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A Large Review of the Pre Treatment

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1. Introduction

Desalination using seawater reverse osmosis (SWRO) technology is an important option available to water-scarce coastal regions. Worldwide sea water desalination is a very effective and economical way of producing potable water for drinking and industries. Reverse osmosis plants to convert sea water to potable drinking water and for other usages have been prevalent throughout the world for more than 4 decades. Design and operation of seawater reverse osmosis plants strongly depend on the raw seawater quality to be treated. The performance of desalination reverse osmosis (RO) systems relies upon the production of high quality pre treated water, and the selection of the best pre treatment technology depends on the raw seawater quality and its variations. Number of full-scale experiences has shown that pre treatment is the key for this application of reverse osmosis technology. It is why during these last years, an import effort has been done to identify and to characterise the diverse organic and mineral components present in the seawater in a view to optimise the seawater pre-treatment and to develop advanced analytical methods for feed water characterization, appropriate fouling indicators and prediction tools.

This Chapter describes firstly a comprehensive approach to characterize raw seawater samples through analytical tools which allow the knowledge of the characterization of seawater from many aspects:

(a) inorganic content, (b) natural organic matter, (c) enumeration of micro-organisms and phytoplankton.

Secondly, this Chapter describes the effect of each of these parameters on the fouling of the reverse osmosis membrane. Finally, this chapter describes the different possible pre-treatments available to reduce or remove the elements or substances up-stream reverse osmosis stage.

2. Sea water characterization

Seawater is a mixture of various salts, organic substances, algae, bacteria and micro particles present in the water. Advanced analytical tools have been developed to allow thorough characterization of seawater samples from many aspects: (a) inorganic content,(b) natural organic matter,(c) enumeration of micro-organisms and phytoplankton.

The types of foulants (figure 1,table 1) most commonly encountered in RO systems include:

- Inorganic & particle fouling: Accumulation of particles on the membrane surface not removed from the raw water during the filtration process in the pre-treatment. The indicators of sufficient reduction of suspended solids and particles are turbidity values

of less than 0.5 Nephelometric Turbidity Unit (NTU) and silt density index (SDI) values of less than 4.

- Colloidal fouling: Deposition of metal oxides, proteins, silicates, organic matter, and clay creating a colloidal slime on the membrane surface. Colloidal fouling is due to the presence of suspended solids in water, such as mud and silt, and tends to cause gross plugging of the device rather than fouling of the membrane surface.
- Biological fouling: Build-up of a microbial community on the membrane surface including microbes and their by-products, resulting in a slime layer. Bio-fouling is a special case of particulate fouling that involves living organisms and can be a serious problem. Biological material growing on membrane surfaces not only causes loss of flux but may physically degrade certain types of membranes.
- Organic fouling: Adsorption of organic matter, particularly humic and fulvic acids, on the membrane surface. Organic fouling is most complex in nature and can cause hydrocarbon oils (naturally occurring or as a result of pollution) and have been known to cause performance deterioration.
- Scaling of RO membrane surfaces is caused by the precipitation of sparingly soluble salts from concentrated brine.

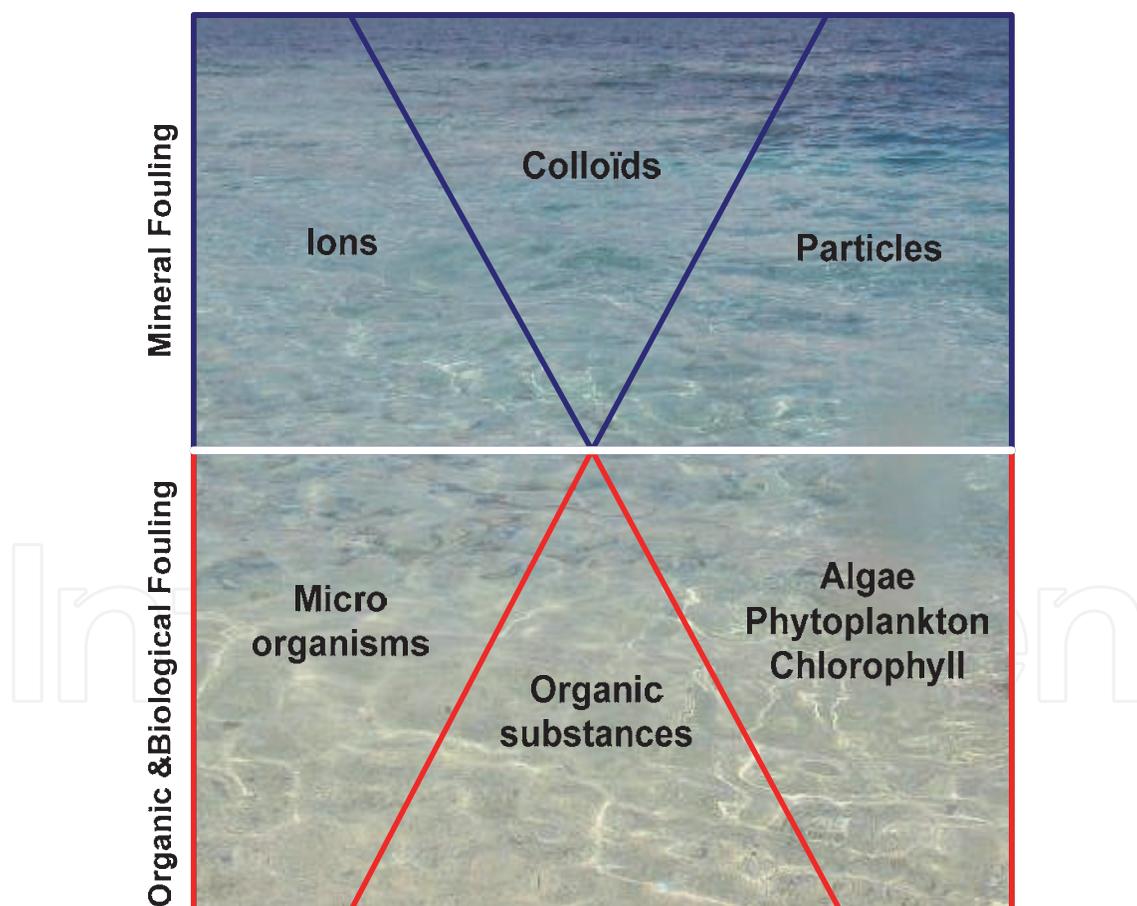


Fig. 1. Fouling potential

The quality will be determined by analysis of physical, chemical, and bacteriological contents to determine the level of treatment to supply the necessary water quality for the reverse osmosis membranes

Inorganic	Organic	Biological
Silica Quartz Silt Carbonates/sulphates	Lipids Proteins Polysaccharides	Algae Plankton Unicellular organisms

Table 1. Seawater constituents and potential membrane foulants

2.1 Physical characteristics

2.1.1 Density

At zero degrees Celsius liquid water turns into ice and has a density of approximately 917 kilograms per cubic meter. Liquid water at the same temperature has a density of nearly 1,000 kilograms per cubic meter. The density of seawater generally increases with decreasing temperature, increasing salinity, and increasing depth in the ocean. The density of seawater at the surface of the ocean varies from 1,020 to 1,029 kilograms per cubic meter. Highest densities are achieved with depth because of the overlying weight of water. In the deepest parts of the oceans, seawater densities can be as high as 1,050 kilograms per cubic meter.

The other physical characteristics of the sea water that must be evaluated are total suspended solids (TSS) and temperature, Turbidity and silt density index (SDI).

2.1.2 Total suspended solids

The total suspended solids level must be evaluated to determine the level of pre-treatment processes required. Sea water having low total suspended solids levels generally requires less pre-treatment.

2.1.3 Temperature

The temperature of the sea water source must be matched to the specific desalination process because this parameter may control the desalination process design. The evolution of the temperature during the year must be made prior to determine the seasonal maximum and minimum water temperatures of the sea water.

2.1.4 Turbidity

This parameter provides the amount of fine particulate matter in the water. Turbidity is measured in Nephelometric Turbidity Units (NTU).

2.1.5 Fouling index

Fouling is the major issue when using membranes for water treatment. Several parameters have been proposed for measuring a fouling potential and using it as a predictive tool for assessing the adequacy of pre-treatment. The Silt Density Index (SDI) and the Modified Fouling Index (MFI) are presently the only standard methods, even if they do not reflect the real potential of fouling because particles smaller than 0.45 μm responsible for fouling are not taken into consideration. Their limitations have been evidenced by several studies [Khirani et al., 2005; Junga & Son, 2009; Hong et al., 2009].

2.1.5.1 Silt density index (SDI)

Silt density index (SDI) is a parameter characterising the fouling potential of water. Particulate, colloidal matter and micro-organisms (figure 2) have a natural tendency to deposit themselves on the membrane, thus impairing its effectiveness. It is one of the most important parameter for the design and operation of reverse osmosis membrane process. SDI analytical protocol is standardized in the ASTM D 4189-95, re-approved 2002, and it evaluates the amount of 0.45-micron filter plugging caused by passing a sample of water through the filter for 15 minutes. SDI is recognised as the standard test to estimate membrane fouling potential (Iwahori et al., 2003; Kim et al., 2006, Kremen & Tanner, 1998; Mosset et al., 2008). It is strongly depending on the amount of particles but also representative of other fouling compounds

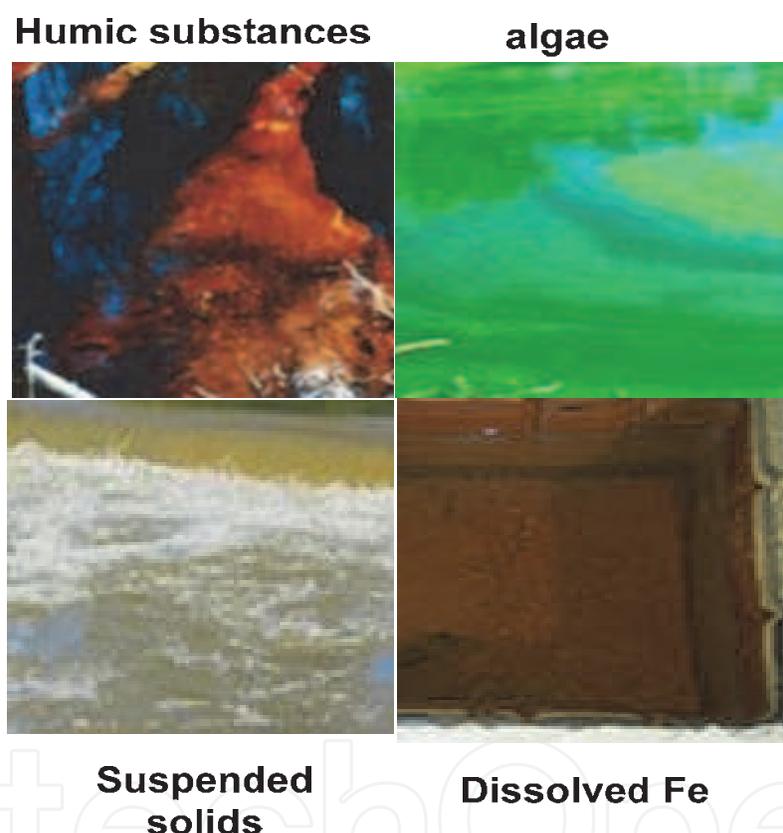


Fig. 2. Origin of the fouling compounds according to SDI membrane appearance

The protocol for this measurement is standardised (see Standard ASTM-D4189-07). The SDI must be as low as possible to limit the fouling of the filtration membranes. The principle of this protocol is to measure the time required to filter a clearly defined volume of water (500 ml) with a new test membrane and then compare this with the time required to filter the same volume after 15 minutes of filtration. The increase in the time required for filtration of the 500 ml is used to calculate an index (figure 3). The minimum SDI_{15} value is 0 and the maximum value, corresponding to an infinite filtration time, is 6.67. In practice, it is never possible to obtain $SDI_{15} = 0$. The test is carried out at a pressure of 2.05 bars through a membrane with a cut-off threshold of $0.45\mu\text{m}$. Conventionally, the measurement is made over a period of 15 minutes (SDI_{15}) on the pre treated water. When the water has very high

fouling properties, it may be made over a period of 10, 5 or 3 minutes. Note that the ranges of values are not at all the same for different measurement periods (SDI₃: 0→33.3; SDI₅: 0→20; SDI₁₀: 0→10; SDI₁₅: 0→6.67). It is therefore expressed in %/min.

Because the filter is more or less plugging versus time, the rate of plugging (SDI) is more or less important. SDI is then calculated according to the following formula:

$$SDI_{Td} = \frac{100}{Td} \times \left(1 - \frac{T_i}{T_f} \right)$$

Where:

Td is the overall filtration time (3, 5, 10, 15 minutes)

T_i is the initial time (in s) to filter 500 ml of water on a 0.45 μm membrane at 2.05 bar

T_f is the final time (in s) to filter 500 ml after 15 min.

Standard ASTM D 4189 does not stipulate the material of the test membrane or its supplier. The nature of the test membrane is a critical parameter because it has been demonstrated that the choice of type of membranes used for the test is primordial. An SDI value given without specifying the type of membrane used for the measurement is meaningless.

The Factors interfering with SDI measures are:

The influence of **pH** shows an increase of SDI values from 4 to 6 when pH is increased from 7 to 8 and is mainly explained by the presence of dissolved substances (Ca, Mg...), which precipitate with the increasing of the pH.

The type of **Membrane** is determinant for SDI values. A comparative study between hydrophobic and hydrophilic membrane (figure 3) shows that higher results are obtained for hydrophobic membrane compared to hydrophilic membrane.

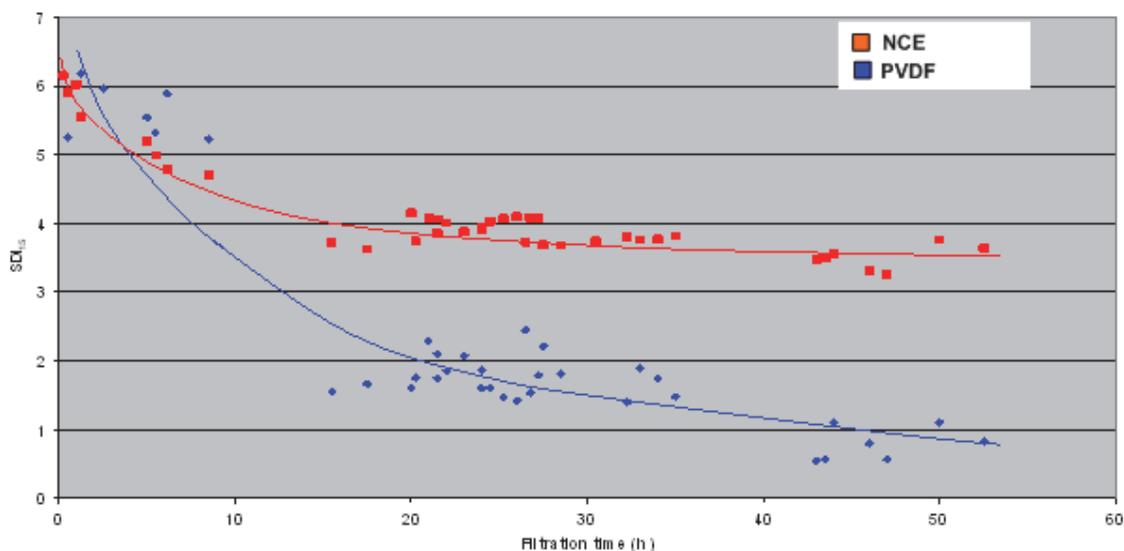


Fig. 3. SDI 15 Comparison Nitrocellulose membrane vs PVDF membrane

SDI is the essential parameter to control the fouling potential of water. Compared to others parameters like turbidity or suspended solids, it is more sensitive. The figures 4 & 5 show the evolution of the SDI during spring and autumn on a site located on the Mediterranean sea. This evolution could influence the pre treated water quality if the selected technology

and the design are not based on the worst and the most disadvantageous values. The operation of the plant concluded that raw water quality seems to be the most obvious answer. The SDI results for the 3-minute test are significant only if inferior to 33. Therefore, all measured values superior to 33 for seawater were discarded. When looking at the evolution over the seasons, it can be observed that, during the autumn and winter months, the average SDI is low with little evolution. On the contrary, during the spring the SDI becomes higher and varies greatly.

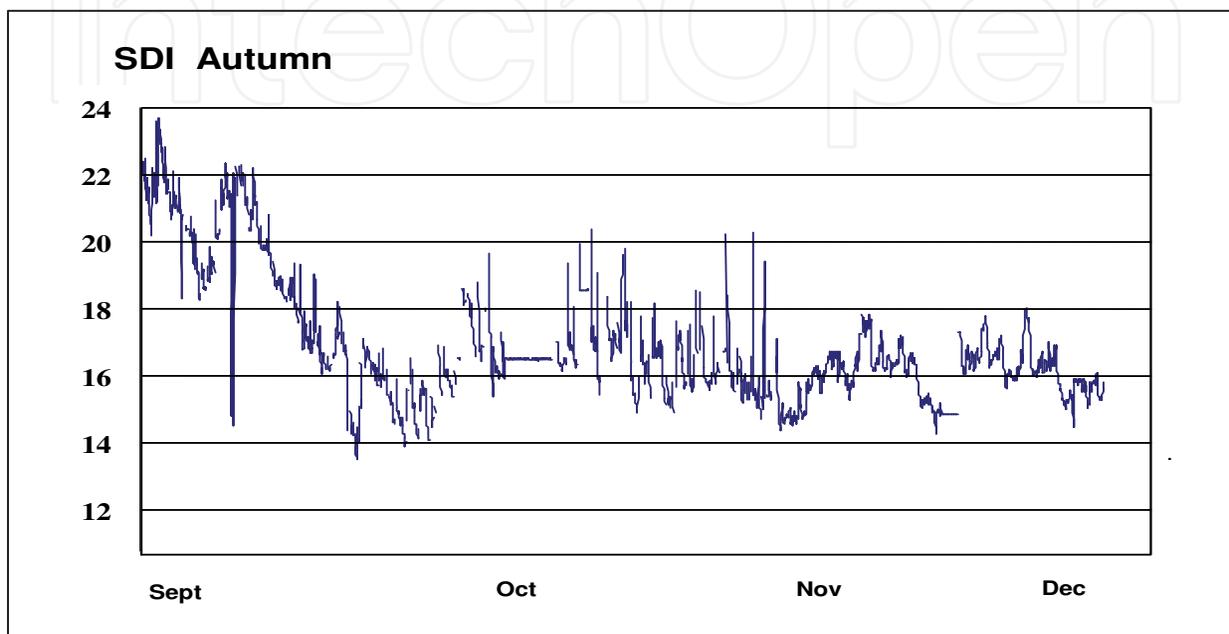


Fig. 4. SDI₃ of seawater from September to December (Mediterranean Site)

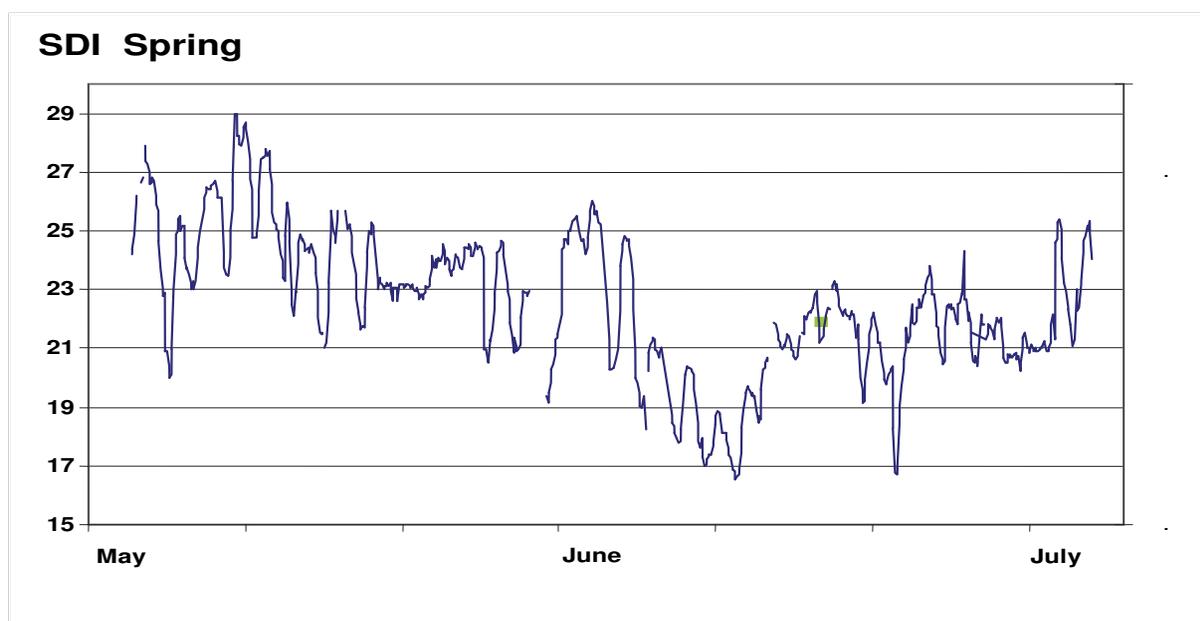


Fig. 5. SDI₃ of seawater from May to July (Mediterranean Site)

2.1.5.2 Modified Fouling Index

Schippers & Verdouw have proposed a fouling index called “Modified Fouling Index” (MFI) which takes into account fouling mechanisms (Schippers & Verdouw, 1980). They considered that the fouling of a flat-sheet membrane in dead-end filtration at constant transmembrane pressure takes place in three steps: (1) pore blocking, (2) formation of an incompressible cake and (3) formation of a compressible cake. This mechanism is based on the laws of dead-end filtration at constant transmembrane pressure or constant flux which give explicit relationships between filtration time and permeate flow rate (Boerlage et al., 1997; 2002a ; 2002b; 2004). This is illustrated by figure 6 which represents the evolution of the ratio t/V as a function of V , where t is the filtration time and V the cumulated permeate volume.

