DOKUZ EYLUL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

APPLICATION OF ULTRAFILTRATION TO AN ORGANIZED INDUSTRIAL DISTRICT WASTEWATER TREATMENT PLANT EFFLUENT FOR WATER REUSE

by

Nevin Özalp

October , 2010

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APPLICATION OF ULTRAFILTRATION TO AN ORGANIZED INDUSTRIAL DISTRICT WASTEWATER TREATMENT PLANT EFFLUENT FOR WATER REUSE

A Thesis Submitted to the
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M. Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"APPLICATION OF ULTRAFILTRATION TO AN ORGANIZED INDUSTRIAL DISTRICT WASTEWATER TREATMENT PLANT EFFLUENT FOR WATER REUSE"** completed by **NEVİN ÖZALP** under supervision of **ASSOC. PROF. DR. NURDAN BÜYÜKKAMACI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Nevin ÖZALP

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ABSTRACT

In this study, it is intended to investigate the possibility of reusing the effluents originated from Organized Industrial District (OID) Wastewater Treatment Plant as process water after ultrafiltration. Secondary treatment effluent samples were taken from an OID, which was selected as pilot plant, and Prep/Scale® Spiral Wound Ultrafiltration Modules (Millipore) were chosen as UF membrane system. Three different sizes of UF membrane cartridges with a molecular weight cut-off (MWCO) of 100 kDa, 30 kDa, and 1 kDa, which are made form regenerated cellulose material, were used. The effect of ultrafiltration on polishing of secondary treatment effluent of OID was evaluated in terms of chemical oxygen demand (COD), suspended solid (SS), electrical conductivity (EC), and pH depending on transmembrane pressure (TMP), which varied between 0 to 2 bars. The results indicated that examined UF membranes are very effective for SS removal; however removal of organics is not sufficient. After UF applications, maximum 67% COD removal efficiency could be obtained. Similarly, significant EC reduction could not be achieved. Therefore, the quality of permeates can not meet the requirements of some industries located in the OID and further treatment should be applied before reuse depending on the required process water qualities.

Keywords: reuse, ultrafiltration, membrane, organized industrial district

ORGANİZE SANAYİ BÖLGESİ ATIKSU ARITMA TESİSİ ÇIKIŞ SULARININ YENİDEN KULLANIMI İÇİN ULTRAFİLTRASYON UYGULAMASI

ÖZ

Bu çalışmada, Organize Sanayi Bölgesi (OSB) Atıksu arıtma Tesisinden çıkan arıtılmış suların Ultrafiltrasyon (UF) sistemi kullanılarak yeniden kullanımını araştırmak hedeflenmiştir. Pilot tesis olarak seçilen OSB Atıksu Arıtma Tesisi son çökeltim ünitesi çıkışından numuneler alınmış ve UF membran sistem olarak "Prep/Scale® Spiral Wound Ultrafiltrasyon Modülü (Millipore)" seçilmiştir. UF membran sisteminde rejenere selüloz maddeden yapılmış, moleküler ağırlık kesim boyutu (MWCO) 100 kDa, 30 kDa ve 1 kDa olan üç farklı membran kartuş kullanılmıştır. Membran sistemi çıkış sularının özellikleri KOİ, AKM, pH ve iletkenlik parametreleri göz önünde bulundurularak değerlendirilmiştir. Sistemde 0-2 bar aralığında membran geçiş basınçları (TMP) uygulanmıştır. Elde edilen sonuçlara göre, UF membran çalışmaları AKM gideriminde oldukça etkili olmuştur ancak KOİ giderimi yeterli değildir. UF uygulamasından sonra maksimum %67 KOİ giderme verimi sağlanmıştır. Aynı şekilde belirgin bir iletkenlik düşüşü gözlenmemiştir. Deneysel çalışmaların sonuçlarına göre; mevcut atıksu arıtma tesisi çıkış sularının denenen ultrafiltrasyon membran sistemine verilmesi durumunda incelenen OSB içerisinde yer alan bazı endüstriler için uygun kalitede proses suyu elde edilemediği, bu şekilde daha iyi kalitede suya ihtiyaç duyan endüstriler için daha farklı ileri arıtma metotlarının kullanılması gerekliliği olduğu sonucuna varılmıştır.

Anahtar Sözcükler: yeniden kullanım, ultrafiltrasyon, membran filtre sistemleri, organize sanayi bölgesi

CONTENTS

CHAPTER ONE
INTRODUCTION

The growth in industry and the changes in manufacturing processes have resulted in an increase in the volume and complexity of wastewater discharges to the environment. Many traditional and novel treatment processes are being modified and developed to try to eliminate the release to surface waters of the diverse chemical substances found in wastewater discharges (Üstün, Solmaz & Birgül 2007).

Implementation and enforcement of stringent environmental regulations over the last two decades has created opportunities for industries to reduce and reuse wastewater from their manufacturing processes. Even though the cost benefits of reusing wastewater may not be realized immediately, the intangible benefits of preventing contamination of the environment on a short-or-long term basis can be significant (Ersu, Braida, Chao & Ong, 2003).

Turkey is not a water-rich country; approximately 1.500 m^3 per capita is available annually for consumption. It is estimated that water availability in Turkey will fall below 1.000 m^3 per capita by 2025 (WHO, 2007). Therefore, in order to meet water demand in the future, the treated wastewater has to be reused and the ways to reuse the effluent from several wastewater treatment plants have to be developed. Industry accounts for about 11% of all water consumption in Turkey (www.dsi.gov.tr) and reclaimed water is ideal for many industries where processes do not require water of potable quality.

Turkey is a developing country and environmental problems increase with increasing industrialization and urbanization. To overcome these problems, some industrial facilities are located in organized industrial districts. In Turkey, the first organized industrial district (OID) was established in 1962. Nowadays, although the amount of planned OID is about 250, only 70 of them are in operation all throughout Turkey. Some of them have a centralized wastewater treatment plant and they must meet discharge standards given in Water Pollution Control Regulation (WPCR, 2008). However, some OID managers are willing to reuse of treated water instead of discharge.

The suitability of reclaimed water for use in industrial processes depends on the particular use. Thus, in investigating the feasibility of industrial reuse with reclaimed water, potential users must be contacted to determine the specific requirements for their process water (EPA, 2004). Since different industrial facilities are placed in OIDs, quality of process water required for each sector will vary.

In order to obtain high quality reclaimed water as process water for some industries, such as textile, pulp and paper, and electronic, membrane systems can be evaluated as a superior alternative. Membrane filtration systems, especially ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) have been widely used for wastewater reclamation and reuse purposes (Juanga et.al., 2007, Gozálvez-Zafrilla et.al., 2008, Arévalo et.al., 2009). Among these systems, UF appears to be more attractive because they promise high fluxes at relatively low pressures (Kang & Choo, 2003).

Although, there are several reuse studies with membrane applications to various industrial effluents, such as textile industry (Bes-Piá et.al., 2009, Gozálvez-Zafrilla et.al., 2008, Arnal et.al., 2008), food processing industry (Hafez et al., 2007), dairy industry (Vourch et.al., 2008), tannery industry (Mendoza-Roca et.al., 2010), pulp and paper industry (Pizzichini et.al., 2005), there are limited studies with organized industrial district effluent in the literature (Juang et.al., 2007, Lei et.al., 2010). The aim of this study was to evaluate the reuse possibility of the secondary effluent of an organized industrial district (OID) as process water at some industrial facilities located in the OID. Spiral wound ultrafiltration (UF) membrane system was applied to improve existing central wastewater treatment plant effluent qualities. Permeate qualities were assessed depending on COD, SS, EC, and pH parameters.

CHAPTER TWO

AN OVERVIEW OF MEMBRANE SYSTEMS

2.1 Introduction

A membrane can be defined as a thin film separating two phases and acting as a selective barrier to the transport of matter (Figure 2.1). This definition includes the definition of a perm-selective membrane and implies that a chemical potential difference exist between the two phases. It is very important to point out here that a membrane is not defined as a passive material but better as a functional material. In other words, even if (perm-selective) membranes may be characterized by their structure, their performances in terms of fluxes and selectivity are mainly dependent on the nature of the elements contained in the two phases and on the nature of the elements contained in the two phases and on the driving force which is applied. This is why we choose to classify membranes according to the type of separation they are able to perform rather than according to their structure, and only then discuss the structure best adopted to improve the performances of the separations (Aptel & Buckley, 1996).

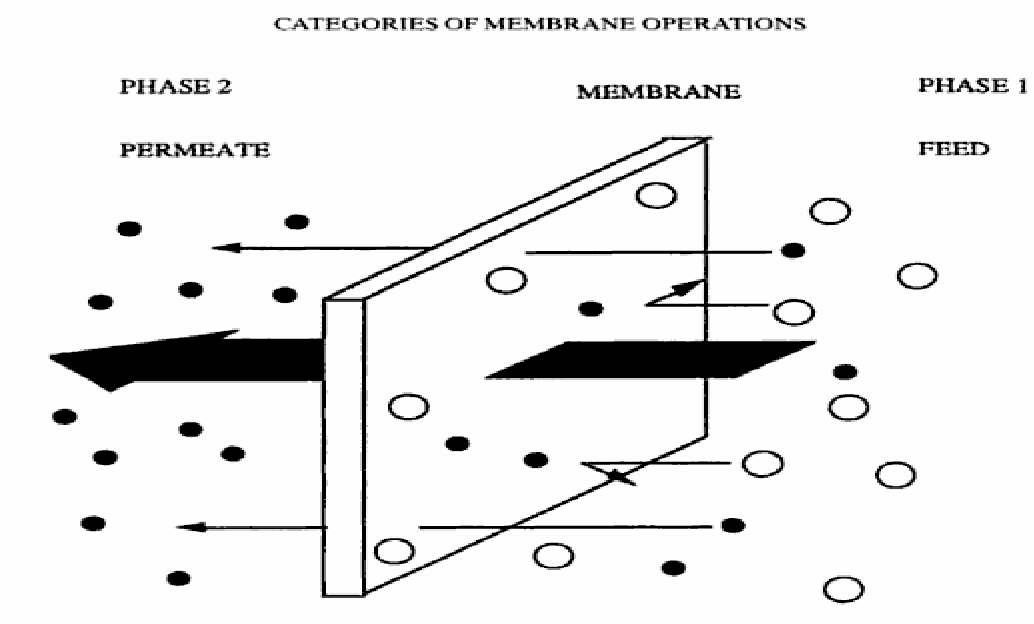

Figure 2.1 Definition of a perm-selective membrane (Aptel & Buckley, 1996).

To be effective for separation membrane materials should ideally posses the following properties:

- Chemical resistance (to both feed and cleaning fluids)
- Mechanical stability,
- Thermal stability,
- High permeability,
- High selectivity,
- Stable operation (Scott & Hughes, 1996).

A membrane operation can be defined as an operation where a feed stream is divided into two streams: permeate containing material which has passed through the membrane and a retentate containing the nonpermeating species (Figure 2.2). Membrane operations can be used to concentrate or to purify a solution or a suspension (solvent-solute or particle separation) and to fractionate a mixture (solute-solute separation). Among the separation operations, membrane offers basic advantages:

● Separation takes place at ambient temperature without phase change, which offers an energetic advantage compared to distillation. This explains, for example the success of reverse osmosis and electrodialysis for water desalination.

● Separation takes place without accumulation of products inside the membrane. Membranes are then well adopted to be run continuously without an elution cycle as in chromatography.

● Separation does not need the addition of chemical additives, as is the case with azeotropic distillation or in water clarification by settlement or conventional filtration. This gives advantages for the quality of the product and leads to less pollutant wastes and explains the success of pervaporation for the fractionation of azeotropic mixtures and ultrafiltration for water clarification **(**Aptel & Buckley, 1996).

