DOKUZ EYLUL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

WASTEWATER REUSE AND WATER OPTIMISATION AT THE PULP AND PAPER INDUSTRY

by
Murat YARAR

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WASTEWATER REUSE AND WATER OPTIMISATION AT THE PULP AND PAPER INDUSTRY

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M. Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"WASTEWATER REUSE AND WATER OPTIMISATION AT THE PULP AND PAPER INDUSTRY"** completed by **MURAT YARAR** 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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ABSTRACT

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. Several researches have been carried out about this subject.

The pulp and paper industry has a high fresh water demand. In the case of water shortage, paper production could not be performed. Therefore, additional sufficient amount of qualified water sources should be found. Reclaimed water reuse as process water could be one of the feasible solution. In this thesis, evaluation of this alternative is aimed.

The experimental studies were carried out with the samples taken from the effluent of the chemical treatment unit and discharge point of the wastewater treatment plant of a pulp and paper industry. Firstly, properties of these two effluents were compared with the required process water quality for direct reuse of the effluents in the process. After then, a laboratory scale membrane filter system was applied to the effluents as an advanced treatment. TOC, COD, SS, pH, and conductivity analysis were carried out on the influent and effluent of the membrane. The experimental results were evaluated in term of utilization of membrane technology to reclaim water for reuse as process water.

Keywords: Paper industry, wastewater reuse, membrane filter systems

KAĞIT ENDÜSTRİSİNDE ATIKSU GERİ KULLANIMI VE SU OPTİMİZASYONU

ÖZ

Doğal su kaynaklarının miktarı gün geçtikçe azalmakta ve dünyanın büyük bir kesiminde su kıtlığı problemi yaşanmaktadır. Atıksuların yeniden kullanılması su kıtlığı probleminin çözümünde yardımcı bir etmen olarak düşünülmektedir. Bu konuda yapılmış ve yapılmakta olan pek çok araştırma mevcuttur.

Kâğıt sanayi çok fazla temiz su ihtiyacı olan endüstrilerden biridir. Su kıtlığı olması durumunda, kâğıt üretiminin yapılması mümkün değildir. Bu nedenle, istenen kalitede yeterli miktarda ilave su kaynaklarının bulunması gereklidir. Arıtılmış suyun işlem suyu olarak kullanılması olası bir alternatif olarak düşünülebilir. Bu tez kapsamında, bu alternatifin değerlendirilmesi amaçlanmıştır.

Deneysel çalışmalar, pilot tesis olarak seçilen bir kâğıt fabrikası atıksu arıtma tesisinin deşarj noktası ve kimyasal arıtma ünitesi çıkışından alınan numunelerle yürütülmüştür. İlk olarak, bu iki noktadan alınan su örneklerinin özellikleri istenen işlem suyu özellikleri ile karşılaştırılmıştır. Daha sonra, her iki noktadan alınan örneklere ileri arıtma uygulanmıştır. Bu amaçla, laboratuvar ölçekli membran filtre sistemi kullanılmıştır. Membran ünitesi giriş ve çıkışından alınan numunelerde TOK, KOİ, AKM, PH ve iletkenlik analizleri yapılmıştır. Elde edilen sonuçlara göre, geri kazanılmış atıksuyun işlem suyu olarak yeniden kullanılabilirliği değerlendirilmiştir.

Anahtar Sözcükler: Kâğıt sanayi, yeniden kullanım, membran filtre sistemleri

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 Overview

At the present time, the world is facing a critical water shortage problem. The Second World Water Forum in Hague in March 2000 showed very clearly to the world public that water will be one of the central issues of the 21st century of this globe and the life of billions of people will depend on the wise management of this source. Water is an essential and basic human need for urban, industrial and agricultural use and has to be considered as a limited resource. In this sense, only 1% of the total water and in 2025 nearly one-third of the population of developing countries, some 2.7 billion people will live in regions of severe water scarcity. They will have to reduce the amount of water used in irrigation and transfer it to the domestic, industrial, and environmental sector (Seckler, Amarasinghe, Molden, De Silva, & Barker, 2000).

Inadequate water supply and water quality deterioration represent serious contemporary concerns for municipalities, industries, agriculture, and the environment in many parts of the world. Factors contributing to these problems include continued population growth in urban areas, contamination of surface water and groundwater, uneven distribution of water resources, and frequent droughts caused by extreme global weather patterns (Asano & Cotruvo, 2004).

Our present environmental problems are originated from unplanned utilization of natural sources depending on the especially industrialization. Increase in variation of products, more benefit wishes of industrialists, incorrect applications and deficiencies of regulations are the major reasons of the industrial wastewater pollution. To overcome the water shortage related with industries following items should be taken into consideration;

- Improvements in the efficiency of water use
- Efficient management and modern technology utilization

- Water reuse and desalination

In many situations in developing countries, especially in arid and semi-arid areas, wastewater is simply too valuable to waste. 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. Appropriate wastewater collection systems and wastewater treatment systems are often not exist in developing countries, and wastewater inadvertently provides an essential source for water and fertilizers (Asano, 1998).

Wastewater reclamation and reuse have become significant elements in water resources planning and management, particularly in arid and semi-arid regions. Proper and integrated planning the reuse of reclaimed water may provide sufficient flexibility to respond the short-term needs as well as to increase to long-term reliability of water supply. Moreover, water quality criteria, economic analyses and project management, in the context of water resources, are essential components in the implementation of such a project is the capability of producing water of a desired quality to provide adequate public health protection and meet the environmental and socio-economic goals than can be practically achieved at given time. There are many methods of water treatment. Different methods can be employed to renovate effluent for utilization for agricultural, industrial, environmental and domestic applications. Direct human consumption of the treated effluent, although it is possible to obtain, will be very rarely applied due to psychological and probably religious reasons (Urkiaga, 2002).

Numerous approaches, modern and traditional, exist throughout the world for efficiency improvements and augmentation. Among such approaches, 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, 2002a).

The foundation of water reuse is built upon three principles; (1) providing reliable treatment of wastewater to meet strict water quality requirements for the intended reuse application, (2) protecting public health, and (3) gaining public acceptance. Water reuse accomplishes two fundamental functions ; (1) the treated effluent is used as a water resource for beneficial purposes, and (2) the effluent is kept out of streams, lakes, and beaches; thus, reducing pollution of surface water and groundwater (Asano, 1998).

For more than a quarter of a century, a recurring thesis in environmental and water resources engineering has been that it is feasible to treat wastewater to high enough quality that it is a resource that could be put to beneficial use rather than wasted (Asano, 1998).

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.

Pulp and paper industry has high amount of fresh water demand for production. The quality and quantity of process water changes depending on the production methods. Different pulp and paper production methods are available throughout the world. The Kraft pulp process is the most commonly applied technique. In addition, it is also possible to mention ground wood and soda-sulphite process. These techniques produce different quality pulp and paper and hence the quality of the water used in the process also differs from one plant to another. Water is mainly used for cooking and digestion of wood chips during Kraft pulping process as well as washing of the cooked pulp for whitening. In addition a certain amount of water also reserved for boiler feed to supply energy requirements of the plants. In general, pulp and paper industry process water must be very high quality. Specifically suspended material is not acceptable in waters as it decreases brightness, affects coloring and interferences with uniformity of the paper. Similarly hardness is also unacceptable parameter due to precipitation of calcium carbonate on the paper slurry. For high grade papers, turbidity and color can create significant problems and can result in quality failure of the produced paper.

1.2 Aim and Scope of the Thesis

In this thesis, investigation of reusability of the wastewater produced from a pulp and paper industry as a process water was aimed. For this purpose, one pulp and paper factory was selected as a pilot plant. Chemically treated wastewater and effluent of the treatment plant of this factory were used during the experimental studies. Different ultrafiltration membrane filters, which have different molecular weight cut-off, were examined separately using a complex membrane filter system. Results obtained from experimental studies were compared to required process water quality for paper production.

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CHAPTER TWO
AN OVERVIEW OF WATER REUSE

2.1 Introduction

Wastewater from point sources such as sewage treatment plants and industries can provide excellent reusable water because this water is usually available a reliable basis and has a known quality. 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).

Collection and treatment of wastewater as well as subsequent reclamation and reuse in one or more ways becomes a feasible method these days. 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 (http://www.watercorporation.com).

The source of wastewater can vary from industrial discharges to urban effluent. The treated wastewater can be used for a range of purposes, from such high-quality uses as indirect potable use to lower quality requirements such as water for agricultural or industrial purposes or for toilet flushing and cooling water (Davis & Hirji, 2003).

2.2 Water Sources and Water Shortage

A third of the world's population is suffering from a shortage of water, raising the prospect of "water crises" in countries such as China, India and the US. Scientists had forecast in 2000 that one in three would face water shortages by 2025, but water experts have been shocked to find that this threshold has already been crossed. About a quarter of the world's population lives in areas of "physical water shortage", where natural forces, over-use and poor agricultural practices have led to falling groundwater levels and rivers drying up. But a further 1 billion people face "economic water shortages", because lack the necessary infrastructure to take water from rivers and aquifers (http://www.ft.com).

The amount of water needed to grow food could be halved, scientists have told an international conference on water in Stockholm, which on Monday heard that one in three of the planet's inhabitants were short of water. Although there was sufficient water for human needs, including agriculture and sanitation, poor management and distribution of water supplies had led to scarcities in large parts of the world (http://www.ft.com).

Fresh water is vital to sustain human life, however, only 3% of total water on earth is fresh water and two-thirds of that is in frozen forms such as the polar ice caps, glaciers and icebergs. The remaining 1% of the total fresh water is either surface water or ground water; ground water consists of two-thirds of this amount. Water is supplied and removed from the earth's surface by various processes forming a continuous recycling of water. Precipitation includes all forms of moisture falling on the ground including rain, snow, dew, hail and sleet. Precipitation is distributed between surface runoff and groundwater. Some portion of precipitation is intercepted by buildings, trees, shrubs and plants and eventually evaporated. Another portion infiltrates into the ground. The plant roots consume some portion of this water and the remaining water becomes groundwater. It may ultimately appear as the base flow in streams. The destination of water is open bodies of water such as oceans, seas and lakes. Water is transferred to the earth's atmosphere through two processes: evaporation and transpiration. Evaporation refers to water lost from the soil and surface water bodies, and transpiration refers to water lost from plants. The term evapotranspiration (ET) is used for water lost by both evaporation and transpiration. As moist air rises, it cools and forms clouds. Eventually, these clouds produce precipitation such as rain and snow. Within the hydrologic cycle, fresh water occupies small portion, however, this water has to be withdrawn to meet water demands. Also, the total amount of this water is heavily dependent on precipitation. In order to ensure there is a sufficient quantity of fresh water to meet our increasing water demand, wastewater has to be purified before going back into the hydrologic cycle and the practice or reusing wastewater must be implemented (http://www.onsiteconsortium.org,).

Freshwater is an important resource. Population growth in water scarce regions will only increase its value. 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. This number does not include people living in arid regions of large countries where there is enough water, but distribution patterns are uneven e.g. China, India, and the United States. In many areas of the world, aquifers that supply drinking water are being used faster than they recharge. Not only does this represent a water supply problem, it may also have serious health implications. Moreover, in coastal areas, saline intrusion of potable aquifers occurs as water is withdrawn faster than it can naturally be replaced. Increasing salinity makes water unfit for drinking and for other purposes such as irrigation (Meeting Report of WHO, 2001).

Half the world's population will not have enough water by 2025 unless governments lift their development and investment priorities, a senior official of the World Water Council said "Thirty percent of the world is living under water stress. They do not have enough water to live or wash, and if we continue at that rhythm, it will become more than 50% in 2025. It is not sustainable," William Cosgrove, vice president of the World Water Council, told reporters in Tokyo (www.abc.net.au).

Years of rapid population growth and increasing water consumption for agriculture, industry, and municipalities have strained the world's freshwater resources. In some areas the demand for water already exceeds nature's supply, and a growing number of countries are expected to face water shortages in the near future (http://www.infoforhealth.org).

Water-related problems are increasingly recognized as one of the most immediate and serious environmental threats to humankind. Water use has more than tripled globally since 1950, and one out of every six persons does not have regular access to safe drinking water. Lack of access to a safe water supply and sanitation affects the health of 1.2 billion people annually (WHO, & UNICEF, 2000).

The latest Global Environment Outlook of the United Nations Environmental Program (UNEP) reports that about one third of the world's populations currently live in countries suffering from moderate-to-high water stress, where water consumption is more than 10% of renewable freshwater resources (UNEP, 2002a).

The availability of freshwater in sufficient quality and quantity is critical to meet human domestic, commercial, and industrial needs. Although over 70% of the earth's surface is covered with water, less than 1% is readily accessible freshwater as either ground water or surface water (Allen, 2002). As with any resource in finite availability, water is not just a natural commodity, it is also an economic and political commodity. The scarcity of water–even in water-rich regions, it is not always in the location where it will be utilized–gives it a value clearly recognizable in both the enormous costs of water resource projects and the complexities of laws governing its uses (Bellandi, 2004).

Globally, water use has increased ten-fold between 1900 and 2000. The industrial activity over the last century has not only increased fresh water consumption, but in turn, has impacted these same fresh water sources through the increases in industrial wastewater discharges. The US Department of Commerce estimates that the major industrial water users discharge approximately 285 billion gallons of wastewater each day (Schmidt, 2004).

Thus, it can been seen that increasing concerns regarding the available water quantity and quality is driving industries to consider both business economics, as well as community and environmental good-stewardship practices for sustainable operation and development. Some of the more water intensive industries include power generation, pulp & paper, food & beverage, electronics, and automotive (Scott, & O'Brien, 2001).

Degrading catchments and water shortage are the most immediate and arguably the biggest environmental issues affecting the world today (Stagnitti, Hamilton, Versace, Ierodiaconou, 2002).

Countries can be classified according to their water wealth:

- **Poor:** Annual water volume per capita is less than 1,000 m^3
- **Insufficient / Water Stress:** Annual water volume per capita is less than 2,000 m^3
- **Rich:** Annual water volume per capita is more than 8,000- 10,000 m^3

Turkey is not a rich country in terms of existing water potential. Turkey is a water stress country according to annual volume of water available per capita. The annual exploitable amount of water has recently been approximately 1,500 m^3 per capita.

The State Institute of Statistics (DIE) has estimated Turkey's population as 100 million by 2030. So, the annual available amount of water per capita will be about 1,000 m^3 by 2030. The current population and economic growth rate will alter water consumption patterns. As population increases, annual allocated available amount of water per person will decrease. The projections for future water consumption would be valid on the condition that the water resources were protected from pollution at least for the next 25 years. It is imperative that available resources be evaluated rationally so as to provide clean and sufficient water resources for the next generation (http://www.dsi.gov.tr).

2.3 Wastewater Reuse

As water resources become more limited and waste discharge becomes increasingly expensive, the concept of water reclamation or water "reuse" is gaining acceptance in industry. Depending on the cost of water and sewer, and even more expensive costs such as surcharges and hauling costs, the concept of water reuse is often already economically justified. This is especially true in cases where the waste is considered "hazardous," requiring hauling and disposal at specifically classified hazardous waste disposal sites. There are often cases where the waste stream can be concentrated to a point where the material can actually be recovered for reuse. In such cases, depending on the value of the recovered material, the economics of water reuse technologies become quite attractive (http://water.environmental-expert.com).

2.3.1 Wastewater Reuse in Industry

As water supplies become scarce and more expensive, utilities and industries must find more innovative ways of water recycling to reduce their total water demand (Krishna, 2002).

Wastewater reuse opportunities exist in almost all industrial plants. In most industries, cooling waters create the largest demand for water within the plant. Many industrial users of fresh water are under increasing pressure to reuse water within their facilities. Their goal is to minimize the amount of water that is discharged, either to a receiving stream or publicly owned treatment works. Using wastewater instead of fresh water not only enables water conservation but also can lead to overall cost reduction for plant operation (James, & McLntyre, 1998).

Industrial reuse has increased substantially since the early 1990s for many of the same reasons urban reuse has gained popularity, including water shortages and increased populations, particularly in drought areas, and legislation regarding water conservation and environmental compliance. To meet this increased demand, many states have increased the availability of reclaimed water to industries and have installed the necessary reclaimed water distribution lines. Petroleum refineries, chemical plants, and metal working facilities are among other industrial facilities benefiting from reclaimed water not only for cooling, but for process needs as well (EPA, WRH, 1998).