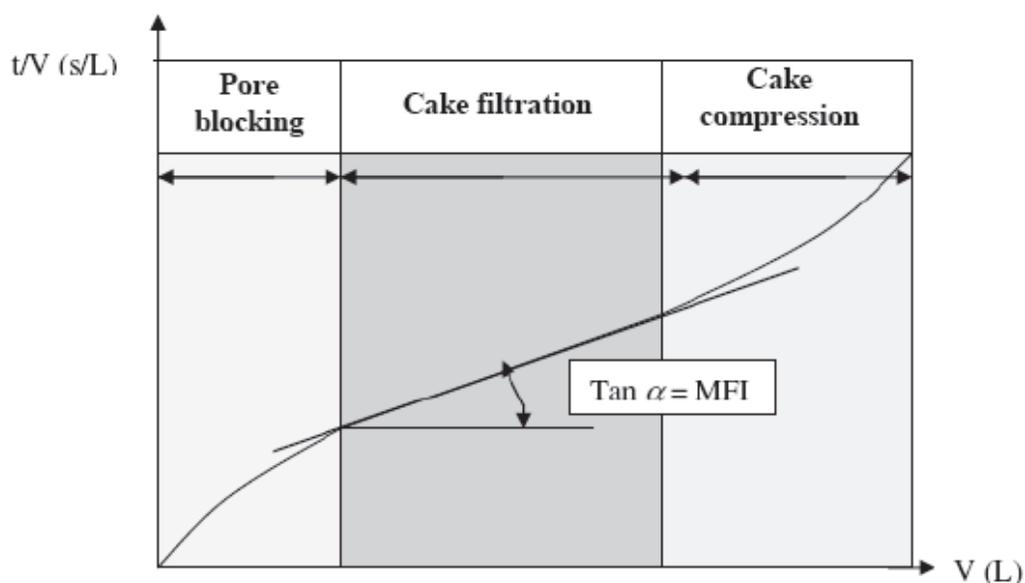


Fig. 6. Evolution of the t/V ratio vs. Volume

Theoretical background making the hypothesis that the only mechanism that increases the apparent resistance during the filtration test is the formation of a cake on the membrane surface. The global relation is given by :

$$\frac{t}{V/A} = \frac{\eta R_m}{\Delta P} + MFI \frac{V}{A} \quad \text{with} \quad MFI = \frac{\eta \alpha C_p}{2\Delta P}$$

where t is filtration time (s), V/A is the permeate volume produced per membrane area (m^2), ΔP is the TMP (Pa), A the membrane area (m^2), R_m the resistance of the membrane (m^{-1}), R_c the resistance of the cake (m^{-1}), α is the specific cake resistance, C_p is the concentration of particles in the feed water, and η is the dynamic viscosity of the water ($N \cdot s \cdot m^{-2}$).

The MFI could be represented by the value of the specific resistance of the cake formed by the fouling components of the water deposited on a membrane during a standard filtration test. The main advantage of the MFI over SDI thus lies in the fact that MFI is a dynamic index which takes into account the evolution of membrane fouling all along a filtration test whereas SDI is only based on an initial and a final measurement.

2.2 Chemical constituents

The chemical constituents of the raw water must be determined to provide information for the pre treatment selection.

2.2.1 Ions content

2.2.1.1 Total dissolved solids (TDS)

Most of the dissolved chemical constituents or salts found in seawater have a continental origin. Only six **elements** and **compounds** comprise about 99% of sea salts: chlorine (Cl⁻), sodium (Na⁺), sulphates (SO₄⁻²), magnesium (Mg⁺²), calcium (Ca⁺²), and potassium (K⁺). Because salinity is directly proportional to the amount of chlorine in sea water, and because chlorine can be measured accurately by a simple chemical analysis, salinity *S* was redefined using chlorine content. The following relation is often used:

$$S(\text{g/L}) = 1.80655 \text{ Cl}(\text{g/L})$$

The TDS of sea water (usually 35 g/L) is made up by all the dissolved salts present in the water. Landlocked seas like the Black Sea and the Baltic Sea have differing concentrations. This world map shows how the TDS of the oceans changes slightly from around 32 g/L (3.2%) to 40 g/L (4.0%). Low TDS is found in cold seas, particularly during the summer season when ice melts.

High salinity is found in the ocean coinciding with the continental deserts. Due to cool dry air descending and warming up, these desert zones have very little rainfall, and high evaporation. The Red Sea located in the desert region but almost completely closed shows the highest salinity of all (42 g/L) but the Mediterranean Sea follows as a close second (38 g/L). Lowest salinity is found in the upper reaches of the Baltic Sea (5 g/L). The Dead Sea is 240 g/L saline, containing mainly magnesium chloride MgCl₂. Shallow coastal areas are 2.6-3.0 g/L saline and estuaries 1-3g/L. The overall ion content of the Arabian Gulf is higher as compared to the oceans and the Mediterranean Sea, the sites located on the Pacific Ocean and the Atlantic Ocean show a slightly lower salt content than the Mediterranean Sea, and this could impact in some cases the design of the RO systems, notably with respect to the boron removal. Overall, these differences of salt content will not impact the selection of the pre treatment strategy, but will impact the sizing of the reverse osmosis systems (Blute et al., 2008).

However, if the major part of ions analysed in the sea water will not impact the pre treatment design, iron and manganese have to be removed before the water feeds the reverse osmosis membrane. The explanation is presented above.

2.2.1.2 Specific ions: Iron & manganese

Iron oxides as well as manganese play an important role in the removal of trace elements from seawater. In the sediments, iron and manganese oxides transported with settling particles are reduced to ferrous and manganous ions during oxidation of organic matter. Ferrous and manganous ions diffuse upward through interstitial water and are transformed again to iron and manganese oxides at the sediment-water interface. Iron and manganese oxides take up dissolved trace elements released from settling particles during diagenesis.

2.2.1.2.1 Iron (Fe)

The behavior of iron is greatly different from that of manganese. Iron chemistry, such as inorganic speciation and organic complexes, in seawater is very complex and not yet fully

understood. The hypothesis that dissolved iron concentration is a key variable that controls phytoplankton processes in ocean surface waters is proved today. Iron is an essential micronutrient for phytoplankton growth, as an important component of such biochemical processes as photosynthetic and respiratory electron transport, nitrate and nitrite reduction, chlorophyll synthesis, and a number of other biosynthetic or degradative reactions (Weinberg, 1989; Kuma, 1996; Geider & Roche, 1994).

The oxidation rate constant of Fe^{2+} tends to increase with increasing pH and temperature, and decrease with increasing salinity (ionic strength). Millero (Millero, 1980) proposes the relationship given by:

$$\text{Log } k = 21.56 - 1.545/T - 3.29 I^{1/2} + 1.52 I$$

where k is the oxidation rate constant, T is the absolute temperature and I is the ionic strength.

The inorganic speciation of Fe^{3+} in seawater is dominated by its hydrolysis behavior and ready tendency to nucleate into particulate Fe^{3+} hydroxides. In general, iron in oxic seawater around pH 8 is present predominantly in the particulate iron oxyhydroxide (FeOOH), which has an extremely low solubility, (Millero, 1987, 1988) and thermodynamically stable. Numerous studies of both the solubility of iron in seawater and of the detailed hydrolysis behavior of Fe^{3+} as a function of pH have been undertaken over the last 25 years. Number of studies of the Fe^{3+} hydroxide solubility in seawater suggest that the Fe^{3+} solubility is controlled by organic complexation (Kuma et al., 1996; Millero, 1998; Liu & Millero, 2002; Tani et al., 2003), which, subsequently, regulates dissolved iron concentrations in seawater (Kuma et al., 1998, 2003; Johnson et al., 1997; Archer & Johnson, 2000; Nakabayashi et al., 2001). In general, the dissolved Fe concentrations in the surface mixed layer were lower than those in mid- depth and deep waters and the values of Fe^{3+} solubility in the surface water, resulting from the active biological removal of dissolved Fe and excess concentration of Fe-binding organic ligands (Rue & Bruland, 1995 & 1997; Kuma et al., 1998). The dissolved Fe profiles generally show low concentrations at the surface (0.2 – 50 $\mu\text{g/L}$), abroad maximum from 500 m to 1000 m (10 –150 $\mu\text{g/L}$). The vertical profiles are similar to those of Fe^{3+} solubility, suggesting that dissolved Fe concentrations in deep ocean waters are controlled primarily by the Fe^{3+} complexation with natural organic ligands, which were released through the oxidative decomposition and transformation of biogenic organic matter in mid-depth and deep waters. In oxic seawater, iron is present predominantly in the insoluble (extremely low solubility). Therefore, phytoplankton growth is controlled by the Fe^{3+} solubilities and the iron dissolution rates of colloidal Fe^{3+} phases (Wells et al., 1983, Stumm & Lee, 1961; Gabelich et al., 2005)).

In previous studies (Kuma et al. 1999 & 2000), it has been suggested that the natural organic- Fe^{3+} complexes and acidic Fe^{3+} supplied by river inputs play an important role in supplying supersaturated bioavailable Fe^{3+} , above the equilibrium concentration of Fe^{3+} , in estuarine mixing systems and coastal waters through its dissociation and hydrolytic precipitation at high pH of seawater and high levels of seawater cations (Stumm & Morgan 1962). The exchange reaction between organic- Fe^{3+} complex and major alkaline earth metals (such as Ca^{2+} and Mg^{2+}) in seawater is one of the most important processes resulting in dissociation of organic- Fe^{3+} complexes and subsequent Fe^{3+} hydrolytic precipitation. The high concentration of alkaline earth cations in seawater probably caused the dissolution of organic Fe^{3+} complexes through the metal exchange reaction. In estuarine and coastal

waters, the natural dissolved organic-Fe³⁺ complexes supplied by river input such as fulvic-Fe³⁺ may play an important role in the supply of biological available iron by heightening the dissolved inorganic Fe³⁺ concentration, through the dissociation of organic-Fe³⁺ complexes during mixing with seawater.

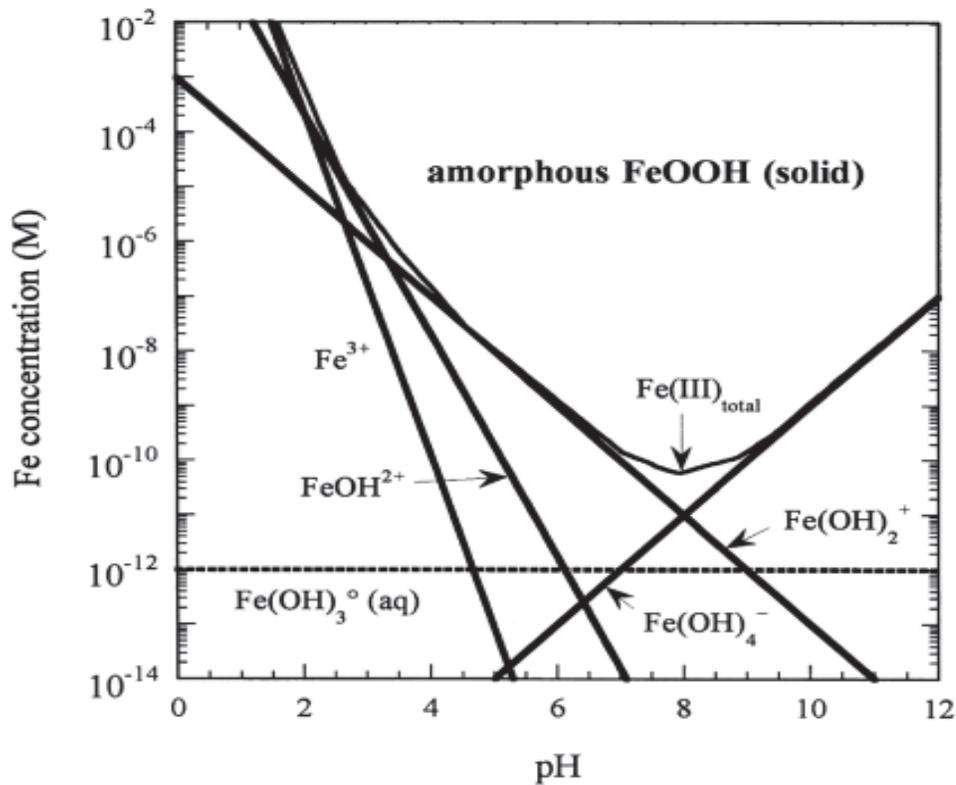


Fig. 7. Iron solubility of solid amorphous FeOOH



Fig. 8. Iron deposit on RO membrane

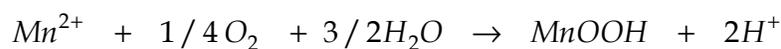
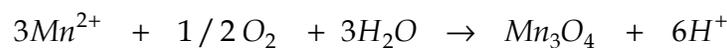
The limitation recommended by the membrane suppliers for iron is low than 50 $\mu\text{g/l}$ due to its possible oxidation on the membranes which damages irreversibly the membrane surface.

2.2.1.2.2 Manganese (Mn)

The chemistry of manganese in seawater is complex and is largely governed by pH and redox conditions. Mn^{2+} dominates at lower pH and redox potential, with an increasing proportion of colloidal manganese oxyhydroxides above pH 5.5 in non-dystrophic waters (Lazerte & Burling, 1990). Oxidation rates of manganese increase with increasing pH. The Mn^{2+} ion is more soluble than Mn^{4+} , therefore, manganese will tend to become more bio-available with decreasing pH and redox potential. The presence of chlorides and sulphates increases manganese solubility (Schaanning et al., 1988).

Manganese exists in the seawater in two main forms: Mn^{2+} and Mn^{4+} . Transition between these two forms occurs via oxidation and reduction reactions.

Based on laboratory experiments, the oxidation of Mn^{2+} to Mn^{4+} occurs as a two-step process in which solid phase Mn-bearing oxides (e.g., Mn_3O_4) or oxyhydroxides (e.g., β - $MnOOH$)



are initially formed and then undergo slower disproportionation or protonation reactions, ultimately forming Mn^{4+} oxides (MnO_2) (Tebo et al., 2004).

Then, the stoichiometry of Mn^{2+} oxidation based on measurements of O_2 consumption and H^+ production follows the chemical reaction typically written for Mn^{2+} oxidation (de Vrind et al. 1986, Adams & Ghiorse 1988):

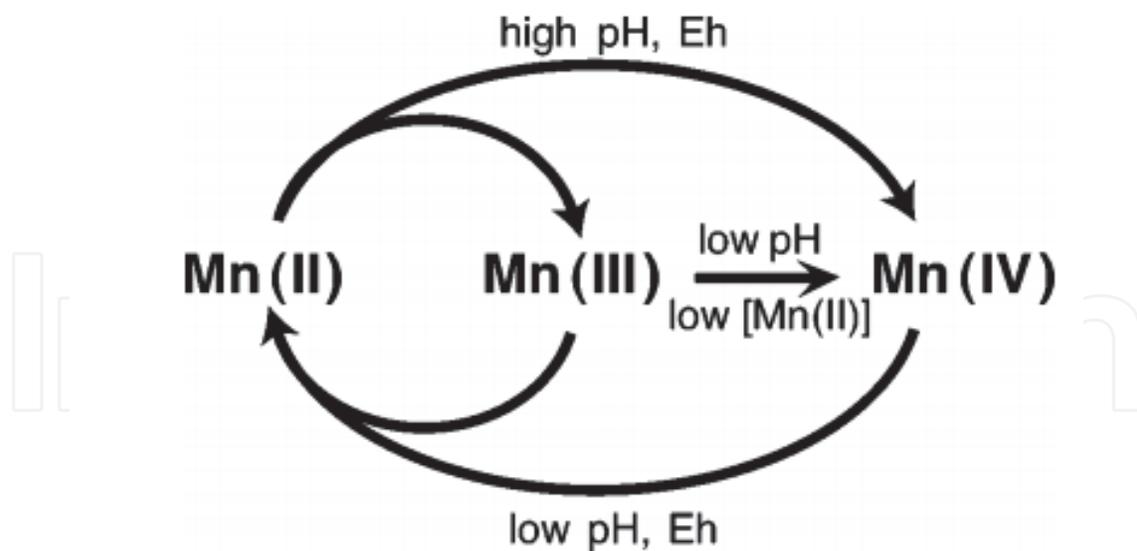
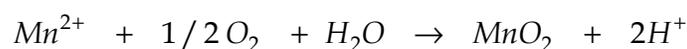


Fig. 9. The Mn cycle of oxidation states

In oxygenated waters, Mn^{2+} is thermodynamically unstable with respect to the oxidation to insoluble manganese oxides. However, owing to the relatively slow kinetics of oxidation of Mn^{2+} in seawater, the low equilibrium concentrations are rarely attained. The ocean distribution of the metal appears to be dominated by external input sources which lead to maxima in the surface waters.

Concentrations of manganese in open seawater range from 0.4 to 10 $\mu\text{g}/\text{litre}$. In the North Sea, the north-east Atlantic Ocean, the English Channel, and the Indian Ocean, manganese content was reported to range from 2 to 230 $\mu\text{g}/\text{litre}$. Levels found in coastal waters of the Irish Sea and in the North Sea off the coast of the United Kingdom ranged from 2 to 25.5 $\mu\text{g}/\text{litre}$ (Alessio et al.,2007). Hypoxic concentrations below 16% saturation can increase the concentration of dissolved manganese above that normally found in seawater to concentrations approaching 1500 $\mu\text{g}/\text{litre}$ (Mucci,2004). The concentration of dissolved Mn^{2+} in the anoxic waters is probably limited by its solubility with respect to MnCO_3 .