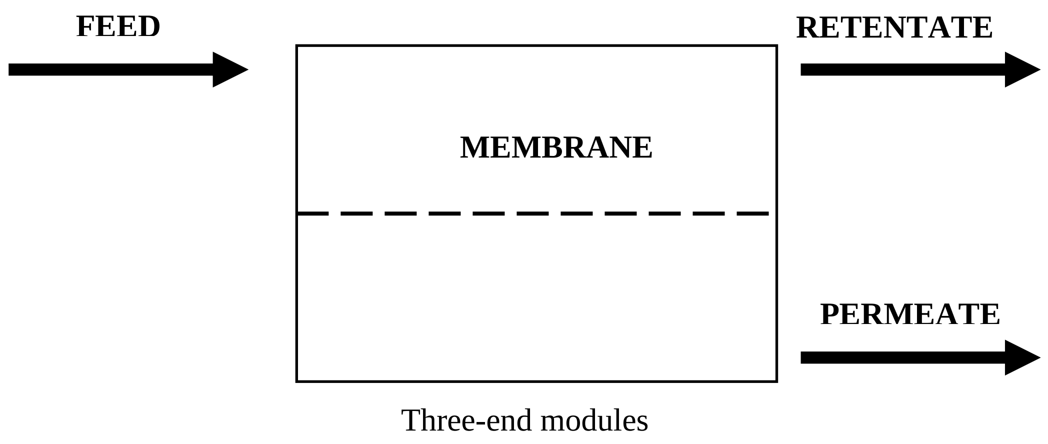

Figure 2.2 Principle of a membrane operation (Aptel & Buckley, 1996)

2.2 Classification of Membrane Separation Processes

Improvements and advances in membrane technology over the last two decades have seen applications expand in many industrial sectors; chemical, petrochemical, mineral and metallurgical, food, biotechnology, pharmaceutical, electronics, paper and pulp and water etc. Membrane separations are in competition with physical methods of separation such as selective adsorption, absorption, solvent extraction, distillation, crystallisation, cryogenic gas separation etc. The feature which distinguishes membrane separations from other separation techniques is the provision of another phase, the membrane. This phase, solid, liquid or gaseous, introduces an interface(s) between the two bulk phases involved in the separation and can give advantages of efficiency and selectivity. The membrane can be neutral or charged and porous or non-porous and acts as a perm-selective barrier.

Transport of selected species through the membrane is achieved by applying driving force across the membrane. This gives a broad classification of membrane separations in the way or mechanism by which material is transported across a membrane. The flow of material across a membrane has to be kinetically driven, by the application of mechanical, chemical or electrical work.

The driving forces are pressure, concentration, temperature or electrical potential in many cases the transport rate (permeation) is proportional to the driving force and the membrane can be categorized in terms of an appropriate permeability coefficient. The use of driving force as a means of classification is not altogether satisfactory because apparently different membrane processes can be applied for the same separation, for example electrodialysis, reverse osmosis and pervaporation in the desalination of water. From the view of applications, classification in terms of suspended solids, colloids or dissolved solutes, etc. is preferred (see Figure 2.3) thus we see techniques of microfiltration and ultrafiltration (and electro-osmosis and electrophoresis) employed in the category of suspended solid separation. All these processes use membranes which are microporous in nature. These are the simplest form of membrane regarding mode of separation and consist of a solid matrix with defined pores ranging from 100 nm to 50 μm in size. A second classification of membranes under homogeneous films encompasses the separations, gas permeation, pervaporation, reverse osmosis (and ultrafiltration). Separation in these cases is related directly to the transport rate of species in the membrane, determined by their diffusivity and concentration in the membrane phase. These membranes are often in the form of composites of a homogeneous film on a microporous support as used in hyperfiltration and pervaporation. These latter two processes are used for similar separations, typically the removal of water to concentrate solutions of ionic or organic solutes. Gas permeation is clearly as a special case which again uses homogeneous membranes which separate species in terms of diffusivity and concentration in the membrane.

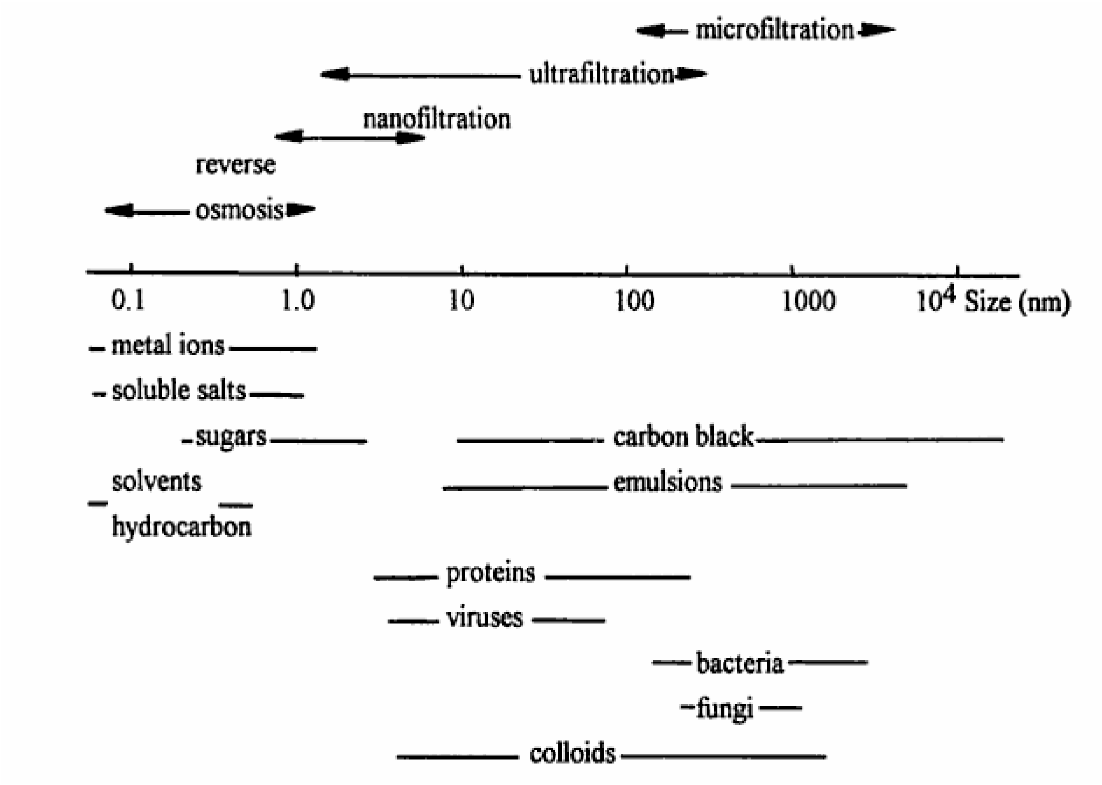

Figure 2.3 Application size range of membrane filtration processes (Scott & Hughes, 1996)

The third and final general classification of membranes is those that are electrically charged. These membranes carry either fixed positive or negative charges and separate by exclusion of ions of the same charge as carried in the membrane phase.

It should be already apparent that one is not merely restricted to a single type of membrane process for a particular separation. The appropriate method of separation will be determined by a range of technical factors such as size, susceptibility of feed to electrical work, etc. and, of course, relative cost (Scott & Hughes, 1996).

2.3 Membrane Processes

2.3.1 Microfiltration

Microfiltration (MF) is the process of removing particles or biological entities in the 0.025 μm to 10.0 μm range from fluids by passage through a microporous medium such as a membrane filter. Although micron-sized particles can be removed by use of non-membrane or depth materials such as those found in fibrous media, only a membrane filter having a precisely defined pore size can ensure quantitative retention. Membrane filters can be used for final filtration or prefiltration, whereas a depth filter is generally used in clarifying applications where quantitative retention is not required or as a prefilter to prolong the life of a downstream membrane. Membrane and depth filters offer certain advantages and limitations. They can complement each other when used together in a microfiltration process system or fabricated device (Millipore, 2004).

In membrane microfiltration (MF) the filter is generally made from a thin polymer film with a uniform pore size and a high pore density of approximately 80%. The principle method of particle retention (Figure 2.4) is characterized as sieving although the separation is influenced by interactions between the membrane surface and the solution (Scott, 1996).

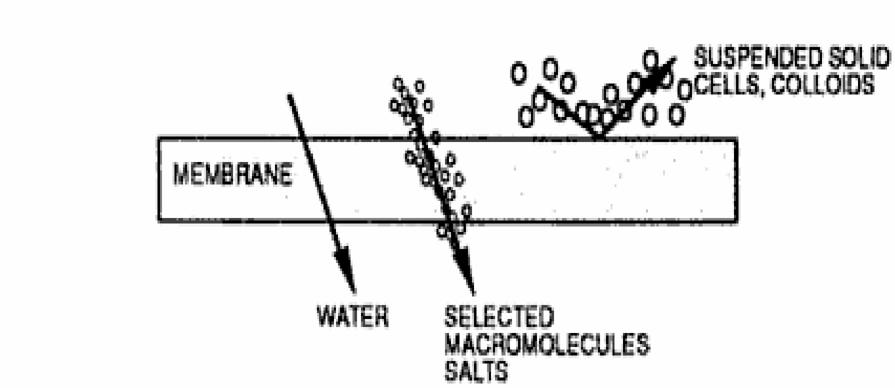

Figure 2.4 Separation using microfiltration membranes (Scott, 1996)

The irregular nature of the pores of the membrane and the often irregular shape of the particles being filtered mean there is not a sharp cut off size during filtration. With symmetric membranes some degree of in-depth separation could occur as particles move through the tortuous flow path. To counteract this effect, asymmetric membranes, which have surface pore sizes much less than those in the bulk of the membrane, have been introduced. These entrap the particles almost exclusively at the surface layers (the membrane skin) whilst still offering low hydrodynamic resistance.

Microfiltration is most widely applied in a dead-end mode of operation. In this the feed flow is perpendicular to the membrane surface and the retained (filtered) particles accumulate on the surface forming a filter cake. The thickness of this cake therefore increases with time and permeation rate correspondingly decreases. Eventually the membrane filter reaches an impractical or uneconomic low filtration rate and is either cleaned or replaced. Typical filters come in the form of readily replaceable screw-in cartridges (Aptel & Buckley, 1996).

Applications of microfiltration are varied and include:

- Food, Sugar & Starch for wet corn milling, corn syrup clarification, modified starch filtration, fructose polishing, cane & beet sugar clarification, scums filtration, caustic recovery, etc.
- Pharmaceutical/ Biotech for fermentation broth concentration & clarification, protein separation & recovery, etc.
- Chemical for solvent recovery, catalyst recovery, chemical clarification, etc.
- Textile for synthetic warp size recovery, dye recovery, caustic recovery, etc.
- Nuclear Power for enriched uranium recovery, low-level rad-waste concentration, etc.
- Waste Treatment for hazardous waste concentration, sludge dewatering, hot wash/ waste water recycle, waste oil recovery, etc.
- Metal Finishing for oil removal, alkaline degreaser recovery, caustic recovery, etc (www.ameridia.com).

2.3.2 Ultrafiltration

Ultrafiltration (UF) is the process of separating extremely small particles and dissolved molecules from fluids. The primary basis for separation is molecular size, although in all filtration applications, the permeability of a filter medium can be affected by the chemical, molecular or electrostatic properties of the sample (Millipore, 2004). Ultrafiltration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. Ultrafiltration can only separate molecules which differ by at least an order of magnitude in size. Typically, ultrafiltration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. Low molecular-weight organics and ions such as sodium, calcium, magnesium chloride, and sulfate are not removed. Because only high-molecular weight species are removed, the osmotic pressure differential across the membrane surface is negligible. Low applied pressures are therefore sufficient to achieve high flux rates from an ultrafiltration membrane. Flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time. Generally flux is expressed as gallons per square foot per day (GFD) or as cubic meters per square meters per day (m^3/m^2.d) (www.appliedmembranes.com).

2.3.2.1 Ultrafilter vs. Conventional Filter

Ultrafiltration, like reverse osmosis, is a cross-flow separation process. Here liquid stream to be treated (feed) flows tangentially along the membrane surface, thereby producing two streams. The stream of liquid that comes through the membrane is called permeate. The type and amount of species left in permeate will depend on the characteristics of the membrane, the operating conditions, and the quality of feed. The other liquid stream is called concentrate and gets progressively concentrated in those species removed by the membrane. In cross-flow separation, therefore, the membrane itself does not act as a collector of ions, molecules, or colloids but merely as a barrier to these species.

Conventional filters such as media filters or cartridge filters, on the other hand, only remove suspended solids by trapping these in the pores of the filter-media. These filters therefore act as depositories of suspended solids and have to be cleaned or replaced frequently. Conventional filters are used upstream from the membrane system to remove relatively large suspended solids and to let the membrane do the job of removing fine particles and dissolved solids. In ultrafiltration, for many applications, no prefilters are used and ultrafiltration modules concentrate all of the suspended and emulsified materials (www.appliedmembranes.com).