Industrial water use accounts for approximately 20% of global freshwater withdrawals. Power generation constitutes a large share of this water usage, with up to 70% of total industrial water used for hydropower, nuclear, and thermal power generation, and 30 to 40% used for other, non-power generation processes. Industrial water reuse has the potential for significant applications, as industrial water demand is expected to increase by 1.5 times by 2025 (Shiklomanov, 1999).

Industrial water reuse has the following specific benefits,

- Potential reduction in production costs from the recovery of raw materials in the wastewater and reduced water usage;
- Heat recovery;
- Potential reduction in costs associated with wastewater treatment and discharge.

Water reuse and recycling for industrial applications have many potential applications, ranging from simple housekeeping options to advanced technology implementation. Wastewater reuse for industry can be implemented through the reuse of municipal wastewater in industrial processes, internal recycling and cascading use of industrial process water, and non-industrial reuse of industrial plant effluent, as summarized in Table 2.1 (UNEP Report, 1998).

Table 2.1.Types and Examples of Industrial Water Reuse (Asano, & Levine, 1998)

Types of water reuse	**Examples**
Reuse of municipal wastewater	Cooling tower make-up water Once-through cooling Process applications
Internal recycling and cascading use of process water	Cooling tower make-up water Once-through cooling and its reuse Laundry reuse (water, heat, and detergent recovery) Reuse of rinse water Cleaning of premises
Non-industrial use of effluent	Heating water for pools and spas Agricultural applications

2.3.1.1 Cooling Water

For the majority of industries, cooling water is the largest use of reclaimed water because advancements in water treatment technologies have allowed industries to successfully use lesser quality waters. These advancements have enabled better control of deposits, corrosion, and biological problems often associated with the use of reclaimed water in a concentrated cooling water system. There are two basic types of cooling water systems that use reclaimed water: (1) once-through and (2) recirculating evaporative. The recirculating evaporative cooling water system is the most common reclaimed water system due to its large water use and consumption by evaporation (EPA WRH, 1998).

2.3.1.2 Boiler Make-Up Water

The use of reclaimed water for boiler make-up water differs little from the use of conventional public water supply; both require extensive additional treatment. Quality requirements for boiler make-up water depend on the pressure at which the boiler is operated. Generally, the higher the pressure, the higher the quality of water required (EPA WRH, 1998).

In general, both potable water and reclaimed water used for boiler water make-up must be treated to reduce the hardness of the boiler feed water to close to zero. Removal or control of insoluble scales of calcium and magnesium, and control of silica and alumina, are required since these are the principal causes of scale buildup in boilers. Depending on the characteristics of the reclaimed water, lime treatment (including flocculation, sedimentation, and recarbonation) might be followed by multi-media filtration, carbon adsorption, and nitrogen removal. High-purity boiler feed water for high-pressure boilers might also require treatment by reverse osmosis or ion exchange. High alkalinity may contribute to foaming, resulting in deposits in the super heater, reheater, or turbines Bicarbonate alkalinity, under the influence of boiler heat, may lead to the release of carbon dioxide, which is a source of corrosion in steam-using equipment. The considerable treatment and relatively small amounts of makeup water required normally make boiler make-up water a poor candidate for reclaimed water (EPA WRH, 1998).

2.3.1.3 Industrial Process Water

The suitability of reclaimed water for use in industrial processes depends on 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, potential users must be contacted to determine the specific requirements for their process water. Table 2.2 presents industrial process water quality requirements for a variety of industries (EPA WRH. 1998).

Table 2.2 Industrial Water Quality Requirements (EPA WRH. 1998)

Parameter*	Pulp & paper			Chemical	Petroleum & Coal	Textiles		Cement
	Mechanical Pulping	Chemical, Unbleached	Pulp Paper Bleached			Sizing suspension	Scouring, Bleach & Dye	
Cu	-	-	-	-	0.05	0.01	-	-
Fe	0.3	1.0	0.1	0.1	1.0	0.3	0.1	2.5
Mn	0.1	0.5	0.05	0.1	-	0.05	0.01	0.5
Ca	-	20	20	68	75	-	-	-
Mg	-	12	12	19	30	-	-	-
Cl	1.000	200	200	500	300	-	-	250
HCO_3	-	-	-	128	-	-	-	-
NO_3	-	-	-	5	-	-	-	-
SO_4	-	-	-	100	-	-	-	250
SiO_2	-	50	50	50	-	-	-	35
Hardness	-	100	100	250	350	25	25	-
Alkalinity	-	-	-	125	-	-	-	400
TDS	-	-	-	1.000	1.000	100	100	600
TSS	-	10	10	5	10	5	5	500
Color	30	30	10	20	-	5	5	-
pH	6-10	6-10	6-10	6.2-8.3	6-9	-	-	6.5-8.5
CCE	-	-	-	-	-	-	-	-

*All values in mg/l except color and pH

2.3.1.3.1 Pulp and Paper Industry. The historical approach of the pulp and paper industry has been to internally recycle water to a very high degree. The pulp and paper industry has long recognized the potential benefits associated with water reuse. At the turn of the century, when the paper machine was being developed, water use was approximately 625 liters per kilogram. By the 1950s, the water usage rate was down to 145 liters per kilogram. (Wyvill, Adams, & Valentine, 1984). An industry survey conducted in 1966 showed the total water use for a bleached Kraft mill to be 750 liters per kilogram (Haynes, 1974). Modern mills approach a recycle ratio of 100 percent, using only 67 to 71 liters freshwater per kilogram (NCASI, 2003). The pulp and paper process water quality requirements are given in Table 2.3.

Table 2.3.Pulp and Paper Process Water Quality Requirements (Adamski, Gyory, Richardson & Crook, 2000)

Parameter [a]	Mechanical Pulping	Chemical, Unbleached	Pulp and Paper, Bleached
Iron	0.3	1	0.1
Manganese	0.1	0.5	0.05
Calcium	-	20	20
Magnesium	-	12	12
Chlorine	1.000	200	200
Silicon Dioxide	-	50	50
Hardness	-	100	100
TSS	-	10	10
Color	30	30	10
pH	6-10	6-10	6-10

(a) All values in mg/L except color and pH

In 1998, about a dozen pulp and paper mills used reclaimed water. Less than half of these mills used treated municipal wastewater. Tertiary treatment was generally required. The driver was usually an insufficient source of freshwater (EPA, WRH, 1998).

Some of the reasons that mills choose not to use treated municipal wastewater include (EPA WRH, 1998):

- Concerns about pathogens
- Product quality requirements that specifically preclude its use
- Possibly prohibitive conveyance costs

- Concerns about potentially increased corrosion, scaling, and biofouling problems due to the high degree of internal recycling involved

2.3.1.3.2 Chemical Industry. The water quality requirements for the chemical industry vary greatly according to production requirements. Generally, waters in the neutral pH range (6.2 to 8.3) that are also moderately soft with low turbidity, suspended solids (SS), and silica are required; dissolved solids and chloride content are generally not critical (EPA WRH, 1998).

2.3.1.3.3 Textile Industry. Waters used in textile manufacturing must be non-staining; hence, they must be low in turbidity, color, iron, and manganese. Hardness may cause curds to deposit on the textiles and may cause problems in some of the processes that use soap. Nitrates and nitrites may cause problems in dyeing (EPA WRH, 1998).

2.3.1.3.4 Petroleum and Coal Industry. Processes for the manufacture of petroleum and coal products can usually tolerate water of relatively low quality. Waters generally must be in the 6 to 9 pH range and have moderate suspended solid (SS) of no greater than 10 mg/L (EPA WRH, 1998).

2.4 Agricultural Application of Reclaimed Wastewater

Treated wastewater, also known as reclaimed water, is a valuable resource for agricultural reuse in irrigation. In both industrialized and developing countries, treated wastewater has been used successfully for the irrigation of a wide range of crops, including fresh eaten fruits and vegetables. The advances in wastewater treatment have improved the capacity to generate reclaimed water of a quality that can be used in both non-potable and potable uses (Asano and Levine 1998).

Required water quality changes depending on the type of plants. High quality water is necessary for sensitive crops. Salinity, total dissolved solids, boron, sodium, potassium, phosphorus, and heavy metal contents of the water are important parameter for agricultural irrigation.

2.5 Groundwater Recharge with Reclaimed Wastewater

Various sources of water are available for groundwater recharge but, in recent years, the use of non conventional water resources such as recycled municipal wastewater, has received increasing attention. The primary reasons for considering use of recycled water in groundwater recharge are that recycled wastewater is available for reuse at a relatively low cost and that it provides a dependable source of water even in drought years (Angelakis, & Aertgeerts, 2003).

The purposes of groundwater recharge using reclaimed water may be: (1) to establish saltwater intrusion barriers in coastal aquifers, (2) to provide further treatment for future reuse, (3) to augment potable or nonpotable aquifers, (4) to provide storage of reclaimed water for subsequent retrieval and reuse, or (5) to control or prevent ground subsidence (EPA WRH 1998).

Pumping of aquifers in coastal areas may result in saltwater intrusion, making them unsuitable as sources for potable supply or for other uses where high salt levels are intolerable. A battery of injection wells can be used to create a hydraulic barrier to maintain intrusion control. Reclaimed water can be injected directly into an aquifer to maintain a seaward gradient and thus prevent inland subsurface saltwater intrusion. This may allow for the additional development of inland withdrawals or simply the protection of existing withdrawals. Infiltration and percolation of reclaimed water takes advantage of the natural removal mechanisms within soils, including biodegradation and filtration, thus providing additional *in situ* treatment of reclaimed water and additional treatment reliability to the overall wastewater management system. The treatment achieved in the subsurface environment may eliminate the need for costly advanced wastewater treatment processes. The ability to implement such treatment systems will depend on the method of recharge, hydrogeological conditions, requirements of the down gradient users, as well as other factors. Aquifers provide a natural mechanism for storage and subsurface transmission of reclaimed water. Irrigation demands for reclaimed water are often seasonal, requiring either large storage facilities or alternative means of disposal when demands are low. In addition, suitable sites for surface storage facilities may not be available, economically feasible, or environmentally acceptable. Groundwater recharge eliminates the need for surface storage facilities and the attendant problems associated with uncovered surface reservoirs, such as evaporation losses, algae blooms resulting in deterioration of water quality, and creation of odors (EPA WRH, 1998).

2.6 Other Applications

2.6.1 Landscape Irrigation

Landscape irrigation includes the irrigation of parks; playgrounds; golf courses; freeway medians; landscaped areas around commercial, office, and industrial developments; and landscaped areas around residences. Many landscape irrigation projects involve dual distribution systems, which consist of one distribution network for potable water and a separate pipeline to transport reclaimed water (Asano, 1998).

2.6.2 Recreational and Environmental Uses

Constitute the fifth largest use of reclaimed water in industrialized countries and involve non-potable uses related to land-based water features such as the development of recreational lakes, marsh enhancement, and stream flow augmentation. Reclaimed water impoundments can be incorporated into urban landscape developments. Man-made lakes, golf course storage ponds and water traps can be supplied with reclaimed water. Reclaimed water has been applied to wetlands for a variety of reasons including: habitat creation, restoration and/or enhancement, provision for additional treatment prior to discharge to receiving water, and provision for a wet weather disposal alternative for reclaimed water (Asano, 1998).

2.6.3 Non-potable Urban Uses

Include fire protection, air conditioning, toilet flushing, construction water, and flushing of sanitary sewers. Typically, for economic reasons, these uses are incidental and depend on the proximity of the wastewater reclamation plant to the point of use. In addition, the economic advantages of urban uses can be enhanced by coupling with other ongoing reuse applications such as landscape irrigation (Asano, 1998).

2.6.4 Potable Reuse

Another water reuse opportunity, which could occur either by blending in water supply storage reservoirs or, in the extreme, by direct input of highly treated wastewater into the water distribution system (Asano, 1998).

2.7 Wastewater Reuse Regulations

Policies of creating public awareness and putting in place the necessary infrastructure to treat water and dispose of wastewater are essential to reduce the pressure on the environment. Wastewater reuse is a potentially viable component of integrated water resources management along with demand-and supply-side management. Wastewater reuse can help to maximize the use of limited water resources and contribute to economic development (Janosova, Miklankova, Hlavinek & Wintgens, 2003)

2.7.1 Water Reuse Guidelines

2.7.1.1 Environmental Protect Agency (EPA)

In 1992, EPA developed the Guidelines for Water Reuse, a comprehensive, technical document. Some of the information contained in this document includes a summary of state reuse requirements, guidelines for treating and reusing water, key issues in evaluating wastewater reuse opportunities, and case studies illustrating legal issues, such as water rights, that affect wastewater reuse. The guidelines also include recommended treatment processes, reclaimed water quality limits, monitoring frequencies, setback distances, and other controls for water reuse applications. The guidelines were updated in 2004 (Technical Guidelines, MEDAWARE).

2.7.1.2 World Health Association (WHO)

Other important guidelines that exist for wastewater reuse are the ones published by the World Health Organization (WHO), and are mainly focused on the needs of developing countries. WHO guidelines specify the microbiological quality and the treatment method required to achieve this quality, which is limited to the use of stabilization ponds since it is cheaper, simpler and ensure removal of parasites which is the most infectious agent in the developing world (Technical Guidelines, MEDAWARE, 2005)

The main features of the WHO (1989) guidelines for wastewater reuse in agriculture are therefore as follows:

- Wastewater is considered as a resource to be used, but used safely.
- The aim of the guidelines is to protect exposed populations (consumers, farm workers, populations living near irrigated fields) against excess infection.
- Fecal coliforms and intestinal nematode eggs are used as pathogen indicators.

- Nematodes are included in the guidelines since infectious diseases in developing countries are mainly due to the presence of parasites which are more resistant to treatment.
- Measures comprising good reuse management practice are proposed alongside wastewater quality and treatment goals; restrictions on crops to be irrigated with wastewater; selection of irrigation methods providing increased health protection, and observation of good personal hygiene (including the use of protective clothing) (Technical Guidelines, MEDAWARE).

2.7.1.3 European Union (EU)

Identification of a competent authority or authorities is the responsibility of each individual state in the context of the implementation of the European Water Framework Directive. Each European country has its own water management system consisting of the state water departments and the local authorities. The Ministries of the Environment, Agriculture, and Health are the main state water departments that issue statutes and water policies as well as implement water related legislation. Most of the regulations are under the umbrella of the EU water framework directive (WFD) and represent the major advance in the European policy with the concept of good ecological status and water management at the river basin level (Janosova, Miklankova, Hlavinek & Wintgens, 2002).

It is currently essential to look at the local authorities in European regions, who are mostly responsible for the supervision of collection, treatment and disposal of wastewater. These water authorities on a local scale and the effectiveness of a participatory approach in water planning could help to achieve a “cultural shift” to recognize the potential benefits which water reuse programs can bring (Dube & Swatuk, 2001).

In Europe, most of the northern European countries have abundant water resources and they all give priority to the protection of water quality. In these countries, the need for extra supply through the reuse of treated wastewater is not considered as a major issue, but on the other hand, the protection of the receiving environment is considered important. However, industry is generally encouraged to recycle water and to reuse recycled wastewater. The situation is different in the southern European countries, where the additional resources brought by wastewater reuse can bring significant advantages to agriculture (e.g. crop irrigation) and tourism (e.g. golf course irrigation). Some of water recycling and reuse technologies have been practiced in Mediterranean region since ancient civilizations but nowadays wastewater recycling and reuse is increasingly integrated in the planning and development of water resources (Urkiaga, 2002).

2.7.1.4 Turkey

Water reuse has been officially legitimized in 1991 through the Regulation for irrigational wastewater reuse issued by the Ministry of Environment. Since then, there have been no changes and revisions of the regulation, however, the applications have not been satisfactorily realized so far. The most important criteria for evaluating the suitability of treated wastewater for irrigation use are: public health aspects, salinity (especially significant in arid regions), heavy metals and harmful organic substances. In addition to standards, regulations can include best practices for wastewater treatment and irrigation techniques as well as regarding crops and areas to be irrigated. In Turkey, the WHO standards have been adopted except the limits for the intestinal nematodes and the residual chlorine. Concerning the microbiological standards, the Turkish regulation consists of only fecal coliform parameter and, it seems to be insufficient and needs to be revised in terms of health aspects (Technical Guidelines, MEDAWARE, 2005).

