UK. The brackish water was treated using granular activated carbon followed by UF membranes prior to desalination on Reverse Osmosis (RO). The process was found to save approximately 50% of the potable water supply. Tsujimoto et al. (169) showed that the pre-treatment of river water by granulated activated carbon and UF membrane brought stable operation for 530 days without chemical cleaning. According to Siddiqui et al. (167) the use of polymers and coagulants upstream of MF did not pose any operational problems and they enhanced the removal of particles by tightening the sheet membranes inside the MF module. UF or possibly MF could be used instead of chemical treatment prior to NF.

Tomaszewska and Mozia (170) conducted laboratory-scale UF membrane experiments to determine the effect of the presence of powdered activated carbon (PAC) on the UF process performance, in terms of flux decline and the possibilities of membranes cleaning during backwash. The application of PAC/UF system was very effective in the removal of organic substances having both low and high molecular weights. 90% of HA was removed for a PAC dosage equal to 100 mg PAC/l compared with 40% rejection without PAC. The PAC cake prevents the HA adsorption/deposition onto the membrane surface and plugging the pores of the membrane. Combining PAC adsorption prior to MF in spring water treatment stabilizes the permeability of the membrane. PAC will not affect fouling as long as the turbidity is law ($<$5NTU) (90). Konieczny and Klornfas (171) compared MF with MF supported with powdered or granulated activated carbon for river water treatment. The hybrid process was superior to the MF alone process, producing higher retention of TOC.

Schafer et al. (115) compared MF, UF, and NF membrane processes available for water treatment in terms of intrinsic rejection, variation of rejection due to membrane fouling and increase in rejection by ferric chloride pre-treatment. Twelve different membranes were compared on the basis of their membrane pore size. Results showed that coagulation pre-treatment allowed a higher rejection of organics by MF and UF and the cut-off criterion due to initial membrane pore size is no longer valid. In NF, natural organics rejection was high and no coagulation pre-treatment was required. However, since coagulation targets large, hydrophobic organics which foul NF membranes by precipitation and gel layer formation, coagulation pre-treatment can control fouling. Ruohomaki et al. (27) investigated two types of UF membranes and NF membrane combined with either coagulation or adsorption. Coagulation was tested with six metal salts: NaCl, KCl, $CaCl_2$, $AlCl_3$, and $FeCl_3$. Adsorption of humic acid was also tested on active carbon. In the filtration tests the interest was focused on how pH, pressure and salts affects the retention and permeate fluxes in filtration of humic substances. The removal of HS was improved the most using $AlCl_3$. Adsorption was the highest at pH 3, which was near the isoelectric point of humic acid. When pH increased no severe adsorption occurred.

Park et al. (172) investigated coagulation with only rapid mixing in a separate tank (ordinary coagulation) and coagulation with no mixing tank (in-line coagulation) prior to an inside-out type hollow fiber UF membrane. Pre-coating the surface of the membranes with metal hydroxide particles of coagulants was also examined. Polyaluminum chloride (PACl) was used as a coagulant as well as aluminium oxide (Al_2O_3) and ferric chloride ($FeCl_3$). In the cross-flow mode the filterability of the ordinary coagulation was superior to that of in-line coagulation. In the pre-coating experiments filterability using PACl at 4.1 ppm was worse than that of ordinary or inline coagulation conditions. However, the reduction of the dosage to 2.0 and 1.0 ppm caused a reasonable improvement in filterability. Thus, it appears that the pre-coating method could lead to decrease in the consumption of coagulant. Meanwhile filterability for 13.0 ppm $FeCl_3$ was better than that for 4.1 ppm PACl. Thus, in the application of the pre-coating method as a membrane pre-treatment, iron hydroxide particles were found to be more suitable than aluminium hydroxide particles.

Suzuki et al. (173) studied the performance of hybrid MF membrane system to treat river water at a pilot scale. PAC was intermittently added to the system for adsorbing the natural organic matter, mainly humic substances.

Humic substances with smaller size than the micro pores of MF membranes were adsorbed by PAC, which were then completely separated by the MF membranes. In the hybrid MF membrane system, the decreasing rate of membrane permeability was much less than that of a conventional MF membrane process.

Advanced oxidation processes (AOPs) and manganese (Mn) sand self-catalytic oxidations were studied by Teng et al. (174) for the removal of manganese from ground water. The study concluded that the oxidation speed of Mn by H_2O_2 was found to be proportional to the concentration of H_2O_2 and pH. The results of Bowen et al. (175) investigation on the effect of PSU/SPEEK blend UF/NF membranes in HA removal showed that the HA rejection increased slightly and the recoverable flux ratio decreased slightly in the presence of coagulants such as $FeCl_3$ and $AlCl_3$. However, the effects were not great and the effect of $MnCl_2$ was insignificant.