2.3.2.2 Concentration Polarization

When a membrane is used for a separation, the concentration of any species being removed is higher near the membrane surface than it is in the bulk of the stream. This condition is known as concentration polarization and exists in all ultrafiltration and reverse osmosis separations. The result of concentration polarization is the formation of a boundary layer of substantially high concentration of substances being removed by the membrane. The thickness of the layer and its concentration depend on the mass of transfer conditions that exist in the membrane system. Membrane flux and feed flow velocity are both important in controlling the thickness and the concentration in the boundary layer. The boundary layer impedes the flow of water through the membrane and the high concentration of species in the boundary layer produces permeate of inferior quality in ultrafiltration applications relatively high fluid velocities are maintained along the membrane surface to reduce the concentration polarization effect (www.appliedmembranes.com).

2.3.2.3 Recovery

Recovery of an ultrafiltration system is defined as the percentage of the feed water that is converted into permeate, or:

$$R = P/F * 100$$

Where;

R= Recovery rate

P= Volume of permeate

F= Volume of feed

The ultimate aim of ultrafiltration is to maximize recovery of solutes of interest, but there are many membrane characteristics that affect that goal. Factors affecting recovery include:

- Nominal molecular weight limit (NMWL)/nucleotide cut-off (NCO)
- Retention
- Concentration polarization
- Flux (Millipore, 2004)

2.3.2.4 Ultrafiltration Membranes

Ultrafiltration Membrane modules come in plate-and-frame, spiral-wound, and tubular configurations. All configurations have been used successfully in different process applications. Each configuration is specially suited for some specific applications and there are many applications where more than one configuration is appropriate. For high purity water, spiral-wound and capillary configurations are generally used. The configuration selected depends on the type and concentration of colloidal material or emulsion. For more concentrated solutions, more open configurations like plate-and-frame and tubular are used. In all configurations the optimum system design must take into consideration the flow velocity, pressure drop, power consumption, membrane fouling and module cost (www.appliedmembranes.com).

2.3.2.5 Membrane Materials

A variety of materials have been used for commercial ultrafiltration membranes, but polysulfone and cellulose acetate are the most common. Recently thin-film composite ultrafiltration membranes have been marketed. For high purity water applications the membrane module materials must be compatible with chemicals such as hydrogen peroxide used in sanitizing the membranes on a periodic basis (www.appliedmembranes.com).

2.3.2.6 Molecular-Weight Cutoff

Pore sizes for ultrafiltration membranes range between 0.001 and 0.1 micron. However, it is more customary to categorize membranes by molecular-weight cutoff. For instance, a membrane that removes dissolved solids with molecular weights of 10,000 and higher has a molecular weight cutoff of 10,000. Obviously, different membranes even with the same molecular-weight cutoff will have different pore size distribution. In other words, different membranes may remove species of different molecular weights to different degrees. Nevertheless, molecular-weight cutoff serves as a useful guide when selecting a membrane for a particular application (www.appliedmembranes.com).

2.3.2.7 Factors Affecting the Performance of Ultrafiltration

There are several factors that can affect the performance of an ultrafiltration system. A brief discussion of these is given here.

Flow across the Membrane Surface: The permeate rate increases with the flow velocity of the liquid across the membrane surface. Flow velocity if especially critical for liquids containing emulsions or suspensions. Higher flow also means higher energy consumption and larger pumps. Increasing the flow velocity also reduces the fouling of the membrane surface. Generally, an optimum flow velocity is arrived at by a compromise between the pump horsepower and increase in permeate rate.

Operating Pressure: Permeate rate is directly proportional to the applied pressure across the membrane surface. However, due to increased fouling and compaction, the operating pressures rarely exceed 100 psig and are generally around 50 psig. In some of the capillary-type ultrafiltration membrane modules the operating pressures are even lower due to the physical strength limitation imposed by the membrane module.

Operating Temperature: Permeate rates increase with increasing temperature. However, temperature generally is not a controlled variable. It is important to know the effect of temperature on membrane flux in order to distinguish between drops in permeate due to a drop in temperature and the effect of other parameters.

Operation and Maintenance: Ultrafiltration system operation and maintenance is similar to that of reverse osmosis systems. Daily records of feed and permeate flow, feed pressure and temperature, and pressure drop across the system should be kept. Membranes should be cleaned when the system permeate rate drops by 10% or more. Feed flow is critical to the operation of ultrafiltration systems. A drop in feed flow may be due to a problem in the prefilter (if any), with the flow control valve, or with the pump itself. When the system is shut down for more than two days, a bacteriocide should be circulated through the membranes. At restart, permeate should be diverted to drain until all the bacteriocide is removed (www.appliedmembranes.com).

2.3.3 Nanofiltration

Nanofiltration (NF) is similar to reverse osmosis (RO) and is a pressure –driven process applied in the area between the separation of capabilities of reverse osmosis membranes and ultrafiltration membranes that is in the separation of ions from solutes such as small molecules of sugar. It has only recently achieved success due to developments in thin film non-cellulose membranes. Membranes can be formed by interfacial polymerisation on a porous substrate of polysulphane or polyethersulphone. Generally this opens up the possibilities for process efficiency improvements and the production of new products particularly in the food and biotechnology industries. Nanofiltration systems typically operate at lower pressure than reverse osmosis (e.g. 5 bar) but yield higher flowrates of water, albeit of a different quality to reverse osmosis.

Nanofiltration is used when high sodium rejection, typical of reverse osmosis, is not needed but where other salts such as Mg and Ca (i.e. divalent ions) are to be removed. The molecular weight cut-off the nanofiltration membrane is around 200. Typical rejections are (5 bar, 2000 ppm solute) 60% for NaCl, 80% for calcium bicarbonate and 98% for magnesium sulphate, glucose and sucrose (Scott & Hughes, 1996).

2.3.4 Reverse Osmosis

Reverse osmosis, also known as hyperfiltration, is the finest filtration available today. It is the most common treatment technology used by premium bottled water companies. It is effective in eliminating or substantially reducing a very wide array of contaminants, and of all technologies used to treat drinking water in residential applications, it has the greatest range of contaminant removal. Reverse osmosis will allow the removal of particles as small as individual ions. The pores in a reverse osmosis membrane are only approximately 0.0005 micron in size (bacteria are 0.2 to 1 micron & viruses are 0.02 to 0.4 microns).

There are two types of reverse osmosis membranes commonly used in home water purification products: Thin Film Composite (TFC) and Cellulose Triacetate (CTA). TFC membranes have considerably higher rejection rates (they will filter out more contaminants) than a CTA membrane, however, they are more susceptible to degradation by chlorine. This is one of the reasons why it is important that a reverse osmosis system include quality activated carbon pre-filters.

A typical RO system is composed of an array of granular activated carbon (GAC) pre-filters, the reverse osmosis membrane, a storage tank, and a faucet to deliver the purified water to your countertop. Reverse osmosis systems vary in membrane quality, output capacity, and storage capacity.

Reverse osmosis uses a membrane that is semi-permeable, allowing pure water to pass through it, while rejecting the contaminants that are too large to pass through the tiny pores in the membrane (figure 2.5). Quality reverse osmosis systems use a process known as crossflow to allow the membrane to continually clean itself. As some of the fluid passes through the membrane the rest continues downstream, sweeping the rejected contaminants away from the membrane and down the drain. The process of reverse osmosis requires a driving force to push the fluid through the membrane (the pressure provided by a standard residential water system is sufficient - 40 psi+) (www.home-water-purifiers-and-filters.com).

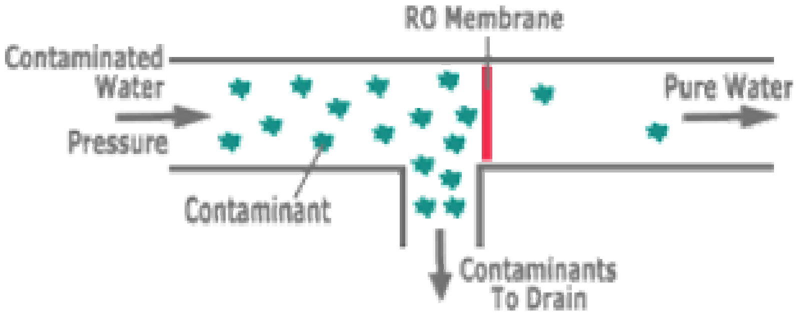

Figure 2.5 Mechanism of RO (www.home-water-purifiers-and-filters.com)

2.3.4.1 Application

Reverse osmosis is an excellent choice for almost all home water purification needs. It is the most recommended solution for individuals on a pre-treated municipal water system. While reverse osmosis can be very effective in removing bacteria and viruses, it is not recommended that reverse osmosis be the only level of purification for water that contains or may contain biological contaminants (untreated well or lake water, for instance). For these applications consider a combined reverse osmosis / ultraviolet system or the addition of a complementary whole-house ultraviolet system for maximum effectiveness and protection against bacteria and viruses. Since membranes are subject to degrading by chlorine, iron, manganese, and hydrogen sulfide, and to bacterial attack, sediment pre-filter and an activated carbon pre-filter and/or post-filter should be included with your reverse osmosis system. Water softeners can be used in advance of the RO system when household water is excessively hard to prevent pre-filter and membrane fouling. RO systems are generally the best choice for water contaminated with high nitrite levels as might be found in agricultural areas (www.home-water-purifiers-and-filters.com).

2.3.4.2 What Contaminants Does Reverse Osmosis Remove?

Reverse osmosis (RO) units remove substantial amounts of most inorganic chemicals (such as salts, metals, minerals), most microorganisms including cryptosporidium and giardia, and most (but not all) inorganic contaminants. Reverse osmosis successfully treats water with dissolved minerals and metals such as aluminum, arsenic, barium, cadmium, chloride, chromium, copper, fluoride, magnesium, iron, lead, manganese, mercury, nitrate, selenium, silver, sulfate, and zinc. RO is also effective with asbestos, many taste, color and odor-producing chemicals, particulates, total dissolved solids, turbidity, and radium. When using appropriate activated carbon pre-filtering, additional treatment can also be provided for such "volatile" contaminants (VOCs) as benzene, MTBE, trichloroethylene, trihalomethanes, and radon. Essentially, reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, heavy metals, chlorine and related by-products, and other contaminants that have a molecular weight of greater than 150-250 daltons. The separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as organics. The larger the charge and the larger the particle, the more likely it will be rejected (Table 2.1).

Table 2.1 Species separation during pressure-driven membrane processes (www.home-water-purifiers-and-filters.com)

Arsenic	Bacteria and Viruses	Bad Tastes & Odors	Chlorine	Fluoride	Hydrogen Sulfide	Heavy Metals	Nitrates	Radon	Sediment	Iron	VOC's
●	●	●	●	●	◐	●	●	○	●	●	◐

● = Effectively Removes ◐ = Significantly Reduces ○ = Minimal or No Removal

Even though reverse osmosis is effective in removing bacteria and viruses, it is not recommended that rely upon reverse osmosis solely if your water is contaminated with bacteria or viruses. Ultraviolet (UV) purification is also recommended.

2.3.4.3 Advantages and Disadvantages of RO

Advantages and disadvantages of RO systems are given below:

Advantages:

- very high rejection rate for a wide array of contaminants
- very cost effective in the long term, costing as little as 5 cents per gallon of pure water once maintenance and water costs are factored in

Disadvantages:

- requires sediment and carbon pre-filtration (generally included as part of the system) to prevent membrane fouling
- because reverse osmosis works against standard osmotic pressure, the process is generally fairly slow, producing roughly 15 gallons of purified water per day, and may require from 3 to 10 gallons of untreated water to make a single gallon of purified water (www.home-water-purifiers-and-filters.com).

2.4 Membrane Fouling

2.4.1 Type of Membrane Fouling, Water Quality Indicators, and Control Measures

According to the type of fouling materials, four categories of membrane fouling are generally recognized. They are (a) inorganic fouling/scaling, (b) particle/colloids fouling, (c) microbial fouling, and (d) organic fouling. A brief description on the nature of fouling, relevant water quality as indicators, and control measures are summarized below for each type of membrane fouling.

a) Inorganic Fouling/Scaling

Inorganic fouling or scaling is caused by the accumulation of inorganic precipitates such as metal hydroxides, and “scales” on membrane surface or within pore structure. Precipitates are formed when the concentration of chemical species exceeding their saturation concentrations. Scaling is a major concern for reverse osmosis (RO) and nanofiltration (NF). RO and NF membranes reject inorganic species. Those species form a concentrated layer in the vicinity of membrane-liquid interface - a phenomenon referred to “concentration polarization”. For microfiltration (MF) and ultrafiltration (UF), inorganic fouling due to concentration polarization is much less profound, but can exist most likely due to interactions between ions and other fouling materials (i.e., organic polymers) via chemical bonding. Some pretreatment processes for membrane filtration, such as coagulation and oxidation, if are not designed or operated properly, may introduce metal hydroxides on membrane surface or within pore structure. Inorganic fouling/scaling can be a significant problem for make-up water of caustic solutions prepared for chemical cleaning.

b) Particulate/colloid Fouling

Algae, bacteria, and certain natural organic matters fall into the size range of particle and colloids. However, they are different from inert particles and colloids such as silts and clays. To distinguish the different fouling phenomena, particles and colloids here are referred to biologically inert particles and colloids that are inorganic in nature and are originated from weathering of rocks.