CHAPTER THREE
PULP AND PAPER INDUSTRY

3.1 Introduction

Paper is essentially a sheet of fibers with a number of added chemicals that affect the properties and quality of the sheet. Besides fibers and chemicals, manufacturing of pulp and paper requires a large amount of process water and energy in the form of steam and electric power. Pulp for papermaking may be produced from virgin fiber by chemical or mechanical means or may be produced by the re-pulping of recovered paper. A paper mill may simply reconstitute pulp made elsewhere or may be integrated with the pulping operations on the same site. Non-integrated pulp mills (market pulp) are only manufacturing pulp that is then sold on the open market. Nonintegrated paper mills are using purchased pulp for their paper production. In integrated pulp and paper mills the activities of pulp and papermaking are undertaken on the same site. Kraft pulp mills are operating in both non-integrated and integrated manner whereas sulphite pulp mills are normally integrated with paper production. Mechanical pulping and recycled fiber processing is usually an integrated part of papermaking but has become a stand-alone activity in a few single cases. Consequently, the main environmental issues associated with pulp and paper production are emissions to water**,** emissions to air, and energy consumption. Waste is expected to become a gradually increasing environmental issue of concern (European Commission, 2001).

3.2 Description to Process

Pulp and paper are manufactured from raw materials containing cellulose fibers, generally wood, recycled paper, and agricultural residues. In developing countries, about 60% of cellulose fibers originate from non wood raw materials such as bagasse (sugar cane fibers), cereal straw, bamboo, reeds, esparto grass, jute, flax, and sisal. The main steps in pulp and paper manufacturing are raw material reparation, such as wood debarking and chip making; pulp manufacturing; pulp bleaching; paper manufacturing; and fiber recycling. Pulp mills and paper mills may exist separately or as integrated operations (PP&AH, 1998). The Summary of the pulping techniques is shown in Figure 3.1.

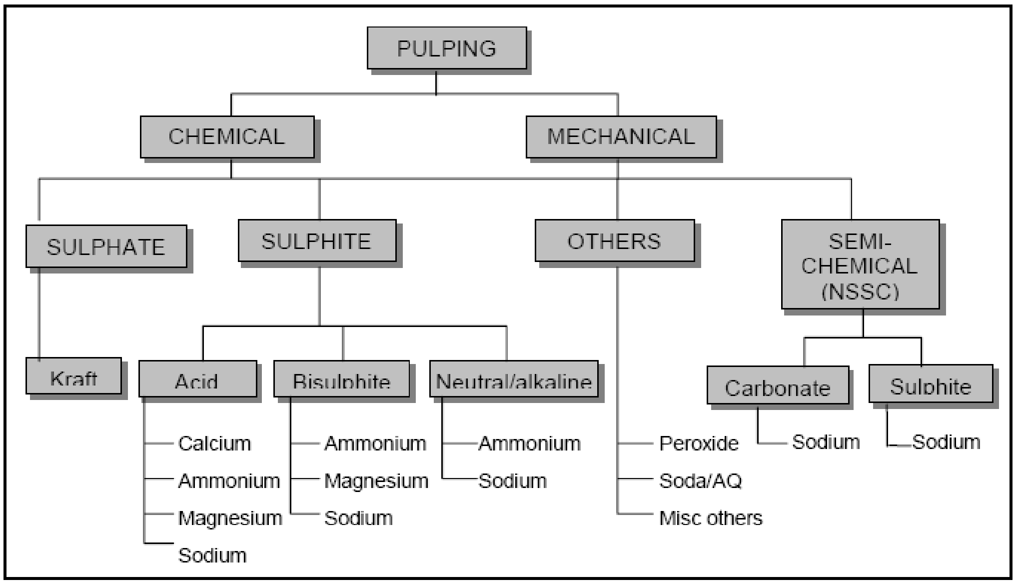

Figure 3.1 Summary of the pulping techniques Integrated Pollution Prevention Control (*IPPC*), 2000

Manufactured pulp is used as a source of cellulose for fiber manufacture and for conversion into paper or cardboard. Pulp manufacturing starts with raw material preparation, which includes debarking (when wood is used as raw material), chipping, and other processes. Cellulosic pulp is manufactured from the raw materials, using chemical and mechanical means. The manufacture of pulp for paper and cardboard employs mechanical (including thermo-mechanical), chemi-mechanical, and chemical methods. Mechanical pulping separates fibers by such methods as disk abrasion and billeting. Chemi-mechanical processes involve mechanical abrasion and the use of chemicals. Thermo-mechanical pulps, which are used for making products such as newsprint, are manufactured from raw materials by the application of heat, in addition to mechanical operations. Chemi-mechanical pulping and chemi-thermo-mechanical pulping (CTMP) are similar but use less mechanical energy, softening the pulp with sodium sulfite, carbonate, or hydroxide. Chemical pulps are made by cooking (digesting) the raw materials, using the Kraft (sulfate) and sulfite processes.

Kraft processes produce a variety of pulps used mainly for packaging and high-strength papers and board. Wood chips are cooked with caustic soda to produce brownstock, which is then washed with water to remove cooking (black) liquor for the recovery of chemicals and energy. Pulp is also manufactured from recycled paper. Mechanical pulp can be used without bleaching to make printing papers for applications in which low brightness is acceptable primarily, newsprint. However, for most printing, for copying, and for some packaging grades, the pulp has to be bleached. For mechanical pulps, most of the original lignin in the raw pulp is retained but is bleached with peroxides and hydrosulfites. In the case of chemical pulps (Kraft and sulfite), the objective of bleaching is to remove the small fraction of the lignin remaining after cooking. Oxygen, hydrogen peroxide, ozone, peracetic acid, sodium hypochlorite, chlorine dioxide, chlorine, and other chemicals are used to transform lignin into an alkali-soluble form. An alkali, such as sodium hydroxide, is necessary in the bleaching process to extract the alkali-soluble form of lignin. Pulp is washed with water in the bleaching process. In modern mills, oxygen is normally used in the first stage of bleaching. The trend is to avoid the use of any kind of chlorine chemicals and employ "total chlorine-free" (TCF) bleaching. TCF processes allow the bleaching effluents to be fed to the recovery boiler for steam generation; the steam is then used to generate electricity, thereby reducing the amount of pollutants discharged. Elemental chlorine-free (ECF) processes, which use chlorine dioxide, are required for bleaching certain grades of pulp. The use of elemental chlorine for bleaching is not recommended. Only ECF processes are acceptable and from an environmental perspective, TCF processes are preferred. The soluble organic substances removed from the pulp in bleaching stages that use chlorine or chlorine compounds, as well as the substances removed in the subsequent alkaline stages, are chlorinated. Some of these chlorinated organic substances are toxic; they include dioxins, chlorinated phenols, and many other chemicals. It is generally not practical to recover chlorinated organics in effluents, since the chloride content causes excessive corrosion. The finished pulp may be dried for shipment (market pulp) or may be used to manufacture paper on site (in an "integrated" mill). Paper and cardboard are made from pulp by deposition of fibers and fillers from a fluid suspension onto a moving forming device that also removes water from the pulp. The water remaining in the wet web is removed by pressing and then by drying, on a series of hollow-heated cylinders (for example, calendar rolls). Chemical additives are added to impart specific properties to paper, and pigments may be added for color (PP&AH, 1998). The Pulping and Papermaking activities are shown in Figure 3.2 and 3.3.

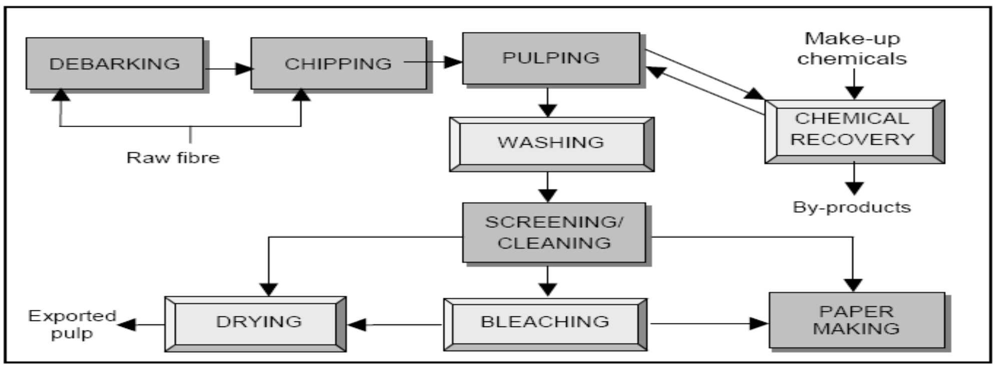

Figure 3.2 Pulping activities Integrated Pollution Prevention Control (*IPPC),* 2000

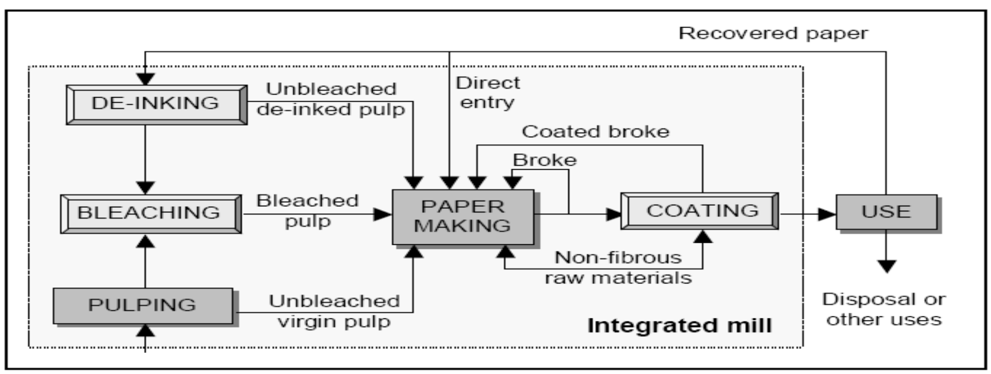

Figure 3.3 Papermaking activities Integrated Pollution Prevention Control (*IPPC),* 2000

3.2.1 The Kraft (Sulphate) Pulping Process

The sulphate or kraft process accounting for ca. 80% of world pulp production is the most applied production method of chemical pulping processes. The importance of the sulphite process has decreased steadily over the last years. Today, only 10% of the world production is obtained by this method. The term “sulphate” is derived from the make up chemical sodium sulphate, which is added in the recovery cycle to compensate for chemical losses. In the chemical pulping process the fibers are liberated from the wood matrix as the lignin is removed by dissolving in the cooking chemical solution at a high temperature. Part of the hemicelluloses is dissolved as well in the cooking. In the Kraft pulp process the active cooking chemicals (white liquor) are sodium hydroxide (NaOH) and sodium sulphide (Na_2S). As a result of the large amount of sodium hydroxide used, the pH value at the start of a cook is between 13 and 14 (alkaline pulping process). It decreases continuously during the course of cooking because organic acids are liberated from lignin and carbohydrates during the pulping reaction (http://aida.ineris.fr).

Today the Kraft process is the dominating chemical pulping process worldwide due to the superior pulp strength properties compared with sulphite process, its application to all wood species, as well as to the efficient chemical recovery systems that have been developed and implemented. But the chemistry of the Kraft process carries with it an inherent potential problem of malodorous compounds. (http://aida.ineris.fr)

As a result of chemical reactions in the cooking stage, chromophoric groups of the residual lignin are formed thus causing the pulp to become darker in colour than the original wood. Because of the higher pH, the Kraft pulping process induces more chromophores than sulphite pulping and unbleached Kraft pulp has a considerably lower initial brightness than unbleached sulphite pulp. The main unit processes of manufacturing of kraft pulp mills are shown in Figure 3.4 (http://aida.ineris.fr).

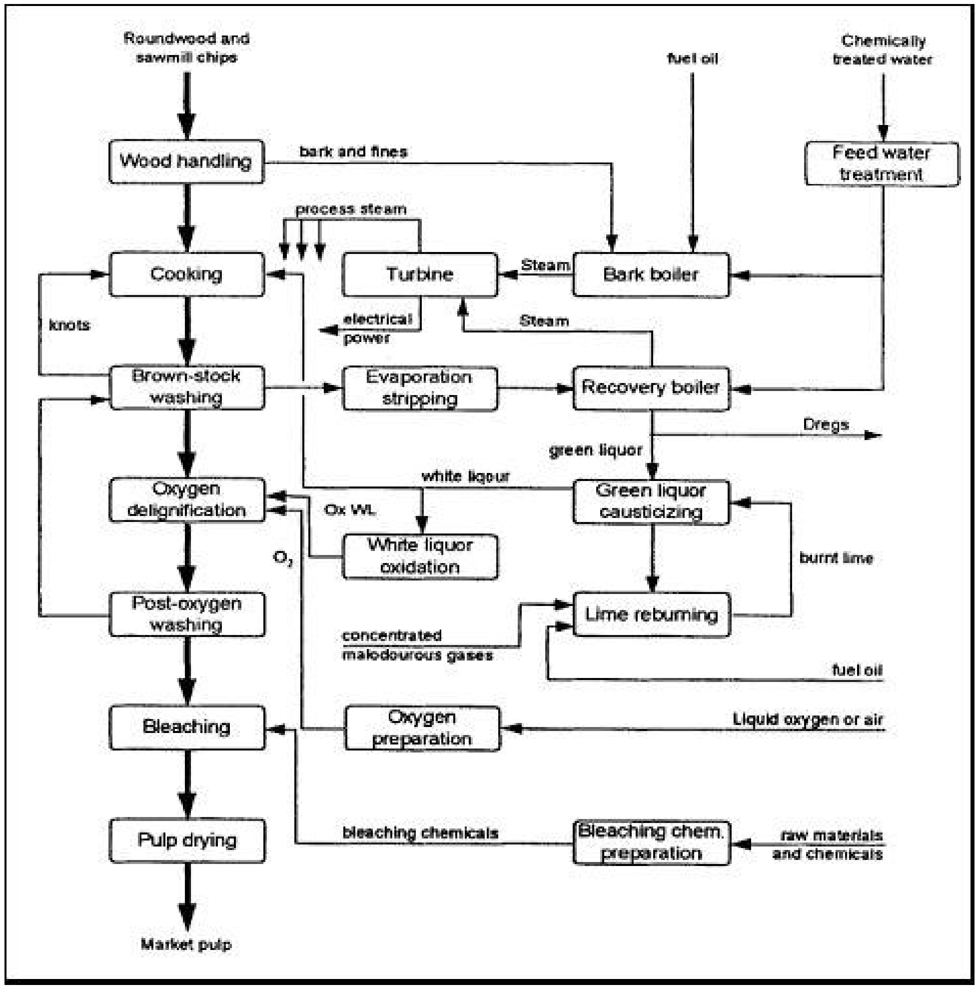

Figure 3.4 Overview of the processes of a Kraft pulp mill (SEPA-Report 713-2, 1997)

3.2.2 The Sulphite Pulping Process

The production of sulphite pulps is much smaller than the production of Kraft pulps and sulphite pulps are more used in special purposes in papermaking rather than being an alternative market pulp grade for Kraft pulps. Very little unbleached sulphite pulp is made and the yield is a little higher which can be attributed to the lower pH in the cooking.

The main reasons of more limited applicability of sulphite pulps are as follows:

- it is not possible to use pine as raw material in the acid cooking process which limits the raw material base of sulphite pulping

- the strength properties of the pulps as measured by the papermaker are generally not as good as those of Kraft pulp, although for some specialty pulps these properties may be equally good or even better
- Environmental problems have in many cases been more expensive to solve and this has decreased the cost-competitivity compared to the Kraft pulping.

The sulphite process is characterized by its high flexibility compared to the Kraft process, which is a very uniform method, which can be carried out only with highly alkaline cooking liquor. In principle, the entire pH range can be used for sulphite pulping by changing the dosage and composition of the chemicals. Thus, the use of sulphite pulping permits the production of many different types and qualities of pulps for a broad range of applications. The sulphite process can be distinguished according to the pH adjusted into different types of pulping the main of which sulphite in Europe are compiled in Table 3.1 (http://aida.ineris.fr).