Results revealed about 500% increase in steady state flux during cationic polyelectrolyte coagulation-microfiltration process. Moreover, integration of microfiltration with coagulation also improved the quality of effluent, in terms of turbidity and COD removals. About 50–60% and 75% removals were recorded for COD and turbidity, respectively during coagulation-microfiltration which was greater than those obtained during microfiltration alone (176). The rates of fouling were relatively low for the strong and weak hydrophobic fractions, and for the charged hydrophilic fraction. Although partial NOM removal was achieved using either an adsorbent or a coagulant, only the latter treatment option reduced the rate of fouling (125). The added metals ($FeCl_3$), which possess generally coagulating properties, seemed not to increase the rejection of NOM at this pH (5.5) by the membrane used (PS). Flux reduction increased when ion exchanged humic water was filtered after the addition of ferric iron. It is obvious that ferric iron which was expected to prevent the transmission of NOM through some kind of complex formation, did not fully succeed in retention because of the relative large pore size of the actual membrane (129). Pre-treatment of natural brackish water with metal-ions ($AlCl_3$) before UF, influenced the rate of flux decline. The results indicated that a reduction in NOM concentration, by pre-coagulation with metal-ions before filtration, could not reduce or prevent membrane fouling. In fact, irreversible membrane fouling was much worse (119) high ferric chloride dose lead to a positively charged deposit and thus an increase in rejection for the cations and a decrease for the negatively charged organics (76).

CONCLUSIONS

This review shows the importance of pre-treatment for reverse osmosis (RO) and thermal desalination processes. It also demonstrates that membrane (MF, UF, and NF) pre-treatment is superior to other conventional pre-treatment methods in terms of feed quality and over-all operational costs for highly fouling feed. Most studies have used Ferric Chloride and Aluminium Chloride as coagulation agents to improve membrane pre-treatment. It can be concluded from previous studies mentioned in this review that it is important to understand the characteristics and interaction of the feed constituents in order to be able to design an appropriate pre-treatment system.

ABBREVIATIONS

RO	Reverse osmosis
NOM	Natural organic matter
SDI	Silt density index
DOM	Dissolved organic matter
HS	Humic substances
FA	Fulvic acid
HA	Humic acid
NF	Nanofiltration
UF	Ultrafiltration
MF	Microfiltration
MWCO	Molecular weight cut-off
TOC	Total organic carbon

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REFERENCES

1. El-Dessouky, H.T. and Ettouney, H.M. (2002) *Fundamentals of Salt Water Desalination*, Vol. 1, 1st ed.; Amsterdam: Elsevier.
2. Marcovecchio, M.G., Mussati, S.F., Aguirre, P.A., Nicolas, J., and Scenna, N.J. (2005) Optimization of hybrid desalination processes including multi stage flash and reverse osmosis systems. *Desalination*, 182: 107–118.
3. Ebensperger, U. and Isley, P. (2005) Review of the current state of desalination, *Water Policy Working Paper 2005-008*.
4. Borsani, R. and Rebagliati, S. (2005) Fundamentals and costing of MSF desalination plants and comparison with other technologies. *Desalination*, 182: 29–37.
5. Semiat, R. (2000) Desalination: present and future. *International Water Resources Association*, 25: 54–65.
6. Nicolaisen, B. (2002) Developments in membrane technology for water treatment. *Desalination*, 153: 355–360.

7. Hassan, A.M. and Al-Sofi, M.A.K., Al-Amoudi, A.S. et al. (1998) A new approach to membrane and thermal seawater desalination processes using nanofiltration membranes (Part 1). *Desalination*, 118: 35–51.
8. Ghabayen, S., McKee, M., and Kemblowski, M. (2004) Characterization of uncertainties in the operation and economics of the proposed seawater desalination plant in the Gaza Strip. *Desalination*, 161: 191–201.
9. Sikora, J., Hansson, C., and Ericsson, B. (1989) Pretreatment and desalination of mine drainage water in a pilot plant. *Desalination*, 75: 363–373.
10. Redondo, J.A. (2001) Brackish-, sea- and wastewater desalination. *Desalination*, 138: 29–40.
11. Schäfer, A.I., Schwicker, U., Fischer, M.M., et al. (2000) Microfiltration of colloids and natural organic matter. *Membrane Science*, 171: 151–172.
12. Wilkinson, K.J., Negre, J.C., and Buffle, J. (1997) Coagulation of colloidal material in surface water: the role of natural organic matter. *Contaminant Hydrology*, 26: 229–243.
13. Van Hoof, S.C.J.M., Hashim, A., and Kordes, A.J. (1999) The effect of ultrafiltration as pre-treatment to reverse osmosis in wastewater reuse and seawater desalination applications. *Desalination*, 124: 231–242.
14. Vial, D. and Doussau, G. (2002) The use of microfiltration membranes for seawater pre-treatment prior to reverse osmosis membranes. *Desalination*, 153: 141–147.
15. Teng, C.K., Hawlader, M.N.A., and Malek, A. (2003) An experiment with different pre-treatment methods. *Desalination*, 156: 51–58.
16. Yiantsios, S.G., Sioutopoulos, D., and Karabelas, A.J. (2005) Colloidal fouling of RO membranes: an overview of key issues and efforts to develop improved prediction techniques. *Desalination*, 183: 773–788.
17. Karabelas, A.J. (2003) Critical assessment of fouling indices. *MEDRC Series of R&D Reports*. Project: 98-BS-034.
18. Costa, A.R. and De Pinho, M.N. (2002) The role of membrane morphology on ultrafiltration for natural organic matter removal. *Desalination*, 145: 299–304.
19. Xu, W., Chellam, S., and Clifford, D.A. (2004) Indirect evidence for deposit rearrangement during dead-end microfiltration of iron coagulated suspensions. *Membrane Science*, 239: 243–254.
20. Hong, S. and Elimelech, M. (1997) Chemical and physical aspects of natural organic matter (NQM): Fouling of nanofiltration membranes. *Membrane Science*, 132: 159–181.
21. Raspor, B. (1989) Adsorption of humic substances from seawater at differently charged surfaces. *The Science of the Total Environment*, 81/82: 319–328.
22. Zeng, K., Hwang, H., and Yu, H. (2002) Effect of dissolved humic substances on the photochemical degradation rate of 1-Aminopyrene and Atrazine. *Int. J. of Molecular Science*, 3: 1048–1057.
23. Alpatova, A., Verbych, S., Bryk, M., et al. (2004) Ultrafiltration of water containing natural organic matter: Heavy metal removing in the hybrid complexation-ultrafiltration process. *Separation and Purification Technology*, 40: 155–162.
24. Kam, S. and Gregory, J. (2001) The interaction of humic substances with cationic polyelectrolytes. *Wat. Res.*, 35: 3557–3566.
25. Aiken, G.R., McKnight, D.M., Wershaw, R.L., and MacCarthy, E. (1985) *Humic Substances in Soil, Sediment and Water*; Wiley: New York.
26. Bjelopavlic, M., Newcombe, G., and Hayes, R. (1999) Adsorption of NOM onto activated carbon: Effect of surface charge, ionic strength, and pore volume distribution. *Colloid and Interface Science*, 210: 271–280.