In most cases, particles and colloids do not really foul the membrane because the flux decline caused by their accumulation on the membrane surface is largely reversible by hydraulic cleaning measures such as backwash and air scrubbing. A rare case of irreversible fouling by particles and colloids is that they have smaller size relative to membrane pore size. Therefore, those particles and colloids can enter and be trapped within the membrane structure matrix, and not easily be cleaned by hydraulic cleaning.

c) Microbial/Biological Fouling

Microbial fouling is a result of formation of biofilms on membrane surfaces. Once bacteria attach to the membrane, they start to multiple and produce extracellular polymetric substances (EPS) to form a viscous, slimy, hydrated gel. EPS typically consists of heteropolysaccharides and have high negative charge density. This gel structure protects bacterial cells from hydraulic shearing and from chemical attacks of biocides such as chlorine.

Severity of microbial fouling is greatly related to the characteristics of the feed water. Water quality parameters that indicate the potential of microbial fouling are classified into three categories:

(a) Parameters indicating the abundance of microbes,

(b) Parameters indicating nutrient availability,

(c) Parameters indicating environmental conditions for microbial growth.

d) Organic Fouling

Organic fouling is profound in membrane filtration with source water containing relatively high natural organic matters (NOM). Surface water (lake, river) typically contains higher NOM than ground water, with exceptions. For source water high in NOM, organic fouling is believed to be the most significant factor contributed to flux decline. Microfilters usually remove insignificant amount of organic matter, as measured by dissolve organic carbon (DOC). DOC as an indicator for organic fouling is probably neither proper nor adequate. Efforts to identify the effects of subgroups of NOM on membrane fouling have yet been able to draw definitive conclusions (Liu, Caothien, Hayes & Caothuy, n.d.).

2.5 Membrane Cleaning

In order to operate membranes efficiently, appropriate cleaning procedures must be applied. Otherwise, the membrane life may be shortened. The membrane cleaning procedure must be specified by the vendor. There are a number of cleaning techniques for the removal of membrane fouling, such as forward flush, backward flush, air flush, and chemical cleaning.

2.5.1 Forward Flush

When forward flush is applied in a membrane, the barrier that is responsible for dead-end management is opened (Figure 2.6). At the same time the membrane is temporarily performing cross-flow filtration, without the production of permeate. The purpose of a forward flush is the removal of a constructed layer of contaminants on the membrane through the creation of turbulence. A high hydraulic pressure gradient is in order during forward flush.

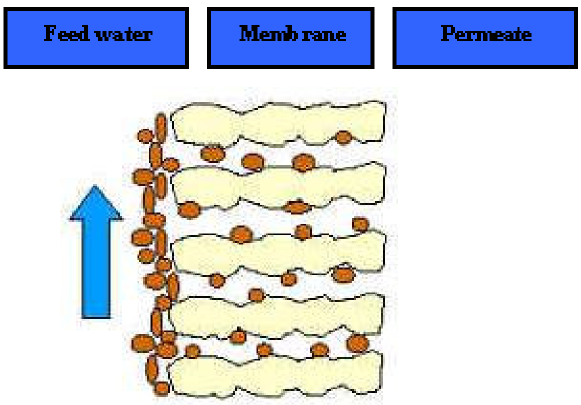

Figure 2.6 Forward flushing (www.lenntech.com)

2.5.2 Backward Flush

When backward flush is applied the pores of a membrane are flushed inside out. The pressure on the permeate side of the membrane is higher than the pressure within the membranes, causing the pores to be cleaned. A backward flush is executed under a pressure that is about 2.5 times greater than the production pressure. Permeate is always used for a backward flush, because the permeate chamber must always be free of contagion (Figure 2.7). A consequence of backward flush is a decrease in recovery of the process. Because of this, a backward flush must take up the smallest possible amount of time. However, the flush must be maintained long enough to fully flush the volume of a module at least once.

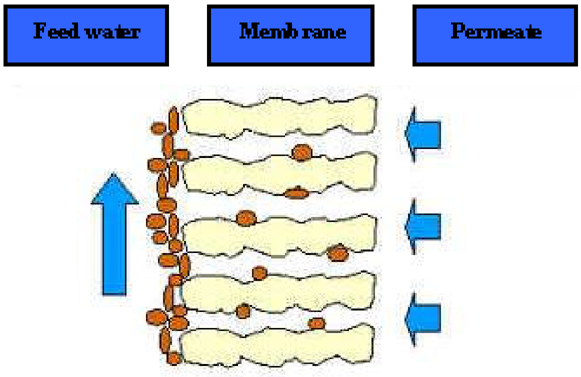

Figure 2.7 Backward flushing (www.lenntech.com)

2.5.3 Air Flush or Air/ Water Flush

Fouling on the membrane surface needs to be removed as effectively as possible during backward flush. The so-called air flush, a concept developed by Nuon in cooperation with DHV and X-flow, has proved to be very useful to perform this process. Using air flush means flushing the inside of membranes with an air/ water mixture. During an air flush air is added to the forward flush, causing air bubbles to form, which cause a higher turbulence. Because of this turbulence the fouling is removed from the membrane surface. The benefit of the air flush over the forward flush is that it uses a smaller pumping capacity during the cleaning process. Air or air/water flushing is shown in Figure 2.8.

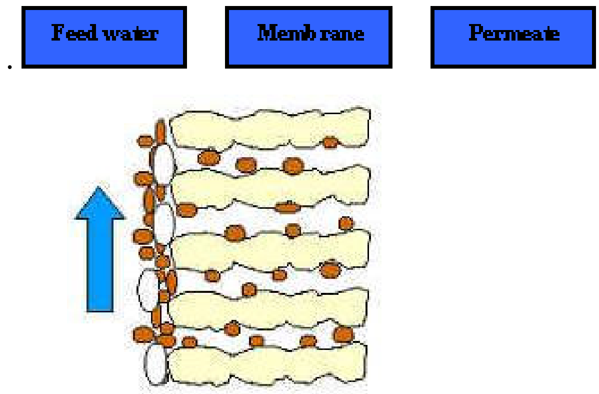

Figure 2.8 Air or air/water flushing (www.lenntech.com)

2.5.4 Chemical Cleaning

When the above-mentioned cleaning methods are not effective enough to reduce the flux to an acceptable level, it is necessary to clean the membranes chemically. During chemical cleaning chemicals, such as hydrogen chloride (HCl) and nitric acid (HNO_3), or disinfection agents, such as hydrogen peroxide (H_2O_2) are added to the permeate during backward flush. As soon as the entire module is filled up with permeate, the chemicals need to soak in. After the cleaning chemicals have fully soaked in, the module is flushed and, finally, put back into production. Cleaning methods are often combined. For example, one can use a backward flush for the removal of pore fouling, followed by a forward flush or air flush. The cleaning method or strategy that is used is dependent on many factors. In practice, the most suitable methods are determined by trial and error (practice tests) (www.lenntech.com).

There are a lot of studies related with the chemical cleaning of membranes. Avet et al. (2009) reported the cleaning results with sodium hydroxide for a 0.1 μm tubular ceramic microfiltration membrane fouled with a 3.5 wt% whey protein concentrate suspension. Alkaline cleaning was also examined for removing oil from contaminated seawater for polyethylene hollow fiber microfiltration membranes and it showed higher recovery of operating cycle time but lower permeate flux recovery than acid cleaning (Al-Obeidani et al., 2008). In addition to conventional cleaning agents, enzyme cleaning is also used for membrane cleaning purposes (Muñoz-Aguado et al., 1996; Argüello et al., 2003; Petrus et al., 2008). Petrus et al. (2008) reported that compared to other typical cleaning agents, application of enzyme in cleaning of membranes fouled with protein solution promised the high cleaning efficiencies with lower environmental impact.

2.6 Membrane Applications in Wastewater Reuse

Natural water resources become insufficient and water scarcity problems are widespread all over the world. Water reuse is considered as one of the supplementary solution to water shortage (Yarar, 2009). In several parts of the world, water reuse is becoming an important issue to satisfy future water demands (Reissmann & Uhl, 2006). Within the next fifty years, it is estimated that 40% of the world's population will live in countries facing water stress or water scarcity (Aertgeerts & Angelakis, 2003). A continuously increasing world population as well as higher quality standards and expenses for drinking water lead to numerous efforts to apply water reuse systems (Reissmann & Uhl, 2006).

Implementation and enforcement of stringent environmental regulations over the last two decades has created opportunities for industries to reduce and reuse wastewater from their manufacturing processes. Even though the cost benefits of reusing wastewater may not be realized immediately, the intangible benefits of preventing contamination of the environment on a short- or long-term basis can be significant (Ersu, Braida, Chao & Ong, 2003). Water resources in developing countries in arid and semi-arid regions of the world with rapidly growing populations and limited economic resources need special attention (Asano & Levine, 1998).

Wastewater reuse has become increasingly important in water resource management for both environmental and economic reasons. Wastewater reuse has a long history of applications, primarily in agriculture, and additional areas of applications, including industrial, household, and urban, are becoming more prevalent. Of them all, wastewater reuse for agriculture still represents the large reuse volume, and this is expected to increase further, particularly in developing countries (UNEP, 2002).

Wastewater reuse cannot only help to maintain downstream environmental quality and reducing the demand for fresh water sources, but can also offer committees opportunity for pollution abatement by reducing effluent discharge to surface waters (Davis & Hirji, 2003). Wastewater reuse is an opportunity to shorten the hydrological cycle until the water is used again and can be utilized when it offers sufficient environmental, social, economic, and political benefits (www.watercorporation.com).

The choice of the right wastewater treatment technologies is the most important thing in planning the water reuse system because they are the important way of decreasing or eliminating the environmental risk. The environmental risk is connected with the contamination that can be finding in the upgraded wastewater and generally risk can be divided into chemical and microbiological. The fundamental purpose of water treatment is to protect the consumer from pathogens and from impurities in the water that may be injurious to human health or offensive. Where appropriate, treatment should also remove impurities which, although not harmful to human health, may make the water unappealing, damage pipes, plant or other items with which the water may come into contact, or render operation more difficult or costly (Urkiaga, n.d.).

Membrane processes are thus increasingly popular for wastewater reuse applications, since they could play a key role in removing the complex components of dissolved and particulate matter contaminants in wastewater (Kang & Choo, 2003). On comparison with traditional physical/chemical treatment processes, membrane processes have the advantages of approving water quality, saving space, saving chemical dosage, and reducing sludge production. Among the membrane processes, crossflow UF and RO are pressure driven separation processes widely used in concentrating and purifying or separating molecules, colloids, suspended particles, and salts from solutions in many industrial fields. Moreover, membrane processes also is a better choice over the traditional separation methods due to their unique properties, such as no phase change, no chemical addition, and simple operation (Juang, Tseng & Lin, 2007). As advances are made in the technology and science underlying membranes, it is proving feasible to replace portions of the conventional wastewater treatment train with membrane processes (Bourgeous, Darby & Tchobanoglous, 2001).

Micro and ultrafiltration are used for both industrial and non-industrial applications of water reuse. They can be utilised as tertiary treatments due to microbiological retention (< 0.45 μm). As physical barriers they can guarantee the suitable microbiological quality without eliminating other valuable compounds as for example nutrients or fertilisers. In the same way, in the industry they can be used for process water recycling, for example in the case of rinsing baths in order to recycle or recover valuable substances (raw material, chemical agents, detergents, heat, etc.). These treatments can be used as single processes or as pre-treatment for other processes as for example nanofiltration or reverse osmosis. Reverse osmosis as final step will produce regenerated water of a very high quality. Reverse osmosis has been extensively used for seawater desalination but some authors have verified that reverse osmosis from wastewater is more cost effective than from seawater. The improvements in the technology and the increase of reverse osmosis utilisation have contributed to a very important decrease of the cost of this process (Urkiaga, n.d.).