Seawater	Manganese concentration ($\mu\text{g}/\text{L}$)	Iron Concentration ($\mu\text{g}/\text{L}$)
North Sea	< 5 to 4	5 to 4
Indian Ocean,	2 to 180	2 to 220
north-east Atlantic Ocean,	5 to 80	25 to 230
English Channel	3 to 4	3 to 4
Irish Sea	2 to 25	2 to 25
Arabian sea	< 5	< 10
Red sea	5-10	5 - 100
Mediterranean sea	5 - 10	< 15
Oman sea	< 5	< 10

Table 2. Evolution of the Fe & Mn concentrations in different seawaters

Neutral streams with elevated levels of iron and manganese can develop blooms of ferromanganese-depositing bacteria with oxide deposition zones. The limitation recommended by the membrane suppliers for manganese is 20 $\mu\text{g}/\text{L}$, due to its possible oxidation on the membrane which will damage irreversibly the membrane surface. The following figures (figures 10 & 11) show the damage observed on the reverse osmosis membrane due to the oxidation of Mn^{2+} into Mn^{4+} . Scanning Electron Microscopy - Energy Dispersive X-ray Analysis (SEM-EDXA) are used also to study membrane surface and identify the elemental composition of the foulant.



Fig. 10. Deposit of MnO_2 on RO membrane

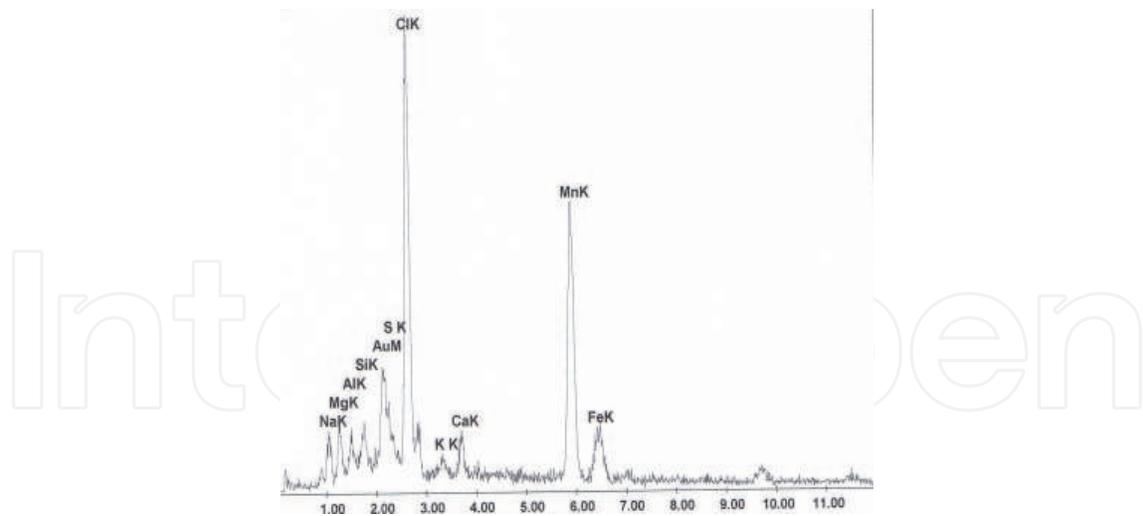


Fig. 11. Abnormal presence of Mn on RO membrane

Elemental determination with the SEM-EDXA system is based on analysis of X-rays produced via electron beam excitation of a sample area. This technique allows analysis of a sample in selective areas. The limited depth of analysis (typically a few microns), and the possibility to select the area of interest under the electron beam, allows for local analysis to reveal differences in composition.

The identification and measurement of individual peak intensities in the X-ray spectrum is done with a computerized multi-channel analyzer. Samples are covered by gold (Au) for analysis.

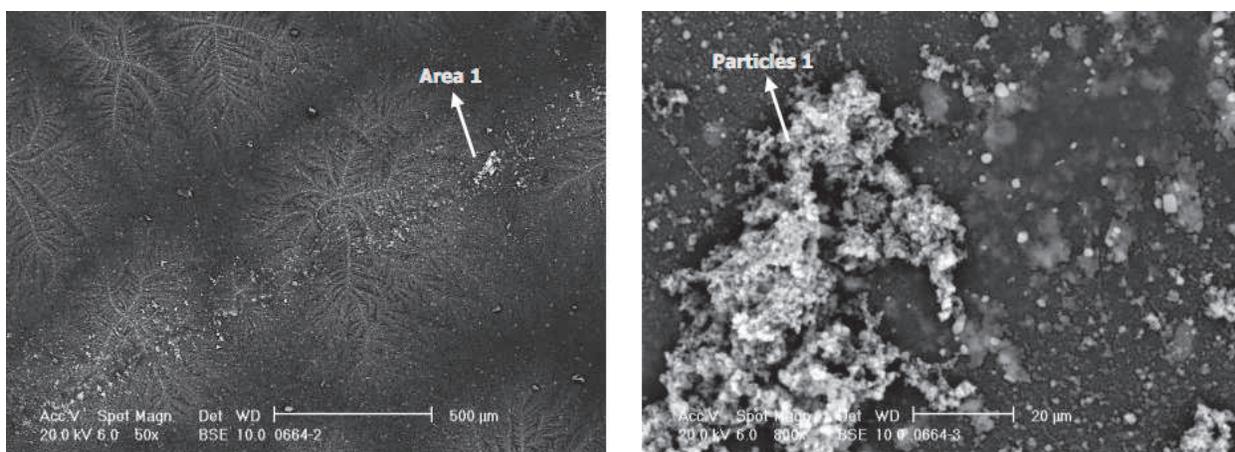


Fig. 12. Microphotographs 1 & 2 General view of membrane and its foulant.

The microphotographs show membrane surface which is completely covered by a deposit, composed of granulated particles (figure 12). EDX analysis on the particles show the presence of chlorine (Cl), sodium (Na), manganese (Mn), sulphur (S), magnesium (Mg), iron (Fe), calcium (Ca) and potassium (K). A survey of the Mn concentration in the feed water before the RO membrane is recommended.

2.3 Organic substances

It is well known that fouling in Reverse osmosis membranes causes serious problems including a gradual decline of membrane flux thereby decrease in permeate production, an

increase in AP thereby increasing requirement of high pressure pump rating and a degradation of membrane itself. All these factors reflect on the cost of water production. Hence, now-a-days attempts are being made to deplete the concentration of organic from the feed to RO to overcome these problems by various pre-treatment methods. Various studies have been carried out to find the factors affecting organic fouling. In order to understand organic fouling, it has been necessary to thoroughly characterize organic matters.

The dissolved organic matter is not a single substance but a mixture of many aliphatic and aromatic compounds. However, among the total dissolved organic substance in seawater, 90% of them are represented by the humic materials or substances. Number of studies (Amy,2008) have demonstrated that the two main types of bulk organic matter (OM) of interest in seawater desalination plant are:

Allochthonous natural organic matter (NOM) dominated by humic substances and Autochthonous or algal organic matter mainly consisting of extra cellular macromolecular and cellular debris.

Moreover, organic matters usually have functional groups such as carboxyl (-COOH) and phenolic groups (-OH). It has been known that these functional groups play a key role in organic fouling since the functionality could change depending on water chemistries. Humic substances (HS) are generated from the degradation of organic matter and represent a significant fraction of the total organic matter in water. The HS are mostly constituted of humic acids (HA) and fulvic acids (FA) in natural water. Humic and fulvic acids possess a significant negative charge density and a bulky macromolecular shape. Subsequently, humic and fulvic acids are not as easily adsorbed onto such a membrane, even if it is intrinsically hydrophobic. Natural Organic matters exhibit relatively high specific UV absorbance values and contain relatively large amounts of aromatic carbon. It has been known that the rate and extent of organic fouling tends to be accelerated with decreasing pH, increasing ionic strength and increasing divalent cations. The electrostatic repulsion was increased at low pH condition, almost completely deprotonating carboxylic and phenolic groups. The electrostatic repulsion was reduced at higher ionic strengths and higher divalent cation concentrations, due to electric double layer around charged organic matters is compressed (Kim et al.,2009b, Krasner et al.,1996)).

There are several measurement procedures for the OM used for the characterization of the organic substances present in the seawater, including:

- Total organic Carbon (TOC) representing the total amount of OM including the particles content
- Dissolved organic Carbon (DOC) representing the amount of OM dissolved in the raw water UVA absorbance @254 nm, reflecting the aromatic character of OM
- SUVA (ratio UVA_{254}/DOC) representing the part of the humic substances versus the non-humic substances.

The LC-OCD stands for "Liquid Chromatography-Organic Carbon Detection". It consists of a size exclusion chromatography column, which separates hydrophilic organic molecules according to their molecular size. Its values refer to "mass of organic bound carbon" (OC), not to total mass of compounds. The underlying principle is the diffusion of molecules into the resin pores (Her et al.,2002; Serkis & Purdue,1990). This means that larger molecules elute first as they cannot penetrate the pores very deeply, while smaller molecules take more time to diffuse into the pores and out again. The separated

compounds are then detected by two different detectors: a UV detector (absorption at 254 nm) and a DOC detector (after inorganic carbon purging). Depending on the size of the molecules, the composition of the organic matter can be obtained (figure 13). With a bespoke algorithm program, the different peaks can be integrated to evaluate the proportion of each organic fraction. The Dissolved Organic Carbon measurement can be carried out using a by-pass mode. In this case, the samples go straight through the TOC reactor and analyzer. Figure 15 depicts a typical chromatograph with the different peaks and their associated organic fractions.

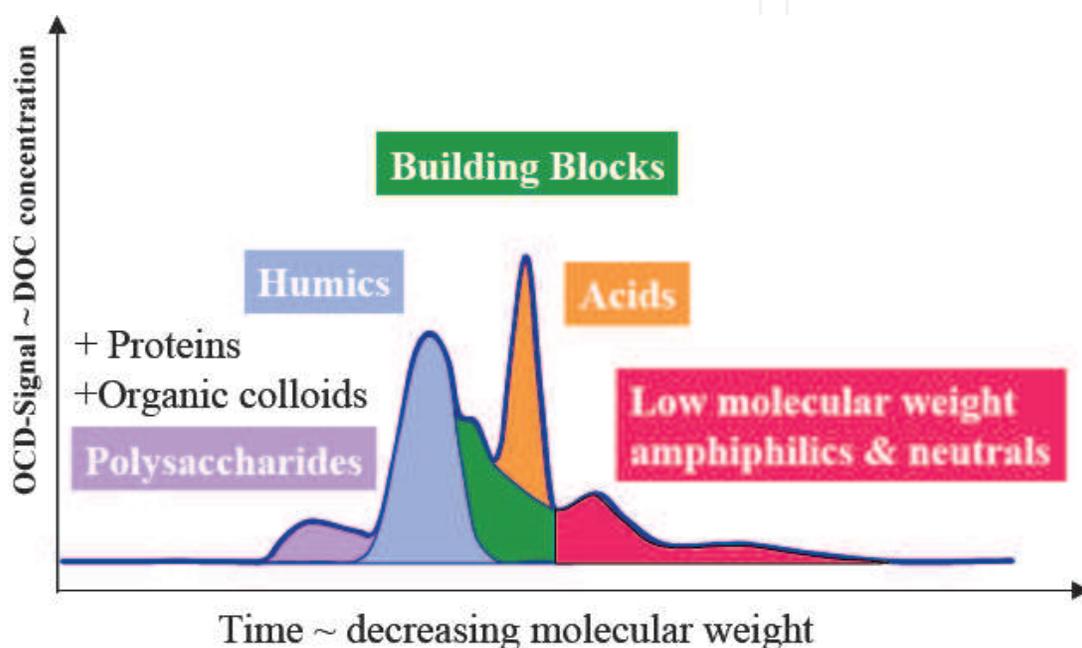


Fig. 13. Chromatograph obtained with LC-OCD chromatography

Biopolymers (polysaccharides amino sugars, polypeptides, proteins; "EPS"): This fraction is very high in molecular weight (100.000 - 2 Mio. g/mol), hydrophilic, not UV-absorbing. Polysaccharides exist only in surface waters.

Humics (HS): There is a tight definition for HS based on retention time.

Building Blocks (HS-Hydrolysates): The HS-fraction is overlain by broad shoulders which are sub-units ("building blocks") of HS with molecular weights between 300-450 g/mol. Building Blocks are perhaps weathering and oxidation products of HS.

LMW (Low Molecular Weight) & Organic Acids: In this fraction, all aliphatic low-molecular-mass organic acids co-elute due to an ion chromatographic effect.

LMW Neutrals: Only low-molecular weight weakly charged hydrophilic or slightly hydrophobic compounds appear in this fraction, like alcohols, aldehydes, ketones, amino acids. The hydrophobic character increases with retention time, e. g. pentanol at 120 min.

A number of membrane related studies have demonstrated the use of LC-OCD in characterising dissolved organic matter (DOM) in surface waters (LeParc et al.,2007; Hong & Elimeleh,1997; Kim et al.,2009) and to identify the constituents that cause organic fouling.

DOC fractions	Size range (Da)	Composition
Biopolymers	> 20 000	Polysaccharides (e.g;TEP) & proteins
Humic substances	~ 1000	Humic and fulvic acids
Building Blocks	300 - 500	Oxidation products of humics
LMW organic acids	< 350	All aliphatic low molar weight organic acids
LMW neutrals	< 350	Alcohols, aldehydes, ketones and amino acids

Table 3. Typical sizes of DOC fractions detected by LC-OCD

Each LC-OCD system has an online organic carbon detector (OCD) that can measure carbon down to a low ppb-range. An online organic nitrogen detector is also connected to the system to measure levels of organic nitrogen. (Passow,2000,2002 ; Wotton,2004,LeParc et al.,2007):

1. Total exopolysaccharides (TEP) monitoring showed that colloidal TEP (82-93%) was more abundant than particulate TEP (7-18%) in the coastal seawater source.
2. The observed increase of total TEP in the raw water in spring coincided with an increase in chlorophyll-a and TOC.
3. LC-OCD analysis results show that biopolymers in the raw water, which were dominated by polysaccharides, doubled during spring and summer periods.

Seawaters collected from open intakes at various sites had a fairly low and stable TOC levels, ranging from 0.8 to 1.5 mg/L (LeParc et al., 2007). Figures 15 & 16 demonstrate the advantage of using beach well as seawater feed as compared to open intake. Firstly, the TOC levels of beach well seawater are slightly lower, but most importantly, the polysaccharides are almost completely removed through the slow filtration occurring when beach wells are used. Beach wells are therefore an excellent line of defense against organic and biological fouling on the RO membranes as polysaccharides are easily absorbed onto spiral-wound membranes. Then, polysaccharides foster the microbial attachment onto the reverse osmosis membranes, and these high molecular weight compounds can also be used as nutrients by the bacteria, thus facilitating the development of a biofilm onto the membranes.

The NOM characterization through LC-OCD chromatography allows to demonstrate that the NOM content (Her et al.,2002; Mitra et al.,2009) may vary depending on the seasons. Figure 5 notably shows that samples collected during fall have lower polysaccharides levels than samples during summer (LeParc et al.,2007). These lower polysaccharides levels during colder seasons correspond also with lower $SDI_{3 \text{ min}}$ values, and lower bacterial counts. It already appears that the bacterial and algal activities, enhanced with warmer water temperatures and higher sun exposure, are major water quality factors impacting the fouling potential of open intake seawaters, and therefore, will impact the selection of the pre treatment strategy.

NOM can be fractionated into hydrophobic, transphilic and hydrophilic acid fractions according to the XAD-8/4 resin method (Krasner et al.1996). Conventional methods such as coagulation or filtration through activated carbon are efficient to remove a part of the organic load from the feed of RO.

2.4 Algae

Algae, dinoflagellates and cyanobacteria are a large and varied group of photosynthetic organisms that are found in oceans. Algal and cyanobacterial cells contain chlorophyll and other photosynthetic pigments. They exist in a wide variety of forms; from single cells and strings of cells, through to complex multicellular seaweeds. The most familiar algae are red, brown and green seaweeds, which are part of a group of large multicellular algae known as macroalgae. However, the majority of algae and cyanobacteria are single-celled species that float freely in the water column; they are invisible to the naked eye and collectively form a group known as phytoplankton. Excessive growth of phytoplankton can occur in coastal seawater and estuaries causing the seawater to appear coloured typically red, or brown close to the surface of the seawater (figure 14) due to the density and numbers of algae.

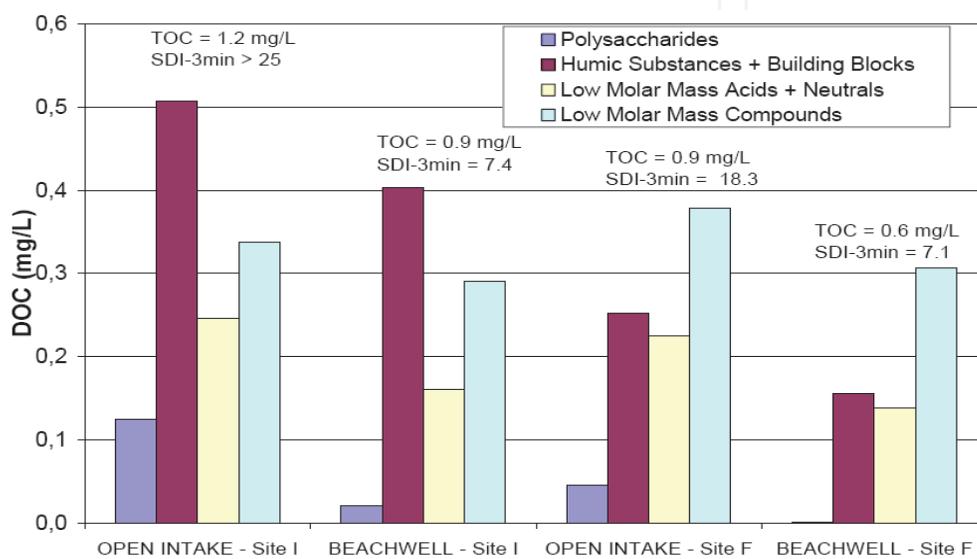


Fig. 14. Impact of the seawater intake type on the NOM content

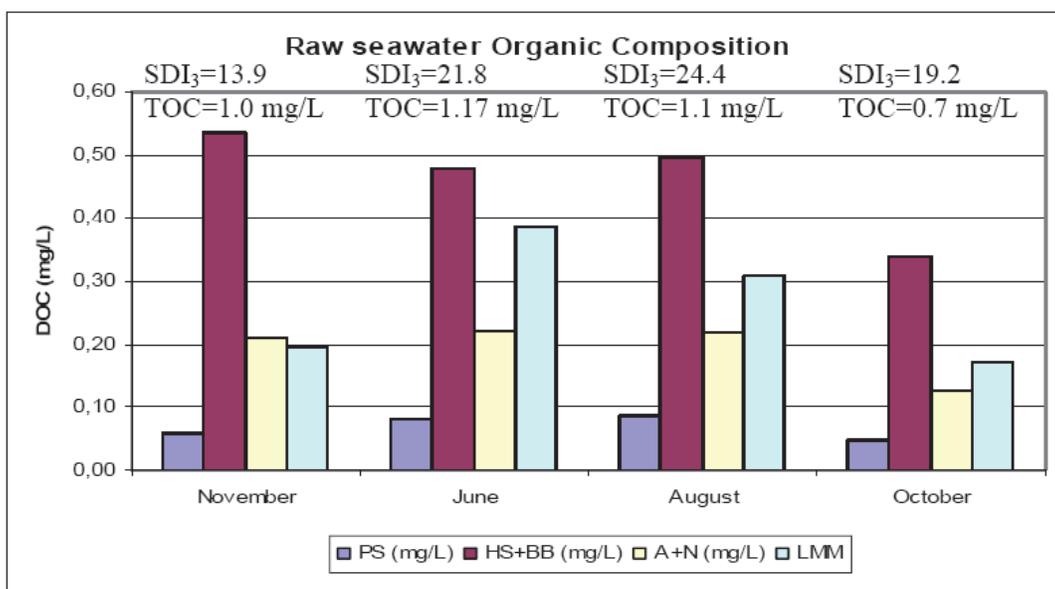


Fig. 15. Seasonal variations of the NOM content of the raw seawater- Mediterranean Sea - Open Intake

This is commonly referred to as an algal bloom. Strictly speaking the most accurate term is “phytoplankton bloom”. Algal blooms can pose problems to the operation of a desalination plant. Extremely high algal numbers result in a high suspended solids load and organics. Most marine algal blooms are harmless, resulting only in a discolouration of the water. Algae exist in natural waters in a variety of sizes, geometric structures and cell wall materials. (figures 16 & 17). Although most algae are microscopic (ranging from 2 μm to 100 μm), a number of forms are macroscopic, with some species growing to lengths over 100 ft (Brock & Clyne, 1984). Plankton organisms are classified by size from femtoplankton (smaller than 0.2 μm), picoplankton (0.2-2 μm) to megaplankton (0.2-2mm). Phytoplankton consists of organisms from bacteria to diatoms and large dinoflagellates (like sea spark, *Noctiluca scintillans*). Their biomass can be estimated by measuring their chlorophyll (green pigment) from light measurements. However, other pigments (brown, red) are also common and the amount of chlorophyll is only a small part of biomass. So, even quantifying the amount of phytoplankton is almost impossible.