Table 3.1 Main sulphite pulping processes in Europe (Uhlmann, 1991)

Process	pH	Base	Active reagent	Cooking temp ^{o}C	Pulp yield %	Applications
Acid (bi)sulphite	1-2	Ca^{2+}, Mg^{2+} Na^{+}	SO_2*H_2O, H^{+}, HSO_3^{-}	125-143	40-50	Dissolving pulp,tissue, printing paper,special paper
Bisulhite (Magnefite)	3-5	Mg^{2+}, Na^{+}	HSO_3^{-}, H^{+}	150-170	50-65	Printing paper, tissue
Neutral sulphite (NSSC)[2]	5-7	Na^{+}, NH_4^{+}	HSO_3^{-}, SO_3^{2-}	160-180	75-90	Corrugate medium, semi-chemical pulp
Alkaline sulphite	9-13.5	Na^{+}	SO_3^{2-}, OH^{-}	160-180	45-60	Kraft-type pulp

The sulphite cooking process is based on the use of aqueous sulphur dioxide (SO_2) and a base-calcium, sodium, magnesium or ammonium. The specific base used will impact upon the options available within the process in respect of chemical and energy recovery system and water use. Today, the use of the relatively cheap calcium base is outdated because the cooking chemicals cannot be recovered. In Europe there is still one mill (FR) using ammonium as a base. The dominating sulphite pulping process in Europe is the magnesium sulphite pulping with some mills using sodium as base. Both magnesium and sodium bases allow chemical recovery. The lignosulphonates generated in the cooking liqueur can be used as a raw material for producing different chemical products. Because of its importance in terms of capacity and numbers of mills running in Europe in the following the focus is on magnesium sulphite pulping. The main unit processes of manufacturing of magnesium sulphite pulp are shown in Figure 3.5 (http://aida.ineris.fr).

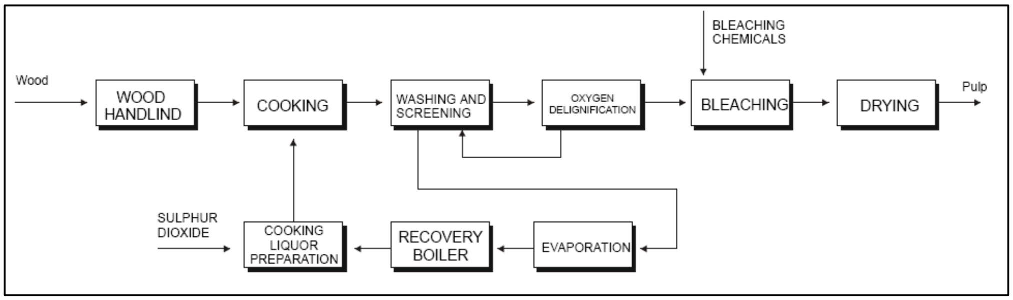

Figure 3.5 Main unit processes of manufacturing of magnesium sulphite pulp (CEPI, 1997b)

3.2.3 Mechanical Pulping and Chemi-Mechanical Pulping

In mechanical pulping the wood fibers are separated from each other by mechanical energy applied to the wood matrix causing the bonds between the fibers to break gradually and fiber bundles, single fibers and fiber fragments to be released. It is the mixture of fibers and fiber fragments that gives mechanical pulp its favorable printing properties. In the mechanical pulping the objective is to maintain the main part of the lignin in order to achieve high yield with acceptable strength properties and brightness. Mechanical pulps have a low resistance to ageing which results in a tendency to discolor. There are two main processes used for the manufacturing of mechanical pulping. In the stone ground wood process (SGW) or in the pressurized ground wood process (PGW) logs are pressed against a rotating grinder stone with simultaneous addition of water. Refiner Mechanical Pulps (RMP, Thermo-Mechanical Pulps = TMP) are produced by defiberizing wood chips between disc refiners. The elements causing the mechanical action – grits on a pulp stone in the grinder and bar edges on a steel disc in the refiner – will give the resulting pulps a typical blend of fibers and fiber fragments. Ground wood pulp has a higher proportion of fine material and damaged fibers giving the pulp good optical and paper-surface properties. The more gentle treatment in the refiners produces a higher yield of intact long fibers which gives the pulp higher strength, which is valuable in furnishes for products with a high requirement on run ability.

The characteristics of the pulp can be affected by increasing the processing temperature and, in the case of refining, by the chemical treatment of the chips. Both steps will increase the energy consumption as well as the pollutant level because of a lower pulping yield. The chemithermo-mechanical pulping process (CTMP), in which the wood is pre-softened with chemicals, is generally considered to be a mechanical pulping technique since the chemicals principally soften the lignin prior to the mechanical stage rather than fully dissolve it out as in true chemical pulping processes. Most mechanical pulping is integrated with paper manufacture. Mechanical pulp is typically included in a paper furnish to increase the opacity of the paper product (http://aida.ineris.fr).

3.2.4 Recovered Paper Processing

Recovered fiber has become an indispensable raw material for the paper manufacturing industry, accounting about one-third of the total raw materials because of the favorable price of recovered fibers in comparison with the corresponding grades of market pulp and because of the promotion of wastepaper recycling by many European countries. In Europe there is an average utilization rate of recovered paper of 43 %. But is has to be taken into account that the maintenance of the fiber cycle relies on the feed of a certain amount of primary fibers to ensure the strength and other properties of the paper to be produced. For effective use of recovered paper it is necessary to collect, sort and classify the materials into suitable quality grades. Therefore, after collection recovered paper is brought to the collection yards where it is sorted. Detrimental substances as e.g. plastics, laminated papers etc. are removed before balling as well as possible. The sorted recovered paper is usually compacted by balling machines. Industrial recovered paper from large generators is usually delivered to and processed in recovered paper yards integrated in the paper mill (PP&AH, 1998).

3.2.5 Wastewater Treatment Technologies for Pulp and Paper Industry

The most significant environmental issues are the discharge of chlorine-based organic compounds (from bleaching) and of other toxic organics. The unchlorinated material is essentially black liquor that has escaped the mill recovery process. Some mills are approaching 100% recovery. Industry developments demonstrate that total chlorine free bleaching is feasible for many pulp and paper products but cannot produce certain grades of paper. The adoption of these modern process developments, wherever feasible, is encouraged (PP&AH, 1998).

Wastewater treatment typically includes (a) neutralization, screening, sedimentation, and floatation/hydrocycloning to remove suspended solids and (b) biological/secondary treatment to reduce the organic content in wastewater and destroy toxic organics. Chemical precipitation is also used to remove certain cations. Fibers collected in primary treatment should be recovered and recycled. A mechanical clarifier or a settling pond is used in primary treatment. Flocculation to assist in the removal of suspended solids is also sometimes necessary. Biological treatment systems, such as activated sludge, aerated lagoons, and anaerobic fermentation, can reduce BOD by over 99% and achieve a COD reduction of 50% to 90%. Tertiary treatment may be performed to reduce toxicity, suspended solids, and color (PP&AH, 1998). Due to high amount of water that use in pulp and paper industry, it is cost efficient to use membrane filtration techniques for reuse of wastewater. Some membrane process applications in pulp and paper industry are given in Table 3.2 (Pourcelly, 2005).

Table 3.2 Membrane processes in the Pulp & Paper industry (Poucelly, 2005)

Separation	**Application**
UF of Kraft	Effluent from the first stage of caustic extraction during pulp bleaching
UF of process effluent spent sulphite liquors	Digested liquors from spent sulphite chemical pulping. Recovery of lignosulfonates and sugars
UF of Kraft black liquor	Recovery of alkali lignins
RO of sulphite liquors	Concentration of spent 31ulphite liquors
RO of paper machine effluents	Recycling of water
RO of wash waters	Pre-concentration of sulphite contaminated wash water before evaporation.

CHAPTER FOUR
MEMBRANE SYSTEMS

4.1 Introduction

Membrane technology has become a dignified separation technology over the past decennia. The main force of membrane technology is the fact that it works without the addition of chemicals, with a relatively low energy use and easy and well-arranged process conductions.

Membrane technology is a generic term for a number of different, very characteristic separation processes. These processes are of the same kind, because in each of them a membrane is used. Membranes are used more and more often for the creation of process water from groundwater, surface water or wastewater. Membranes are now competitive for conventional techniques. The membrane separation process is based on the presence of semi permeable membranes. The principle is quite simple: the membrane acts as a very specific filter that will let water flow through, while it catches suspended solids and other substances. There are various methods to enable substances to penetrate a membrane. Examples of these methods are the applications of high pressure, the maintenance of a concentration gradient on both sides of the membrane and the introduction of an electric potential. Membranes occupy through a selective separation wall. Certain substances can pass through the membrane, while other substances are caught. Membrane filtration can be used as an alternative for flocculation, sediment purification techniques, adsorption (sand filters and active carbon filters, ion exchangers), extraction and distillation.

There are two factors that determine the affectivity of a membrane filtration process; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor (expressed by the unit $l/m^2 \cdot h$). Productivity is expressed as a parameter called flux (expressed by the unit $l/m^2 \cdot h$). Selectivity and productivity are membrane-dependent. Membrane filtration can be divided up between micro and ultra filtration on the one hand and Nanofiltration and Reverse Osmosis (RO or hyper filtration) on the other hand. When membrane filtration is used for the removal of larger particles, micro filtration and ultra filtration are applied. Because of the open character of the membranes the productivity is high while the pressure differences are low. When salts need to be removed from water, Nanofiltration and Reverse Osmosis are applied. Nanofiltration and RO membranes do not work according to the principle of pores; separation takes place by diffusion through the membrane. The pressure that is required to perform Nanofiltration and Reverse Osmosis is much higher than the pressure required for micro and Ultrafiltration, while productivity is much lower (www.lenntech.com).

Membranes may be classified according the driving force at the origin of the transport process:

- A pressure differential leads to Microfiltration, Ultrafiltration, Nanofiltration and Reverse Osmosis;
- A difference of concentration across the membrane leads to diffusion of a species between two solutions (dialysis);
- A potential field applied to an ion exchange membrane leads to migration of ions through the membrane (electrodialysis, electro-electrodialysis and electrochemical devices).

Membrane separation defined according to the mechanism of separation is given in Table 4.1 and main solid/liquid and liquid/liquid membrane separation process is given in Tables 4.2. Species separation during pressure-driven membrane process (normal or perpendicular flow conditions) is given in Figure 4.1 (Pourcelly, 2005).

Table 4.1 Membrane separation according to the mechanism of separation (Pourcelly, 2005)

Separation mechanism	**Membrane separation process**
Size exclusion (filtration)	Nanofiltration (NF), Ultrafiltration (UF), Microfiltration (MF)
Solubility/diffusivity	reverse osmosis (RO), gas separation (GS), pervaporation (PV), Liquid/liquid membranes (LM)
Charge	electrodialysis (conventional and bipolar)

Table 4.2 Main Solid/Liquid and Liquid/Liquid Membrane Separation Process (Pourcelly, 2005)

Membrane process	Pore size	Membrane type	Driving force	Main applications
Microfiltration MF	50 nm -5 µm	Symmetric and asymmetric microporous	Hydrostatic pressure 0.5-5 bars	Clarification, sterile filtration
Ultra filtration UF	5 – 100 nm	Asymmetric microporous	Hydrostatic pressure 1-9 bars	Separation of macromolecular solutions
Nanofiltration (NF)	1 – 5 nm	Asymmetric	Hydrostatic pressure 4-20 bars	Separation of small organic compounds and multivalent ions
Reverse Osmosis (RO)	dense	Asymmetric, composite with homogeneous layer	Hydrostatic pressure > 20 bars	Production of "pure" water
Dialysis (D)	dense	Symmetric microporous	Concentration gradient	Separation of micro-solutes and salts from macromolecular solutions
Membrane distillation (MD)	10 – 100 nm	Microporous	Temperature	Separation of water from non-volatile solutes
Electrodialysis (ED)	dense	Charged membrane	Electric field	Separation of ions from water and non-ionic solutes
Electro-electrodialysis (EED)	dense	Charged membrane	Electrical field	Separation of ions from water and ionic solutes
Liquid membranes (LM)	10 – 100 nm	Microporous, liquid carrier	Concentration, reaction	Separation of ions and solutes from aqueous solutions

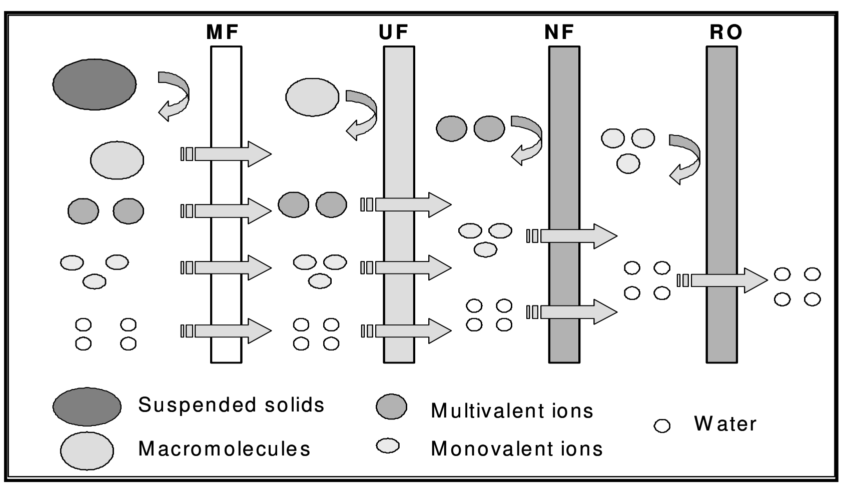

Figure 4.1 Species separation during pressure-driven membrane process (normal or perpendicular flow conditions) (Pourcelly, 2005)

Membrane filtration has a number of benefits over the existing water purification techniques:

- It is a process that can take place while temperatures are low. This is mainly important because it enables the treatment of heat-sensitive matter.
- It is a process with low energy cost. Most of the energy that is required is used to pump liquids through the membrane. The total amount of energy that is used is minor, compared to alternative techniques, such as evaporation.
- The process can easily be expanded.

Membrane filtration is the separation of the components of a pressurized fluid performed by polymeric membranes. The openings in the membrane matrices (pores) are so small that significant fluid pressure is required to drive liquid through them; the pressure required varies depending on the size of the pores. RO membranes have the smallest pores, while MF membranes have the largest pores. Normal particle filtration has historically not been run in a cross-flow design, “perpendicular flow” may be the most appropriate term, with the solution to be filtered approaching the filter media in a perpendicular direction. The entire influent stream passes through the filter media. In this perpendicular flow design, there are only two streams, the influent and the effluent. Separation is effected in the micron range or greater with certain depth filter media achieving as low as a nominal one micron separation (www.lenntech.com).

4.2 Membrane Systems

The choice for a certain kind of membrane system is determined by a great number of aspects, such as costs, risks of plugging of the membranes, packing density and cleaning opportunities. Membranes are never applied as one flat plate, because this large surface often results in high investing costs. That is why systems are built densely to enable a large membrane surface to be put in the smallest possible volume. Membranes are implemented in several types of modules. There are two main types, called the tubular membrane system and the plate & frame membrane system. Tubular membrane systems are divided up in tubular, capillary and hollow fiber membranes. Plate & frame membranes are divided up in spiral membranes and pillow-shaped membranes.

Tubular membranes: Tubular membranes are not self-supporting membranes. They are located on the inside of a tube, made of a special kind of material (Figure 4.2). This material is the supporting layer for the membrane. Because the location of tubular membranes is inside a tube, the flow in a tubular membrane is usually inside out. The main cause for this is that the attachment of the membrane to the supporting layer is very weak. Tubular membranes have a diameter of about 5 to 15 mm. Because of the size of the membrane surface, plugging of tubular membranes is not likely to occur. A drawback of tubular membranes is that the packing density is low, which results in high prices per module.

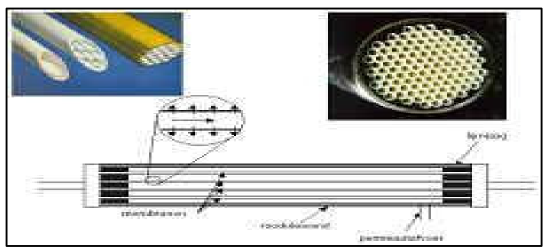

Figure 4.2 Tubular Membrane

Capillary membranes: With capillary membranes the membrane serves as a selective barrier, which is sufficiently strong to resist filtration pressures (Figure 4.3). Because of this, the flow through capillary membranes can be both inside out and outside in. The diameter of capillary membranes is much smaller than that of tubular membranes, namely 0.5 to 5 mm. Because of the smaller diameter the chances of plugging are much higher with a capillary membrane. A benefit is that the packing density is much greater.

