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# UNESCO-IHE INSTITUTE FOR WATER EDUCATION



## Effect of Soil Aquifer Treatment Effluent on Performance of MF/UF Membranes

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MSc Thesis MWI 2008/01  
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# Effect of Soil Aquifer Treatment Effluent on Performance of MF/UF Membranes

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The findings, interpretations and conclusions expressed in this study do neither necessarily reflect the views of UNESCO-IHE, Institute for Water Education, nor of the individual members of the MSc committee, nor of their respective employers.

*I want to dedicate this work to my whole family  
Specially to my parents  
who have always been anywhere I am, guiding me throughout each  
step of my life*



## Abstract

As the world population is growing and the demand for water is increasing, there is a need to look for alternate sources for water. Re-use of treated wastewater has been gaining increasing attention these days as an alternative to natural source of water for potable or non-potable reuse. However, while promoting wastewater reuse it is important that, there is proper treatment of these water sources in order to ensure proper operation of the distribution system and no adverse impact on the health of the population served.

Soil Aquifer Treatment (SAT) is an the emerging managed aquifer recharge technology, which in combination with other available wastewater treatment technologies could produce effluent of acceptable quality for indirect potable reuse. It is a low cost and appropriate option for wastewater reclamation in developing countries that ensures sustainability of both surface water and groundwater sources with in the context of integrated water resources management. The EfOM content of SAT effluent might influence the subsequent treatment processes in drinking water production namely MF/UF. The effect of SAT effluent on the performance of MF/UF membrane systems has not been fully understood, Organic matter present in SAT effluent may foul these membranes and influence their performance.

The main goal of this study was to develop the technology for reuse of wastewater by using SAT as pre-treatment of MF/UF membrane system. The specific objectives included analysis of DOC removal, MFI reduction and removal of different organic matter fractions by different types of membranes with or without SAT pre-treatment.

Laboratory-scale soil column and stirred cell experiments were conducted using two types of water; (i) SE+DCW, (ii) SE, and different types of membranes: 0.1  $\mu\text{m}$  pore size MF membranes and 100, 50, 10 kD UF membranes.

The average DOC removal from wastewater treatment plant effluents for different types of membranes alone ranged from 12 to 22%. SAT pre-treatment of these effluents increased the DOC removal by MF/UF membranes to 30 to 46%.

SAT helps to improve performance of MF/UF by reducing the fouling up to 73% for SE+DCW and 57% for SE. The different types of membranes have characteristic for removal of organic matter and have different value of MFI. MFI reduction was bigger when the MWCO of the membranes was smaller. The maximum protein removal with 10 kD UF membrane was 30% without SAT, and for fulvic and humic-like organic matter removal is 22% without SAT pre-treatment.

This study clearly showed that SAT pre-treatment of wastewater treatment plant effluents not only improves the DOC removal by MF/UF membranes but also reduces the fouling potential of these membranes. Furthermore, combination of SAT and UF removes different organic matter fractions substantially thus increasing the potential for water reuse.

SAT can help to reduce water scarcity for the developing countries like Yemen, because the technology is low cost and sustainable. Furthermore SAT is good option as pretreatment for removal of non-humic substances for water reuse application.



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## List of Symbols and Abbreviations

|                |   |
|----------------|---|
| A              | Membrane surface area (m <sup>2</sup> )             |
| C <sub>b</sub> | Concentration of particles in the feed water (mg/l) |
| d <sub>p</sub> | Particle size diameter (m)                          |
| J              | Flux (l/m <sup>2</sup> .h)                          |
| Q              | Flow (ml/s)   |
| R <sub>c</sub> | Cake resistance (1/m)                               |
| R <sub>m</sub> | Clean membrane resistance (1/m) computed from MFI   |
| R <sub>b</sub> | Blocking resistance (1/m)                           |
| R <sub>t</sub> | Total resistance (1/m)                              |
| t              | Filtration time (s)                                 |
| T              | Temperature (°C)                                    |
| V              | Filtration volume (m <sup>3</sup> )                 |
| w              | Cake mass (mg)                                      |
| h <sub>f</sub> | Friction loss (mwc)                                 |
| h <sub>m</sub> | Minor loss (mwc)                                    |
| Re             | Reynolds number (-)                                 |

## Greek symbols

|                             |                                       |
|-----------------------------|---------------------------------------|
| $\alpha$                    | Specific cake resistance (m/g)        |
| $\Delta P$                  | Transmembrane pressure (kPa)          |
| $\eta_{20^{\circ}\text{C}}$ | Viscosity at 20°C (Pa.s)              |
| $\eta_T$                    | Viscosity at T°C (Pa.s)               |
| $\rho_p$                    | Particle density (kg/m <sup>3</sup> ) |
| $\lambda$                   | Friction factor (-)                   |
| $\xi$                       | Minor loss factor (-)                 |

## List of Abbreviations

|        |   |
|--------|---|
| SAT    | Soil aquifer treatment  |
| NF     | Nano-filtration   |
| UF     | Ultra-filtration  |
| RO     | Reverse osmosis   |
| WSE    | Water supply engineering  |
| MDG    | Millennium Development Goals                                    |
| SANDEC | Department of water and SANitation in DEveloping Countries      |
| UN     | United Nations  |
| UNEP   | United Nations Environmental Programme                          |
| UNESCO | United Nations Educational Scientific and Cultural Organization |
| WHO    | World Health Organization                                       |
| EfOM   | Effluent organic matter   |
| NOM    | Natural organic matter  |
| DOC    | Dissolved organic carbon  |
| FTIR   | Fourier transform infrared                                      |

|         |  |
|---------|--|
| SMP     | Soluble microbial products                                     |
| DBP     | Disinfection by-product  |
| SOCs    | Synthetic organic compounds                                    |
| MilliQ  | Deionised water with a resistance of less than 18.2 MΩ at 25°C |
| MFI     | Modified Fouling Index   |
| MFI0.45 | Modified Fouling Index determined using a 0.45 µm membrane     |
| MFI-UF  | Modified Fouling Index using ultrafiltration membranes         |
| UV254   | UV absorbance at 254 nm  |

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# **1. Introduction**

## **1.1. Background**

In September 2000, the United Nations (UN) General Assembly adopted the Millennium Declaration (Resolution 55/2) to crystallise the agenda of human development. International goals – the Millennium Development Goals (MDGs) were thus set, namely:

1. Eradicate extreme poverty and hunger
2. Achieve universal primary education
3. Promote gender equality and empower women
4. Reduce child mortality
5. Improve maternal health
6. Combat HIV/AIDS, malaria and other diseases
7. Ensure environmental sustainability
8. Develop a global partnership for development

The MDG 7 is to ensure environmental sustainability. One of its targets (target 10) is directly related to this research: "Halve, by 2015, the proportion of people without sustainable access to safe drinking water and basic sanitation" (MDG's (2007).

This research aims to help to achievement of MDG 7 (target 10), by improving the methods of wastewater treatment and reuse. This research focuses on the effect of Soil Aquifer Treatment (SAT) on performance of MF/UF membrane. In this approach, SAT is the pre-treatment for wastewater treatment plant effluent to promote potable reuse.

SAT relies on natural processes to polish treated wastewater. The performance of SAT system is affected by several engineering design and operational factors. These include:

- The degree of wastewater treatment that precedes SAT (pretreatment),
- Certain physical characteristic of the SAT system such as to groundwater and distance to recovery wells, and
- The operational schedule of SAT infiltration basin.

Wastewater constituents of primary concern include residual organic material, nitrogen, trace organic and pathogenic microorganisms.

Membrane filter is being extensively used for treatment of wastewater for reuse. A major limitation in membrane filtration of wastewater effluent during wastewater reclamation/ reuse is significant reduction of permeate flux caused by membrane fouling. In the operation of a membrane system, membrane fouling is dependent on many parameters. Like membrane characteristics; source (feed) water characteristics, and hydraulic conditions of the system. Among these, organic constituents contained in wastewater effluent, designated as effluent organic matter (EfOM), are found to play an important role as membrane foulants (Shon, 2006). Effluent organic matter (EfOM) represents a range of soluble organic compounds present in biologically treated wastewater.

These complex and heterogeneous compounds can be classified into 3 different groups according to their origins: (Shon, 2006).

1. Refractory natural organic matter (NOM) derived from drinking water sources.
2. Synthetic organic compounds (SOC) produced during domestic use and disinfection by-products (DBPs) generated during disinfection processes of water and wastewater treatment, and
3. Soluble microbial products (SMP) derived during biological processes of wastewater treatment. The SMP is typically divided into two groups: 1. BAP (biomass associated products) mainly generated from biomass decay. 2. UAP (utilization associated products) mainly generated from substrate uptake and biomass growth.

## **1.2. Problem Description**

Wastewater reuse is an attractive option to reduce water scarcity; however, it needs to be treated properly before reuse. There are different treatment methods for wastewater effluent before reuse. Soil Aquifer Treatment (SAT) followed by membrane is one of the most attractive & promising hybrid technologies.

SAT is an emerging treatment technology which in combination with other wastewater treatment technologies could remove multiple contaminants from wastewater and serve as an effective barrier and environmental buffer for indirect potable reuse. The effectiveness of SAT depends on the quality of wastewater applied, process conditions applied and the local hydrogeology.

The complexity and heterogeneity of the EfOM contribute to varying physical and chemical behaviors in membrane fouling, making it difficult to explain membrane fouling mechanisms. Effect of EfOM on the performance of different types of membrane is not fully understood. Selection of proper SAT pre-treatment system and proper membrane type for subsequent treatment is very important to minimize the costs and to produce water of required quality.

To understand these problems, analysis of organic matter before and after SAT and after MF/UF treatment is required to determine the real effect of SAT on performance of membranes, specially MF/UF membranes.

## **1.3. Goal and Objectives**

The main goal of this research was to develop the technology for reuse of wastewater by using the SAT as pretreatment and MF/UF membranes as main treatment .

The specific objectives of this research are:

1. To investigate the fate of EfOM in secondary effluent during SAT followed by MF/UF process as post treatment by conducting lab-scale experimental studies.

2. To characterize the EfOM removed during MF/UF membrane process with or without SAT pre-treatment.
3. To analyses the impact of effluent organic matter present in SAT effluent on the performance of the MF/UF membrane systems by studying development of transmembrane pressure and fouling of the membranes.



## 2. Literature Review

### 2.1. General Overview of Wastewater Treatment by SAT

Soil aquifer treatment (SAT) of wastewater relies on extensive biogeochemical processes in the soil and aquifer to achieve large-scale and economic reclamation of municipal effluents. In general, it can be concluded that SAT technology has the capacity for removing organic matter from both primary and secondary effluent. Organic matter is effectively removed in the upper layer of infiltration primarily by biodegradation and complimented by filtration and adsorption.

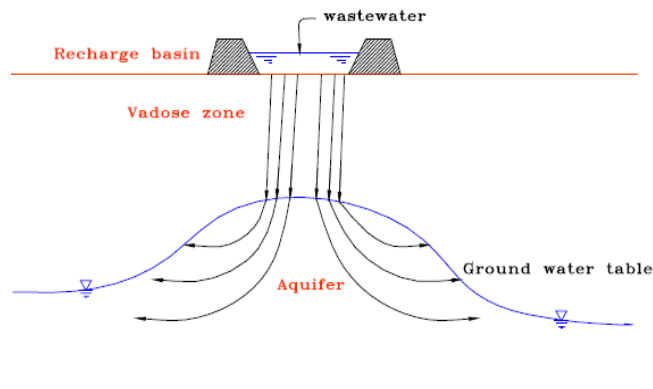


Figure 2.1 Schematic representation of SAT system with flow lines

(Source: Nema et al., 2001)

Large-scale reclamation and reuse of municipal wastewater is increasingly practiced in many locations. SAT is an economical approach to reclamation involving an initial treatment of the municipal wastewater to secondary effluent level followed by recharge into a local aquifer by means of large scale recharge basins for further treatment, quality improvement and storage. In essence, this method activates biogeochemical processes in soils for effluent purification. After a period of detention in the aquifer the reclaimed water are recovered and reused mainly for unlimited irrigation (Bouwer, 1996).

SAT evolved as a result of increased need to augment existing drinking water supplies due to the high industrial and agricultural water demand, the contamination of groundwater and surface water sources and the uneven distribution of water resources. Potable water reuse has been through infiltration or injection of effluents below the surface. Currently, indirect potable reuse projects especially in the United States of America (USA) apply SAT after conventional secondary wastewater treatment followed by tertiary filtration (Drewes et al., 2003). SAT enhances aesthetics and public acceptance of water reuse since water is obtained through recovery wells instead of an advanced wastewater treatment system (Bouwer, 1996).



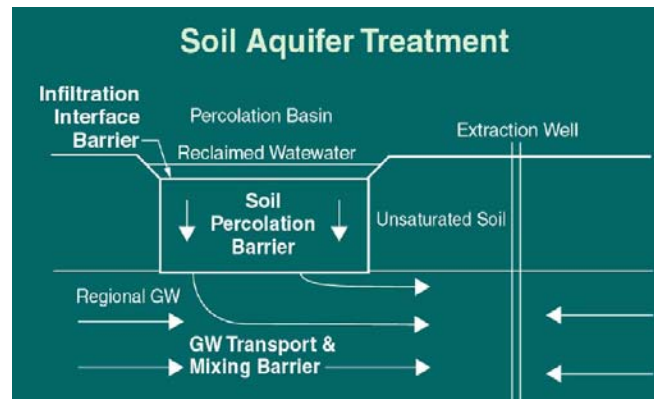


Figure 2.2 Soil aquifer treatment technology (Source: Amy, 2005)

### 2.1.2 Methods and Process of SAT

Soil aquifer treatment helps to augment aquifer based potable and non-potable water supplies. This type of treatment allows treated municipal wastewater discharges in basins to infiltrate through the vadose zone and eventually the saturated unconfined aquifer. It, therefore, improves water quality through physiochemical and biological treatment in both saturated and unsaturated zones. The process is a cycle of wetting and drying periods to allow re-aeration, which increases the redox potential (Montgomery-Brown et al., 2003). This technology is comparable to riverbank infiltration except that it is discontinuous.

Figure 2-3 below shows the operational cycle of an infiltration basin with operational period in the order of days to weeks. After reaching the ground water table, the water will flow in all directions or radially away from recharge areas before conforming to the natural ground water flow pattern at greater distances. There may also be some lateral flow in the vadose zone where perched water table of phreatic surface occurs.

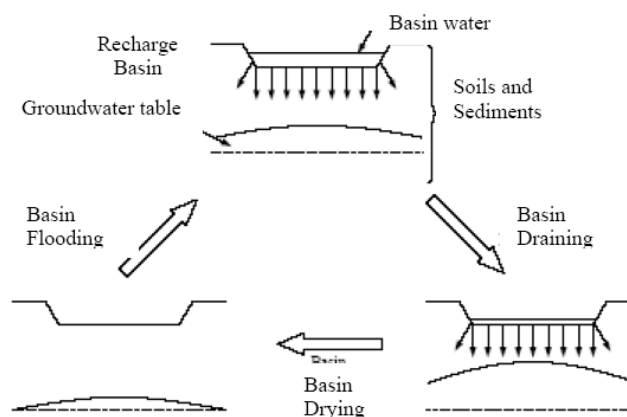


Figure 2. 3 A schematic representation of infiltration basin operation (Source: Montgomery-Brown et al., 2003)

### 2.1.3 Factors Effecting SAT

#### 2.1.3.1 Influent Wastewater Quality

Influent wastewater quality parameters namely organic matter, suspended solids and nitrogen influence the quality of SAT effluent. The organic matter components and their

characteristics differ considerably in groundwater, primary effluent, and secondary effluent and reclaimed wastewater. The difference is attributed to organic compounds added by consumers and soluble microbial products (SMPs) generated in wastewater treatment processes. The organic loading in the incoming water exerts an oxygen demand resulting in depletion of oxygen and development of anoxic conditions with  $\text{NO}_3^-$  as the electron acceptor (Drewes and Fox, 1999).

Suspended solids may not have a significant effect on infiltration rates. Infiltration rate for primary and secondary effluents were comparable under previous studies carried out using high rate filtration columns (Nema et al., 2001). However, the characteristics of raw wastewater in terms of suspended solids determine the settling efficiency and hence primary clarification to make it suitable for soil aquifer treatment.

Higher nitrogen removal is likely to be achieved using primary effluents as compared to secondary effluents. This is attributed to the availability of the carbon source for denitrification in primary effluents due to high organic concentration; 1 mg/L nitrate nitrogen requires about 2.5 mg/L BOD to be denitrified. Higher nitrogen removal could be achieved with higher C:N ratio with evidence of nitrification from the increased  $\text{NO}_3\text{-N}$  concentration. In addition, Phosphorous and virus removal with both effluent types showed no difference (Nema et al., 2001).

Physical factors that affect SAT processes include temperature, pH, oxygen concentration and electrical conductivity. The DOC of removal increases with increasing temperature. Increase in temperature increases the microbial activity resulting in a fast biodegradation process.

### 2.1.3.2 Hydraulic Parameters

The main hydraulic parameters that affect SAT process include infiltration rate, permeability or porosity of the soil and hydraulic retention time.

#### Infiltration rate

Reduction in infiltration rates leads to development of anaerobic conditions. This caused by physical clogging due to high-suspended solids (SS) concentration and biological clogging during long flooding or wetting period even under low SS concentration. Infiltration rate has a direct impact on retention time and hence other DOC removal processes with the time dependant behavior more pronounced up to 1.5 m depth in the vadose zone (Drewes and Fox, 1999).

#### Permeability

Permeability depends type of soil and porosity. The size of pore space and interconnectivity of the spaces help determine permeability. It determines the hydraulic conductivity of the vadose zone and hence the retention time of the applied wastewater. Therefore permeability affects the percolation through the unsaturated zone and the treatment processes after rapid infiltration from recharge basins (Nema et al., 2001). Table 2.1 & 2.2 below show typical permeability and porosity values respectively of various soil sediments.

Table 2.1 Typical permeability values for natural soil sediments

(Source: Nema et al., 2001)

| Material                              | Permeability or Hydraulic Conductivity (cm/s) |
|---------------------------------------|---|
| Well-sorted gravel                    | 10 <sup>-2</sup> to 1                         |
| Well-sorted sands, glacial outwash    | 10 <sup>-3</sup> to 10 <sup>-1</sup>          |
| Silt sands, fine sands                | 10 <sup>-5</sup> to 10 <sup>-3</sup>          |
| Silt, sandy silts, clayey sands, till | 10 <sup>-6</sup> to 10 <sup>-4</sup>          |
| Clay                                  | 10 <sup>-9</sup> to 10 <sup>-6</sup>          |

Table 2. 2 Typical porosity values for natural soil sediments

(Source: Nema et al., 2001)

| Material                   | Porosity (%) |
|----------------------------|--------------|
| Well-sorted sand or gravel | 25-50        |
| Sand and gravel, mixed     | 20-35        |
| Glacial till               | 10-20        |
| Silt                       | 35-50        |
| Clay                       | 33-60        |

### Detention Time and Hydraulic Loading Rate

Detention times have significant effect on the treatment processes. Microbial activity in degradation of organic matter requires time for growth of microbial population under optimum conditions. Also nitrification-denitrification process and COD conversion will not be complete under short retention time. Removal of refractory organics usually requires long periods. An increase in hydraulic loading rate reduces the empty bed contact time (EBCT) resulting in reduced microbial formation of adsorbed DOC (Amy, 2005).

Typical hydraulic loading rate for SAT systems ranges from 0.1 to 3 m/day to achieve acceptable effluent quality depending the hydrogeological properties. The distance and travel times between recharge basins and wells should be at least 50-100 m and approximately 6 months (retention time) for adequate SAT (Asano and Cotruvo, 2004).

#### 2.1.3.3 Soil Types

The nature of soils beneath in the vadose zone affect the filtration rate. Fine clay result in low filtration rates (Fox et al., 2001a). Soil samples from infiltration basins have been found to contain pollutants but confined largely to 5-10 cm depth of penetration after determining the volatile matter content of the soil (Nema et al., 2001). Depending on the soil type, removal of DOC is rapid during percolation through the first 1.5 m (Quanrud et al., 2003). Therefore, SAT technology can be applied in tertiary wastewater treatment without polluting the deeper soil layers. However, soil characteristics vary from place to place with the depth making the rational design and operation of SAT systems difficult since it would require detailed hydrogeological investigations for each site. Quanrud et

al. (2003) found out that there was little benefit of using media of finer grains during SAT for optimum removal of EfOM. It was also established that increase in frequency of wetting cycles during SAT increase total hydraulic loading rates with no effect on dissolved organic removal efficiency.

#### **2.1.3.4 Aerobic, Anoxic and Anaerobic Conditions**

The period of wetting and drying cycles during SAT has a significant effect on removal of organic matter during biodegradation and on nitrogen removal during nitrification – denitrification processes. During SAT with the surface covered, dissolved oxygen is depleted due to nitrification and DOC oxidation and replenishment is only possible through applied wastewater. Kim et al. (2004) found out that oxygen supply from water in the saturated zone doesn't satisfy the oxygen demand exerted under high pollutant loading.

Nema et al., (2001) showed that oxygen concentration of 2-6.3 mg/L in renovated water which suggests that the unsaturated soil zone provided enough oxygen for biochemical processes which is in contrast with results for a covered surface. It can therefore be deduced that applying aerobic wastewater will not necessarily lead to anoxic conditions in the deeper parts of the soil matrix without control of oxygen concentration entering the system.

When oxygen is depleted, denitrification is enhanced under anaerobic conditions resulting in reduced nitrate and DOC concentrations; oxygen concentration is a key factor in predicting the production and removal of nitrate (Kim et al., 2004).

Under aerobic conditions, there is nitrification in the unsaturated zone and part of the nitrogen adsorbed on soil particles undergoes nitrification. Denitrification occurs under anoxic conditions and has been reported to occur in limited anaerobic pockets in the aerobic zone making it localized and partial (Idelovitch et al., 2003). This probably accounts for the fluctuation of nitrate concentrations indicated in literature. However according to Nema et al. (2004), the occurrence of anaerobic conditions can be expected in a rapid filtration system at least at microsites during the next application cycle or flooding period. In the first application cycle, ammonia is adsorbed to soils during the early part of flooding period after which soil microbes convert ammonia to nitrate under aerobic conditions in the drying period. Nitrifying and denitrifying bacteria are common soil organisms that play a big role in the nitrogen cycle.

## **2.2 Overview of Membrane Technology**

### **2.2.1 Historical Development of Membranes**

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. (Baker, 2004)

Systematic studies of membrane phenomena can be traced to the eighteenth century philosopher science. Through the nineteen and early twentieth centuries, membranes had no industrial or commercial uses, but were used as laboratory tools to develop physical/chemical theories.

By 1960, the elements of modern membrane science had been developed, but membranes were used in only a few laboratory and small, specialized industrial applications.

The period from 1960 to 1989 produced a significant change in the status of membrane technology. Building on the original Loeb- Sourjan technology, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high performance membranes. The final development of the 1980s was the introduction by GFT, a small German Engineering company, of the first commercial pervaporation system for dehydration of alcohol. (Mallevialle, *et al*, 1996)

## 2.2.2 Type of Membranes

The principle types of membrane are shown schematically in figure 2-4 and are described briefly below.

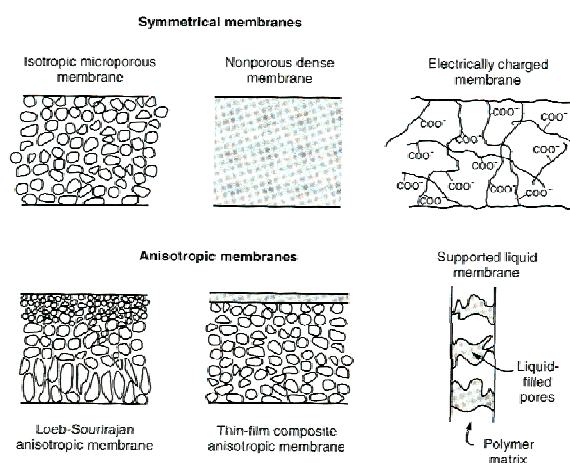


Figure 2.4 Schematic diagrams of the principal type of membrane  
(Source: Baker, 2004)

### Isotropic Membrane

#### Microporous Membranes

It is rigid, highly voided structure with randomly distributed, interconnected pores. However, these pores differ from those in a conventional filter by being extremely small, on the order of 0.01 to 10 $\mu$ m in diameter.

### Nonporous, Dense Membranes

It consist of a dense film through which permeates are transported by diffusion under the driving force of a pressure, concentration, pr electrical potential gradient. Usually these membranes have an anisotropic structure to improve the flux.

### Electrically Charged Membranes

It can be dense or Microporous, but are most commonly very finely Microporous, with the pore walls carrying fixed positively or negatively charged ions. They are used for processing electrolyte solutions in electrodialysis (Mallevalle, *et al*, 1996).

### Anisotropic Membranes

The transport rate of a species through a membrane is inversely proportional to the membrane thickness. Conventional film fabrication technology limits manufacture of mechanically strong, defect-free film to about 20  $\mu\text{m}$  thickness. The advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial processes use such membranes (Baker 2004).

### Ceramic, Metal and Liquid Membranes

The discussion so far implies that membrane materials are organic polymers and, in fact, the vast majority of membranes used commercially are polymer-based. However, in recent years, interest in membranes formed from less conventional materials has increased. Ceramic membranes, a special class of Microporous membranes, are being used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required. Dense metal membranes, particularly palladium membrane are being considered for the separation of hydrogen from gas mixtures, and supported liquid films are being developed for carrier- facilitated transport processes ( Benefield, *et al*, 1999).

#### 2.2.3 Membrane Process

The four developed industrial membrane separation processes are (i) microfiltration, (ii) ultrafiltration, (iii) reverse osmosis, and (iv) electrodialysis. These processes are all well established, and the market is served by a number of experienced companies. The range of application of the three pressure-driven membrane water separation is presented on figure 2-5. Microfiltration and ultrafiltration are basically similar in that the mode of separation is molecular sieving through increasingly fine pores. Microfiltration membranes filter colloidal particles and bacteria from 0.1 to 10  $\mu\text{m}$  in diameter. Ultrafiltration membranes can be used to filter dissolved macromolecules, such as proteins, from solutions. The mechanism of separation by reverse osmosis membranes is quite different. In RO membranes, the membrane pores are so small, from 3 to 5  $\text{\AA}$  in diameter that they are within the range of thermal motion of the polymer chains that form the membranes. The accepted mechanism of transport through these membranes is called the solution-diffusion model (Baker 2004).

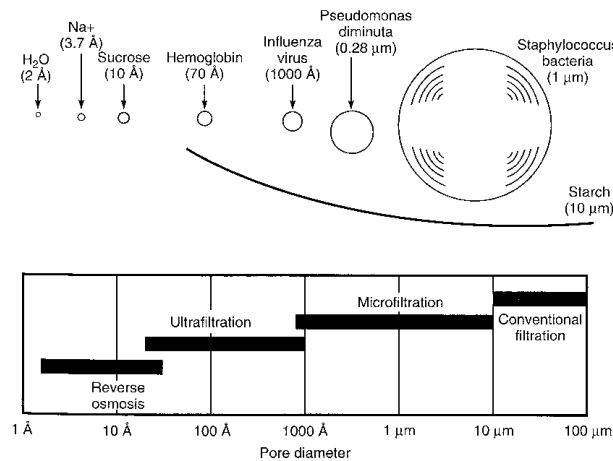


Figure 2.5 MF/UF and conventional filtration are related processes differing principally in the average pore diameter of the membrane filter (Source: Benefield, et al, 1999).

Its small size, easier maintenance and superior water quality produced by membrane filtration has made this advanced technology possible to replace conventional treatment processes that consist of ozonation, precipitation, coagulation, flocculation, chlorination and gravel filtration. In addition, the membrane filtration process offers the extra advantages over conventional treatment such as a small footprint, compact module, lower energy consumption, environmental friendliness and the capability of handling wide fluctuations in feed quality. Membrane filtration processes involving microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) in potable water production have increased rapidly over the past decade. MF and UF are employed to remove microparticles and macromolecules, which generally include inorganic particles, organic colloids (i.e., microorganisms) and DOM. However, the use of membrane processes does not directly eliminate the problem of DBPs; even though MF, UF, NF or RO have excellent performance on the removal of microbial particles, the disinfection process is still necessary. Typically the cost of membrane treatment increase as the size of the solute removed decreases (Baker 2004).

Table 2.3 The size range of membrane processes (Source: Baker 2004)

| Process               | μm           | nm          |
|-----------------------|--------------|-------------|
| Microfiltration, MF   | 0.02 - 10    | 20 - 10,000 |
| Ultrafiltration, UF   | 0.005 - 0.02 | 5 - 20      |
| Nanofiltration, NF    | < 0.001      | < 1         |
| Reverse Osmosis, RO * | < 0.001      | < 1         |

The membrane processes normally used to the ionic range for removal macromolecules and fine particles encompasses potable water solutes such as sodium, chloride, total hardness, most total dissolved solids, and smaller DBPs. The macromolecular range includes larger and small colloids, bacteria, viruses, and color. The fine particles range includes larger turbidity producing particles, most total suspended solids, cysts and largerm bacteria (Benefield et al., 1999). Table 2.3 shows the size range of membrane processes.

| Size $\mu\text{m}$                          | Ionic /molecule | macromolecular |                 | colloids        | suspended | settable |     |
|---|-----------------|----------------|-----------------|-----------------|-----------|----------|-----|
|   | 0.001           | 0.01           |                 | 0.1             | 1.0       | 10       | 100 |
| Approx. MW                                  | 100             | 1K             | 10K             | 100K            |           |          |     |
| Relative size of various materials in water | Salts           | Viruses        |                 | Cell fragments  | Bacteria  | Protozoa |     |
|   |                 | Polysaccharide |                 |                 |           |          |     |
|   | Fatty acids     | Protein        |                 |                 |           | Algae    |     |
|   |                 | Humics         |                 |                 |           |          |     |
| Pressure [bar]                              | 100             |                |                 |                 |           |          |     |
|   | 10              | Nanofiltration |                 |                 |           |          |     |
|   | 1               |                | Ultrafiltration |                 |           |          |     |
|   | 0.1             |                |                 | Microfiltration |           |          |     |

Figure 2.6 Classification of membrane and colloidal/macromolecular organic matter in ground and surface water (Source: Benefield et al., 1999)

## 2.3. Ultrafiltration

### 2.3.1. Introduction

Ultrafiltration (UF) uses a finely porous membrane to separate water and microsolutes from macromolecules and colloids. The average pore diameter of the membrane is in the 10-1000Å range. The principal problem inhibiting wider application of the technology is membrane fouling. The problem is controlled, but not eliminated, by module and system design and by regular membrane cleaning protocols. Development of membranes with surface properties designed to minimize fouling has also helped. Recently, several companies have developed ceramic-based ultrafiltration membranes. Although much more expensive than their polymeric equivalents, these have found a place in applications that require resistance to high temperature or require regular cleaning with harsh solutions to control membrane fouling (Benefield, et al, 1999).

