DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

APPLICATION OF MEMBRANE PROCESSES FOR THE TREATMENT OF HIGH STRENGTH WASTEWATERS

by
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October, 2007
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APPLICATION OF MEMBRANE PROCESSES FOR THE TREATMENT OF HIGH STRENGTH WASTEWATERS

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in Environmental Engineering, Environmental Technology Program

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November, 2007
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PhD THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"APPLICATION OF MEMBRANE PROCESSES FOR THE TREATMENT OF HIGH STRENGTH WASTEWATERS"** completed by **EZGİ OKTAV AKDEMİR** under supervision of **Prof. Dr. ADEM ÖZER** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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ACKNOWLEDGMENTS

The author is thankful to Prof. Dr. Adem ÖZER, the advisor of the thesis, for his guidance, motivation and valuable advises throughout the preparation of this thesis. The author greatly acknowledges the effort of Prof. Dr. Füsun ŞENGÜL, for her invaluable advices, considerable concern in beginning of the thesis.

The author is thankful to Prof. Dr. Ayşe FİLİBELİ and Prof. Dr. Kadir YURDAKOÇ for their advices, comments and evaluations throughout the conduct of the study.

The author is thankful to Dr. Zihni YILMAZ, Technician Yılmaz SAĞER and Orhan ÇOLAK for their helps in experimental studies.

The author is also thankful to her friends Ebru ÜLENGİN, Ebru Ç. ÇATALKAYA, Özlem T. GÜRLEK, Neval BAYCAN, Cemile YÜCEL, Nurdan BÜYÜKKAMACI, Gülbin E. KAYNAK, Özlem S. KUŞÇU, İlgi K. KAPDAN, Yaşariye OKUMUŞ for their support, morale motivation and friendship.

The author finally would like to thank to her family, especially her mother Sevim OKTAV and her husband Özay AKDEMİR for their love, moral support and encouragement.

Ezgi OKTAV AKDEMİR

APPLICATION OF MEMBRANE PROCESSES FOR THE TREATMENT OF HIGH STRENGTH WASTEWATERS

ABSTRACT

In the content of this PhD thesis, membrane processes, such as microfiltration, ultrafiltration and nanofiltration were applied for the treatment of cheese whey effluents and olive oil mill wastewaters. Before membrane processes, different physical and chemical pretreatment experiments were done in order to avoid membrane fouling.

In this respect, this thesis is composed of two main parts. In the first part of the experimental studies, cheese whey effluents were examined. Maximum removal efficiencies were obtained by combination of physical pretreatment, microfiltration and ultrafiltration processes. 99% of SS reduction and 98% of oil and grease reduction were achieved. However, COD concentration was as high as 22000 mg/L with 66% removal efficiency.

In the second part of this thesis, treatment of olive oil mill wastewater (OMWW) was investigated. If chemical coagulation with H_2SO_4 at pH=2, cartridge filter and filter cloth filtration, ultrafiltration and then nanofiltration processes were applied, 3700 mg/L,1083 mg/L, 30 mg/L, and 40 mg/L concentrations were achieved for COD, TOC, SS, oil and grease, respectively. With another OMWW sample, application of two step pH adjustment and cartridge filter filtration, and then nanofiltration process gave 1600 mg/L, 948 mg/L, 40 mg/L, 80 mg/L concentrations for COD, TOC, SS and oil and grease parameters, respectively. The results obtained show that NF treatment is a possible and acceptable method for treatment of olive oil mill wastewater.

Key Words: Cheese whey effluent, olive oil mill wastewater, pre-treatment, microfiltration, ultrafiltration, nanofiltration.

YÜKSEK KİRLİLİK İÇEREN ATIKSULARIN ARITIMINDA MEMBRAN İŞLEMLERİNİN UYGULANMASI

ÖZ

Bu doktora tezi kapsamında, peynir altı suyu ve zeytinyağı endüstrisi atıksularının arıtımı amacıyla mikrofiltrasyon, ultrafiltrasyon ve nanofiltrasyon işlemleri uygulanmıştır. Membran tıkanmasını engellemek amacıyla, membran filtrasyon işlemlerinden önce fiziksel ve kimyasal ön arıtım denemeleri yapılmıştır.

Tez iki ana kısımdan oluşmaktadır. Ilk kısımda, peyniraltı suyu atıksularının arıtılabilirliği incelenmiştir. Maksimum giderme verimleri fiziksel ön arıtım, mikrofiltrasyon ve ultrafiltrasyon işlemlerinin kombinasyonuyla elde edilmiştir. Bu durumda %99 AKM, %98 yağ-gres giderme verimi elde edilmesine rağmen KOİ konsantrasyonu 22000 mg/L gibi yüksek bir değerdedir. KOİ için elde edilen giderme verimi %66'dır.

Tezin ikinci kısmında, zeytinyağı endüstrisi atıksularının (karasu) arıtılabilirliği incelenmiştir. pH=2'de H_2SO_4 ile koagülasyon, kartuş filtreden ve filtre bezlerinden filtrasyon, ultrafiltrasyon ve nanofiltrasyon işlemlerinin arka arkaya uygulanmasıyla, 3700 mg/L KOİ, 1083 mg/L TOK, 30 mg/L AKM ve 40 mg/L yağ-gres konsantrasyonlarına ulaşılmıştır. Başka bir karasu numunesiyle yapılan çalışmada, iki kademe pH ayarlaması, kartuş filte filtrasyonu ve nanofiltrasyon ile ulaşılan kirlilik konsantrasyonları, KOİ için 1600 mg/L, TOK için 948 mg/L, AKM için 40 mg/L ve yağ-gres için 80 mg/L'dir. Elde edilen sonuçlar, nanofiltrasyon işleminin karasuyun arıtımı için uygun ve kabul edilebilir bir yöntem olduğunu göstermektedir.

Anahtar Kelimeler: Peyniraltı suyu, zeytinyağı endüstrisi atıksuyu, ön arıtım, mikrofiltrasyon, ultrafiltrasyon, nanofiltrasyon.

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CHAPTER ONE
INTRODUCTION

1.1 General Information about Membrane Processes

1.1.1 Membrane Technology

Membrane filtration processes are gaining popularity in a wide range of applications to remove a variety of chemical and biological contaminants of the wastewaters. Membrane technologies offer a number of distinct advantages including more compact installation, absolute barrier for certain microorganisms, less chemical requirements, greater reliability and little restriction to presence of toxic compound (Hong, 2003).

Even though significant development of membrane technology has been made, membrane fouling remains to be one of the biggest challenges for its wider application in water and wastewater treatment. Generally, membrane fouling refers to the adsorption or accumulation of retained substances within the membrane pore or on the membrane surface, thereby, causing a gradual decline in permeate flux and reducing the efficiency of membrane filtration. A wide spectrum of constituents such as less soluble salts, dissolved organic compounds, colloidal and particulate mater and biological growth could all cause the membrane fouling. The phenomena involved are very complex, because of the nature of complicated physicochemical and biological interactions between the fouling-causing materials and membrane surfaces. This places a substantial economic restriction on membrane plant operation because the excessive fouling requires frequent backwash and even membrane replacement (Baker et. al., 1995).

Membrane can be broadly defined as a separation process that uses a semi-permeable membrane to divide the feed stream into two portions: permeate that contains the material pass through the membranes and retentate consisting of the species left behind. The processes can be classified in many different ways according

to the driving force used for separating materials (i.e. transmembrane pressure, temperature, concentration and electrical potential), separation mechanism, membrane structure and its chemical composition or membrane construction geometry. Among them, pressure-driven membrane separation processes have been recognized as the most promising membrane processes for water and wastewater treatment (Wiesner et. al., 1994; Macrorie et. al., 2000).

Various membrane materials have been proposed for water and wastewater treatment. Depending on the applications, both organic polymers and inorganic materials with wider pH and temperature range have become available. Proper selection of membrane material is one key factor in using the membrane processes successively. Ideally, the membrane to be used should have high permeate flux, good contaminant rejection, great durability, strong chemical resistance and low cost (Hong, 2003).

1.1.2 Membrane Separation Processes

Membrane processes can be divided into four groups, depending on membrane pore size and separation mechanism: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Microfiltration and ultrafiltration are often operated at very low transmembrane pressure and have been widely used to remove particles and microorganisms. Reverse osmosis process is mainly used to desalinize brackish water and sea water. Because of its small pore size, reverse osmosis process has also been used to remove natural organic matter, synthetic organic and other inorganic chemicals. Nanofiltration process uses the membrane with the pore size between reverse osmosis and ultrafiltration. It has been used to remove calcium ions, magnesium ions and disinfection by-products precursors (Jacangelo et. al., 1995). General information about these four groups is given below.

1.1.2.1 Microfiltration (MF)

MF membrane is generally porous enough to pass molecules of true solutions, even if they are large. Microfilters can also be used to sterilize solutions, as they are prepared with pores smaller than 0.3 microns, the diameter of the smallest bacterium, pseudomonas diminuta. The MF membranes are made from natural or synthetic polymers such as cellulose nitrate or acetate, polyvinylidene difluorie (PVDF), polyamides, polysulfone, polycarbonate, polyproppylene. The inorganic materials such as metal oxides, glass, zirconia coated carbon are also used for manufacturing the MF membranes (www.osmonics.com).

1.1.2.2 Ultrafiltration (UF)

UF is most commonly used to separate a solution that has a mixture of some desirable components and some that are not desirable. UF is somewhat dependent on charge of the particle, and is much more concerned with the size of the particle. Typical rejected species include bio-molecules, polymers and colloidal particles. UF processes operate at 2-10 bars though in some cases up to 25-30 bars have been used. UF throughput depends on physical properties of the membrane, such as permeability, thickness, process and system variables like feed consumption, feed concentration, system pressure, velocity and temperature. Polymeric materials, polysulfone, polypropylene, nylon, polytetrafluoroethylene (PTFE), PVC, acrylic copolymer has been used successfully as UF membranes. Inorganic materials such as ceramics, carbon based on membranes, zirconia, have been commercialized by several vendors (Gould et. al., 2003).

1.1.2.3 Nanofiltration (NF)

NF is a form of filtration that uses membranes to separate different fluids or ions. NF is capable of concentrating sugars, divalent salts, bacteria, proteins, particles, dyes and other constituents that have a molecular weight greater than 1000 daltons.

Membranes used for NF are cellulose acetate and aromatic polyamide type having characteristics as salt rejections (www.osmonics.com).

1.1.2.4 Reverse Osmosis (RO)

Unlike water filtration, that can only remove some suspended materials larger than 1 micron, the process of RO will eliminate the dissolved solids, bacteria, viruses and other germs contained in the water. RO is essentially a pressure driven membrane diffusion process for separating dissolved solutes. The RO is generally used for desalination seawater for its conversion into potable water. Reverse osmosis uses high pressures to force permeate through the membrane, producing a concentrate containing high levels of dissolved salts. RO membranes are made from polymers, cellulose acetates, and polyamide types (www.osmonics.com).

1.1.3 Membrane Configuration

The shape of a membrane is essential to the proper and reliable operation of a membrane filtration plant. The following membrane modules are most frequently used: Plate and frame, spiral wound, hollow fiber, and tubular.

1.1.3.1 Plate and Frame Module

In typical plate and frame module, the feed is pumped trough two membrane surfaces. Permeate is collected on the other side. Membrane surfaces are kept on a certain distance by a spacer plate. The spacer consists of filtrate paper with a very open structure. This way stacked membranes are placed between the two end-plates. The typical total surface of such a membrane module is about 100-400 m^2/m^3. This device incorporates sheet membrane that is stretched over a frame to separate the layers and facilitate the collection of the permeate. Schematic demonstration of this module is given in Figure 1.1.

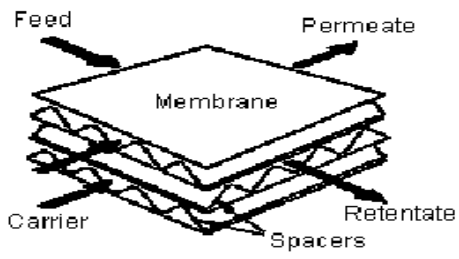


Figure 1.1 Plate and frame module
(www.osmonics.com)

1.1.3.2 Spiral Wound Module

Spiral modules are made by placing a woven plastic mesh which acts as the permeate channel between two membrane layers and sealing three sides. The fourth side of this sandwich is attached to the permeate tube. Another plastic mesh, which acts as the feed channel is laid over it and the assembly is wrapped around the central permeate tube. This module also can withstand high pressures but is susceptible to fouling of feed channels by suspended particles. Spiral module is given in Figure 1.2.

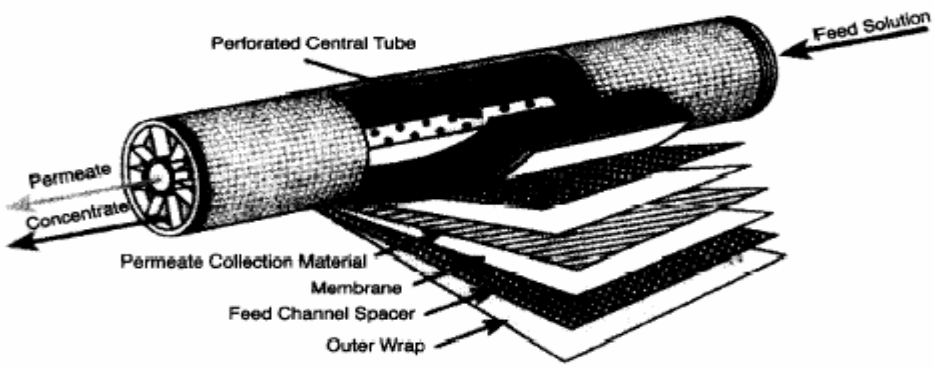


Figure 1.2 Spiral wound module (Nicolaisen, 2002)

1.1.3.3 Hollow Fiber Module

Hollow fiber module consists of bundles of hollow fibers typically 0.5 to 3 mm diameter sealed into plastic headers and assembled in permeates casings. The feed passes through the central bore and permeate collects in the outer casing. Hollow fibers are self-supporting hence these modules are for use in low pressure applications only. These can accommodate moderate levels of suspended particles. Similar to the tubular elements in design, hollow fibers are generally much smaller in diameter and require rigid support such as is obtained from potting of the bundle inside a cylinder. As with tubular elements, feed flow is usually down the interior diameter of the fiber. Schematic diagram of hollow fiber module is given in Figure 1.3.

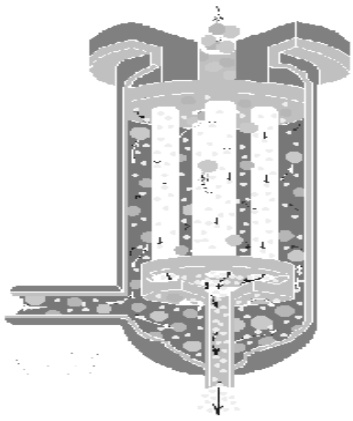


Figure 1.3 Hollow fiber module
(www.osmonics.com)

1.1.3.4 Tubular Module

Tubular module consists of tubular membranes held inside individual perforated support tubes. Several such tubes are assembled onto common headers and permeate vessels to form a module. A variation of tubular geometry is the monolithic construction where several channels are formed in a porous block of material. These modules can withstand high pressures and accommodate suspended particles. Schematic diagram of tubular module is given in Figure 1.4.