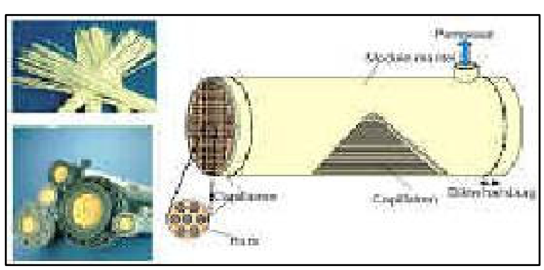

Figure 4.3 Capillary Membrane

Hollow fiber membranes: Hollow fiber membranes are membranes with a diameter of below 0.1 μm. consequentially, the chances of plugging of a hollow fiber membrane are very high (Figure 4.4). The membranes can only be used for the treatment of water with low suspended solids content. The packing density of a hollow fiber membrane is very high. Hollow fiber membranes are nearly always used merely for nano filtration and Reverse Osmosis (RO).

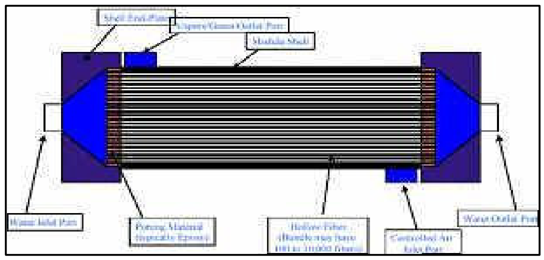

Figure 4.4 Hollow Fiber Membranes

Spiral membranes: Spiral membranes consist of two layers of membrane, placed onto a permeate collector fabric. This membrane envelope is wrapped around a centrally placed permeate drain (Figure 4.5). This causes the packing density of the membranes to be higher. The feed channel is placed at moderate height, to prevent plugging of the membrane unit. Spiral membranes are only used for nano filtration and Reverse Osmosis (RO) applications.

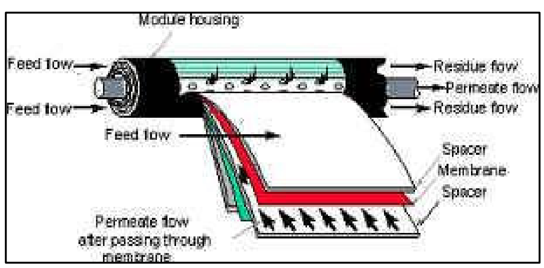

Figure 4.5 Spiral membrane

Pillow-shaped membranes: Membranes that consist of flat plates are called pillow-shaped membranes. The name pillow-shaped membrane comes from the pillow-like shape that two membranes have when they are packed together in a membrane unit. Inside the 'pillow' is a supporting plate, which attends solidity. Within a module, multiple pillows are placed with a certain distance between them, which depends on the dissolved solids content of the wastewater. The water flows through the membranes inside out. When treatment is done, permeate is collected in the space between the membranes, where it is carried away through drains (www.lenntech.com).

Often it is possible to choose between two or more different types which are competitive with each other, for example hollow fibre and spiral wound modules for seawater desalination and pervaporation. In diary applications or in the pulp and paper industries, tubular or plate-and-frame modules are used. In electro-membrane processes (electrodialysis and electro-electrodialysis), the plate-and-frame module is recommended. Plate-and-frame module (for electrodialysis or electro-electrodialysis) is shown in Figure 4.6 (Pourcelly, 2005).

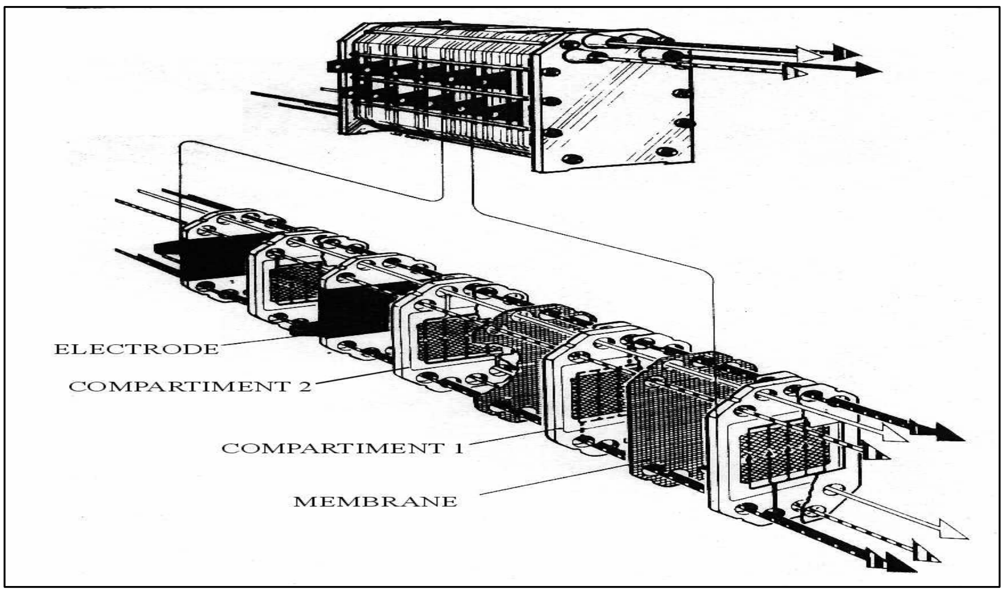

Figure 4.6 Plate-and-frame modules (for electrodialysis or electro-electrodialysis) (Pourcelly,2005)

4.2.1 Microfiltration

Micro filtration is pressure-dependent process. The principle of micro filtration is physical separation. Membranes with a pore size of 0.1 – 10 µm perform micro filtration. Micro filtration membranes remove all bacteria. Only part of the viral contamination is caught up in the process, even though viruses are smaller than the pores of a micro filtration membrane. This is because viruses can attach themselves to bacterial biofilm. Micro filtration can be implemented in many different water treatment processes when particles with a diameter greater than 0.1 mm need to be removed from a liquid.

Examples of micro filtration applications are:

- Cold sterilization of beverages and pharmaceuticals
- Clearing of fruit juice, wines and beer
- Separation of bacteria from water (biological wastewater treatment)
- Effluent treatment
- Separation of oil/ water emulsions
- Pre-treatment of water for nanofiltration or Reverse Osmosis
- Solid-liquid separation for pharmacies or food industries

4.2.2 Ultrafiltration

Ultra filtration is pressure-dependent process. The principle of ultra filtration is physical separation. For complete removal of viruses, ultra filtration is required. The pores of ultra filtration membranes can remove particles of 0.001 – 0.1 µm from fluids.

Examples of fields where ultra filtration is applied are:

- The dairy industry (milk, cheese)
- The food industry (proteins)
- The metal industry (oil/ water emulsions separation, paint treatment)
- The textile industry

Ultrafiltration is generally defined as affecting separation in the 0.002 to 0.2 micron range. This is perhaps more usefully described as the 500 to 300.000 molecular weight cut-off (MWCO) range, requiring pore sizes of from 15 to 1.000 Angstroms.

4.2.3 Nanofiltration

Nanofiltration is a technique that has prospered over the past few years. Today, nanofiltration is mainly applied in drinking water purification process steps, such as water softening, decolouring and micro pollutant removal. During industrial processes Nanofiltration is applied for the removal of specific components, such as colouring agents. Nanofiltration is a pressure related process, during which separation takes place, based on molecule size. The technique is mainly applied for the removal of organic substances, such as micro pollutants and multivalent ions. Nanofiltration membranes have a moderate retention for univalent salts.

Other applications of Nanofiltration are:

- The removal of pesticides from groundwater
- The removal of heavy metals from wastewater
- Wastewater recycling in laundries
- Water softening
- Nitrates removal

4.2.4 Reverse Osmosis (RO)

Reverse Osmosis is based upon the fundamental pursuit for balance. Two fluids containing different concentrations of dissolved solids that come in contact with each other will mix until the concentration is uniform. When these two fluids are separated by a semi permeable membrane (which lets the fluid flow through, while dissolved solids stay behind), a fluid containing a lower concentration will move through the membrane into the fluids containing a higher concentration of dissolved solids. After a while the water level will be higher on one side of the membrane. The difference in height is called the osmotic pressure. By pursuing pressure upon the fluid column, which exceeds the osmotic pressure, one will get a reversed effect. Fluids are pressed back through the membrane, while dissolved solids stay behind in the column. Using this technique, a larger part the salt content of the water can be removed.

Mechanism of RO;

1. Water flows from a column with low dissolved solids content to a column with a high dissolved solids content
2. Osmotic pressure is the pressure that is used to stop the water from flowing through the membrane, in order to create balance
3. By pursuing pressure that exceeds the osmotic pressure, the water flow will be reversed; water flows from the column with high dissolved solids content to the column with a low dissolved solids content. Mechanism of Reverse Osmosis is shown that in Figure 4.6

1	2	3

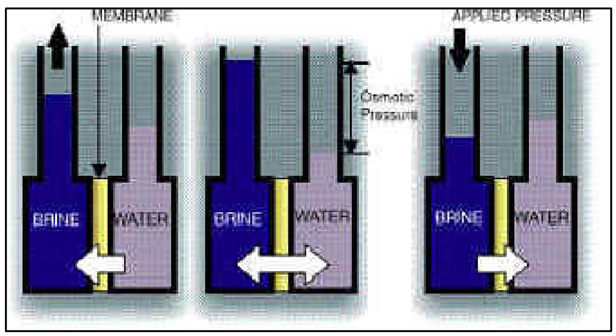

Figure 4.7.Mechanism of Reverse Osmosis

Reverse Osmosis is a technique that is mainly applied during drinking water preparation. The process of drinking water preparation from salty seawater is commonly known. Besides that, Reverse Osmosis is applied for the production of ultra pure water and boiler feed water. It is also applied in the food sector (concentration of fruit juice, sugar and coffee), in the galvanic industry (concentration of wastewater) and in the dairy industry (concentration of milk for cheese production) (www.lenntech.com).

The applications of Reverse Osmosis application are:

- Water softening
- Drinking water production
- Process water production
- Ultra pure water production (electronic industries)
- Concentration of molecular solvents for food and dairy industries

4.3 Process Management of Membrane Filtration Systems

Membrane systems can be managed either through dead-end filtration or through cross-flow filtration.

Dead-end filtration: When dead-end filtration takes place, all the water that enters the membrane surface is pressed through the membrane. Some solids and components will stay behind on the membrane while water flows through. This depends on the pore size of the membrane. Consequentially, the water will experience a greater resistance to passing through the membrane. When feed water pressure is continual, this will result in a decreasing flux. After a certain amount of time the flux has decreased to such an extent, that the membrane will need cleaning. Dead-end management is applied because the energy loss is less than when one applies a cross-flow filtration. This is because all energy enters the water that actually passed the membrane. The pressure that is needed to press water through a membrane is called Trans Membrane Pressure (TMP). The TMP is defined as the pressure gradient of the membrane, or the average feed pressure minus the permeate pressure. The feed pressure is often measured at the initial point of a membrane module. However, this pressure does not equal the average feed pressure, because the flow through a membrane will cause hydraulic pressure losses. During cleaning of a membrane, components are removed hydraulically, chemically or physically. When the cleaning process is performed, a module is temporarily out of order. As a result, dead-end management is a discontinuous process. The length of time that a module performs filtration is called filtration time and the length of time that a module is cleaned is called cleaning time. In practice one always tries to make filtration time last as long as possible, and apply the lowest possible cleaning time. When a membrane is cleaned with permeate, it does not have a continuous production of water. This results in a lower production. The factor that indicates the amount of production is called recovery. Dead-end filtration is shown in Figure 4.8.

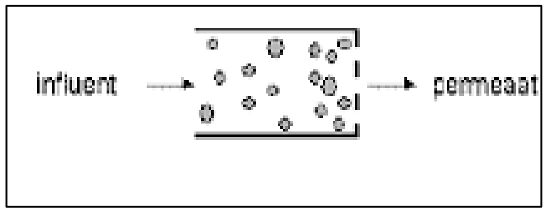

Figure 4.8 Dead-end filtration

Cross-flow filtration: When cross-flow filtration takes place, feed water is recycled. During recirculation the feed water flow is parallel to the membrane. Only a small part of the feed water is used for permeate production, the largest part will leave the module. Consequentially, cross-flow filtration has a high energy cost. After all, the entire feed water flow needs to be brought under pressure. The water speed of the feed water flow parallel to the membrane is relatively high. The purpose of this flow is the control of the thickness of the cake. Consequentially to the flow speed of the water, flowing forces are high, which enables the suspended solids to be carried away in the water flow. Cross-flow management can achieve stable fluxes. Still, the cleaning of cross-flow installations needs to be applied from time to time. Cleaning is performed by means of backward flushing or chemical cleaning. The cross-flow system is applied for Reverse Osmosis, nano filtration, ultra filtration and micro filtration, depending on the pore size of the membrane. Cross-flow membrane filtration is fundamentally different in design, in that the influent stream is separated into two effluent streams, known as permeate and concentrate. Permeate is that fraction which has passed through the “semi-permeable” membrane. The concentrate is that stream which has been enriched in the solutes or suspended solids, which have not passed through the membrane. Membrane is a surface filtration media, which affects separation in the ionic and molecular range as well as the macromolecular and particle range. The advantage of this design approach is that the membrane media is operated in a continuously self-cleaning mode, with solutes and solids swept away by concentrate stream, which is running parallel to the membrane. Hence the term "crossflow," and the advantage of this approach for separation in the micron, sub-micron, molecular and ionic range. The feed solution flows under pressure between the two membranes depicted, and as it flows over the membranes, permeate passes through. The rate of permeation is known as flux. The concentrated fraction of the stream exits through the same flow channel as the feed enters, carrying away concentrated solutes and particles (www.lenntech.com).

Cross-flow (tangential flow) membrane filtration is generally considered to be the most efficient configuration as it reduces membrane fouling and provides a more consistent flux. Cross-flow filtration process is shown in Figure 4.9. Comparison of cross-flow membrane configurations are shown in Table 4.3. Typical process conditions and applications of four pressure-driven membrane processes as depicted in Figure 4.1 and reported in Table 4.4 (classic cross-flow) (Pourcelly, 2005).

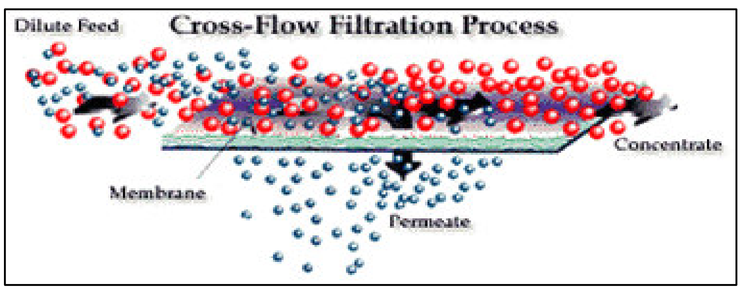

Figure 4.9 Cross-flow filtration process (Pourcelly, 2005)

Table 4.3 Comparison of cross-flow membrane configurations (Pourcelly, 2005)

	Cost	**Packing density**	**Operating pressure capacity**	**Membrane types**	**Fouling resistance**	**Cleanability**
Spiral wound	Low	High	High	Many	Fair	Fair
Hollow fibre	Low	UF high RO v high	UF low RO high	Few	UF good RO poor	UF good, RO poor
Tubular	High	Low	UF moderate	Few	Very good	Very good
Plate & frame	High	Moderate	High	Many	Fair	Fair

Table 4.4 Cross-flow membrane processes (Pourcelly, 2005)

Process	Component retained	Transmembrane pressure	Process applications
RO	99% of most ions, most organics over 150 MW	15 – 70 bars	Brackish sea water, desalting, boiler feed purification, pre-treatment to ion exchange, ultra-pure water production
NF	95% of divalent ions, 40% of monovalent ions, organics greater than 200 – 300 MW	9 – 20 bars	Hardness removal, organic and microbiological removal, dye desalt-ing, colour removal
UF	Most organics over 1000 MW	2 – 9 bars	Pre- and post-treatment to IX, beverage clarification, concentration of industrial organics and dilute suspended oils, removal of pyrogens, bacteria, viruses, and colloids
MF	Small suspended particles greater than 0.1 mm	1.5 – 4 bars	High volume removal of small suspended solids.