### 2.3.2 Characterization of UF Membranes

Ultrafiltration membranes are usually anisotropic structure made by the loeb-Sourirajan process. They have a finely porous surface layer or skin supported on a much more open Microporous substrate. The finely porous surface layer performs the separation; the Microporous substrate provides mechanical strength. The membranes discriminate between dissolved macromolecules of different sizes and are usually characterized by their molecular weight cut-off, a loosely defined term generally taken to mean the molecular weight of the globular protein molecule that is 90% rejected by the membrane. UF and MF are related processes – the distinction between the two lies in the pore size of the membrane (Baker 2004).



### 2.3.3. Concentration Polarization and Membrane Fouling

A key fact determining the performance of UF membranes is concentration polarization, which causes membrane fouling due to deposition of retained colloidal and macromolecular material on the membrane surface. The pure water flux of UF membranes is often very high – greater than  $1 \text{ cm}^3/\text{cm}^2 \cdot \text{min}$  ( $350 \text{ gal}/\text{ft}^2 \cdot \text{day}$ ). However, when membranes are used to separate macromolecular or colloidal solutions, the flux falls within seconds, typically to  $0.1 \text{ cm}^3/\text{cm}^2 \cdot \text{min}$ . This immediate drop in flux is caused by the formation of a gel layer of retained solutes on the membrane surface due to concentration polarization. This gel layer forms a secondary barrier to flow through the membrane, as illustrated in Figure 2-11 and described in detail below.

This first decline in flux is determined by the composition of the feed solution and its fluid hydrodynamics. Sometimes the resulting flux is constant for a prolonged period, and when the membrane is retested with pure water, its flux returns to the original value. More commonly, however, a further slow decline in flux occurs over a period of hours to weeks, depending on the feed solution. Most of this second decrease in flux is caused by slow consolidation of the secondary layer formed by concentration polarization on the membrane surface.

Formation of this consolidated gel layer, called membrane fouling, is difficult to control. Control techniques include regular membrane cleaning, back flushing, or using membranes with surface characteristic that minimize adhesion. Operation of the membrane at the lowest practical operating pressure also delays consolidation of the gel layer. (Jacangelo J.G, 1995)

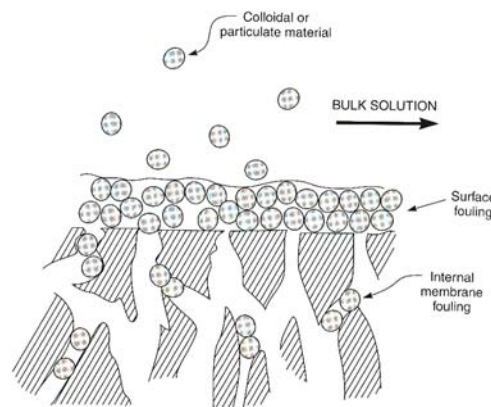


Figure 2.7 Schematic representation of fouling on an UF membrane. Surface fouling is the deposition of solid material on the membrane that consolidates over time. (Source Jacangelo J.G., 1995)

### 2.3.4 Operational Modes

UF is a membrane filtration process where particles and molecules in a fluid are forced through a membrane and separated, fractionated or concentrated by the membrane. UF is a pressure-driven water separation process. It uses a fine pore membrane to separate water and micro-solutes (micromolecules) from macromolecules and colloids. The average diameter of a UF membrane is in the range of  $1 - 100 \text{ nm}$  or  $0.5\text{-}300 \text{ kDa}$  (Schäfer, 2001). These limits are neither precise nor universally agreed upon, so the

range overlaps that of nanofiltration at the lower end and microfiltration at the upper end (Table 2.4).

Table 2.4 Overview of membrane treatment processes and solute/particle dimensions (Source: Schafer et al. 2001)

|                             | Atomic force microscopy  | Electron microscope                       | Optical microscope  | Visible  |
|-----------------------------|--|---|---|--|
|                             | Dissolved matter   |   | Colloids  | Suspended matter   |
|                             | Ions   | Molecules                                 | Macromolecules  | Microparticles   |
| Molecular weight, Da        | 100  | 1000                                      | 10000   | 100000   |
| Size, $\mu\text{m}$         | 0.001  | 0.01                                      | 0.1   | 1  |
| Solute/particle dimension   | Mineral salts<br>Fulvic Acid<br>Humic Acid<br>Metal ions<br>Pesticides<br>Amino Acids<br>Polysaccharides | Proteins<br>Pyrogens<br>Virus<br>Colloids | Red Blood Cells<br>FeCl <sub>3</sub> flocs<br>Bacteria, Micro Algae | Algae, Protozoa<br>Macrophytes, Zooplankton<br>Clay, sand<br>Pollens |
| Membrane separation process | RO<br>NF<br>UF<br>Dialysis<br>Electrodialysis  |   | MF  |  |

UF membranes therefore retain particulate matter, ionic and non-ionic organic species depending on the molecular weight cut-off (MWCO) of the membrane. However, most of the inorganic species (especially small ions) pass through the membrane (Mallevalle et al., 1996). MWCO is the molecular mass of a macro- solute (polyethyleneglycol, dextran or protein) for which the membrane has a retention capacity greater than 90%. MWCO can be regarded as a measure of membrane pore dimensions (Mallevalle et al., 1996).

UF is considered a physical disinfection technique, with the exception of possible imperfection of membranes and depending on the membrane selected. It is effective in the removal of protozoa, bacteria and other parasites (whose diameters are greater than pore size) from the water. UF fairs well in virus removal if a good pre-treatment (e.g. coagulation) exists (Jacangelo J.G, 1995).

Ultrafiltration can be divided down into two different operational modes dead-end filtration and cross flow filtration. The difference in fluid flow between these two modes is illustrated in Fig. 2.12.

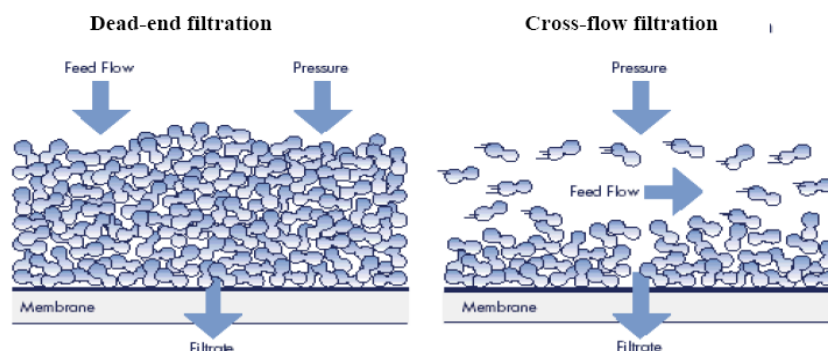


Figure 2.8 Comparison of dead-end and cross-flow filtration (Source: Millipore 2005)

In dead-end filtration, fluid is convected directly toward the membrane under an applied pressure. Particulates that are too large to pass through the pores of the membrane accumulate at the membrane surface or in the depth of the filtration media, while smaller molecules pass through to the downstream side.

In cross flow filtration, the fluid is pumped tangentially along the surface of the membrane. An applied pressure serves to force a portion of the fluid through the membrane to the filtrate side. As in dead-end filtration, particulates and macromolecules that are too large to pass through the membrane pores are retained on the upstream side. However, in this case the retained components do not build up at the surface of the membrane. Instead, they are swept along by the tangential flow. This feature of cross flow filtration makes it an ideal process for finer sized-based separations.

## 2.4. The Fouling

### 2.4.1. Membrane Fouling

The fouling of membranes elements may cause operational problems of membrane installations (e.g. increase of pressure drop and/or decrease of flux). Fouling increases the cost of plant operation and can be a threat for the production of drinking water. Fouling can ultimately lead to an early replacement of membrane elements. The fouling mechanisms of spiral wound membranes include scaling (inorganic, organic and colloidal) and biofouling. Scaling by inorganic compounds is usually controlled by the use of a scale inhibitor (polymer, acid) and scaling by colloidal material can be controlled by pre-treatment (e.g. ultrafiltration). Biological filtration processes removing biodegradable compounds as pre-treatment can reduce the risk on biofouling.

Fouling occurs when rejected solids are not transported from the surface of the membrane back into the bulk flow stream. As a result, both the dissolved salts and suspended solids accumulate at the membrane surface. Deposition of solids on the membrane causes an increase in resistance of water flow to the membrane and inhibits diffusion of dissolved solids from the membrane surface. As a result, permeate quality and productivity decrease. In addition, because the solid deposits occupy space in the brine channel, there is an increased restriction to flow and a rise in differential pressure across the membrane sometimes can be observed (Graham et al., 1989).

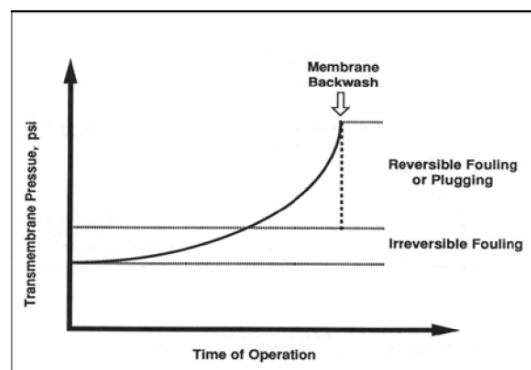


Figure 2.9 Schematic of membrane fouling (source: Ismail et al., 2006)

The increased pressure is the evidence of the accumulation and/or adsorption of materials on the membrane surface. Reversibility of this phenomenon is characterized as based on the backwash efficacy to restore the flux. Thus, the fraction of pressure that can be recovered using a backwash describes the reversible fouling. Irreversible fouling is then determined by the increase of pressure after a backwash.

Five different types of fouling have been identified: particulate, inorganic, biological, and organic and NOM fouling (Lee N. et al., 2004)

#### 2.4.1.1 Particulate Fouling

This fouling is due to suspended and colloidal matter (e.g. clay minerals, coagulants, algae, extra cellular polymer substance, and transparent exopolymer particles). Colloids are defined as particles which are between one nanometer and one micrometer in size. Colloidal foulants typically seen in membrane systems include silica, clay and silt. The most common mode of fouling from colloidal material is soiling. The particle fouling mechanisms are showed in figure 2-13.

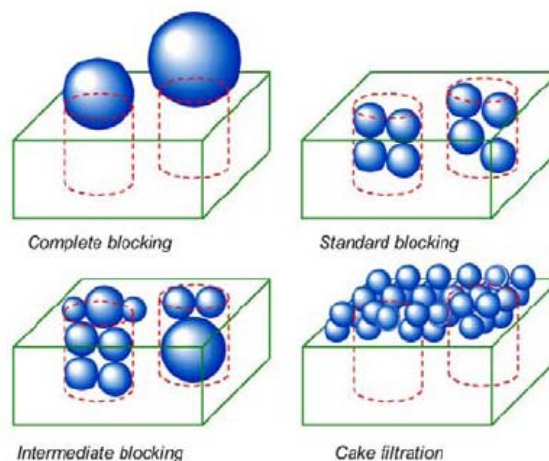


Figure 2.10 Particle fouling mechanisms (Source: Laine, 2003)

Filtration is the way how particulate fouling is reached. Two filtration mechanisms are identified: pore blocking and cake formation. Pore blocking is subdivided in complete blocking, standard blocking and intermediate blocking while cake filtration is subdivided in cake formation without compression cake and cake formation with compression cake.

Complete blocking or -pore blocking phenomenon- represents each particle reaching the membrane surface and blocking a pore or more without superposition of particles. Standard blocking or - internal adsorption - describes particles reaching the membrane surface and depositing onto the internal pore walls leading to a decreasing of the pore volume.

Intermediate blocking or - long-term blocking phenomenon- represents each particle arriving and settling on previous particles which already are blocking pores or some membrane area.

#### 2.4.1.2 Inorganic Fouling

Inorganic foulants are defined as those that are non-carbon based. Common inorganic foulants seen in membrane systems include salts such as calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate and calcium fluoride, as well as metal hydroxides such as iron hydroxide and aluminum hydroxide. The most common mode of fouling with inorganic foulants is precipitation.

In groundwater, inorganic fouling is due to adsorption of soluble iron (II) and soluble manganese (II), and their subsequent oxidation to  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2$  forms. Occurrence of inorganic fouling is governed by the presence of oxygen in water and the presence of iron and manganese in the soil. To avoid inorganic fouling, oxygen has to be excluded completely from entering the feed water in the well and plant. (Schipper and Kennedy 2006).

#### 2.4.1.3 Biofouling

Biofouling is the accumulation of biomass (difficult to quantify) on a membrane surface by growth and/or deposition to such a level that it is causing operational problems. However, the diagnosis “biofouling” is only justified when a relation is found between the encountered operational problems and biomass accumulation as determined with adequate parameters.

Biofouling of surfaces involves living matter (either micro or macro organisms). The former are small, often single cell entities (e.g., bacteria, fungi, or algae), and the latter are larger creatures (such as mussels and barnacles). Laîné, (2003) established that the initial bonding of the bacteria to the surface is reversible, but, after a period of time, the adhesion becomes more substantial and irreversible. Bacteria finding themselves in crevices are more likely to form a permanent bond compared with those residing on an “exposed” part of the surface, because they have more opportunity to do so. It is possible that the more permanent condition arises from a chemical bridging between the cell and the adsorbed macromolecules.

The general development of a biofilm with time is shown in figure 2-7. After the conditioning and initiating of biofilm growth, there is a rapid development in biofilm thickness. After a further period, the thickness of the biofilm becomes stabilized about a mean value. At the plateau, it is considered that the factors that enhance growth (e.g., nutrient availability) are offset by the removal forces owing to the fluid shear.

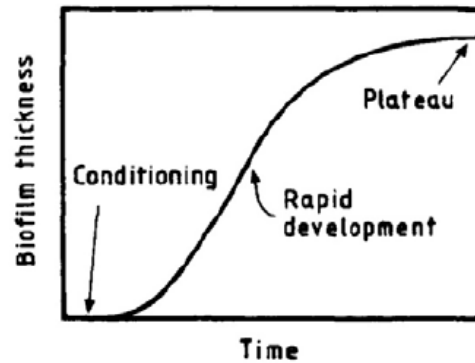


Figure 2.11 Idealized biofilm development curve (Source: Melo and Bott, 1997)

The morphology of a biofilm that may be observed on a surface is very dependent on the prevailing conditions (e.g., nutrient availability, water flow rate, temperature, and pH). The biofilm can contain strands of cells or clusters that grow out from the surface toward the bulk liquid or it can be irregular with interstices. The compactness of the biofilm, therefore, is variable, and it will generally contain in excess of 90% water. The morphology and structure of a biofilm is likely to change as the biofilm ages and will be dependent on external conditions, particularly with respect to nutrient availability and velocity of flow over the biofilm (Melo and Bott, 1997).

#### 2.4.1.4 Organic Fouling

Organic foulants are those which are carbon based, but non-living. Some common organic foulants include humic acids, oil, hydrocarbons and polymers. Organic materials can foul membranes via soiling as well as absorption.

#### 2.4.1.5 NOM Fouling

Fouling of NOM occurs due to many factors and mechanisms. The factors affecting NOM and membrane interactions include NOM characteristics, operating conditions, membrane characteristics and solution chemistry. NOM fouling occurs when dissolved organic or inorganic solute is adsorbed or deposited on the membrane. The adsorption mechanism happens more quickly compared to cake formation but depends on the membrane properties, ionic strength, pH and presence of divalent cations (Ismail et al, 2006).

For NOM fouling prevention is important to know the NOM fractions that are causing the fouling in the membranes. Thus, what is needed is more information on the composition of NOM.

#### 2.4.1.6 Factors Affecting Fouling

Related to membrane materials, based on a review of available research Zularisam et al., (2006) stated, that membrane properties such as MWCO (pore size), surface charge and roughness, porosity, and hydrophilicity/hydrophobicity contribute to determination of membrane fouling types. They concluded that fouling is higher with negatively charged membranes when they are exposed to neutral (hydrophilic) materials and protein (bases)

compared to highly negatively charged material (humic substances), though they possessed high adsorptive behaviour due to their high hydrophobicity.

This is contradicted by Jung et al., (2006), who observed that the effect of membrane properties on the adsorption of organic fractions was greater for the hydrophobic membrane than for the hydrophilic membrane regardless of the kind of organic fractions. A tendency of electrostatic repulsion between membranes with negative surface charge and NOM constituents with a high charge density is observed (Liu et al., 2001). This usually happens in nature pH conditions of water. Therein the electrostatic charge of the membrane surface is conditioned to be negatively charged, where else colloids, particles and dissolved organic matter carries a negative charge too.

pH conditions of the source water are also reported to have influence on fouling. For instance Jung et al., (2006) reported variation of total resistance in filtration of raw water at different pH, where the resistance for lower pH increased more rapidly. At neutral pH, the membrane rejected less NOM, but with the decrease of pH, the removal efficiency could be increased markedly.

Fouling is furthermore influenced by chemical and physical factors of foulants. Foulants are characterized according to their molecular structure, molecular size, surface charge, charge density, and the content in terms of functional groups (Zularisam et al., 2006). They also state that the presence of divalent ions and the pH of the water are of influence to fouling.

Jung et al., (2006) mentioned that hydrophobic organics adsorbed much more quickly than hydrophilic organics, by using regenerated cellulose and polysulfone UF membranes with different levels of hydrophilicity in a stirred cell arrangement.

Lee et al., (2004) found that high hydrophilic (HPI) fraction content of NOM resulted in significant flux decline. In their experiments macromolecules of a relatively hydrophilic character (e.g. polysaccharides) were effectively rejected by low-pressure membranes, suggesting that macromolecular compounds and/or colloidal organic matter in the hydrophilic NOM fraction may be a problematic foulant of low-pressure membranes. They further concluded that MF membrane fouling may be caused by pore blockage associated with large (macromolecular) hydrophilic molecules and/or organic colloids.

Another factor responsible for the extent of fouling are operation conditions. Applied fluxes, the frequency of backwashing, their intensity, and cleaning are crucial to fouling.

#### **2.4.1.7 Fouling Prediction**

As mentioned, particulate fouling mainly causes decline in permeate flux in MF and UF. Particulate fouling refers to deposit and adsorption of colloids, suspended solids, and microbial cells on and inside the membrane pores. Water quality parameters such as turbidity, suspended matter and particle counting cannot be used to estimate the particulate fouling potential of a feedwater. Nevertheless, from design, economical and operational points of view it is important to predict and control membrane fouling. Cleaning frequencies, pre-treatment requirement, operating condition, cost and performance are affected by membrane fouling (Mallevalle et al., 1996). For the purpose of fouling prediction methods have been developed using the basic resistance

model to predict particulate fouling. This process in MF and UF is described by pore blocking and cake filtration mechanism.

**Silt Density Index** The Silt Density Index (SDI) as a method designed to measure the particulate fouling potential of feedwater is employed with special equipment. A specific 0.45 micron microfiltration membrane with a diameter of 45 mm and appliance of a pressure of 3 psig is used to determine the SDI. One shortcoming of the SDI is that it does not measure the rate of change of resistance during duration of the test, but only at view preset intervals throughout the procedure.

**Modified Fouling Index** The Modified Fouling Index, derived by (Schipers and Verdouw, 1980) form the SDI, and was aimed to predict the rate of fouling for RO membranes. For determination of the MFI the same equipment and procedure as the SDI is applied. Hence, the volume is recorded in an interval of 30 seconds over a 15 minutes filtration period.

The MFI is based on the physical laws of filtration theory derived by Darcy and Hagen-Poiseulle. The thickness of the cake layer formed at the membrane is in direct proportion with the filtered volume, as a homogenous distribution of particle in the feed water is assumed. The total resistance is the sum of the initial membrane resistance and the cake resistance. Boerlage, (2001) pointed out that the MFI is based only on cake filtration mechanism, though depth filtration and pore blocking is happening during the initial stage of the filtration cycle. The total resistance building up is dependent on the particle size through the Carmen- Kozeny equation for specific cake resistance. The linear relation between the index and the concentration of colloidal and suspended matter leads to the conclusion that smaller particles present in the cake result in higher MFI values.

$$\frac{dV}{Adt} = \frac{Q}{A} = \frac{\Delta P}{\eta^* (R_m + R_c)} \quad \text{..... 2. 1}$$

The permeability of a clean membrane is a function of the filter properties, such as filter thickness, surface porosity, pore radius, and tortuosity, and can be defined by Poisseulle's law and the resistance in series model.

The resistance of the cake formed during constant pressure filtration is proportional to the amount of cake deposited at the filter medium, provided that the retention of particles and  $\alpha$  is constant (Schipers and Verdouw, 1980).

$$R_c = \frac{V}{A} \cdot \alpha \cdot C_b \quad \text{..... 2. 2}$$

By rearranging and substitution of  $C_b$  with the coagulant dose in g/m<sup>3</sup> the specific cake resistance over the filtration cycle is calculated.

$$\frac{t}{V} = \frac{\eta \cdot R_m}{\Delta P A} - \frac{\eta \alpha C_b}{2 \Delta P A^2} * V \quad \text{..... 2. 3}$$



### 2.4.1.8 Blocking Filtration

Hermans and Bredee in (1936) first distinguished the previously mentioned fouling and filtration mechanisms retaining particles on porous media during constant pressure filtration in dead end mode. They found a way to mathematically describe those four mechanisms, based on parallel capillary filter tubes as describe by Poiseulle, thus leading to the general equation for the rate of blocking (second derivative model)

$$\frac{d^2t}{dV^2} = Kb \left( \frac{dt}{dV} \right)^\beta \quad \text{..... 2. 4}$$

The coefficients  $\alpha$  is a constant depending on the initial flow rate (except for intermediate blocking). The exponent  $\beta$  describes the prevailing filtration mechanism. Values for  $\beta$  of 0 define cake, for 1 intermediate blocking, for 1.5 standard and for 2 complete blocking filtration. The rate of blocking increases in the order of: complete > standard > intermediate > cake blocking filtration.

Hermia reanalyzed the filtration laws of Hermans and Bredee in 1982, and developed physical models for the transition states between these mechanisms. He confirmed the previously established proof for the respective laws, when linearity is given for certain plots. With constant pressure filtration complete blocking is leading to a linear decrease of flux over time, hence a linear relation can be obtained when plotting  $\exp(t)$  over filtered volume.

$$K_b V = \frac{dV_0}{dt_0} (1 - \exp(-K_b t)) \quad \text{..... 2. 5}$$

To prove standard blocking a linear relation can be obtained when plotting  $dt/dV$  over filtered volume.

$$K_s t = \frac{2t}{V} - \frac{2dt_0}{dV_0} \quad \text{..... 2. 6}$$

Intermediate blocking, gives a linear relation between  $dt/dV$  (resistance of the filter) over filtration time  $t$ .

$$K_i V = \ln(1 + K_i Q_0 t) \quad \text{..... 2. 7}$$

Cake filtration is given when a linear relation between  $t/V$  plotted against  $V$  is obtained.

$$K_c V = \frac{2t}{V} - \frac{2}{Q_0} \quad \text{..... 2. 8}$$

#### **2.4.1.9 Cake Compression**

At the beginning of filtration the membrane resistance controls the rate of flow, and the whole of the pressure drop occurs in the membrane. As filtration continues and a cake builds up a proportion of the pressure drop is absorbed by the cake. At a given point the membrane resistance becomes negligible. A hydraulic pressure gradient over the cake depth develops resulting in an increase in the viscous drag at the particle surfaces over which the fluid flows. If the shape of the particles or their physical strength is such that the packing arrangement in the cake formed on the membrane can sustain this drag force without significant deformation, the cake is regarded as incompressible. The porosity of the cake and its specific resistance are then independent of imposed pressure (Boerlage, 2001).

Practically few cakes are incompressible. Those composed of clays and microbial cells which are highly compressible. As the pressure drop increases over the cake during filtration (or for a test conducted at higher pressure) the cake porosity reduces as particles compress (creating a non-uniform porosity distribution in the direction of flow). In addition, the filtration of fine particles in the cake structure may also be responsible for an increase in the specific cake resistance over time. Fine particles will block or narrow the voids present in the cake (cake clogging), hence increasing the specific cake resistance. As a consequence the specific cake resistance increases (Boerlage, 2001).

Lee et al., (2003) concluded that compressibility is strongly influenced by trans-membrane pressure (TMP), particularly for smaller floc sizes. The deposition of highly porous aggregates onto the membrane results in the formation and maintenance of a highly porous cake layer, provided a low TMP (<10 kPa) is applied. Rapid compression of the cake occurs at higher TMP's (>60 kPa) as shown by the significantly lower porosity of the cake.

In UF applications the extent of pretreatment is highly dependent on the quality of the feedwater, and the need for pretreatment will increase as the cross section of the membrane flow channel is decreased. NOM are of great importance in potential fouling of the UF membrane and consequently, in permeate flux that can be used under normal operation conditions. Thus it is an interesting design option to pretreat the water to remove natural organic matter and consequently decrease the surface of membrane needed, due to the higher flux that is possibly obtained in this case.

#### **2.4.2. Influence of NOM on Membrane Fouling**

Concentration polarization is the accumulation of retained materials in the boundary layer above the membrane due to osmotic pressure and the hydraulic resistance effect. Increments and variation of hydraulic resistances may come from a variety of organic substances, inorganic particles, colloids and microorganisms with different fouling behaviors. Fouling behaviors are found to be significantly influenced by various chemical and physical factors of the foulants. The foulant can be characterized according to its molecular structure, surface charge, molecular size and functional groups. One of the most important identified foulants found in surface water filtration is NOM (Ismail et al., 2006).

Macromolecule NOM plays a significant role since the colloidal NOM are normally macromolecule. At the beginning of membrane fouling, macromolecule particles have been demonstrated to be the crucial foulant blocking the membrane pores followed by the adsorption of small foulant particles, which lead to further compactness of fouling layer.

Previous studies in NOM characterization done in raw sources waters, UF concentrates, UF permeates, and cakes accumulated at the membrane surface proved the presence of polysaccharides (PS), polyhydroxyaromatics (PHA), proteins and amino sugars in all types of natural waters. The differences in the NOM characteristics of the raw and the permeate water indicated that the PHA and PS concentrated in the cake deposited onto the membrane surface. In addition, elemental analysis of the cake indicated that around half of the material deposited was inorganic (clays, carbonates and hydroxides). Furthermore, the results from scanning electronic microscopy confirmed that the fouling cake consisted of a deposit 30 to 50 microns thick, based on clay particles bounded by a NOM-based gel. Waters with a high PHA concentration have an irreversible fouling potential higher than waters with a high PS concentration. This was observed for comparable total organic content waters, hence demonstrating that the characteristics of NOM had a strong impact on fouling (Lainé et al., 2003).

#### **2.4.3. Membrane Fouling Potential**

The fouling potential can be estimated using fouling indices and selected water quality parameters or properties. The most commonly used fouling indices include: Silt Density Index (SDI), Modified Fouling Index (MFI), Mini Plugging Factor Index (MPFI) and MFI-Ultrafiltration (MFI-UF). Water quality parameters such as UVA, color, TOC, SUVA, humic content and properties such as SEC-UV absorbance ratio index (SECURI), SEC-fluorescence, colloid size, Assimilable Organic Carbon (AOC) and Bio-film Formation Rate (BFR) are also useful.

#### **2.4.4. Membrane Cleaning**

Membrane cleaning is defined as the process where a membrane is relieved of a substance which is not an integral part of the material. Graham et al. (1989) stated that periodic cleaning is an essential maintenance procedure in any RO and NF plant experiencing fouling. The decision criteria for instituting a cleaning procedure should be based on loss of plant performance relative to a set of standard conditions. This requires normalization of operating data to account for changes in salinity, temperature and pressure. Because a RO and NF membranes are in risk of permanent damage if fouling is allowed to progress beyond reasonable limits, normalization procedures should be incorporated into an operator's daily routine.

Generally speaking, membranes should be cleaned when the permeate rate drops off or when the differential pressure ( $\Delta P$ ) across the membrane array increases. Many membrane system operators follow a 10 percent rule; i.e. if the permeate rate drops by 10% or the  $\Delta P$  increases by 10%, they clean the system. Similarly, if the feed pressure required to produce a given amount of permeate increases by 10%, a cleaning should be initiated.

## 2.5. Secondary Wastewater Effluent

Wastewater reclamation and reuse has been recognized as important alternative for water resources preservation and water pollution control. Advances in wastewater treatment technologies have improved the capacity to produce reclaimed wastewater and more reliable cost effective technologies are needed for acquiring new water supplies and protecting existing water sources from pollution (Asano and Contruvo, 2004).