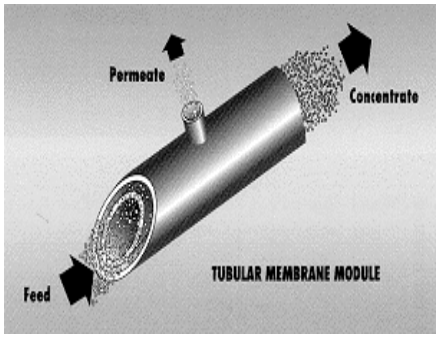
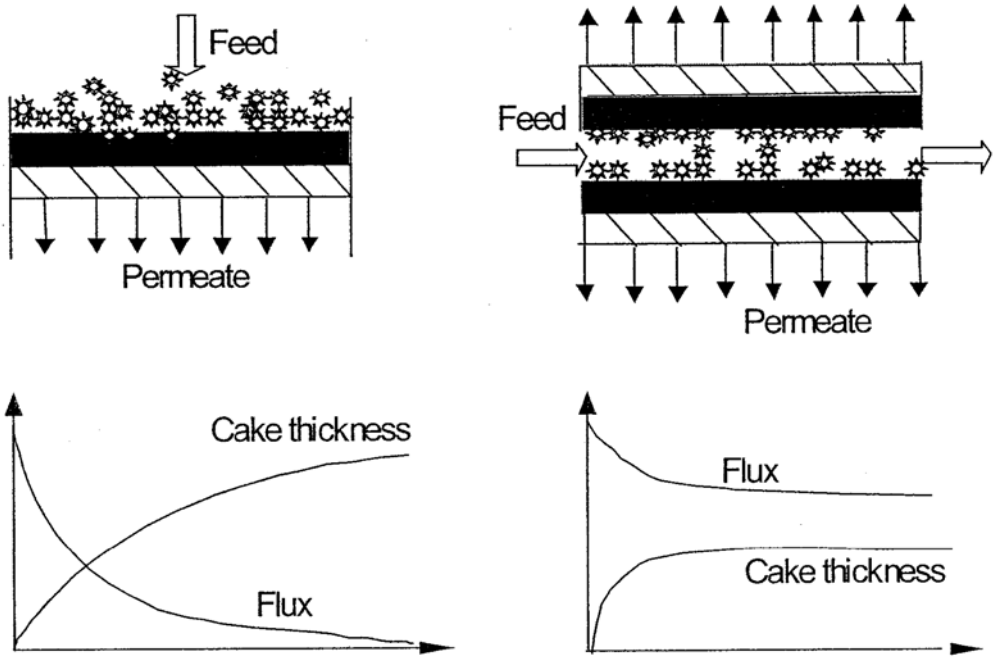


Figure 1.4 Tubular module
(www.osmonics.com)

Manufactured from ceramics, carbon or any number of porous plastics, these tubes have inside diameters ranging from 1/8 inch (3.2 mm) up to approximately 1 inch (2.54 cm). The membrane is typically coated on the inside of the tube, and the feed solution flows through the interior from one end to other, with the permeate or filtrate passing through the wall to be collected on the outside of the tube.

1.1.4 Types of Filtration

There are two ways to operate filtration equipment which are given in Figure 1.5.: the dead-end or cross flow mode. Some equipment such as pleated cartridges is operated in the dead-end mode, in which the feed is pumped directly towards the filter. There is one stream entering the filter module and only one permeate stream leaving the filter. However, most ultrafiltration and microfiltration modules are operated in the cross flow mode, in which the feed is pumped across or tangentially to the membrane surfaces. In this mode, there is one stream entering the module and two streams leaving the module: the retentate and the permeate.



(a) (b)

Figure 1.5 Schematic showing of the filtration types (a) dead-end filtration, (b) cross flow filtration (Hong, 2003)

The main advantage of the dead-end filtration mode is simplicity. The feed suspension is not recycled or passed across the membrane. However, intensive concentration polarization and fouling can occur under these conditions. In contrast, the cross flow membrane filtration will continuously scour the rejected contaminants away from the membrane surface, thereby, minimizing the buildup of contaminants on the membrane surface and the extent of membrane fouling. Although membrane cleaning is still periodically required, the self cleaning nature of cross flow filtration lengthens the filtration cycle prior to backwash. Thus, it has been widely used in nearly all commercial large scale pressure driven membrane plants (Gould et. al., 2003).

1.1.5 Membrane Fouling

The feasibility of membrane technology is largely limited by membrane fouling. Membrane fouling generally refers to a gradual decline in permeate flux due to adsorption of foulants to the membrane surface or within the membrane pores. Deposition of foulants also results in the formation of a cake layer.

It has been observed that less soluble salts, dissolved organic compounds, colloidal and particulate matter, and biological growth could also cause membrane fouling. Each of these foulants has different effects on membrane fouling and flux recovery. Fouling inside membrane pores by salts and small colloids often considered as an irreversible process and is responsible for long term flux decline unless they are dissolved by cleaning agents in backwash water. In contrast, a flux decline due to the development of a surface cake is largely reversible (Belfort et. al., 1994).

A number of studies have been taken a fundamental approach to predict the flux decline or fouling (Field et. al., 1995; Bowen & Jenner, 1995; Choo & Lee, 1998). The fluid dynamics of the membrane system, the membrane chemistry and the nature of the foulants could affect the transport of foulants to the membrane and their accumulation on and within the membrane. Efforts to predict permeate flux decline are complicated by the simultaneous occurrence of different fouling mechanisms: gravity, van der Waals attraction, permeation drag, buoyancy, electrical double layer repulsion, Brownian diffusion, shear induced diffusion, inertial migration and other mechanisms. As such, no single mechanism can fully explain the permeate flux decline.

The successful operation of a membrane plant requires the careful management of membrane fouling. Its complete elimination is not possible, but its impact can be controlled by a variety of techniques. For this reason, evaluation of optimal conditions in each membrane plant is necessary.

One of the most important reasons why membrane processes are not more extensively used is the flux decline during the filtration. The flux decline is caused by several phenomena in, on and near the membrane. These phenomena can also cause a loss in selectivity or an additional undesired selectivity. The predicting of permeate flux decline is essential for keeping economical and reliable operating conditions. There have been many theoretical approaches to predicting permeate flux decline. Theoretical models describing permeate flux decline in membrane filtration of macromolecular and colloidal suspensions are: Particle trajectory model, traditional filtration theory, concentration polarization model (film theory) and resistance-in-series model.

1.1.6 Parameters Affecting Membrane Performance

The membrane filtration process involves a number of particle transport mechanisms and foulant-membrane interactions. As a result, many factors will affect the performance of cross flow membrane filtrations under various conditions (Zhang & Song, 2000; Williams & Wakeman, 2000; Schafer et. al., 2000). These factors are feed concentration, transmembrane pressure (TMP), recycling flow rate or cross flow velocity, particle size or molecular weight cut off (MWCO), pH of feed solution and ionic strength of feed solution

1.1.6.1 Feed Concentration

The permeate flux decreases with increasing feed concentration. Experimental studies reported by Zhang & Song (2000) showed that the permeate flux for a higher feed concentration declines faster than that for a lower feed concentration. The lower feed concentration shows a higher permeate flux at steady state. In another study, the effect of organic concentration for colloid rejection was investigated by Schafer et. al. (2000). They suggested when particles mixed with the organics and then with the salt solution, the organic concentration affects the particle charge and aggregation, result in flux decline.

1.1.6.2 Transmembrane Pressure (TMP)

The importance of TMP in membrane filtration was investigated by many researchers (Lee & Clark, 1998; Zhang & Song, 2000; Schafer et. al., 2000). The permeate flux increases with increasing TMP. However, there is a negative effect of a higher TMP. The cake layer on the membrane surface may become more compact as the TMP increase, so greater flux reduction is occurred. Zhang & Song (2000) demonstrated flux rate declines with time under different TMPs. It showed that a higher permeate flux results in a higher decline rate and permeate flux when steady state condition is TMP dependent. Schafer et. al. (2000) studied the effect of TMP with and without organics. The results showed that TMP increase leads to the break-up of aggregated organics, which affect the deposition of colloids.

1.1.6.3 Cross flow Velocity

One important feature of cross flow membrane filtration is that it produces shear along the membrane surface. The cross flow carries the retained particles away from the filter surface and reduces membrane fouling. As the cross flow velocity increases, the particle concentration at the membrane surface is expected to decrease. So, permeate flux increases.

1.1.6.4 Particle Size

The particle size is another important parameter affecting flux decline. In the initial stage of filtration, the permeate flux for small particles decline faster than that for the larger ones. Zhang & Song (2000) showed that permeate flux for large particles are lower than those for small particles when the filtration time is sufficiently long. They suggested that there is an equilibrium region in the cross flow filtration channel and an equilibrium time. The time to reach equilibrium is longer for larger particles.

1.1.6.5 pH and Ionic Strength of Feed Solution

The solution pH and ionic strength are important to understand fouling behavior because these factors affect the surface charge of particles and the solubility of many solutes (Schafer et. al., 2000). Braghetta et. al. (1997) suggested that the charged polymers come apart at high pH and/or low ionic strength, thus increasing water permeability. These same conditions would also favor an increased thickness of the diffuse double layer and therefore greater rejection of charged matters.

1.2 Treatment of Cheese Whey Effluent

Cheese whey is the aqueous phase that separates from the curds during cheese making or casein production. Whey contains 93-94% water, 63-67 g/L dry matter, 45-50 g/L lactose, 7-9 g/L protein, 6-8 g/L salts, and 1-2 g/L fat. The pollutant load represents 30-50 g/L BOD_5, 60-65 g/L COD and 1.2 g/L suspended matter. The production of 1 kg of pressed cheese generates 9 to 10 liters of whey according to the amounts of water used in the production process (Bonnet et. al., 1999).

Treatment or utilization of cheese whey was not a concern in cheese making for many years, the whey being simply discarded with no preliminary treatment. Today various technologies of ranging complexity, reliability and cost have been developed to forestall pollution by waste whey and to find uses for this by-product. These treatments very often involve separating the major components, first of all to eliminate water. The extraction of lactose, proteins and salts affords various substances that are useful in the food and pharmaceutical industries. Other technologies (anaerobic digestion, various fermentations, use of plants) can also be used. These processes, which mostly rely on industrial technology, are generally not suitable for small production units. However, small dairy farms cannot be left to go on discarding crude whey into the environment, which most often means slow-flowing waterways (Mawson, 1994).

Membrane technology is finding interesting applications in the water industry. Developments in membrane technology have created the opportunity for an entirely new approach to cheese technology. Membrane processes have some advantages that make the membrane treatment attractive such as continuous operation, no pollution of the environment, small space requirements, suitable for high salt contents, easy transportation, simple operation, no civil construction necessary at the site and reduced cost with technological environments (Koyuncu et. al., 2000).

The application of the membrane technology for the treatment of cheese whey was discovered in the last decades (Maubois, 1991). Several membrane operations have been proposed for the treatment of cheese whey: one-stage operations like ultrafiltration, nanofiltration, reverse osmosis or two-stage operations like ultrafiltration and nanofiltration, nanofiltration and reverse osmosis or in combination with membranes and biological treatment named as membrane bioreactors.

Koyuncu et. al. (2000) used two alternative membrane processes. Nanofiltration membranes were applied to the existing treatment plant effluents in different operating conditions. Batch runs were carried out successively and serious membrane fouling appeared not to be a problem with treatment plant effluents. During the runs, flux values ranged from 16 to 51 $L/m^2.h$, while pressures were changed from 5 to 12 bar. Excellent rejections had been achieved. Approximately 90% of the treatment plant effluent was recovered for reuse. In the second part of their study, two pass reverse osmosis membranes were applied to the raw wastewater of the dairy industry. At first stage, flux values ranged from 14 to 32.8 $L/m^2.h$, while pressure ranged from 6 to 18 bar. A very good removal of COD was obtained. Concentration level of COD has decreased to approximately 100–200 mg/L in the permeate. At second stage, the initial permeate flux was about 45 $L/m^2.h$ and at the end of the run, 39.5 $L/m^2.h$, constant values had been observed. Feed COD was about 100–200 mg/L. This concentration level of COD has decreased to approximately 1–2 mg/L in the permeate.

Balannec et. al. (2002) were compared eight nanofiltration and reverse osmosis membranes by dead-end filtration. Cross-flow experiments with nanofiltration and reverse osmosis spiral-wound membranes were confirmed the results obtained by dead-end filtration. For dead-end filtration nanofiltration and reverse osmosis, COD removal efficiencies were ranging between 98.9–99.8 % and 99.88–99.96 %, respectively. For cross-flow nanofiltration and reverse osmosis, COD removal efficiencies were around 99.7 % and 99.96 %, respectively. Their results showed that one single membrane operation allowed the milk constituents to be concentrated in the retentate. However, reusable water of composition complying with the standard of purified water from process water was not reached. A finishing step such as reverse osmosis or other was needed for the production of reusable water.

Ateş (2001) investigated the treatability and reuse of dairy industry wastewater using membrane processes. Nanofiltration and reverse osmosis were evaluated for the treatment of the effluent of chemical–biological treatment plant and the original effluent of dairy industry, respectively. In this study, permeate flux declined rapidly at the beginning of the run and then appeared remain approximately constant after 60 h of operation at different pressures. Specific energy consumption increased as a function of time and decreased with increasing pressure for each membrane. The average of specific energy consumption was obtained at 6 and 1 kWh/m^3 for nanofiltration and reverse osmosis, respectively. Therefore, nanofiltration and reverse osmosis operational costs were estimated at U.S. \$ 0,45/m^3 and U.S. \$ 0,75/m^3, respectively. The operational costs of treatment of the dairy industry effluent with chemical–biological process (U.S. \$ 0,30/m^3) followed by nanofiltration membrane and with only reverse osmosis membrane were nearly equal. COD removal efficiency of Nanofiltration and reverse osmosis was 95–98 % and 92–95 %, respectively. Therefore, it was found that the product water had reuse potential for dairy industry.

If it was aimed to treat cheese whey with membrane processes, the greatest problem is membrane fouling that drastically reduces the efficiency of permeation and also changes its selectivity. In this case, pre-treatment step is necessary to

decrease membrane fouling and to increase filtration efficiency. Before membrane processes, chemical precipitation of protein can be applied. Treatment of dairy wastewaters by chemical treatment is only removes albumins and other suspended solids, does not remove dissolved organic compounds (Şengül, 1991).

Traditional coagulants, such as ferric chloride and alum, result in a high metal content in the sludge, which is undesirable in food (Odegard, 1987). Rusten et. al. (1992) tested four different combinations of coagulants: H_2SO_4-ferric chloride (JKL), H_2SO_4-lignosulfonic acid (LSA), H_2SO_4- carboxy methyl cellulose, and lactic acid-carboxy methyl cellulose. They used COD_f/COD_t (filtered/total chemical oxygen demand) ratio for controlling the protein removal efficiency. Using JKL resulted in poor solid separation and lower total COD removal efficiency than with any of the other coagulants (20-40%). Sulphuric acid plus CMC gave the best removal efficiencies (30-70 %) at a COD_f/COD_t ratio of 0.6. However, total COD removal efficiencies with lactic acid plus CMC were only a few percent below the removal efficiencies obtained with sulphuric acid plus CMC (25-65%). 20-60% COD removal efficiencies were achieved with sulphuric acid plus LSA.

Some researchers investigated the efficiency of a process using chitosan as an alternative to the CMC process. Chitin and chitosan are fibers derived from marine animals. Chitin is a polysaccharide that naturally occurs in the hard outer shell of insects, shellfish such as crab, lobster, and shrimp, and marine coral. Chitin is chemically similar to cellulose and starch, the abundant plant fibers. It is used to make various other substances, including chitosan, which is derived from chitin by heating it with a chemical solution. Chitosan has the advantage of being more soluble in water compared to chitin. It has been used to treat the waste effluents a wide number of food process applications including egg breaking, vegetable, cheese, meat, beer and apple juice process. In these operations, chitosan was demonstrated to be a very good coagulating agent. The minimum suspended solid removal efficiency was reported as 70% (Xue, 1998).