4.4 Membrane Fouling

During membrane filtration processes membrane fouling is inevitable, even with a sufficient pre-treatment. The types and amounts of fouling are dependent on many different factors, such as feed water quality, membrane type, membrane materials and process design and control. Particles, biofouling and scaling are the three main types of fouling on a membrane. These contaminants cause that a higher workload is required, to be able to guarantee a continuous capacity of the membranes. At a certain point the pressure will rise so much that it is no longer economically and technically accountable (www.lenntech.com).

4.5 Membrane Cleaning

There are a number of cleaning techniques for the removal of membrane fouling, such as forward flush, backward flush and air flush.

Forward flush: When forward flush is applied in a membrane, the barrier that is responsible for dead-end management is opened (Figure 4.10). 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.

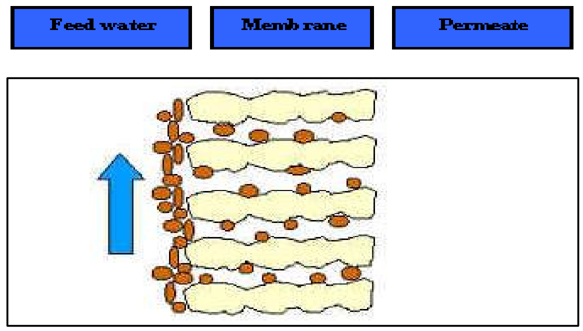

Figure 4.10 Forward Flushing

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 a bout 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 4.11). 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.

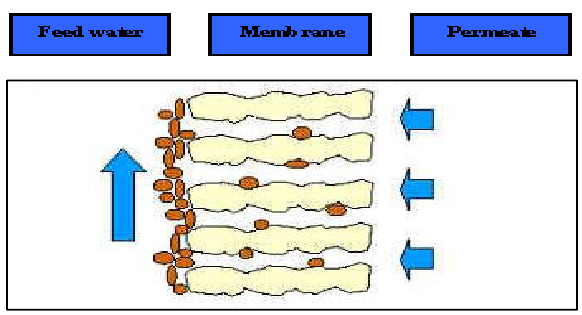

Figure 4.11 Backward Flushing

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 4.12.

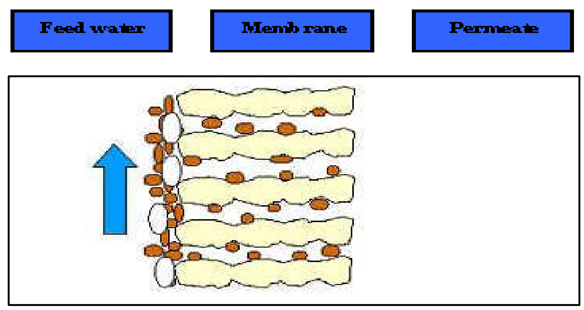

Figure 4.12 Air or Air/Water Flushing

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 is determined by trial and error (practice tests) (www.lenntech.com).

4.6 Protection of Membranes

Ultra filtration can also be applied for pre-treatment of water for Nanofiltration or Reverse Osmosis. Pre-treatment of water is very important when these filtration techniques are applied, because membrane fouling can easily disturb the purification process. Pre-treatment is not only important for Nanofiltration and Reverse Osmosis processes, but also for the above-mentioned micro filtration and ultra filtration processes. Pre-treatment needs to be determined as soon as the composition of the wastewater is known. To prevent plugging or damaging of membranes by hard and sharp particles from the feed water, water needs to be pre-filtered before micro filtration or ultra filtration processes take place. The pores of the pre-filtration unit need to be between 0.5 and 1.0 mm, depending on the composition of the wastewater. Further pre-treatment will not be necessary when micro filtration or ultra filtration is performed. Reversed Osmosis membranes and other membrane systems need periodic cleaning and servicing. For optimal performance specific chemicals are required, depending on the cause of the pollution. Scaling is concerned with the seclusion of suspended inorganic particles, such as calcium carbonate, barium sulphate and iron compounds. Fouling is concerned with the seclusion of organic, colloidal and suspended particles. Bacteria and other microorganisms that decompose these particles will create substrates. As a consequence they will grow and develop further. The processes that are mentioned above will cause a decrease in capacity and/ or an increase of the pressure and, as a result, of the energy use. It is very important to purify the membrane preventively. In many cases regular mild cleaning is better than cleaning periodically with an aggressive cleaning product. The membrane will than last longer. The pretreatment of feed water for nanofiltration or Reverse Osmosis installations greatly influences the performance of the installation. The required form of pretreatment depends on the feed water quality.

The organic matter content and the amounts of bacteria should be as low as possible to prevent the so-called biofouling of membranes. The application of a pretreatment has several benefits:

- Membranes have a longer life-span when pretreatment is performed.
- The production time of the installation is extended.
- The management tasks become simpler.
- The employment costs are lower

Next to pretreatment one can perform a chemical dosage (acid, anti-scalent), to prevent scaling and precipitation of insoluble solids, such as calcium carbonate and barium sulphate on the membrane surface. The applied acids are hydrochloric acid (HCl) and sulphuric acid (H_2SO_4). Sulphuric acid is the most widely used chemical for this purpose. However, hydrochloric acid is applied more and more because sulphuric acid can negatively influence the fouling speed of a membrane. When the feed water contains high amounts of sulphate ions, hydrochloric acid replaces sulphuric acid. The dosage of sulphuric acid would enhance the chances of scaling by sulphate ions on the membranes in this case (www.lenntech.com).

CHAPTER FIVE
MATERIALS AND METHODS

5.1 Introduction of the Pilot Plant

In this study, a pulp and paper industry located in Izmir was selected as a pilot plant. Throughout the explanation of the study, name of this plant will not be expressed. Its production capacity is 20,500 tons/year. Huge amount of water, which is about 3700 m^3/day, is used for production. The process water is abstracted from four deep wells and flow rate of three of them is 22 L/s and one of them is 12 L/s. General properties of water withdrawn from the well are given in Table 5.1. This data was taken from the plant.

Table 5.1 General Properties of Well Waters of the Pilot Plant

Parameters	**Unit**	**Value**	**Parameters**	**Unit**	**Value**
Ammonia (NH_3)	mg/L	1.73	Magnesium (Mg)	mg/L	39.1
Ammonium (NH_4^+)	mg/L	1.83	Magnesium Hardness	mg/L	160.3
Bicarbonate (HCO^-_3)	mg/L	281	Manganese (Mn)	mg/L	0.56
Vaporization Residual	mg/L	923	Organic material	mg/L	3.3
Ferrous (Fe)	mg/L	1.232	pH (26.6 °C)	----	7.81
Fe^{+2}	mg/L	0.03	Sulphate (SO^{-2}_4)	mg/L	36
Phosphate (PO^{-3}_4)	mg/L	1.47	Total alkalinity	mg/L	313
Conductivity (26.6 °C)	µS/cm	1230	Total dissolved solids	mg/L	984
Calcium (Ca^{2+})	mg/L	47.8	Bicarbonate hardness	°FS	27.8
Calcium Hardness	mg/L	191.2	Total hardness	°FS	28.05
Carbonate (CO_3^{-2})	mg/L	32	Silicium Dioxide (SiO_2)	mg/L	61.2
Chloride (Cl^-)	mg/L	210	Nitrate (NO_3^-)	mg/L	2.21
Sodium chloride (NaCl)	mg/L	346.2	Nitrite (NO_2^-)	mg/L	0.02

Water withdrawn from the wells is directly used in the process. Any pretreatment operations are not applied. In pulp and paper industry, process water must be limpid and odorless. It must not be included turbidity and suspended solids and its hardness must be 15-16 dH (a German dH is 17.8 ppm $CaCO_3$). The wastewater generated from the production is treated by chemically and biologically. The chemical treatment operations include slow mixing and rapid mixing tank followed by chemical sedimentation tank. Chemically treated wastewater is then treated by conventional activated sludge system. After then effluent is discharged to the receiving media. The wastewater treatment plant flow scheme is given in Figure 5.1.

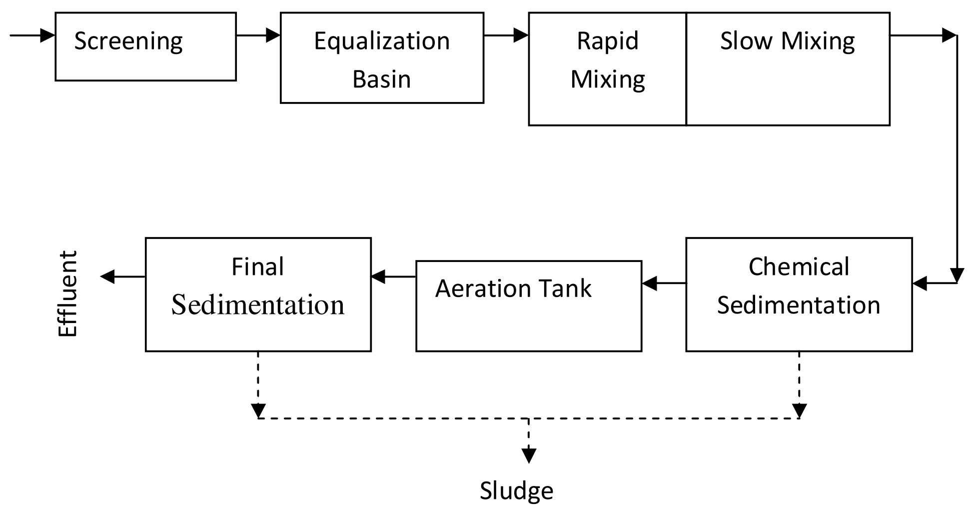

Figure 5.1 Wastewater Treatment Plant Flow Scheme of the Pilot Plant

5.2 Laboratory Scale Membrane System

In this study, chemically treated wastewater (CW) and effluent of the treatment plant (EW) were 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. Although the maximum inlet pressure of the system is given as 5.5 bar (80 psi), the system could be operated at the maximum pressure of 3.5 bar. During the experiments the inlet pressure was kept constant at 2 bar.

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 5.1, photo of the membrane module and membrane cartridges are given. The retentate (concentrate) and permeate collected after each run were analyzed.

Figure 5.1 Laboratory Scale Membrane System and Cartridges

5.3 Analytical Procedure

In the experimental studies, chemical oxygen demand (COD), suspended solid (SS), pH, conductivity (EC), temperature, and total organic carbon (TOC) 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). TOC analyses were done using a DOHRMANN DC-190 high temperature analyzer. pH and conductivity were measured by WTW model 340i multi analyzer.

CHAPTER SIX
RESULTS AND DISCUSSIONS

6.1 Introduction

Experimental studies were planned and carried out considering the following steps:

- The determination of the chemically treated wastewater properties
- The determination of the effluent of the wastewater treatment plant properties
- The comparison of these two treated wastewater properties with the required process water quality
- An advanced treatment application using the lab scale membrane module
- The evaluation of the membrane studies results.

6.2 Advanced Treatment Application

In order to produce high quality of paper, process water must also be high quality. It must be limpid, odorless, and soft. It must not be included turbidity and suspended solids and its pH must be neutral. However, the properties of effluent have not required quality except pH parameter. Therefore, if the treated wastewater is used as process water, additional organic matter and suspended solids removal operations must be applied. At these situations, application of the one of the advanced treatment operations should be good choice. In this study, membrane filter systems were considered as an advanced treatment to achieve further organic material and suspended solids removal.

6.2.1 Determination of the Membrane System Properties

The factor which has the greatest influence on the membrane system design and operation is the fouling tendency of the feed water. Membrane fouling is caused by particles and colloidal material which are present in the feed water and are concentrated at the membrane surface. The concentration of the fouling materials at the membrane surface increases with increasing permeate flux (the permeate flow rate per unit membrane area) and increasing the ratio of permeate flow rate to feed flow rate. Systems with high permeate flux rates are, therefore likely to experience higher fouling rates and more frequent chemical cleaning. The average flux of the system, i.e. the system permeate flow rate related to the total active membrane area of the system, is a characteristic number of a design. The system flux is a useful number to quickly estimate the required number of elements for a new project (http://www.dow.com).

Table 6.1Results of Flux Experiments

Membrane Filter	Influent P (bar)	Effluent P (bar)	Pressure Losses (bar)	Flux ($L/m^2.h$)
1 kDa	0.25	0.2	0.05	0
	0.5	0.3	0.20	9.11
	1.2	0.6	0.60	10.67
	2.1	1.3	0.80	14.67
	3.5	3.2	0.30	15.2
30 kDa	0.1	0.009	0.09	34
	0.6	0.21	0.39	126.67
	1	0.3	0.70	150
	2.1	1.7	0.40	270.8
	2.5	2.1	0.40	325
	3	2.6	0.40	386.23
	3.5	2.9	0.60	421.4
100 kDa	0.1	0.08	0.02	47.78
	0.25	0.1	0.15	88.89
	0.7	0.19	0.51	133.32
	1	0.27	0.73	400
	1.5	0.33	1.17	500

In this study, membranes were not operated continuously and recycle was not used. Therefore, flux decreases depending on the fouling could not be observed. However, flux is the one of the most important parameter for the membrane systems. Therefore, the experimental studies were started with the flux experiments. The effect of pressure on flux was investigated for each membrane cartridge. The inlet pressure was controlled at 0.1 and 3.5 bars. In order to decide the flux of the clean membrane without fouling, fresh water was used during the flux trials. The flux experiments results are given in Table 6.1.

The permeate flux increased with increasing pressure for all cartridges as expected. The membrane having 1 kDa MWCO has smaller pore size than the others. Therefore permeate flux of this membrane cartridge is lower. However if the pressure of the system was increased, permeate quality decreased as seen following sections.

6.2.2 Results of the Advanced Treatment Applications

As indicated before, both chemically treated wastewater (1) and effluent of the treatment plant (2) is further treated with the membrane system. Location of the sampling point is presented in Figure 6.1.

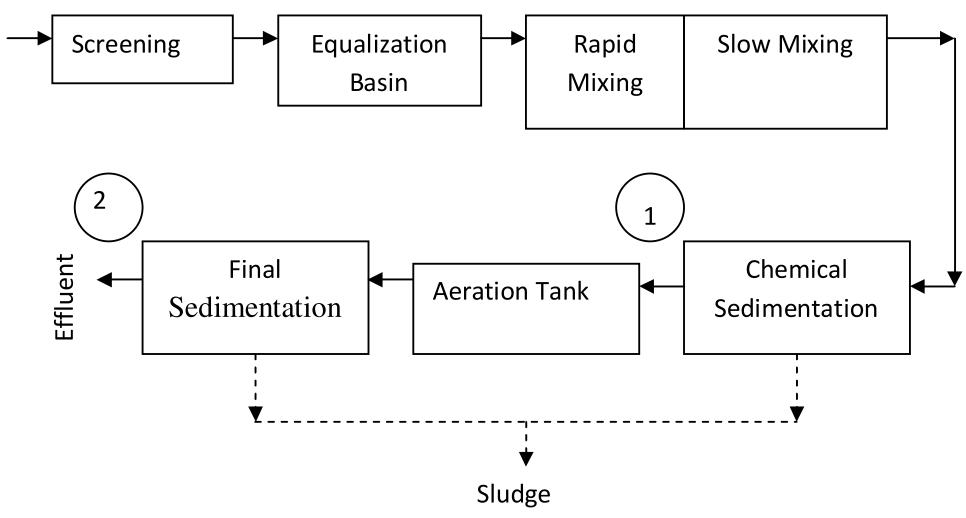

Figure 6.1 Sampling point location

Membrane performances were evaluated considering SS, COD, and TOC parameters. The results of experimental studies carried out with three different membrane filters are discussed below. In addition, all results are also given as table form at Appendix. Some abbreviations are used to give results. These are given below:

- 100KO, 30KO, 1KO : Influents of membrane filters
- 100KR, 30KR, 1KR : Retantate of membrane filters
- 100KP, 30KP, 1KP : Permeate of membrane filters

"O", "R", and "P" indicate influent, retantate, and permeate, respectively. "100K", "30K", and "1K" indicate membrane cartridge having MWCO of 100 kDa, 30 kDa, and 1 kDa, respectively.