From the time when a combined activated sludge/UF process had been developed for domestic wastewater treatment in the 1960s (Smith et al., 1969), the activated sludge process has been commonly used in combination with the membrane process because of its wide range of treatment ability. Seo et al., (1996) incorporated powdered activated carbon (PAC) into UF or MF for removing dissolved organic contaminants from natural water. Consequently, from the viewpoints of stability and economy, such combination of the membrane process with stable pre-treatment technologies is interesting on wastewater treatment and reuse (Seo et al., 1996).

Membrane separation technology, which is increasingly adopted in the field of water and wastewater treatment, has shown good performance for removing these kinds of contaminants (Seo et al., 1996) being RO is one of the membrane technologies of particular interest to be used in advanced wastewater reclamation using secondary wastewater effluent as source water.

A typical scheme for advanced wastewater reclamation involves the following steps: (i) biological wastewater treatment, (ii) pre-treatment of the secondary effluent with MF/UF to remove suspended and colloidal matter, (iii) treatment of effluent with RO, and (iv) UV disinfection of product water. Pre-treated secondary effluent, however, still contains considerable amount of organic macromolecules, designated as effluent organic matter (EfOM), which are problematic due to their potential contribution to organic fouling of RO membranes. Therefore, understanding the causes of RO membrane fouling by EfOM and developing strategies for fouling control are of paramount importance for successful application of RO technology in water reuse (Lee et al., 2006)

### 2.5.1 Effluent Organic Matter (EfOM)

EfOM is one of the parameters of concern for human and environmental health and it is originated from wastewater treatment plant (WWTP) effluents. This EfOM should be carefully characterized in order to find an optimum treatment method for wastewater reuse (Shon et al., 2006).

EfOM is a complex heterogeneous mixture of multiples organic components, often measured as dissolved organic carbon (DOC), ranging from low to high molecular weight compounds. Examples of such compounds include polysaccharides, proteins, amino-sugars, nucleic acids, humic and fulvic acids, organic acids, and cell components (Barker et al., 2004). Among these, polysaccharides are some of the most ubiquitous hydrophilic macromolecules in secondary effluent. Polysaccharides are produced during

biological wastewater treatment processes and they are part of the so-called soluble microbial products (SMP) (Barker R.W., 2004).

The presence of trace organic pollutants in wastewater has been the cause of increasing public concern in recent decades due to potential health risks. EfOM in wastewater consists of both particulates and dissolved substances, which has been found to include several trace organic contaminants, including endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs). EfOM can be summarized into three general classes based on their origins:

- NOM derived from drinking-water sources.
- Synthetic organic compounds (SOC) produced during domestic use and disinfection by-products generated during disinfection processes of water and wastewater treatment.
- Soluble microbial products derived during biological processes of wastewater treatment (Drewes and Fox, 1999).

The constituents that are found in biologically treated sewage effluent (BTSE) are shown in Figure 2-12. The fraction of POC measured as suspended solids (SS) includes protozoa, algae, bacterial floc and single cells, microbial waste products, and other miscellaneous debris. DOC (smaller than 0.45  $\mu\text{m}$ ) are typically cell fragments and macromolecules. Thus, EfOM can be classified into two main groups by size groupings:

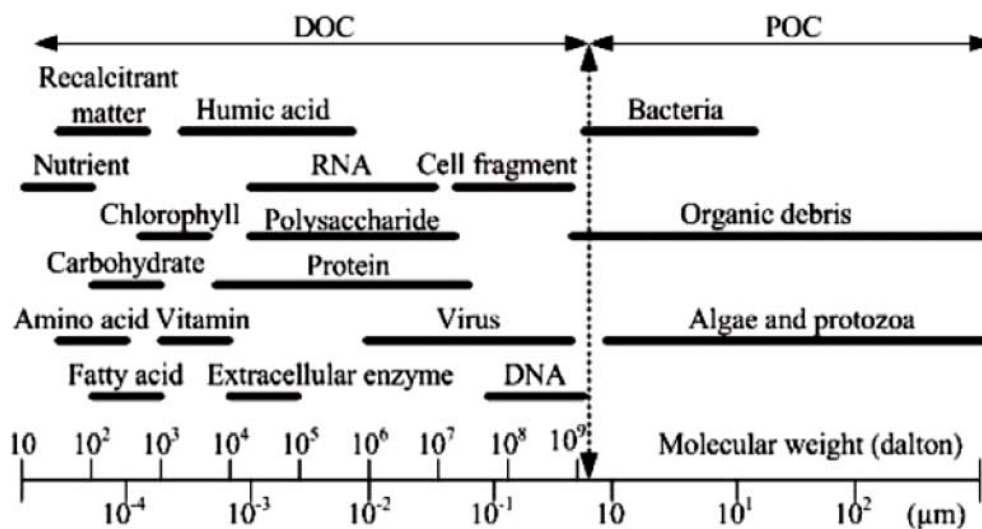


Figure 2.12 Typical organic constituents in BTSE and their size ranges  
(Source: Graham et al., 1989)

### 2.5.2 Soluble Microbial Products (SMP)

During biological wastewater treatment, biomass not only consumes organic material present in the wastewater, but also produces soluble microbial products (SMP) and extra cellular polymeric substances (EPS). These classes of compounds appear to be cellular

components that are released during cell lysis, compounds that diffuse through the cell membrane, or compounds that are excreted from some other purposes (Graham et al., 1989). These cellular products are ubiquitous in biological treatment and constitute the majority of the effluent COD. EfOM was mainly composed of high molecular weight materials employing low aromaticity. These compounds are corresponding to proteins, polysaccharides, and/or aminosugars, possibly originated from cell components during biological processes.

Formation of SMP during biological degradation of organic compounds in a sequencing batch reactor (SBR) was investigated using high performance liquid chromatography-size exclusion chromatography (HPSEC) as well as other organic matter characterization tools. Results showed that carbon compounds in a glucose feed solution were totally transformed to other organic products classified biomass-associated products (BAP). The SMP-BAP contained in the SBR effluent consisted mainly of high-molecular weight (MW) fractions of organic matter, possibly originating from cell lysis. These compounds exhibited a low specific ultraviolet absorbance (SUVA) and a hydrophilic character. In addition, the characteristics of bulk effluent organic matters (EfOM) samples from wastewater treatment facilities were studied. It was observed that EfOM consisted of humic-like and hydrophobic (HPO) compounds, derived from the corresponding drinking water source, in addition to SMP-BAP. A superimposition of SEC chromatograms of the SMP-BAP and humic-like compounds represented a fingerprint of EfOM (Jarusutthirak and Amy 2006).

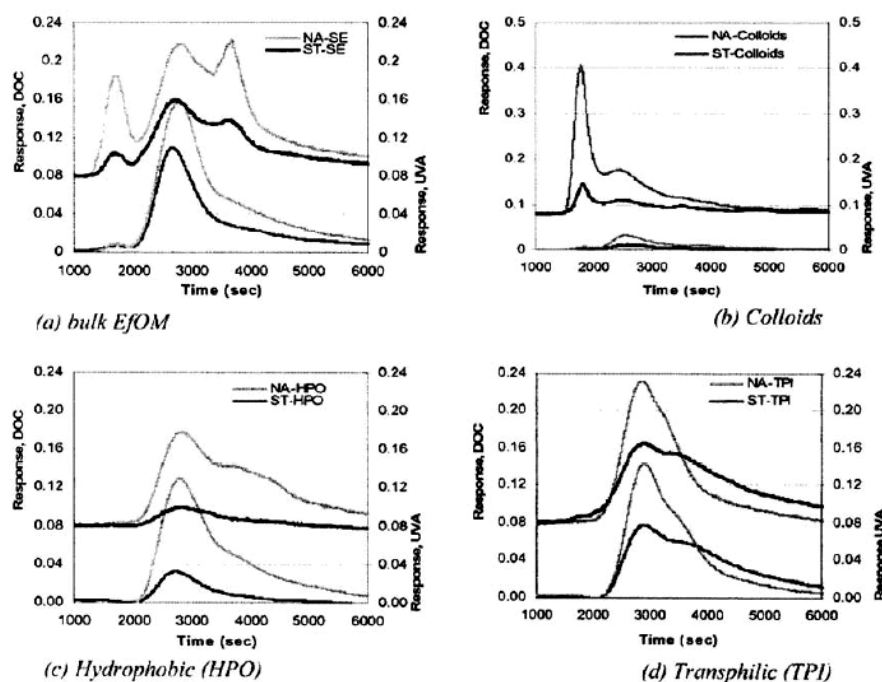


Figure 2.13 SEC chromatograms of EfOM bulk waters and associated EfOM isolates

(Source: Jarusutthirak et al., 2002)

Polysaccharides are present in the EfOM fractions. It was found that polysaccharides were contained in colloids at a higher amount than in transphilic and hydrophobic fractions (Figure 2-13). Polysaccharides have a significant contribution of hydrophilic character to so-called hydrophilic colloids. A major source of polysaccharides in

hydrophilic colloids is likely to be the bacterial cell wall, released during the endogenous phase of microbial growth.

Toxicity of SMP is of increasing concern. These products may actually be more toxic than the original organic compounds present in BTSE. Mutagenic response is higher in BTSE than in the primary effluent (Graham et al., 1989).

### **2.5.3 Role of Soluble Microbial Products (SMP) in Membrane Fouling and Flux Decline**

Soluble microbial products (SMP), a significant component of effluent organic matter (EfOM), play an important role in membrane fouling and flux decline in wastewater reclamation/reuse applications. The SMP compounds of a microbial origin are derived during biological processes of wastewater treatment. They exhibit the characteristics of hydrophilic organic colloids and macromolecules. These high molecular weight compounds play an important role in creating high resistance of the membrane, leading to a reduction of permeate flux. The SMP fouling of RO, NF, and tight UF membranes is associated with formation of a cake/gel layer due to size (steric) exclusion. FTIR spectra of SMP- and EfOM-fouled membranes exhibited foulants' composition, consisting of polysaccharides, proteins, and/or aminosugar-like compounds. This finding reveals the important role of the SMP components as factors in membrane fouling and flux decline associated with EfOM source waters. Solids retention time (SRT) affects the characteristics and amounts of SMP, however, SRT did not affect flux decline trends of RO and NF membranes. (Jarusutthirak and Amy (2006)

## **2.6. MDG Achievement**

### **2.6.1. MDG Targets and Indicators**

One of the aims of the MDG goal 7, target 10 is to provide basic improved sanitation to people in urban and rural areas. Sanitation is an important component which directly or indirectly contributes the other targets coverage and improving indicator values. The targets and indicators which are directly connected to the sanitation are listed in Annex No. 7

### **2.6.2. Global Level**

Access to safe water and sanitation are human needs as well as basic human rights. They are essential elements of human development and poverty alleviation and component of primary health care. "There is evidence that provision of adequate sanitation services, safe water supply, and hygiene education represents an effective health intervention that reduces the mortality caused by diarrhoeal disease by an average of 65% and the related morbidity by 26%" (WHO/UNICEF 2006). Most of children die every year from diseases associated with lack of safe drinking water, adequate

sanitation and poor hygiene in developing countries. Inadequate sanitation, hygiene and water result not only in more sickness and death, but also in higher health costs, lower worker productivity, and lower school days of children. shows child mortality versus sanitation coverage in global level.

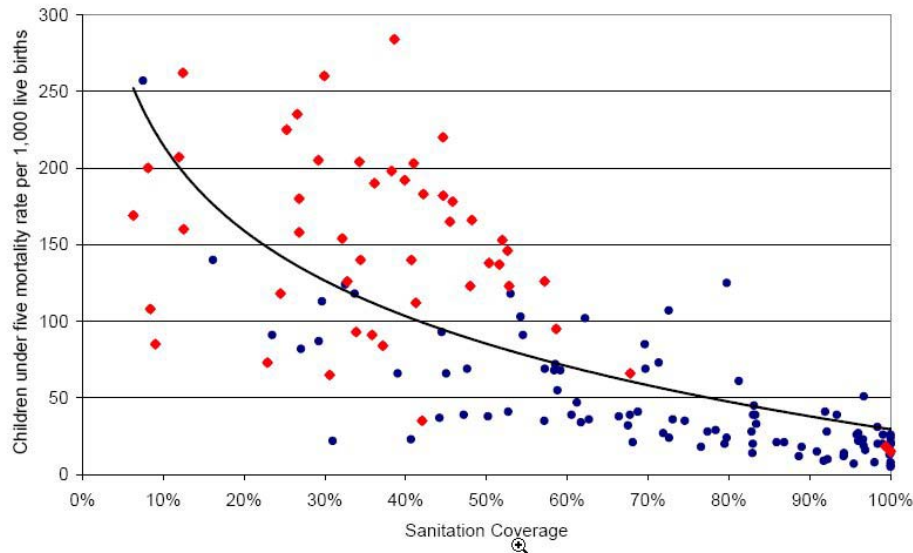


Figure 2.14 Child mortality versus sanitation coverage at global level (Source SEI 2005)

WHO/UNICEF (2006) states that the estimated population growth in 2015 is 1.1 billion people, 88% of whom will live in urban areas and thereafter all the population expansion will be concentrated in cities. By 2015, water supply services will be provided to an additional 739 million urban dwellers and 489 million rural inhabitants. Considering that the current urban and rural populations without improved water service are 173 million and 926 million, respectively.

It is obvious that the past pace of providing improved water supply and sanitation services will be insufficient to cope with the projected population growth. Unless the pace is increased, the number of people without access will increase sharply in water and sanitation sector.

It seems that the world is on the track to meet the MDG target for drinking water however, the slow progress has shown been in Sub-Saharan Africa. The situation is serious in South Asia, Sub-Saharan Africa, Western Asia, Eurasia and Oceania on sanitation. Because none of them are in the sanitation target track for meeting MDG target.

The figures 2.15 & 2.16 show more details of MDG target sanitation coverage in 2002 and 2015.



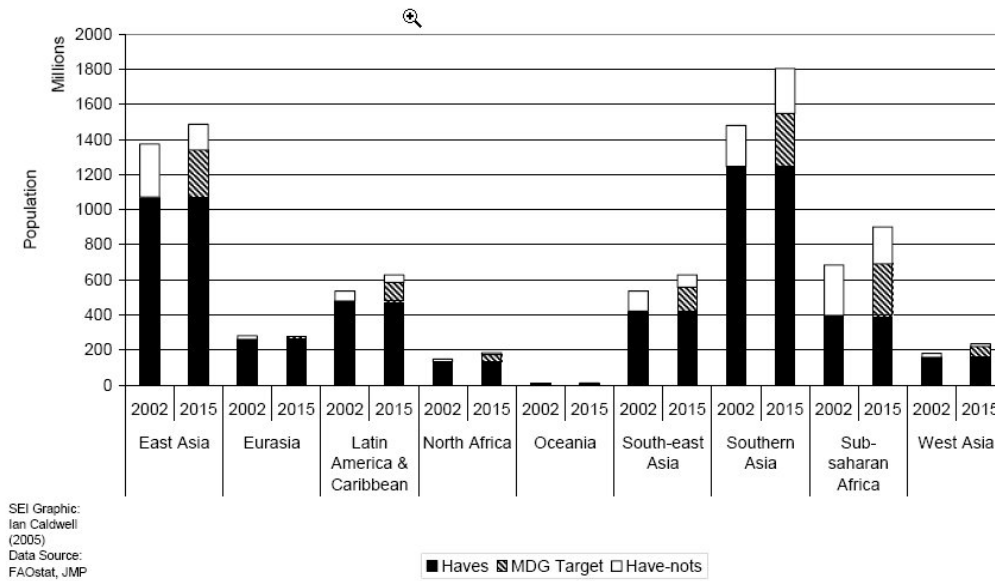


Figure 2.15 Global water coverage in 2002 and 2015 (Source: SEI 2005)

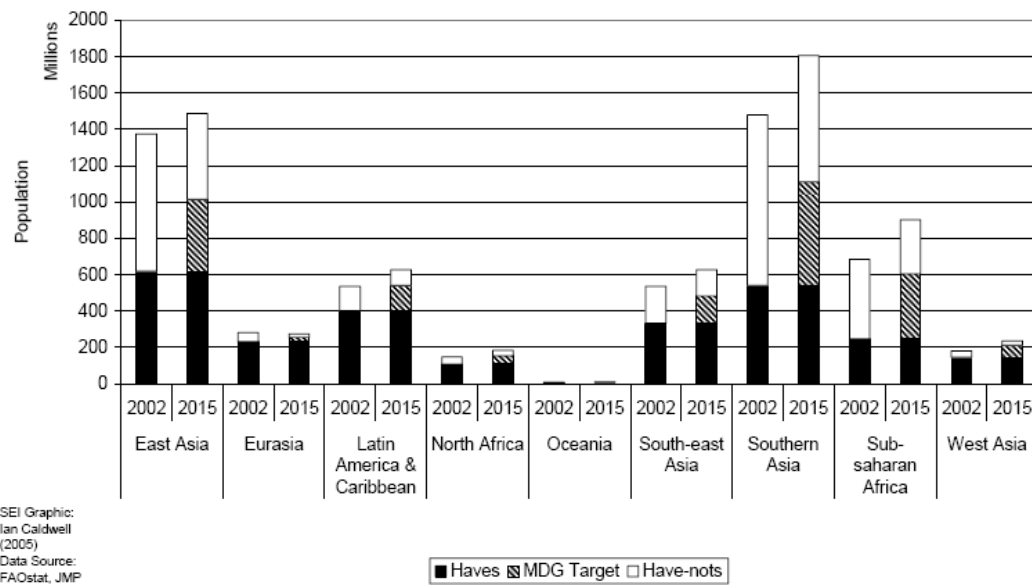


Figure 2.16 Global sanitation coverage in 2002 and 2015 (Source: SEI 2005)

### 2.6.3. Current Status and Trends of MDG in Yemen

Activities related to 8 main goals of MDG's in Yemen are explained in the following paragraphs (MDG's , 2007).

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### 2.6.3.1 Goal No. 1 Poverty Eradication

During the first half of the 1990s, the Yemeni economy encountered several crises, which contributed to increasing the poverty levels, and to the deterioration of living conditions of the majority of the population. The HBS (1998) results indicated that the highest poverty level reached 41.8% of the population (6.9 million people). On the income distribution, the survey found that 20% of the population earns no more than 8% of the gross income, the Gini coefficient of expenditure amounted to 0.343. Consequently, the percentage of population living on less than a dollar per day did not exceed 10.7% of the population while 47% of the population is living on less than two dollars a day, based on the Purchasing Power Parity (PPP) terms. Poverty in Yemen is a rural phenomenon. Indicators show that 83% of the poor people live in rural areas. This reflects the reality that Yemen is a rural society, as 76% of the population live in rural areas according to 1994 census.

### 2.6.3.2 Goal No. 2 Primary Education

Official and public efforts in the 1990s resulted in an increase in primary education net enrolment rate from 52.7% in 1990 to 59.5% in 2000. This means that a significant proportion of children at school age (6-14 years) are not enrolled in primary education, and are likely to join the ranks of the illiterate population in the near future.

Average net enrolment rates differ from a governorate to another. The majority of governorates have registered a net enrolment rate of less than 50% as compared to the national net enrolment rate, except for Aden, where the net enrolment rate was 85.7% in the year 2000 compared to 20.8% in Sa'ada governorate. This huge disparity requires tremendous efforts and resources to bridge the enrolment gap. Gender-based disparity demonstrates itself clearly when comparing the net enrolment rates for boys and girls. The net enrolment rate among girls for the same age-group (6-14 years) is 44.7%, in comparison with 72.2% for boys. In conclusion, these indicators suggest that Yemen is still far from achieving the Universal Primary Education goal by 2015, unless major qualitative steps to advance basic education for both girls and boys are implemented. This, in turn, requires expansion in the construction of school buildings, and improving facilities in school buildings. It also requires increasing the number of female and male teachers and providing them with incentives for rural education, as well as improving quality of education and school curricula.

### 2.6.3.3 Goal No. 3 Promote Gender Equality and Empower Women

Despite an increase in female enrolment rates since 1990, male enrolment rates remain higher.

Girls enrolment in basic education increased from 44.6% in 1990 to 55.7% in 2000.

In the secondary level, girls enrolment rates are still low despite the improvements of the 1990s. Girls enrolment rates in secondary education increased from 13.7% in 1990 to 36.6% in 2000, and so was the case with higher education, with enrolment rates rising from 28% in 1990 to 32.3% in 2000.

Nevertheless, indicators show that a significant proportion of girls are still out of school, particularly in the primary education stage, despite the State's commitment to provide equal opportunities for boys and girls alike. Data also shows disparities between rural and urban areas. Girls average enrolment rate in rural areas was 29.5%, as compared to 73.2% in urban areas. Therefore, it is difficult to achieve equality in basic, secondary and higher education. This requires continuous Women empowerment is progressing slowly as big proportion of this segment of the population is illiterate.

#### **2.6.3.4 Goal No. 4 Reduce Child Mortality**

Statistical data show that almost 50% of the population are covered by health services, and that health coverage has not yet reached the targeted levels. Moreover, contagious and endemic diseases are widespread in the country. The demographic survey indicators of 1997 indicate that the under-five mortality rate (U5MR) has dropped down from 122 per 1,000 in 1900 to 105 in 1997 (112 in rural areas and 98 in urban areas). In light of this slow progress, Yemen will not be able to achieve a 2/3 reduction in U5MR by 2015. The Demographic Surveys of 1992 and 1997 have found that fever, diarrhea, respiratory infections were the most killer diseases among children under-five.

#### **2.6.3.5 Goal No.5 Improve Maternal Health**

Despite improvements of several indicators related to reproductive and public health during the 1990s, Yemen is still one of the countries grappling with health problems affecting the entire population, particularly maternal and child health. The maternal mortality in 1997 was 351 per 100,000 births, according to DHS (1997). No updated MMR for 2000 are available. Many factors, including early marriage and pregnancy, malnutrition, poor quality health services, anemic pregnant women and low levels of health coverage are the direct causes of high MMR. Prevalence of traditional contraceptives during the 1990s was low. Data suggests that the prevalence rate of contraceptives was as low as 10% in 1992, but increased to 22% in 1997, while the prevalence rate of modern contraceptives increased from 6.1% in 1992 to 10% in 1997.

#### **2.6.3.6 Goal No.6 Combat HIV/AIDS, Malaria and other Diseases**

The pandemic of the Acquired Immune Deficiency Syndrome (AIDS), based on recent African experience, is no longer only a health problem, but also a complex socio-economic issue. So far, the pandemic is not widely spread in Yemen. Official data indicates an increasing number of registered HIV/AIDS cases from one in 1990 to 874 cases in 2000. Men account for 77% of the cases, compared to 23% for women. Incidence rate among the Yemeni nationals was 44.5% as opposed to 55.5% among the foreigners living in Yemen during 2000. Two HIV/AIDS Situation Analysis Studies were conducted in 2000/01 covering five highly populated cities. The Situation Analysis cited existing factors that would facilitate the spread of HIV in the country, both among high risk and vulnerable groups as well as the population in general. Recently, the government has approved a National Strategy to Combat HIV/AIDS, which was prepared in cooperation with international organizations, key line ministries and Civil Society Organizations to address the findings of the two Situation Analysis Studies.

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### **2.6.3.7 Goal No.7 Ensure Environmental Sustainability**

Yemen is facing enormous severe environmental problems, which can be summarized as following:

1. Water crisis: Yemen is one of the countries with the scarcest water resources in the world. This is due to the dry climate prevailing in 90% of Yemen's total area, and to high evaporation rates, in addition to the over-utilization and excessive pumping of ground water. The average drop of water levels in most basins ranges between 1-8 meters per year.
2. Degradation of soil resources: Yemen's cover of soil resources is extremely limited. Arable land constitutes 2% of the total area of land. The cultivated land is 1.3 million hectares, i.e. 2.4% of the total area and 68.8% of the arable land. Therefore, the deterioration of soil resources poses a genuine environmental threat, due to high salinity of soil and desertification, which threatens approximately 97% of the land throughout the country and destroys almost 3 - 5% of arable land every year.
3. Forests: The annual depletion rate of forest areas during the period 1990-2000 was 1.04% due to a host of factors including agricultural activities, over-grazing and wooding. Statistics indicate that 60% of the population is still using wood as fuel. What is so alarming is that the plant cover is being over depleted. Depletion exceeds tree-planting by far thus creating a serious environmental situation

### **2.6.3.8 Goal No.8 Development of the Global Relationship**

Since 1990, Yemen has been facing great internal and external shocks, which have greatly affected the performance of the national economy, thus leading to remarkable shortfalls in the various economic balances. To address these shortfalls, the government has prepared the First Five-Year Development Plan (1996/2000) and Second Five Year Development Plan (2001/05). At the same time, the government has adopted Economic, Financial and Administrative Reform Programme in 1995, which includes several policies and measures, including:

1. Reform the central budget and tax and customs systems;
2. Reform the monetary sector (the central bank, other banks and financial market);
3. Reform of the foreign trade (exchange rates system, customs tariff, importation and exportation transactions); and
4. Improve management of foreign and domestic debt.

### **2.6.4. Wastewater Treatment in Yemen**

In Yemen, due to the urban development and high population growth, the water and wastewater network were constructed during the nineties, the water served to the households. This led into a wastewater disposal to the cesspits (2 to 3 m surface are with

up to 20 m depth). In most cases the cesspits is flooded into the streets in several of main and secondary cities, while in some other cases, it was connected to an overloaded wastewater treatment system which over flow with the pollution. In some other places, there is no wastewater treatment and the wastewater is discharged into the sea as the case of Al-Mukalla. The extension in building more WWTP led into production of more sludge which has become a cumbersome in most cases especially for the case of mechanical treatment such as the case in Sana'a and Ibb where there is a hundreds of tons of sludge which could not be disposed (Al-Nozaily 2006).

#### **2.6.4.1 The Level of Coverage by the Water and Wastewater Services**

It is estimated that 75% of the population in Yemen lack the service in wastewater while 50% of them can not get safe drinking water. This percentage is decreasing with time due to the continuous population growth and urban development which does go with extension of services at the same rate. For example, the percentage coverage in urban areas was decreased from 50% water ; 26% sanitation in 2000 to 47% water and 25% sanitation in 2002.

Water scarcity in Yemen and its depletion is considered as a reason which led into not enough water reaching consumers. The consumption rate in rural mountainous places was about 30l/c.d while in the urban mountainous places was 70 l/c.d with a little bit more in the coastal hot areas.

This low water consumption has led into an increase in the pollutants in the wastewater. The wastewater BOD in the mountainous cities is three to four times the highest known concentration in the world while it reached only two times in case of coastal areas although there is enough water is available to some extent.

#### **Technologies and problems in Sanitation in Yemen:**

In some rural areas, the dry sanitation is still applied which separates the solid part (Faeces) from the liquid (urine, washing, cleaning and ablution) and utilization of the water for irrigation while solids is used for fertilizer. However, due to the increasing in use of water and the unhygienic situation of application of solid part, this method is almost abandoned from the urban areas and still being used in some rural areas.

Therefore, the sanitation problem in rural areas is considered as big problem where the solid part is thrown to the backside of the houses or buried in holes in the ground, which become a health hazard to the population. In some rural and urban areas, cesspits is used as a mean of wastewater disposal. Even in some places the people are using the dried well as a cesspit which will be of a threat to the groundwater basins (Al-Nozaily 2006).

On the other hand, waste water stabilization ponds (WSP) is easy to operate and maintain and there effluent is considered safe for irrigation provided that the retention time is at least higher than 10 days in order to have enough time for treatment and subjection to the sunshine. Although these systems are easy, the water and wastewater corporations face a lot of difficulties in having enough available areas which stands as a problem preventing introducing and extending these systems. Moreover, the

corporations are not takinn seriously the proper operation of these systems although very simple as the case in Al-Hodiedah, Taiz and Dhamar.

Other problem facing the treatment process is the scarcity of water and lower consumption which is increasing with time. This low water consumption causes increase in wastewater pollutants concentrations (Al-Nozaily 2006).



### 3. Materials & Methods

This chapter presents the details of the experimental setups used in this research, the procedures followed to conduct the experiments, equipment used for analysis and the equations used for the data analysis.

#### 3.1. Experimental Setup

In this research the experiments were divided into two stages. First, laboratory-scale SAT simulated soil columns were used as pre-treatment of wastewater effluent impacted surface water and wastewater effluent. Second, pretreated samples (SAT effluents) were introduced as feed water for the different type of membranes (MF/UF) to investigate membrane fouling and flux decline and the effect of SAT on flux decline.

##### 3.1.1 Soil Aquifer Treatment Setup:

Laboratory-scale column studies, simulating SAT were conducted using the experimental setup shown in Figure 3.1 & 3.2. There were two sets of column. The soil columns are constructed with PVC. The bottom of each column is packed with filter media support of 15 cm thick graded gravel and then fill with prewash silica sand sized between 0.8 and 1.25 mm. Each set consisted of two columns, with each 2.5 m in height, connected in series to simulate a 5 m depth of aquifer. Each soil column consisted of 14 sampling ports located along the columns, and a number of sampling ports is higher in the first column than in the second column.

The first set of soil column was of 100 mm diameter and was fed with mixture of Delft Canal Water (DCW) and Secondary Effluents (SE) under anoxic conditions.

The second set of soil column was of 54 mm diameter and was fed of SE only under oxic conditions.