Industrial wastewater reuse is one of the important components of water reuse. The suitability of reclaimed water for use in industrial processes depends upon the particular use. For example, the electronics industry requires water of almost distilled quality for washing circuit boards and other electronic components. On the other hand, the tanning industry can use relatively low-quality water. Requirements for textiles, pulp and paper and metal fabricating are intermediate. Thus, in investigating the feasibility of industrial reuse with reclaimed water, the potential users must be contacted to determine specific requirements for process water (Yarar, 2009).

Reclaimed water can be used for several purposes, such as landscape and agricultural irrigation, industrial processing, heating and cooling, dust suppression and soil compaction, flushing toilets in commercial buildings, wetland enhancement, stream flow augmentation, and groundwater recharge. Among these, industrial usage of reclaimed water is one of the important components of water reuse applications. Reclaimed water for industrial reuse may be derived from in-plant recycling of industrial wastewaters and/or municipal water reclamation facilities. The suitability of reclaimed water for use in industrial processes depends upon the particular use. Some industries, such as electronics industry, require high quality water. On the other hand, the tanning industry can use relatively low-quality water. Requirements for textiles, pulp and paper and metal fabricating are intermediate. Therefore, in order to determine specific requirements for process water, the feasibility of reuse of reclaimed water in any industrial facility must be determined with the potential users.

CHAPTER THREE

INTRODUCTION TO ORGANIZED INDUSTRIAL DISTRICT

3.1 Definition of an Organized Industrial District

Organized industrial districts can also be called as an organized industrial zone (OIZ) or industrial parks. In fact, industrial park is the general term which is used for the area zoned and planned for the purpose of industrial development. There are mainly six types of industrial parks in Turkey (www.turkisheconomy.org.uk).

1) Free Trade Zones
2) Organized Industrial Districts/Zones
3) Technology Development Zones
4) Industrial Zones
5) Industrial Sites
6) Trade and production centers composed of workshops

OIDs operate in line with Law No. 4562 dated 2000 and regulating establishment, building and operation of OID's defines them as follows:

Organized Industrial Districts/Zones (OIZs): The good and service production zones, which are formed by allocating the land parcels, the borders of which are approved, for the industry in a planned manner and within the framework of certain systems by equipping such parcels with the necessary administrative, social, and technical infrastructure areas and repair, trade, education, and health areas as well as technology development regions within the ratios included in zoning plans and which are operated in compliance with the provisions of the Law no 4562 in order to ensure that the industry gets structured in approved areas, to prevent unplanned industrialization and environmental problems, to guide urbanization, to utilize resources rationally, to benefit from information and informatics technologies, and to ensure that the types of industries are placed and developed within the framework of a certain plan (Organized Industrial Zones Implementation Regulation, 2009).

An OID is a production park and the followings are targeted:

- Enabling the industry to be structured in appropriate areas in a sound manner,
- Managing the urbanization process in the country,
- Preventing the environmental problems,
- Benefiting from information and communications technologies,
- Integrating the economic actors in the local areas,
- Facilitating the transfer of know-how among small and medium sized organizations,
- Providing all necessary infra and supra structure services at very reasonable costs (www.turkisheconomy.org.uk).

OIDs help prepare the industrial infrastructure for investment (roads, drinking water, water for business use, electricity, communications, waste treatment). Industrialists thus move to these zones with infrastructure to start up their operations (www.yoikk.gov.tr).

OIDs are accepted a crucial industrialization and city and region planning tool. As a city and region planning tool, industrial parks are: controlling industrial development, obtaining systematic urbanization, balancing regional development and pioneering new cities establishment and improvement. As an industrialization tool, industrial parks are provided great economic advantages and encouragements for entrepreneurs. Firms existing in industrial parks benefit from external and agglomeration economies so their competition power increase. In addition to being an effective means of practicing macro policies, the policy of industrial parks, is accepted as a considerable way of industrialization by improving industry, modernizing industry establishments according to increasing productivity and profit, decreasing costs and improving quality of products (Türk, 2006).

OIDs offer many economic advantages to industrialists, local communities and countries. The economic benefits of OIDs arise to an important degree from the following:

1. Economies of scale derived from the development of the park
2. External economies accrued largely from the aggregation of enterprises
3. Provision of certain services which become feasible as a result of an aggregation of a sufficient large number of firms (Türk, 2006).

3.2 OIDs in the World

In Hong Kong, industrial parks are usually known as industrial estates. In the United Kingdom small industrial parks containing multiple units all of the same style is known as trading estates. A more "lightweight" version is the business park or office park, which has offices and light industry, rather than heavy industry (http://en.wikipedia.org/wiki/Industrial_park).

OIDs began to appear just over 110 years ago in the United Kingdom and the United States. Development of OIDs had been slow until the Second World War. However, industrial parks have been used with increasing success since the Second World War in Europe and other developed countries. But some of Europe countries like Germany, Austria, The Netherlands and Scandinavia frequently, cities have promoted industrial zones which in concept have approached what are called industrial tract in the United States. That are areas have been set aside for industrial use and municipalities have been taken the initiative to provide them with the utilities required for manufacturing. In Italy and the United Kingdom, OIDs have been used for promoting and guiding industrialization in undeveloped regions (Türk, 2006).

OIDs in developing countries, which adopt planned development as means of development in developing countries have taken encouragement precautions in order to have balanced development among regions, active resources in developing regions, stop unemployment so that reduce the social cost that emerged by industry and relocate industry in undeveloped regions (Türk, 2006)

In European Union, “Opinion of the European Economic and Social Committee on ‘The role of technology parks in the industrial transformation of the new Member

States (2006/C 65/11)'" was published. Some examples taken from this document are given below:

In the Czech Republic, 82 industrial zones were set up through Czech Invest, the government agency to promote investment, in the framework of the governments program to support the development of industrial zones. In 2001 further sub-programs on Regenerating industrial zones, Building and regenerating leasable properties and Accreditation of industrial zones were added.

There are several types of industrial park in Estonia, denoted and defined in various ways. Some of them have been set up with the support of local/regional authorities and other organizations; primarily concerned with research and development, they operate in cooperation with major universities.

Most 'industrial parks' in Poland were set up over the past few years. At present, their economic impact is negligible, primarily because the main channels for investment, and foreign investment in particular, are the 14 Special Economic Zones (SEZ). These zones were set up by government acts in 1995-97 for a period of 20 years in industrially underdeveloped regions or regions in need of industrial restructuring, as part of support for regional development. Initially they offered investors 100 % exemption from corporate tax for the first ten years, and 50 % over the next ten years, together with full exemption from property tax. On 1 January 2001, these incentives were brought into line with EU legislation. Given that the special status of SEZs will expire by December 2017 at the latest, the quantity, role and land area of industrial parks is likely to grow.

In Latvia parks are referred to as 'business parks', and they attract companies by means of favorable infrastructure and administrative conditions. The Latvian Innovation Act provides for a national research and development program.

In Lithuania, decisive government efforts aimed at stimulating development of labor-intensive, relatively high value- added industries (automotive electronics,

electronics) and knowledge-based industries and services (biotechnology, IT, laser technology) have significantly contributed to industrial restructuring. The program, launched in the late 1990s, to build ‘industrial parks’ with proper infrastructure near cities, was designed to develop Lithuania's economy, focusing as it did on industrial development in the immediate vicinity of urban centers, in view of the availability of skilled labor there.

In Hungary, the government has been operating a system to develop industrial parks since 1997. Individual parks submit their long-term development plans for assessment by the Ministry of Economic Affairs, and if they are of a sufficiently high standard, they are awarded the title of industrial park. The objectives of industrial parks are to enhance competitiveness, to create jobs, and to put in place the conditions for environmentally friendly industrial activity, as well as logistical and other services which comply with EU standards. There are approximately 2 500 companies, both multinationals and Hungarian small and medium enterprises, with over 140 000 employees, in Hungarian industrial parks.

In Malta, economic statistics from recent years show that industrial manufacturing makes a relatively substantial contribution to the economy. Malta Enterprise, a company whose objective is to promote investment, has set up a Business Incubation Centre to support pioneering projects in fields such as IT, telecommunications, mechanical and electrical engineering design, industrial design, renewable energy sources and biotechnology. The Incubation Centre provides facilities for investment or financing, together with a wide range of infrastructure services, to companies operating in the above sectors.

Support for industrial parks in Slovakia is regulated by Act No 193 on support for industrial parks, adopted in 2001 and amended in 2003 and 2004. This act defines an industrial park as an area designated in the spatial plan in which one or more enterprises is engaged in industrial manufacture. Local and regional authorities can set up industrial parks on land owned by them; the Act also provides for joint establishment of industrial parks on the basis of a contract between two or more authorities.

In Slovenia, parks are referred to as ‘technology parks’. Their purpose is to act as a catalyst for business ideas making use of state-of-the-art technology and a high degree of scientific know-how. In addition, they put in place the physical and intellectual infrastructure for such initiatives with particular attention to the needs of small and medium enterprises, and liaise between businesses and institutions of higher education. The Ministry of Economic Affairs defines a technological park as a legal entity which assists in the execution of projects, in contrast to incubators, which are also legal entities, but only create the starting conditions for projects (EU, 2006/C 65/11).

According to studies made by the United Nations; an often-quoted estimate from 1996 puts the number of parks globally at more than 12000. Growth in the developing countries of Asia has been rapid and recent estimates indicate that there may now be more than 20000 OIDs globally by 2000 in China and over 5000 parks in other parts of the region. The numbers of industrial parks have been increasing worldwide with a particular interest in the industrializing countries (Türk, 2006).

Another term, eco-industrial park (EIP), is also used in the world. EIP is an industrial park in which businesses cooperate with each other and with the local community in an attempt to reduce waste and pollution, efficiently share resources (such as information, materials, water, energy, infrastructure, and natural resources), and help achieve sustainable development, with the intention of increasing economic gains and improving environmental quality. An EIP may also be planned, designed, and built in such a way that it makes it easier for businesses to co-operate, and that results in a more financially sound, environmentally friendly project for the developer (http://en.wikipedia.org/wiki/Eco-industrial_park).

3.3 OIDs in the Turkey

In Turkey, the first organized industrial district (OID) was established in 1962. Nowadays, although the amount of planned OID is about 250, only 70 of them are in operation all throughout Turkey. To overcome some environmental pollution problems, OIDs are considered as a good choice. Organized pattern of these industrial zones is an advantage to the Turkish economy as the country is rapidly industrializing. Unless such incentives are given to the financiers' environmental control costs to be added to the product costs will not easily let industries compete in the interest rates, operating costs are not small and with the influence of the European Market subsidies must come down soon. Therefore, the only way out for competing international markets is using the wisdom and knowledge in better industrial planning to optimize the use of common infrastructure and minimize pollution control costs. Among these costs shared costs of water supply and wastewater collection/treatment systems make up a good proportion of the overall investments (Filibeli, Sengül & Müezzinoglu, 1996).

In Turkey, the OID policy has been constituted in the Five Year Development Plans by State Planning Organization (SPO) since 1970. These objectives have been; achieving balanced regional development, using industrial parks as an urban development planning tool, directing industrial development, decentralizing industry and reducing unemployment by providing incentives and disincentives for manufacturing firms. Nevertheless, they have not been achieved yet. But on the contrary, manufacturing firms have selected location in the provinces of most developed regions of Turkey, Marmara and Aegean Regions. This practice was contrast to the industrial park policy of SPT. Thus the Ministry of Industry and Trade became a law of industrial park in 2000. Aim of the law is to regulate location selection, establishment and management of industrial parks as an urbanization and industrialization planning tool. Just now the developed cities have too many established and establishing parks that cause unexpected and uncontrolled urban growth, social problems, less economic growth and idle capacity. Thus, structure and historical development of manufacturing industry of each city should be analyzed and an industrial park planning should be made based on the law and the objectives of SPO (Türk, 2006).