27. Ruohomaki, K., Vaisanen, P., Metsamuuronen, S., Kulovaara, M., and Nystrom, M. (1998) Characterization and removal of humic substances in ultra- and nanofiltration. *Desalination*, 118: 273–283.
28. De Paolis, F. and Kukkonen, J. (1997) Binding of organic pollutants to humic and fulvic acids: Influence of pH and the structure of humic material. *Chemosphere*, 34: 1693–1704.
29. Amy, G.L., Collins, M.R., Kuo, C.J., and King, P.H. (1987) Comparing gel permeation chromatography and ultrafiltration for the molecular weight characterization of aquatic organic matter. *Am. Water Works Assoc.*, 79: 43–49.
30. Rao, L. and Choppin, G.R. (1995) Thermodynamic study of the complexation of neptunium(V) with humic acids. *Radiochim Acta*, 69: 87–95.
31. Aiken, G.R. and Malcolm, R. (1987) Molecular weights of aquatic fulvic acids by vapor pressure osmometry. *Geochim Cosmochim Acta.*, 51: 2177–2184.
32. Becktt, R., Zhang, J., and Giddings, J.C. (1987) Determination of molecular weight distributions of fulvic and humic acids, using flow field-flow fractionation. *Environ. Sci. Technol.*, 21: 289–295.
33. Reid, P.M., Wilkinson, A.E., Tipping, E., and Jones, M.N. (1990) Determination of molecular weights of humic substances by analytical (UV scanning) ultracentrifugation. *Geochim. Cosmochim. Acta.*, 54: 131–138.
34. Chiang, P.C., Chang, E.E., and Liang, C.H. (2002) NOM characteristics and treatabilities of ozonation processes. *Chemosphere*, 46: 929–936.
35. Pokrovsky, O.S. and Schott, J. (2002) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology*, 190: 141–179.
36. Gavriil, A.M. and Angelidis, M.O. (2005) Metal and organic carbon distribution in water column of a shallow enclosed Bay at the Aegean Sea Archipelago: Kalloni Bay, island of Lesvos, Greece. *Estuarine, Coastal and Shelf Science*, 64: 200–210.
37. Munksgaard, N.C. and Parry, D.L. (2001) Trace metals, arsenic and lead isotopes in dissolved and particulate phases of North Australian coastal and estuarine seawater. *Marine Chemistry*, 75: 165–184.
38. Rangaraj, S., Kim, Y., Joo, C.K., and Yi, J. (2004) Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: Kinetics and equilibrium. *Colloid and Interface Science*, 273: 14–21.
39. Yates, D.M., Joyce, K.J., and Heaney, P.J. (1998) Complexation of copper with polymeric silica in aqueous solution. *Applied Geochemistry*, 13: 235–241.
40. Abu Qdais, H. and Moussa, H. (2004) Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination*, 164: 105–110.
41. Rengaraj, S. and Moon, S. (2002) Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins. *Water Research*, 36: 1783–1793.
42. Harmant, P. and Aimar, P. (1998) Coagulation of colloids in a boundary layer during cross-flow filtration. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 138: 217–230.
43. Kretzschmar, R. and Sticher, H. (1998) Colloid transport in natural porous media: Influence of surface chemistry and flow velocity. *Phys. Chem. Earth*, 23: 133–139.
44. Tipping, E., Lofts, S., and Lawlor, A.J. (1998) Modelling the chemical speciation of trace metals in the surface waters of the Humber system. *The Science of the Total Environment*, 210/211: 63–77.
45. Martell, A. (1957) The chemistry of metal chelates in plant nutrition. *Soil Science*, 84: 13–26.