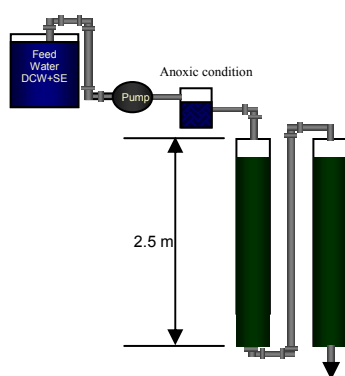


Figure 3.1 Schematic diagram of the soil column experimental setup (1) for SE+DCW (SC1)

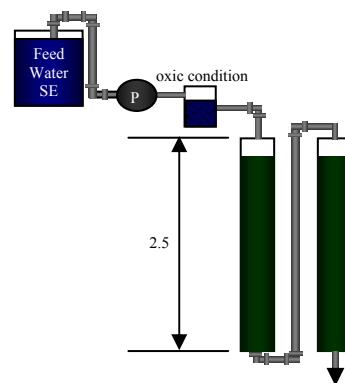


Figure 3.2 Schematic diagram of the soil column experimental setup (2) for SE (SC2)



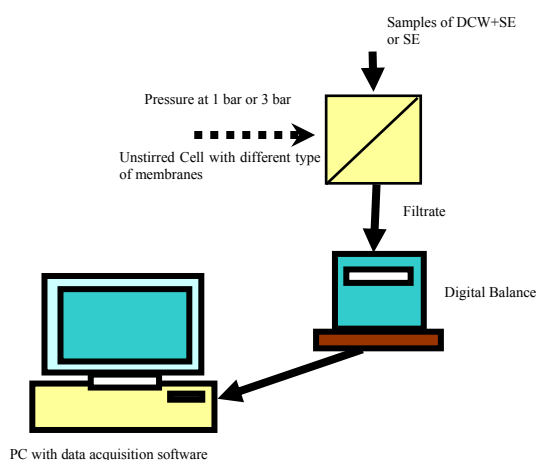
The main characterises of the effluent used are summered in the table 3.1 below:

*Table 3. 1 Characterises of water quality in this study*

| Parameters         | Units          | DCW   | SE    |
|--------------------|----------------|-------|-------|
| pH                 |                | 7.2   | 7.82  |
| Temperature        | C <sup>0</sup> | 6.6   | 12.5  |
| O <sub>2</sub>     | mg/L           | 7.7   | 1.7   |
| EC                 | μS/cm          | 1257  | 1000  |
| DOC                | mg/L           | 17.42 | 14.04 |
| UV <sub>254</sub>  | cm-1           | 0.541 | 0.441 |
| SUVA               | L/mg-m         | 3.21  | 3.18  |
| NH <sub>4</sub> -N | mg/L           | 0.603 | 0.154 |
| NO <sub>3</sub> -N | mg/L           | 2.23  | 1.81  |
| PO <sub>4</sub> -P | mg/L           | 1.1   | 0.33  |
| SO <sub>4</sub>    | mg/L           | 74.5  | 97.7  |

### 3.1.2 Membrane Setup for MF/UF

Membrane filtration tests were conducted using a (un)stirred cell device. Figures 3.3 & 3.4 show the photograph and schematic of filtration setup.



*Figure 3.1 MF/UF experimental filtration setup      Figure 3.2 Scheme of filtration setup*

Batch experiments were conducted using Amicon cells (8200) with a maximum process volume of 200 ml. The stirring assembly is entirely removed from the cell in order to keep the cake layer intact. Filtration is achieved under dead-end, constant pressure mode. Required pressure is achieved by applying nitrogen gas and is adjusted by a pressure valve. Permeate from the cell is collected in a beaker set on an electronic balance (Mettler Toledo, Model PB 602-S). The scale has an RS 232 interface with a computer. Data sets of collected filtrate weight and filtration time are recorded and imported into an MS Excel spread sheet by data acquisition software (Win Wedge, [www.taltech.com](http://www.taltech.com)). Recording interval could be adjusted (minimum interval of 1 second) prior to the

filtration run, and is constant throughout the length of a run. A typical output of the software is shown in annex 3.

One of the drawbacks of the digital scale is its very low capacity of 610 grams, which prevents continuous filtration. Another major drawback is that the readability of the balance is 0.01g, which proved to be not precise enough for distinguishing different filtration mechanisms.



Figure 3.3 Pressure sustaining valve



Figure

To make filtration of larger volumes possible, pressure vessel (steel) with a volume of 3.875 litres were used. The MQ water (1000 ml) was fed to the reservoir which is pressurized and connected to the cell as shown in figure 3.5

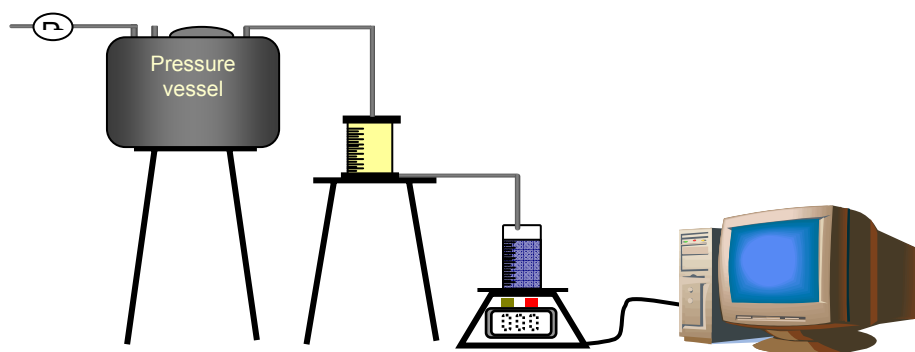


Figure 3.4 Filtration setup with feed reservoir (pressure vessel)

The alternative setup is shown schematically in Figure 3-8, whereby the filtration cell is filled up with feed solution and pressure is applied directly to the cell. The volume which may be filtered with this setup is limited to 180 ml (cell capacity).

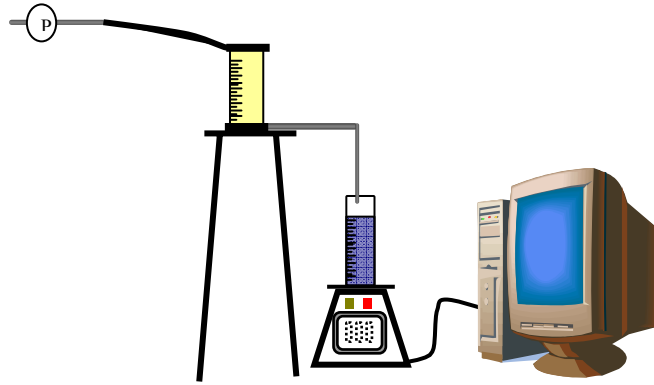


Figure 3.5 Filtration setup without feed reservoir (pressure vessel)

### 3.2. The Characteristic of Membrane Materials

The membrane characteristics for MF/UF membranes used in this study are shown in table 3.2 below, and the other characteristics installed in Annex 7.

Table 3. 2 Characteristics of MF/UF membranes used in research

| Type                           | Filter Material  | Filter Diameter |
|--------------------------------|------------------|-----------------|
| 0.1 $\mu\text{m}$ pore size MF | PVDF             | 90.0 mm         |
| 100,000 Dalton UF              | Polyethersulfone | 63.5 mm         |
| 50,000 Dalton UF               | Polyethersulfone | 63.5 mm         |
| 10,000 Dalton UF               | Polyethersulfone | 63.5 mm         |
| 5,000 Dalton UF                | Polyethersulfone | 63.5 mm         |

### 3.3. Experiment Procedures

The experiments involved two main steps: (i) Pre-filtration with SAT, and (ii) Filtration with MF/UF membranes.

#### (i) Pre-filtration with SAT.

In this stage the soil column experiments are divided in two types with different kind of samples quality (shown in figure 3.1&3.2), which were operated under a down-flow mode, and the flow rate (hydraulic loading rate) was controlled at 1.25 m<sup>3</sup>/day by the valves located at the outlet of the soil columns.

The first set of soil (SC1) (figure 3.1) was acclimated for one month period with secondary wastewater effluent. The wastewater effluent was used instead of DCW to

enhance biomass accumulation on sand. After the columns showed steady state performance with respect to DOC reduction, SC1 was fed with wastewater effluent from a wastewater treatment plant (Hoek van Holland, The Netherlands) with NOM rich Delft canal water (1:1) and NOM-rich DCW, respectively. DCW was collected from Oude Delft near the UNESCO-IHE building (Delft, The Netherlands). All influents were filtered through a microsieve (38  $\mu\text{m}$ ) prior to infiltration to prevent physical clogging on the top layers of soil column.

The second set of soil column (SC2) (figure 3.2) was acclimated for one month period with secondary wastewater effluent (SE). After the columns showed steady state performance with respect to DOC reduction, SC2 was fed with secondary effluent from a wastewater treatment plant (Hoek van Holland, the Netherlands).

## (ii) Filtration MF/UF membranes

In the second stage the experiments included:

- a) Using the influent of SAT with MF/UF system to determine the characteristics of wastewater before the SAT for comparing with the effluent of SAT later.
- b) Using the effluent SAT with MF/UF membranes as post filtration for wastewater to find the characteristics of effluent with these technologies.

## - The steps of MF/UF membranes experiments

1. Cleaning the system of MF/UF and the other equipments which we used during the experiments firstly with tap water and then with demineralized water to ensure every things are clean, because that can effect on the quality of water.
2. Taking about 250 ml of samples from influent and effluent of SC1 & SC2.
3. Determining the pH, EC, temperature, DOC,  $\text{UV}_{254}$  and EEM for all samples before and after membranes filtration.
4. Soaking the membranes in the MQ water for 5 to 24 hours before it is used.
5. Filling the pressure vessel with approximately 1200 ml of MQ water for flushing of membrane.
6. After that the filter were kept in the stirred cell, and the clean membrane experiment was started. Then approximately 180 ml of the influent and effluent was transferred to the stirred cell. This was done with utmost care using a plastic ladle with rounded edges to avoid any disturbance.
7. The outlet of the cell was plugged and opened only when set on the stand and connected to pressure. At this stage pressure was applied and the recording software started.
8. Each set of experiments were conducted three times to ensure the reproductively of the results and the average values were used for preparing graphs and calculation.

**Pressure:** MFI tests performed at a pressure of 2 bars. In this study applied pressure of 1 bar was chosen for 0.1  $\mu\text{m}$  pore size MF membrane and 3 bars was chosen for the other type of UF membranes, because of its close proximity to the pressure applied in MFI tests. As it is, at 1 bar, the clean water flux (at the start of a filtration run) is approximately between 720-1450  $\text{lmh}$  for different type of membranes, which is unusually high as compared to values applied in practice (50-80  $\text{lmh}$  for surface water, 60-120  $\text{lmh}$  for pretreated surface water).

### 3.4. Computational Procedure

#### 3.4.1 Determination of Clean Water Flux

Prior to the filtration of each feed solution, the filter was conditioned, whereby approximately 1.2 litres of MQ water was filtered through the membrane at 1 and 3 bar applied pressure. Membrane resistance was then calculated from the following equation:

$$R_m = \frac{\Delta P}{\eta J} \quad \text{..... 3. 1}$$

Where  $R_m$  ( $\text{m}^{-1}$ ) is the clean membrane resistance

$\Delta P$  (bar) is the pressure.

$J$  is the flux  $\text{m}^3/\text{m}^2.\text{s}$

$\eta$  is the viscosity (Pa.s), all the other symbols with their units are included in the list of symbols and abbreviations.

Ideally membrane resistance should be calculated from equation 3.2, which allows for membrane resistance as a function of filter properties such as filter thickness ( $\Delta x$ ), surface porosity ( $\epsilon$ ), pore radius ( $r$ ) and tortuosity ( $\tau$ ) and is defined by Poiseuille law:

$$R_m = \frac{8\Delta x \tau}{\epsilon r p^2} \quad \text{..... 3. 2}$$

Most of these parameters are very difficult to determine, and some are not provided by the membrane manufacturer/supplier. Hence in accordance with Darcy's law and the resistance in series model membrane resistance is determined by equation 3.1.

#### 3.4.2 Computation of the Modified Fouling Index

The Modified Fouling Index (MFI) was introduced by Schippers (1980) as an index of the fouling potential of a feed water containing particles, when fixed reference values are used for pressure (2bar), temperature (20°C) and membrane surface area ( $13.8 \times 10^{-4} \text{ m}^2$ ). It is based on the well known filtration equation (Eq 3.6), which is itself based on the fundamental equation for the rate of flow through a porous medium (Eq 3.3) and the definition of cake resistance (Eq 3.4) presented by Ruth (1933).

$$J = \frac{dV}{Adt} = \frac{\Delta P}{\eta(R_m + R_b + R_c)} \quad \text{..... 3. 3}$$

$$R_c = \frac{V}{A} \times \alpha C_b \quad \text{..... 3. 4}$$

In the absence of pore blocking, combining equations 3.3 and 3.4 results in:

$$\frac{dt}{dV} = \frac{\eta Rm}{\Delta P A} + \frac{\eta \alpha C_b}{\Delta P A^2} V \quad \text{..... 3. 5}$$

Integration at constant pressure from  $t = 0$  to  $t = t$ , assuming time independent permeability and uniform porosity characteristics throughout the depth of the cake (i.e. no compression of the cake), results in the well known filtration equation:

$$\frac{t}{V} = \frac{\eta Rm}{\Delta P . A} + \frac{\eta \alpha C_b}{2 \Delta P . A^2} . V \quad \text{..... 3. 6}$$

When  $t/V$  is plotted against  $V$ , a graph such as the one shown in Figure 3-9 may be obtained, depending on the occurrence of various filtration mechanisms. The portion of the line with a constant slope (straight line) represents cake filtration. The gradient of this line was adopted by Schippers (1980) to define the MFI.

In the MFI equation (Eq 3.7), product of the specific resistance of the cake and the concentration of particles in the feed water is taken to equal 'I' the fouling index, and is assumed to be independent of pressure. An advantage of using 'I' is that in most cases it is impossible to determine  $C$  and  $\alpha$  accurately.

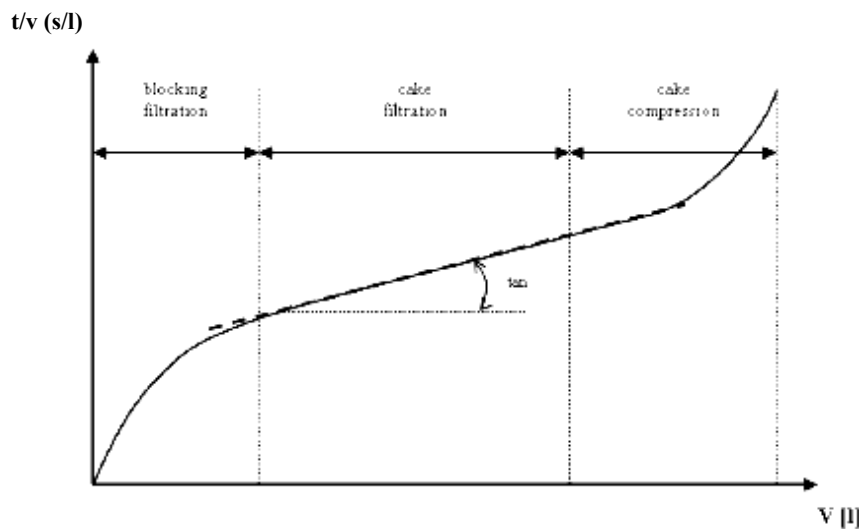


Figure 3.6 Ratio of filtration time and volume as a function of total filtrate volume

$$MFI = \frac{\eta \alpha C_b}{2 \Delta P . A^2} = \frac{\eta I}{2 \Delta P . A^2} = \tan \alpha \quad \text{..... 3. 7}$$

Specific resistance may be defined by the Carmen-Kozeny relationship (Eq 3.8). This relation clearly shows that a reduction in cake porosity or a decrease in particle size, increases the specific resistance and hence the MFI is increased.

$$\alpha = \frac{180(1 - \varepsilon)}{p_p d_p^2 \varepsilon^3} \quad \text{..... 3. 8}$$

Where  $\varepsilon$  is the cake porosity and  $p_p$  is the particle density.

Using the available filtration setup (described in the previous section), errors are introduced during filtration, which affect the obtained results especially at the start (first few recordings). These errors may be defined as one or a combination of the following factors:

- Air is trapped in the cell (CO<sub>2</sub> bubbles may be present in the solution after the acid dosing step), in the membrane and in the hose leading to the balance, which escapes at the start of a filtration run rendering the early readings inaccurate.
- The software and the pressure switch may not be run simultaneously; hence there is always a lapse between the actual start of the filtration and the first recording.
- Influence of the permeate stream hitting the collecting beaker randomly, which is quite strong at the start of the filtration when the beaker is empty and may result in superficially high values at the beginning and would persist throughout a filtration run.

When such errors are identified, the erroneous results must be excluded from the calculations. This is achieved by using equation 3.5 instead of equation 3.6 for the calculation of MFI. However, it must be noted that the two equations differ by a factor 2, which must be considered while correcting calculated MFI values to MFI-UF, by applying a correction factor. MFI-UF (Eq. 3.9) includes correction factors to standard reference conditions.

$$MFI - UF = \frac{\eta_{20c}}{\eta_r} \left( \frac{\Delta P}{\Delta P_0} \right) \left( \frac{A}{A_0} \right)^2 \tan \alpha \quad \text{..... 3. 9}$$

Where the temperature correction factor corrects the feed water viscosity to 20°C, the pressure correction factor corrects the applied transmembrane pressure to 2 bar ( $\Delta P_0$ ) and the area correction factor corrects the filter area to the reference surface area of the MFI0.45 microfiltration membrane ( $A_0 = 13.8 \times 10^{-4} \text{m}^2$ ).

### 3.5. Analytical Methods and Equipment

Some parameters were determined during experiments to find the effect SAT on performance of membranes. These parameters are;

### (i) pH, Turbidity and Conductivity/Temperature

The pH of samples was measured using a Metrohm 691 pH-meter while the conductivity and temperature were measured with a WTW cond 330i conductivity meter. Turbidity was measured using a Dr Lange Trubungsphotometer LTP 4 turbidity meter.

### (ii) DOC/TOC

The dissolved organic carbon (DOC) and total organic carbon (TOC) were measured using a Total Organic Carbon (TOC) analyser (O x I Corporation Model 700). For DOC, the samples were pre-filtered with cleaned cellulose acetate 0.45  $\mu$  m filters.

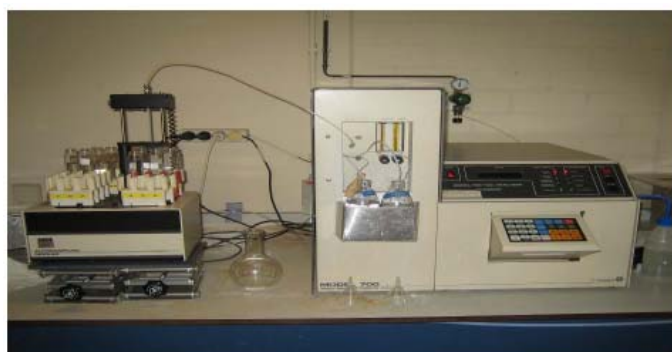


Figure 3.7 A 700 Model TOC analyzer

### (iii) UV<sub>254</sub>/SUVA

NOM can be characterized by spectrophotometric analysis. Ultraviolet (UV) light absorbance by sample waters is attributed to the aromatic chromophores present in NOM molecules (mainly humics) dissolved in water. UV measures the aromatic compounds preferentially and does not give correct results if the aromaticity is altered. Values will be overestimated, as most treatment processes preferentially remove aromatic compounds (Schäfer, 2001). Specific UV absorbance (SUVA or SUVA 254) is defined as the sample's UV absorbance at 254 nm divided by the DOC concentration of the sample. SUVA indicates the level of aromaticity of compounds in the DOC and can be used to estimate the chemical nature of the DOC. A  $SUVA \leq 3$  L/m-mg C indicates non-humic NOM while SUVA 4-5 L/m-mg C indicates humic NOM (Edzwald and van Benschoten, 1990).

### (iv) Fluorescence EEM

The fluorescence Excitation-Emission Matrix (EEM) spectra of the different samples were measured using a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer with a xenon lamp as the excitation source. Sample preparation for the analysis was done in a uniform manner. The protocol adapted was based on previous work by Westerhoff et al. (2001). Based on the measured DOC level, filtered water samples were diluted to  $\sim 1.0$  mg/L of DOC with 0.01M KCl solution whose pH was pre-adjusted to 2.8 ( $\pm 0.1$ ) using



HCl. In addition, all sample measurements were performed at room temperature. The range of the wavelength used was as follows: Excitation: 240-450 nm (10 nm intervals), Emission: 290-530 nm (2 nm intervals). EEMs of each sample were subtracted with the EEM of the 0.01M KCl (pH 2.8 adjusted with HCl) solution (set as a blank EEM) to remove raman scatter peaks. Correction steps were applied to each blank-subtracted EEM using emission and excitation correction factors provided by the manufacturer. This enabled the DOM fractions to be categorized in terms of protein-like material, humic-like material and fulvic-like acids. Figure 3-8 shows the set-up that was used for the EEM measurements.



*Figure 3.8 A Horiba Jobin Yvon FluoroMax-3 spectrofluorometer used for FEEM measurements*

## 4. Results and Discussion

### 4.1 Introduction

In this chapter, the results of the different experiments carried out in this study are provided and discussed. The first part presents results from the analysis of DOC, pH, EC and TDS for different types of water with and without SAT and MF/UF. The second part shows the results from the MF/UF membranes carried out during the same experiments and analysis of the performances of different membranes.

### 4.2 DOC Removal by Different Membranes with and without SAT

DOC removal by different membranes were analysed with or without SAT pre-treatment by conducting (un)stirred cell experiments in the laboratory. Results of DOC analysis for each type of membrane is illustrated separately. The experiments were conducted in triplicate and the average results of three runs are presented in the graph and tables.

#### 4.2.1 DOC Removal by 0.1 $\mu\text{m}$ MF Membrane

Figure 4.1 & 4.2 show the DOC of two different influent water after different treatment steps.

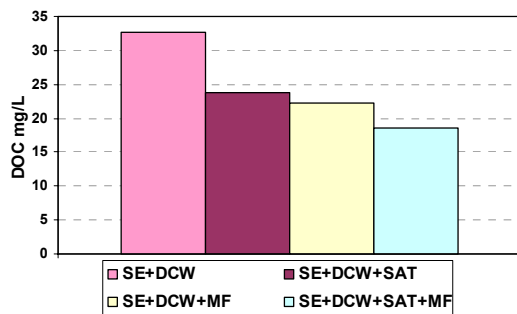


Figure 4. 1 DOC of SE+DCW before and after different treatment steps.

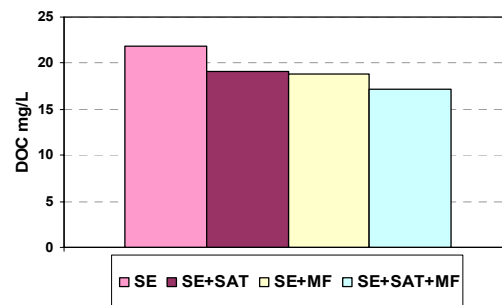


Figure 4. 2 DOC of SE before and after different treatment steps.

From the figures, it is clear that for both type of influent performance of SAT + MF is better than SAT alone or MF alone. However the main goal is not to removal DOC in general, but rather, problematical DOC foulants (like protein or humic etc.)

Table 4.1 Presents DOC removal % for 0.1  $\mu\text{m}$  membrane with or without SAT

Table 4. 1 Percentage DOC removal for 0.1  $\mu\text{m}$  MF membrane with or without SAT

| Treatment | Influent |      |
|-----------|----------|------|
|           | SE + DCW | SE   |
| SAT       | 25.5     | 17.4 |
| MF        | 12.5     | 13.8 |
| SAT + MF  | 36.9     | 30.4 |

Table 4.1 shows that DOC removal from SAT alone is 25.5% and 17.4% for SE+DCW and SE respectively. DOC removals with UF alone (without SAT pre-treatment) were 12.5% and 13.8% respectively. However, for SAT pre-treated water DOC removal after UF increased by 10.4% and 13.8% respectively. These results clearly show that SAT pre-treatment of wastewater treatment plant effluent improves the overall DOC removal of subsequent UF membranes.

In addition to DOC,  $\text{UV}_{254}$ , pH, EC and  $\text{Ca}^{+2}$  concentrations of the samples were also measured; the results are presented in Annex 3. Table 4.2 summarises the change in SUVA values after different treatment.

Table 4. 2 SUVA ( $\text{Lm}^{-1}\text{mg}^{-1}$ ) for 0.1  $\mu\text{m}$  membrane with or without SAT

| Treatment | Influent |     |
|-----------|----------|-----|
|           | SE + DCW | SE  |
| Influent  | 1.6      | 2.0 |
| SAT       | 1.8      | 2.2 |
| MF        | 2.0      | 2.2 |
| SAT + MF  | 2.2      | 2.3 |

SUVA indicates the level of aromaticity of compounds in the DOC and can be used to estimate the chemical nature of the DOC. Table 4.2 shows the increase of SUVA with SAT only were 11 % and 9 % for SE+DCW and SE respectively, and for UF only were 20 % and 9 % for SE+DCW and SE respectively. These results show that both in SAT and MF, there is preferential removal of non-humic.

Furthermore, it was observed that EC,  $\text{UV}_{254}$  and  $\text{Ca}^{+2}$  were decreasing after SAT and /or UF treatment. However there was no clear trend with respect to change in pH, though the change in pH observed was minimal ( $\pm 0.2$  units).

#### 4.2.2 DOC Removal by 100 kD UF Membrane

Similarly DOC removal analysis was conducted for sample with or without SAT pre-treatment with 100 kD UF membrane. The results of the DOC removal is summarised in table 4.3.

Table 4. 3 Percentage DOC removal for 100 kD UF membrane with or without SAT

| Treatment | Influent |      |
|-----------|----------|------|
|           | SE + DCW | SE   |
| SAT       | 25.2     | 15.3 |
| UF        | 13.3     | 16.9 |
| SAT + UF  | 34.8     | 31.4 |

Table 4.3 shows that DOC removal from SAT alone is 25.5% and 15.3% for SE+DCW and SE respectively. DOC removals with UF alone (without SAT pre-treatment) were 13.3 % and 16.9 % respectively. These results clearly show that SAT pre-treatment of wastewater treatment plant improves the overall DOC removal of subsequent UF membranes.

For the other measurements DOC,  $UV_{254}$ , pH, EC and  $Ca^{+2}$  concentrations of the samples were also measured; the results are presented in Annex 3. Table 4.4 summarises the change in SUVA values after different treatment.

Table 4. 4 SUVA ( $Lm^{-1}mg^{-1}$ ) for 100 kD UF membrane with or without SAT

| Treatment | SE + DCW | SE  |
|-----------|----------|-----|
| Influent  | 3.0      | 2.3 |
| SAT       | 3.5      | 2.6 |
| UF        | 3.4      | 2.6 |
| SAT + UF  | 3.9      | 2.8 |

Table 4.4 shows the increase of SUVA with SAT only were 14.2 % and 11.5 % for SE+DCW and SE respectively, and for UF only were 13.3 % and 11.5 % for SE+DCW and SE respectively. These results show that SAT and UF are equally effective in removing non-humic part of natural organic matter.

#### 4.2.3 DOC Removal by 50 kD and 10 kD UF Membranes

In case of 50 and 10 kD membranes the DOC removal analysis was conducted for sample with or without SAT pre-treatment. The results of the DOC removal is summarised in table 4.5.

Table 4. 5 Percentage of DOC removal for 50 &amp; 10 kD membranes with or without SAT

| Treatment | Influent |       |       |       |
|-----------|----------|-------|-------|-------|
|           | SE + DCW |       | SE    |       |
|           | 50 kD    | 10 kD | 50 kD | 10 kD |
| SAT       | 25.5     | 22.7  | 16.4  | 15.9  |
| UF        | 18.3     | 20.5  | 17.4  | 21.5  |
| SAT + UF  | 36.9     | 38.5  | 28.5  | 33.1  |

Table 4.5 shows that DOC removal from UF (50 & 10 kD) alone is increasing from 18.3% to 20.5% and from 17.4% to 21.5% for SE+DCW and SE respectively. For DOC removal with SAT alone is the same % removal as the above results. These results clearly show that UF post-treatment of wastewater treatment plant using 50 or 10 kD membrane improves the overall DOC removal up to 22%.

Table 4.6 summarises the change in SUVA values after different treatment for 50 & 10 kD membranes.

Table 4. 6 SUVA ( $Lm^{-1}mg^{-1}$ ) for 50 & 10 kD membrane with or without SAT

| Treatment | SE + DCW |       | SE    |       |
|-----------|----------|-------|-------|-------|
|           | 50 kD    | 10 kD | 50 kD | 10 kD |
| Influent  | 3.1      | 3.4   | 1.9   | 3.0   |
| SAT       | 3.5      | 3.8   | 2.1   | 3.3   |
| UF        | 3.7      | 3.9   | 2.2   | 3.4   |
| SAT + UF  | 4.1      | 4.4   | 2.4   | 3.7   |

Table 4.6 shows that increase of SUVA with SAT only were approximately 11 % and 9 % for SE+DCW and SE respectively. For UF (50 & 10 kD) only, SUVA were changed from 16.25 to 12.8 % and 13.6 % to 11.8 % for SE+DCW and SE respectively.

For the parameters like pH and  $UV_{254}$  there was no clear indication about the percentage change of these parameters, but EC and TDS appeared to be affecting of removals of DOC on this types of membranes. The related results for these parameters are included in the tables and figures in Annex.3.

As a comparison between the different types of membranes, table 4.7 and figure 4.3 show the summary for the percentage DOC removal with the different membranes.