Increases in the amount of OID will cause an increase the usage of water. The State Statistics Institute has regularly performed periodical surveys on OIDs. Depending on these surveys obtained from 70 OIDs whose substructures were finished, the amount of discharged wastewater from these OIDs was 75.315 Mm^3 and 107.577 Mm^3 in 2000 and 2002, respectively (Ustun and Solmaz, 2007). Only 66% of all wastewater was treated but it was not evaluated for reuse possibility. Reclamation and reuse of wastewater are of great interest and viable options for many industrial sectors and countries which suffer from water scarcity problems (Solmaz, Üstün, Birgül, & Taşdemir, 2007). Ciner and Eker (2007) reported that 216 different scale unified (i.e. tanneries, textile) or mixed OIDs have been planned up in Turkey and more than 59 of them have been constructed and activated by 2004. It is the fact that 17 of them have their own constructed treatment plants and 9 of them discharge the wastewater directly into the municipal sewerage system or wastewater treatment plants while the rest still discharge into receiving waters without treatment.

CHAPTER FOUR
MATERIALS AND METHODS

4.1 Introduction of the Pilot Plant

In this study, an Organized Industrial District (OID) was selected a pilot plant. There are many companies here on the Zone that are both leaders within their sectors and stand among the largest companies of Turkey. The list of companies on this OID is given in Table 4.1.

Table 4.1 The list of companies on an OID

Sector	Number of Sector	Sector	Number of Sector
Automotive Sub-Industry	15	Bycyle Sector	1
Cement Industry	1	Chemistry Industry	2
Construction & construction materials	1	Electrical Devices Industry	1
Electrical Machinery Industry	2	Electronics Industry	17
Food Industry	6	Forestry Industry	5
Glass Sector	1	Heatproof Lining Materials Manufacturing Industry	1
Heating Devices Industry	2	Machine Mould Industry	5
Iron & Stell Industry	5	Hardware Industry	10
Miscelleneous Manufacturring Industry	2	Moulding Industry	4
Non-ferrous Metal Industry	24	Packaging Sector	2
Paper & Paper Products Industry	2	Paper-Packaging Industry	4
Petro-Chemical Industry	1	Plastic Industry	12
Printing Sector	4	Terracotta-cement-appliances Industry	1
Textile & Clothing Industry	9	Tobacco & Tobacco Products Industry	1
White Goods Sector	5	White Goods Sub-Sector	16

The OID have a central biological and chemical wastewater treatment plant with a capacity of 6500 m^3/day that was completed in June 1993; it has been working efficiently to the present day.

The continued industrial development in the Organized Industrial Zone has resulted in an increase in the amount of wastewater being discharged. Over time the capacity of OID existing wastewater treatment plant became insufficient to handle the volume; therefore it was decided to construct Part II of the wastewater treatment facility. Wastewater treatment plant with a capacity of 5.000 m^3/day; the extended facility came into operation in December 2001.

The infrastructure of the zone is still expanding; therefore the wastewater plant has been developed to handle the anticipated volume that will be created from the development of Phases IV and V, to obviate the need for any additional investment. The plant extends over an area of 51.460 m^2 and has a total capacity of 21.500 m^3/day. The OID wastewater treatment plant flow scheme is given in Figure 4.1.

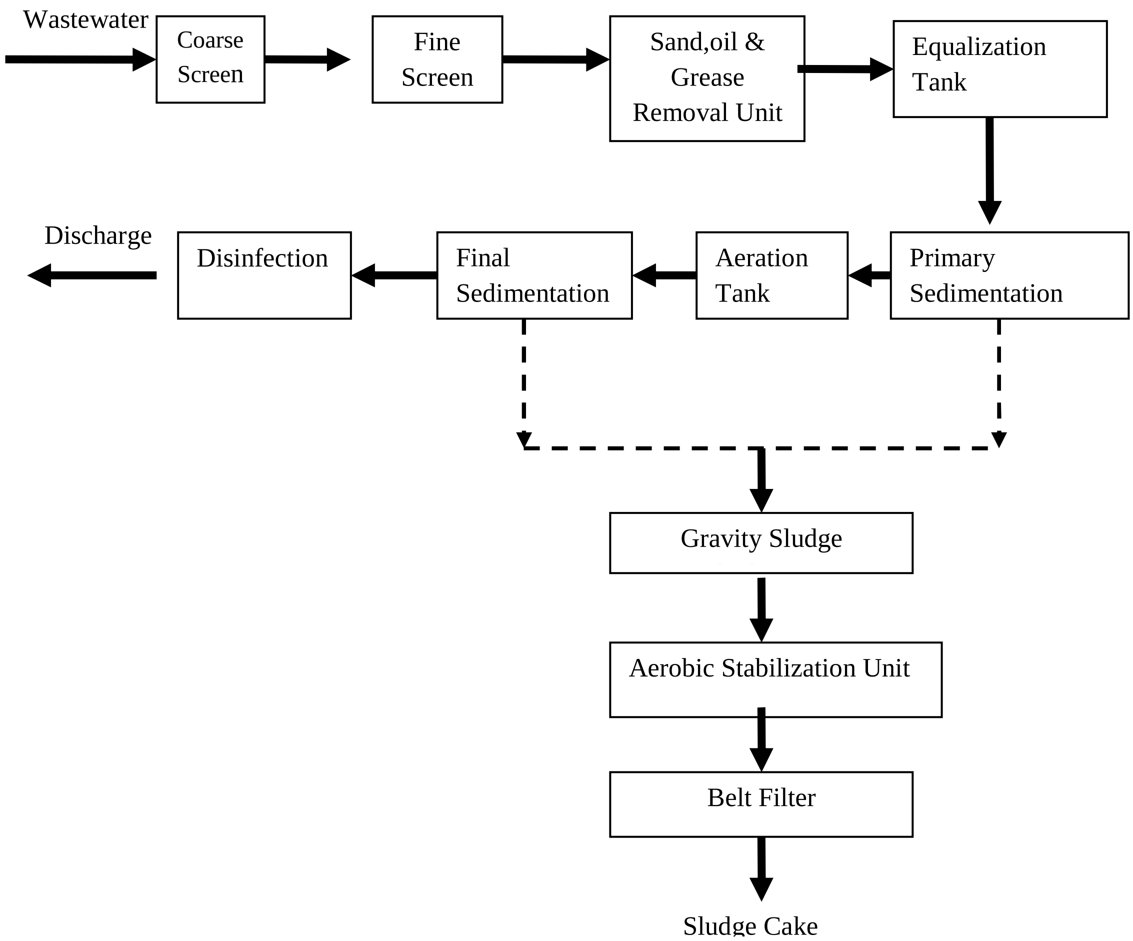

Figure 4.1 Wastewater treatment plant flow scheme of the OID

The quality of treated effluent of the OID's wastewater treatment plant was compared with the Regulation Standards (Water Pollution Control Regulation, 2004). This comparison can be seen in Table 4.2. This data was taken from the plant.

Table 4.2 The comparison of the quality of treated effluent of the OID Wastewater Treatment Plant with the obligated standard values in regulation standards.

Parameters	**Unit**	**Design Concentration Inlet**	**Regulation Standards**		**Plant Effluent**
			Composite Sample (2hr)	**Composite Sample (24 hr)**	
COD	mg/L	2700	400	300	100
SS	mg/L	800	200	100	25
Oil & Grease	mg/L	400	20	10	7
Total P	mg/L	20	2	1	1
Total Cr	mg/L	2	2	1	0.06
Cr^{+6}	mg/L	2	0.5	0.5	0.01
Pb	mg/L	2	2	1	0.3
Total CN	mg/L	1	1	0.5	0.03
Cd	mg/L	1	0.5	-	0.03
Fe	mg/L	2	10	-	1
F	mg/L	2	15	-	1.25
Cu	mg/L	2	3	-	0.25
Zn	mg/L	2	5	-	0.1
Hg	mg/L	0.05	-	0.05	-
SO_4	mg/L	-	1500	1500	220
TKN	mg/L	-	20	15	3
Fish Bioassay	-	-	10	10	5
pH	-	7.9	6-9	6-9	7.5

4.2 Laboratory Scale Membrane System

In this study, effluent of the treatment plant (EW) was subjected to the laboratory scale membrane system (Millipore) using Prep/Scale® Spiral Wound Ultrafiltration Modules. This system has a simple design for easy set-up. A peristaltic pump is used for wastewater pumping to the membrane. Inlet and outlet pressure is measured using pressure measurement devices attached to the module.

Ultrafiltration (UF) membranes are rated according to the nominal molecular weight limit (NMWL), also sometimes referred to as molecular weight cut-off

(MWCO). The NMWL indicates that most dissolved macromolecules with molecular weights higher than the NMWL will be retained. An ultrafiltration membrane with a stated NMWL should retain (reject) at least 90% of a globular solute of that molecular weight in Daltons (Millipore catalogue). In this study, three different size of UF with a molecular weight cut-off (MWCO) of 100 kDa, 30 kDa, and 1 kDa were used. Effective filtration area of this membrane system is 0.54 m^2. The membranes are made from regenerated cellulose material. In Figure 4.2, photo of the membrane module and membrane cartridges are given. The retentate (concentrate) and permeate collected after each run were analyzed. Membrane cartridges were cleaned with 0.1 N NaOH solutions.

Figure 4.2 Laboratory Scale Membrane System and Cartridges

4.3 Analytical Procedure

In the experimental studies, chemical oxygen demand (COD), suspended solid (SS), pH and conductivity (EC) analysis were taken into consideration. SS and COD analyses were done according to Standard Methods that published by American Public Health Association, American Water Works Association, & Water Environment Federation (APHA, AWWA, WEF, 2005). pH and conductivity were measured by WTW model 340i multi analyzer.

CHAPTER FIVE
RESULTS AND DISCUSSIONS

5.1 Characteristics of an OID Wastewater Treatment Plant Effluent

Experimental studies were carried out with the samples taken from the OID wastewater treatment plant effluent. General properties of the effluent are given in Table 5.1. The measurements were done three times.

Table 5.1 General characteristic of the OID wastewater treatment plant effluent

Parameter	Value
Suspended solids (mg/L)	20±5
Chemical oxygen demand (mg/L)	100±20
Conductivity (mS/cm)	3.2±0.1
T-N(mg/L)	3.4±0.1
T-PO_4-P(mg/L)	0.3±0.01
TOC	78.5±0.5
pH	7.5±0.5

5.2 Determination of the Membrane System Properties

During Ultrafiltration, it is important to balance speed with retention to obtain optimal performance. A membrane’s flux is defined as the flow rate divided by the membrane area. Using membrane with higher nominal molecular weight limit (NMWL) ratings will increase the flow, but at the same time lower the retention. A membrane should be selected for required rejections, consistent with desired flow rate. This is determined by surface area, macrosolute type, solubility, concentration and diffusivity, membrane type, temperature effects on viscosity and, to some extend, pressure. When concentration polarization is rate-controlling, flux is affected by solute concentration, fluid velocity, flow channel dimensions, and temperature.

In general, flux increases with increasing transmembrane pressure (TMP). These effects are most apparent when operating under controlled positive pressure, such as when using a stirred cell. When the process is membrane-controlled (i.e., when the resistance of the gel layer is much smaller than that of the membrane), the flux-pressure relationship is linear. When the process is controlled by polarization (e.g., when the resistance of the gel layer is much larger than that of the membrane), flux will reach a plateau and may actually decrease with increases in pressure. When concentration of the retained species is very low, flux is independent of concentration. As solute concentration rises during operation, increased viscosity and the polarization effect cause flux to decrease (Millipore, 2004).

Permeate flux is one of the most important operating parameter during membrane filtration. Flux changes were monitored depending on the various transmembrane pressures (TMP) for each membrane cartridge. The results showed that the membrane with MWCO 100 kDa gave higher fluxes compared to the others (Figure 5.1). Almost linear relationship between TMP and permeate flux was obtained for 30 kDa (R^2 = 0.98) and 100 kDa (R^2 = 0.95) membranes. It can be observed that permeate flux increases proportionally with TMP in these two membranes. However, flux values were almost kept constant for 1 kDa membrane at all TMP. Recovery rate and flux values are dependent variables. For the membrane 1 kDa, very low recovery rates were obtained (2.5 % - 5.3%). Better results were achieved with 30 kDa and 100 kDa membrane. The maximum recovery rate was 26.8 % and 35.3 % for 30 kDa and 100 kDa membrane, respectively.