Olsen et. al. (1996) used chitosan as a biological cationic polymer for the treatment of dairy industry wastewater at different pH values (4.5-5.25) by coagulation. They obtained 60 % removal efficiencies of phosphates and COD_t, and 90 % removal efficiencies of suspended solids at pH=5.25. Chitosan can efficiently function at pH ranges even as high as 5.25, while other chemical polymers, such as CMC functioned only at pH below 4.5. Chitosan usage can save almost 50% of pH-adjusting acid and base consumption. Chitosan sludge can be used as an animal food additive.

Ekdal (2000) investigated the chemical treatability of dairy wastewater and determined whether the chemically treated wastewater meet the discharge standards for industries, in terms of COD parameter. Ferric chloride, ferrous sulfate and alum were used as coagulants in the jar tests experiments. However, also chemical treatability of wastewater had been performed with just acid addition and pH adjustment. Characterization studies demonstrated that wastewater characteristics varied within a wide range. COD removal efficiencies varied between 33% and 45% in the studies which had been performed with pH adjustment. Maximum COD removal efficiencies were 72%, 59% and 54% for ferric chloride, ferrous sulfate and alum, respectively at the optimum dosages and pH values. COD removal efficiencies obtained during experimentation, were found to be inadequate to meet the discharge standards for industries. This condition demonstrated that chemical treatment was insufficient by itself for discharging dairy wastewater into the sewerage.

1.3 Treatment of Olive Oil Mill Wastewaters (OMWW)

Olive oil production is an important economic activity of Mediterranean countries and this activity leads to significant liquid and solid pollutant wastes. Especially the liquid phase, olive oil mill wastewater (OMWW) is the major environmental problem of these countries. The environmental impact of the OMWW is considerable with the dangerous effects, such as coloring of natural waters, threat to the aquatic life, causing surface and ground water pollution, changing soil quality and plant growth and causing odours. The difficulties of treatment of olive mill effluents are

mainly related to: (a) high organic loading, (b) seasonal operation, (c) high territorial scattering and (d) presence of organic compounds which are hard to biodegrade, such as long-chain fatty acids and phenolic compounds (Ergüder et. al., 2000).

Many different processes have been proposed to treat the OMWW: lagooning or direct watering on fields, co-composting, physico-chemical methods (flocculation, coagulation, filtration, open evaporating ponds and incineration), ultrafiltration/reverse osmosis, chemical and electrochemical treatments and manufacture into animal food (Ün et. al, 2006). The treatment of OMWW by a combination of chemical or physical processes and a biological process has not been completely successful, and a longer lag phase has been found to be necessary for biological treatment. In Mediterranean countries, olive oil production and the subsequent wastes are widespread in small locations, resulting in intensive local pollution problems (Drouiche et. al., 2004).

OMWW contain significant amounts of suspended and colloidal matter at concentrations as high as 190 g/L (Mulinacci et al., 2001). So, successful treatment may require a preconditioning stage to remove the suspended and colloidal fractions which typically consist of pectins, proteins, oils and tannins. This can be done by means of separation processes especially membrane processes and several case studies have been reported in the literature.

Turano et. al. (2002) developed a two stage centrifugation and ultrafiltration process consists in a preliminary centrifugation step, in which the suspended solids are removed, and in an actual selective separation phase, carried out by ultrafiltration of the centrifuge supernatant. The combination of centrifugation and ultrafiltration allows a TSS and COD reduction of about 80% and 90%, respectively. Interestingly, fats could easily be recovered as they were completely rejected by the membrane.

Canepa et. al. (1988) studied combined application of membranes and adsorption processes to the treatment of vegetation waters coming from olive oil factories. They used polysulfone ultrafiltration membranes for absorbing polymers and

polypiperazine amide. The influent COD concentration of the plant was 90000 mg/L and 99% COD reduction was obtained.

In Italy, an olive oil mill wastewater treatment plant was operated with 300 m^3/d capacity. This plant was based on the following steps: Dirty water storage, oil removal system, settling of suspended solids, tangential filtration on polymeric membrane, eluate treatment by means of polymeric membranes in a double-step biological process complying with Italian standards. COD concentration of raw OMWW was 78000 mg/L. After oil removal and suspended solids settling, it decreased to 52000 mg/L. COD concentration of ultrafiltration permeate was measured as 31000 mg/L with 60% removal efficiency (Borsani & Ferrando, 1996).

In order to prevent membrane fouling, different physical and chemical treatment methods can be applied. There are several applications of physical and chemical treatment methods for OMWW. Al-Malah et. al. (2000) described a three-stage process comprising centrifugation, filtration and adsorption on bentonite clay to treat OMWW. Centrifugation and filtration resulted in nearly complete TSS removal followed by only about 25% COD and 60% phenols removal. However, clay adsorption was capable of decreasing the residual COD and phenolic contents by as much as 70% and 80%, respectively.

The use of sodium polyacrylate super-absorbent polymers to detoxify OMWW has been reported in a recent study (Davies et. al., 2004). The absorbent was capable of retaining the polyphenolic fraction inside the polymeric chains, while large molecules such as proteins were concentrated in the residual liquid phase whose phyto-toxicity was substantially reduced. Coagulation with materials such as lime, alum, ferric chloride and ferrous sulphate has also been extensively employed in water/wastewater treatment.

Beccari et. al. (1999) proposed a process comprising OMWW pretreatment by means of lime coagulation and adsorption on bentonite followed by anaerobic digestion. Pretreatment was capable of removing oleic acid, polyphenols and COD

by as much as 99.5%, 43% and 55%, respectively. The resulting effluent was subject to 1:1.5 dilution and then treated anaerobically. For the same dilution ratio, the original untreated OMWW was not suitable to anaerobic degradation.

In a study, centrifugation of OMWW was investigated. Centrifugation proved capable to fully separate suspended solids, which in turn significantly improved COD removal and oil recovery. Changes in the chemical environment of OMWW had a considerable influence on the centrifugation efficiency. So, pH of OMWW was adjusted to 2 by H_2SO_4. At pH = 2 the highest oil recovery (47 %) and a simultaneous high COD decrease (68 %) were achieved. Furthermore, the sediment obtained from centrifugation at pH = 2 had 15% solid and 80% water content (Mitrakas et. al., 1996).

In further studies (Aktas et. al., 2001), the impact of lime pre-treatment on total solids, COD and polyphenols removal for 17 different OMWW was evaluated. After lime precipitation process, COD values of the wastewater samples reduced by 42–46 %. The average removal percentage of the other parameters are 29–47 % for total solids, 41–53 % for volatile solids, 74–37 % for reduced sugar, 95–96 % for oil-grease, 74–63 % for polyphenols, 38–32 % for volatile phenols and 61–80 % for nitrogenous compounds, respectively.

1.4 Objectives and Scope of the Thesis

This thesis is designed to investigate pretreatment and/or treatment alternatives of cheese whey effluents and olive oil mill wastewaters. Investigation of effluent characteristics, examining the possible wastewater treatment methods that would result the best reduction in pollution content were the main aims of this thesis. Major objectives of this thesis can be summarized as follows:

1. To investigate the effects of physical pretreatment before membrane processes for the treatment of cheese whey effluent and olive oil mill wastewater.

2. To find an effective chemical coagulant, acid and alkali dosage for chemical precipitation of cheese whey effluent and olive oil mill wastewater.

3. To investigate the effectiveness of membrane processes in the treatment of cheese whey effluent and olive oil mill wastewater after physical and/or chemical pretreatment.

4. To determine the most appropriate wastewater treatment option for cheese whey effluent and olive oil mill wastewater.

The ultimate goal is to maximize the removal efficiencies and minimize the number and total treatment stage. Depending on the wastewater composition, the number and order of treatment stages vary and optimal conditions can only be determined for a given composition. Experiments were performed by using different physical and chemical pretreatment steps, and different membranes such as microfiltration, ultrafiltration and nanofiltration.

CHAPTER TWO
MATERIALS AND METHODS

2.1 Characterization of Wastewater Samples Used in the Thesis

Two types of strong wastewater were used in the experimental studies. One of them was cheese whey effluent which is a by product of cheese production. The other one was olive oil mill wastewater which is produced as liquid waste with high suspended solid content during olive oil production.

2.1.1 General Characteristics of Cheese Whey Effluents

Two different cheese whey effluents numbered as sample I and sample II were used in the pretreatment and membrane experiments. They were taken from Ege University Food Engineering Department. The experimental studies were carried out as soon as possible after taking sample. However when it was necessary to keep the wastewater, it was kept in refrigerator at 4°C and no pH adjustment was made to keep the samples for a long time, since pH value of samples was between pH=4–5. Physical and chemical compositions of these samples are given in Table 2.1.

Table 2.1 Physical and chemical characteristics of cheese whey effluents

Sample Number	pH	COD (mg/L)	TOC (mg/L)	SS (mg/L)	Oil and Grease (mg/L)
Sample I	5.1	65600	23150	2667	1782
Sample II	4.7	60000	22210	2513	1650

2.1.2 General Characteristics of Olive Oil Mill Wastewater

Four types of olive oil mill wastewater (OMWW) samples used in the experimental studies were taken from a 3-phase continuous olive oil mill plant located in Bornova-Izmir. Samples were collected in December from the effluent of

the horizontal decanter. Fresh sample was kept in dark at 4°C. General characteristics of OMWW samples are given in Table 2.2.

Table 2.2 Physical and chemical characteristics of olive oil mill wastewater

Sample Number	pH	COD (mg/L)	TOC (mg/L)	SS (mg/L)	Oil and Grease (mg/L)
Sample I	4.4	120000	46340	18600	2870
Sample II	5.1	100000	21870	17600	3070
Sample III	4.8	84000	25542	11200	2510
Sample IV	5.0	120000	31650	33200	11940

2.2 Pretreatment Experiments

One common problem of membrane filtration of strong wastewaters is the membrane fouling that drastically reduces the efficiency of permeate and changes its selectivity. Therefore, a pre-treatment step is necessary to decrease membrane fouling and to increase filtration efficiency. By considering this fact, physical and chemical pretreatment steps were applied before membrane filtration experiments.

2.2.1 Pretreatment of Cheese Whey Effluents

Physical and chemical pretreatment methods were applied on cheese whey effluents.

2.2.1.1 Physical Pretreatment of Cheese Whey Effluents

Cartridge filter and filter cloth filtration experiments were done as physical pretreatment studies. First of all, cheese whey was filtered through a 25 μm cartridge filter. This filter was inserted into the influent line to protect the membranes from suspended solids.

After the cartridge filter filtration, the effluent was successively filtered through four different filter cloths with different air and water permeability, in membrane cell. Two important parameters in filter cloths are air permeability and water permeability. The former one is air permeability that is air flux which passes through the cloth with 0.5 inch water column (w/c) head loss. The later one is water permeability which determined using laboratory scale membrane system. During water permeability determination, headloss was 10 cm (w/c) which is negligible compared to 1 bar. Air and water permeabilities of filter clothes are given in Table 2.3. Pore sizes of the filter clothes were not available. All filter cloths were made from polyester fabric. Filtration experiments were done at 100 L/h flow rate and the concentrate flow control valve (CFCV), which was shown in Figure 2.1, was kept open.

Table 2.3 Air and water permeability of four different filter cloths

Filter Cloth Number	**Air Permeability ($L/dm^2.h$)**	**Water Permeability ($L/m^2.h$)**
Number I	15	1190
Number II	12	952
Number III	7.2	571
Number IV	3.2	254

2.2.1.2 Chemical Pretreatment of Cheese Whey Effluents

2.2.1.2.1 Coagulation Experiments. In the first pretreatment study with cheese whey samples I, different combinations of coagulants shown in Table 2.4 for chemical pretreatment of cheese whey were tested. Jar tests were done to determine the dose of the chemicals, pH and COD removal efficiency.

Table 2.4 Different chemical combinations for cheese whey treatment

Alternative	**pH Adjustment Chemical**	**Coagulant**
1	H_2SO_4	$FeCl_3$
2	H_2SO_4, NaOH	$Al_2(SO_4)_3$
3	H_2SO_4	Carboxy Methyl Cellulose (CMC)
4	H_2SO_4	CMC + $FeCl_3$
5	-	Chitosan
6	H_2SO_4	Chitosan
7	H_2SO_4	Chitosan + $FeCl_3$

Jar test procedure was: a) Addition of 1 L dairy wastewater sample to each vessel, b) pH adjustment, if it is necessary, c) Coagulant addition, d) Rapid mixing at 225 rpm for 5 minutes, e) Slow mixing at 25 rpm for 45 minutes, f) Sedimentation for 2 hours, g) Withdrawal of effluent sample from mid-depth when the water phase appeared clear.

2.2.1.2.2 The Steffen Process. The Steffen process is a method for lactose recovery from cheese whey. Reducing lactose are more sensitive to alkaline reagents than non-reducing sugars; therefore, the complete process must be carried out at low temperature. The procedure of this process is as follows: Fresh acid whey is cooled to 3-5°C and maintained at that temperature for all subsequent operations. Two hundred milliliters of whey (contain 9.5 g lactose) and 12.5 g of finely powdered CaO (130 parts of CaO to 100 parts of lactose) are mixed together and vigorously stirred with a mechanical stirrer for 45-60 min and then centrifuged (Cerbulis, 1973).

Application of Steffen process for the recovery of lactose, protein and also for the reduction of COD and TOC in whey was aimed in this thesis. Fresh acid whey (sample-II) with pH=4.7 was cooled to 3-5°C and maintained at that temperature with ice bath for all operations. Different dosages of $Ca(OH)_2$ and CaO were mixed with cooled cheese whey and vigorously stirred with a mechanical stirrer for 60-90 minutes and then centrifuged at 6500 rpm for 15-30 minutes. For the another

separation of liquid and solid particles, mixed liquor was left 1 day settling and supernatant was filtered through cartridge filter.

2.2.2 Pretreatment of Olive Oil Mill Wastewater

Physical and chemical treatment experiments were also done for pretreatment of olive oil mill wastewater.

2.2.2.1 Physical Pretreatment of Olive Oil Mill Wastewater

Cartridge filter filtration and filter cloth experiments were also done as physical pretreatment studies for OMWW like in pretreatment of cheese whey effluents. Only the pore size of cartridge filter was different from the first one. A 20 μm cartridge filter was used as first step of physical pretreatment. Effluent of cartridge filter then filtered from four different filter cloths with different pore size in membrane cell as mentioned in section 2.2.1.1. In some experiments, physical pretreatment is used after chemical treatment. In some of these experiments, only cartridge filter filtration was used.

2.2.2.2 Chemical Pretreatment of Olive Oil Mill Wastewater

Chemical coagulation-flocculation-sedimentation experiments were done with sample I. In order to select the optimum coagulant for OMWW, the coagulation tests were conducted with different coagulants. The selection based on the COD, SS, oil and grease concentration of supernatant after jar test procedure including rapid mixing at 225 rpm for 5 minutes, slow mixing at 25 rpm for 45 minutes and sedimentation for 2 hours.

$FeCl_3$, $FeSO_4$, chitosan, H_2SO_4 and $Ca(OH)_2$ were used as coagulants and pH adjustment chemicals for chemical pretreatment of OMWW. pH value of the raw OMWW was 4.4. For this reason, no pH adjustment was done during $FeCl_3$, $FeSO_4$ and chitosan experiments.

pH adjustment was applied on all OMWW samples. pH of sample I was adjusted from 4.4 to 2 by adding 98 % H_2SO_4 solution and then 7 by adding 10 % (w/v) $Ca(OH)_2$ in order to achieve neutral pH. Jar test procedure was applied after all pH adjustment steps. For sample II, only pH=2 adjustment was done and then jar test procedure was carried out. Two step pH adjustment with H_2SO_4 and $Ca(OH)_2$ were also done with sample III and IV. Cartridge filter filtration was applied instead of jar test procedure after all pH adjustments for these samples.