Table 4.7 Average DOC removals for both type of water with different type of treatment

| UF Type           | DOC Removal by UF only | DOC Removal by SAT+UF |
|-------------------|------------------------|-----------------------|
| 0.1 $\mu\text{m}$ | 12 - 13%               | 30 - 37%              |
| 100 kD            | 13 - 16%               | 31 - 40%              |
| 50 kD             | 17 - 20%               | 34 - 44%              |
| 10 kD             | 18 - 22%               | 35 - 46%              |

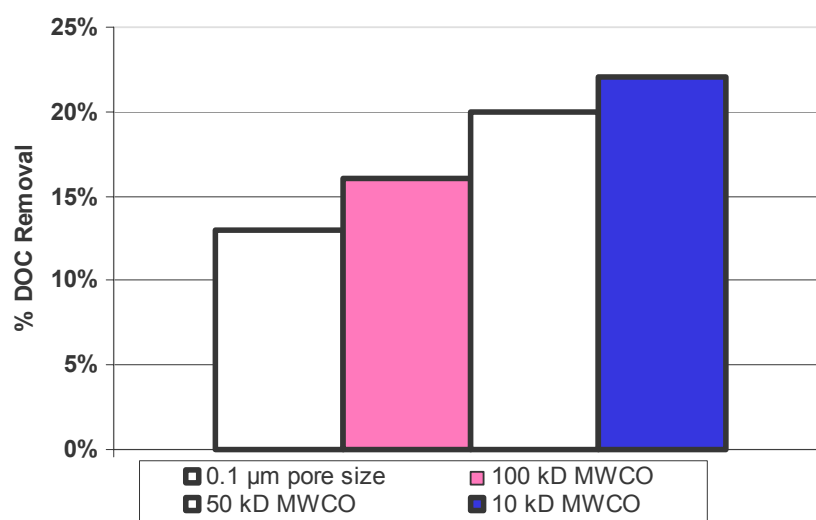


Figure 4.3 Average DOC removal for both type of water with different type of UF membranes (without SAT)

Table 4.7 and figure 4.3 show that 10 kD membranes gives the highest DOC removal 22% without SAT and increasing up to 46% DOC removal with SAT pre-treatment. As expected DOC removal was higher for UF membranes with low MWCO. These results clearly demonstrate SAT pre-treatment of wastewater treatment plant effluent improves the overall DOC removal and decreasing of non-humic substances which helps the performance of UF membranes.

### 4.3 Analysis of Clean Membrane Resistance

The clean membrane resistances ( $R_m$ ) were measured using MQ water under pressure 1 bar and 3 bars ( see 3.3),  $R_m$  is the one of the important parameter in this research; it gives us the characterisation of membranes and the idea about the suitable pressure for full operation of each types of membranes.

For the determination of actual membrane resistance, MilliQ water was filtered through the fresh membrane in its unfouled state, until a steady permeate flux was observed. This value represents the pure water flux of each particular piece of membrane. The

average of these resistances was taken as the clean membrane resistance (Tabatabai, 2007).

Filtration results for all filters showed a similar trend as that shown in Figure 4.4. A decrease in resistance was observed for the first few hundred milliliters of filtered water, after which filter resistance became rather stable.

Figure 4.4 shows the decline in filtration for filtration with MQ water under 1.0 bar pressure with 0.1  $\mu\text{m}$  pore of membrane.

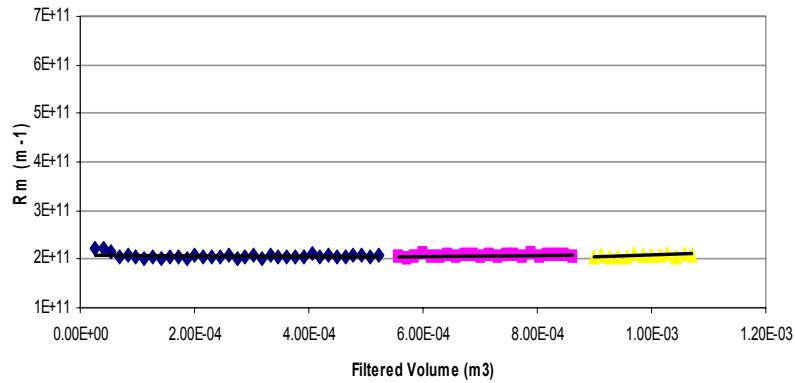


Figure 4. 4 Decline in filter resistance for filtration with MQ water at 1.0 bar and 0.1  $\mu\text{m}$  pore of membrane

Gaps in volume axis in figure 4.4 were, caused as the maximum capacity for the digital balance is 610 g. For that we needed to change the full container with the empty one to continue the experiment.

The decreasing trend did not persist for volumes larger than 600 ml. This is in accordance with the findings of Gaulinger (2007). This is attributed to the fact that a certain volume of water is required to wet (open) all the internal pores of a filter. When the membrane is already fully wetted, this effect should not be seen (Persson, 1995). Table 4.8 shows the values of membrane resistances for 3 runs for 0.1  $\mu\text{m}$  pore of membrane.

Table 4. 8 Membrane resistances measured from filtration with MQ water at 1.0 bar and 0.1  $\mu\text{m}$  pore size of membrane

|         | $R_m \text{ (m}^{-1}\text{)}$ |
|---------|-------------------------------|
| Run1    | 2.27E+11                      |
| Run2    | 2.11E+11                      |
| Run3    | 2.08E+11                      |
| Average | 2.14E+11                      |

Table 4.8 shows that the  $R_m$  was calculated as  $2.18 \times 10^{11} \text{ m}^{-1} (\pm 4.4\%)$  for this type of membrane.

For 100 kD membrane, the pressure was 1.0 bar, figure 4.5 shows the decline in filter resistance.

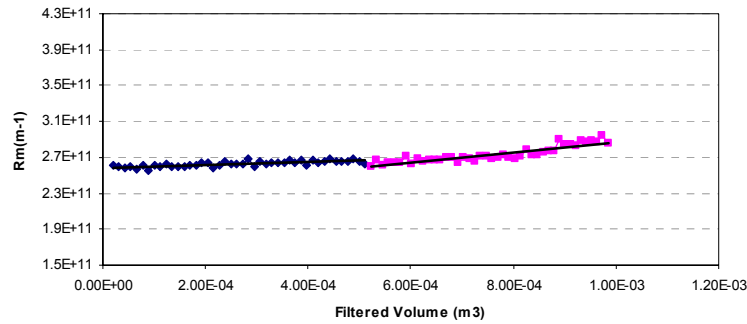


Figure 4. 5 Decline in filter resistance for filtration with MilliQ water at 1.0 bar and 100kD MWCO of membrane

Figure 4.5 shows slightly increasing  $R_m$  after 600 ml of MQ water filter, that happened with 100, 50 and 10 kD membrane, that increasing in  $R_m$  is around 10%, the main cause for that is the MQ water was NOT completely clean 100% and the pressure vessel was corrosion, that cause the fouling in the membranes and  $R_m$  was increased. The figures for decline in filtration resistances for filtration with MQ water for 50 and 10 kD membranes are shown in Annex 4.

Table 4.9 shows the values of membrane resistances for 100 kD membrane under pressure 1.0 bar.

Table 4. 9 Membrane resistances measured from filtration with MQ water at 1.0 bar and 100 kD membrane

|         | $R_m$    |
|---------|----------|
| Run1    | 2.77E+11 |
| Run2    | 2.61E+11 |
| Run3    | 2.99E+11 |
| Run4    | 2.69E+11 |
| Average | 2.76E+11 |

Table 4.9 shows that the  $R_m$  was calculated as  $2.89 \times 10^{11} \text{ m}^{-1} (\pm 4.2\%)$  for this type of membrane.

As comparison between different types of membranes, table 4.10 lists the average of the clean membrane resistances for each type.



Table 4. 10 The clean membranes resistance for each type of membranes.

| UF Type     | Clean membrane resistance ( $m^{-1}$ ) | Pressure (bar) | Water clean Flux(lmh) |
|-------------|--|----------------|-----------------------|
| 0.1 $\mu m$ | 2.08 – 2.27 E+11                       | 1.0            | Up to 1500            |
| 100 kD      | 2.60 – 3.00 E+11                       | 1.0            | Up to 1200            |
| 50 kD       | 5.5 – 6.80 E+11                        | 3.0            | Up to 1100            |
| 10 kD       | 9.00 E+11– 1.45 E+12                   | 3.0            | Up to 800             |

Comparison between the  $R_m$  for manufacturing specification for these types of membrane and the experimental result show that there results are 10% higher than the manufacturing results. It is likely as the experiments conditions are different and there are calculation errors in temperature, which has effect on water viscosity and the membrane performance.

#### 4.4 Analysis of MFI for Different Membranes

The modified fouling index (MFI) was used in this research to analyse the effect of SAT on performance of the membranes. For calculation of MFI, we need accuracy considerations and calculation to reach reliable results (see 3.4.2). As accuracy considerations relationship  $t/V$  over  $V$  vs.  $\Delta t/\Delta V$  over  $V$  were used.

In all experiments conducted with the available filtration setup, the first few time/volume recordings are much higher than the values that follow. This happens due to the presence of air in the filtration cell at the very beginning and cannot be avoided. Another reason for the introduction of error in the first recordings of volume is that the pressure valve cannot be released simultaneously with the recording button of the software. This results in lower recordings or in other words higher resistance at the start of the filtration. Therefore, the first few recordings in all tests are artefacts and should be eliminated from the calculations (Tabatabai, 2007).

$t/V$  is the cumulative reciprocal flow rate and if calculations are done with reference to the first erroneous value, the error will be carried through in all calculations that follow and hence the plot of  $t/V$  against  $V$  is not enough to be accepted our results for that the calculation of  $\Delta t/\Delta V$  over  $V$  was taken in this study to ensuring the MFI results.  $\Delta t/\Delta V$ , however, is the difference between each two consecutive recordings of time and volume and thus errors in the first recorded value will not affect the rest of the calculations. These discussions are further illustrated in light of the following sections.

##### 4.4.1 Analysis of MFI for 0.1 $\mu m$ Membrane

This section shows all results about the MFI for 0.1 $\mu m$  MF membrane and the accuracy consideration that was taken for calculations.

**(i) MFI for SE+DCW with or without SAT pre-treatment**

Figure 4.6 shows the results for 3 runs conducted for  $t/V$  over  $V$  vs.  $\Delta t/\Delta V$  over  $V$  graphs for SE+DCW samples without SAT pre-treatment under 1.0 bar for 0.1  $\mu\text{m}$  MF membrane.

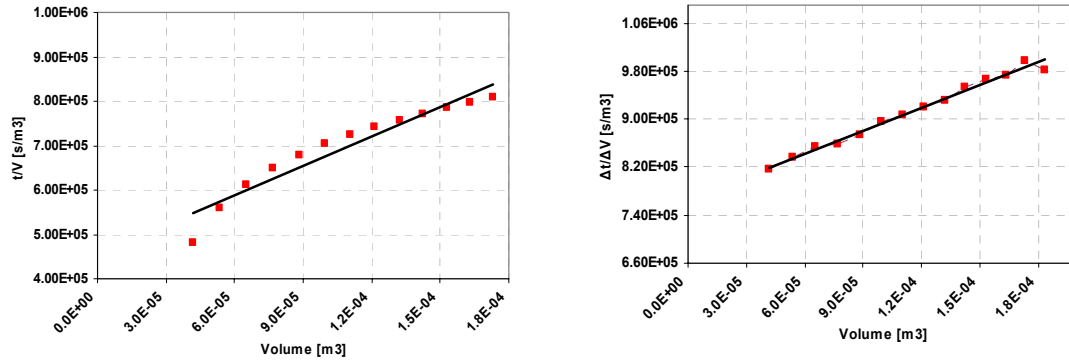


Figure 4. 6(a)  $t/V$  versus  $V$  and (b)  $\Delta t/\Delta V$  versus  $V$  graphs for SE+DCW samples without SAT pre-treatment at 1.0 bar and 0.1  $\mu\text{m}$  MF membrane

In Figure 4.6(a) cumulative reciprocal flow rates are plotted against volume for one test series. Figure 4.6(b) shows  $\Delta t/\Delta V$  versus  $V$  graphs for the same test series. It shows that the  $\Delta t/\Delta V$  versus  $V$  graphs is the approximately same as that for  $t/V$  versus  $V$  graphs, however because error is neglected from subsequent points on the graph, an apparent difference in slope is observed. For the SE+DCW samples with SAT pre-treatment, the graphs for  $t/V$  versus  $V$  and (b)  $\Delta t/\Delta V$  versus  $V$  are shown in Annex.4

The importance of the proper choice of graph for MFI calculations for SE+DCW samples is illustrated in Table 4.11 & 4.12 where the slope of the linear approximation (MFI) along with  $R^2$  values are presented for both  $t/V$  versus  $V$  and  $\Delta t/\Delta V$  versus  $V$  graphs.

Table 4.11 Comparison of MFI obtained from the plot of  $t/V \sim V$  and  $\Delta t/\Delta V \sim V$  for SE+DCW samples without SAT pre-treatment at 1.0 bar and 0.1  $\mu\text{m}$  MF membrane

|      | $t/V \sim V$              |       |                                   | $\Delta t/\Delta V \sim V$ |       |                                   |
|------|---------------------------|-------|-----------------------------------|----------------------------|-------|-----------------------------------|
|      | MFI<br>( $\text{s/L}^2$ ) | R2    | Y-intercept<br>( $\text{s/L}^2$ ) | MFI<br>( $\text{s/L}^2$ )  | R2    | Y-intercept<br>( $\text{s/L}^2$ ) |
| Run1 | 503                       | 0.976 | 1.33E9                            | 520                        | 0.986 | 2.64E9                            |
| Run2 | 1090                      | 0.986 | 5.98E8                            | 1117                       | 0.997 | 1.01E9                            |
| Run3 | 567                       | 0.978 | 1.30E9                            | 585                        | 0.996 | 2.43E9                            |

Table 4. 12 Comparison of MFI obtained from the plot of  $t/V \sim V$  and  $\Delta t/\Delta V \sim V$  for SE+DCW samples with SAT pre-treatment at 1.0 bar and 0.1  $\mu\text{m}$  MF membrane

|      | t/V vs. V                  |       |                                    | $\Delta t/\Delta V$ vs. V  |       |                                    |
|------|----------------------------|-------|------------------------------------|----------------------------|-------|------------------------------------|
|      | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) |
| Run1 | 314                        | 0.946 | 2.82E8                             | 320                        | 0.942 | 5.61E8                             |
| Run2 | 572                        | 0.987 | 3.71E8                             | 583                        | 0.978 | 6.26E8                             |
| Run3 | 232                        | 0.956 | 1.30E9                             | 244                        | 0.941 | 2.13E9                             |

Table 4.11 & 4.12 showed that the plot of  $t/V$  versus  $V$  and  $\Delta t/\Delta V$  over  $V$  gives approximately equal for  $R^2$  value, therefore MFI was calculated for all other results from this method ( $t/V$  versus  $V$ ). Otherwise the reduction of MFI between SE+DCW samples with and without SAT pre-treatment is about 40 – 60%; These results clearly show that SAT pre-treatment of wastewater treatment plant effluent decreases the overall MFI of subsequent UF membranes and increases of efficiency of membranes.

#### (ii) MFI for SE with or without SAT pre-treatment

The plot of  $t/v$  versus  $V$  gave approximately same  $R^2$  value for the plot  $\Delta t/\Delta V$  over  $V$  and therefore the plot of  $t/v$  versus  $V$  are presented below. Figure 4.7 shows  $t/V$  versus  $V$  and graphs for SE samples with or without SAT pre-treatment at 1.0 bar and 0.1  $\mu\text{m}$  of membrane.

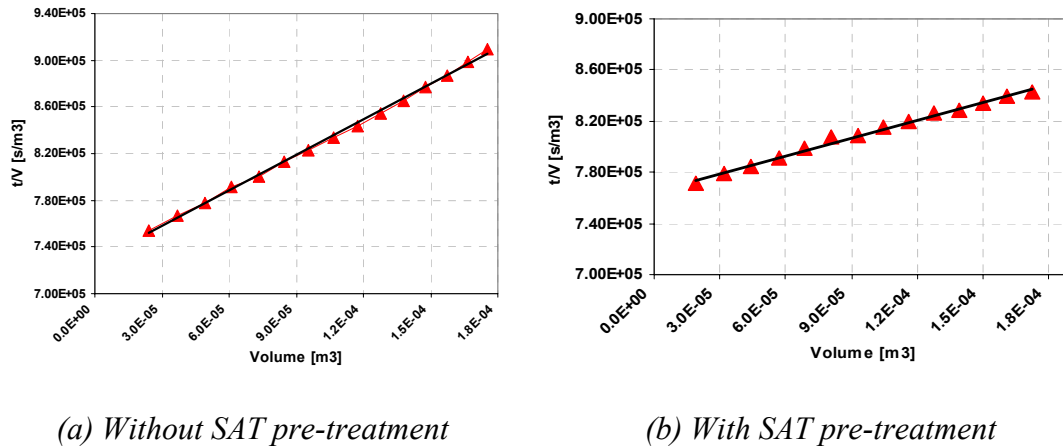


Figure 4. 7  $t/V$  versus  $V$  and graphs for SE samples at 1.0 bar and 0.1 MF  $\mu\text{m}$  membrane

In Figure 4.7 cumulative reciprocal flow rates are plotted against volume for one test series. Those graphs were average of 3 runs with the same type of membranes and samples. It shows that the blocking filtration and cake compression did NOT appear in this type of membranes, because the flux is high and the blocking filtration occurs very fast before it could be captured during the experiment.

Table 4.13 shows the comparison of  $R^2$  and MFI for SE samples under 1.0 bar with 0.1  $\mu\text{m}$  MF membrane.

Table 4.13 Comparison of MFI obtained from the plot of  $t/V \sim V$  for SE samples without or with SAT pre-treatment at 1.0 bar and 0.1  $\mu\text{m}$  MF membrane

|      | SE only                    |       |                                    | SE + SAT                   |       |                                    |
|------|----------------------------|-------|------------------------------------|----------------------------|-------|------------------------------------|
|      | t/V vs. V                  |       |                                    | t/V vs. V                  |       |                                    |
|      | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) |
| Run1 | 471                        | 0.976 | 4.43E8                             | 278                        | 0.993 | 3.75E8                             |
| Run2 | 749                        | 0.994 | 4.65E8                             | 372                        | 0.977 | 2.28E8                             |
| Run3 | 1030                       | 0.983 | 1.00E9                             | 441                        | 0.986 | 5.0E8                              |

Table 4.13 shows that differences MFI between SE samples with and without SAT is around 41 – 57 %, that means SAT helps to reduce the fouling up to 57%. It clearly shows MFI for SE is more than MFI for SE+DCW, DWC make as adulation for SE.

#### 4.4.2 Analysis of MFI for 100 kD UF Membrane

Similarly as in the section before the results of MFI for 100 kD membrane, are presented below.

##### (i) MFI for SE+DCW with or without SAT pre-treatment

Figure 4.8 shows  $t/V$  versus  $V$  and graphs for SE+DCW samples with or without SAT pre-treatment at 1.0 bar and 100 kD UF membrane.

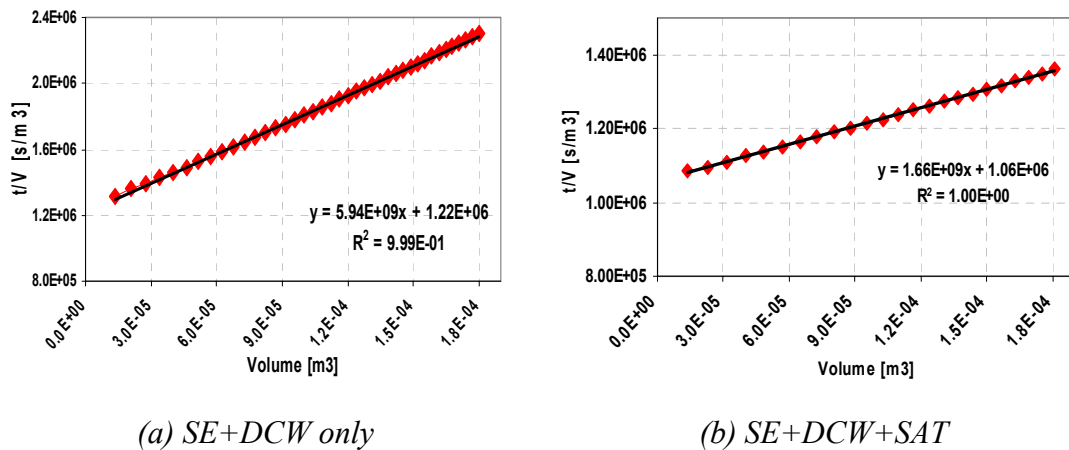


Figure 4.8  $t/V$  versus  $V$  and graphs for SE+DCW samples with or without SAT pre-treatment respectively at 1.0 bar with 100 kD UF membrane

In Figure 4.8, it can be seen that the cake filtration appeared without any indication to blocking filtration and cake compression. Otherwise the cake compression was not reached, maybe the because of the small quantity of sample and the time of experiment was not long (few minutes only).

Table 4.14 shows the comparison of MFI between SE+DCW samples under 1.0 bar.

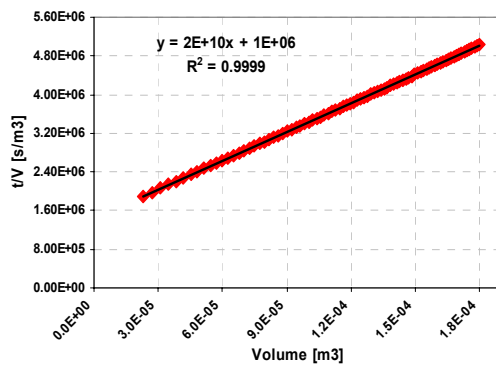
*Table 4.14 Comparison of MFI obtained from the plot of  $t/V \sim V$  for influent and effluent of SE+DCW samples at 1.0 bar and 100 kD UF membrane*

|      | SE+DCW only                |                |                                    | SE+DCW+SAT                 |                |                                    |
|------|----------------------------|----------------|------------------------------------|----------------------------|----------------|------------------------------------|
|      | $t/V$ vs. $V$              |                |                                    | $t/V$ vs. $V$              |                |                                    |
|      | MFI<br>(s/L <sup>2</sup> ) | R <sup>2</sup> | Y-intercept<br>(s/L <sup>2</sup> ) | MFI<br>(s/L <sup>2</sup> ) | R <sup>2</sup> | Y-intercept<br>(s/L <sup>2</sup> ) |
| Run1 | 1.41E+04                   | 0.999          | 6.06E9                             | 3.91E+03                   | 1.00           | 1.82E9                             |
| Run2 | 1.45E+04                   | 0.999          | 5.94E9                             | 4.11E+03                   | 0.998          | 1.66E9                             |

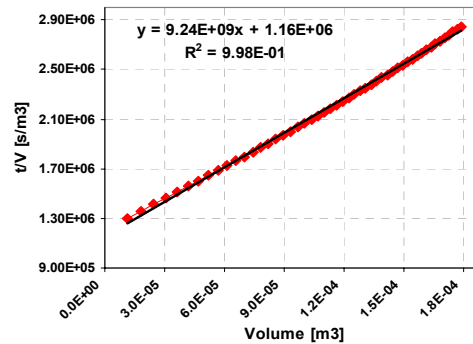
Table 4.14 shows R<sup>2</sup> is very high, so, the accuracy for calculation of MFI will be high or more reliable. It shows the MFI are 1.45E+04 s/L<sup>2</sup> and 4.11E+03 s/L<sup>2</sup> for samples without and with SAT pre-treatment respectively. The differences MFI between SE+DCW samples with and without SAT is around 72 % that means the SAT pre-treatment is likely to help to reduce the fouling in membrane up to 72%.

#### (i) MFI for SE with or without SAT pre-treatment

Figure 4.9 shows  $t/V$  versus  $V$  and graphs for SE samples at 1.0 bar and 100 kD UF membrane. The MFI and R<sup>2</sup> are shown in table 4.15



(a) Without SAT pre-treatment



(b) With SAT pre-treatment

*Figure 4. 9  $t/V$  versus  $V$  and graphs for SE samples with or without SAT respectively at 1.0 bar with 100 kD UF membrane*

Figure 4.9 shows the same behaviour as figure 4.8, the cake filtration is clear, but the blocking and cake compression did not appear because of the same reason.

Table 4.15 Comparison of MFI obtained from the plot of  $t/V \sim V$  for SE samples with or without SAT at 1.0 bar and 100 kD UF membrane

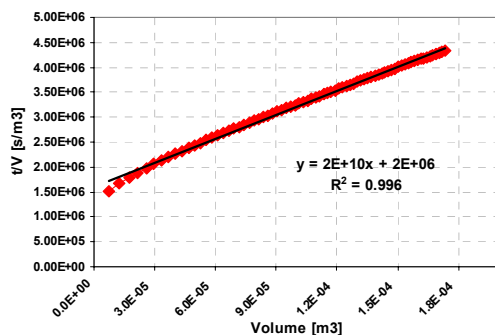
|      | SE only                    |       |                                    | SE+SAT                     |       |                                    |
|------|----------------------------|-------|------------------------------------|----------------------------|-------|------------------------------------|
|      | $t/V$ vs. $V$              |       |                                    | $t/V$ vs. $V$              |       |                                    |
|      | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) |
| Run1 | 3.40E+04                   | 0.996 | 1.41E10                            | 2.32E+04                   | 0.996 | 9.94E9                             |
| Run2 | 4.61E+04                   | 0.999 | 2.00E10                            | 2.15E+04                   | 0.998 | 9.24E9                             |

Table 5.15 shows MFI for SE samples with or without SAT pre-treatment as two runs conducted experiments, where MIF are 4.61E+04 s/L<sup>2</sup> and 2.15E+04 s/L<sup>2</sup> respectively. The differences MFI between influent and effluent is around 47%, it can be seen that the MFI for SE sample is higher than MFI for SE+DCW. However the percentage removal for SE+DCW samples is higher than that for SE samples. That was due to difference on the quality of water samples and the efficiency of the SAT pre-treatment. However MFI for SE is more than MFI for SE+DCW.

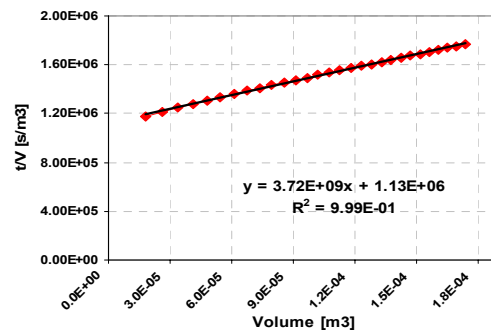
#### 4.4.3 Analysis of MFI for 50 kD Membrane

##### (i) MFI for SE+DCW with or without SAT pre-treatment

For this 50 kD membrane, the experiments were conducted at the pressure of 3.0 bars, Figure 4.9 shows  $t/V$  versus  $V$  and graphs for SE influent and effluent samples at 1.0 bar and 50 kD UF membrane.



(a) Without SAT pre-treatment



(b) With SAT pre-treatment

Figure 4. 10  $t/V$  versus  $V$  and graphs for SE+DCW samples at 3.0 bars with 50 kD UF membrane

Figure 4.10 (a) for influent samples without SAT pre-treatment shows blocking filtration and cake filtration. That happened in this type of membrane because the flux became smaller than in case of the previous membranes. But with SE+DCW samples with SAT pre-treatment samples can not be controlled on the first points to get the blocking filtration.

Table 4.16 shows the MFI results for one run only, because the other runs are similar.

Table 4. 16 Comparison of MFI obtained from the plot of  $t/V \sim V$  for SE+DCW samples at 3.0 bar and 50 kD UF membrane

|      | SE+DCW only        |       |                            | SE+DCW+SAT         |       |                            |
|------|--------------------|-------|----------------------------|--------------------|-------|----------------------------|
|      | $t/V$ vs. $V$      |       |                            | $t/V$ vs. $V$      |       |                            |
|      | MFI<br>( $s/L^2$ ) | R2    | Y-intercept<br>( $s/L^2$ ) | MFI<br>( $s/L^2$ ) | R2    | Y-intercept<br>( $s/L^2$ ) |
| Run1 | 9.50E+04           | 0.996 | 2.00E10                    | 2.54E+04           | 0.999 | 3.72E9                     |

Table 4.16 summarises the MFI results, where MFI are  $9.50E+04 \text{ s/L}^2$  and  $2.54E+04 \text{ s/L}^2$  respectively. The MFI difference between samples with or without SAT pre-treatment is around 77 %, otherwise the MFI will be higher with the smaller of the MWCO of membranes.

### (ii) MFI for SE with or without SAT pre-treatment

Similarly figure 4.11 shows the  $t/V$  versus  $V$  and graphs for SE samples with or without SAT pre-treatment at the pressure 3.0 bar with 50 kD UF membrane.

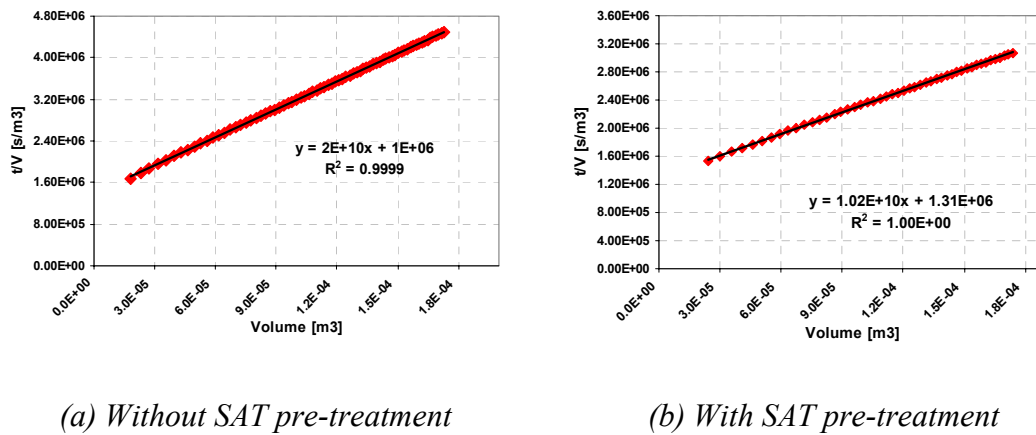


Figure 4.11  $t/V$  versus  $V$  and graphs for SE samples at 3.0 bar with 50 kD UF membrane

In the above figure, the blocking filtration did not appear for the same reasons mentioned above.  $R^2$  is very high it approximately equal one.

A comparison between MFI for SE samples with or without SAT pre-treatment, it is presented in table 4.17.