46. Eyrolle, F. and Benaim, J. (1999) Metal available sites on colloidal organic compounds in surface waters (Brazil). *Water Research*, 33: 995–1004.
47. Bryan, N.D., Jones, M.N., Birkett, J., and Livens, F.R. (2001) Application of a new method of analysis of ultracentrifugation data to the aggregation of a humic acid by copper(II) ions. *Analytica Chimica. Acta.*, 437: 281–289.
48. Hamilton-Taylor, J., Postill, A.S., Tipping, E., and Harper, M.P. (2002) Laboratory measurements and modeling of metal-humic interactions under estuarine conditions. *Geochimica et Cosmochimica Acta*, 66: 403–415.
49. Van Houtte, E., Verbauwhede, J., Vanlerberghe, F., Demunter, S., and Cabooter, J. (1998) Treating different types of raw water with micro- and ultrafiltration for further desalination using reverse osmosis. *Desalination*, 117: 49–60.
50. Pervov, A.G., Andrianov, A.P., Efremov, R.V., et al. (2003) A new solution for the Caspian Sea desalination: Low-pressure, mernbranes. *Desalination*, 157: 377–384.
51. Teuler, A., Glucina, K., and Laine, J.M. (1999) Assessment of UF pre-treatment prior RO membranes for seawater desalination. *Desalination*, 125: 89–96.
52. Van der Bruggen, B. and Vandecasteele, C. (2003) Removal of pollutants from surface water and groundwater by nanofiltration: Overview of possible applications in the drinking water industry. *Environmental Pollution*, 122: 435–445.
53. Conlon, W.J. and McClellen, S.A. (1989) Membrane softening: treatment process comes of age. *AWWA*, 81: 47–51.
54. Linde, K. and Jonsson, A. (1995) Nanofiltration of salt solutions and landfill leachate. *Desalination*, 103: 223–232.
55. Glucina, K., Laine, J.M., and Durand-Bourlier, L. (1998) Assessment of filtration mode for the ultrafiltration membrane process. *Desalination*, 118: 205–211.
56. Majewska-Nowak, K., Kowalska, I., and Kabsch-Korbutowicz, M. (2005) Ultrafiltration of SDS solutions using polymeric membranes. *Desalination*, 184: 1395–1402.
57. Hilal, N., Al-Zoubi, H., Darwish, N.A., and Mohammad, A.W. (2005) Characterisation of nanofiltration membranes using atomic force microscopy. *Desalination*, 177: 187–199.
58. Schaifer, A.I., Fane, A.G., and Waite, T.D. (1998) Nanofiltration of natural organic matter: Removal, fouling and the influence of multivalent ions. *Desalination*, 118: 109–122.
59. Xu, L., Shiyong, W., and Zeng, X. (2005) The maltitol purification and concentration by nanofiltration. *Desalination*, 184: 1275–1283.
60. Cho, J., Amy, G., and Pellegrino, J. (1999) Membrane filtration of natural organic matter: Initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. *Water Research*, 33: 2517–2526.
61. Hoek, E.M.V. and Elimelech, M. (2003) Cake-enhanced concentration polarisation: A new fouling mechanism for salt-rejecting membranes. *Environ. Sci. Technol.*, 37: 5581–5588.
62. Vela, M.C.V., Blanco, S.A., and Garcia, J.L. (2005) Crossflow ultrafiltration of cake forming solutes: a non-steady state model. *Desalination*, 184: 1327–1336.
63. Her, N., Amy, G., and Jarusutthirak, C. (2000) Seasonal variations of nanofiltration (NF) foulants: Identification and control. *Desalination*, 132: 143–160.
64. Manttari, M., Puro, L., Nuortila-Jokinen, J., and Nystrom, M. (2000) Fouling effects of polysaccharides and humic acid in nanofiltration. *Membrane Science*, 165: 1–17.