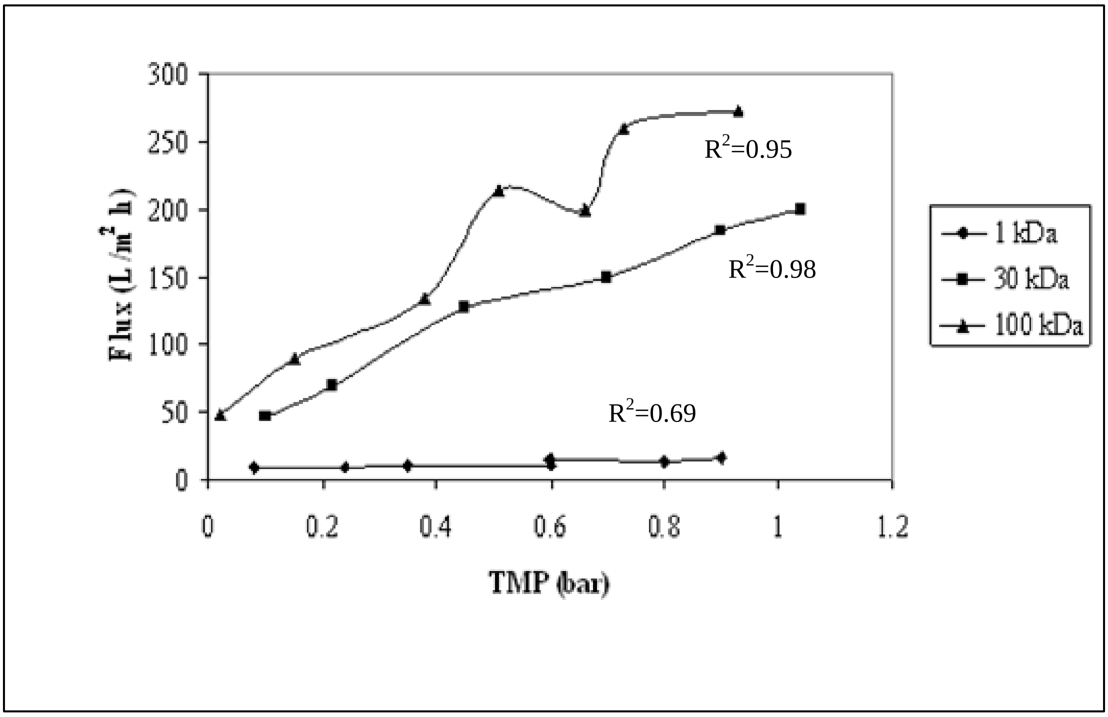

Figure 5.1 Fluxes versus TMP

5.3 Effect of TMP on Permeate Quality

5.3.1 Suspended solids

Required process water quality changes depend on the each plant. For example; SS concentration of process water should be lower than 10 mg/L, 5 mg/L, and 500 mg/L for pulp and paper, chemical and textile, and cement industry, respectively (EPA, 2004). In general, industrial plants need process water having less suspended solids (SS).

SS content of the secondary effluent of the OID wastewater treatment plant is about 25 mg/L. In order to remove SS, several filtration methods, such sand filtration (Mulligan et al., 2009, Healy et al., 2007) and membrane filtration (Li et al., 2008, Viadero and Noblet, 2002) have been applied. Ultrafiltration membrane system can produce high quality water, free of suspended solids, colloidal material and bacteria

(Taylor and Wiesner, 1999). Suspended solids concentrations after membrane applications versus TMP are given in Figure 5.2. For all membrane MWCO sizes, SS removal efficiencies decreased with increasing pressure. The lowest SS removal efficiencies were obtained at highest TMP for all membrane types and 100% SS removal efficiencies were obtained at lower TMP for each membrane.

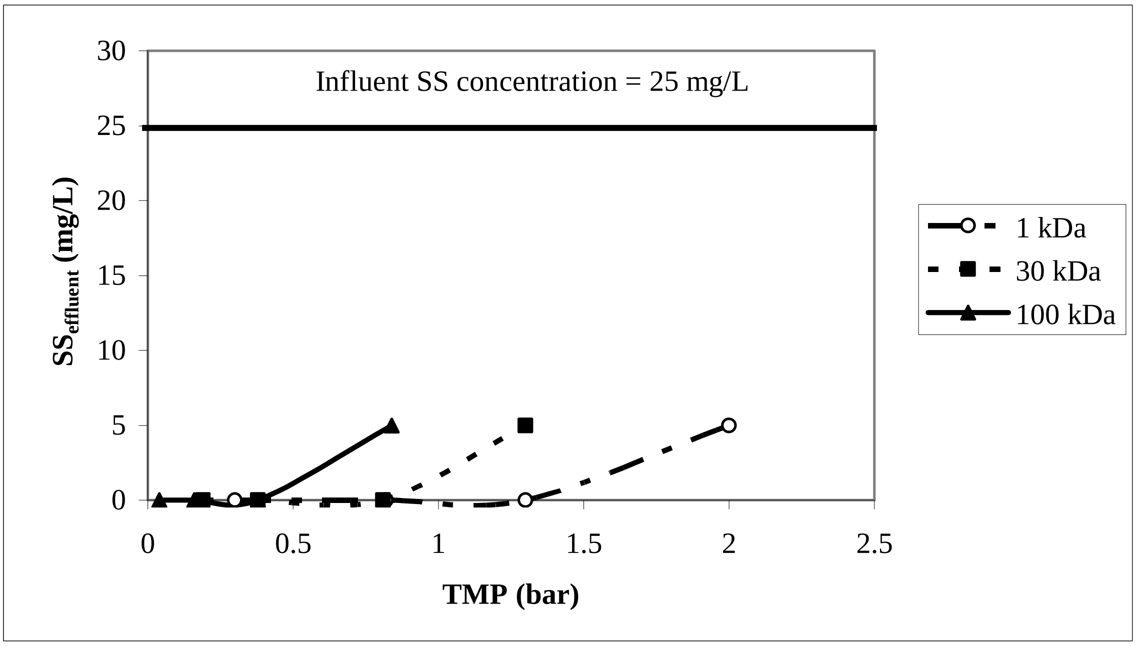

Figure 5.2 Permeate SS concentrations depending on TMP

5.3.2 Organic material

In general, process water must be low in organic matter. Therefore, good organic substances removal is essential in reclamation facilities. For the selected pilot plant, effluent COD concentration of the wastewater treatment plant is about 120 mg/L. After UF applications, maximum 67% COD removal efficiency could be obtained. This means that, the lowest COD concentration of permeate was about 40 mg/L for all tested membranes (Figure 5.3). The final level of COD is still high for some industries and may require further treatment before reuse depending on the required process water qualities. This result was not a surprise. UF is very effective for the removal of bacteria and suspended particles; however removal of organics is generally low. This is because organics that are smaller than the pore size can pass through the membrane. Arnal et al. (2008) obtained the COD rejections in the range of 35–50% with a 4-inch spiral-wound UF membrane module (IRIS 3028 10 kDa). In another study, although almost 100% COD removal efficiencies were obtained with NF, it was not possible to decrease COD with UF membranes of 5 to 100 kDa MWCO (Bes-Piá et al., 2002).

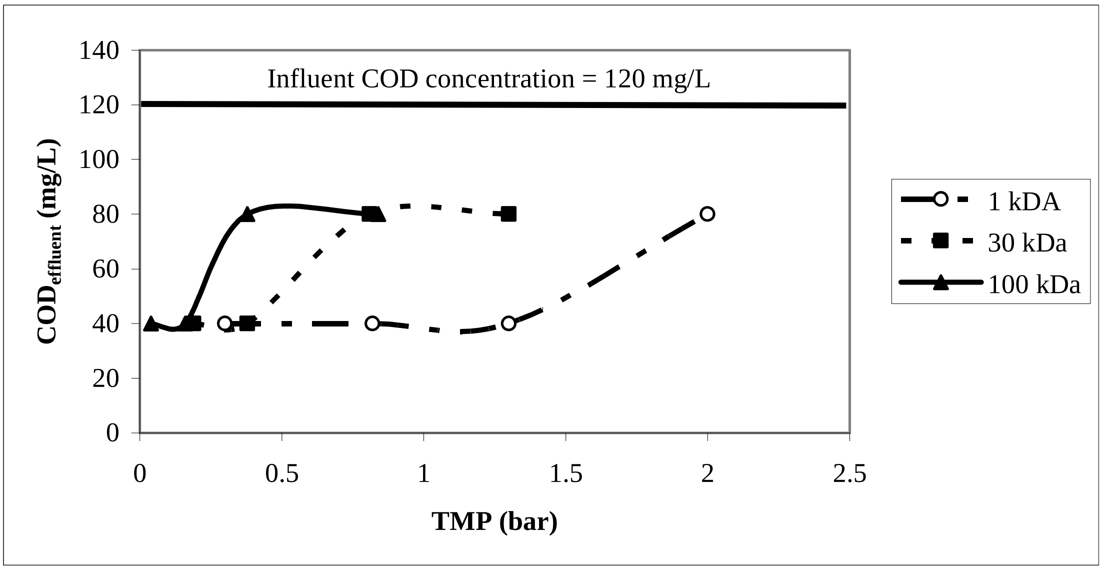

Figure 5.3 COD concentrations versus TMP

5.3.3 EC and pH

Conductivity is used as an indicator of total dissolved solids (TDS) (Metcalf and Eddy, 1991). Most of the industries require process water with low EC, e.g. it must be lower than 1.5, 0.16, and 0.94 mS/cm for chemical industry, textile industry, and cement industry, respectively (EPA, 2004). EC of fresh water and wastewater treatment plant effluent of the selected OID is 0.42 mS/cm and 3.2 mS/cm, respectively. Effluent EC value is very high for various industries. As a result of the experimental studies, significant EC reduction could not be achieved. As it is seen from Figure 5.4, permeate EC values were almost same with feed water. Pores of UF membranes are too large to reject significant amounts of TDS. In order to reduce EC of treated wastewater until this level, nanofiltration (NF) or reverse osmosis (RO) should be applied.

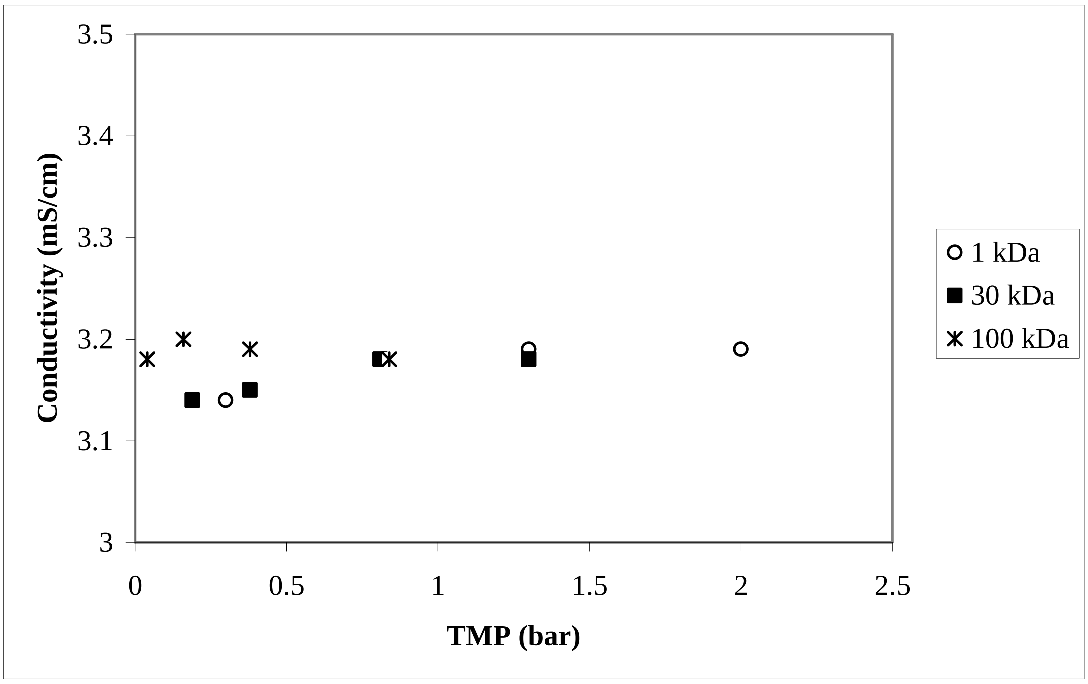

Figure 5.4 Conductivity versus TMP

In general, neutral pH is necessary for most of process water. pH of the feed water is about 8 and after UF applications, slight increases in pH were observed (Figure 5.5). However, permeate pH was always below 8.3. Therefore, reuse of permeates as process water is not problem in terms of pH parameter.