Table 4.17 Comparison of MFI obtained from the plot of  $t/V \sim V$  for SE samples at 3.0 bar and 50 kD UF membrane

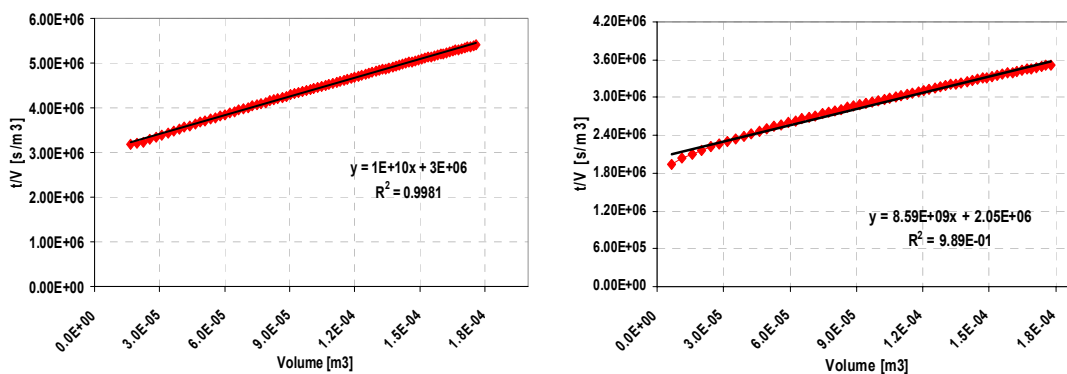
|      | SE only                    |       |                                    | SE+SAT                     |      |                                    |
|------|----------------------------|-------|------------------------------------|----------------------------|------|------------------------------------|
|      | t/V vs. V                  |       |                                    | t/V vs. V                  |      |                                    |
|      | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) | MFI<br>(s/L <sup>2</sup> ) | R2   | Y-intercept<br>(s/L <sup>2</sup> ) |
| Run1 | 1.26E+05                   | 0.999 | 2.0E10                             | 7.09E+04                   | 1.00 | 1.02E10                            |

Table 4.17 shows MFI are 1.26E+05 s/L<sup>2</sup> and 7.09E+04 s/L<sup>2</sup> for SE samples without and with SAT pre-treatment respectively. The difference MFI is around 44%. It shows clearly the SAT has effect on the performance of membrane especially in reducing the fouling.

#### 4.4.4 Analysis of MFI for 10 kD UF Membrane

Similarly as in the case of previous types of membranes, the MFI for 10 kD UF membrane type are presented below.

##### (i) MFI for SE+DCW with or without SAT pre-treatment



(a) Without SAT pre-treatment

(b) With SAT pre-treatment

Figure 4. 12  $t/V$  versus  $V$  graphs for SE+DCW samples at 3.0 bars with 10 kD UF membrane



Figure 4.13 shows the  $t/V$  versus  $V$  for SE+DCW samples with or without SAT pre-treatment. The blocking filtration is slightly appearing, but can not accept as well, because there were 3 points which give us the curve as blocking filtration curve. For that those points can not be accepted as the blocking filtration curve.

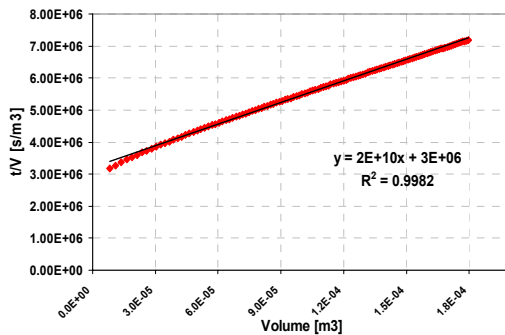
Table 4.18 shows comparison of MFI of SE+DCW samples with or without SAT pre-treatment.

Table 4.18 Comparison of MFI obtained from the plot of  $t/V \sim V$  for SE+DCW samples at 3.0 bar and 10 kD UF membrane

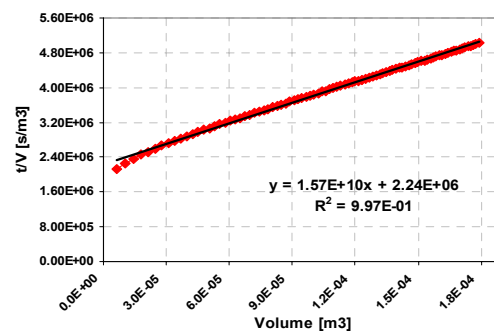
|      | SE+DCW only                |       |                                    | SE+DCW+SAT                 |       |                                    |
|------|----------------------------|-------|------------------------------------|----------------------------|-------|------------------------------------|
|      | $t/V$ vs. $V$              |       |                                    | $t/V$ vs. $V$              |       |                                    |
|      | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) |
| Run1 | 1.09E+05                   | 0.998 | 1.00E10                            | 5.84E+04                   | 0.989 | 8.59E9                             |

Table 4.18 shows MFI are 1.09E+05 s/L<sup>2</sup> and 5.84E+04 s/L<sup>2</sup> for samples without or with SAT pre-treatment respectively, where difference MFI is around 40 %. It shows clearly the SAT has effects on the performance of membranes.

## (ii) MFI for influent and effluent of SE



(a) Without SAT pre-treatment



(b) With SAT pre-treatment

Figure 4. 13  $t/V$  versus  $V$  and graphs for SE samples respectively at 3.0 bar with 10 kD UF membrane

Figure 4.14 show the same accuracy results for R<sup>2</sup> and the plot of  $t/V$  versus  $V$  for SE samples. It shows no significant difference for blocking filtration appearance.

Table 4.19 shows comparison of MFI of SE samples with or without SAT pre-treatment.

*Table 4.19 Comparison of MFI obtained from the plot of  $t/V \sim V$  for SE samples at 3.0 bar and 10 kD UF membrane*

|      | SE only                    |       |                                    | SE+SAT                     |       |  |
|------|----------------------------|-------|------------------------------------|----------------------------|-------|--|
|      | t/V vs. V                  |       |                                    | t/V vs. V                  |       |  |
|      | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-intercept<br>(s/L <sup>2</sup> ) | MFI<br>(s/L <sup>2</sup> ) | R2    | Y-<br>intercept<br>(s/L <sup>2</sup> ) |
| Run1 | 1.58E+05                   | 0.998 | 2.0E10                             | 1.12E+05                   | 0.997 | 1.57E10                                |

Table 4.19 shows MFI are 1.58E+05 s/L<sup>2</sup> and 1.12E+05 s/L<sup>2</sup> for SE samples without or with SAT pre-treatment respectively, where the difference MFI is around 30 %. It shows clearly the SAT has effects on the performance of membranes. But the decrease in MFI is not effected with the type of membrane, it is mainly depending on the SAT pre-treatment and the water quality used.

#### 4.4.5 Summary of MFI Analysis for Different Membranes

Table 4.20 shows the analysis summary for MFI for different types of membranes with or without SAT pre-treatment for different type of water.

*Table 4.20 Summary for MFI with or without SAT per-treatment for different types of membranes*

|            |                   | Membranes types |          |          |          |
|------------|-------------------|-----------------|----------|----------|----------|
| Water Type |                   | 0.1 $\mu$ m     | 100 kD   | 50 kD    | 10 kD    |
| SE+DCW     | With out SAT      | 1090            | 1.45E+04 | 9.50E+04 | 1.09E+05 |
|            | With SAT          | 572             | 4.11E+03 | 2.54E+04 | 5.84E+04 |
|            | Difference in MFI | 47.5%           | 71.7%    | 73.3%    | 46.4%    |
| SE         | With out SAT      | 1030            | 4.61E+04 | 1.26E+05 | 1.58E+05 |
|            | With SAT          | 441             | 2.15E+04 | 7.09E+04 | 1.12E+05 |
|            | Difference in MFI | 57.2%           | 53.4%    | 43.7%    | 29.1%    |

Table 4.20 shows clearly the differences of MFI between the different type of water with or without SAT. The difference in percentage depends on the quality of water applied to the membrane. But the comparison between the membranes shows clearly very big difference between them. The MFI is increasing when the MWCO is

decreasing. In general this is 47 to 73 % reduction of MFI for SE+DCW and 29 to 57 % MFI reduction for SE.

However, it is to be noted that MFI is not generally used as a parameter for analysing fouling of ultrafiltration membranes in practice, as they are backwashed. Even then MFI-UF could give good information about filterability of the water or the fouling potential. Therefore, based on this study it can be concluded that higher the MWCO, higher will be the removal of material with high fouling potential and SAT- pre-treatment improves the filterability and decreases the fouling potential of water for MF/UF membranes.

## **4.5 Analysis of Removal of Different Organic Matter Fractions by Fluorescence EEM**

The EEM plots and maximum peaks corresponding to different OM fractions were identified in the samples from MF/UF with or without SAT pre-treatment. EEM spectra, representing a 3-dimensional plot of fluorescence intensity versus excitation and emission wavelengths, was used to reveal removals of protein-like organic matter (corresponding to an EEM peak at lower excitation/emission wavelengths) and humic-like organic matter (corresponding to an EEM peak at higher excitation/emission wavelengths).

The interpretations of the EEM data obtained in this study were based on the protocol developed by previous researchers who identified the peaks in position Ex=330-350/250-260 and Em=420-480/380-480 to be signatures of fulvic-like and humic-like material respectively and peaks at Ex=270-280 and Em=300-320/320-350 as tyrosine/tryptophan protein-like material (Leenheer and Croue, 2003).

### **4.5.1 Fluorescence EEM for 0.1µm MF Membrane samples**

Characterisation of organic matter removal for MF/UF samples with or without SAT pre-treatment was one of the main objectives. Analysis of removal of different organic matter fractions was achieved by using fluorescence EEM, distinguishing humic-like organic matter from protein-like organic matter. Fluorescence index (FI is the ratio of the fluorescence intensity at Em=450 nm and Em=500 nm at Ex=370 nm), which distinguishes between autochthonous organic matter (microbially derived, with higher FI 1.4-1.7) and allochthonous organic matter (from terrestrial plant origin, with low FI 1.3-1.4).

#### **(i) Fluorescence EEM for SE+DCW with or without SAT pre-treatment**

Figures 4.14 & 4.15 show Fluorescence EEM for SE+DCW samples with or without SAT for 0.1µm MF membrane.

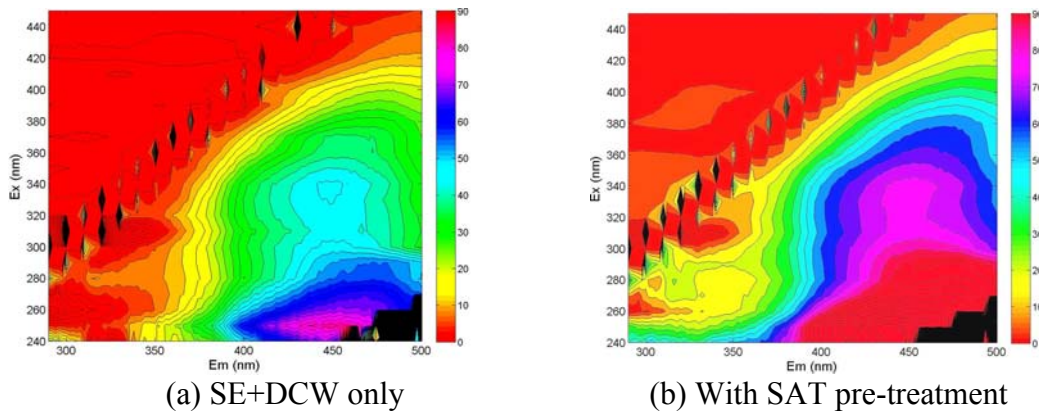


Figure 4.14 Fluorescence EEM references of (a) SE+DCW without SAT (b) SE+DCW with SAT

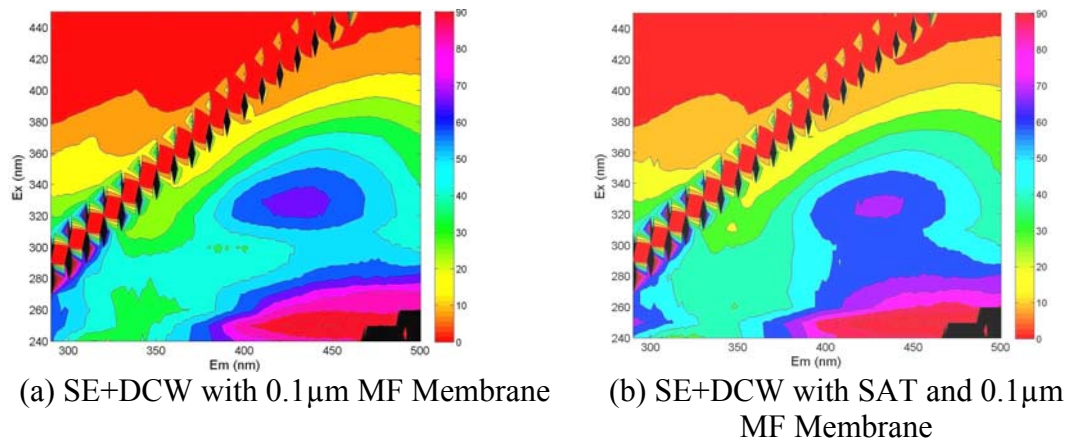


Figure 4.15 Fluorescence EEM references of (a) SE+DCW with 0.1µm Membrane (b) SE+DCW with SAT and 0.1µm Membrane

Figures 4.14 & 4.15 show Fluorescence EEM was carried out for each of the samples on the different sampling and the EEM plots and maximum peaks were identified. Table 4.21 summarises the intensities of FEEM peaks for different organic matter fractions for SE+DCW samples.

Table 4.21 The intensities of different fractions for SE+DCW samples with or without SAT and 0.1µm MF membrane

| Type          | Fluorescence intensities |             |            |      |
|---------------|--------------------------|-------------|------------|------|
|               | Protein                  | Fulvic-like | Humic-like | FI   |
| SE+DCW        | 9.7                      | 47.7        | 84.7       | 1.36 |
| SE+DCW+SAT    | 1.6                      | 45.3        | 82.2       | 1.30 |
| SE+DCW +MF    | 8.9                      | 46.2        | 82.6       | 1.33 |
| SE+DCW+SAT+MF | 1.0                      | 43.9        | 80.3       | 1.28 |

Based on the above results, the following were observed:

- The protein-like peaks were decreasing during SAT from 9.7 to 1.6; overall the removal efficiency was 84%. With 0.1 $\mu$ m membrane the decrease was very small, it was around 7.6%. Totally with SAT and 0.1 $\mu$ m Membrane the removal efficiency was 90%.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 47.7 to 45.3. With 0.1 $\mu$ m membrane it decreased from 47.7 to 46.2, Overall the removal efficiency was 8.0 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 5.0 %.
- A decrease in fluorescence intensity (FI) from 1.36 to 1.28 was obtained; it shows to allochthonous organic matter, that means water from terrestrial plant origin.

## (ii) Fluorescence EEM for SE with or without SAT pre-treatment

Figures 4.16 & 4.17 show Fluorescence EEM for SE samples with or without SAT for 0.1 $\mu$ m membrane.

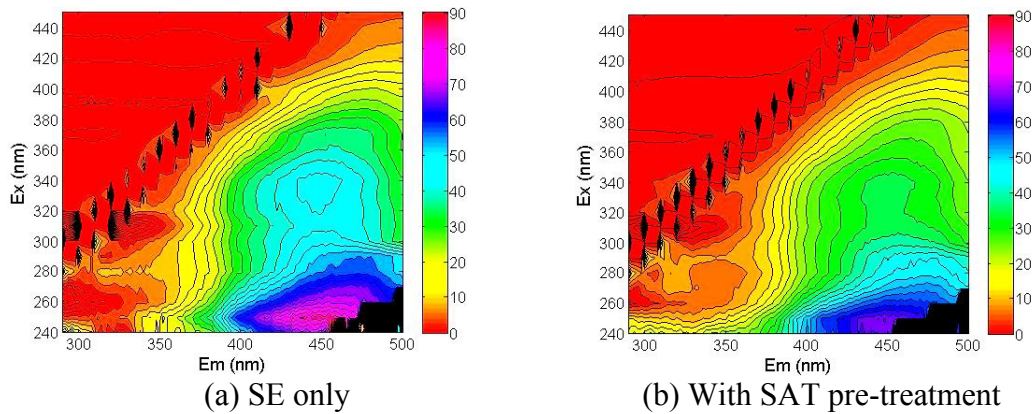


Figure 4.16 Fluorescence EEM references of (a) SE without SAT (b) SE with SAT

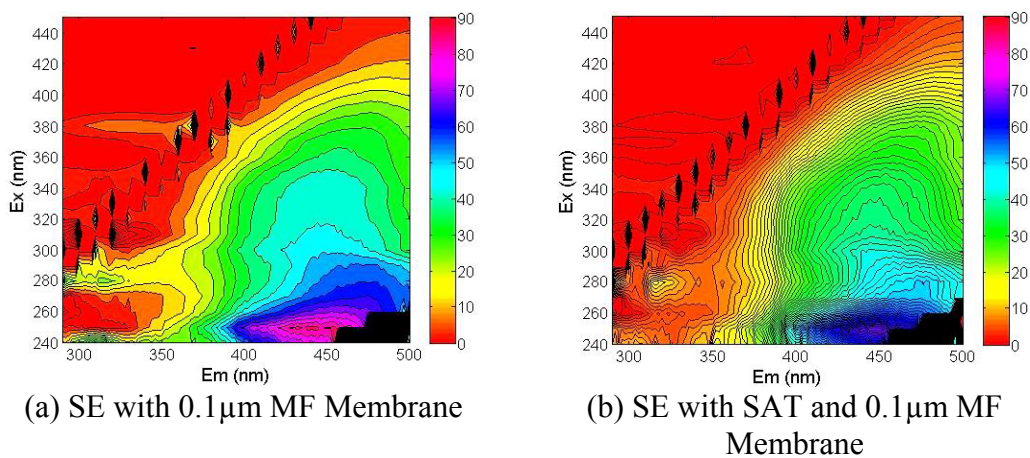


Figure 4.17 Fluorescence EEM references of (a) SE with 0.1 $\mu$ m Membrane (b) SE with SAT and 0.1 $\mu$ m MF membrane

Table 4.22 shows peaks intensities for protein, fulvic and humic-like for SE samples with SAT and 0.1 $\mu$ m MF membrane.

*Table 4.22 The intensities for SE samples with or without SAT pre-treatment and 0.1 $\mu$ m MF membrane*

| Type      | Fluorescence intensities |             |            |      |
|-----------|--------------------------|-------------|------------|------|
|           | Protein(1)               | Fulvic-like | Humic-like | FI   |
| SE        | 17.8                     | 61.5        | 80.1       | 1.40 |
| SE+SAT    | 1.7                      | 58.1        | 77.7       | 1.32 |
| SE+MF     | 15.8                     | 57.3        | 76.2       | 1.36 |
| SE+SAT+MF | ND                       | 54.3        | 73.7       | 1.30 |

Table 4.22 shows the intensities of SE samples for both treatments, the explanation about these results are summarized below:

- The protein-like peaks were decreasing during SAT from 17.8 to 1.7; the removal efficiency was 90%. With 0.1 $\mu$ m membrane the decrease was very small, it was around 10%. With SAT and 0.1 $\mu$ m Membrane, the protein was not detected in the EEM measurements.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 61.5 to 58.1, and with using 0.1 $\mu$ m membrane decreased from 61.5 to 57.3. Overall the removal efficiency was 11.7 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 8.0 %.
- A decrease in fluorescence intensity (FI) from 1.40 to 1.30 was obtained; it shows to allochthonous organic matter that means water is from terrestrial plant origin. It also reflects that there is significant degree of wastewater treatment.

#### 4.5.2 Fluorescence EEM for 100 kD UF Membrane

In the following type of membranes, the removal of protein, fulvic-like and humic-like for SE+DCW and SE samples with SAT were same for all, the difference was with the UF membranes. For that the results and plot for SAT pre-treatment are included in Annex 6.

##### (i) Fluorescence EEM for SE+DCW with or without SAT pre-treatment

Figure 4.16 shows Fluorescence EEM for SE samples without SAT for 100 kD UF membrane.



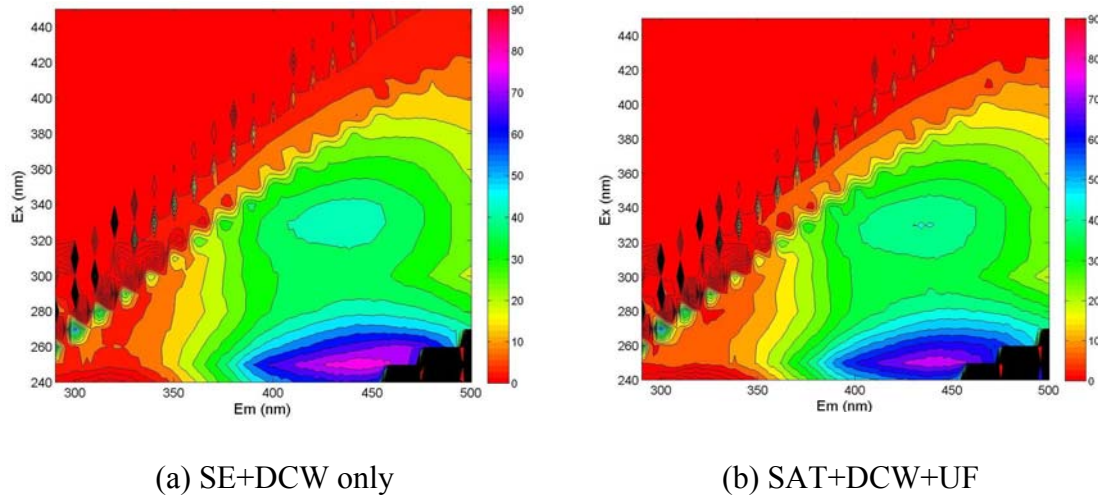


Figure 4.18 Fluorescence EEM references of (a) SE+DCW only (b) SE+DCW with UF

Table 4.23 shows peaks intensities in the figure 4.18 for protein, fulvic and humic-like for SE+DCW samples with SAT and 100 kD UF membrane.

Table 4.23 The intensities for SE+DCW samples with or without SAT and 100 kD UF membrane

| Type          | Fluorescence intensities |             |            |      |
|---------------|--------------------------|-------------|------------|------|
|               | Protein(1)               | Fulvic-like | Humic-like | FI   |
| SE+DCW        | 8.3                      | 45.2        | 77.8       | 1.37 |
| SE+DCW+SAT    | 0.8                      | 42.1        | 74.6       | 1.33 |
| SE+DCW +UF    | 7.0                      | 41.2        | 70.6       | 1.35 |
| SE+DCW+SAT+UF | ND                       | 37.6        | 66.5       | 1.30 |

Based on figure 4.18 and table 4.23, the following observations were made

- The protein-like peaks were not detected in the EEM measurements with SAT and UF.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 45.2 to 42.1, and with 100 kD membrane decreased from 45.2 to 41.2, Overall the removal efficiency was 17 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 14.5 %.
- A decrease in fluorescence intensity (FI) from 1.37 to 1.30 was obtained. it shows to allochthonous organic matter.

#### (ii) Fluorescence EEM for SE with or without SAT pre-treatment

Figure 4.19 shows the Fluorescence EEM for SE samples without SAT and with UF only. The plot for the Fluorescence EEM for SE with SAT and SE with both treatments are included in Annex 6.

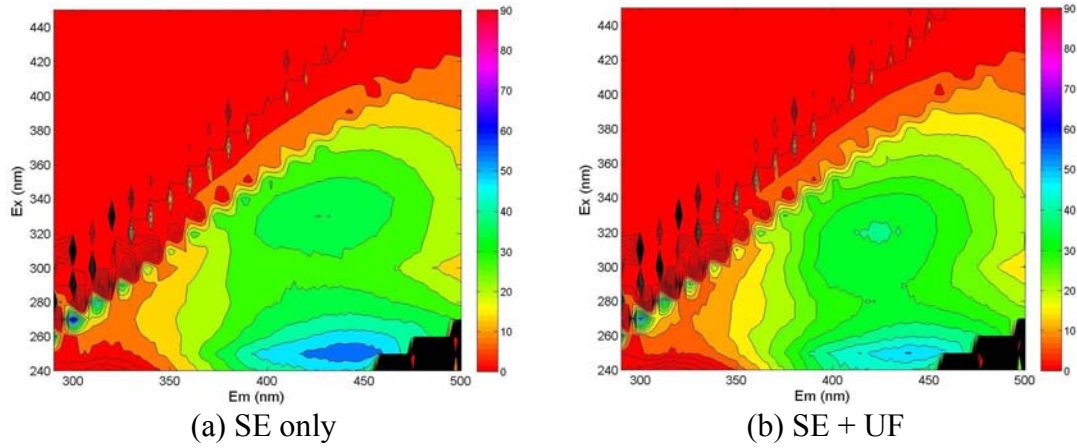


Figure 4.19 Fluorescence EEM references of (a) SE without SAT (b) SE without SAT and with 100 kD UF membrane

Table 4.24 summarises the peaks intensities for protein, fulvic and humic-like for SE samples with SAT and 100 kD UF membrane.

Table 4.24 The intensities for SE samples with or without SAT pre-treatment and 100 kD UF membrane

| Type      | Fluorescence intensities |             |            |      |
|-----------|--------------------------|-------------|------------|------|
|           | Protein(1)               | Fulvic-like | Humic-like | FI   |
| SE        | 14.7                     | 40.5        | 59.3       | 1.4  |
| SE+SAT    | 1.4                      | 38.1        | 57.4       | 1.35 |
| SE+UF     | 12.2                     | 36.7        | 53.8       | 1.37 |
| SE+SAT+UF | -                        | 33.5        | 50.8       | 1.34 |

From Figure 4.19 and table 4.24, the following were observed

- The protein-like peaks were not detected in the EEM measurements with SAT and UF.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 40.5 to 38.1, and with using 100 kD membrane decreasing from 40.5 to 36.7, Overall the removal efficiency was 17.2 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 14.4 %.
- A decrease in fluorescence intensity (FI) from 1.4 to 1.34 was obtained. it shows to allochthonous organic matter.



### 4.5.3 Fluorescence EEM for 50 kD UF Membrane

For this type of membrane, the removal of protein, fulvic-like and humic-like for SE+DCW and SE samples with SAT were as same as with 0.1 $\mu$  and 100 kD membrane. The difference was with the UF membranes. All plots for Fluorescence EEM are included in Annex 6.

#### (i) Fluorescence EEM for SE+DCW with or without SAT pre-treatment

Table 4.25 shows peaks intensities for protein, fulvic and humic-like for SE+DCW samples with SAT and 50 kD membrane.

*Table 4.25 The intensities for SE+DCW samples with or without SAT pre-treatment and 50 kD UF membrane*

| Type          | Fluorescence intensities |             |            |      |
|---------------|--------------------------|-------------|------------|------|
|               | Protein(1)               | Fulvic-like | Humic-like | FI   |
| SE+DCW        | 13.8                     | 80.8        | 92.0       | 1.4  |
| SE+DCW+SAT    | 0.9                      | 76.3        | 88.5       | 1.33 |
| SE+DCW +UF    | 11.1                     | 69.8        | 79.9       | 1.36 |
| SE+DCW+SAT+UF | ND                       | 64.5        | 75.7       | 1.32 |

Table 4.25 summarises the analysis of Fluorescence EEM for SE+DCW samples with or without SAT and 50 kD membrane. The following were observed:

- The protein-like peaks were not detected in the EEM measurements with SAT and UF as the previous membranes.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 80.8 to 76.3, and with 50 kD membrane, it decreased from 80.8 to 69.8, Overall the removal efficiency was 20.2 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 17.7 %.
- A decrease in fluorescence intensity (FI) from 1.4 to 1.32 was obtained. It shows to allochthonous organic matter.

#### (ii) Fluorescence EEM for SE with or without SAT pre-treatment

Table 4.26 shows peaks intensities for protein, fulvic and humic-like for SE samples with SAT and 50 kD UF membrane.

Table 4.26 The intensities for SE samples with or without SAT and 50 kD UF membrane

| Type      | Fluorescence intensities |             |            |      |
|-----------|--------------------------|-------------|------------|------|
|           | Protein(1)               | Fulvic-like | Humic-like | FI   |
| SE        | 12.13                    | 65.3        | 90.9       | 1.40 |
| SE+SAT    | 1.1                      | 61.5        | 86.5       | 1.34 |
| SE+UF     | 9.68                     | 56.0        | 79.4       | 1.36 |
| SE+SAT+UF | ND                       | 51.7        | 74.2       | 1.32 |

Based on table 4.26, the following can be observed:

- The protein-like peaks were not detected in the EEM measurements with SAT and UF as the previous membranes, but with UF only the removal efficiency was 20.2%.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 65.3 to 61.5, and with using 50 kD membrane decreasing from 65.3 to 61.5, Overall the removal efficiency was 21 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 18.4 %.
- A decrease in fluorescence intensity (FI) from 1.4 to 1.32 was obtained.

#### 4.5.4 Fluorescence EEM for 10 kD UF Membrane

##### (i) Fluorescence EEM for SE+DCW with or without SAT pre-treatment

Table 4.27 shows peaks intensities for protein, fulvic and humic-like for SE+DCW samples with SAT and 10 kD UF membrane. All plots for Fluorescence EEM for this type of membrane is included in Annex 6.

Table 4.27 The intensities for SE+DCW samples with or without SAT pre-treatment and 10 kD UF membrane

| Type          | Fluorescence intensities |             |            |      |
|---------------|--------------------------|-------------|------------|------|
|               | Protein(1)               | Fulvic-like | Humic-like | FI   |
| SE+DCW        | 16.95                    | 68.0        | 85.56      | 1.38 |
| SE+DCW+SAT    | 1.54                     | 63.7        | 81.86      | 1.32 |
| SE+DCW +UF    | 12.24                    | 54.1        | 69.92      | 1.33 |
| SE+DCW+SAT+UF | ND                       | 48.7        | 65.26      | 1.30 |

Based on table 4.27 and EEM plots, the following were observed.