65. Kaiya, Y., Itoh, Y., Fujita, K., and Takizawa, S. (1996) Study on fouling materials in the membrane treatment process for potable water. *Desalination*, 106: 71–77.
66. Isaias, N.P. (2001) Experience in reverse osmosis pre-treatment. *Desalination*, 139: 57–64.
67. Choksuchart, P., Heran, M., and Grasmick, A. (2002) Ultrafiltration enhanced by coagulation in an immersed membrane system. *Desalination*, 145: 265–272.
68. Brehant, A., Bonnelye, V., and Perez, M. (2002) Comparison of MF/UF pretreatment with conventional filtration prior to RO membranes for surface seawater desalination. *Desalination*, 144: 353–360.
69. Cho, J., Amy, G., Pellegrino, J., and Yoon, Y. (1998) Characterization of clean and natural organic matter (NOM) fouled NF arid UF membranes, and foulants characterization. *Desalination*, 118: 101–108.
70. Thorsen, T. (2004) Concentration polarisation by natural organic matter (NOM) in NF and UF. *Membrane Science*, 233: 79–91.
71. Shaalan, H.F. (2002) Development of fouling control strategies pertinent to nanofiltration membranes. *Desalination*, 153: 125–131.
72. Derradji, A.F., Taha, S., and Dorange, G. (2005) Application of the resistances in series model in ultrafiltration. *Desalination*, 184: 1357–1364.
73. Bowen, W.R., Jones, M.G., and Yousef, H.N.S. (1998) Prediction of the rate of crossflow membrane ultrafiltration of colloids: A neural network approach. *Chemical Engineering Science*, 53: 3793–3802.
74. Bowen, W.R., Mongruel, A., and Williams, P.M. (1996) Prediction of the rate of cross-flow membrane ultrafiltration: A colloidal interaction approach. *Chemical Engineering Science*, 51: 4321–4333.
75. Hilal, N., Ogunbiyi, O.O., Miles, N.J., and Nigmatullin, R. (2005) Methods employed for control of fouling in MF and UF membranes: A comprehensive review. *Separation Science and Technology*, 40: 1–49.
76. Schafer, A.I., Fane, A.G., and Waite, T.D. (2000) Fouling effects on rejection in them membrane filtration of natural waters. *Desalination*, 131: 215–224.
77. Cho, J., Amy, G., and Pellegrino, J. (2000) Membrane filtration of natural organic matter: comparison of flux decline, NOM rejection, and foulants during filtration with three UF membranes. *Desalination*, 127: 283–298.
78. Marchese, J., Ponce, M., Ochoa, N.A., et al. (2003) Fouling behaviour of polyethersulfone UF membranes made with different, PVP. *Membrane Science*, 211: 1–11.
79. Clever, M., Jordt Knauf, R., et al. (2000) Process water production from river water by ultrafiltration and reverse, osmosis. *Desalination*, 131: 325–336.
80. Bottino, A., Capannelli, C., Del Borghi, A., et al. (2001) Water treatment for drinking purpose: Ceramic microfiltration application. *Desalination*, 141: 75–79.
81. Stover, R.L., Ameglio, A., and Khan, P.A.K. (2005) The ghalilah SWRO plant an overview of the solutions adopted to minimize energy consumption. *Desalination*, 184: 1197–1201.
82. Gille, D. and Czolkoss, W. (2005) Ultrafiltration with multi bore membranes as seawater pre-treatment. *Desalination*, 182: 295–301.
83. Halpern, D.F., McArdle, J., and Antrim, B. (2005) UF pre-treatment for SWRO: Pilot studies. *Desalination*, 182: 317–326.
84. Kothari, N. and Taylor, J.S. (1998) Pilot scale microfiltration at Manitowoc. *Desalination*, 119: 93–102.
85. Wang, K.Y., Matsuura, T., Chung, T., and Guo, W.F. (2004) The effects of flow angle and shear rate within the spinneret on the separation performance

of poly (ethersulfone) (PES) ultrafiltration hollow fiber membranes. *Journal of Membrane Science*, 240: 67–79.

86. Rashid, M.A. (1970) Role of humic acid of marine origin their different molecular weight fractions in complexing di- and tri-valent metals. *Soil Science*, 3: 298–305.
87. Bodzek, M. and Konieczny, K. (1998) Comparison of various membrane types and module configurations in the treatment of natural water by means of low-pressure membrane method. *Separation and Purification Technology*, 14: 69–78.
88. Hagen, K. (1998) Removal of particles, bacteria and parasites with ultrafiltration for drinking water treatment. *Desalination*, 119: 85–91.
89. Mavrov, V., Chmiel, H., Kluth, J., et al. (1998) Comparative study of different MF and UF membranes for drinking water production. *Desalination*, 117: 189–196.
90. Pianta, R., Boller, M., Janex, M., et al. (1998) Micro- and ultrafiltration of karstic spring water. *Desalination*, 117: 61–71.
91. Madaeni, S.S., Fane, A.G., and Grohmann, G.S. (1995) Virus removal from water and wastewater using membranes. *Membrane Science*, 102: 65–75.
92. Kim, S. and Yoor, J. (2005) Optimization of microfiltration for seawater suffering from red-tide contamination. *Desalination*, 182: 309–315.
93. Hsu, B. and Yeh, H. (2003) Removal of giardia and cryptosporidium in drinking water treatment: A pilot-scale study. *Water Research*, 37: 1111–1117.
94. Thompson, M.A., Kelkar, U.G., and Vickers, J.C. (1995) The treatment of groundwater containing hydrogen sulphide using microfiltration. *Desalination*, 102: 287–291.
95. Cote, P., Siverns, S., and Monti, S. (2005) Comparison of membrane-based solutions for water reclamation and desalination. *Desalination*, 182: 245–251.
96. Wolf, P.H., Siverns, S., and Monti, S. (2005) UF membranes for RO desalination pre-treatment. *Desalination*, 182: 289–296.
97. Kruithof, J.C., Schippers, J.C., Kamp, P.C., et al. (1998) Integrated multi-objective membrane systems for surface water treatment: Pre-treatment of reverse osmosis by conventional treatment and ultrafiltration. *Desalination*, 117: 37–48.
98. Schäfer, A.I. and Richards, B.S. (2005) Field testing of a hybrid membrane system for groundwater desalination. *Desalination*, 183: 1–8.
99. Glueckstern, P., Priel, M., and Wilf, M. (2002) Field evaluation of capillary UF technology as a pre-treatment for large seawater RO systems. *Desalination*, 147: 55–62.
100. Murrer, J. and Rosberg, R. (1998) Desalting of seawater using UF and RO–results of a pilot study. *Desalination*, 118: 1–4.
101. Hofman, J.A.M.H., Beumer, M.M., Baars, E.T., et al. (1998) Enhanced surface water treatment by ultrafiltration. *Desalination*, 119: 113–125.
102. Hassan, A.M., Farooque, A.M., Jamaluddin, A.T.M., et al. (2000) A demonstration plant based on the new NF-SWRO process. *Desalination*, 131: 157–171.
103. Ericsson, B., Hallberg, M., and Wachenfeldt, J. (1997) Nanofiltration, of highly colored raw water for drinking water production. *Desalination*, 108: 129–141.
104. Jucker, C. and Clark, M.M. (1994) Adsorption of aquatic hnmic substances on hydrophobic ultrafiltration membranes. *Membrane Science*, 97: 37–52.
105. Mohsen, M.S., Jaber, J.O., and Afonso, M.D. (2003) Desalination of brackish water by nanofiltration and reverse osmosis. *Desalination*, 157: 167.