6.2.2.1. The Effect of the Membrane Application on Suspended Solids Reduction

As general, all membrane systems have high suspended solids removal capacities. Because pulp and paper industry requires process water containing no suspended solids, this parameter is very important.

Wastewater samples firstly were treated by 100 kDa. After then, 100 kDa effluents were treated by 30 kDa and 30 kDa effluents were treated by 1 kDa membrane. Results are given in Figure 6.2.

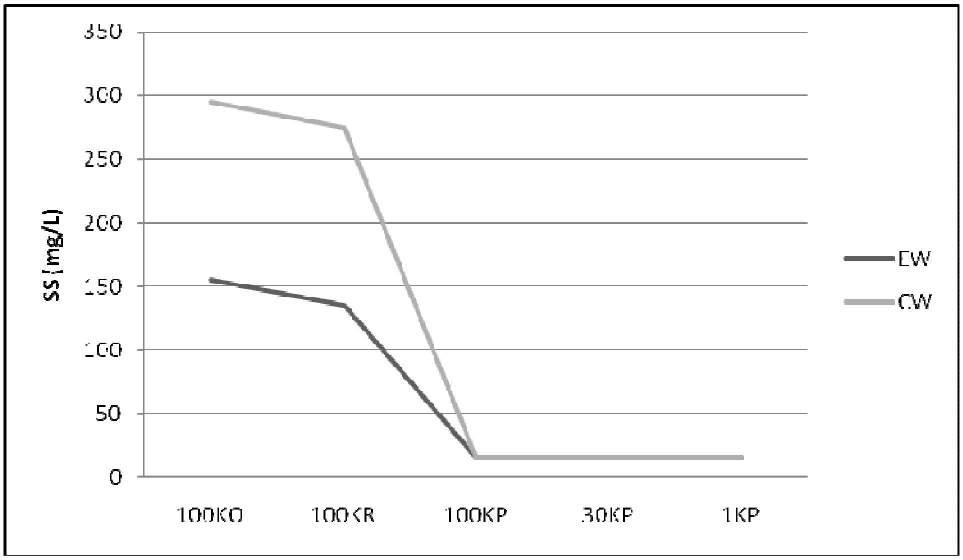

Figure 6.2 Effect of 100 kDa membrane on suspended solid removal

When 100 kDa membranes were used alone, suspended solids removal efficiency was 95 and 90% for CW and EW, respectively. SS concentration can be reduced to till 15 mg/L for both CW ($SS_{influent}$ = 295 mg/L) and EW ($SS_{influent}$ = 155 mg/L) samples. In order to decrease SS concentration to less than 15 mg/L, permeate of the 100 kDa membrane was pumped to 30 kDa and 1 kDa membranes. However, SS concentration could not be decreased to below 15 mg/L using these membranes.

Wastewater samples were then treated by 30 kDa membrane. After then, permeate of this membrane was pumped to 1 kDa membrane. Figure 6.3 shows the results of these experiments.

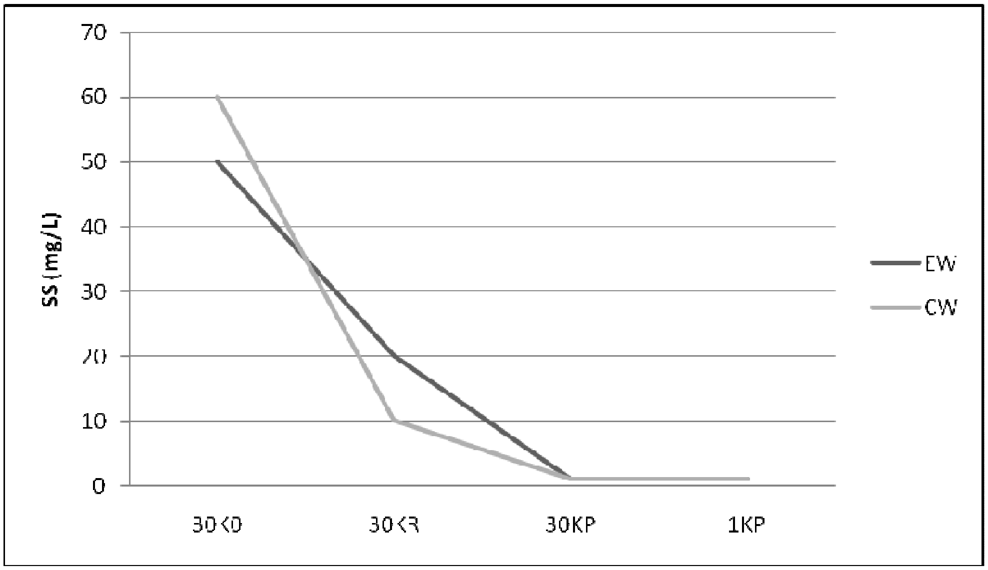

Figure 6.3 Effect of 30 kDa membrane on suspended solid removal

At these experiments, quality of wastewater samples taken from the plant was better. Suspended solid concentration of CW and EW was 60 and 50 mg/L, respectively. When 30 kDa membrane was applied, approximately 98% SS removal efficiencies were obtained and SS concentration of permeate of two wastewaters were decreased to 1 mg/L. Any SS reductions were obtained with 1 kDa membrane used after 30 kDa membrane.

In order to evaluate the 1 kDa membrane usage effect on SS removal, wastewater samples were also directly pumped to this membrane. Results of these experiments are given in Figure 6.4.

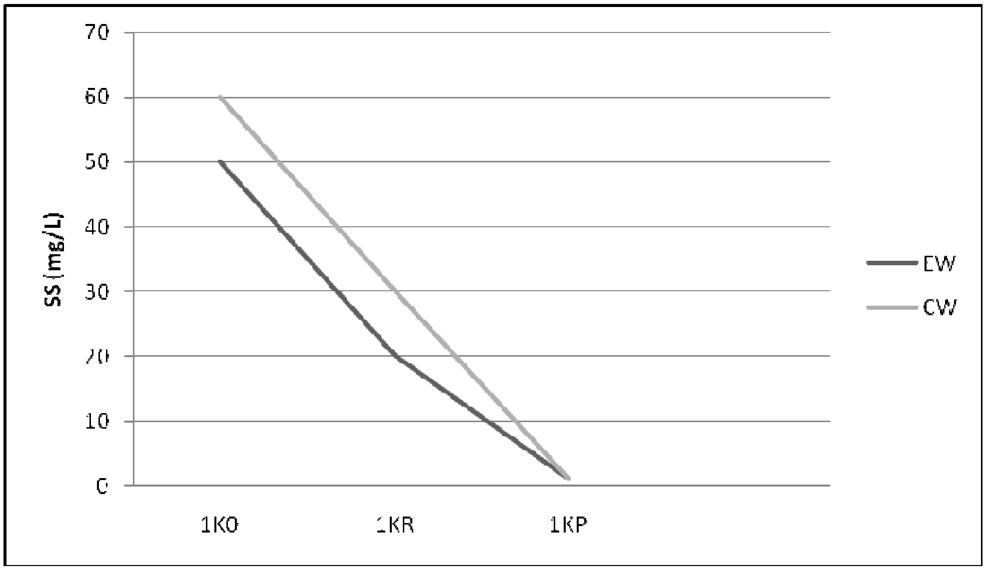

Figure 6.4 Effect of 1 kDa membrane on suspended solid removal

When 1 kDa membrane was used alone, SS concentrations could be reduced to 1 mg/L. Similar results were obtained with previous experiments.

Considering all experiments, it can be said that 100 kDa membranes is sufficient for SS removal. Therefore usage of 30k and 1k membrane is not necessary.

6.2.2.2 The Effect of the Membrane Application on Organic Material Reduction

The effect of membrane on organic material was evaluated by TOC and COD parameters. Results are given as separate two subsections below.

6.2.2.2.1 The Effect of the Membrane Application on TOC. CW and EW wastewaters were treated using 100 kDa, 30 kDa, and 1 kDa membrane in series. Figure 6.5 represents the results of TOC measurements of permeate of these applications. Low TOC removal efficiencies were obtained. At the end of the 1 kDa membrane application, only 44 and 7% TOC removal efficiency was achieved for CW and EW wastewater, respectively.

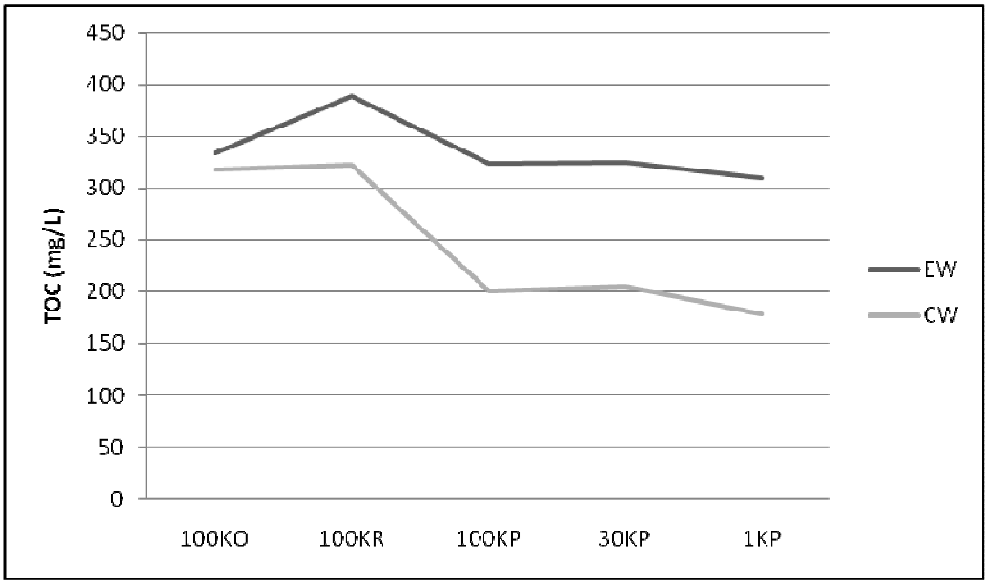

Figure 6.5 Effect of 100 kDa membrane on TOC removal

In order to evaluate the effect of 30 kDa membrane on TOC removal, wastewater samples were directly pumped to this membrane. Permeate of 30 kDa membrane was further filtered using 1 kDa membrane. Figure 6.6 shows the results of these experiments. With these experiments, only 12 and 6% TOC removal efficiencies could be obtained for CW and EW, respectively.

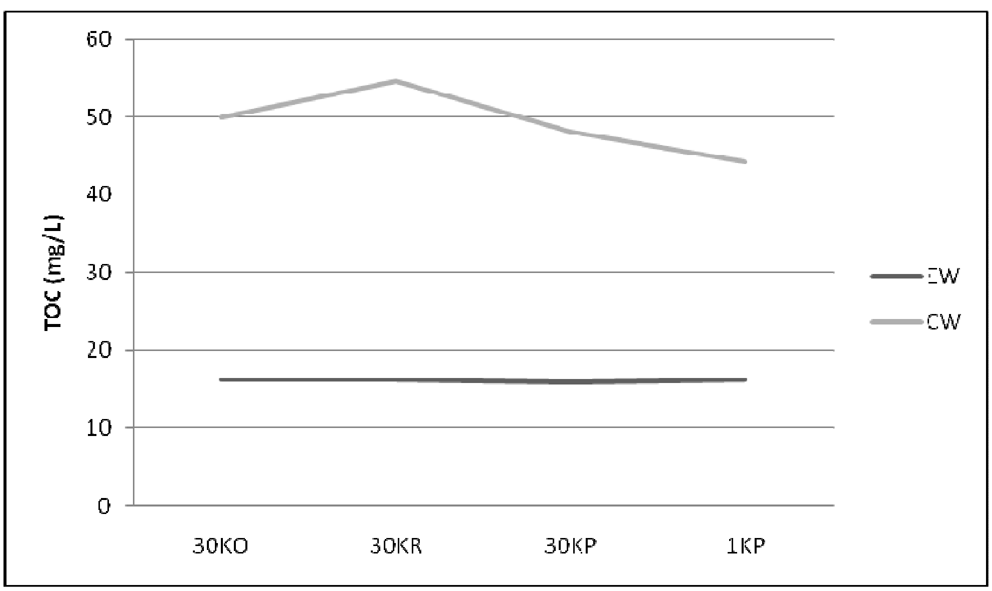

Figure 6.6 Effect of 30 kDa membrane on TOC removal

To evaluate the effect of 1 kDa membrane on TOC removal, it was used alone. As do in previous experiments, only just TOC removal could be achieved. 13% TOC removal efficiency was obtained for CW and 0.6% TOC removal efficiency was obtained for EW. Results are given in Figure 6.7.

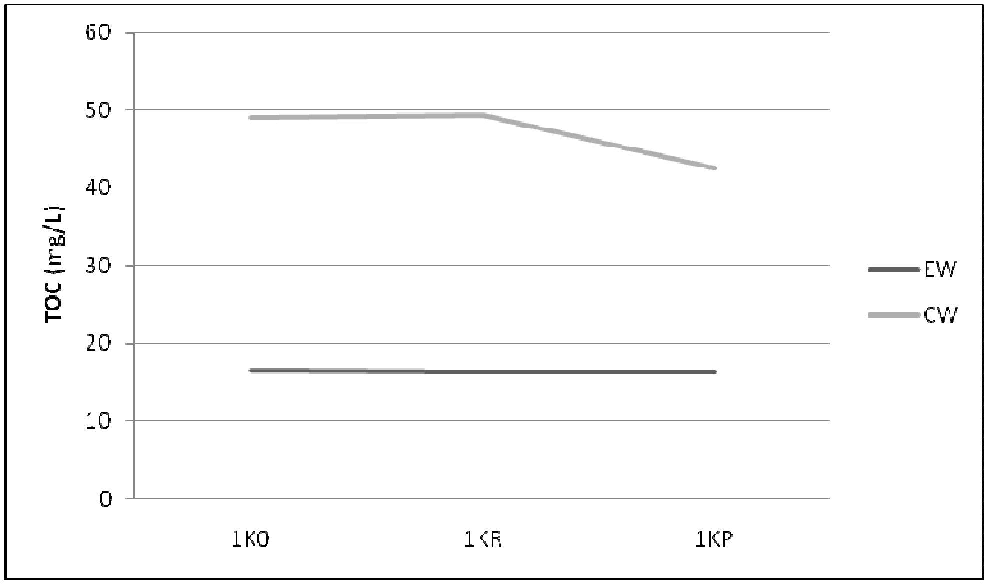

Figure 6.7 Effect of 1 kDa membrane on TOC removal

6.2.2.2.2 The Effect of the Membrane Application on COD. In addition to TOC parameters, organic matter removal was also monitored by COD parameter. Similar analysis procedure was applied for COD parameters. 100 kDa, 30 kDa, and 1 kDa membranes were used in series for both CW and EW wastewaters. COD concentrations of permeate of these experiments are given in Figure 6.8. Higher COD reductions were obtained compared to TOC. At the end of the 1 kDa membrane application, 80 and 58% COD removal efficiency was achieved for CW and EW wastewater, respectively.