2.3 Experimental Set-Up

The membrane experiments were carried out in a laboratory-scale cross flow membrane system. The feed stream was pumped from the feed vessel to the feed inlet. A portion of the solution permeated through the membrane and flowed into the permeate receiver. The concentrate stream flowed back to the 25 liters feed vessel. Osmonics Sepa CF II membrane cell, which consists of two elements (cell body and cell holder), was used. Hydraulic pressure was applied to the top of the holder. This pressure causes the piston to extend downward and compress the cell body against the cell holder. A single piece of rectangular membrane was installed in the bottom cell body with a feed spacer. A heat exchanger in the feed vessel was used in all filtration experiments to keep the temperature at 22-24°C. Schematic flow diagram of experimental set-up is depicted in Figure 2.1.

At the beginning of the experiments, pretreated effluent was filled into feed vessel of experimental set-up. Permeate from membrane was collected in the permeate collection vessel. With one hour interval, permeate in the collection vessel was poured into the feed vessel. The pressure and the recycle flow rate were controlled by regulation valves. During the filtration experiments, weight of permeate in permeate carrier was continuously monitored with 5 minutes interval.

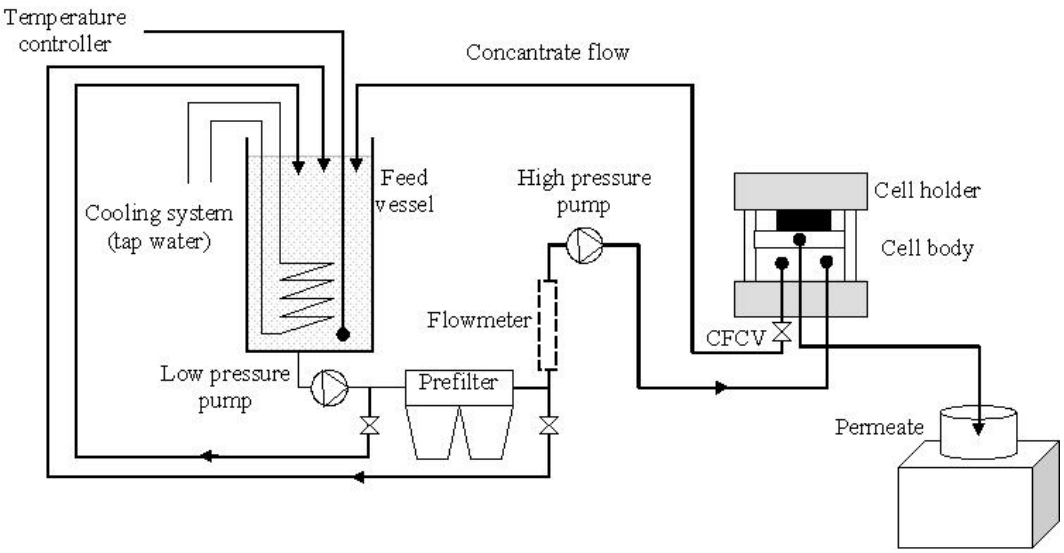


Figure 2.1 Schematic flow diagram of the experimental set-up used in studies

2.4 Technical Characteristics of the Membranes

Polymeric microfiltration, ultrafiltration and nanofiltration membranes, which were supplied by Osmonics as a flat sheet, were used in this study. Technical properties of used membranes are given in Table 2.5.

Table 2.5 The technical characteristics of the membranes used during experiments

	Microfiltration membrane	**Ultrafiltration membrane**	**Ultrafiltration membrane**	**Nanofiltration membrane**
Designation	JX	JW	MW	DK
Polymer type	PVDF	PVDF	Ultrafilic	TF
MWCO	0.3 micron	15-25 kDa	50-100 kDa	150-300 Da
Area, m^2	0.0155	0.0155	0.0155	0.0155
pH range	2-11	1-11	1-10	2-11

2.5 Analytical Methods

pH, COD, SS, oil and grease, TOC measurements were done on the wastewater samples. COD, SS, oil and grease measurements were carried out according to Standard Methods (APHA, AWWA & WEF, 1992).

2.5.1 pH Analysis

pH 890 pH METER was used for pH analysis.

2.5.2 Chemical Oxygen Demand (COD) Analysis

COD was determined according to 5220 C method of Standard Methods (APHA, AWWA & WEF, 1992).

2.5.3 Suspended Solid (SS) Analysis

SS analysis was applied according to 2540 D method of Standard Methods (APHA, AWWA & WEF, 1992).

2.5.4 Oil and Grease Analysis

Oil and grease analysis was applied according to 5520 D method of Standard Methods (APHA, AWWA & WEF, 1992).

2.5.5 Total Organic Carbon (TOC) Analysis

TOC analysis was done by DOHRMANN DC–190 high temperature TOC analyzer.

CHAPTER THREE
RESULTS AND DISCUSSIONS

3.1 Cheese Whey Effluent

Two sets of experimental treatability studies were realized with cheese whey effluents named as sample I and sample II. In the first study with sample I, treatment steps were pretreatment + microfiltration + ultrafiltration. Two different pretreatment steps are physical pretreatment (cartridge filter filtration and four different filter cloth filtration successively), and coagulation + physical pretreatment (determination of suitable coagulant and pH, coagulation under suitable conditions, cartridge filter filtration, four different filter cloth filtration successively). In the first part of study with sample I, physical pretreatment were selected as pretreatment and then microfiltration and ultrafiltration processes were applied. In the second part, only microfiltration process was applied after coagulation experiments.

In the second study with cheese whey effluent, sample II was used. The Steffen process was applied as chemical pretreatment step. Centrifugation, sedimentation and cartridge filter filtration processes were used for the separation of solid and liquid phases. After pretreatment, only microfiltration was used. Ultrafiltration step was not applied, because the volume of sludge was too much to use this method as pretreatment step.

3.1.1 Physical Pretreatment and/or Chemical Coagulation + Microfiltration + Ultrafiltration Experiments

In the first part of the experimental studies with cheese whey, firstly the physical pretreatment and/or chemical coagulation experiments were done. Microfiltration process was applied to two different pretreated samples with physical treatment methods and chemical coagulation. The last step was ultrafiltration process which

was applied after microfiltration of pretreated sample with physical treatment methods. The schematic diagram of the all treatment steps are given in Figure 3.1.

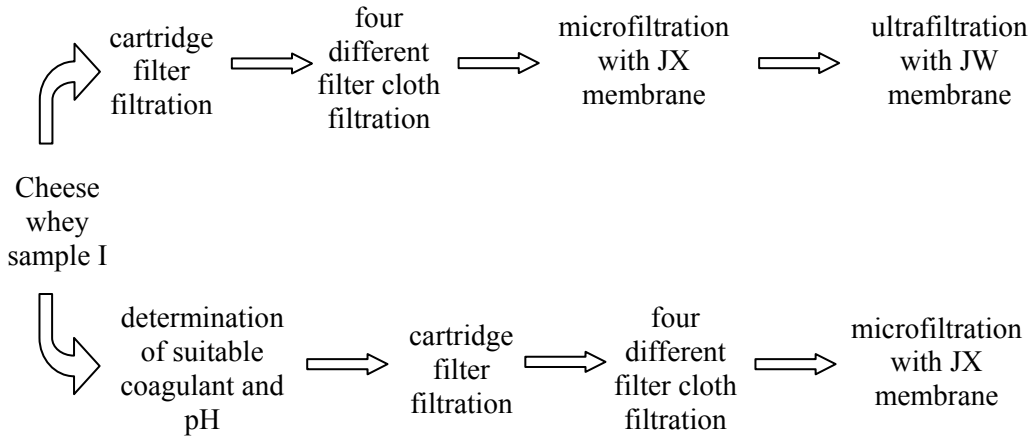


Figure 3.1 Schematic flow diagram of the treatment steps for cheese whey sample I

3.1.1.1 Physical Pretreatment Experiments

Cartridge filter filtration and filter cloth experiments were done as physical pretreatment studies. First of all, raw cheese whey was filtered from a 25 μm cartridge filter. Filtered wastewater was collected in a tank for using in following experiments.

Cheese whey was filtered sequentially from four different filter cloths with different permeability, in membrane cell. Effluent form cartridge filter was used during experiments. Filter cloths were used successively from more permeable to less permeable filter cloth. Experiments were done at 100 L/h flowrate and the concentrate flow control valve (CFCV) was kept open. Characteristics of wastewater after cartridge filter and filter cloth filtration experiments are given in Table 3.1.

3.1.1.2 Chemical Coagulation Experiments

In the chemical coagulation experiments, ferric chloride ($FeCl_3.6H_2O$), alum ($Al_2(SO_4)_3.18H_2O$), carboxy methyl cellulose (CMC), and chitosan were used as coagulants, sulfuric acid (H_2SO_4), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used as pH adjustment chemicals in the treatment of cheese whey effluent. Jar tests were done to determine the optimum dosage of the used chemicals. The most effective chemical and suitable dosages were chosen after jar tests comparing the COD removal efficiencies.

Table 3.1 Results of cartridge filter and four different filter cloth filtration

Parameter	**Raw Water**	**Cartridge Filter**	**Filter Cloth I**	**Filter Cloth II**	**Filter Cloth III**	**Filter Cloth IV**
COD (mg/L)	65600	64000	60800	54400	49600	46400
COD removal efficiency (%)	-	2	7	17	24	29
SS (mg/L)	2667	2333	2122	1902	1685	1467
SS removal efficiency (%)	-	13	20	29	37	45
Oil and grease (mg/L)	1782	1655	1311	1012	880	650
O-G removal efficiency (%)	-	7	26	43	51	64

*3.1.1.2.1 Experimental Studies with $FeCl_3$*6 H_2O.* Ferric chloride ($FeCl_3$*6 H_2O) was added to sample at different pH values between 4 and 8 to determine the optimum pH value. H_2SO_4 solution with 98% purity and 1 N NaOH was used for pH adjustment. Rusten et. al. (1992) was reported that 200 mg/L $FeCl_3$ was optimum dosage for cheese whey effluent. So, in this study firstly only this dosage was used. Jar test was done for the optimization of pH and results are given in Table 3.2. As it can be seen from Table 3.2, optimum pH was found as pH=4.

Table 3.2 Optimization of pH for $FeCl_3$ treatment

pH	pH Adjustment Chemical	Chemical Dosage (mg/L)	COD Concentration of Effluent (mg/L)	COD Removal Efficiency (%)
5.1	-	-	65600	-
4	H_2SO_4	8	47000	28
5	H_2SO_4	1	48800	26
6	NaOH	29	51200	22
7	NaOH	60	59200	10
8	NaOH	91	53600	18

After optimization of pH, investigation of optimum $FeCl_3$ dosage was aimed. For this reason, different dosages of $FeCl_3$ between 100 and 500 mg/L were added to sample at the pH value of 4 and jar test was done. The results of optimization of $FeCl_3$ dosage are given in Table 3.3. COD removal efficiency of $FeCl_3$ was variable at different dosages. Maximum efficiency was achieved with 200 mg/L $FeCl_3$ as 29%. This result is in accordance with the other authors (Rusten et. al, 1992).

Table 3.3 COD removal efficiency of coagulation experiments with $FeCl_3$

$FeCl_3$ Dosage (mg/L)	COD Concentration of Effluent (mg/L)	COD Removal Efficiency (%)
-	65600	-
100	52500	20
200	46800	29
300	51600	21
400	50500	23
500	48600	26

COD, SS, oil and grease analysis of effluent were also done at optimum pH (pH=4) and $FeCl_3$ dosage (200 mg/L) and results are given in Table 3.4. Maximum removal efficiency was achieved in SS parameter as 70%.

Table 3.4 Results of $FeCl_3$ treatment (pH=4, $FeCl_3$ dosage=200 mg/L)

Parameter	Influent Concentration	Effluent Concentration	Removal Efficiency (%)
COD (mg/L)	65600	47000	28
SS (mg/L)	2667	800	70
Oil and grease (mg/L)	1782	1490	16

3.1.1.2.2 Experimental Studies with $Al_2(SO_4)_3$. $Al_2(SO_4)_3$ (alum) was added to cheese whey sample as a coagulant in different doses between 100-300 mg/L. pH value of wastewater was decreased from 5.1 to 4 with the addition of H_2SO_4, and increased from 5.1 to 7 with NaOH solution. Jar test was also done for optimization of pH and alum dosage. Obtained COD concentrations and removal efficiencies are given in Table 3.5. Optimum pH and alum dosage was found as pH=4 and 200 mg/L, respectively.

Table 3.5 COD removal efficiency of coagulation experiments with alum

pH	pH Adjustment Chemical	Alum Dosage (mg/L)	COD Concentration of Effluent (mg/L)	COD Removal Efficiency (%)
5.1	-	-	65600	-
4	H_2SO_4	100	50800	23
4	H_2SO_4	200	48600	26
4	H_2SO_4	300	64800	1
7	NaOH	100	54400	17
7	NaOH	200	62400	5
7	NaOH	300	88800	-

COD, SS, oil and grease concentration were also measured at optimum alum dosage and pH, and results are given in Table 3.6. Results are similar with $FeCl_3$

treatment experiments. Maximum removal efficiency was also achieved with SS parameter at pH=4 and 200 mg/L alum dosage.

Table 3.6 Results of alum treatment (pH=4, alum dosage=200 mg/L)

Parameter	**Influent Concentration**	**Effluent Concentration**	**Removal Efficiency (%)**
COD (mg/L)	65600	48600	26
SS (mg/L)	2667	1608	40
Oil and grease (mg/L)	1782	1342	25

3.1.1.2.3 Experimental Studies with Carboxy Methyl Cellulose (CMC). CMC is used together with H_2SO_4 in a commercially available process for protein recovery from food industry effluents, especially for dairy industry wastewaters (Rusten et. al., 1992). For this reason CMC is used in this study as a chemical coagulant. Different dosages of CMC, using different pH values were tested in this section. Rusten et. al. (1992) studied chemical pretreatment of dairy wastewater with CMC at pH=4. In this thesis, pH level of sample was adjusted to pH=4 with the addition of 8 mg/L H_2SO_4 solution (98% pure). CMC was added to wastewater in different doses between 5 – 20 mg/L, and then jar test was carried out. After precipitation, samples were taken from mid-depth of wastewater and COD analyses were done. Experimental results are given in Table 3.7. Optimum CMC dosage was found as 10 mg/L.

Table 3.7 COD removal efficiency of coagulation experiments with CMC (pH=4)

CMC Dosage (mg/L)	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
0	64000	-
5	56000	13
10	50400	21
15	73600	-
20	75000	-

In order to optimize pH value of wastewater, optimum dosage of CMC, which was 10 mg/L, was taken into consideration. pH adjustment was done with H_2SO_4 solution (98% pure). Acid volume, COD concentrations and COD removal efficiencies are given in Table 3.8. The COD removal efficiency of CMC was variable at different pH values. The maximum COD removal efficiency was 24 % at the pH=4.

Table 3.8 Optimization of pH value for the chemical treatment of cheese whey with CMC (CMC dosage=10mg/l)

pH	**Acid usage (mg/L)**	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
5.1	-	64000	-
4.5	4	52000	21
4.0	8	50000	24
3.5	12	60000	9
3.0	16	70000	-
2.0	24	76000	-

CMC is generally used for protein recovery from food industry effluents. In this thesis, the main purpose is to maximize removal efficiency. In order to increase removal efficiency, $FeCl_3$ was used together with CMC. 10 mg/L CMC and different dosage of $FeCl_3$ were added to sample at the pH = 4.0 and the same procedure was applied. However, no significant decrease in COD was observed compared to $FeCl_3$ usage solely. Results are shown in Table 3.9. COD, SS, oil and grease concentration of optimum conditions (pH=4, CMC dosage=10 mg/L, $FeCl_3$ dosage=200 mg/L) are given in Table 3.10.