106. Gwon, E., Yu, M., Oh, H., and Ylee, Y. (2003) Fouling characteristics of NF and RO operated for removal of dissolved matter from groundwater. *Water Research*, 37: 2989–2997.
107. Eriksson, P., Kyburz, M., and Pergande, W. (2005) NF membrane characteristics and evaluation for sea water processing applications. *Desalination*, 184: 1261–1274.
108. Liikanena, R., Miettinen, I., and Laukkanen, R. (2003) Selection of NF membrane to improve quality of chemically treated surface water. *Water Research*, 37: 864–872.
109. Sato, Y., Kang, M., Kamei, T., and Magara, Y. (2002) Performance of nanofiltration for arsenic removal. *Water Research*, 36: 3371–3377.
110. Van der Bruggen, B., Hawrijk, L., Cornelissen, E., and Vandecasteele, C. (2003) Direct nanofiltration of surface water using capillary membranes: Comparison with flat sheet membranes. *Separation and Purification Technology*, 31: 193–201.
111. Khalik, A. and Praptowidodo, V.S. (2000) Nanofiltration for drinking water production from deep well water. *Desalination*, 132: 287–292.
112. Agenson, K.O., Oh, J., and Urase, T. (2003) Retention of a wide variety of organic pollutants by different nanofiltration/reverse osmosis membranes: Controlling parameters of process. *Membrane Science*, 225: 91–103.
113. Anne, C.O., Trebouet, D., Jaouen, P., and Quemeneur, F. (2001) Nanofiltration of seawater: fractionation of mono and multi-vaient cations. *Desalination*, 140: 67–77.
114. Al-Sofi, M.A.K., Hassan, A.M., Hamed, O.A., et al. (2000) Optimization of hybridized seawater desalination process. *Desalination*, 131: 147–156.
115. Schafer, A.I., Fane, A.G., and Waite, T.D. (2001) Cost factors and chemical pretreatment effects in the membrane filtration of waters containing natural organic matter. *Water Research*, 35: 1509–1517.
116. Assemi, S., Newcombe, G., Hepplewhite, C., and Beckett, R. (2004) Characterization of natural organic matter fractions separated by ultrafiltration using flow field-flow fractionation. *Water Research*, 38: 1467–1476.
117. Speth, T.F., Gusses, A.M., and Summers, R.S. (2000) Evaluation of nanofiltration pre-treatments for flux loss control. *Desalination*, 130: 31–44.
118. Yiantsios, S.G. and Karabelas, A.J. (2001) An experimental study of humid acid and powdered activated carbon deposition on UF membranes and their removal by backwashing. *Desalination*, 140: 195–209.
119. Maartens, A., Swart, P., and Jacobs, E.P. (1999) Feed-water pre-treatment: methods to reduce membrane fouling by natural organic matter. *Membrane Science*, 163: 51–62.
120. Teixeira, M.R. and Rosa, M.J. (2002) pH adjustment for seasonal control of UF fouling by natural waters. *Desalination*, 151: 165–175.
121. Childress, A.E. and Elimelech, M. (1996) Effect of solution chemistry on the surface charge of polymeric reverse osmosis and naanofiltration membranes. *Membrane Science*, 119: 253–268.
122. Guo, L., Wen, L., Tang, D., and Santschi, P.H. (2000) Re-examination of cross-flow ultrafiltration for sampling aquatic colloids: Evidence from molecular probes. *Marine Chemistry*, 69: 75–90.
123. Lee, S., Cho, J., and Elimelech, M. (2004) Influence of colloidal fouling and feed water recovery on salt rejection of RO and NF membranes. *Desalination*, 160: 1–12.