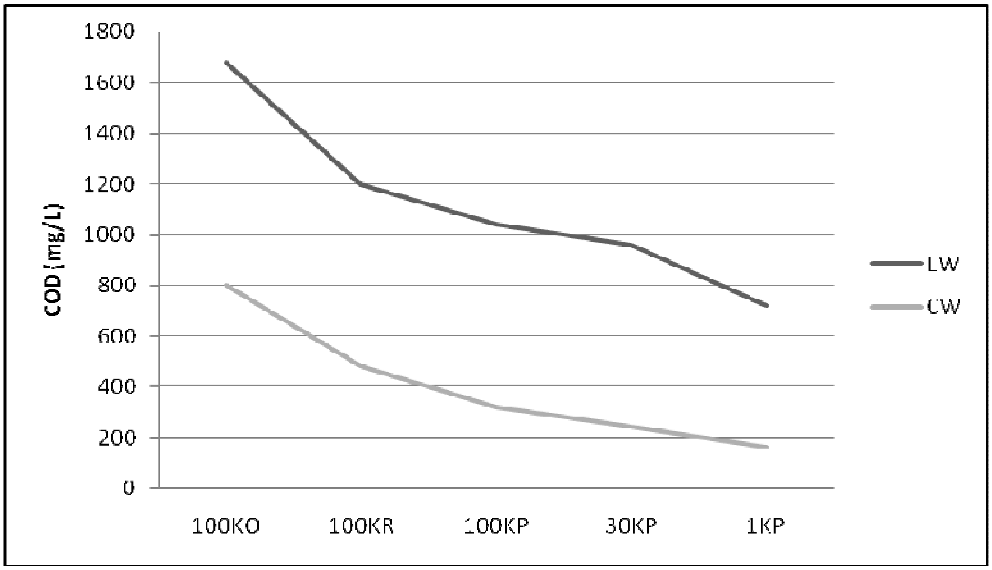

Figure 6.8 Effect of 100 kDa membrane on COD removal

The effect of 30 kDa membrane on COD removal was also evaluated. Wastewater samples were directly pumped to this membrane. After then permeate of 30 kDa membrane was further filtered using 1 kDa membrane. Figure 6.9 shows the results of these experiments. 87.5% and 75% COD removal efficiencies were achieved for CW and EW, respectively. COD concentration of CW reduced to 80 mg/L after 30 kDa and 1 kDa membrane applications in series.

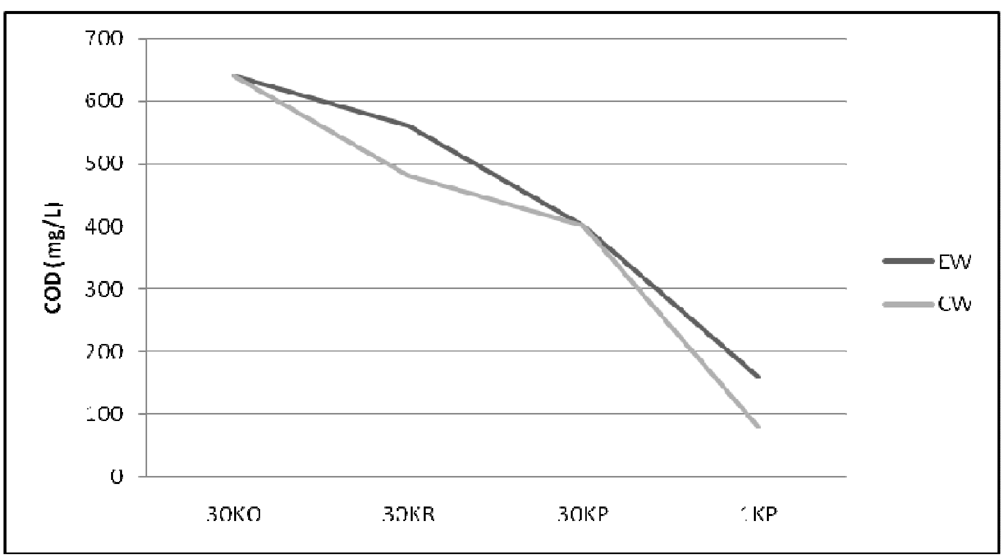

Figure 6.9 Effect of 30 kDa membrane on COD removal

When the 1 kDa membrane was used alone, similar result was obtained for EW but lower COD removal efficiencies were obtained for CW (Figure 6.10). 82 and 75% COD removal efficiency was obtained for CW and EW, respectively.

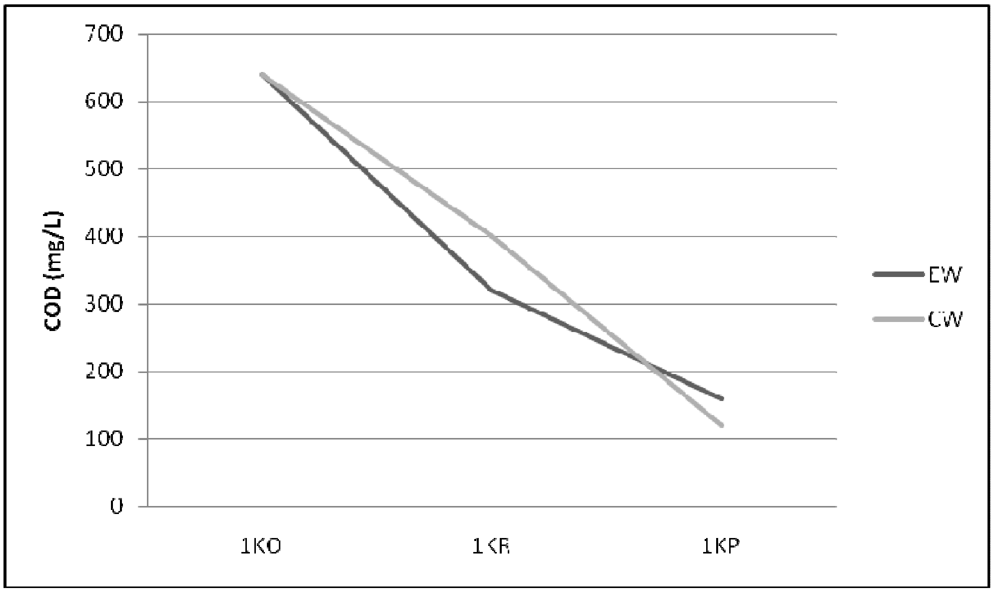

Figure 6.10 Effect of 1 kDa membrane on COD removal

6.2.2.2.3 The Effect of the Membrane Application on pH and Conductivity. Since the pH and conductivity of process water is very important, these parameters were also checked. 100 kDa, 30 kDa, and 1 kDa membranes were used in series for this aim. PH of permeates changed between 6.5 and 6.9 for CW while it changed between 7.2 and 7.5 for EW (Figure 6.11). Conductivity of permeates were very low. All permeate conductivities were below than 2.5 mS/cm (2500 µS/cm). However, conductivity of well water, which is used in process, is 1230 µS/cm. Therefore additional total dissolved solid removal method, i.e. reverse osmosis, can be used.

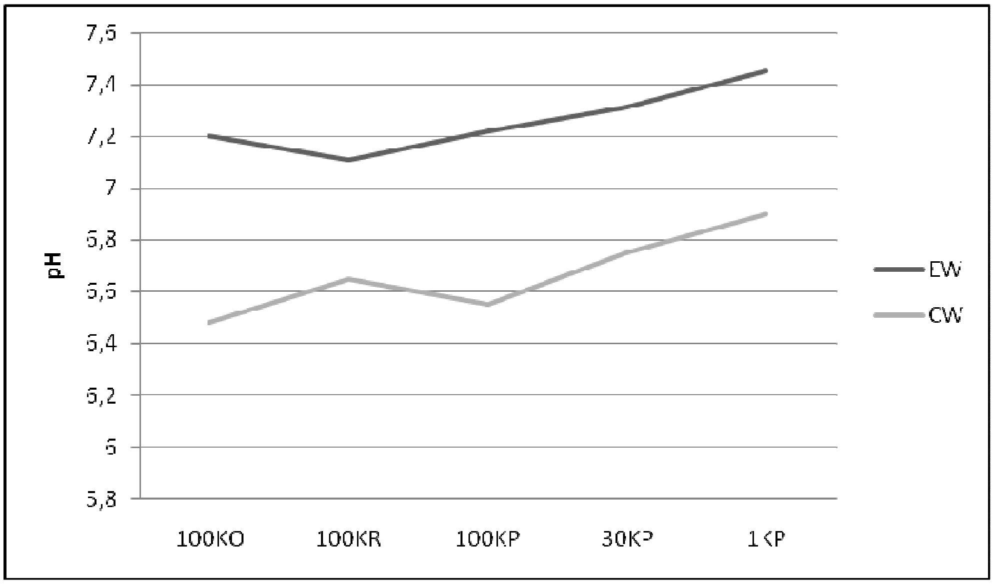

Figure 6.11 Effect of membrane application on pH

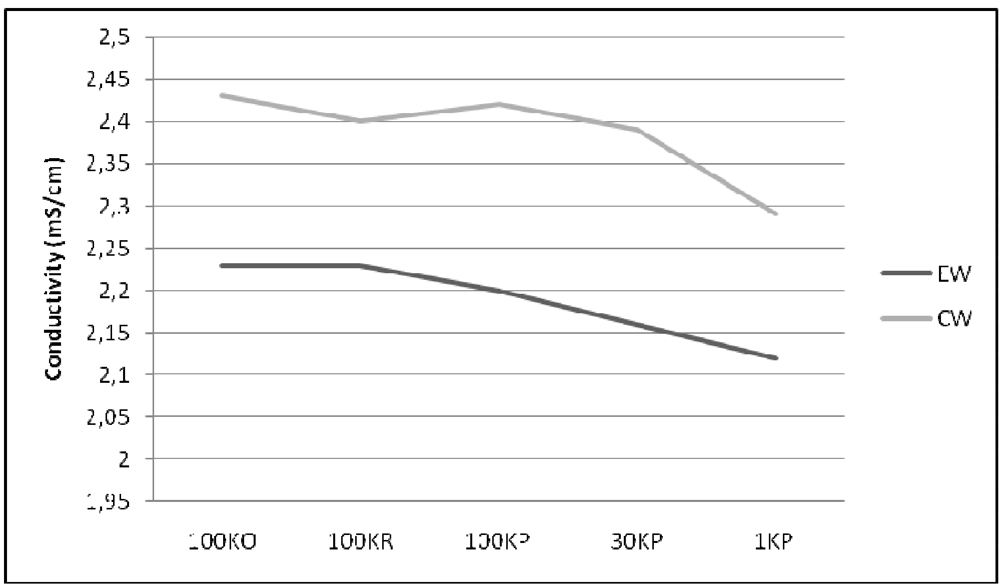

Figure 6.12 Effect of membrane application on conductivity

6.2.3 Summary of the All Experiments and Evaluation of the Results

The results of all experiments described above are summarized in Table 6.2 and Table 6.3. Considering these results, it can be said that, membrane system used in this study, is not sufficient for organic matter removal. However, sufficient SS removal efficiencies were obtained for both two wastewaters. Investment cost of membrane increases with decreasing pore size. Therefore, cost of 1 kDa membrane is higher than others. Almost similar results were obtained with 1 kDa and 30 kDa membrane. So, it is not necessary to use of 1 kDa membrane to obtain process water from treated wastewater.

In this study, two effluents (chemically treated wastewater, CW, and effluent of the treatment plant, EW) and three ultrafiltration membrane systems were used. SS concentrations of EW lower than CW samples. This property can help choosing the most appropriate filter type. It can be considered this difference for choosing takepoint of clarified wastewater. As seen from Figure 6.2, 6.3 and 6.4, suspended solid concentration difference between two types of wastewater is very high. Since clogging is the one of the most important parameter for membrane operation, low SS concentration of influent is more suitable for effective membrane operation. The less SS concentration, the more long-life membrane system. Depend on low SS concentration, period of cleaning and clearing of membrane system is also extended and cost of management is reduced. SS removal efficiencies of three type membrane filter used in this study were almost same. This provides elasticity to choose membrane filter type. However, in the economical point of view, 100 kDa membranes can be used alone for sufficient SS removal. But, in order to obtain sufficient organic material removal, all membranes could not give required efficiency.

Wastewater samples were taken from the pilot plant in different days. Therefore, there were some differences between their properties. Especially, the quality of the first sample was very worse than others. Effluent quality changed depending on the influent wastewater properties. Nonetheless, average COD removal efficiencies were about 80-87% and 75% for CW and EW, respectively. These results were fine for membrane systems. However, sufficient TOC reduction could not achieved with membrane filters. In order to reduce TOC into required value, nanofiltration or reverse osmosis can be used. A high amount of dissolved colloidal substances results in a high COD (chemical oxygen demand) load in the process water and in a loss of quality of the mechanical pulp, e. g. strength properties.

PH values were 7-7.5 and 6.5-7 for EW and CW, respectively. Membrane filters used in this study can be operated at pH 2 to 14. Therefore, any problem related to pH was not existed.

Ultrafiltration is not sufficient for removal of dissolved solids. Therefore, required conductivity results could not be obtained. Nanofiltration or reverse osmosis can be used for this aim. Helik says about conductivity; “Inorganic dissolved substances, i.e. salts, are measured as increased conductivity. Salts are also detrimental to the process performance and potentially for the paper properties. Electrolytes reduce the swelling potential of fibers and chloride especially leads to corrosion of machine parts” (Helik H.; 2006).

Table 6.2 Removal efficiencies of membrane system for CW

Parameter	Membrane Type		
	100K	30K	1K
COD	80 %	87.5 %	82 %
TOC	44 %	12 %	13 %
SS	95 %	98 %	98 %

*pH average: 6.6 *Conductivity average: 2.4 ms/cm

Table 6.3 Removal efficiencies of membrane system for EW

Parameter	Membrane Type		
	100K	30K	1K
COD	58 %	75 %	75 %
TOC	<10	<10	<10
SS	90 %	98 %	98 %

*pH average: 7.2 *Conductivity average: 2.2 ms/cm

CHAPTER SEVEN
CONCLUSIONS AND RECOMMEDATIONS

7.1 Conclusions

Wastewater is too valuable to waste in most areas of the world. Fresh water sources can be conserved using reclaimed water in appropriate places. Wastewater may be reused up to a dozen times or more before being discharged to the receiving media. Industrial wastewaters reuse one of the possible reuse options. But, wastewater for reuse must be adequately treated to obtain required water quality. The suitability of reclaimed water for use in industrial processes depends upon the particular use. Therefore, each industry should be evaluated separately and in investigating the feasibility of industrial reuse with reclaimed water, the potential users must be contacted to determine specific requirements for process water. In this study, the possibility of industrial wastewater reuse for process water in a pulp and paper industry was evaluated. According to the experimental results, the conclusion remarks from this study could be given as follows:

- The main problem of the effluents of the pilot pulp and paper industry is high concentrations of suspended solids, organic material, and conductivity.
- Ultrafiltration system with 100 kDa membrane can be used for SS removal. 95-98% SS removal efficiencies were obtained.
- Almost similar results were obtained for 1 kDa, 30 kDa, and 100 kDa membranes.
- COD and TOC parameters were used for organic material detection. Although better results were obtained for COD than TOC, sufficient organic material reduction could not be achieved.
- Required conductivity results, which are necessary for the production of high quality paper, could not be achieved.

7.2 Recommendations

- The effectiveness of membrane systems should be evaluated in continuous operation.
- Pilot plant studies should be done to evaluate the usability of membrane filter systems in paper industries.
- Water reuse alternatives should be evaluated considering the different stages of the treatment plant.
- The combination of different membrane systems should be examined. Particularly to prevent clogging, ultrafiltration used in this study can be used as pretreatment step.
- Ultrafiltration system used in this experiment can be used for lower quality paper production.
- Organic matter and conductivity values could not be reduced to required values by using ultrafiltration membrane system. So, nanofiltration or reverse osmosis can also be examined.

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APPENDIX

Table 1. Result of Experimental Studies Suspended Solids

Types of Membrane	Discharge (mg/L)	Chemical Unit Effluent (mg/L)
100KO	155	295
100KR	135	275
100KP	15	15
30KP	15	15
1KP	15	15
30KO	50	60
30KR	20	10
30KP	1	1
1KP	1	1
1KO	50	60
1KR	20	30
1KP	1	1

Table 2. Results of Experimental Studies for TOC

Types of Membranes	Discharge (mg/L)	Chemical Unit Effluent (mg/L)
100KO	333.6	318
100KR	388.2	322.2
100KP	323.7	309.85
30KP	324.9	204.84
1KP	309.6	178.23
30KO	16.258	49.86
30KR	16.256	54.6
30KP	15.86	48.06
1KP	16.202	44.18
1KO	16.42	49
1KR	16.36	49.26
1KP	16.32	42.56

Table 3 Results of Experimental Studies for COD

Types of Membranes	Discharge (mg/L)	Chemical Unit Effluent (mg/L)
100KO	1680	800
100KR	1200	480
100KP	1040	320
30KP	960	240
1KP	720	160
30KO	640	640
30KR	560	480
30KP	400	400
1KP	160	80
1KO	640	640
1KR	320	400
1KP	160	120