Table 3.9 COD removal efficiency of coagulation experiments with CMC and $FeCl_3$ (pH=4, CMC dosage=10 mg/L)

$FeCl_3$ Dosage (mg/L)	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
-	64000	-
100	50400	21
200	43200	33
300	49600	23
400	48000	25
500	45600	29

Table 3.10 Results of CMC treatment (pH=4, CMC dosage=10 mg/L, $FeCl_3$ dosage=200 mg/L)

Parameter	**Raw Water**	**After CMC Treatment**	**Removal Efficiency (%)**	**CMC + $FeCl_3$**	**Removal Efficiency (%)**
COD (mg/L)	65600	51000	22	43200	33
SS (mg/L)	2667	2440	9	2240	16
Oil and grease (mg/L)	1782	1522	15	1296	27

3.1.1.2.4 Experimental Studies with Chitosan. Some researchers investigated the efficiency of a process using chitosan as an alternative to the CMC process. Chitosan has been used to treat the waste effluents a wide number of food process. In these operations, chitosan was demonstrated to be a very good coagulating agent (Xue, 1998). In this study, chitosan was also used instead of CMC in chemical precipitation experiments.

Olsen et. al. (1996) reported that chitosan can achieve results similar that CMC process even at pH as high as 5.3. Thus, no pH adjustment was done in this experiment. Chitosan was added to wastewater in different doses between 5 – 25 mg/L and then jar test was carried out. After precipitation, samples were taken and

COD analyses were done. Experimental results are depicted in Table 3.11. Maximum COD removal efficiency was achieved at 15 mg/L chitosan dosage.

Table 3.11 COD removal efficiency of coagulation experiments with chitosan

Chitosan Dosage (mg/L)	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
0	65600	-
5	57600	12
10	47200	28
15	42400	35
20	60000	9
25	63200	4

In order to see the effects of pH variation on COD removal efficiency, pH value of wastewater was adjusted with H_2SO_4 solution (98% pure). 15 mg/L of chitosan dosage, which gave maximum COD removal efficiency, was applied. Acid volume, COD concentrations and COD removal efficiencies are given in Table 3.12. Results are in accordance with CMC pretreatment. Optimum pH value for chitosan was also found as pH=4.

Table 3.12 Optimization of pH value at 15 mg/L chitosan dosage

pH	**Acid Usage (mg/L)**	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
5.1	-	42400	35
5.0	1.0	40000	39
4.0	8.0	32000	51
3.0	16.0	42000	36
2.0	24.0	46000	30

In order to increase COD removal efficiency, $FeCl_3$ was also used with chitosan. Chitosan and $FeCl_3$ dosages, which were the optimum dosages for cheese whey treatment, were 15 mg/L and 200 mg/L, respectively. pH value of wastewater was adjusted with H_2SO_4 solution from 5.1 to 5, 4, 3, and 2. pH value, COD concentration after chitosan addition and COD concentration after chitosan and $FeCl_3$ addition are depicted in Table 3.13. Combination of chitosan and $FeCl_3$ gave the maximum COD removal efficiency of all chemical pretreatment experiments.

Table 3.13 COD removal efficiency of coagulation with chitosan and $FeCl_3$ at different pH

pH	**COD Concentration (Chitosan) (mg/L)**	**COD Removal Efficiency (%)**	**COD Concentration (Chitosan + $FeCl_3$) (mg/L)**	**COD Removal Efficiency (%)**
5.1	42400	35	36500	44
5.0	40000	39	33000	50
4.0	32000	51	28000	57
3.0	42000	36	36000	45
2.0	46000	30	41000	38

At the combination of chitosan and $FeCl_3$, the last experiment was done to determine the removal of COD, SS and oil and grease concentrations. First, 15 mg/L chitosan and 200 mg/L $FeCl_3$ was added to cheese whey sample at the pH value of 4. Then jar test was carried out. Results are given in Table 3.14.

3.1.1.2.5 General Evaluations for Chemical Coagulation Experiments. Chemical coagulation of cheese whey effluent was tested with $FeCl_3$, alum, CMC and chitosan at different dosage and pH. In the experimental studies with $FeCl_3$ and alum, maximum COD removal efficiencies were 28% and 26%, respectively at the dosage of 200 mg/L and pH value of pH=4. In the CMC experiments, the maximum COD removal efficiency was 24 % at the dosage of 10 mg/L CMC at pH=4. If the combination of CMC and $FeCl_3$ was examined, COD removal efficiency increased to

33 % at the dosage of 10 mg/L CMC and 200 mg/L $FeCl_3$. The combination of 15 mg/L of chitosan and 200 mg/L of $FeCl_3$ had COD removal efficiency of 57 % at the pH=4. Also chitosan had 51 % COD removal efficiency at the dosage of 15 mg/L at the same pH value by itself. General evaluations of all chemical coagulation experiments are given in Table 3.15.

Table 3.14 Results of chitosan treatment

Parameter	**Raw Water**	**After Chitosan Treatment**	**Removal Efficiency (%)**	**Chitosan + $FeCl_3$**	**Removal Efficiency (%)**
COD (mg/L)	65600	32200	51	28000	57
SS (mg/L)	2667	1467	45	880	67
Oil and grease (mg/L)	1782	1422	20	1127	37

Table 3.15 Removal efficiencies of different chemical coagulation chemicals

Treatment Chemicals	**COD (mg/L)**	**COD Rem. Eff. (%)**	**SS (mg/L)**	**SS Rem. Eff. (%)**	**Oil and Grease (mg/L)**	**O-G Rem. Eff. (%)**
Raw wastewater	65600	-	2667	-	1782	-
$FeCl_3$	47000	28	800	70	1490	16
Alum	48600	26	1608	40	1342	25
CMC	51000	22	2440	9	1522	15
CMC + $FeCl_3$	43200	33	2240	16	1296	27
Chitosan	32200	51	1467	45	1422	20
Chitosan + $FeCl_3$	28000	57	880	67	1127	37

3.1.1.2.6 Chemical Coagulation + Physical Pretreatment Experiments. As a result of all chemical coagulation experiments, maximum removal efficiencies in all parameters were achieved for chitosan + $FeCl_3$ treatment. For this reason, microfiltration process was applied on coagulated cheese whey with chitosan and $FeCl_3$.

Before microfiltration process, coagulated wastewater was filtered through cartridge filter and four different filter cloths in order to prevent membrane fouling. COD concentrations and COD removal efficiencies of wastewater after chemical coagulation with chitosan + $FeCl_3$ and filtration are given in Table 3.16.

Table 3.16 COD concentrations of wastewater after chemical treatment and filtration

Treatment Steps	**COD Concentration (mg/L)**	**COD Removal Efficiency (%)**
Raw wastewater	65600	-
Chitosan + $FeCl_3$	28000	57
Cartridge filter	27050	59
Filter cloth I	26500	60
Filter cloth II	25300	61
Filter cloth III	24800	62
Filter cloth IV	23500	64

The results of the experiments indicated that, removal efficiencies for COD and SS parameters in chemical coagulation and physical pretreatment are higher than that of physical pretreatment (See Table 3.1 and Table 3.16). But oil and grease removal efficiency of chemical pretreatment is less than physical pretreatment. This result can be explained as that oil and grease are stabilized or dispersed by coagulants and kept in suspension. After addition of coagulants, settling or floating properties of oil and grease become poorer. But in filtration process, oil and grease particles are captured physically. It should be noticed that removal efficiencies for SS and especially for COD are more promising in chemical pretreatment step.

3.1.1.3 Microfiltration Experiments

In this study, two different types of feed solutions were applied to microfiltration membranes which were cheese whey pretreated with only physical treatment methods (filtration from cartridge filter and filter cloth), and pretreated with chemical and physical treatment methods, such as, chemical coagulation with chitosan + $FeCl_3$ and filtration.

3.1.1.3.1 Permeate Flux Experiments. One of the most important parameter in the membrane filtration is permeate flux (Jv) and it depends on the permeate volume, membrane area and filtration time. Permeate flux is given in Equation 3.1.

$$\text{Permeate Flux, Jv} = \frac{\text{Permeate volume (L)}}{\text{Membrane area (m}^2\text{)} \times \text{Time (h)}} \tag{3.1}$$

Permeate flux experiments were carried out with 100 L/h, 150 L/h, and 200 L/h flowrates, at 1 and 2 bar pressures. The influence of the pressure on the permeate flux at 100, 150, and 200 L/h flowrate during the 120 minutes for microfiltration of pretreated cheese whey by physical and chemical treatment methods is depicted in Figure 3.2 and 3.3.

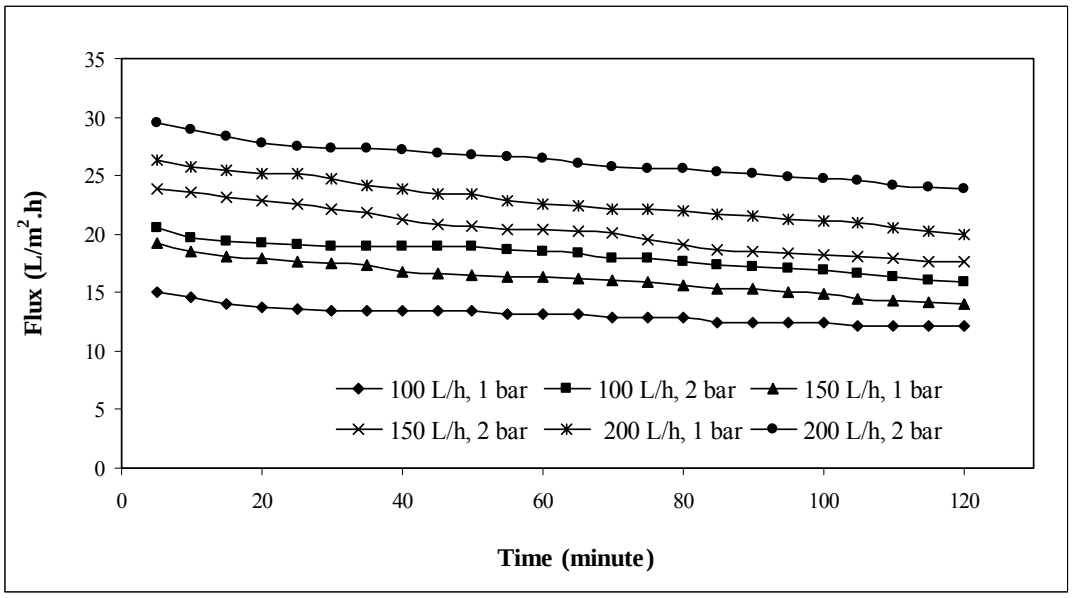


Figure 3.2 Water fluxes of pretreated cheese whey at different flowrate in different pressure after physical pretreatment

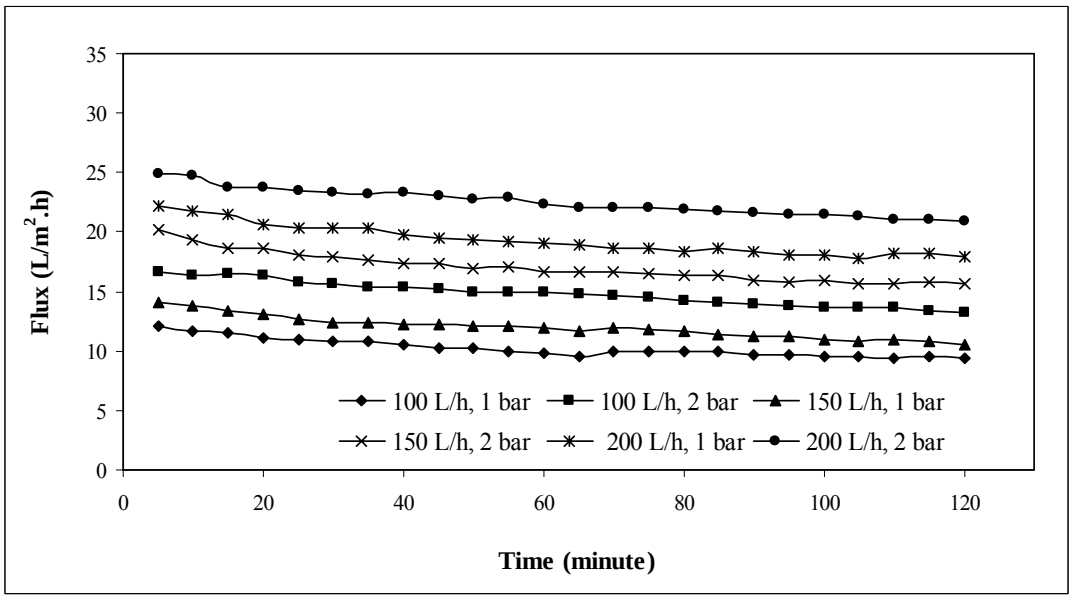
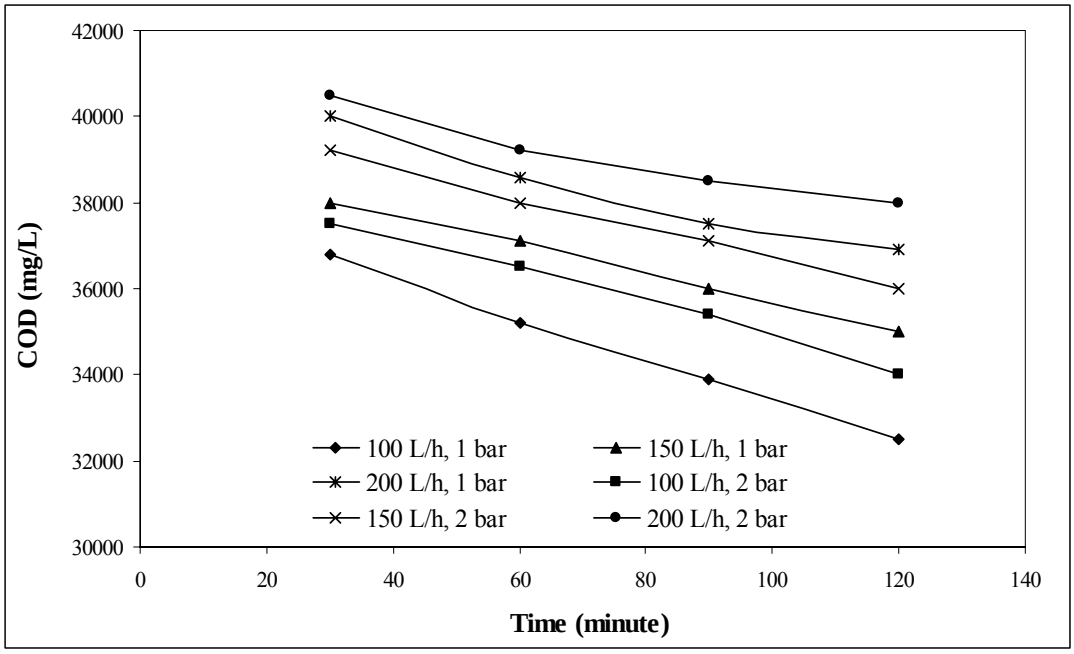


Figure 3.3 Water fluxes of pretreated cheese whey at different flowrate in different pressure after chemical coagulation and physical pretreatment