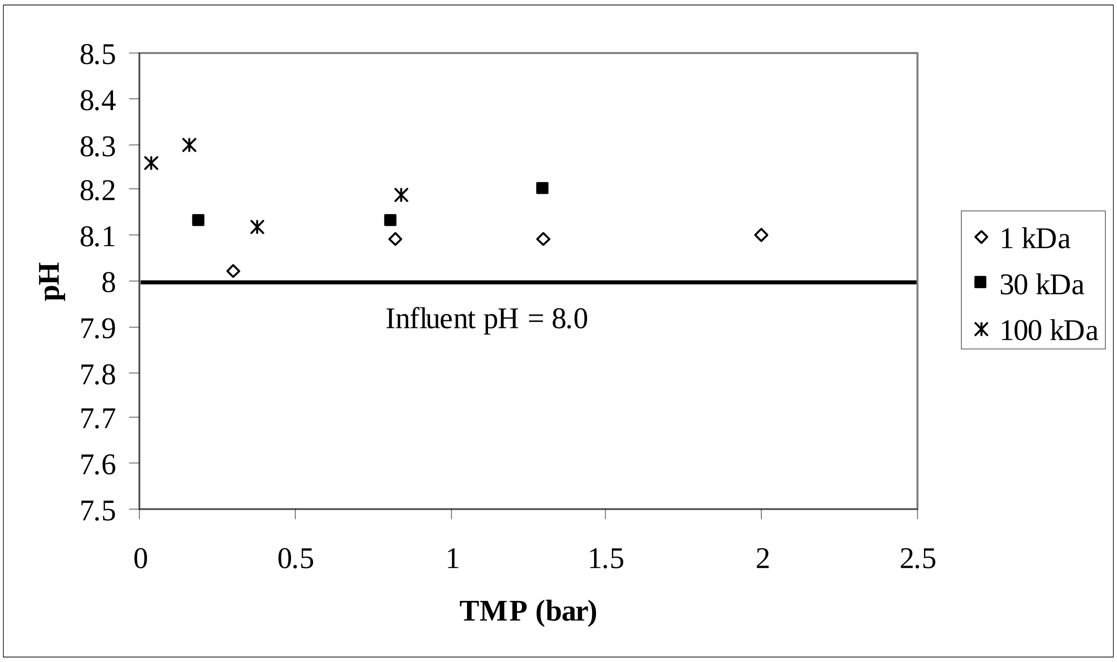

Figure 5.5 pH versus TMP

5.4 Recovery Rate Values

While rejection is used to characterize membrane performance, it does not always directly correlate with solute recovery from a sample or volume. Actual solute recovery the amount of material recovered after ultrafiltration is generally based on mass balance calculations (Millipore, 2004). Higher recovery rate is essential for optimum membrane operations. For this aim, appropriate membrane type should be selected.

Avula, Nelson and Singh (2008) determined spiral membrane modules were less tolerant to suspended solids in feed streams and more susceptible to fouling than hallow fiber modules. The result of concentration scans with two spiral membrane indicated that the fluxes were lower and the flux decline was sharper compared to the characteristics with hallow fiber.

Among the other membrane systems, UF appears to be more attractive because they promise high fluxes at relatively low pressures (Kang & Choo, 2003). In general high flux values can be obtained with UF membrane systems. However, in order to achieve high recovery rate, the quality of feed water must be good. Some pre-treatment processes, such as sand filtration, microfiltration, should applied for this aim. In this study, since wastewater treatment effluent was used as feed water, any pre-treatment process was not used. Therefore some fouling problems occurred and maximum 35% recovery rate could be obtained (Figure 5.6). Avula, Nelson and Singh (2008) reported that 20 and 80% recovery rate at 75 and 40 L/m^{2}h flux values, respectively, can be obtained with spiral membrane modules.

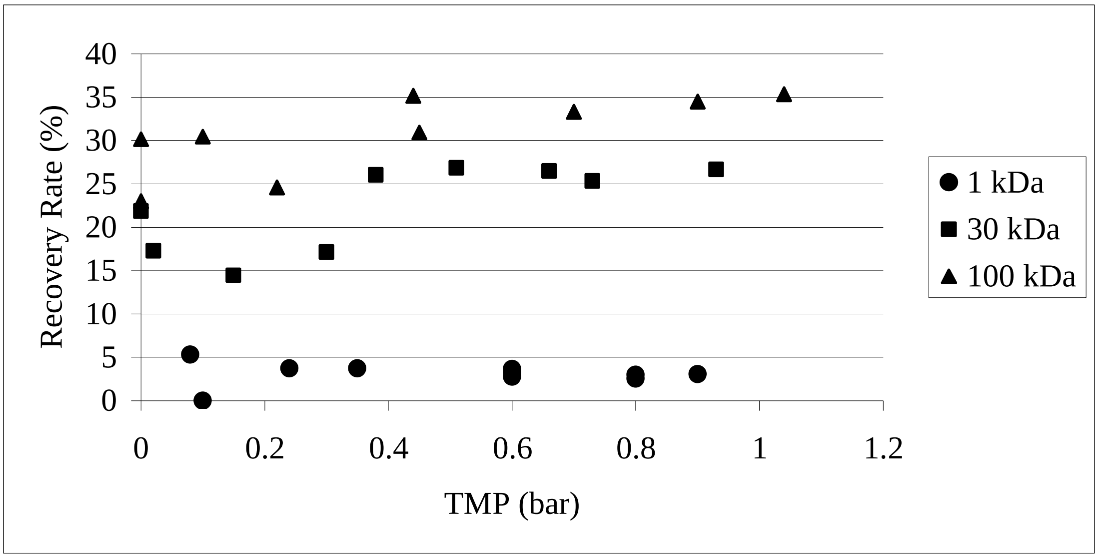

Figure 5.6 Change of recovery rate with TMP

The experimental studies results showed that the membrane with MWCO 100 kDa gave higher recovery rate compared to the others (Figure 5.6). Almost linear relationship between TMP and recovery rate was obtained for 30 kDa and 100 kDa membranes. It can be observed that recovery rate increases proportionally with TMP in these two membranes. However, recovery rate values were almost kept constant for 1 kDa membrane at all TMP. For the membrane 1 kDa, very low recovery rates were obtained (2.5 % - 5.3%). Better results were achieved with 30 kDa and 100 kDa membrane. The maximum recovery rate was 26.8 % and 35.3 % for 30 kDa and 100 kDa membrane, respectively.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this thesis, the effects of ultrafiltration on the quality of secondary effluent of an OID wastewater treatment plant have been investigated. Reuse possibilities of permeates were evaluated as process water for some industries located in the OID. Three membrane cartridges having MWCO of 1 kDa, 30 kDa, and 100 kDa were examined.

According to experimental results, the conclusion remarks from this study could be given as follows:

- The experimental studies results showed that the membrane with MWCO 100 kDa gave higher recovery rate compared to 1 and 30 kDa membranes. Almost linear relationship between TMP and recovery rate was obtained for 30 kDa and 100 kDa membranes. Recovery rate values were very low (2.5 % - 5.3%) and almost kept constant for 1 kDa membrane at all TMP. The maximum recovery rate was 26.8 % and 35.3 % for 30 kDa and 100 kDa membrane, respectively.
- For all membrane MWCO sizes, SS removal efficiencies decreased with increasing pressure. The lowest SS removal efficiencies were obtained at highest TMP for all membrane types and 100% SS removal efficiencies were obtained at lower TMP for each membrane.
- All membranes completely removed suspended solids; but the final level of COD after UF applications, maximum 67% COD removal efficiency could be obtained. This means that, the lowest COD concentration of permeate was about 40 mg/L for all tested membranes.

- The level of EC was still high for some industries and may require further treatment before reuse depending on the required process water qualities to produce a higher quality of permeates.
- pH of the feed water is about 8 and after UF applications, slight increases in pH were observed. Permeate pH was always below 8.3.
- UF membrane system can be considered as pre-treatment steps of NF or RO systems.

6.2 Recommendations

- In the experimental studies, sufficient permeate qualities could not obtained for some industries located in the OID at applied conditions. Hence, other membrane systems or different operational conditions should be examined at further researches.
- Pilot plant studies should be done to evaluate the usability of membrane filter systems.

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APPENDIX

Table 1. Flux and TMP Results

Membrane Filter MWCO	Influent P (bar)	Effluent P (bar)	TMP (bar)	Flux ($L/m^2.h$)
1kDa	0.25	0.17	0.08	9.12
	0.50	0.26	0.24	8.89
	0.80	0.45	0.35	10.67
	1.20	0.60	0.60	9.78
	1.60	1.00	0.60	14.22
	1.90	1.10	0.80	13.33
	2.20	1.30	0.90	16.00
30 kDa	0.002	0.009	0	34.00
	0.20	0.10	0.10	45.67
	0.40	0.18	0.22	68.89
	0.60	0.15	0.45	126.67
	1.00	0.30	0.70	150.00
	1.20	0.30	0.90	183.33
	1.40	0.36	1.04	200.00
100 kDa	0.10	0.08	0.02	47.78
	0.25	0.10	0.15	88.89
	0.50	0.12	0.38	133.33
	0.70	0.19	0.51	213.33
	0.90	0.24	0.66	200.00
	1.00	0.27	0.73	260.00
	1.25	0.32	0.93	273.33

Table 2. SS removal efficiencies

Membrane Filter MWCO	Influent P (bar)	Effluent P (bar)	TMP (bar)	Effluent SS concentration (mg/L)	SS Removal efficiency E (%)
1 kDa	0.40	0.10	0.30	0	100
	1.00	0.18	0.82	0	100
	1.50	0.20	1.30	0	100
	2.30	0.30	2.00	5	80
30 kDa	0.25	0.06	0.19	0	100
	0.50	0.12	0.38	0	100
	1.00	0.19	0.81	0	100
	1.50	0.20	1.30	5	80
100 kDa	0.10	0.06	0.04	0	100
	0.25	0.09	0.16	0	100
	0.50	0.12	0.38	0	100
	1.00	0.16	0.84	5	80

Table 3. Results of Experimental Studies for COD

Membrane Filter MWCO	Influent P (bar)	Effluent P (bar)	TMP (bar)	Effluent COD conc. (mg/L)	COD removal eff. (%)
1 kDa	0.40	0.10	0.30	40	66.7
	1.00	0.18	0.82	40	66.7
	1.50	0.20	1.30	40	66.7
	2.30	0.30	2.00	80	33.3
30 kDa	0.25	0.06	0.19	40	66.7
	0.50	0.12	0.38	40	66.7
	1.00	0.19	0.81	80	33.3
	1.50	0.20	1.30	80	33.3
100 kDa	0.10	0.06	0.04	40	66.7
	0.25	0.09	0.16	40	66.7
	0.50	0.12	0.38	80	33.3
	1.00	0.16	0.84	80	33.3

Table 4. Effect of UF on EC and pH

Membrane Filter	Influent P (bar)	Effluent P (bar)	TMP (bar)	Conductivity (mS/cm)	pH
1kDa	0.40	0.10	0.30	3.14	8.20
	1.00	0.18	0.82	3.18	8.09
	1.50	0.20	1.30	3.19	8.09
	2.30	0.30	2.00	3.19	8.10
30 kDa	0.25	0.06	0.19	3.14	8.13
	0.50	0.12	0.38	3.15	8.11
	1.00	0.19	0.81	3.18	8.13
	1.50	0.20	1.30	3.18	8.20
100 kDa	0.10	0.06	0.04	3.18	8.26
	0.25	0.09	0.16	3.20	8.30
	0.50	0.12	0.38	3.19	8.12
	1.00	0.16	0.84	3.18	8.19

Table 5.Recovery rate

Membran Filter	Influent P (bar)	Effluent P (bar)	TMP (bar)	Recovery Rate (%)
1kDa	0.25	0.17	0.08	5.30
	0.50	0.26	0.24	3.74
	0.80	0.45	0.35	3.72
	1.20	0.60	0.60	2.78
	1.60	1.00	0.60	3.24
	1.90	1.10	0.80	2.99
	2.20	1.30	0.90	3.05
30 kDa	0.002	0.009	0	17.31
	0.20	0.10	0.10	14.47
	0.40	0.18	0.22	17.13
	0.60	0.15	0.45	26.03
	1.00	0.30	0.70	26.50
	1.20	0.30	0.90	25.35
	1.40	0.36	1.04	26.67
100 kDa	0.10	0.08	0.02	22.99
	0.25	0.10	0.15	30.44
	0.50	0.12	0.38	30.93
	0.70	0.19	0.51	35.16
	0.90	0.24	0.66	33.33
	1.00	0.27	0.73	34.52
	1.25	0.32	0.93	35.34