- The protein-like peaks were not detected in the EEM measurements with SAT and UF as the previous membranes, but with UF only the removal efficiency was 28.0%.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 68.0 to 63.7, and with 10 kD membrane decreased from 68.0 to 54.1, Overall the removal efficiency was 28.3 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 24.0 %.
- A decrease in fluorescence intensity (FI) from 1.38 to 1.30 was obtained. It shows to allochthonous organic matter.

## (ii) Fluorescence EEM for SE with or without SAT pre-treatment

Table 2.28 shows the peaks intensities for protein, fulvic and humic-like for SE samples with SAT and 10 kD UF membrane.

*Table 4.28 The intensities for SE samples with or without SAT pre-treatment and 10 kD UF membrane*

| Type      | Fluorescence intensities |             |            |      |
|-----------|--------------------------|-------------|------------|------|
|           | Protein(1)               | Fulvic-like | Humic-like | FI   |
| SE        | 18.13                    | 60.9        | 80.87      | 1.4  |
| SE+SAT    | 1.92                     | 57.1        | 77.12      | 1.34 |
| SE+UF     | 12.7                     | 47.1        | 64.09      | 1.35 |
| SE+SAT+UF | ND                       | 43.2        | 60.43      | 1.33 |

Table 4.28 shows the analysis of Fluorescence EEM for SE samples with or without SAT and 10 kD UF membrane.

- The protein-like peaks were with UF only the removal efficiency was 28.0%, but they were not detected in the EEM measurements with SAT and UF.
- The fluorescence intensity of the fulvic-like peak at Ex-250 decreased during SAT from 60.9 to 57.1, and with 10 kD membrane decreased from 60.9 to 47.1, Overall the removal efficiency was 29.0 %.
- A similar trend was observed with the humic-like peak at Ex-330, where the overall removal efficiency was 25.3 %.
- A decrease in fluorescence intensity (FI) from 1.40 to 1.33 was obtained.

As a comparison for different types of membranes, table 4.29 summarise the removal of protein, fulvic-like, and humic-like for different types of membranes for different types of water, without SAT pre-treatment.

#### 4.5.5 Summary of FEEM Analysis for Different Membranes

Table 4.29 Comparison of organic fractions removal for different types of membranes without SAT pre-treatment by Fluorescence EEM

|        |                       | Membranes types |        |       |       |
|--------|-----------------------|-----------------|--------|-------|-------|
|        | Water Type            | 0.1 $\mu$ m     | 100 kD | 50 kD | 10 kD |
| SE+DCW | % Removal Protein     | 8.3             | 16.0   | 19.4  | 28.0  |
|        | % Removal Fulvic-like | 3.1             | 8.8    | 13.6  | 20.5  |
|        | % Removal Humic-like  | 2.5             | 9.2    | 13.1  | 18.0  |
| SE     | % Removal Protein     | 10.9            | 16.4   | 20.2  | 30.0  |
|        | % Removal Fulvic-like | 6.7             | 9.2    | 14.2  | 22.6  |
|        | % Removal Humic-like  | 4.8             | 9.0    | 12.7  | 20.75 |

Table 4.29 shows the percentage removal of organic matter fractions by different types of membranes used in this study; it clearly shows the increasing of removal for organic matter fraction with decreasing of MWCO for membranes. SAT helps to remove the protein from the secondary effluent. The removal of protein by SAT is up to 94%, and after using the UF membranes, the proteins is removed completely. Otherwise for humic-like and fulvic-like, SAT is poor to remove these type of organic matter fraction, but the UF can remove up to 20 % of these fractions. Comparison between table 4.7 and 4.29, it clearly show the percentage removal of DOC is mainly due to removal of non-humic specially protein removal.

Table 4.30 shows the removal of organic fractions for different types of membranes with SAT pre-treatment

*Table 4.30 Comparison of organic fractions removal for different types of membranes with SAT pre-treatment by Fluorescence EEM*

|        |                       | With SAT pre-treatment |        |       |       |
|--------|-----------------------|------------------------|--------|-------|-------|
|        |                       | Membranes types        |        |       |       |
|        | Water Type            | 0.1 $\mu$ m            | 100 kD | 50 kD | 10 kD |
| SE+DCW | % Removal Protein     | 93                     | 100    | 100   | 100   |
|        | % Removal Fulvic-like | 8                      | 17     | 20.2  | 28.3  |
|        | % Removal Humic-like  | 5                      | 14.5   | 17.7  | 24    |
| SE     | % Removal Protein     | 100                    | 100    | 100   | 100   |
|        | % Removal Fulvic-like | 11.7                   | 17.2   | 21    | 29    |
|        | % Removal Humic-like  | 8                      | 14.4   | 18.4  | 25.3  |

Table 4.30 clearly shows that for system with SAT pre-treatment protein removal by different membrane is almost 100%. Furthermore removal of humics and fulvic were also substantially improved with SAT pre-treatment. There for the % protein removal is much higher than the average DOC removal where as humic or fulvic like organic mater fraction removal is relatively low.

In general, it was observed that higher the protein removal, the higher was the reduction of MFI, however there was no direct linear relationship. This is because MFI not only depends on protein removal but also on the types of membranes used and other water quality treatment.

## **5. Conclusions and Recommendations**

### **5.1 Conclusions**

Based on the experimental results, data analysis and literature review, the following conclusions can be drawn from this research:

- Average DOC removal by SAT alone was 15% to 25% for SE and SE+DCW respectively. SAT helps to improve DOC removal, especially non-humic substances that were shown by increased of SUVA after SAT.
- The average DOC removal from wastewater treatment plant effluents ranged from 12 to 22%. SAT pre-treatment of these effluents increased the DOC removal by MF/UF membranes by 30 to 46%.
- SAT pre-treatment improves the performance of MF/UF membranes by reducing the fouling. This was shown by 47 to 73% reduction of MFI for SE+DCW and 29 to 57% reduction of MFI for SE.
- For the given influent, MFI was different between the different types of membranes. MFI reduction was higher for the membranes with smaller MWCO.
- SAT can remove almost 100% of protein and approximately 6% and 5% of fulvic-like and humic-like organic matter respectively.
- SAT pre-treatment followed by UF removed almost 100% of the protein from wastewater plant effluent. However the removal of fulvic like and humic like organic fractions was limited to 8 to 30% and 5 to 25% respectively.
- The maximum removal for protein, fulvic-like and humic-like by 10 kD UF alone without SAT are 30%, 22%, 21% respectively. This implies that use can get higher removal of different organic matter fractions if smaller MWCO membranes are used.
- This study clearly showed that SAT pre-treatment of wastewater treatment plant effluent not only improves the DOC removal by MF/UF membranes but also reduces the fouling potential of these membranes. Furthermore, there is substantial removal of proteins with the computation of SAT and UF.
- Delft Canal Water used in this study was mixed with SE. DCW+SE showed very good removal of organic matter during SAT. This shows that SAT can be used to recharge the aquifers using wastewater impacted surface water sources.
- SAT can be used for indirect potable reuse and for irrigation to reduce water scarcity, especially in rural areas of developing countries like Yemen which has a good suitable soil for this technology.

## **5.2 Recommendations**

The following is recommended for further improvement and application of SAT system:

- SAT technology needs to be improved for more sustainability of reuse of wastewater, to help the countries which have the real problem with water scarcity like Yemen to reduce using ground water for irrigation and use of the water treatment by SAT.
- Further study should be conducted on use of membranes with MWCO smaller than 10 kD to study their effectiveness in removal of different organic matter fractions and reduction of fouling of these membranes with SAT pre-treatment.

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# Annexes



## 7. Annexes

### Annex 1: Components of Amicon Series 8000 Stirred Cell

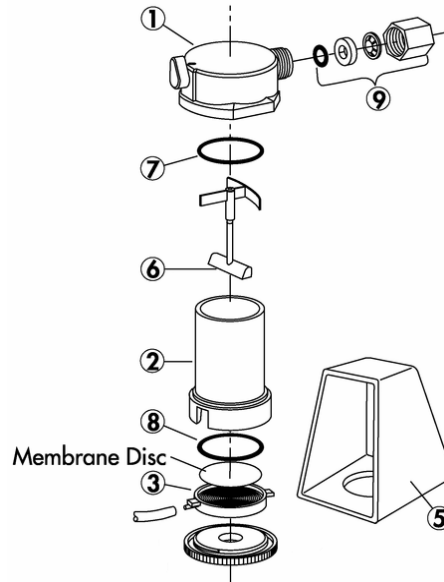


Figure 7.1 Components of Amicon series 8000 stirred cell

Table 7. 1 Specifications for components and materials of Amicon (8000) stirred cells

| Parts                               | Materials                  |
|-------------------------------------|----------------------------|
| (1,9) Cap and tube fitting assembly | Nylon                      |
| (2,3) Cylinder and membrane holder  | Polysulfone                |
| (6) Stirring assembly               | Acetal polysulfone         |
| (7,8) O-rings                       | Silicone rubber            |
| (5) Retaining Stand                 | Anodized aluminum or nylon |

Table 7. 2 Detailed specifications of Amicon stirred cell model 8200

| Parameter               | Unit            | Value |
|-------------------------|-----------------|-------|
| Max. process volume     | ml              | 200   |
| Min. process volume     | ml              | 0.5   |
| Membrane diameter       | Mm              | 63.5  |
| Effective membrane area | cm <sup>2</sup> | 28.7  |
| Hold-up volume          | ml              | 1.2   |
| Height                  | cm              | 12.8  |
| Base                    | cm              | 9*9   |
| Weight                  | kg              | 0.4   |

## Annex 2: A Typical Output of the Software

Table 7.3 A Typical Output of the Software program (Winwedge) at 5 second interval

| Time             | Weight |
|------------------|--------|
| 11/8/07 12:16:12 | 3.650  |
| 11/8/07 12:16:16 | 8.860  |
| 11/8/07 12:16:20 | 14.170 |
| 11/8/07 12:16:24 | 19.150 |
| 11/8/07 12:16:28 | 23.960 |
| 11/8/07 12:16:32 | 28.990 |
| 11/8/07 12:16:36 | 34.130 |
| 11/8/07 12:16:40 | 38.980 |
| 11/8/07 12:16:44 | 43.790 |
| 11/8/07 12:16:48 | 48.580 |
| 11/8/07 12:16:52 | 53.460 |
| 11/8/07 12:16:56 | 58.320 |
| 11/8/07 12:17:00 | 62.920 |
| 11/8/07 12:17:04 | 67.730 |
| 11/8/07 12:17:08 | 72.640 |
| 11/8/07 12:17:12 | 77.280 |
| 11/8/07 12:17:16 | 81.910 |
| 11/8/07 12:17:20 | 86.500 |
| 11/8/07 12:17:24 | 91.210 |
| 11/8/07 12:17:28 | 95.910 |

### Annex 3: Results and Graphs of DOC for Different Membranes

Table 7.4 DOC,  $UV_{254}$ , pH, EC and  $Ca^{+2}$  of SE + DCW samples with and without SAT (anoxic condition) and UF (0.1  $\mu m$  pore size)

| Samples       | Ca+2<br>mg/l | pH    | EC $\mu S/cm$ | TDS<br>mg/l | DOC<br>mg/l | $UV_{254}$ |
|---------------|--------------|-------|---------------|-------------|-------------|------------|
| SE+DCW        | 68           | 8.977 | 958.333       | 690         | 32.7152     | 0.46       |
| SE+DCW+SAT    | 62           | 8.567 | 869           | 625.68      | 23.8059     | 0.42       |
| SE+DCW +UF    | 63.2         | 8.82  | 950.667       | 684.48      | 28.74       | 0.437      |
| SE+DCW+SAT+UF | 59.8         | 8.51  | 861.333       | 620.16      | 19.82       | 0.407      |

Table 7.5 DOC,  $UV_{254}$ , pH, EC and  $Ca^{+2}$  of SE samples with and without SAT (oxic condition) and UF (0.1  $\mu m$  pore size)

| Samples   | Ca+2<br>mg/l | pH   | EC $\mu S/cm$ | TDS<br>mg/l | DOC<br>mg/l | $UV_{254}$ |
|-----------|--------------|------|---------------|-------------|-------------|------------|
| SE        | 58           | 8.39 | 901.32        | 690         | 21.88       | 0.449      |
| SE+SAT    | 52           | 8.37 | 820.74        | 625.68      | 18.07       | 0.412      |
| SE+UF     | 50.1         | 8.34 | 845           | 684.48      | 18.86       | 0.429      |
| SE+SAT+UF | 47           | 8.22 | 768           | 620.16      | 16.1        | 0.399      |

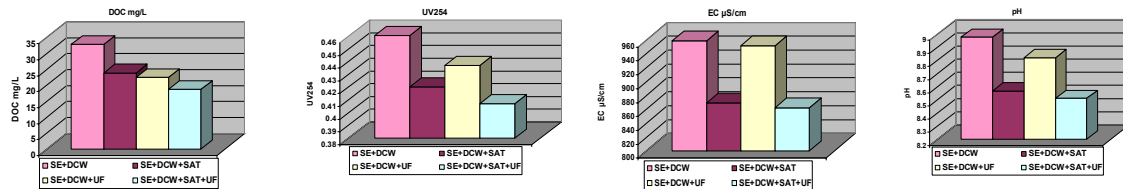


Figure 7.2 DOC,  $UV_{254}$ , pH, EC and  $Ca^{+2}$  of DCW+SE samples with and without SAT (oxic condition) and UF (0.1  $\mu m$  pore size)

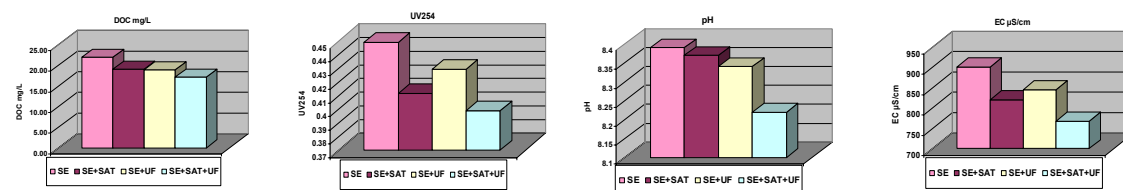


Figure 7.3 DOC,  $UV_{254}$ , pH, EC and  $Ca^{+2}$  of SE samples with and without SAT (oxic condition) and UF (0.1  $\mu m$  pore size)



Table 7.6 DOC,  $UV_{254}$ , pH, EC and  $Ca^{+2}$  of **SE+DCW** samples with and without SAT (anoxic condition) and UF (100kDa MWCO)

| Samples       | Ca+2<br>mg/l | pH    | EC<br>$\mu$ S/cm | TDS<br>mg/l | DOC<br>mg/l | $UV_{254}$ |
|---------------|--------------|-------|------------------|-------------|-------------|------------|
| SE+DCW        | 68           | 8.977 | 958.333          | 690         | 14.3        | 0.4340     |
| SE+DCW+SAT    | 62           | 8.567 | 869              | 625.68      | 10.692      | 0.3790     |
| SE+DCW+UF     | 60.3         | 8.75  | 945.27           | 684.48      | 12.4        | 0.4260     |
| SE+DCW+SAT+UF | 57.4         | 8.51  | 857.15           | 620.16      | 9.32        | 0.3670     |

Table 7.7 DOC,  $UV_{254}$ , pH, EC and  $Ca^{+2}$  of **SE** samples with and without SAT (oxic condition) and UF (100kDa MWCO)

| Samples   | Ca+2<br>mg/l | pH   | EC<br>$\mu$ S/cm | TDS mg/l | DOC<br>mg/l | $UV_{254}$ |
|-----------|--------------|------|------------------|----------|-------------|------------|
| SE        | 58           | 8.39 | 901.32           | 690      | 16.39       | 0.37       |
| SE+SAT    | 52           | 8.37 | 820.74           | 625.68   | 13.88       | 0.36       |
| SE+UF     | 48.5         | 8.25 | 834              | 673.3    | 13.62       | 0.35       |
| SE+SAT+UF | 46.3         | 8.13 | 758              | 613.48   | 11.90       | 0.33       |

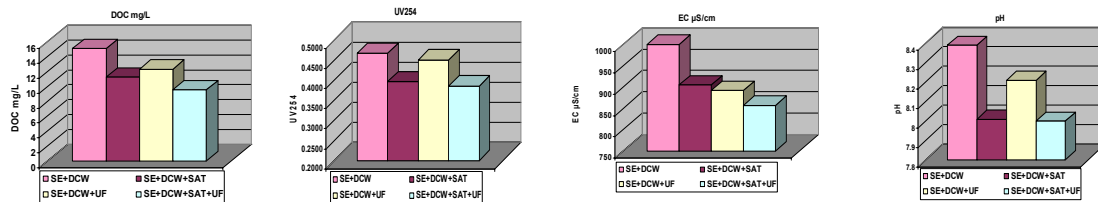


Figure 7.4 DOC,  $UV_{254}$ , pH and EC of **SE + DCW** samples with and without SAT (anoxic condition) and UF (50 kDa MWCO)

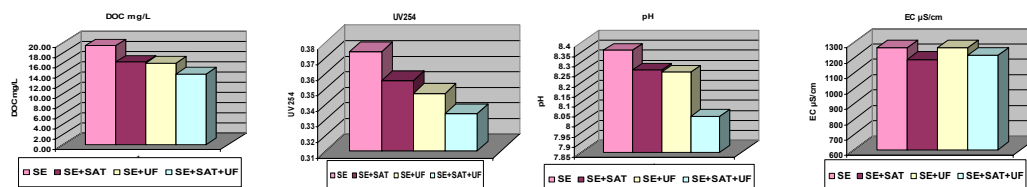


Figure 7.5 DOC,  $UV_{254}$ , pH, and EC of **SE** samples with and without SAT (oxic condition) and UF (50 kDa MWCO)

## Annex 4: Graphs and Tables of $R_m$ for Different Membranes

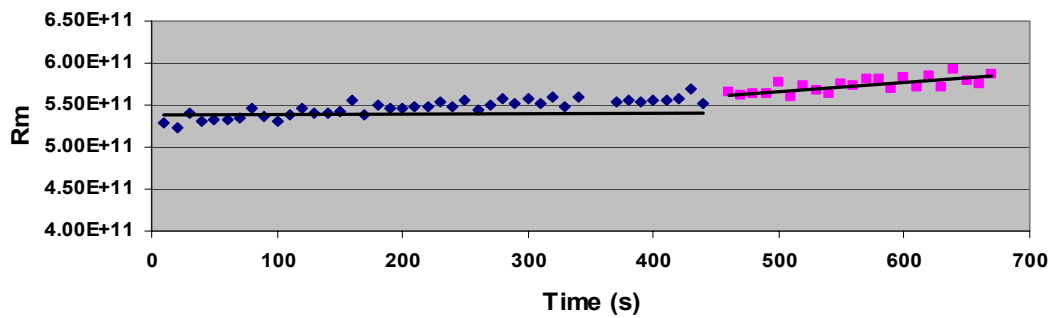


Figure 7.6 Decline in filter resistance for filtration with MilliQ water at 3.0 bar and 50 kD MWCA of membrane

Table 7.8 Membrane resistances measured from filtration with ultra pure water at 3.0 bar and 50 kD MWCA of membrane

|         | $R_m$    |
|---------|----------|
| Run1    | 5.52E+11 |
| Run2    | 5.82E+11 |
| Run3    | 6.16E+11 |
| Run4    | 6.79E+11 |
| Average | 6.07E+11 |

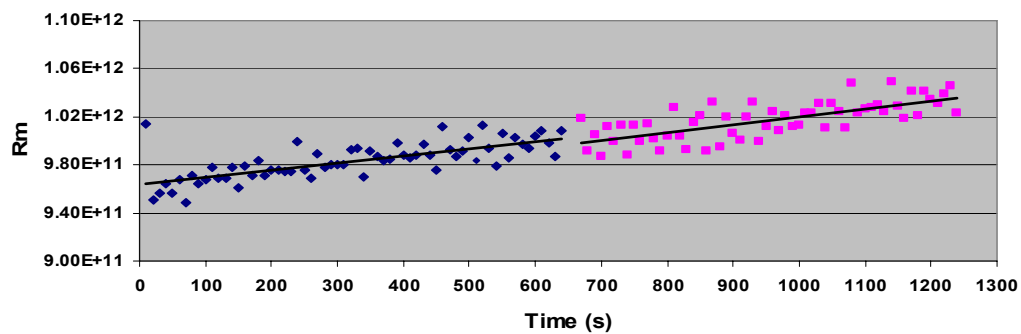


Figure 7.7 Decline in filter resistance for filtration with MilliQ water at 3.0 bar and 10 kD MWCA of membrane

*Table 7.9 Membrane resistances measured from filtration with ultra pure water at 3.0 bar and 10 kD MWCA of membrane*

|                | <b>R<sub>m</sub></b> |
|----------------|----------------------|
| <b>Run1</b>    | 9.96E+11             |
| <b>Run2</b>    | 1.22E+12             |
| <b>Run3</b>    | 1.43E+12             |
| <b>Run4</b>    | 1.10E+12             |
| <b>Average</b> | 1.123E+12            |

## Annex 5: Graphs and Tables of MFI Analysis for Different Membranes

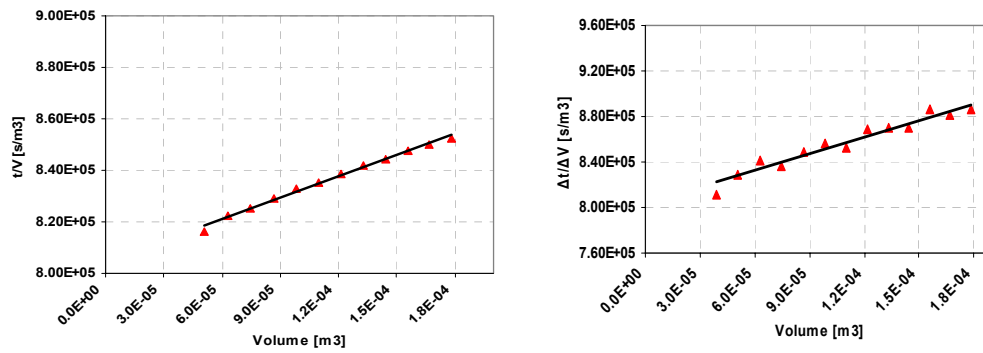


Figure 7. 8 (a)  $t/V$  versus  $V$  and (b)  $\Delta t/\Delta V$  versus  $V$  graphs for SE+DCW effluent samples at 1.0 bar and  $0.1 \mu\text{m}$  of membrane

## Annex 6: Graphs and Tables of EEM Analysis for Different Membranes

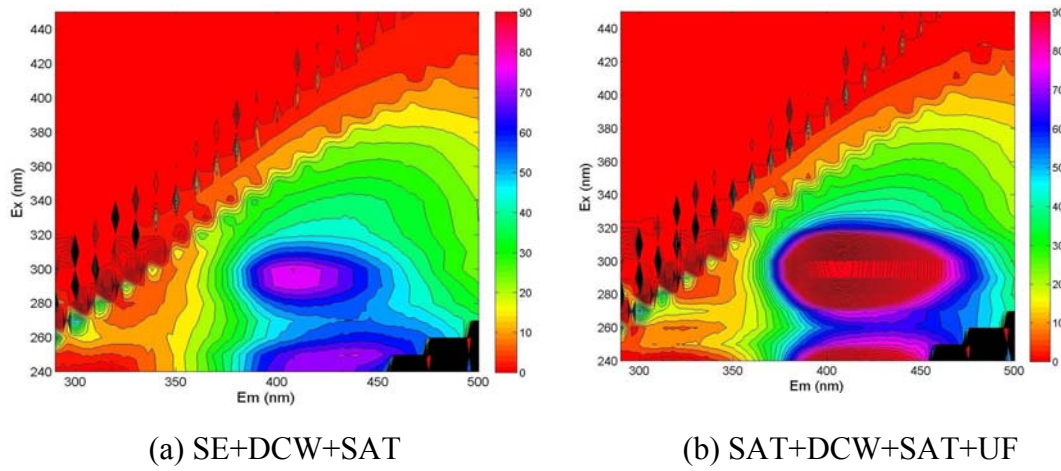


Figure 7.9 Fluorescence EEM references of (a) SE+DCW with SAT pre-treatment (b) SE+DCW with SAT and UF

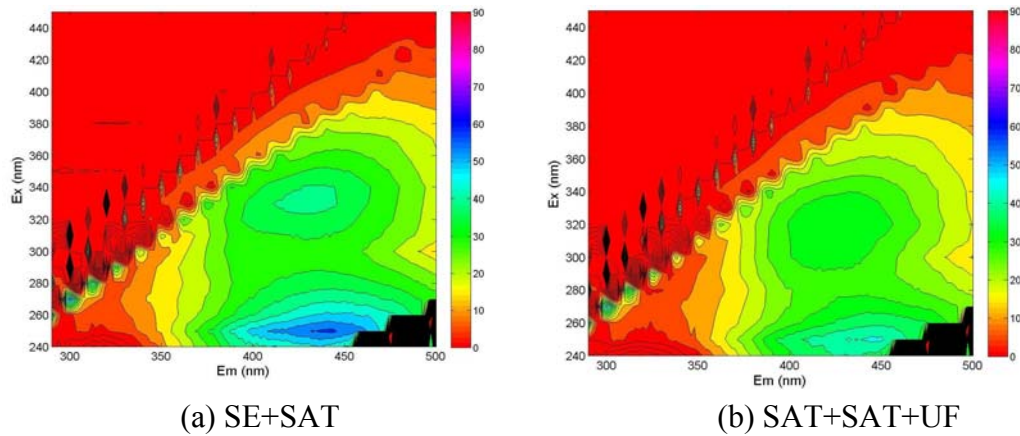


Figure 7.10 Fluorescence EEM references of (a) SE with SAT pre-treatment (b) SE with SAT and UF

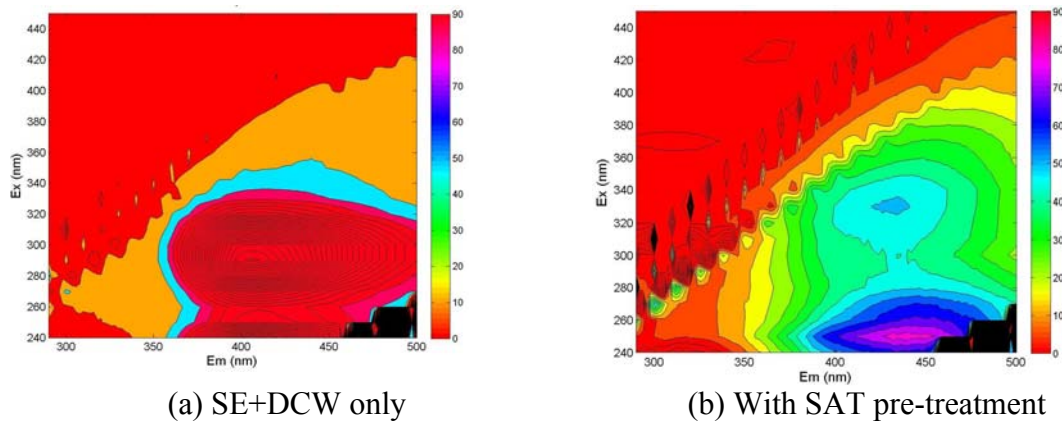


Figure 7.11 Fluorescence EEM references of (a) SE+DCW without SAT (b) SE+DCW with SATF for 50 kD membrane

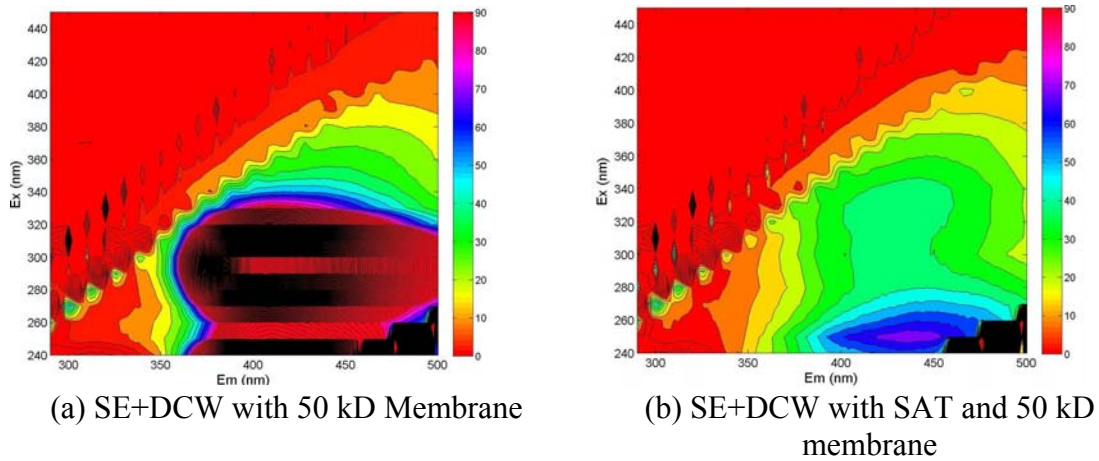


Figure 7.12 Fluorescence EEM references of (a) SE+DCW with 50 kD membrane (b) SE+DCW with SAT and 50 kD membrane