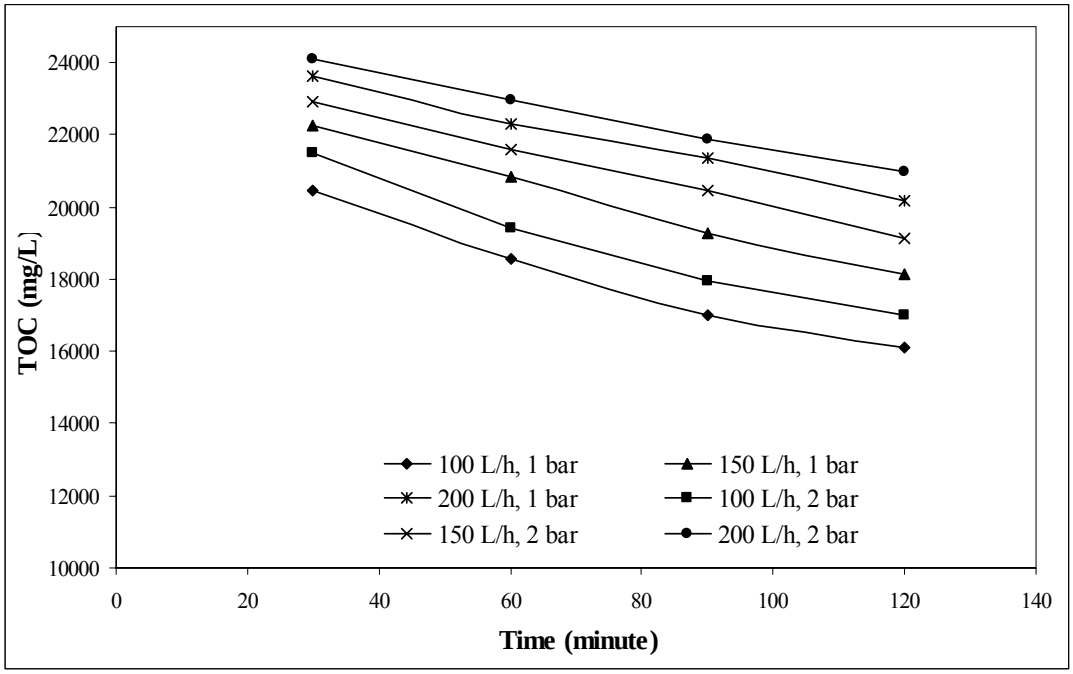
After 120 minutes of operation time, the flux became independent of the time. So, all flux experiments were finished at the end of the 120 minutes. Pressure and recycling flowrate significantly influenced the permeate flux. Higher flowrate at the membrane surface is a very important factor in increasing the permeate flux. The

deposited molecules are continuously removed from the membrane surface by using higher velocity. Thus the hydraulic resistance of the fouling layer is reduced by using higher velocity (Atra et. al., 2005). Increase in pressure also increased water fluxes for all pretreatment options. The water flux obtained for pretreated cheese whey with physical methods was higher than pretreated cheese whey with chemical treatment methods for all flowrate and pressure.

3.1.1.3.2 Treatment Results of Microfiltration Experiments. The performance of microfiltration process was evaluated in terms of COD and TOC removal. pH value of permeate was between 4.04 and 4.11 during all experiments. Temperature of cheese whey in feed tank and permeate was kept 22-24°C by cooling system. Permeate was collected with 30 minutes interval in all experiments. The influence of the flowrate and pressure on the COD and TOC concentrations of physically pretreated effluent are shown in Figure 3.4 (a) and (b).



(a)



(b)

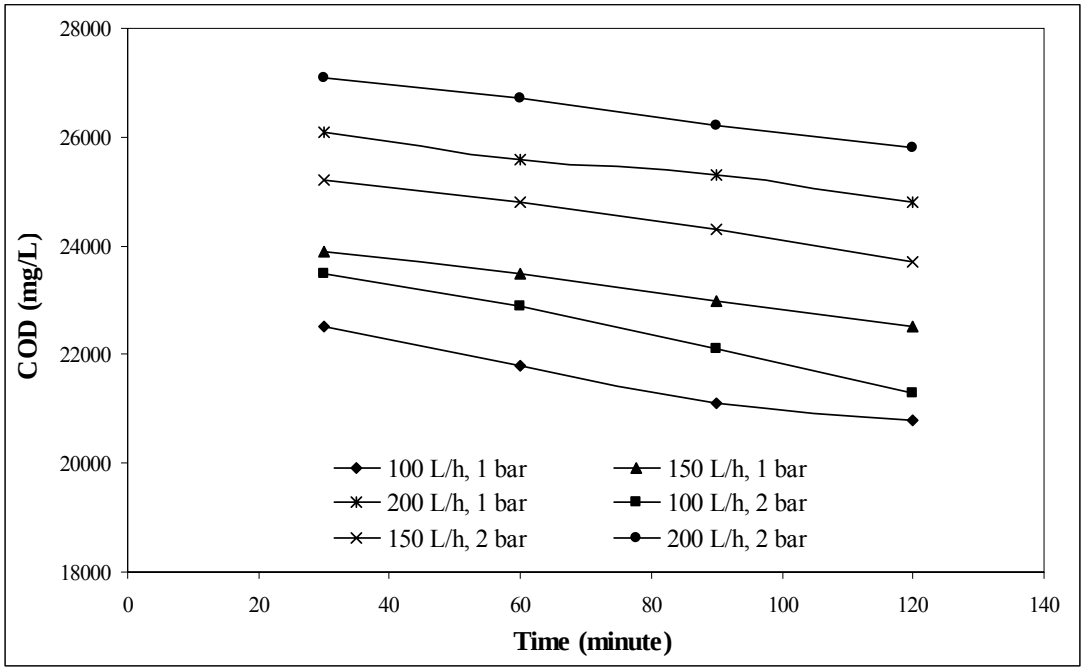
Figure 3.4 COD and TOC concentrations of permeate at different flowrate and pressure after physical pretreatment (a) COD concentration (b) TOC concentration

As it can be seen from Figure 3.4 (a) and (b), if the pressure of system was increased, COD and TOC concentration of effluents also increased. At higher pressures, more organic compounds passed through the membrane because of the pressure effect. In addition, increasing flowrate resulted in increase for COD and TOC concentration. These results are in agreement with results from other authors (Mohammadi et. al., 2005). Maximum removal efficiencies were achieved at 100 L/h flowrate and 1 bar pressure.

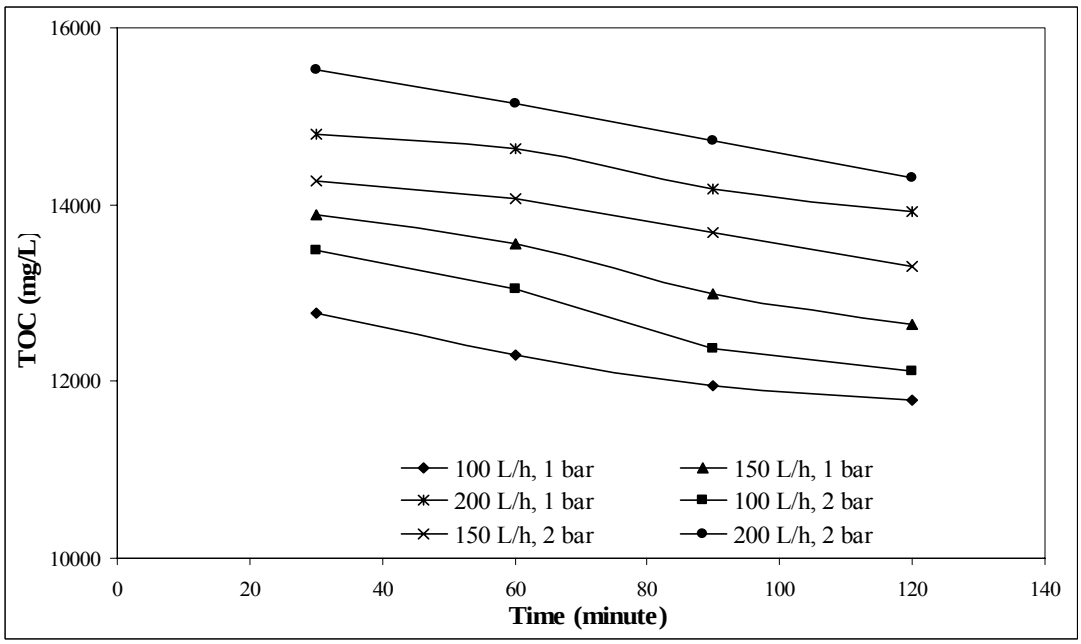
Permeate of all microfiltration experiments were collected in a tank. COD, SS, oil and grease concentrations of all effluents for physical pretreatment and membrane studies are given in Table 3.17. If cheese whey was treated with the combination of physical pretreatment and membrane process, total removal efficiencies of COD, SS, and oil and grease were 54%, 93%, 92%, respectively.

The second microfiltration experiment was microfiltration of cheese whey pretreated with chemical coagulation and physical pretreatment methods. Samples

were also filtered at the same flowrates and pressures, and permeate was collected in 30 minutes interval. Treatability results are given in Figure 3.5 (a) and (b).



(a)



(b)

Figure 3.5 COD and TOC concentrations of permeate at different flowrate and pressure after chemical pretreatment (a) COD concentration (b) TOC concentration

If COD and TOC concentrations of permeate for all flowrate and pressure are investigated, it can be concluded that increase in pressure resulted in increasing COD and TOC concentration of permeate. Increasing flowrate also increased removal efficiencies for microfiltration of pretreated cheese whey with chemical coagulation and physical pretreatment.

Removal efficiencies of chemical coagulation and physical pretreatment combined with microfiltration process are given in Table 3.17. SS and oil-grease removal efficiencies are approximately the same for both pretreatment options. But COD removal efficiency is higher for chemical pretreatment step than physical pretreatment. COD removal efficiency increases from 61% to 65% by using microfiltration process. It should be noticed that the application of microfiltration after chemical coagulation seems to be not feasible.

Energy consumption decreases with the increasing membrane pore size. Energy consumption is higher for microfiltration than that for filter cloth filtration. Also, water fluxes increase with increasing pore sizes under same pressure. Using chemical pretreatment, it is possible to obtain approximately the same removal efficiencies for microfiltration and filter cloth filtration. COD value after filter cloth-IV is 23500 mg/L and 21000 mg/L after microfiltration. Therefore, using filter cloth instead of microfiltration as pretreatment for ultrafiltration seems reasonable for cheese whey effluent treatment. Because filter cloth filtration is done under negligible pressure compared to 1 or 2 bar pressure used for microfiltration. The relatively close treatment efficiencies for filter cloth and microfiltration can be explained by the size of flocs which were large enough to captured by filter cloth. Flocs in the effluent were small enough to pass through microfiltration membrane.

Table 3.17 Treatment results of physical and chemical pretreatment combined with microfiltration

Treatment Steps	COD (mg/L)	COD Rem. Eff. (%)	SS (mg/L)	SS Rem. Eff. (%)	Oil and Grease (mg/L)	O-G Rem. Eff. (%)
Raw wastewater	65600	-	2667	-	1782	-
Physical pretreatment	46400	29	1467	45	650	64
Physical pretreatment + Microfiltration	30400	54	200	93	140	92
Chemical coagulation+ Physical pretreatment	23500	64	880	67	1127	37
Chemical coagulation+ Physical pretreatment + Microfiltration	21000	68	160	94	110	94

3.1.1.4 Ultrafiltration Experiments

Ultrafiltration experiments were carried out after microfiltration with only physical pretreated cheese whey effluent. Physical pretreatment methods are more reasonable than chemical methods, because operational costs of physical treatment methods are lower than chemical treatment methods. In addition, removal efficiencies of two pretreatment methods are not significantly different from each other.

3.1.1.4.1 Permeate Flux Experiments. Three different flowrates (100, 150 and 200 L/h) and four different pressures (1, 2, 3 and 4 bar) were applied with ultrafiltration membrane. Figure 3.6, 3.7 and 3.8 show the flux over the duration of the experiment at different transmembrane pressures. Significant reductions in flux for the first 80 minutes indicate that the development of fouling layer was occurring. At pressure of 2 bar for flow rate of 200 L/h, the permeate flux reduction from 25 to 15 L/m^2.h was

observed. This observation is consistent with Mikulasek et. al. (2004) and Ahmad et. al (2005) findings which concluded that the flux decline was due to cake build-up. In another study, Balakrishnan et. al. (2000) demonstrated that the significant flux decline was due to the deposition of small particles and colloidal on the membrane surface which led to the membrane fouling. The steady-state flux was obtained implying that the fouling layer was almost established after 80 minute operation time for all flow rates. Figures also illustrates that the increase in transmembrane pressure led to an increase in both the initial and final flux values. These data are in agreement with the finding of Sondhi et. al. (2000). Based on Darcy's law, the increasing pressure gradient increases permeate flux.

Figure 3.6, 3.7 and 3.8 also show the flux versus time at different feed flow rates. The permeate flux increased with an increase in flow rate or cross flow velocity. Increasing cross flow velocity could enhance the back diffusion of solute accumulated on the membrane surface, therefore, the permeate flux could be improved. Seidel & Elimelech (2002) explained this phenomenon as increasing cross flow velocity increases the shear rate which mitigates the fouling effect to some extent by reducing the accumulation of natural organic matter on the membrane and arresting the growth of fouling layer.