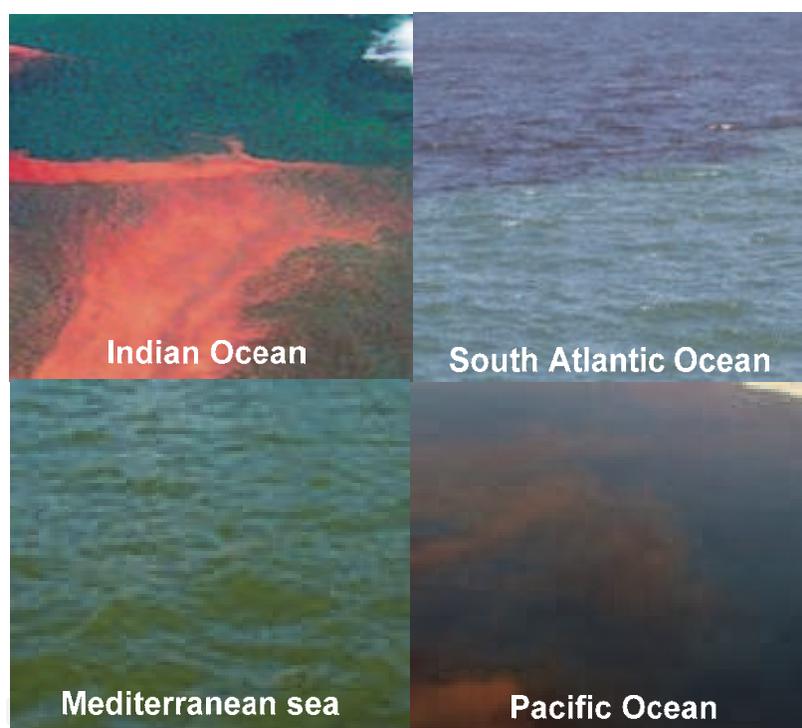


Fig. 16. Algae bloom in different sea waters

Advanced analytical tool was developed to allow thorough characterization of seawater samples the enumeration of phytoplankton and bacteria. Results (Leparc et al.,2007) obtained on raw seawater samples showed that the bacteria and phytoplankton counts appear to be positively correlated with (a) the concentration of polysaccharides, organic compounds highly fouling for reverse osmosis, and with (b) the SDI values of both the raw and pre-treated seawaters. The other conventional water quality parameters such as turbidity and TOC does not show any correlation with the fouling potential of both the raw and pre-treated seawaters. Indeed, biofouling due to bacteria attachment and growth on the membranes is one of a major threat for seawater reverse osmosis plant and the presence of polysaccharides in the pre-treated water increase that threat as these organic compounds are very prone to absorb onto the RO membranes and then be used as nutrients by bacteria.

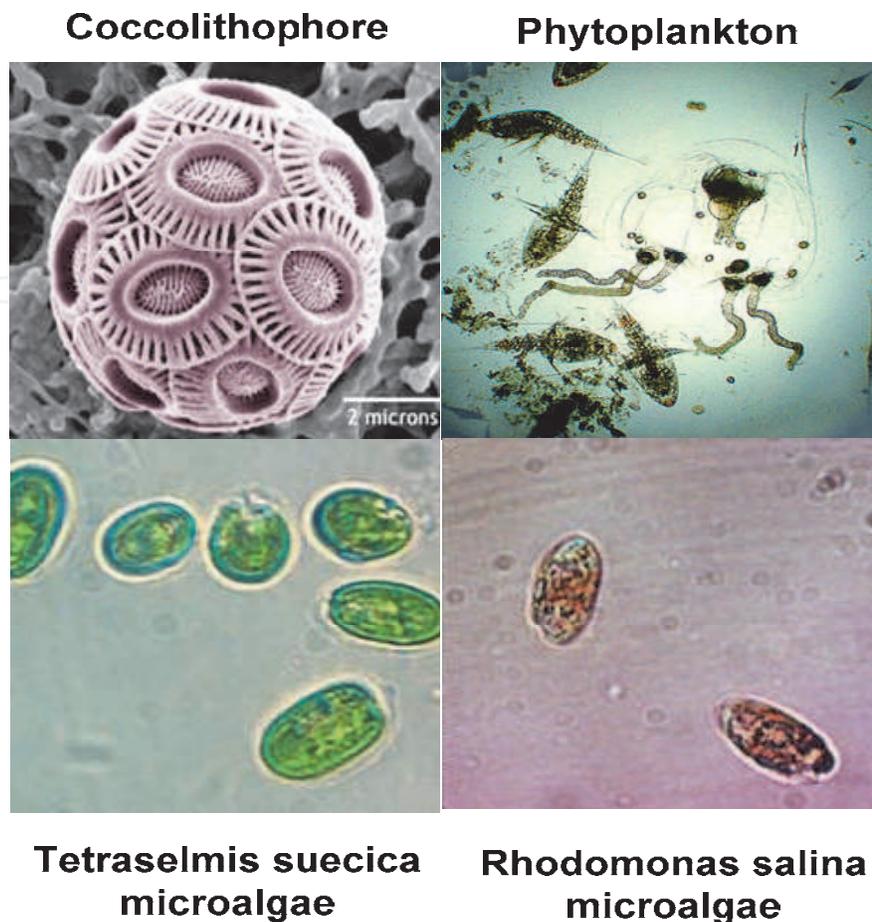


Fig. 17. Types of algae found in the seawater

Overall, the use of these complementary water quality parameters should provide engineers with valuable information to design, build, and operate more efficient and sustainable seawater reverse osmosis plants as future design and operation engineering practices will take into account more detailed information on site-specific water quality challenges.

Picophytoplankton species corresponds to the smaller size species of phytoplankton. The concentrations of picophytoplankton species appeared interesting to be monitored in both raw and pretreated seawaters because phytoplankton species with a size greater than 100 μm are very likely to be removed through the pretreatment processes and therefore, smaller size algal organisms, such as picophytoplankton, are the most likely to pose a threat to the RO membranes.

Figure 18 shows the concentrations of phytoplankton species (Le Parc et al., 2007) at various seawater desalination sites. The following observations can be made:

- the Arabian Gulf seawater has a significantly higher algal activity as compared to the Mediterranean Sea (and other oceans - data not shown),
- the positive impact of the beachwell is again demonstrated, as concentrations of phytoplankton species in beachwell seawater is more than one level of magnitude lower than that of surface seawaters.

Red Tide Events - algae bloom.

Red tide is a complex phenomenon involving many different types of creatures with different characteristics covering large areas. "Red Tide" is a common name for such a

phenomenon where certain phytoplankton species contain reddish pigments and the water appears to be coloured red. They disrupt the ecosystems causing large scale environmental damage. Most of the red tides cause large scale fish kill and the killed fish will be washed to the shores resulting with a bad smell on the beaches. Red tide events may occur in the spring-summer period of the year and may result in increase of algae content in the source water (intake turbidity increases to up to 10 NTU); creased organics (TOC concentration increases to 4 -.5 mg/L) and apparent colour and odour. One or more sequential red tide events may occur per year and each event may last 6 to 8 weeks. Recent red tide in 2006 and 2008 in the Arabian Gulf caused considerable environmental damage and economic losses in the Gulf countries (Bauman et al;2010, Choules et al.,2007) and also in Iran, Iraq and Pakistan.

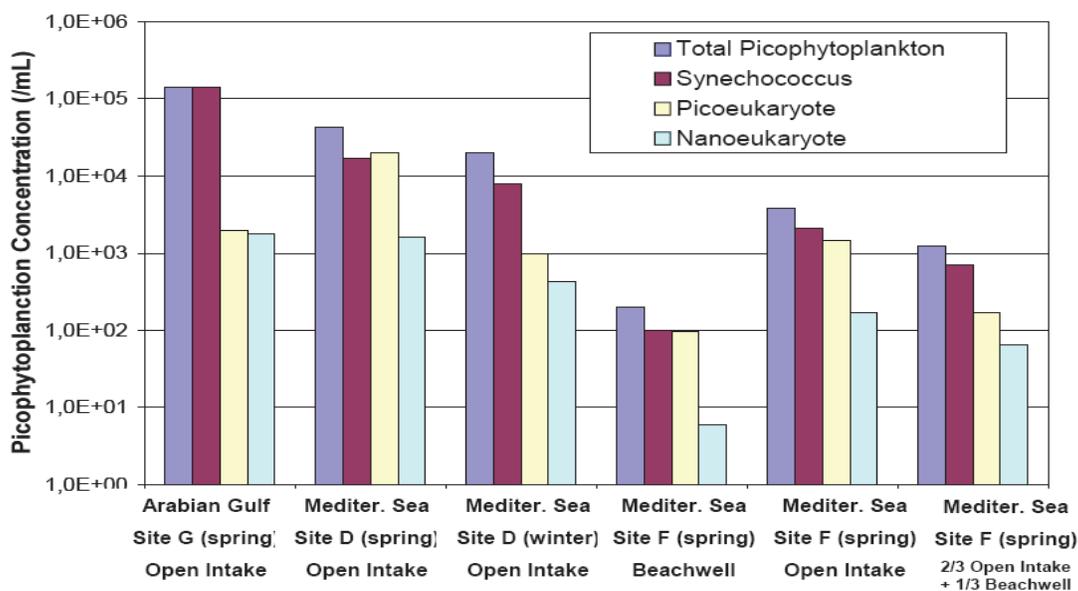


Fig. 18. Phytoplankton concentrations in various raw seawaters (log-scale)

Red tide is not caused by any single organism, although some are more common than others. Many of these species are regional and are quite adoptive. The two main types of toxic red tide creatures are certain phytoplanktons which produce mostly chemical toxins harmful to fisheries and the environment and a group of dinoflagellates that produce mostly neurotoxins harmful to humans and marine mammals. Most of the harmful algal blooms from 1988 to 2008 in Oman were caused by some type of dinoflagellates.

Seawater desalination plants, power plants and other plants that use seawater for cooling purposes were forced to close during the last red tide in the Arabian Gulf region to avoid the fouling and blockage problems.

Algae blooms may occur in freshwater as well as marine environments. Typically only one or a few phytoplankton species are involved and some blooms may be recognized by discoloration of the water resulting from the high density of pigmented cells. Although there is no officially recognized threshold level, algae can be considered to be blooming at concentrations may reach millions of cells per mL, depending on the causative species (figure 20). Colours observed are green, yellowish-brown, or red. As more algae and plants grow, others die. This dead organic matter becomes food for bacteria that decompose it. Algal blooms may also be of concern as some species of algae produce neurotoxins .At the

high cell concentrations reached during some blooms, these toxins may have severe biological impacts on wildlife. Algal blooms (Hallegraeff, G.M.,1993) known to naturally produce biotoxins are often called Harmful Algal Blooms (HABs).

2.5 Oil and chemical spills

Sometimes, oil and chemical spills have been detected in the seawater. The range of the concentration is 0 - 10 mg/L. These can affect the desalination plant. Emulsified oil and grease are the principle sources of immiscible liquid fouling in desalination facilities. Flotation appears as the most efficient treatment for this contaminant. A polishing on granular activated carbon is sometimes used to maintain acceptable levels upstream the reverse osmosis membranes.



Fig. 19. Algal bloom in Fujairah coast

3. Selection of the pre treatment

The characterization of the seawater through the main parameters which could be removed along the pre treatment process such as, Fe, Mn, natural organic matter, SDI, bacteria and algal are very useful from many aspects: - better understanding of site-specific seawater quality and its seasonal variation; - improved assessment tools to evaluate and predict the impact of raw seawater quality on the performance of a conventional pre treatment process, - additional and complementary indicators to the conventional water quality parameters (SDI, turbidity) for quantifying the risks of fouling on the RO units.

Before raw water is desalinated, the undesirable materials will be removed or reduced to acceptable levels. Without adequate pre treatment, desalination facilities are destined for reduced lifetimes, shortened periods of operation, and high maintenance.

After the completion of physical, chemical, and bacteriological analysis of the selected feed water, the type of pre treatment can be examined and is used to bring a saline feed water within limits so that a desalination process can be used. One of the most significant factors in successfully (and cost-effectively) operating a reverse osmosis (RO) desalination plant is the ability of the pre treatment system to consistently produce well-filtered and relatively particle- and microbe-free water for feed to the RO system. Pre treatment is critical in RO applications because it directly impacts fouling of the RO membranes. Fouling of the RO

membranes results in increased operating cost from increased cleaning demands, increased feed pressures, and reduced membrane life. Additionally, fouling can result in reduced permeate water quality and permeate quantity, thereby impacting production from the RO facility.

Parameters to be removed or reduced during the pre-treatment	Limit recommended up stream reverse osmosis membrane
Iron	< 50 µg/L
Manganese	< 20 µg/L
Turbidity	< 0.5 NTU
Suspended solids	< 1 mg/L
SDI	< 4 (95 % of time)
Algae	< 100 u/L
Chlorophyll	< 2 µg/L
Organic substances (Dissolved Organic Carbon)	< 2 mg/L
Hydrocarbons	< 0.1 mg/L

Table 4. Limits recommended up stream RO membranes

Both processes may be implemented in series with other typical water treatment processes such as clarification and flotation. Seawater is usually chemically conditioned as part of the pre-treatment process. This may include pH adjustment, coagulation and flocculant dosing. Physico-chemical selection (figure 21) would depend on process choice, feed water quality and other environmental and design parameters (Gaid & Treal,2007; Choi et al.,2009).

The pre-treatment process would:

- remove Fe, Mn, turbidity , suspended solids & SDI
- manage risks from human activities such as oil leaks from shipping
- manage risks from naturally occurring events such as algal blooms & red tides
- reduce dissolved organic carbon

3.1 Unit operation and process of the pre treatment

To achieve these goals, a variety of treatment operation and processes (figure 20) are utilized, which exploit various physical and chemical phenomena to remove or reduce the undesirable constituents from the water. Each unit operation / process used plays an important role at the various stages of the pre treatment. The predominant role and responsibility of the design engineer is the selection and the design of the appropriate pre treatment operation/ process. The type of pre-treatment required depends on the characteristics of the raw water. The characteristics of the sea water is assessed by taking sample of water from the source during different seasons of the year and analyzing for physical, chemical and bacteriological quality parameters. Initial screening equipment will remove the (mobile) larval stages of these types of organisms from the raw water supply.

3.1.1 Prechlorination

The addition of chemical oxidants, such as chlorine, bromine, iodine, or ozone, can provide biological disinfection before membrane processes. Because, the first stage of fouling formation is an uncontrolled growth of microbial organisms on surfaces, with a preliminary formation of slime, which gives a biofilm, produced by the living cells and their metabolic

by-products. The term biofouling refers to the final deposit, resulting from the mixture of bio-film (microbial and their extra-cellular polymeric substances (EPS), suspended solids, corrosion products and macro-organisms finally adhering and growing on the surface. The fouling layer reaches the maximum development with the adhesion of marine animals (figure 21) such as Crustacea & Molluscs,. Mussels are considered the most characteristic macro-fouling species and are the main species responsible for clogging of industrial pipes. It is very difficult to destroy and detach mussel shells from pipe walls due to their strong adhesion.

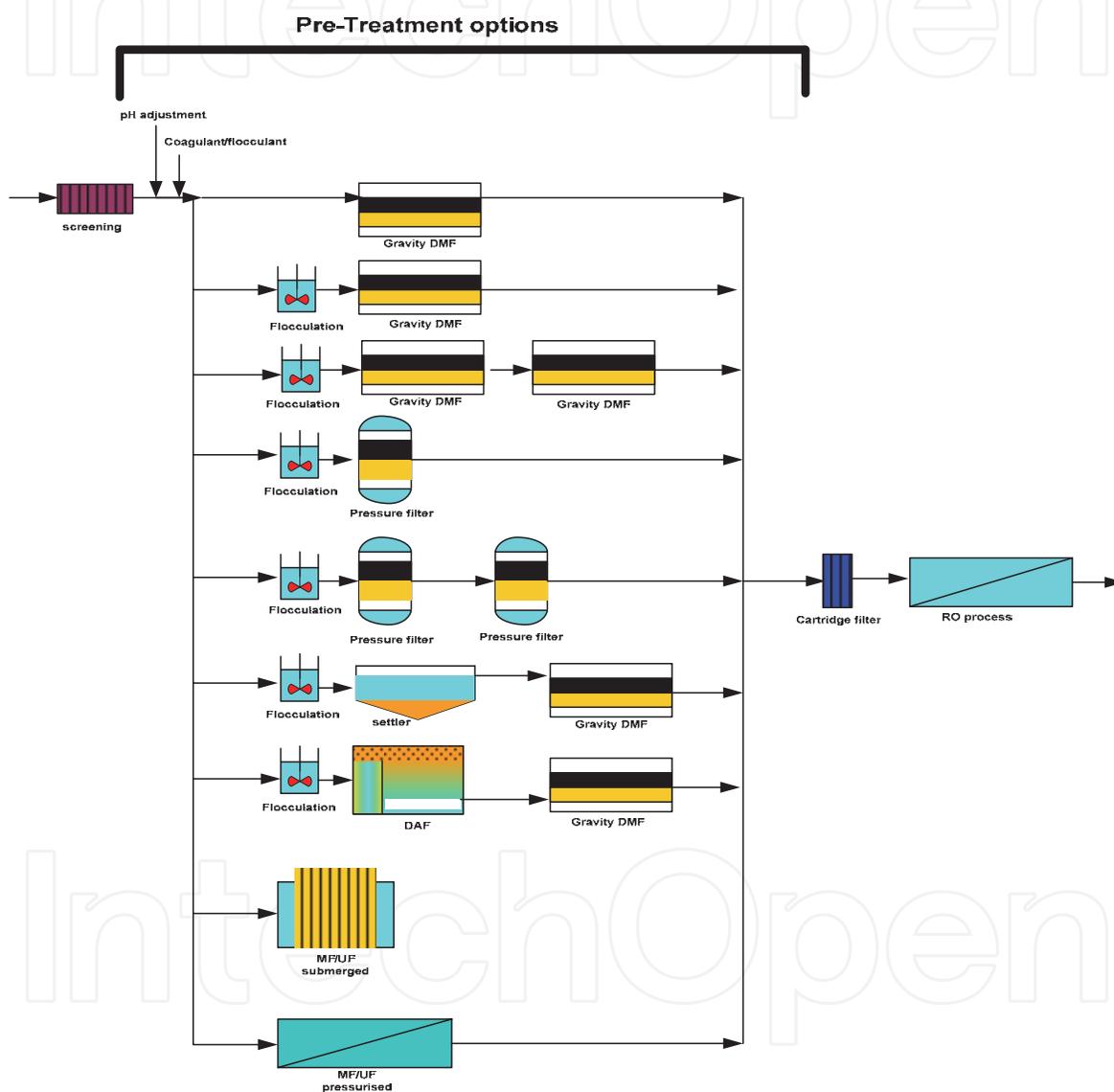


Fig. 20. Pre-Treatment options

Due to the anaerobic conditions, the activity of sulphate reducing bacteria (SRBs) is favoured and allows the corrosion phenomena on metallic surfaces of the pipes. It is why that a critical planning consideration for the full-scale seawater desalination facility is the risk of bio-fouling of intake and membrane equipment caused by marine organisms. The bio fouling risk is dynamic, changing with seasonal variances in source water quality parameters, such as nutrient loading, freshwater inflow, contamination, oil spills, and algae

blooms. To minimize the problems related to micro and macro-fouling in desalination plant, continuous or intermittent injection of oxidant is added into the seawater at the intake. The pre chlorination is the most common method for bio-fouling control in seawater applications, especially where large water quantities are needed for desalination plants. The use of chlorine must be monitored carefully to keep the chlorine below 0.1 milligrams per liter of free chlorine residual that would even damage most of RO membrane used by the constructors. This dechlorination is accomplished chemically through sulfite compound addition. When organic substances are chlorinated, the resulting chlorine oxidation generates halogenated carbon compounds, such as the trihalomethane class of compounds. Complete dechlorination and destruction of the chlorine residual by reducing compounds will ensure that chemicals do not attack these sensitive membrane systems.