124. Lee, H., Amy, G., Cho, J., et al. (2000) Cleaning strategies for flux recovery of an ultrafiltration membrane fouled by natural organic matter. *Water Research*, 35: 3301–3308.
125. Carroll, T., King, S., Gray, S.R., Bolto, B.A., and Booker, N.A. (2000) The fouling of microfiltration membranes by NOM after coagulation treatment. *Wat. Res.*, 34: 2861–2868.
126. Nilson, J.A. and DiGino, E.A. (1998) Influence of NOM composition on nanofiltration. *AWWA*, 88: 53–66.
127. Yiantsios, S.G. and Karabelas, A.J. (1998) The effect of colloid stability on membrane fouling. *Desalination*, 118: 143–152.
128. Jarusutthirak, C., Amy, G., and Croue, P. (2002) Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. *Desalination*, 145: 247–255.
129. Kulovaara, M., Metsamuuronen, S., and Nystrom, M. (1999) Effects of aquatic humic substances on a hydrophobic ultrafiltration membrane. *Chemosphere*, 38: 3485–3496.
130. Khulbe, K.C., Matsuura, T., Singh, S., et al. (2000) Study on fouling of ultraflltration membrane by electron spin resonance. *Membrane Science*, 167: 263–273.
131. Bian, R., Yamamoto, K., and Watanabe, Y. (2000) The effect of shear rate on controlling the concentration polarization and membrane fouling. *Desalination*, 131: 225–236.
132. Hillis, P., Padley, M.B., Powell, N.I., and Gallagher, P.M. (1998) Effects of backwash conditions on out-to-in membrane microfiltration. *Desalination*, 118: 197–204.
133. Kampa, P.C., Kruithof, J.C., and Folmer, H.C. (2000) UF/RO treatment plant Heemskerk: From challenge to full scale application. *Desalination*, 131: 27–35.
134. Nederlof, M.M., Kruithof, J.C., Taylor, J.S., et al. (2000) Comparison of NF/RO membrane performance in integrated membrane systems. *Desalination*, 131: 257–269.
135. Takata, K., Yamamoto, K., Bian, R., and Watanabe, Y. (1998) Removal of humic substances with vibratory shear enhanced processing membrane filtration. *Desalination*, 117: 273–282.
136. Lipp, P. and Baldauf, G. (2002) Application of out-in MF/UF-systems for drinking water treatment with air supported backwash–three case studies. *Desalination*, 147: 63–68.
137. Nakatsuka, S., Nakate, I., and Miyano, T. (1996) Drinking water treatment by using ultrafiltration hollow fiber membranes. *Desalination*, 106: 55–61.
138. Kuo, C. and Amy, G.L. (1998) Factors affecting coagulation with aluminium sulphate-II: Dissolved organic matter removal. *Wat. Res.*, 22: 863–872.
139. Al-Mutairi, N.Z., Hamoda, M.F., and Al-Ghusain, I. (2004) Coagulant selection and sludge conditioning in a slaughterhouse wastewater treatment plant. *Bioresource Technology*, 95: 115–119.
140. Vickers, J.C., Thompson, M.A., and and Kelkar, U.G. (1995) The use of membrane filtration in conjunction with coagulation processes for improved NOM removal. *Desalination*, 102: 57–61.
141. Pikkarainen, A.T., Judd, S.J., Jokel, J., and Gillberg, L. (2004) Pre-coagulation for microfiltration of an upland surface water. *Water Research*, 38: 455–465.
142. Papic, S., Koprivanac, N., Bozic, A.L., and Metes, A. (2004) Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon absorption process. *Dyes and Pigments*, 62: 291–298.