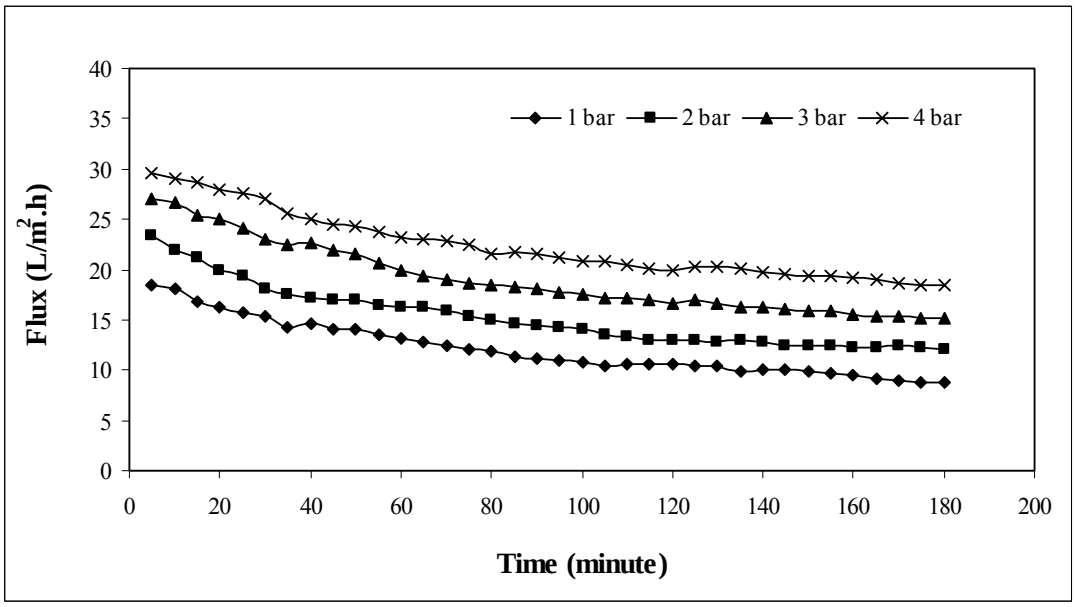


Figure 3.6 Permeate fluxes of cheese whey at 100 L/h flowrate

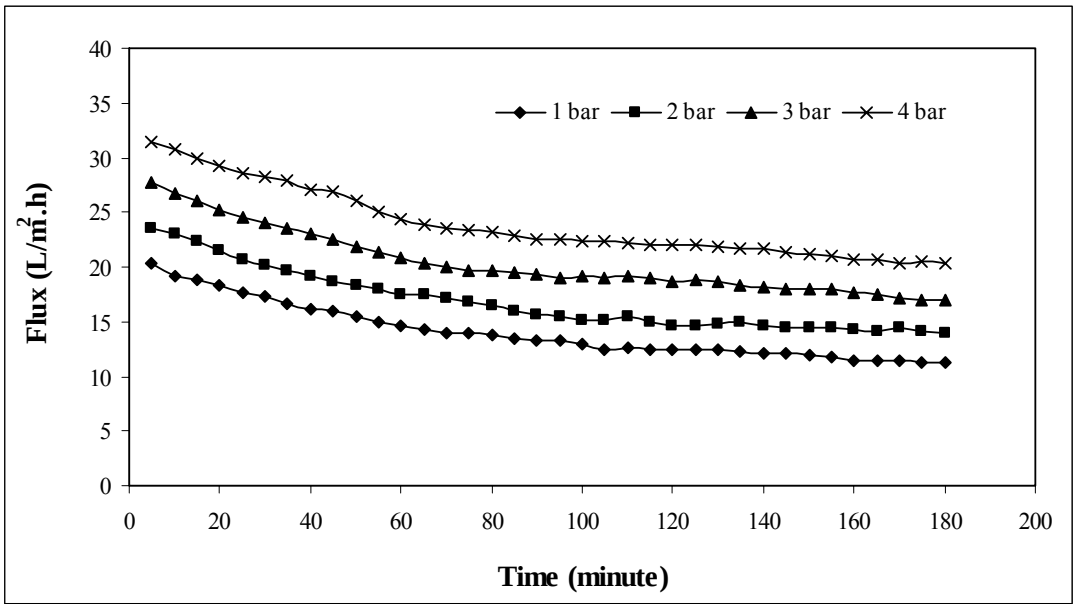


Figure 3.7 Permeate fluxes of cheese whey at 150 L/h flowrate

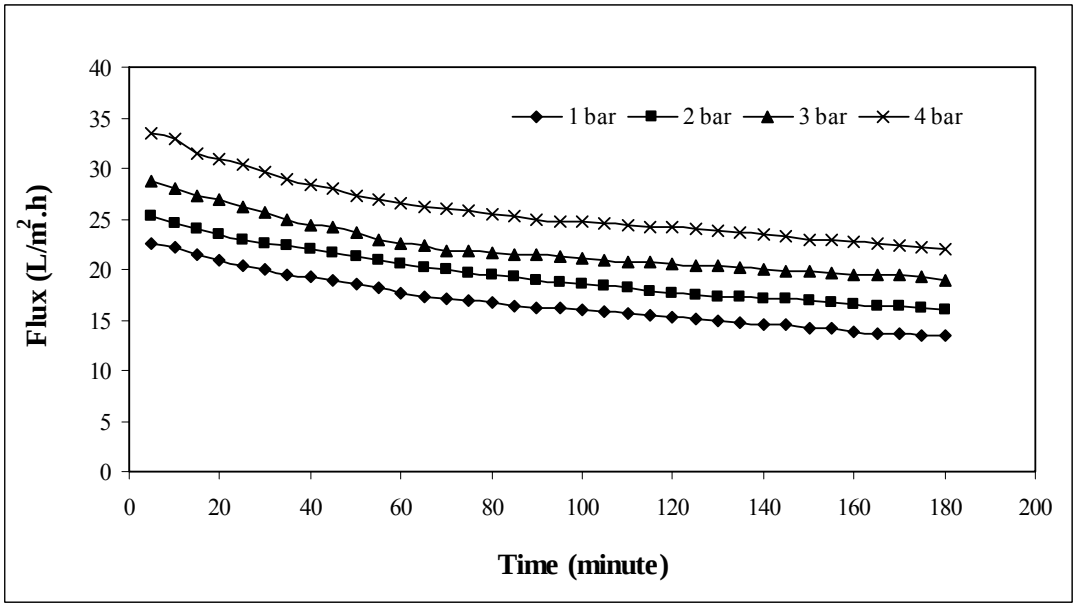


Figure 3.8 Permeate fluxes of cheese whey at 200 L/h flowrate

3.1.1.4.2 Treatment Results of Ultrafiltration Experiments. Ultrafiltration experiments were carried out after microfiltration of physically pretreated cheese whey. COD, SS, oil and grease concentrations of ultrafiltration inlet was 30400 mg/L, 160 mg/L, 110 mg/L, respectively. pH value of permeate was around pH = 5 in all experiments. Temperature of sample was kept 22-24° C by cooling system. Permeates were collected in 30 minutes interval for all experiments. Treatability results of ultrafiltration experiments at 100, 150, and 200 L/h flowrate are given in Figure 3.9, 3.10 and 3.11, respectively. As a result of ultrafiltration study, maximum removal efficiencies for both COD and TOC concentrations were achieved at minimum flowrate and minimum pressure, where the minimum permeate flux obtained. Optimum operation condition was found as 100 L/h flowrate and 1 bar pressure for ultrafiltration process.

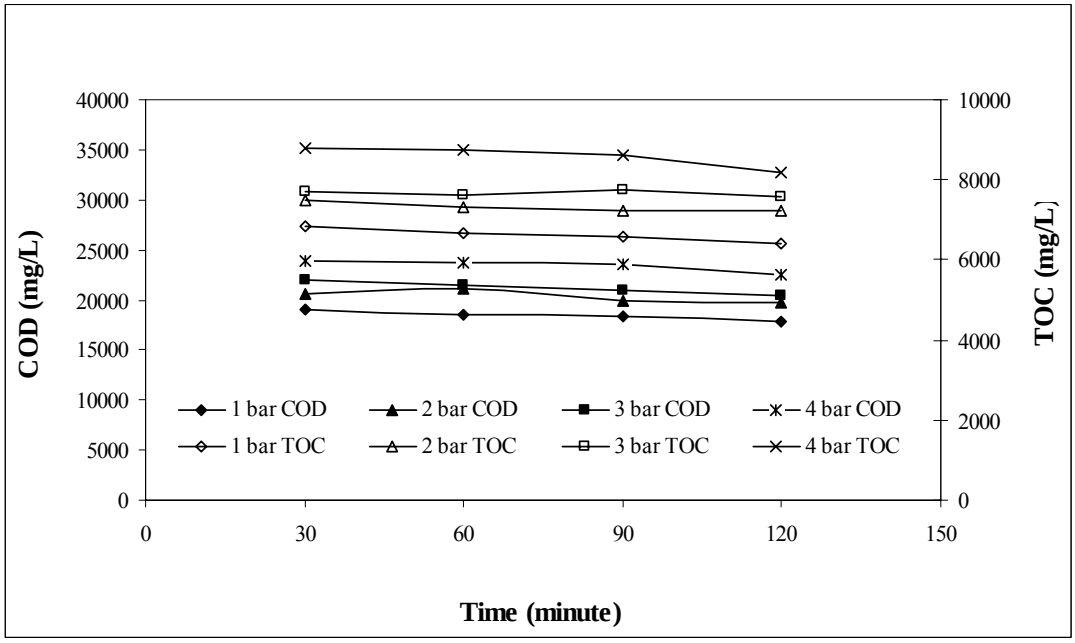


Figure 3.9 COD and TOC concentration of permeate at 100 L/h flowrate

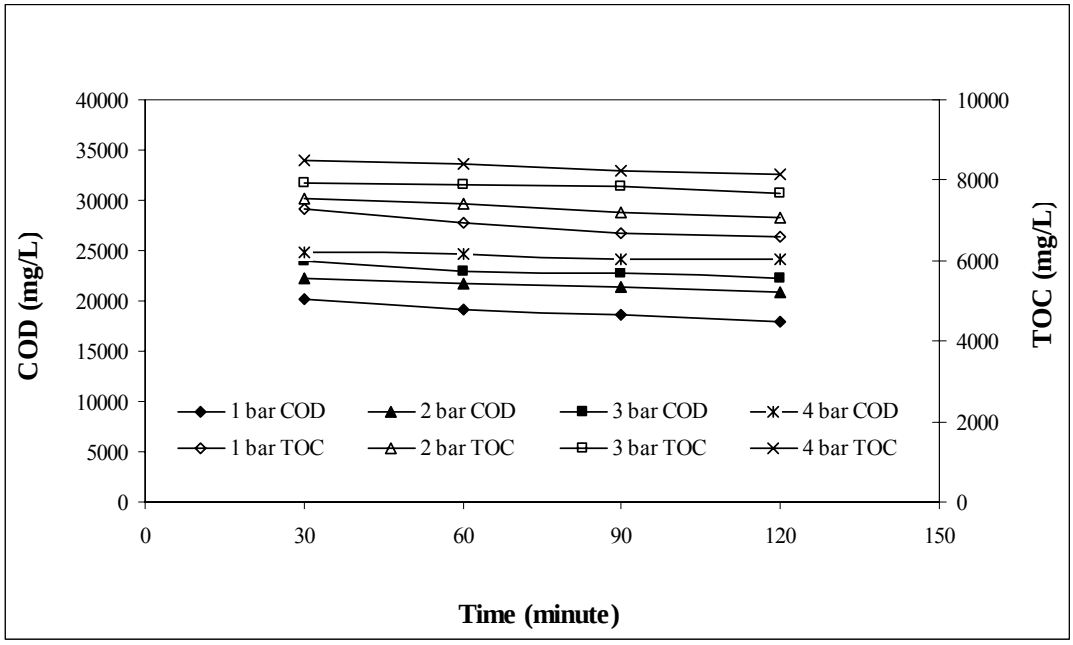


Figure 3.10 COD and TOC concentration of permeate at 150 L/h flowrate

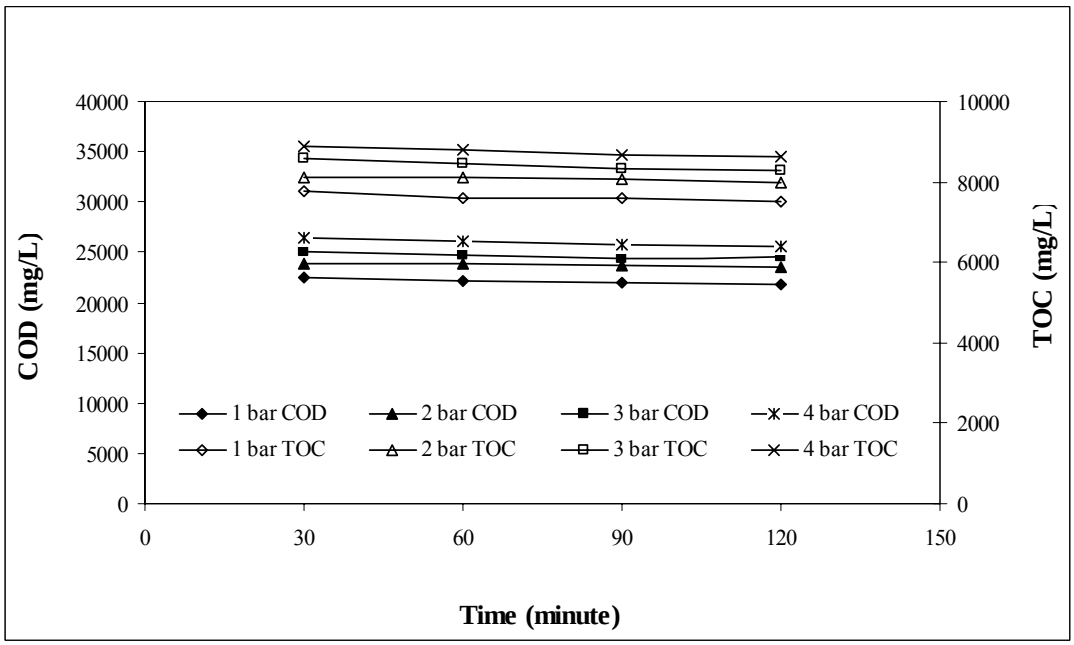


Figure 3.11 COD and TOC concentration of permeate at 200 L/h flowrate

Permeates of ultrafiltration experiments were also collected. COD, SS, oil and grease concentrations of all effluents for physical pretreatment and membrane studies are given in Table 3.18. Total COD removal efficiency of microfiltration and ultrafiltration combination was 66%, while application of only microfiltration process was 54%, after physical pretreatment. Usage of two step membrane process, such as microfiltration and ultrafiltration is not so effective for cheese whey effluent treatment. Only microfiltration seems to be feasible giving 54% removal efficiency for COD.

Table 3.18 Treatment results of physical pretreatment and membrane process

Treatment Steps	**COD (mg/L)**	**COD Rem. Eff. (%)**	**SS (mg/L)**	**SS Rem. Eff. (%)**	**Oil and Grease (mg/L)**	**O-G Rem. Eff. (%)**
Raw wastewater	65600	-	2667	-	1782	-
Physical pretreatment	46400	29	1467	45	650	64
Physical pretreatment + Microfiltration	30400	54	160	94	110	94
Physical pretreatment + Microfiltration + Ultrafiltration	22000	66	47	98	25	99

3.1.2 The Steffen Process + Centrifugation or Sedimentation + Cartridge Filtration + Microfiltration Experiments

Application of Steffen process for the reduction of COD and TOC in whey was aimed in this section. Fresh acid whey with pH=4.7 was cooled to 3-5°C and maintained at that temperature with ice bath for all operations. Cheese whey with different dosages of $Ca(OH)_2$ or CaO were mixed vigorously stirred with a mechanical stirrer for 60-90 minutes and then centrifuged at 6500 rpm for 15-30 minutes. In the other pretreatment experiment, after 60-90 minutes mechanical stirring, 1 day sedimentation and cartridge filter filtration of supernatant was done.

Microfiltration process was applied on the effluent of the Steffen process. The schematic diagram of all these treatment steps is given in Figure 3.12.

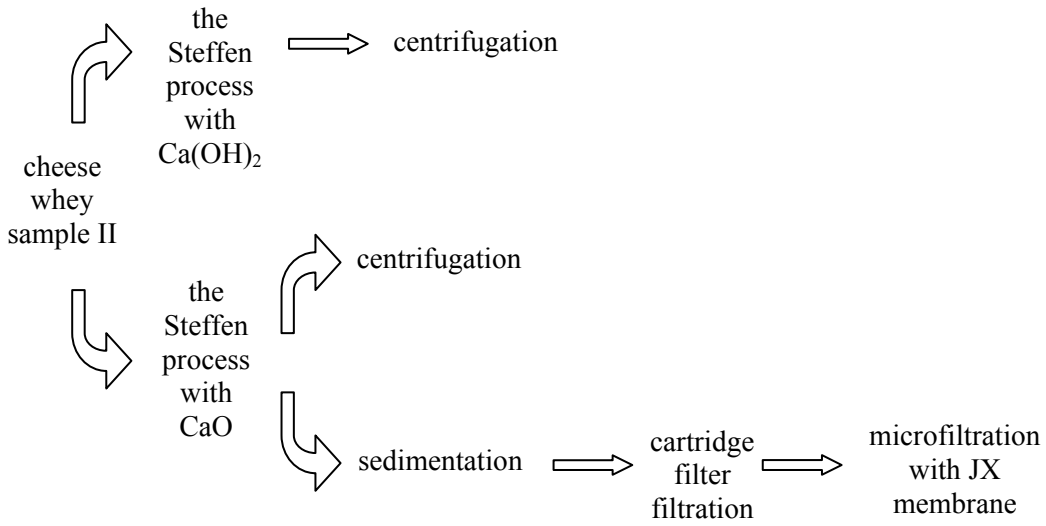


Figure 3.12 Schematic flow diagram of the treatment steps for cheese whey sample II

3.1.2.1 The Steffen Process + Centrifugation or Sedimentation Experiments

3.1.2.1.1 Usage of $Ca(OH)_2$. In the first part of pretreatment experiments, 7 different dosage of $Ca(OH)_2$ were mixed with cooled cheese whey and vigorously stirred with a mechanical stirrer for 60 minutes and then centrifuged at 6500 rpm for 15 minutes. COD and TOC concentration of centrifuged samples are given in Table 3.19. pH values of samples for the all dosage was around pH=12. Maximum removal efficiencies in COD and TOC parameters, which were 50% for each parameter, were achieved with 60 g/L $Ca(OH)_2$ dosage.