Chlorination chemistry

Chlorine is most commonly available as chlorine gas and sodium and calcium hypochlorites. In water, they hydrolyze instantaneously to hypochlorous acid:

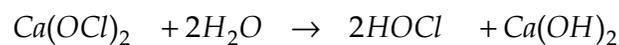
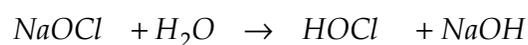
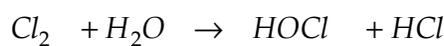
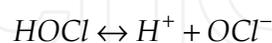
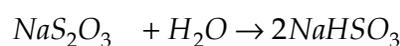


Fig. 21. Mussels development on intake (left) and biofilm on pipes (right)

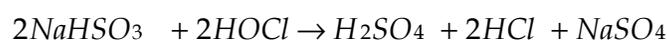
Hypochlorous acid dissociates in water to hydrogen ions and hypochlorite ions:



The sum of Cl_2 , NaOCl , Ca(OCl)_2 , HOCl , and OCl^- is referred to as free available chlorine or free residual chlorine, expressed as mg/L Cl_2 . Sodium metabisulfite (SMBS) is commonly used for removal of free chlorine. Other chemical reducing agents exist (e.g., sulfur dioxide), but they are not as cost-effective as SMBS. When dissolved in water, sodium bisulfite (SBS) is formed from SMBS:



SBS then reduces hypochlorous acid according to:



In theory, 1.34 mg of sodium metabisulfite will remove 1.0 mg of free chlorine. In practice, however, 3.0 mg of sodium metabisulfite is normally used to remove 1.0 mg of chlorine.

Efficient bio-fouling control is achieved at concentrations in the range of 1– 3 mg/l when it is used under a continuous procedure, and in the range of 5-10 mg/l when it is used intermittently for some hours per day. Dechlorination upstream of the membranes is required, however, to protect the membranes from oxidation.

To day, the main question is: Continuous chlorination or intermittent chlorination?

According to seasonal and/or daily parameters (temperature, organisms population, light), to operational parameters, chlorine can be dosed through continuous or intermittent (higher dosages for shorter time at fixed intervals of time) way providing always a good mix with the feed water.

Continuous chlorination

The continuous dosing of chlorine had been confirmed as effective in the long history of RO systems operation.

However, this requires sensitive carefulness in operation. Chlorine is added continuously at the intake, and a reaction time of 20–30 min should be allowed. A free residual chlorine concentration around 0.5 mg/L should be maintained through the whole pretreatment line.

- But, it is well known that very close attention is required to minimize deterioration by oxidization of the membranes if a small residual of free chlorine is still present on the RO feed water.
- There is always a risk that membrane deterioration takes place rapidly under the presence of heavy metals such as Fe, Mn, Cu, Co, and others in the system.
- Bio-fouling problem downstream of the point of dechlorination is still common because the chlorine reacts with the organic matter in the water and breaks it down to more biodegradable fragments. Since there is no chlorine present on the membranes, microorganisms can grow with an enhanced nutrient offering, unless the system is sanitized very frequently. It is why, it is admitted that bio-fouling refers to the undesirable accumulation of a biotic deposit on a surface.

Therefore, the continuous chlorination/dechlorination method is becoming less popular.

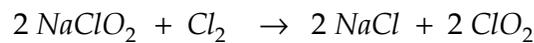
Intermittent or shock chlorination

Instead of continuous chlorination, chlorine is more and more applied preferably periodically. Chlorine is added intermittently for some hours per day at the intake at concentrations in the range of 5 – 10 mg/l. Shock dosages can be extremely effective and provide a high inactivation rate of the organisms. Before the system goes into operation again, all chlorine containing feed water has to be rinsed out carefully, and the absence of chlorine must be verified (e.g., by monitoring of the oxidation-redox potential (ORP)). In the shock dosage, the chlorine dose must satisfy the “chlorine feed water demand” at the forecast contact time and a chlorine residual of about 0.1 mg/L should be present. The shock dosing is carried out for 10 minutes every 12 hours with only 3 ppm dosage. No algae or mussels growth was noticed in the seawater intake therefore the process appears to be very effective (Sommariya et al., 2009)

In order to achieve the long membrane life that is desired for seawater desalination RO modules, optimization of the chlorine injection method becomes indispensable. Therefore, in order to reduce chlorine load to the RO module, the intermittent or shock chlorination method is more and more recommended instead continuous chlorination method.

Chlorine dioxide

Chlorine dioxide (ClO_2) is a greenish-yellow gas, highly soluble in water. It is generated “on site”, mainly according to the following process with sodium chlorite as reagent:



In a pH range of 6–8.5, chlorine dioxide remains in solution as dissolved gas. The Jumeirah Palm project is the first desalination project in the Gulf to adopt chlorine dioxide for both seawater and potable water sterilization (Petrucci & Rosellini, 2005). The limitations of the Chlorine dioxide observed on site are the chlorites (ClO_2^-) production which can be 30 % of the ClO_2 concentrations. Due to the fact that the chlorites are not removed during the pre treatment, their impact on the reverse osmosis membranes through an eventual oxidation is possible but not clearly proved due to the small desalination plants using this oxidant. The second limitation is often due to the operating cost because ClO_2 is more expensive than the sodium hypochlorite.

3.1.2 pH adjustment

The pH adjustment step of pre-treatment must result in the optimal pH level for the desalination system. After coagulants have been added, the pH is often changed significantly. In most cases, the pH must be returned to a neutral or a slightly acid level. Adjustment chemicals to lower the pH include sulfuric acid and hydrochloric acid.

3.2 Filtration

The type and choice of pretreatment depend on the extremes of raw water characteristics. Different source waters require varying levels of pre-treatment to ensure maximum RO membrane. With multiple technologies available for the pre-treatment, desalination engineers can look forward to satisfactory fouling index, efficient down stream RO plant and equipment operation

The most common pre treatment for open seawater is multimedia filters. It is possible to use a single stage filtration if the feed water is constantly of high quality. Double stage filtration is required if the seawater is degraded.

Regarding applications of filtration, it is noted that the extent and complexity of the pre-treatment systems for removing or reducing colloidal and organic fouling depend on site conditions. In case of open seawater intake, reverse osmosis membranes should be protected against a variety of foulants, necessitating an extensive pre-treatment process. For example, the use of coagulants and sedimentation or flotation equipment maybe necessary, followed by media filtration. Alternatively, granular media filtration can be replaced by low pressure membrane systems such as ultrafiltration or microfiltration.

In all water purification processes, filtration will be an integral step if not the main step. Filtration is an essentially mechanical operation and its goal is to trap particles larger than 10 microns (100,000 angstroms). In granular filtration, interception, gravitational sedimentation, and Brownian diffusion are the key mechanisms of colloidal particle transport from the pore fluid to the surface of a filter grain (Yao & Habibian, 1971)

Granular media filters have two different design configurations:

- single media filter or dual media filter
- gravity filter or pressure filter

These two configurations can be also used as single stage filtration or double stage filtration

3.2.1 Single media filter and dual media filter

Single media filter - Gravity filter

Direct filtration is proposed when the seawater presents a low level of particles and low SDI. Single-media filtration is used when the SDI is lower than 10. Dual-media filtration is used when the SDI is lower than 25. The conditions of the use of the direct filtration is summarised on the table 5.

Seawater parameters	Single media filter	Dual media filter
Turbidity, NTU	1 - 2	< 10
Suspended solids, mg/L	< 3	< 15
SDI	10 - 15	30
Algae, u/L	-	2 000
Chlorophyll $\mu\text{g/L}$	-	< 5
DOC, mg/L	< 1.0	< 2.0

Table 5. Limit recommended of the feed water

Single-media filtration consists of one media (figure 22). This media is often small-grained silica sand based on 0.8 m for the effective size and 1.3 for the uniformity coefficient. The height of the media ranges between 1.0 – 1.5 m. This type of filter is mainly proposed when the SDI and the suspended solids are very low. A critical factor in designing pre-treatment is the possible use of an intake well, in particular a beach-well. If such an intake well exists, it is essentially part of the pre-treatment process because of the capacity of the sand (usually present at the sea bed) to act effectively as a first filter medium for the suspended solids in the seawater. Then, a simple form of pre-treatment by granular filter media, even without addition of coagulants, maybe adequate. Very few references exist for open intake and most of references concern groundwater or beach well.

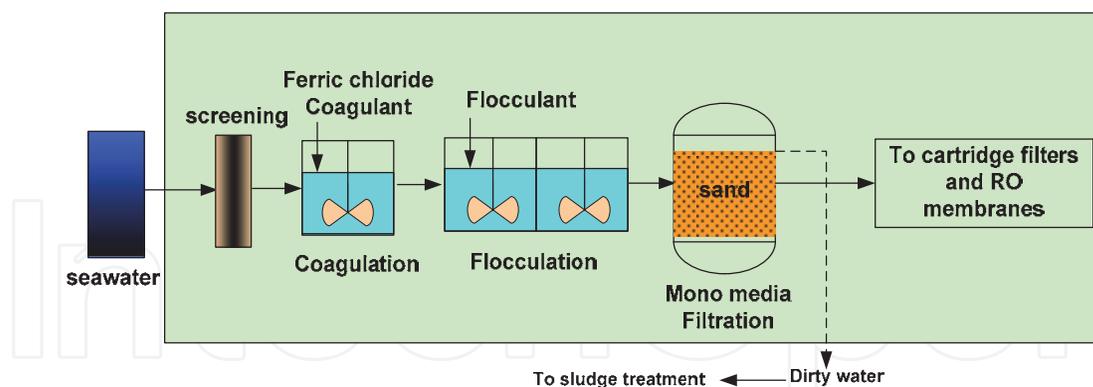


Fig. 22. Principle of coagulation-flocculation-single media filtration

Granular filter media must satisfy various specifications before they can be considered for applications. These include grain size, grain surface condition, density, particle porosity, solubility, durability, settling rate. The void fraction of the granular bed formed by the grains is also important. The shape of the grains used in filtration media mainly depends on the origin of the material. Grains collected from river beds are usually rounded and smooth. Grains resulting from the crushing of larger pieces are jagged and angular. Although inadequately studied so far, improved performance of crushed particles over rounded grains has been demonstrated for water filtration. For instance, the shape of the grains

affects the bulk porosity of the bed, which is strongly related to the increase in head loss that results from deposits in the filter. However, systematic studies on the effect of grain shape on filtration are rather limited. Regarding grain surface roughness effects, although intuition and recent evidence suggest that they should play a significant role in filtration..

Single-media filtration - Continuous backwash up-flow sand filter

The filter is the Continuous Backwash Up-flow Sand Filter, commercially available for over 25 years, and over 8,000 units have been installed worldwide. Treatment begins when influent feed water enters at the top of the filter and flows downward through an annular space between the feed pipe and airlift housing. The feed is then introduced into the media bed through distribution radials, which are open at the bottom. As the influent flows upward through the moving granular bed, the solids are captured in and on the media while clean water continues rising into the filtrate pool above the bed. The filtrate then exits at the top of the filter over the effluent weir. Simultaneously, the granular media is being cleaned and recycled throughout the filter via an airlift pipe and media washer mechanism. The solids-laden filter media is drawn downward towards the intake of the airlift pipe located in the center of the filter bottom. A small, steady stream of compressed air is introduced into the airlift bottom, which draws the granular media and solids into the airlift. The solids-laden media is scoured as it rises in the airlift. Upon reaching the top of the airlift, the solids and granular media are released into the central reject compartment. The heavy filter media grains are returned to the bed after falling through the washer. As the filter media falls through the washer, which consists of several concentric stages, a small amount of filtered water passes upward, hydraulically lifting the solids or "dirt", while allowing the heavier and coarser granular media to fall. This counter-current flow of filtrate quality water is created by a difference in filtrate and reject weir heights. The cleansed media is then deposited at the top of the filter bed. This method of cleaning provides continuous, uninterrupted flows of filtrate and reject water (Dynasand). The application of continuous backwash up-flow for desalination is combined with a second stage filtration.

Single-media filtration - Diatomeceous filter

Diatomaceous earth media is low recommended for primary filtration because of its characteristic high head loss and short run times. The diatomaceous earth precoat filter technology is long-term, established method in conventional water and wastewater treatment. Its use in seawater applications is limited and few references exist worldwide.

Dual media filtration (DMF)

Dual-media filtration consists of two media with different specific gravities (figure 23). The difference creates a two-layer separation effect. Use silica sand for one layer; use anthracite or pumice or equivalent media for the other layer. Anthracite is a black coal which allows for longer run times than can be achieved by sand alone. The use of dual media will allow larger quantities of material to be filtered and will reduce head loss during operation. The first layer is anthracite (or pumice) with a large diameter size which gives to the media bed, larger void spaces with greater solids holding capacity. It acts as a very robust roughing layer capable of handling heavy solids loading conditions associated with certain seasonal conditions such as suspended solids, algae development. The second layer is sand with a smaller diameter which acts as a final barrier for the fine particles responsible of the fouling. Considering an open intake, the seawater would in all cases be chemically conditioned to coagulate and flocculate the suspended matter (colloids, particles, algae) for removal in the

pre-treatment filters. Coagulation is a process where a coagulant (Al or Fe salt) is added to the water to destabilise small particles suspended in the water. Coagulation is a rapid process requiring rapid mixing to disperse the coagulant in the feed water. The coagulation is done through a static mixer (most of cases) or through a coagulation tank with an adapted mixer. Since the pH of coagulation is critical (>8.5), an acid (mainly H_2SO_4) is added prior to coagulation to maintain optimum pH conditions. The coagulated water would discharge to flocculation tanks with mixers to provide gentle mixing of the coagulated water for the destabilised particles to form flocs. At the entry to the flocculation tanks, flocculant (polyelectrolyte) would be added to aid the process. Flocculated water would be removed from the water by passing through the gravity filters filled with sand granular medium for the single media filter and with anthracite (coal) / sand for the dual media filter. Inline coagulation is used and the dosage of the coagulants depends of the seawater quality. The most relevant process conditions for inline coagulation with metal salts are pH, dose, velocity gradient (G), shear rate (Gt) and temperature .pH affects the surface charge of colloids and determines the predominant coagulant species. Therefore, floc size and structure (porosity, density) may differ as a function of pH. Flocs formed at low pH and low dosage are reported to be denser and less porous than those formed at high pH and high dosage (Shin & O'Melia,2006). The physical properties of flocs are sensitive to flocculation conditions such as G and Gt. Increased shear reduces the average steady-state size of flocs. Higher G values lead to larger fractal dimension, which is related. The design of the flocculation tank depends of the seawater parameters. An important consideration in inline coagulation applications is the fate of coagulated & flocculated particles in the pipe network feeding the pre- treatment plant. It is important to consider if the flow regimes in the pipes favour floc growth or break the flocs. Studies on turbulent pipe flow for particle destabilization and aggregation show that for Reynolds number between 8 000 and 16000, the reaction rate for particle aggregation increased. Beyond 16000, the reaction rate decreased and may be attributed to a reduced collision efficiency of the primary particles and/or disruption of microflocs if the turbulence intensity in the pipe reactor exceeds a certain critical value. Reports on flocculation experiments in pipes of various diameters (8-600 mm) show that under steady-state conditions, a decreased floc size is observed with an increasing flow velocity (Johir et al.,2009; Mitrouli et al.,2008)).

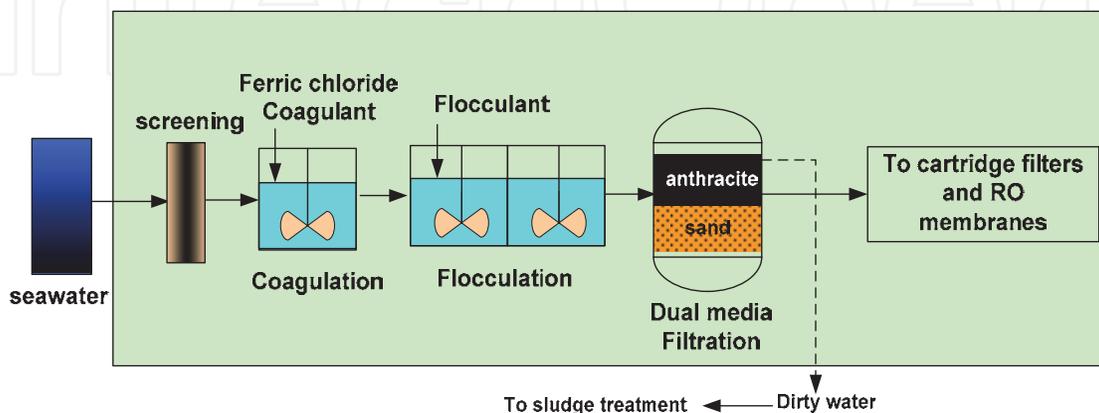


Fig. 23. Principle of coagulation-flocculation-dual media filtration

Anthracite or Pumice can be replaced by Filtralite which has excellent properties for use in pre-treatment filters in desalination plants. Filtralite media is made by burning of clay at about 1200° C, followed by crushing and sieving. The material has a porous structure and when crushed, a large surface area is exposed. The aggregates do not release harmful substances, and the acid solubility is minimal. With Filtralite, time between backwashes can be increased by about 25%, then reducing use of backwash water (Mitrouli et al.,2009).

The use of two media types introduced in a DMF will provide a good coarse-of-fine filtration process for desalination facilities. The total height of the two media ranges between 1.4 - 1.6 m based on a half layer part for each media. Pre-treatment processes are similar to the processes utilised for treating fresh water (in surface water drinking supplies). It is expected that sand and anthracite would be replaced about every 10 years.

A new development of DMF for seawater pre treatment have been proposed based on a total height of the media of 3 m -4 m and related with a higher filtration velocity (15 m/h). A linear relation ship has been demonstrated between the total height of the media , the filtration velocity and the final performance of the DMF.

The pre-treatment filters will also be provided with a backwash system. All chemical feed systems have been designed using prudent engineering practices and providing at least one standby chemical feed pump per system and adequate chemical mixing upstream of the pre-treatment filters.. Filters will be equipped with distribution boxes, crosswalks, wash headers, filtered water weirs, automatic backwash controls, backwash waste piping and valves and cell isolation gates.