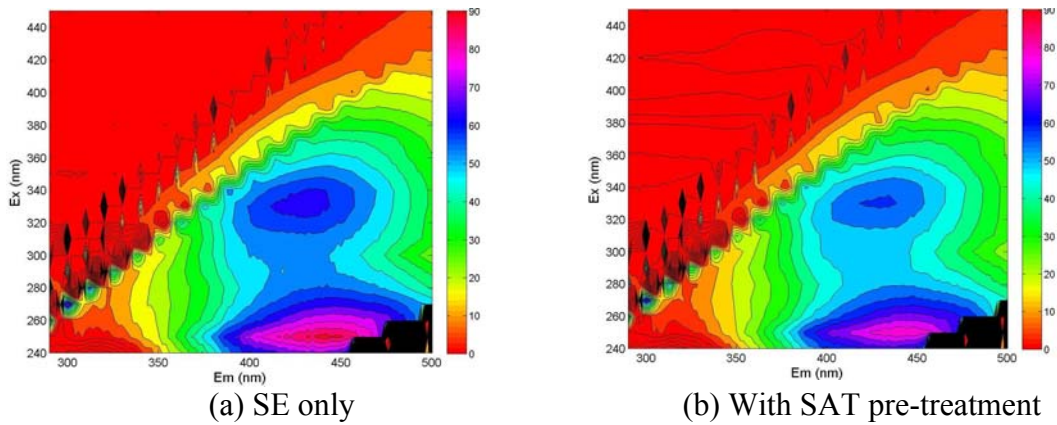


Figure 7.13 Fluorescence EEM references of (a) SE without SAT (b) SE with SATF for 50 kD membrane

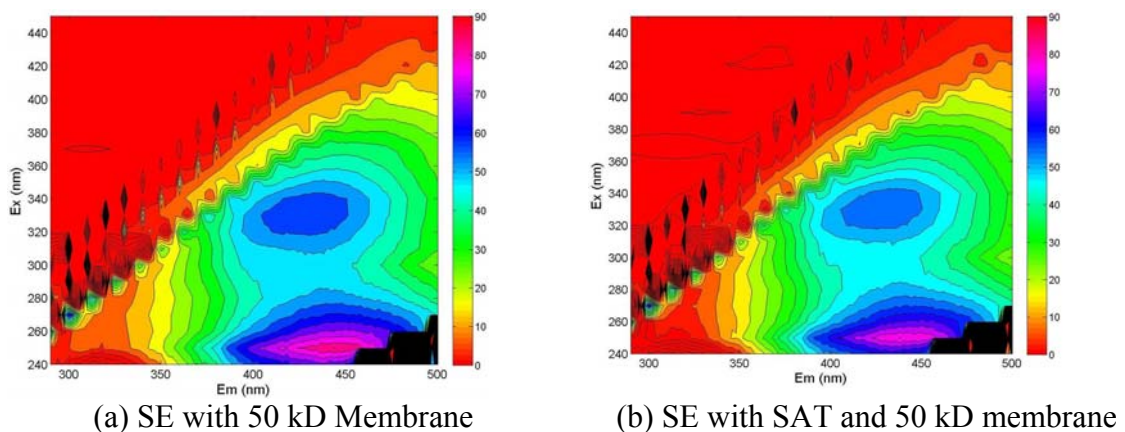


Figure 7.14 Fluorescence EEM references of (a) SE with 50 kD membrane (b) SE with SAT and 50 kD membrane



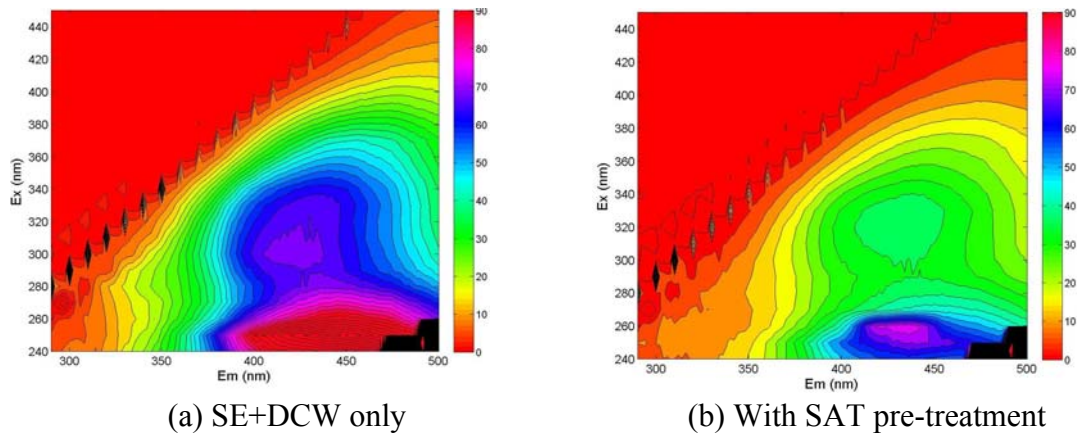


Figure 7.15 Fluorescence EEM references of (a) SE+DCW without SAT (b) SE+DCW with SATF for 10 kD membrane

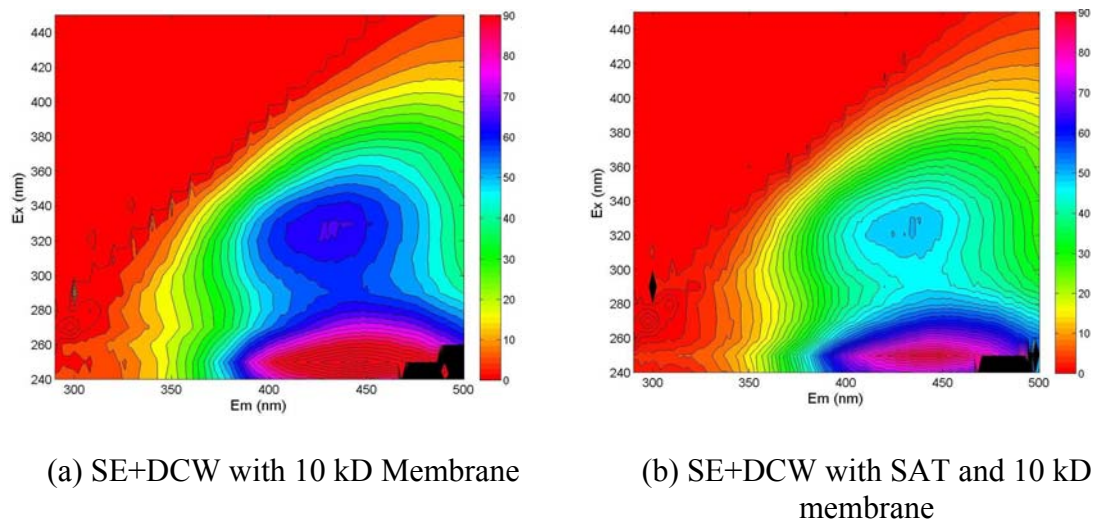


Figure 7.16 Fluorescence EEM references of (a) SE+DCW with 10 kD membrane (b) SE+DCW with SAT and 10 kD membrane

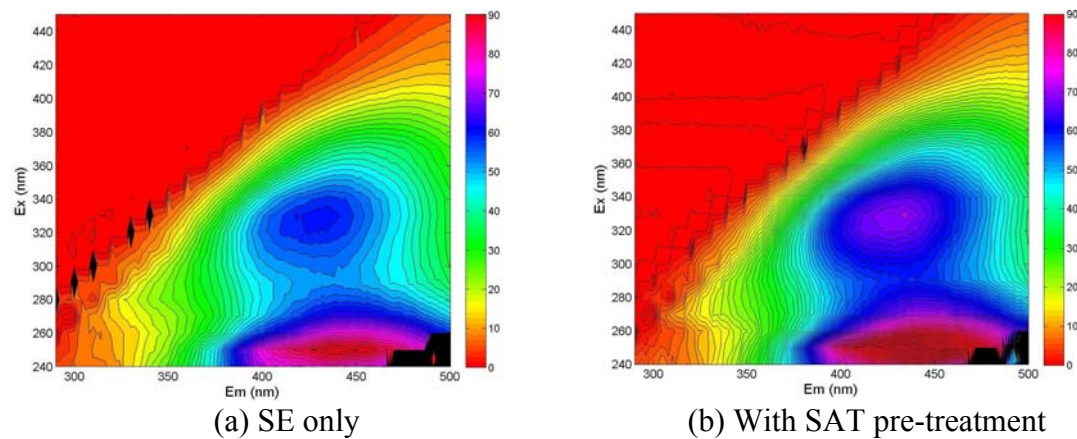
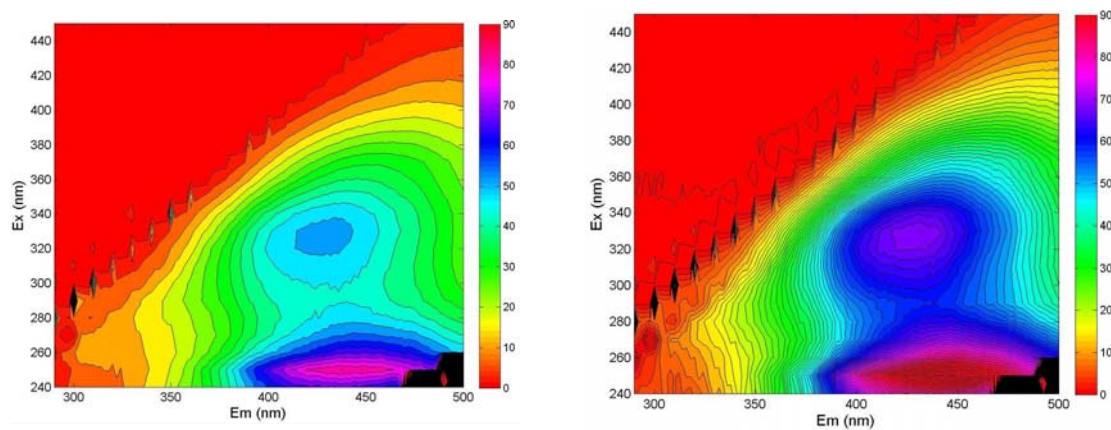


Figure 7.17 Fluorescence EEM references of (a) SE without SAT (b) SE with SATF for 10 kD membrane



(a) SE with 10 kD Membrane

(b) SE with SAT and 10 kD membrane

Figure 7.18 Fluorescence EEM references of (a) SE with 10 kD membrane (b) SE with SAT and 10 kD membrane



## Annex 7: Millipore's Specifications of Different Type of Membrane Filters

Table 7.10 Millipore's specifications of Durapore Membrane Filters (0.1  $\mu\text{m}$ )

| Parameters                                | Value               |
|---|---------------------|
| Air Flow Rate, L/min x cm <sup>2</sup>    | 0.15                |
| Thickness, $\mu\text{m}$                  | 125                 |
| Bubble Point at 23 °C                     | $\geq 4.8$ bars     |
| Gravimetric Extractables, %               | 0.5                 |
| Porosity %                                | 70                  |
| Refractive Index                          | 1.42                |
| Filter Diameter, mm                       | 90                  |
| Filter Surface                            | Plain               |
| Max Operating Temperature, °C             | 85                  |
| Filter Color                              | white               |
| Filter Material                           | Hydrophilic<br>PVDF |
| Filter Type                               | Screen filter       |
| Filter Pore Size, $\mu\text{m}$           | 0.1                 |
| Wettability                               | Hydrophilic         |
| Water Flow Rate, mL/min x cm <sup>2</sup> | 2.5                 |

Table 7.11 Millipore's specifications of Biomax Membrane Filters (100, 50, and 10 kD)

| Parameters                       | Value                           |                                 |                                 |
|----------------------------------|---------------------------------|---------------------------------|---------------------------------|
|                                  | 10 kD                           | 50 kD                           | 100 kD                          |
| Air Flow Rate, ml/min at 30 psig | < 2.5                           | < 2.5                           | < 2.5                           |
| Thickness, $\mu\text{m}$         | 160-320                         | 160-320                         | 160-320                         |
| Bubble Point at 23 °C            | NA                              | NA                              | NA                              |
| Filter Diameter, mm              | 63.5                            | 63.5                            | 63.5                            |
| Filter Surface                   | Plain                           | Plain                           | Plain                           |
| Max Operating Temperature, °C    | 50                              | 50                              | 50                              |
| Filter Color                     | white                           | white                           | white                           |
| Filter Material                  | Hydrophilic<br>Polyethersulfone | Hydrophilic<br>Polyethersulfone | Hydrophilic<br>Polyethersulfone |
| Filter Type                      | Screen filter                   | Screen filter                   | Screen filter                   |
| Filter Pore Size, NMWL           | 10                              | 50                              | 100                             |

## Annex 8: The Targets and Indicators for MDGs

Table 7.12 MDG goals, targets, and indicators directly connected to sanitation  
WHO/UNICEF (2006)

| Goals and targets   | Indicators   |
|---|--|
| <b>Goal 1: Eradicate extreme poverty and hunger</b>   |  |
| Target 1: Halve, between 1990 and 2015 the proportion of people whose income is less than one dollar per day              | 1. proportion of population below \$ 1 (PPP) per day<br>2. Poverty gap ratio (indices x depth of poverty)<br>3. Share of poorest quintile in national consumption                  |
| Target 2: Halve, between 1990 and 2015 the proportion of people who suffer from hunger                                    | 4. Prevalence of underweight children under-five years of age<br>5. Proportion of population below minimum level of dietary energy consumption                                     |
| <b>Goal 4: Reduce child mortality:</b>  |  |
| Target 5: Reduce by two-thirds, between 1990 and 2015, the under-five mortality rate                                      | 13. Under five mortality rate<br>14. Infant mortality rate   |
| <b>Goal 6 : Combat HIV/AIDS, Malaria and other diseases</b>   |  |
| Target 8: Have halted by 2015 and begun to reverse the incidence of malaria and other diseases.                           | 21. Prevalence and death rates associated with malaria<br>22. Proportion of population in malaria – risk areas using effective malaria prevention and treatment                    |
| <b>Goal 7 : Ensure environmental sustainability</b>   |  |
| Target 10: Halve, by 2015 the proportion of people without sustainable access to safe drinking water and basic sanitation | 30. Proportion of population with sustainable access to improved water source, urban and rural<br>31. Proportion of population with access to improved sanitation, urban and rural |
| Target 11: By 2020, to have achieved a significant improvement in the lives of at least 100 million slum dwellers         | 32. Proportion of households with access to secure tenure  |

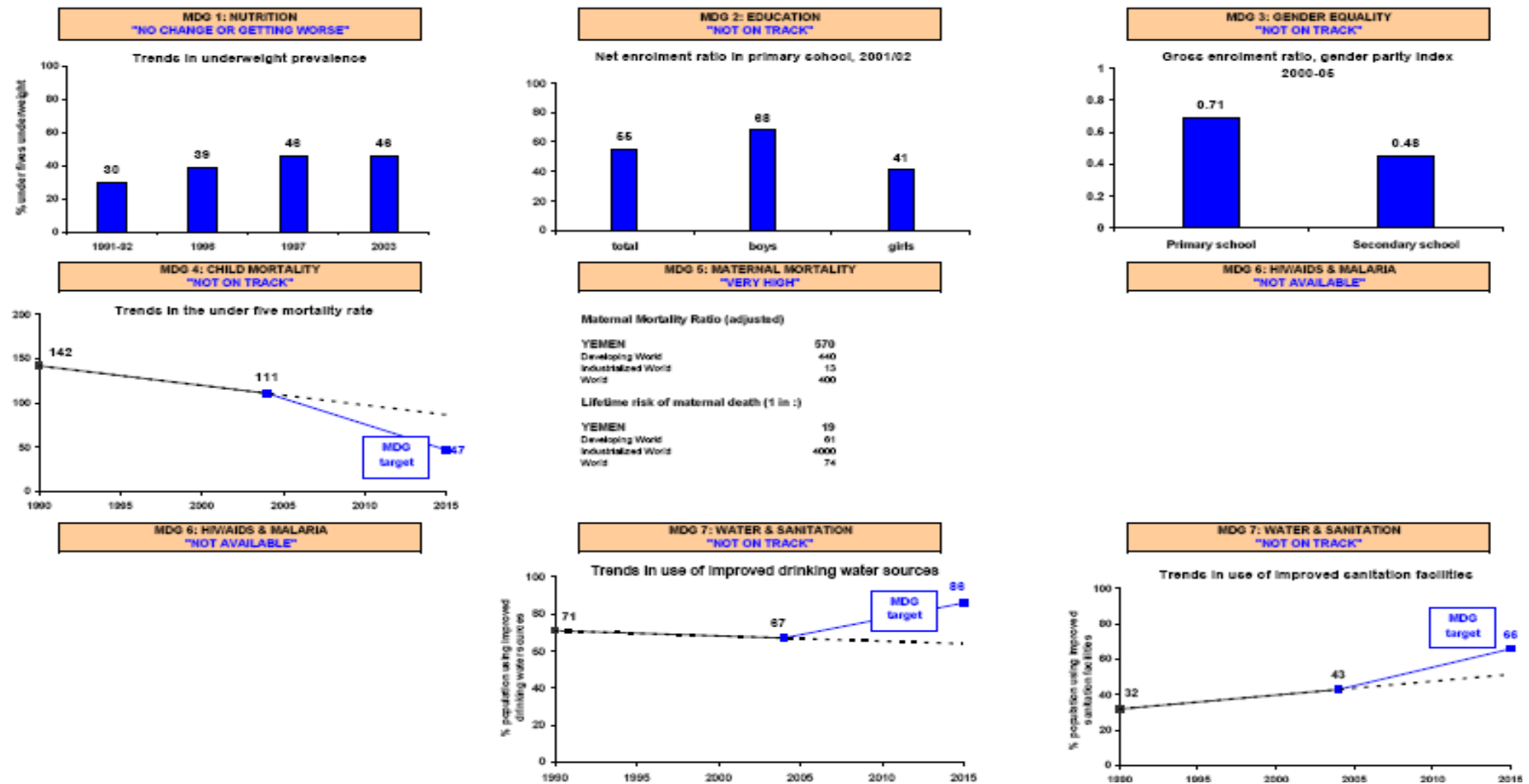
Table 7.13 Contribution of improved drinking and sanitation for other MDGs WHO/UNICEF (2006)

| MDG goals                                       | Contribution of improved drinking water and sanitation  |
|---|---|
| 1. Eradicate extreme poverty and hunger         | <ul style="list-style-type: none"> <li>• The security of household livelihoods rests on the health of its members; adults who are ill themselves or must care for sick children are less productive.</li> <li>• Illnesses caused by unsafe drinking water and inadequate sanitation generate high health cost relative to income for the poor.</li> <li>• Healthy people are better able to absorb nutrients in food than those suffering from water related diseases, particularly helminths, which rob their hosts of calories.</li> <li>• The time lost because of long-distance water collection and poor health contributes to poverty and reduced food security.</li> </ul> |
| 2. Achieve universal primary education          | <ul style="list-style-type: none"> <li>• Improved health and reduced water-carrying burdens improve school attendance, especially among girls.</li> <li>• Having separate sanitation facilities for girls and boys in school increases girls' attendance, especially after they enter adolescence.</li> </ul>   |
| 3. Promote gender equity and empower women      | <ul style="list-style-type: none"> <li>• Reduced time, health and care-giving burdens from improved water services give women more time for productive endeavors, adult education and leisure.</li> <li>• Water sources and sanitation facilities closer to home put women and girls at less risk of assault while collecting water or searching for privacy.</li> </ul>  |
| 4. Reduce child mortality                       | <ul style="list-style-type: none"> <li>• Improved sanitation and drinking water sources reduce infant and child morbidity and mortality.</li> </ul>   |
| 5. Improve maternal health                      | <ul style="list-style-type: none"> <li>• Accessible sources of water reduce labour burdens and health problems resulting from water portage, reducing maternal mortality risks.</li> <li>• Safe drinking water and basic sanitation are needed in health-care facilities to ensure basic hygiene practices following delivery.</li> </ul>   |
| 7. Ensure environmental sustainability          | <ul style="list-style-type: none"> <li>• Adequate treatment and disposal of wastewater contributes to better ecosystem conservation and less pressure on scarce freshwater resources. Careful use of water resources prevents contamination of groundwater and helps minimize the cost of water treatment.</li> </ul>   |
| 8. Develop a global partnership for development | <ul style="list-style-type: none"> <li>• Development agendas and partnerships should recognize the fundamental role that safe drinking water and basic sanitation play in economic and social development.</li> </ul>   |

## Annex 9: Progress Towards the Millennium Development Goals in Yemen

### YEMEN

#### PROGRESS TOWARD THE MILLENNIUM DEVELOPMENT GOALS



## YEMEN

## PROGRESS TOWARD THE MILLENNIUM DEVELOPMENT GOALS

| GOAL  | TARGET             | MEASURE OF TARGET  | 1990   | 2004             | Target 2015          | Actual AARC* | Required AARC* | SUMMARY        | SOURCES  |  |
|-------|--------------------|--|--|------------------|----------------------|--------------|----------------|----------------|--|--|
| MDG 1 | NUTRITION          | Halve between 1990 and 2015 the proportion of people who suffer from hunger  | % children under five who are underweight  | 30<br>(1991-92)  | 46<br>(2003)         | NA           | -3.6%          | 2.8%           | NO CHANGE OR GETTING WORSE   | PAFCHILD 1991-92, MICS 1996, DHS 1997, FHS 2003; UNICEF Progress for Children May 2006   |
| MDG 2 | EDUCATION          | Ensure that by 2015 children everywhere, boys and girls alike, will be able to complete a full course of primary schooling | Net enrollment ratio in primary school (total)**   | 54.6<br>(2001)   | 64.4<br>(2005)       | 100          | 1.95%          | 3.03%          | NOT ON TRACK   | UNICEF Progress for Children April 2005  |
|       |                    |  | Net enrollment ratio in primary school (boys)**  | 67.8<br>(2001)   | 79.5<br>(2005)       | 100          | 2.36%          | 2.14%          |  | UNICEF Progress for Children April 2005  |
|       |                    |  | Net enrollment ratio in primary school (girls)**   | 40.7<br>(2001)   | 48.5<br>(2005)       | 100          | 1.54%          | 3.95%          |  | UNICEF Progress for Children April 2005  |
| MDG 3 | GENDER EQUALITY    | Eliminate gender disparity in primary and secondary education, preferably by 2005, and in all levels by 2015               | Gross enrollment ratio in primary school, gender parity index                                | NA               | 0.71<br>(2000-05)    | 1.00         | NA             | NA             | NOT ON TRACK<br>(On track = GPI is between 0.96 and 1.04 inclusive)  | UNESCO estimates available in SOWC2007   |
|       |                    |  | Gross enrollment ratio in secondary school, gender parity index                              | NA               | 0.45<br>(2000-05)    | 1.00         | NA             | NA             | NOT ON TRACK<br>(On track = GPI is between 0.96 and 1.04 inclusive)  | UNESCO estimates available in SOWC2007   |
| MDG 4 | CHILD MORTALITY    | Reduce by two-thirds, between 1990 and 2015, the under-five mortality rate   | Under-five mortality rate  | 142              | 111                  | 47           | NA             | 7.8%           | NOT ON TRACK   | UNICEF/WHO/World Bank/ UNFPO joint estimates   |
|       |                    |  | YEMEN  | DEVELOPING WORLD | INDUSTRIALIZED WORLD | WORLD        |                |                |  |  |
| MDG 5 | MATERNAL MORTALITY | Reduce by three-quarters, between 1990 and 2015, the maternal mortality ratio  | Maternal mortality ratio:  | 570<br>(2000)    | 440<br>(2000)        | 13<br>(2000) | 400<br>(2000)  |                | VERY HIGH<br>(Latest estimate > 550)   | UNICEF/WHO/UNFPA adjusted estimates of maternal mortality in "Maternal Mortality in 2000: Estimates Developed by WHO/UNICEF/UNFPA" |
|       |                    | Lifetime risk of maternal death (1 in : )  | 19<br>(2000)   | 61<br>(2000)     | 4000<br>(2000)       | 74<br>(2000) |                | VERY HIGH      | UNICEF/WHO/UNFPA adjusted estimates of maternal mortality in "Maternal Mortality in 2000: Estimates Developed by WHO/UNICEF/UNFPA" |  |
|       |                    |  | MEASURE OF TARGET  | 1990             | 2004                 | Target 2015  | Actual AARC*   | Required AARC* |  |  |
| MDG 6 | HIV/AIDS & MALARIA | Have halted and begun to reverse the spread of HIV/AIDS  | HIV prevalence rate among young pregnant women aged 15-24 years (in capital city)            | NA               | NA                   | NA           | NA             | NA             |  | Ministry of Health   |
|       |                    | Have halted and begun to reverse the incidence of malaria and other major diseases   | Incidence estimates not available (see page 3 for key malaria indicators for MDG monitoring) |                  |                      |              |                |                |  |  |
| MDG 7 | WATER & SANITATION | Halve by 2015 the proportion of people without sustainable access to safe drinking water and basic sanitation              | % population using improved drinking water sources   | 71               | 67                   | 88           | NA             | NA             | NOT ON TRACK   | UNICEF/WHO Joint Monitoring Programme (JMP), and UNICEF Progress for Children September 2005                                       |
|       |                    | Halve by 2015 the proportion of people without sustainable access to safe drinking water and basic sanitation              | % population using improved sanitation facilities  | 32               | 43                   | 68           | NA             | NA             | NOT ON TRACK   | UNICEF/WHO Joint Monitoring Programme (JMP), and UNICEF Progress for Children September 2005                                       |

\* AARC = average annual rate of change

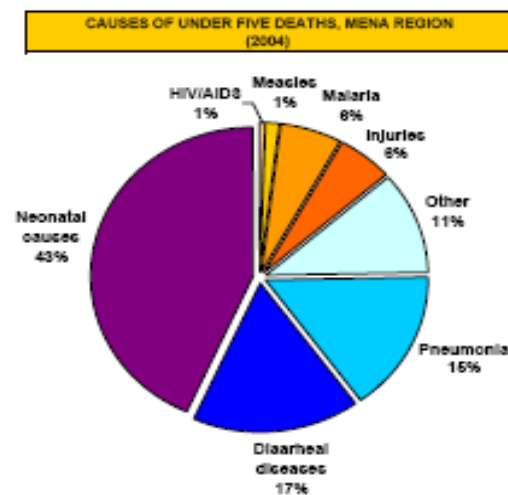
\*\* In some countries the net attendance ratio in primary school is used instead

## YEMEN

## OTHER KEY INDICATORS OF CHILD WELL-BEING

| AREA                    | SUB-AREA                      | KEY INDICATOR   | YEAR & SOURCE                       | YEMEN ESTIMATE | MENA AVERAGE |
|-------------------------|-------------------------------|---|-------------------------------------|----------------|--------------|
| NUTRITION               | VITAMIN A SUPPLEMENTATION     | Vitamin A supplementation coverage rate (6-59 months)   | UNICEF HQ 2004                      | 26             | NA           |
|                         | EXCLUSIVE BREASTFEEDING       | % infants who are exclusively breastfed (first 6 months of life)  | PHS 2003                            | 12             | 30           |
|                         | IODIZED SALT CONSUMPTION      | % households consuming adequately iodized salt (15 parts per million or more)   | PHS 2003                            | 36             | 65           |
|                         | LOW BIRTH WEIGHT              | % infants with low birth weight   | DHS 1997                            | 32             | 15           |
| HEALTH                  | PNEUMONIA                     | % under fives with suspected pneumonia taken to an appropriate health care provider                                     | PHS 2003                            | 47             | 66           |
|                         | DIARRHEA                      | % under fives with diarrhea receiving ORT and continued feeding   | DHS 1997<br>Reanalyzed by UNICEF HQ | 23             | 39           |
|                         | MALARIA                       | % under fives with fever receiving antimalarial drugs   | NA                                  | NA             | NA           |
|                         |                               | % under fives sleeping under an ITN   | NA                                  | NA             | NA           |
| HIV/AIDS                | PREVALENCE                    | Estimated adult HIV prevalence rate (15-49 years)   | NA                                  | NA             | 0.2          |
|                         | PMTCT                         | % HIV-positive pregnant women receiving ARVs to prevent infant HIV infection  | NA                                  | NA             | NA           |
|                         | KNOWLEDGE                     | % of young people who have comprehensive knowledge of HIV   | NA                                  | NA             | NA           |
|                         | CONDOM USE                    | % of young people who used a condom at last high-risk sex   | NA                                  | NA             | NA           |
| IMMUNIZATION            | MEASLES                       | % one year old children immunized against measles   | WHO & UNICEF 2005                   | 76             | 69           |
|                         | DPT3                          | % one year old children immunized with 3 doses of DPT   | WHO & UNICEF 2005                   | 66             | 69           |
| MATERNAL & NEWBORN CARE | SKILLED ATTENDANT AT DELIVERY | % births attended by skilled health personnel (doctor, nurse, midwife)  | PHS 2003                            | 27             | 76           |
|                         | ANTENATAL CARE                | % women aged 15-49 years attended at least once during pregnancy by skilled health personnel (doctor, nurse or midwife) | PHS 2003                            | 41             | 70           |
|                         | CONTRACEPTIVE PREVALENCE      | % women in union aged 15-49 currently using contraception   | PHS 2003                            | 23             | 53           |
| CHILD PROTECTION        | BIRTH REGISTRATION            | % children under five that were registered at the moment of survey  | NA                                  | NA             | NA           |
|                         | FEMALE GENITAL MUTILATION     | % women 15-49 years of age who have been mutilated/cut  | DHS 1997                            | 23             | NA           |
|                         | CHILD LABOR                   | % children aged 5-14 years involved in labor activities at the moment of survey   | NA                                  | NA             | 10           |
|                         | CHILD MARRIAGE                | % women 20-24 years of age that were married or in union before they were 18 years old                                  | DHS 1997                            | 37             | NA           |

| DEMOGRAPHY (2005)         |            |                             |           |
|---------------------------|------------|-----------------------------|-----------|
| Total population          | 20,975,000 | Total under five population | 3,668,000 |
| Under five mortality rate | 102        | Under five mortality rank   | 46        |
| Total births              | 845,000    | Total under five deaths     | 86,000    |



Source: UNICEF, The State of the World's Children 2007; www.childinfo.org

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