143. Abdessemed, D. and Nezzal, G. (2002) Treatment of primary effluent by coagulation-adsorption-ultrafltration for reuse. *Desalination*, 152: 367–373.
144. Ma, J. and Liu, W. (2002) Effectiveness of ferrate(VI) preoxidation in enhancing the coagulation of surface waters. *Water Research*, 36: 4959–4962.
145. Judd, S.J. and HiIlis, P. (2001) Optimisation of combined coagulation and microfiltration for water treatment. *Water Research*, 35: 2895–2904.
146. Gabelich, C.J., Yun, T.I., and Coffey, B.M. (2002) Effects of aluminum sulfate and ferric chloride coagulant residuals on polyamide membrane performance. *Desalination*, 150: 15–30.
147. Huang, C. and Shiu, H. (1996) Interactions between alum and organics in coagulation. *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, 133: 155–163.
148. Low, S.C., Han, H.J., and Jin, W.X. (2004) Characteristics of a vibration membrane in water recovery from fine carbon-loaded wastewater. *Desalination*, 160: 83–90.
149. Bayat, O., Arslan, V., Bayat, B., and Poole, C. (2004) Application of a flocculation-ultrafiltration process for bacteria (Desulfovibrio desulfuricans) removal from industrial plant process water. *Biochemical Engineering*, 18: 105–110.
150. Bolto, B., Abbt-Braun, G., Dixon, D., et al. (1999) Experimental evaluation of cationic polyelectrolytes for removing natural organic matter from water. *Water Science and Technology*, 71–79.
151. Cabane, B., Meireles, M., and Aimar, P. (2002) Cake collapse in frontal filtration of colloidal aggregates: Mechanisms and consequences. *Desalination*, 146: 155–161.
152. McDay, G., Hart, B.T., McKelvie, I.D., and Beckett, R. (1994) Absorption of natural organic matter onto goethite. *Colloids Surf. A*, 89: 1–13.
153. Tipping, E. (1981) The absorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta.*, 45: 191–199.
154. Schlautman, M.A. and Morgan, J.J. (1994) Adsorption of aquatic humic substances on colloidal-size aluminum oxide particles: Influence of solution chemistry. *Geochem. Cosmochim. Acta.*, 58: 4293–4303.
155. Mavrov, V., Erwe, T., Blocher, C., and Chmiel, H. (2003) Study of new integrated processes combining adsorption, membrane separation and flotation for heavy metal removal from wastewater. *Desalination*, 157: 97–104.
156. Ha, T., Choo, K., and Choi, S. (2004) Effect of chlorine on adsorption/ultrafiltration treatment for removing natural organic matter in drinking water. *Colloid and Interface Science*, 274: 587–593.
157. Kanungo, S.B., Tripathy, S.S., and Rajeev. (2004) Adsorption of Co, Ni, Cu, and Zn on hydrous manganese dioxide from complex electrolyte solutions resembling sea water in major ion content. *Colloid and Interface Science*, 269: 1–10.
158. Illés, E. and Tombácz, E. (2004) The role of variable surface charge and surface complexation in the adsorption of humic acid on magnetite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 230: 99–109.
159. Specht, C.H., Kumke, M.U., and Frimmel, F.H. (2000) Characterization of NOM adsorption to clay minerals by size exclusion chromatography. *Water Research*, 34: 4063–4069.
160. Duan, J., Wilson, F., Graham, N., and Tay, J.H. (2002) Adsorption of humic acid by powdered activated carbon in saline water conditions. *Desalination*, 151: 53–66.
161. Kozar, S., Bilinski, H., and Branica, M. (1992) Adsorption of lead and cadmium ions on calcite in the Krka estuary. *Marine Chemistry*, 40: 215–230.

162. Rengaraj, S., Yeon, K., Kang, S., et al. (2002) Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin. *Journal of Hazardous Materials*, 92: 185–198.
163. Matilainen, A., Lindqvist, N., Korhonen, S., and Tuhkanen, T. (2002) Removal of NOM in the different stages of the water treatment process. *Environment International*, 28: 457–465.
164. Zidouri, H. (2000) Desalination in Morocco and presentatio of design and operation of the Laayoune seawater reverse osmosis plant. *Desalination*, 131: 137–145.
165. Naceur, W.M., Messaoudene, N.A., and Aggoun, A. (2003) Microfiltration reinforced adsorption of humic acids onto modified Algerian clay. *Desalination*, 158: 271–276.
166. Karakulski, K., Gryta, M., and Morawski, A. (2002) Membrane processes used for potable water quality improvement. *Desalination*, 145: 315–319.
167. Siddiqui, M., Amy, G., Ryan, J., and Odem, W. (2000) Membrane for the control of natural organic matter from surface waters. *Water Research*, 34: 3355–3370.
168. Smith, A.J., Khow, J., Lodge, B., and Bavister, G. (2001) Desalination of poor quality brackish groundwater for non-potable use. *Desalination*, 139: 207–215.
169. Tsujimoto, W., Kimura, H., Izu, T., and Irie, T. (1998) Membrane filtration and pre-treatment by GAC. *Desalination*, 119: 323–326.
170. Tomaszewska, M. and Mozia, S. (2002) Removal of organic matter from water by PAC/UF system. *Water Research*, 36: 4137–4143.
171. Konieczny, K. and Klomfas, G. (2002) Using activated carbon to improve natural water treatment by porous membranes. *Desalination*, 147: 109–116.
172. Park, P., Lee, C., Choi, S., et al. (2002) Effect of the removal of DOMs on the performance of a coagulation-UF membrane system for drinking water production. *Desalination*, 145: 237–245.
173. Suzuki, T., Watanabe, Y., Ozawa, G., and Ikeda, S. (1998) Removal of soluble organics and manganese by a hybrid MF hollow fiber membrane system. *Desalination*, 117: 119–130.
174. Teng, Z., Huang, J.Y., Fujita, K., and Takizawa, S. (2001) Manganese removal by hollow fiber micro-filter. Membrane separation for drinking water. *Desalination*, 139: 411–418.
175. Bowen, W.R., Doneva, T.A., and Yin, H. (2002) Separation of humic acid from a model surface water with PSU/SPEEK blend UF/NF membrances. *Membrane Science*, 206: 417–429.
176. Katayon, S., Megat Mohd Noor, M.J., Abdul Ghani, L.A., and Ahmad, J. (2005) Influence of cationic polyelectrolyte coagulant on microfiltration performance for treatment of oxidation pond effluent. *Desalination*, 184: 1403–1410.