Algal cells proved difficult to remove by direct filtration. The filter clogging (headloss) as a function of algal content has been evaluated in number studies and proved that this process is limited by this parameter. Petruchevski (Petrusevski et al., 1995) has demonstrated that algal removal efficiency by dual media filters was shown to vary strongly with algal species, suggesting that properties other than size and shape (algal motility, presence of outer mucilaginous layer, algal cell form) may have had a significant impact on filterability.

Parameters	Single media filter	Dual media filter
anthracite		
Height m		0.7 - 0.8
Effective size mm		1.0 - 1.5
Uniformity coefficient		≤ 1.4
sand		
Height m	1.0 - 1.5	0.7 - 0.8
Effective size mm	0.8	0.6
Uniformity coefficient	≤ 1.3	≤ 1.3
Velocity m/h	6 - 8	7 - 10

Table 8. Specification of the single media filter and the dual media filter

Filtration problems caused by algae were grouped into three categories:

1. penetration of stable algal cells into the filter media;
2. interferences with coagulation/flocculation caused by extracellular algal materials; and
3. short filter runs (increased headloss due to filter clogging) with increased need for backwash.



Fig. 24. Single media Pressure filters (Oman Sur desalination Plant)



Fig. 25. Gravity dual media filters (Australian desalination plant)

3.2.2 Double stage filtration

The pre-treatment system can include a double stage filtration (figure 26). The 1st stage filter can be a dual media with 1.2-1.6 m of total effective media depth. The specifications of the two media are summarised on the table 9. The first layer is anthracite (or pumice) with a large diameter size which gives to the media bed, larger void spaces with greater solids holding capacity. The second layer is sand with a smaller diameter which acts as a final barrier for the fine particles responsible of the fouling. The 1st Stage filters operate as roughing filters and are sized for a filtration velocity around 13 m/h. The 2nd Stage filter is a standard-bed sand filter with 1.0 m of effective sand media depth. The 2nd Stage filter uses a smaller diameter sand size (0.4-0.5 mm ES) which maximizes the sand media surface area and subsequently the possibility for attachment of finer particles still in the water. The 2nd Stage acts as a polishing filter to remove the majority of the remaining particles producing an effluent with a low Silt Density Index. The 2nd Stage filters operate as polishing filters and are sized at a greater hydraulic loading rate (16 - 18 m/h). The combination of increased sand media surface area and a higher hydraulic loading rate enables to meet the expected performances. The experiences shows that the 2nd stage filter can remove 0.3 - 0.4 SDI. The seawater would in all cases be chemically conditioned to coagulate colloids and micro particles. The filtration system is sized to optimize solids removal performance.

Parameters	1st stage filtration	2nd stage filtration
anthracite		
Height m	0.5 - 0.7	
Effective size mm	1.0 - 1.2	
Uniformity coefficient	≤ 1.4	
sand		
Height m	0.5 - 0.7	1.0
Effective size mm	0.6	0.4 - 0.5
Uniformity coefficient	≤ 1.3	≤ 1.3
Velocity m/h	10 - 13	14 - 18

Table 9. Specifications of the double stage filtration

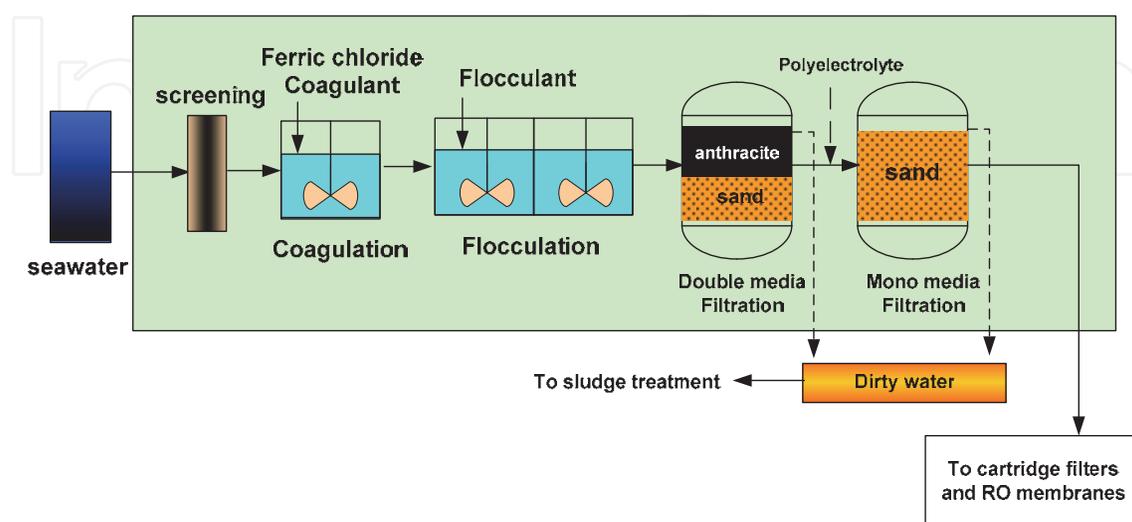


Fig. 26. Double stage filtration system

The figure 27 shows the performance of the double stage filtration for the removal of the SDI₁₅ (Millipore membrane). The SDI₁₅ after the double stage filtration is better than that recorded after a single dual media filter. A difference between 0.4 – 0.5 is observed between the two configurations. The SDI₃ of the raw water was in the range 16 – 29 % .min.

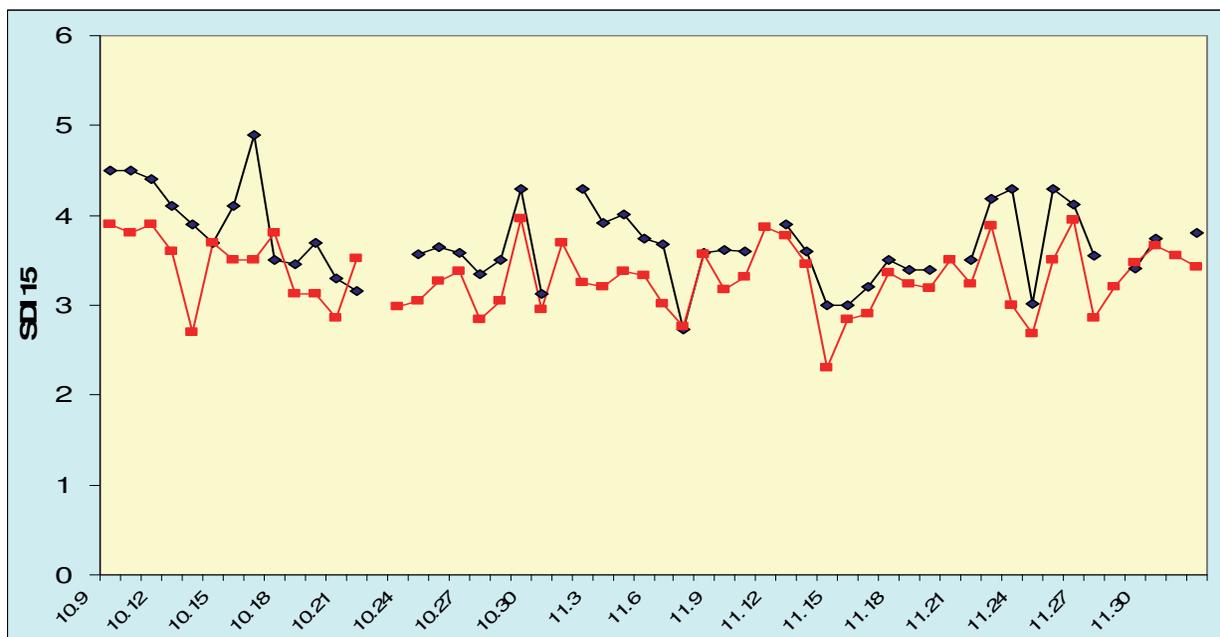


Fig. 27. Comparison of the SDI reduction between single DMF and double stage filtration (red line corresponds to double stage filtration, black line corresponds to DMF)

An in-line SDI monitoring meter is recommended to be installed downstream of each second stage filter cell. If the in-line monitors indicate that the SDI reading is above the design criterion for this parameter (SDI < 3-4), an alarm will give to operators to manually isolate the filter train . An in-line turbidimeter is also recommended to be installed in the first and second stage effluent channel.

Leparc (Leparc & al., 2008) has developed a new concept for the double filtration based on the following advantages points:

- Full-scale application with battery of filters: improved process stability and robustness against upsets of 1st stage
- Improved SDI mainly during first few hours of filtration
- Reduce the size of the 2nd stage (30 – 70% reduction based on raw seawater quality)
- Avoid useless cost for over-quality as compared to a full double stage pretreatment
- Provide better stability of water quality as compared to single-stage filtration

3.2.3 Three media filtration

When three media are used in filters, a better coarse-to-fine filtration pattern can be constructed. High-density silica sand, garnet, and anthracite are commonly used to provide the filter bed. This gradual change in media size provides a gradient from coarse to fine and creates a media flow pattern necessary to achieve a very low silt density index. However, it is observed that after a backwash (air + water), the different media do not stratify completely. Some desalination pre-treatment systems use an alternate media such as greensand to remove iron and manganese compounds.

3.2.4 Gravity filters or pressure filters

The open filter cells will be covered to minimize algae growth. Protective coating suitable for seawater applications will be used in the filter cells as the structural integrity of the concrete structure will be adequate. For example, pressure granular media filters (figure 30) are used for Oman Sur desalination plant (Oman). Pressure filters are also widely used in small plants worldwide because they are cost-competitive, space efficient and easier and faster to install and operate when compared to granular media gravity filters. Often when the source seawater is collected via open intake, two-stage dual media (sand and anthracite) pressure filters are applied.

4. Enhanced coagulation

For a degraded seawater containing high suspended solids, high concentration of algae, oil, organic matter, a pre-treatment including only a direct filtration is not enough. It is necessary to add a solid-liquid separation systems to remove these physico-chemical parameters.

4.1 Flotation

As opposed to settling, flotation is a solid-liquid separation technique that is applied to particles whose density is lower or has been made lower than the liquid they are in. The Dissolved Air Flotation (DAF) process is proving to be a very efficient and cost effective pre-treatment option. Several suppliers have selected the DAF as the preferred pre-treatment provider for a large RO desalination plant.

4.1.1 Principle of flotation

The DAF process is an efficient process for the separation of suspended matter (turbidity, algae etc.) and SDI from seawater following the addition of a coagulant chemical and flocculation (figure 28). Dissolved air flotation (DAF) utilises the property of micro-bubble adherence to suspended solids, increasing the tendency of the particles to float. The flocculated water meets a water flow with supersaturated air (85% to 95%) which is supplied through nozzles. Due to the pressure drop of the supersaturated water at the nozzles, small air bubbles are formed. These micro-bubbles attach themselves to discrete floc particles created in the flocculation process. The rising velocity of the air bubbles is higher than the water velocity and the air bubbles will thus collide with the flocs in water. The density of the aggregates decreases until values below the water density. As a consequence, the aggregates will float on the water surface (Shawwa & Smith, 2000; Edzwald et al., 1999; Haarhoff, 2008; Peleka & Matis, 2008). As they rise to the surface, the buoyant flocs form a stable sludge layer above the water surface. Mechanical scrapers skim the solids from the surface into a collecting bin. When surface scrapers are used a sludge with a dry solids content in excess 2-3% may be produced.

The size of the bubbles greatly affects the efficiency of the flotation process, with bubbles smaller than 100 μm considered the most effective (Edzwald, 1995; 2007a ; 2007b). Air bubbles of 20 to 50 μm are considered the best for the recovery of fats. The air to solids ratio has a major effect on the performance of a DAF unit. The proportion of the TS present as suspended solids is also critical in determining efficiency (Arnold et al, 1995; Edzwald & Wingler, 1990), Depending on the raw water quality and the efficiency of mixing of the recycle stream with the flocculated water, the amount of recycle required typically lies somewhere between 8% and 12% of the influent flow (Peleka & Matis, 2008).

The amount of air that can be dissolved in a certain volume of water depends on the pressure and the water temperature and can be calculated with Henry's law:

$$C_s = k_D C_l = k_D \frac{MW p}{RT}$$

C_s = saturation concentration of gas in water (g/m³), k_D = distribution coefficient, C_l = specific density of air at the prevailing temperature and pressure (g/m³), MW = molecular weight of gas (g/mol), p = total air pressure (Pa), R is the universal gas constant = 8,3142 (J/(°K mol)), T = temperature (K)

Assuming a laminar flow and spherical aggregates, the rising velocity can be calculated with Stokes' law

$$V_{st} = \frac{1}{18} \frac{g}{\nu} \frac{(\rho_w - \rho_a)}{\rho_w} d^2 a$$

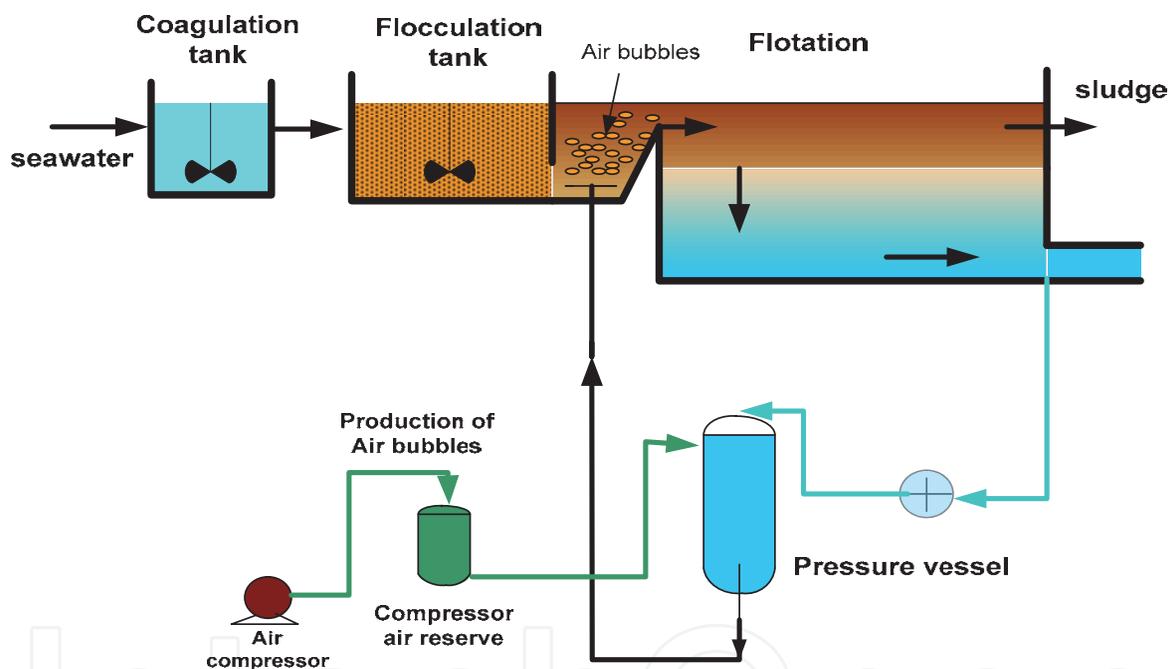


Fig. 28. Schematic of a traditional dissolved air flotation system

V_{st} = rising velocity of the air bubble floc-aggregate (m/s); ρ_a = density of the aggregate (kg/m³); ρ_w = density of the water (kg/m³); d = diameter of the aggregate (m)

For seawater, high rate DAF processes have been developed at loadings of 15 - 50 m³/h. For example, Spidflow™ which works at 30 -40 m³/h for seawater application, comprises a coagulation stage, followed by a flocculation step and a clarification phase through fast flotation (figure 29). The flocculation stage may also use a Turbomix™ when dealing with cold water. The fine air bubbles, formed by pressurising air in water (at pressures of 5 to 6 bar) when producing white water, are injected through specific nozzles into the Spidflow™ flotation units through a dedicated distribution system. This ensures the separation of Suspended Solids (SS), algae, oil, and hydrocarbons, which are trapped in hydroxide flocs formed by the addition of coagulant (figures 30 & 31).

The hydraulic sequencing of the various compartments of the Spidflow™ process has been designed in accordance with specific Computerized Fluid Dynamics (CFD) type studies. Spidflow™ has a floor for the distribution of flocculated water, which is located before the mixing step with white water. It also includes anti-spiral flow plates that break down any short circuits and collection lines which uniformly distribute water flow. This unparalleled process optimisation ensures that Spidflow™ achieves levels of treatment efficiency which allow it to operate at clarification rates between 30 and 50 m/hour.

Spidflow™ fits specifically well seawater desalination pre treatment, as an upstream step of a reverse osmosis membrane treatment chain. Spidflow™ is especially efficient during red tide algal bloom periods. This process significantly maximises filtration cycles duration following pre treatment steps and protects reverse osmosis membranes against ill-timed clogging. As a result, Spidflow™ guarantees very low SDI (Silt Density Index) figures that remain stable over time.

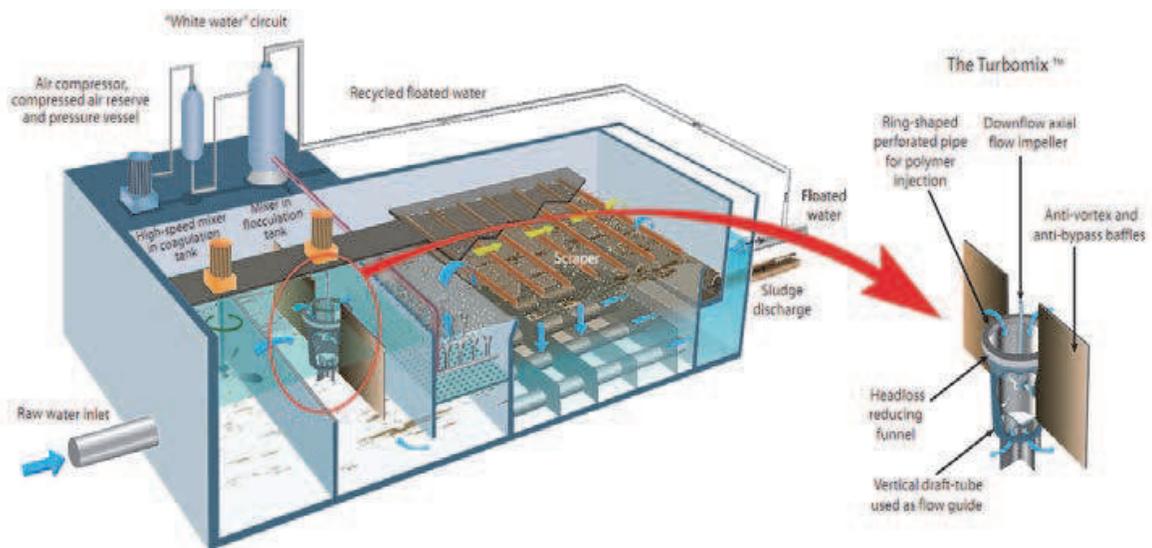


Fig. 29. Spidflow system



Fig. 30. White water formation (Spidflow™)



Fig. 31. Sludge blanket at the top of the flotator (Spidflow™)

4.1.2 Performances expected with the flotation

4.1.2.1 Oil removal

The limit accepted by the RO membranes is 0.1 mg/L. In lot of cases, desalination plants facilities are built in or near industrial zones and draw their raw water from sometimes very busy shipping zones. A carefully designed intake structure is essential and oil has to be removed to ensure the systems do not get damaged. The DAF is one of the best suited to remove oil from sweater. If oil were to get through the flocculation zones onto the flotation zone as free oil it will almost certainly be trapped by the micro bubbles and be floated of into the sludge blanket for removal along with the floc. The percent removal is around 90 %.

The filtration stage will not removed oil content, it is why the DAF has to be well designed to ensure the system against oil presence.

4.1.2.2 SDI removal

Silt density index (SDI, according to ASTM) is an easy and useful tool for particle evaluation and has been widely applied to determine the fouling characteristics of membranes. In principle, the removal efficiency for SDI is largely dependant on the chemical dosing adopted for the plant. If the chemistry is not right, the clarification and filtration plant will not be able to achieve the required treated water standards no matter how high the efficiency of the process or the quality of the equipment. It is now common knowledge that in order to achieve the required SDI levels it is not sufficient to just remove solids and algae from the water. It is important to look at reduction of the dissolved organic matter as well.

4.1.2.3 Dissolved Organic Carbon (DOC)

Dissolved Organic Carbon (DOC) can be reduced using enhanced flocculation (figures 32 & 33). Enhanced flocculation is performed at a lower pH, typically requires a more coagulant (FeCl_3 most of time) and possibly some acid to depress the pH to the right level. Ferric salts are generally considered to be more effective for the removal of organics when compared to Aluminium salts. A coagulation aid polymer can be included in the design. The DAF

process combined with the use of enhanced coagulation, the small foot print and short retention times have also been demonstrated to provide good TOC reduction (resulting in very low SDI's) and minimising the potential for issues such as bio-fouling.

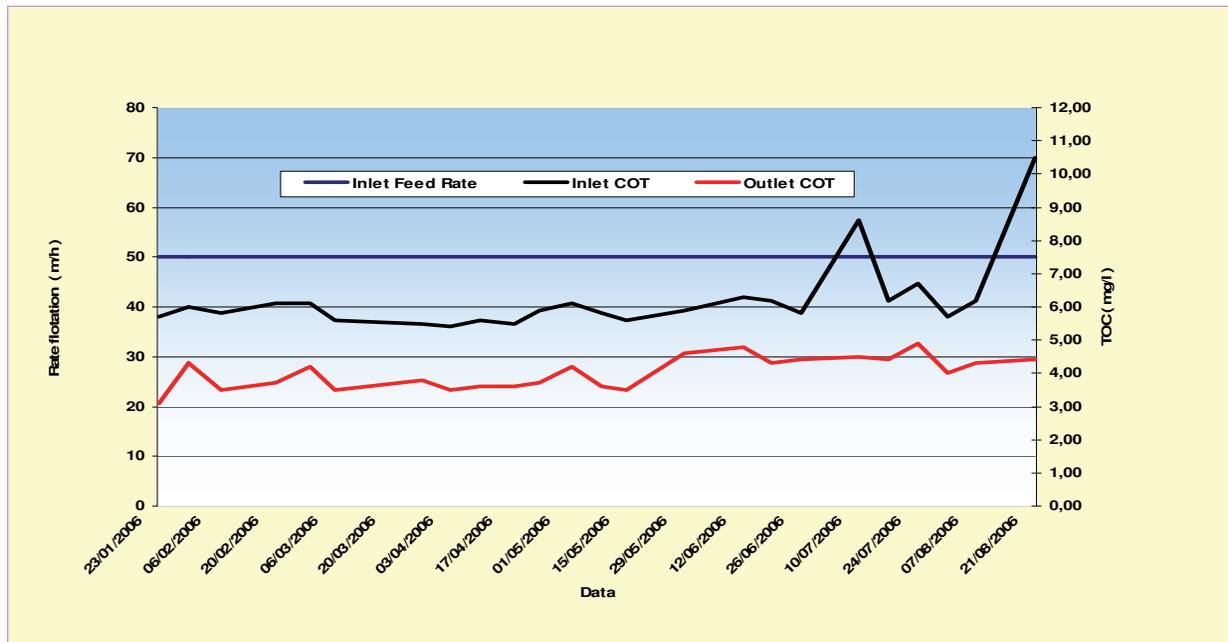


Fig. 32. Performances of the removal of TOC with DAF

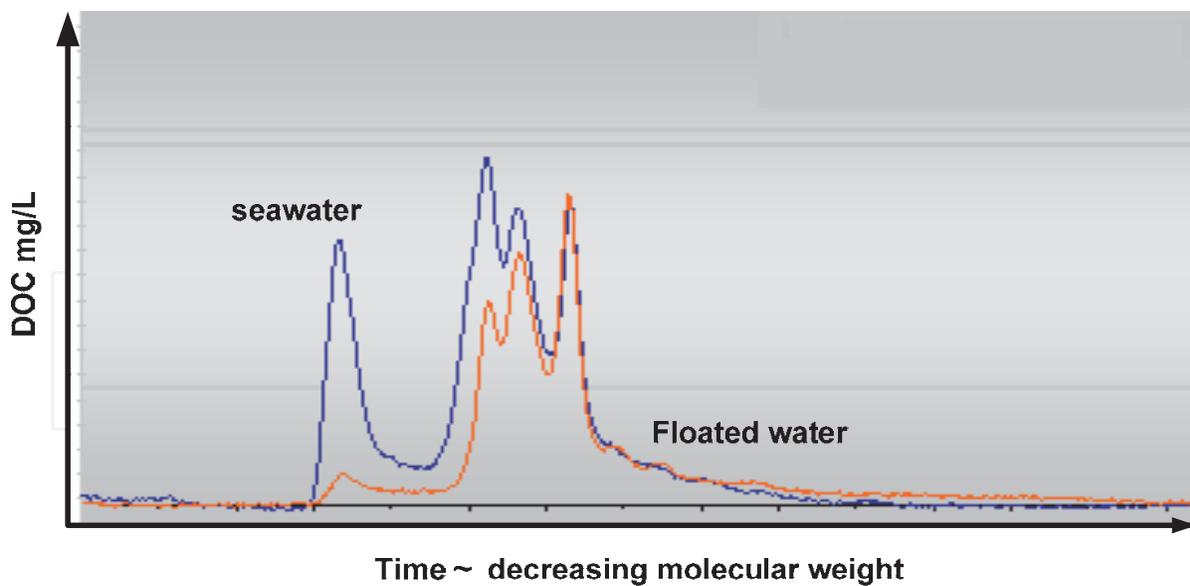


Fig. 33. LC-OCD of the raw water and floated water

4.1.2.4 Algae

One of main applications of DAF is for the removal of algae. Algae are difficult to remove by conventional treatment such as sedimentation, as they are naturally less dense than water so doesn't settle well (Al-Leyla & Middlebrooks, 1974; Vlaski et al., 1997). Algal species

typically are characterized by a negative surface charge in natural water environments. In the work done by Bernhardt and Clasen (Bernhardt & Clasen, 1991), algal destabilization by charge neutralization was achieved through chemical coagulation and flocculation. Maximum filterability of suspended algae was observed when algal cells were destabilized and in aggregate form.

Poor removal of algae (diatoms, green algae, flagellates, blue green algae) can lead to clogging of granular media filters and short filter runs. 99 - 99.9 % removal can be obtained with DAF (figure 34) compared with 90 - 99 % by sedimentation. The removal of algae with flotation is more effective than sedimentation (60 - 90%) depending of the inlet concentration of algae (Henderson et al., 2008, Edwards , 2007a).

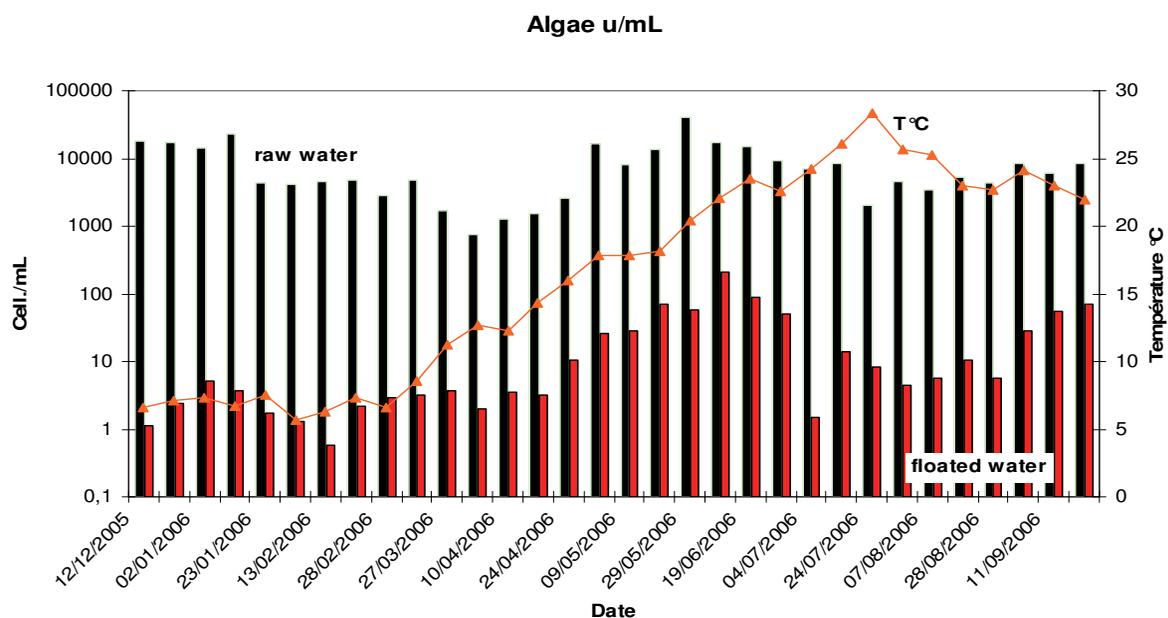


Fig. 34. performances of the removal of algae with DAF

4.1.2.5 Conclusion for flotation process

If the chemistry is right, the chances of achieving the treated water quality is much better with Dissolved Air Flotation followed by Filtration than with any other process and that could possibly include membrane filtration. The reason for this - we believe - is that the very small particles that make up the material that is collected on the filter paper when one analyses for SDI is the very small material that for some reason is not captured in the floc or did break away from the floc and has a density equal to or even a little lighter than water.

In sedimentation processes (in particular the very high rate versions) this material finds its way onto the filters and inevitably a percentage will break through. The chances of capturing these particles in a DAF plant are much better as the particles are small and light.

Low SDI's are further assured by spending some further attention to detail when designing the DAF plant such as: the correct flotation and filtration rates; the method of mixing the saturated water with the flocculated water; the method of removing the collected solids

without disturbing the sludge blanket; distribution of the clarified water over the filter media; washing methods etc.

4.2 Sedimentation

The principles of the coagulation & flocculation are simulars of those described in the flotation chapter. The Coagulation process is the dosing of coagulant in water, resulting into the destabilisation of negatively charged particles. a. Coagulation. Non settleable solids and some suspended materials do not precipitate because of electrical charges on the surface of the particles. If the charges on the particles can be reduced, the particles may precipitate. Chemicals that lower surface charges are lime, alum, ferric salts, and polyelectrolytes (Smoluchowski,1916).

During adsorptive coagulation, micro-particles present in the seawater are adsorbed to the positively charged hydrolysis products. The optimal pH-range for adsorptive coagulation with iron salts is between 6 and 8, the optimal pH-range with aluminium salts is more narrow and is about 7.

Flocs are formed from a combination of suspended materials in the raw water together with adsorbed and precipitate solids gained via coagulation. For seawater pre treatment, frequently iron chloride (FeCl_3) is used as coagulant. Alternatively, aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$) can be applied.

4.2.1 Different types of clarifier used as pre treatment

4.2.1.1 Floc blanket clarifier

The character and behaviour of the suspended bed within a floc blanket clarifier (FBC) lies at the heart of the process. The blanket can be envisaged as being held in place as a result on a balance between the flux of material associated with the upflow velocity and a downward flux associated with sedimentation. It consists of assemblage of flocs whose sizes are relatively large compared with the incoming feed floc and serves as a filter of the incoming material. As collection progresses, there is an accumulation of solids held within the suspension, this manifesting as an increase in the blanket depth. Periodically, excess solids are extracted. The impact of the flocs in the FBC can be examined in term of blanket dynamics and clarification capacity.

When using hydrolysing metal coagulants, the greater the dose, the greater is the propensity to trap water. One of the advantages of optimising the dose and pH is that the floc density appears to be maximised at the optimum conditions. The advantage of using polymer in solid-liquid separation the dose of metal coagulant (by charge neutralisation ,is reduced.

4.2.1.2 Actiflo

Ballasting refers to the use of materials added during flocculation, that increase the density of flocs resulting in faster settlement. The ACTIFLO® process is a high rate settling process that combines the advantages of ballasted flocculation and lamella clarification (figure 35). The aim of Actiflo is to remove suspended solids, reduce turbidity and remove dissolved organic water. The use of microsand gives the Actiflo® process the advantage of treating a wide range of raw water. Density and shape of microsand particles increase the flocculation and settling efficiencies. As a consequence it is easier and faster to create a strong floc, even with lighter solids coming in. Once the floc is formed and attached to the microsand, the floc settling velocity is high enough to allow for high rise rates.

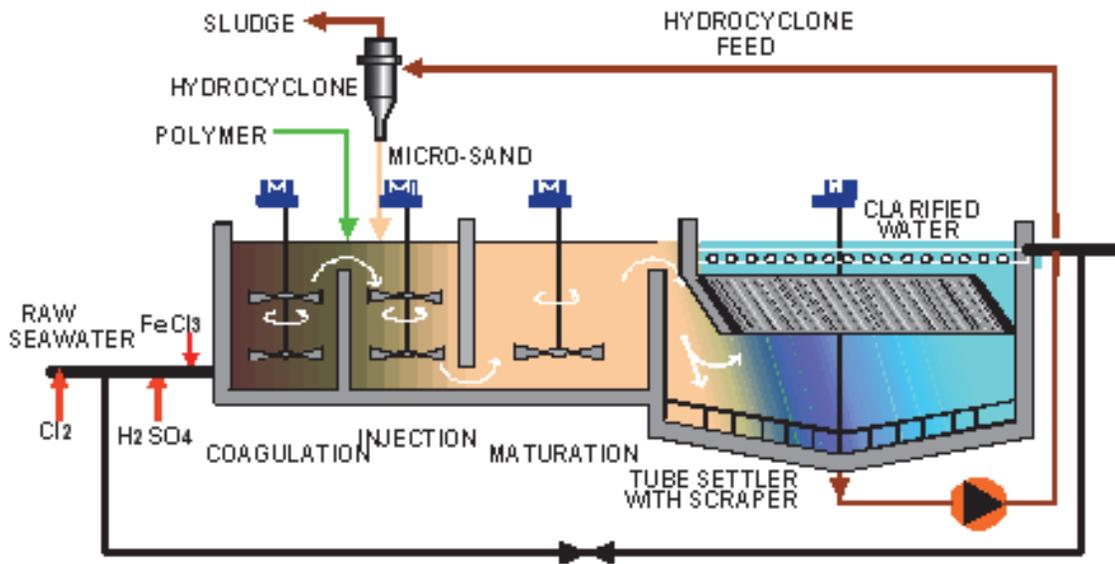


Fig. 35. Actiflo settler

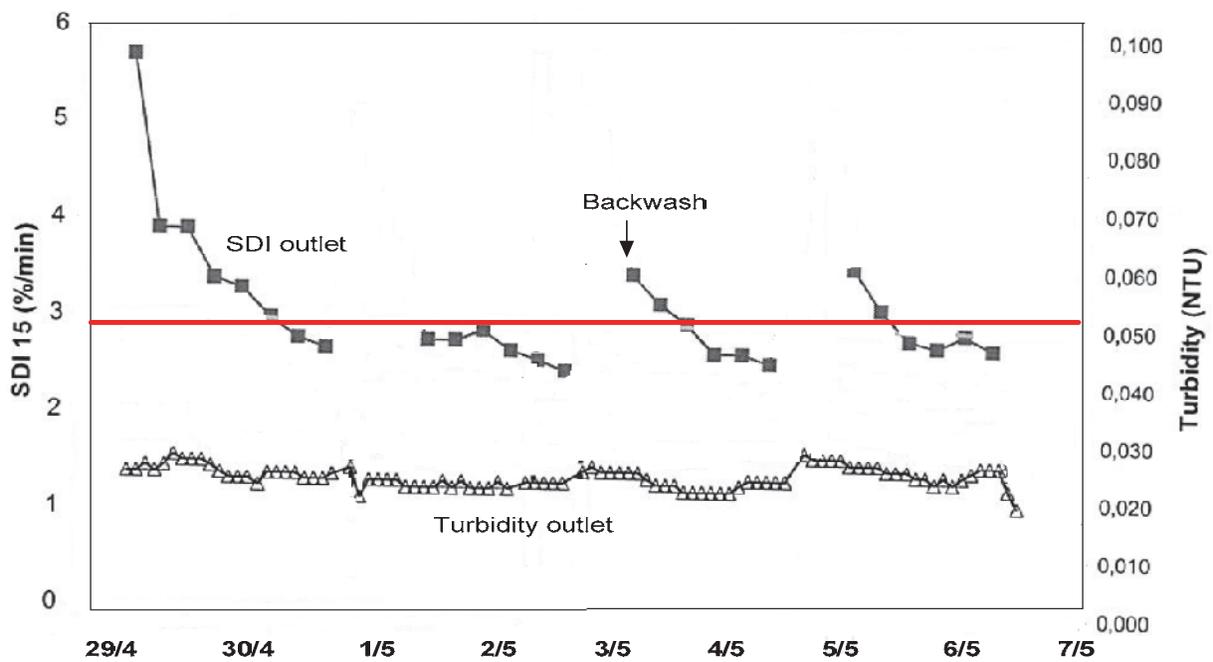


Fig. 36. Performances of Actiflo on SDI and turbidity for seawater pre treatment application

Ferric chloride is injected into the coagulation chamber at a dosing rate of 10 ppm. Rapid mixing in this basin starts the coagulation process. Coagulated raw water then enters the injection tank where micro-sand and polymer are added. Polymer is injected at a dosing rate of 0.2 ppm. Dynamic mixing induces a high probability of contact between coagulated solids, polymer and microsand. Flocculated water enters the maturation chamber where a slow mixing process enables floc maturation and the increase of floc size. The micro-sand then becomes the nucleus of the newly formed floc. Rapid settling of ballasted floc is

achieved in the lamella clarifier section. Micro-sand allows for high rise rate design of the lamellar clarifier. Clarified water is then collected at the surface. Sludge is extracted from the bottom of the clarifier by means of an abrasion-resistant centrifugal pump. Using the centrifugal vortex principle, a hydrocyclone then separates the sludge from the reusable microsand. These microsand particles are discharged through the underflow of the hydrocyclone and recycled in the injection tank. The fine and lighter sludge particles move upwards with the major fraction of the water out through the vortex overflow. The application of the Actiflo process for seawater pre treatment gives a good efficiency for the removal of suspended solids, turbidity, SDI, dissolved organic carbon and algae (figure 36).

5. Membranes (ultrafiltration and microfiltration)

Most of the desalination plants use conventional pre treatment processes (i.e. dual media filtration preceded by coagulation and sometimes by sedimentation or air flotation for more challenging seawaters). Despite these conventional processes are quite efficient in decreasing the fouling ability of the raw seawater, they could present some difficulties to maintain at anytime a SDI below 3 when this low value is required and when high variations of the seawater quality is observed. However, they could easily meet a value of $SDI \leq 4$ which is value largely accepted by the membrane suppliers. The main advantage of the conventional pre treatment processes is the use of adequate and high dosage of the coagulant (such Fe) which implies a reduction of high organic matter which control the bio-film on the RO membranes (Laine et al.,2003).

In drinking water plants fed from surface or ground water, low-pressure membrane processes such as microfiltration (MF) or ultrafiltration (UF) are used to produce high quality water. In the last ten years, ultrafiltration (UF) or microfiltration (MF) pre-treatment has gained widespread attention as potential pre-treatment to seawater desalination by seawater reverse osmosis (SWRO). While in the period until 2002, mostly pilot studies were undertaken, in recent years there have been about 10-15 seawater reverse osmosis (SWRO) plants implemented using ultrafiltration pre-treatment (Bonnélye et al.,2008; Jerowska et al.,2009; Kim & Yoon, 2005).

Membrane filtration pre-treatment involves forcing seawater through a membrane with very fine pores. Particles that are larger than the pores are filtered out. Current large plants utilise low Coagulant dosage since dissolved organics can still pass through the membrane. There has been increasing utilisation of membrane filtration for reverse osmosis systems over the last few years. It is why, low pressure membranes such as ultrafiltration (UF) and microfiltration (MF) are choose for pre-treatment in RO systems (figure 37), primarily due to their effectiveness in removing potential foulants in sea waters. The table 12 summarizes the different specifications of some membranes used for the seawater pre treatment. In treating bad seawater quality, MF and UF are susceptible to fouling for which backwashing without chemicals is sometimes no longer effective. This may result to an increase in chemical consumption for membrane cleaning as well as for in-line coagulation. Several studies reported that polysaccharides are the main cause of fouling in MF/UF membranes (Yoon et al;2004 ; Yang & Kim,2009;Kruithof et al.,1998).

The origin of the flux decline can be accounted for by using different theoretical kinetics models commonly employed for systems showing flux decline (McCabe et al., 1985). Hermia (Hermia,J, 1982) and Van Hoof (Van Hoof et al., 2001) introduced some filtration models: (a) complete blocking, (b) intermediate blocking, (c) standard blocking, and (d) cake filtration

which aim to describe fouling mechanism. The complete blocking model occurs when particles arrive at the membrane and block some pore or pores with no superposition of particles. An intermediate blocking model is when particles can settle on other particles previously arrived that already block some pores. A standard blocking model is when particles arrive at the membrane and are deposited onto the internal pore wall. The cake filtration model is when particles are located on other already arrived and are already blocking some pores. During the filtration mode, all the solids in suspension retain on the membrane surface. These retained solids are generally referred to as fouling and the filtration process cannot be maintained indefinitely, due to the fact that the driving force across the membrane has to be increased constantly to keep the flow through the membrane constant. Hence, the system is backwashed (BW) by reversing the flow direction through the filter at regular intervals (Xia et al.,2004; Teuler et al.,1999). The solids are washed away to drain and the whole process repeats itself. While backwashing can remove most of the solids from the system, chemical cleaning methods have to be applied to completely clean the membrane. Some substances tend to adhere to the membrane surface so they cannot be removed by mechanical force alone. (Boerlage et al.,1997) These substances, often of organic and microbial origin, tend to slowly but surely block the membrane. This blocking of the membrane is what ought to be called fouling since the removal of these particular substances is most often not the main purpose of the process. They are sometimes in solution (small organic compounds) and would pass through the membrane, if not for their strong tendency to adhere to the surface. They could also constitute micro-organisms that are removed by the membrane, but start producing extra cellular substances once they have settled onto the membrane surface. The primary goal of in-line coagulation (Qin et al.,2006) is stabilization of the dead-end UF process between 2 chemical cleanings. Dosing of some ppm's coagulant is stabilizing the dead-end filtration process resulting in a slowly rising resistance-profile in time (Maa et al.,2006; Liang et al.,2008;Chen et al/,2007; Knox-Holmes et al.,1994). A recent study by Villacorte (Villacorte et al.,2009) reported significant amounts of TEP in the raw water and after MF/UF pre treatment. It was also found that acidic polysaccharides smaller were up to 5 times more abundant than those larger than 0.40 μm . The presence of colloidal TEPs is also essential considering that MF/UF pre-treatment may not completely remove this fraction from the RO feed water. Systems composed of ultrafiltration (UF) pre-treatment for seawater reverse osmosis (SWRO) desalination are often termed "integrated membrane system" or "dual membrane system".

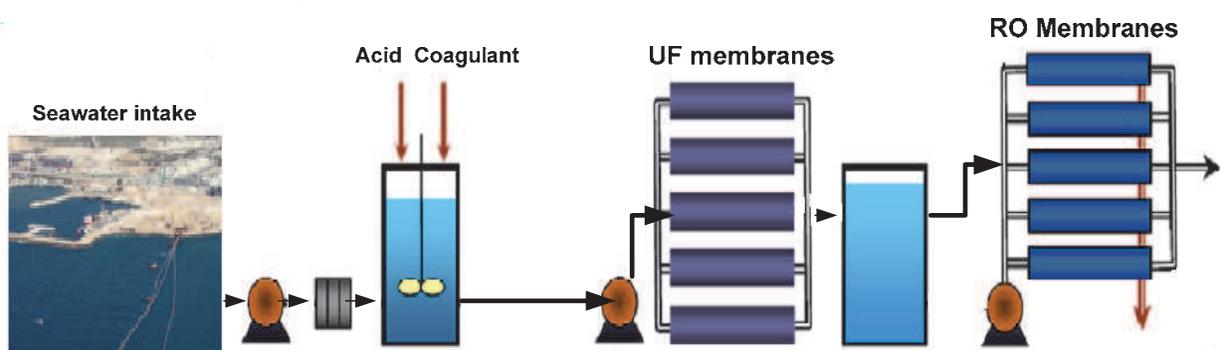


Fig. 37. Systems composed of ultrafiltration (UF) pre-treatment for seawater reverse osmosis (SWRO)

There have been few studies about seawater RO pre-treatment by membrane processes in the past. Kumar (Kumar et al.,2007) compared MF and UF membranes in pre-treatment to determine differences in filtrate quality: 0.1 μm MF and 100 kDa UF membranes showed no difference in term of flux decrease in the RO element, suggesting equal fouling potential of the filtrate. On the contrary, a 20 kDa UF membrane resulted in a reduced flux decline in the RO element, suggesting less membrane fouling. In 2003, Vial & Doussau (Vial & Doussau, 2002) tested 0.1 μm hollow-fibre membranes for the pre treatment of Mediterranean seawater. They observed no influence of turbidity and SDI peaks on permeate turbidity and SDI. In 2004, Pearce (Pearce,2004) used an UF membrane pre treatment at Port Jeddah, Saudi Arabia, as an alternative to its conventional pre treatment facility, which could not meet targeted feed water quality during algal blooms and storms. The implementation of membrane pre treatment with daily air-enhanced backwashes achieved an average filtrate SDI of 2.2, which corresponded to an SDI improvement of two units compared to the previous conventional pre treatment. Higher RO feed water quality hence resulted in reduced fouling of the RO element by 75%.

Most of these studies about seawater RO pre treatment by membrane processes are based on an evaluation of pre treatment performance (Choules et al., 2009); Gaid & Craig,2009) through conventional and limited analytical tools such as SDI, turbidity or particle counts. Moreover, few of these studies presented a side-by-side comparison of conventional and membrane pre treatment fed at the same time by the same seawater.

Membrane element characteristic	ZeeWeed 1000 Ultrafiltration	Norit Ultrafiltration	DOW Ultrafiltration	Hydranautics Ultrafiltration	Pall Microfiltration
Active Membrane Area (m^2)	55.8	40	51	46	50
Flow Path (In-Out; Out-In)	Outside-In	Inside-Out	Outside-In	Inside-Out	Outside-In
Molecular Weight Cutoff (Daltons)	100 000	150 000	150 000	150 000	-
Nominal Membrane Pore Size (microns)	0.02	0.05	0.05	0.05	0.10
Absolute Membrane Pore Size (microns)	0.1	0.075	0.075	0.075	-
Membrane Material	PVdF	PES	PVdF	PES	PVdF
Membrane Hydrophobicity	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophilic	Hydrophobic
Membrane Charge	Slightly negative	Neutral	Neutral	Neutral	Slightly negative
Acceptable Range Operating pH Values	5 - 10	2 -12	2 -12	2 -12	1 - 10
Maximum TMP for System (bar)	0.9	2.5	2.1	2.5	3
Chlorine/Oxidant resistance	Resistant to NaOCl, ClO ₂ , KMnO ₄	200 ppm continuous	>5 000 000 ppm.hrs	200 ppm	Chlorine 10 000 ppm, oxidant resistance
Required Pre screening (microns)	100	100	100	100	200

Table 12. Main characteristics of some membranes used for pre treatment of seawater

5.1 Performances of the ultrafiltration and microfiltration membranes

5.1.1 Biofilm control on Reverse osmosis membranes

Controlling the persistent problem of organic and biological fouling, is still a major challenge in many reverse osmosis (RO) plants (Shon et al.,2009, Wittmann ,2011). A membrane bio-film is known to offer significant advantages for micro-organisms embedded within its matrix, including better stability against mechanical cleaning and higher tolerance to biocides. Bio-film studies cited the importance of extra-cellular polymeric substances (EPS) in the cohesion of microbial cells and other particles, as well as adhesion to surfaces. Whether the accumulation of EPS in RO membranes is mainly due to local production by bio-film micro-organisms or by gradual deposition of EPS from the RO feed water, is still not clearly known (Aleem et al.,1998; Fujiwara & Matsuyama,2008; Tekeuchi et al.,2008)).

Over the last decade, the discovery of a formerly undetectable but abundant type of EPS called transparent exo-polymer particles (TEP), has led to a better understanding of its role in the carbon cycle and biological life in aquatic systems. TEP is distinct among EPSs in many ways. Unlike most EPS, TEP exist as individual particles rather than as cell coatings or dissolved slimes. They have been characterised as transparent, sticky, gel-like substances which are comprised mainly of acidic polysaccharides. TEPs are hydrophilic and known to exist in different shapes (blobs, clouds, sheets, fibers or clumps) and sizes (~0.4 to 200 μm). As a planktonic type of EPS, they are ubiquitous in most fresh (terrestrial/surface) and marine waters and have also been found in wastewater.

Most TEP originates from polysaccharides released by phytoplankton and bacterioplankton, which subsequently coagulates to form TEP. However, they are also exuded or lysed out from macro algae and some higher marine organisms. The majority of TEP are formed abiotically from colloidal polysaccharides, 1-3 nm in diameter by hundreds of nanometers long, which are flexible enough to pass through 8 kDa pore size membranes. Thus, these colloidal polysaccharides or the so called "colloidal TEPs" are capable of passing through MF/UF pre-treatment and may compromise the operation of the reverse osmosis (RO) system downstream.

5.1.2 Algae & membranes

Algal species are larger than the nominal pore size of both microfiltration and ultrafiltration membranes; therefore, rejection of algae occurs to a large extent on the basis of size. However, the trapped cells may release extra-cellular matter that can block the module outlet and lead to severe flux decline or TMP increase. Membrane fouling often occurs as a result of accumulation and/or adsorption of rejected materials at the membrane surface. However, in the presence of algae, the layer of rejected material at the membrane surface should not be considered as a non-adhesive cake layer (Adham S.,1997). In the absence of any pre-treatment, algae cells and organic matter can easily enter the UF module. Organic matter can penetrate within the membrane pore and cause evident flux decline. Live algae cells can also deposit on the surface of membrane and release extra-cellular material during filtration. The released polysaccharides can bond with other organic species and increase the resistance for filtration. For this reason, a direct UF system is not suitable for algae-rich water treatment (Passow, 2000 and 2002; Kwon et al.,2005). Instead, the extra-cellular algal slimes (mucilaginous or gelatinous materials) are likely to serve as "cement" for the particulate material rejected by the membrane surface. The presence of extra-cellular algal slimes is likely to contribute to a greater superimposed resistance to filtration (Thornton, 2004) than would be observed for a non-adhesive cake layer.

Coagulation pre-treatment can improve UF by flocculation of the material depositing on the membrane surface, which can then form a cake layer. The low molecular organic matters can be trapped within this layer and the fouling is reduced. During the algae-rich water treatment, coagulation – flocculation can only adsorb and flocculate the algae cells, while it can not make them inactive. Coagulation pre-treatment alone can not satisfy the needs of UF application in algae-rich water treatment.

5.1.3 Feed back of pilot plants and existing plants

- a. The seawater of the Palm Jumeirah plant (figure 38) is characterized by a very high seawater SDI measured as SDI 2.5 min. Furthermore, as is common in the seawaters of the Gulf, the contribution to the SDI is given by particles of very small size and this accounts for the relatively poor turbidity values observed upstream of the Norit UF membranes. On the other hand excellent permeate quality was obtained during plant operation with excellent permeate SDI regardless of the very high feed seawater quality (around 30 NTU). Measured values of permeate SDI are in range from 0,5 to 3 with the average about 1,6. SDI values obtained during operations (Sommariva et al.,2009). Experiments were performed on site using 10 μ , 5 μ , 1 μ and 0.47 μ test filter papers. It was found that the 10 μ and 5 μ filter papers removed almost no particles at all; the 1 micron filter paper was able to remove around 10% of the particles; a further 45% of particles were removed by the 0.47 μ filter and the remaining 50% had a particle size of less than 0.47 μ . It is possible that some of the particles would be small enough to pass even the UF membrane (or migrate through faulty seals). For this reason a small amount of Ferric Chloride is dosed as a coagulant filtration aid (\sim 0.25 mg/l as total iron was found to be optimal). The high volume of very small particle size silt and the consequent necessity to dose ferric chloride led to deposits forming on the membrane surface and to escalating operating pressure of the UF units as backwashing and CEB could not fully restore the trans-membrane pressure differential. A 'clean-in-place' (CIP) regime was implemented to restore the membranes to their original performance levels. The selected cleaning chemical was a mixture of oxalic acid ($H_2C_2O_4$) and ascorbic acid ($C_6H_8O_6$). The cleaning solution consisted of RO permeate containing 1% oxalic acid and $\frac{1}{4}$ % ascorbic acid heated to 36°C and the procedure was a series of soak and recirculation stages followed by rinsing with fresh, warm RO permeate (Ingham et al. 2009).

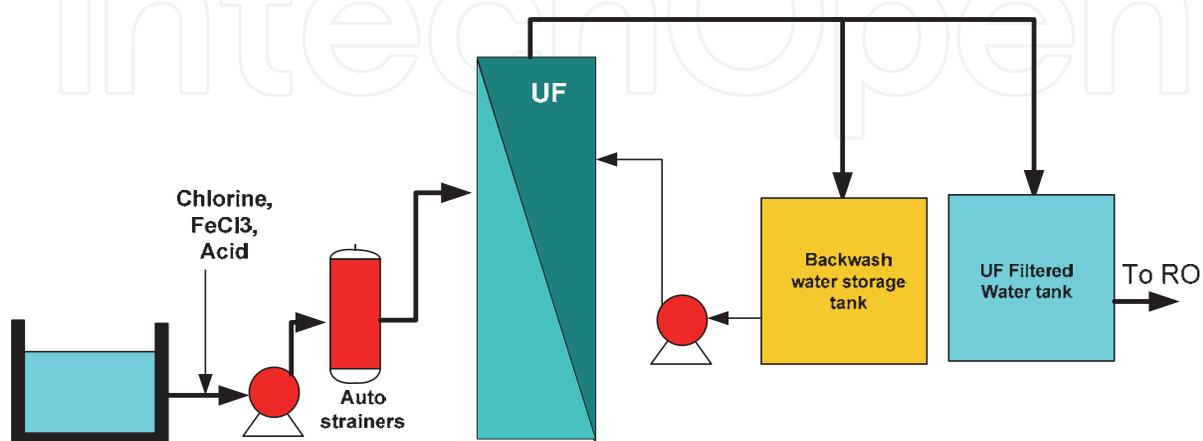


Fig. 38. Palm Jumeirah Pre treatment including Norit X-Flow UF

- b. Codemo (Codemo et al., 2009) said that since UF membranes provide a barrier to particulates, they provide significant benefits to the RO and overall system design. Everybody must be aware that if UF is not handled together with respect RO as one compact system – significant problems in RO performance may occur. RO performance could suffer due to heavy bio-fouling despite the fact that UF filtrate will provide very good membrane feed water with no particulates. But despite this – one important parameter may be out of control – bio-fouling. Bio-fouling is much bigger and more dangerous threat for UF-RO system than i.e. fiber breakage.
- c. Busch (Busch et al., 2009) described the cleaning occurred on Wang Tan power plant where the modules been autopsied and showed a significant amount of fouling on the module. The fouling appeared to be of brown to red colour. After analysis, it was concluded that the colour of the fouling can be explained by the presence of high organic and iron levels. The most appropriate cleaning condition was as follows: oxalic acid 2%, temperature 35°C, circulation time 2 h, then soaking 3 h, then backwashing. It can be seen that after this protocol, the module can be very well cleaned again and the full permeability can be restored.
- d. Knops (Knops & Lintelo, 2009) describe the tests done in 2007 on the Colakoglu steel mill plant where they have observed a loose of the permeability on the seaguard UF Membrane. One membrane element was removed from the UF system and returned to the factory for autopsy. The immediate investigation revealed a dark red discoloration of the membrane element . EDX analysis of the membrane confirmed that the colour was caused by iron, with trace amounts of silica and aluminium being present. This indicated that the most probable cause of the drop in performance was fouling with the inorganic coagulant (FeCl_3). Laboratory scale testing of the performance revealed a sharp drop in permeability when compared to the original value for the new membrane.. A plant cleaning in place (CIP) was performed to remove the bulk of the fouling (Junga & Son, 2009).

5.1.4 Lessons learned from the UF membrane SWRO pre-treatment

If there is any doubt about the long term quality of the feedwater then the following should be considered when designing a desalination plant:

- UF will provide effective treatment of the raw water; therefore the RO stages can therefore be designed quite aggressively.
- Turbidity alone is not a good predictor of fouling potential.
- The UF system should be designed using conservative flux and net recovery assumptions. Physical space should be left for additional UF plant in case anticipated flux values and net recovery are difficult to achieve. Additional capacity should be designed into the screening and straining stage.
- Ultrafiltration provides more stable water quality than a multi media filtration

But an irreversible membrane fouling has to be considered and could be a limitation in the application of this technology depending of the seawater quality. The accumulation of the retained matter on the membrane surface leads to an increase in operating costs, due to progressively increasing energy consumption and the necessity of periodic cleaning. To reduce these operating costs, it is necessary to control the fouling behaviour. This can be achieved by in-line coagulation. In addition to performance enhancement, in-line coagulation promotes the retention of organic macro-molecules and phosphates, which helps to reduce bio-fouling in downstream processes, such as SWRO. However, the

application of in-line coagulation does have drawbacks. Firstly, it forms a large portion of the operating costs, due to chemicals consumption and the increased disposal costs of the concentrate stream. Secondly, coagulant residuals in the permeate, caused by over dosing, reduce the product quality and can lead to issues in downstream processes, for example SWRO (Futelaar et al., 2009; Yacubowicz, 2010).

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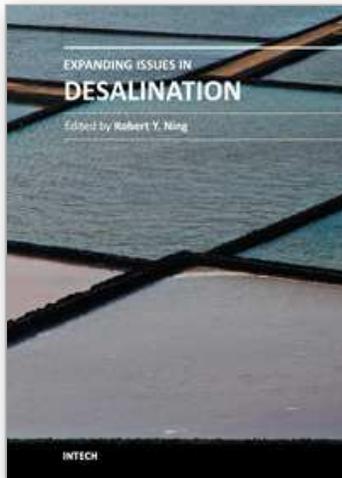
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For this book, the term “desalination” is used in the broadest sense of the removal of dissolved, suspended, visible and invisible impurities in seawater, brackish water and wastewater, to make them drinkable, or pure enough for industrial applications like in the processes for the production of steam, power, pharmaceuticals and microelectronics, or simply for discharge back into the environment. This book is a companion volume to “Desalination, Trends and Technologies”, INTECH, 2011, expanding on the extension of seawater desalination to brackish and wastewater desalination applications, and associated technical issues. For students and workers in the field of desalination, this book provides a summary of key concepts and keywords with which detailed information may be gathered through internet search engines. Papers and reviews collected in this volume covers the spectrum of topics on the desalination of water, too broad to delve into in depth. The literature citations in these papers serve to fill in gaps in the coverage of this book. Contributions to the knowledge-base of desalination is expected to continue to grow exponentially in the coming years.

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