Table 3.19 COD and TOC concentration of the first experiment with $Ca(OH)_2$

$Ca(OH)_2$ Dosage (g/L)	**COD (mg/L)**	**COD Removal Efficiency (%)**	**TOC (mg/L)**	**TOC Removal Efficiency (%)**
-	60000	-	22210	-
10	50000	17	18070	19
15	48000	20	16360	26
20	45000	25	13930	37
30	40000	33	12840	42
40	37000	38	12510	44
50	35000	42	12160	45
60	30000	50	11130	50

Volume of supernatant and sludge for all experiment with different $Ca(OH)_2$ dosage after centrifugation were measured and given in Table 3.20. Water and solid contents of separated sludge after centrifugation were also calculated and given in Table 3.20. Water content of lime sludge was around 71-75 %.

Table 3.20 Supernatant, sludge volume, water and solid content of sludge after centrifugation

$Ca(OH)_2$ Dosage (g/L)	**Supernatant Volume (ml)**	**Sludge Volume (ml)**	**Water Content (%)**	**Solid Content (%)**
30	765	235	75	25
40	755	245	74	26
50	715	285	73	27
60	710	290	71	29

3.1.2.1.2 Usage of CaO. In this part of study, CaO was used instead of $Ca(OH)_2$. The same procedures were applied. 1 L of cheese whey, which was cooled till 3-5°C, was mixed with CaO in different dosage. Samples were rapidly mixed with a mechanical stirrer for 60 minutes and then centrifuged at 6500 rpm for 15 minutes. COD and TOC concentration of supernatant are given in Table 3.21. pH values of

samples for the all dosage was also around pH=12. Maximum removal efficiencies were 67% and 68% for COD and TOC, respectively with 60 g/L CaO dosage.

Table 3.21 COD and TOC concentration of the first experiment with CaO

CaO Dosage (g/L)	COD (mg/L)	COD Removal Efficiency (%)	TOC (mg/L)	TOC Removal Efficiency (%)
-	60000	-	22210	-
30	48000	20	14110	37
40	40000	33	13650	39
50	35000	42	12890	42
60	20000	67	7176	68

Supernatant and sludge volume of all experiments with 30, 40, 50 and 60 g/L CaO dosage after centrifugation were measured and depicted in Table 3.22. Water and solid contents of separated sludge are also given in the same table. Water content of CaO sludge was around 78-81 %. It was found that, sludge volume after usage of CaO was higher than usage of $Ca(OH)_2$. In addition, water content of CaO sludge was also higher than $Ca(OH)_2$ sludge. As a result of all experimental studies with Steffen process, maximum removal efficiency was achieved with 60 g/L CaO dosage.

Table 3.22 Supernatant, sludge volume, water and solid content of sludge after centrifugation

CaO Dosage (g/L)	Supernatant Volume (ml)	Sludge Volume (ml)	Water Content (%)	Solid Content (%)
30	625	375	79	21
40	555	445	80	20
50	565	435	78	22
60	585	415	81	19

In the centrifugation experiments, only 84 ml of sample can be centrifuged for one run. Since the supernatant volume was not sufficient for microfiltration, sedimentation was used instead of centrifugation. 1 L of cheese whey was cooled to 3°C and then 60 g/L CaO was added. After 60 minutes of rapid mixing at 250 rpm, sample was precipitated for 3 days. Sludge volume and COD, TOC concentration of supernatant was measured daily and given in Table 3.23.

Table 3.23 Sludge volume, COD and TOC concentrations of supernatant in sedimentation experiment (volume of sample: 1 liter)

Time (day)	**Volume of Sludge (ml)**	**COD (mg/L)**	**COD Rem. Eff. (%)**	**TOC (mg/L)**	**TOC Rem. Eff. (%)**
0	0	60000	-	22210	-
1	500	25000	58	8343	62
2	480	26000	57	8927	60
3	460	27000	55	9144	59

As a result of all chemical pretreatment experiments, maximum removal efficiency for COD and TOC concentration was achieved with Steffen process. 60 g/L CaO dosage was selected. 15 liter of cheese whey was cooled to 3°C. 900 g of CaO was added to cooled sample and this sample was mixed rapidly for 90 minutes. After that, sample was precipitated for 1 day. 7.5 liter of supernatant was obtained at the end of the 1 day. COD concentration of this sample was 25000 mg/L. Microfiltration process was applied this sample, after cartridge filter filtration.

3.1.2.2 The Steffen Process + Sedimentation + Cartridge Filter Experiments

7.5 liter of pretreated cheese whey with Steffen Process and sedimentation was used in this experiment. This wastewater was filtered from a 25-µm cartridge filter during 30 minutes. Filtered wastewater was collected in a tank for using in microfiltration experiments. Treatment results of filtration from cartridge filter are given in Table 3.24.

Table 3.24 Results of pretreatment experiments

Treatment Steps	COD (mg/L)	COD Rem. Eff. (%)	TOC (mg/L)	TOC Rem. Eff. (%)
Raw wastewater	60000	-	22210	-
The Steffen process + Sedimentation	25000	58	10430	53
The Steffen process + Sedimentation + Cartridge filter filtration	22500	63	8369	62

3.1.2.3 Microfiltration Experiments

In these experiments, pretreatment steps were mixing, sedimentation and cartridge filtration. The microfiltration membrane was operated in a range of transmembrane pressures between 1 and 2 bar and feed flowrates between 100 and 200 L/h. In Figure 3.13, the effect of feed flowrate and pressure on the permeate flux is shown as a function of time. Pressure and the recycle flowrate slightly influenced the permeate flux. If the flux values of microfiltration membrane after the Steffen process was compared to the fluxes of the same membrane after chemical coagulation with chitosan and $FeCl_3$ (Section 3.1.1), very small permeate flux values were obtained with the Steffen process pretreatment. When the feed flowrate was 200 L/h, permeate fluxes were 4.5 and 4 $L/m^2.h$ for 2 and 1 bar transmembrane pressure, respectively for pretreatment with the Steffen process. 24 and 20 $L/m^2.h$ permeate fluxes were obtained at the same conditions, after chitosan and $FeCl_3$ pretreatment. If flowrate was decreased to 100 L/h, obtained fluxes were 2.5 and 2 $L/m^2.h$ for 2 and 1 bar pressure, after the Steffen process; 16 and 10 $L/m^2.h$ for 2 and 1 bar pressure, after chitosan pretreatment. Probably, it is due to the fact that, membrane surface could be covered by CaO, when the Steffen process was applied. So, permeate flux considerably decreased. Therefore application of microfiltration for pretreated cheese whey by the Steffen process is not feasible.

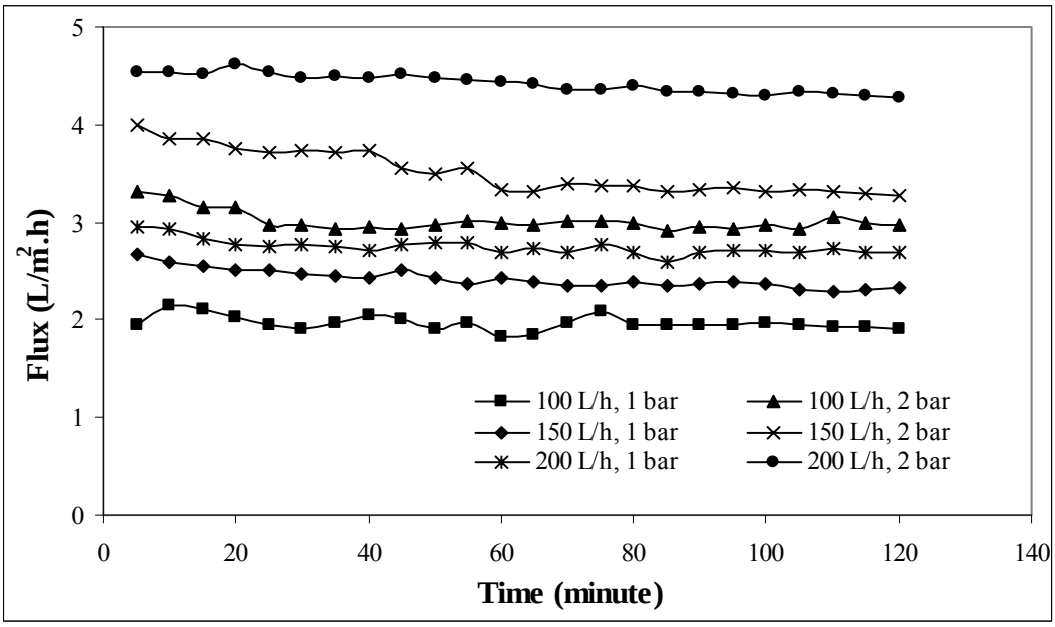
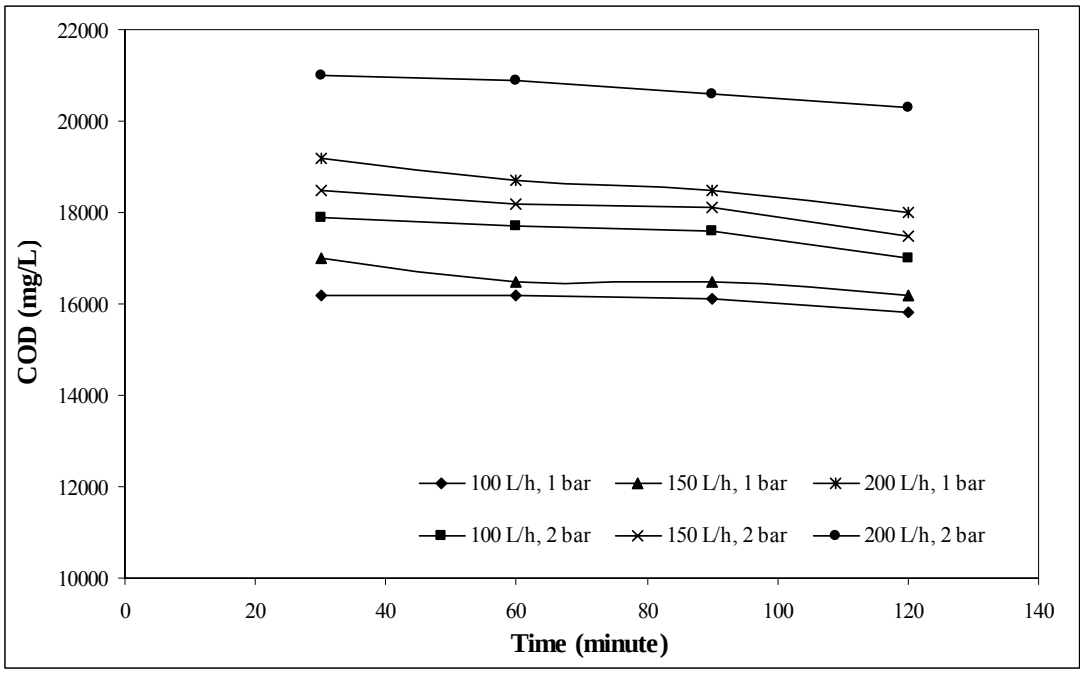


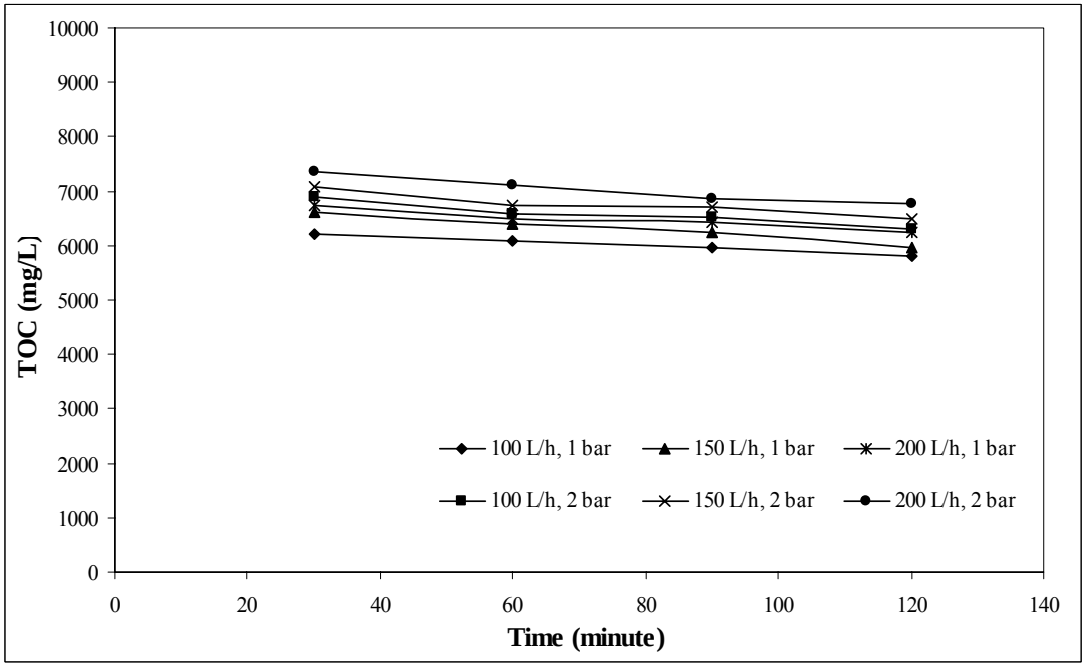
Figure 3.13 Water fluxes of pretreated cheese whey with the Steffen process at different flowrate and different pressure

Treatability results of microfiltration experiments were given in terms of COD and TOC removal. pH value of permeate was between 12.0 and 11.5 during all experiments. Temperature of wastewater in feed tank and permeate was kept 19-20°C by cooling system. Permeate was collected with 30 minutes interval in all experiments. COD and TOC concentration of samples treated with microfiltration membrane at 100, 150, and 200 L/h flowrate are given in Figure 3.14 (a) and (b).

As it can be seen from Figure 3.14 (a) and (b), if the pressure of system was increased, COD and TOC concentration of samples also increased. In addition, increasing flow rate also resulted in increase in COD and TOC concentration. Maximum removal efficiencies were achieved at 100 L/h flow rate and 1 bar pressure. At the end of the all microfiltration experiments, permeate was collected in the same tank and analyzed. COD and TOC concentration of all permeate are given in Table 3.25. Application of microfiltration membrane after the Steffen process was not effectively changed COD and TOC removal efficiencies.



(a)



(b)

Figure 3.14 COD and TOC concentrations of permeate of microfiltration process after the pretreatment with the Steffen process (a) COD concentration (b) TOC concentration

Table 3.25 Treatment results of pretreatment and membrane process

Treatment Steps	**COD (mg/l)**	**COD Rem. Eff. (%)**	**TOC (mg/l)**	**TOC Rem. Eff. (%)**
Raw wastewater	60000	-	22210	-
The Steffen process + Sedimentation	25000	53	10430	53
The Steffen process + Sedimentation + Cartridge filter filtration	22500	58	8369	62
The Steffen process + Sedimentation + Cartridge filter filtration + Microfiltration	17000	72	6430	71

3.2 Olive Oil Mill Wastewater

Four different olive oil mill wastewater (OMWW) samples were used in this thesis. Pretreatment steps were determined considering the information gathered from the earlier samples.

3.2.1 Physical and / or Chemical Pretreatment + Microfiltration or Ultrafiltration Experiments

The treatment experiments of OMWW sample I are given schematically in Figure 3.15.

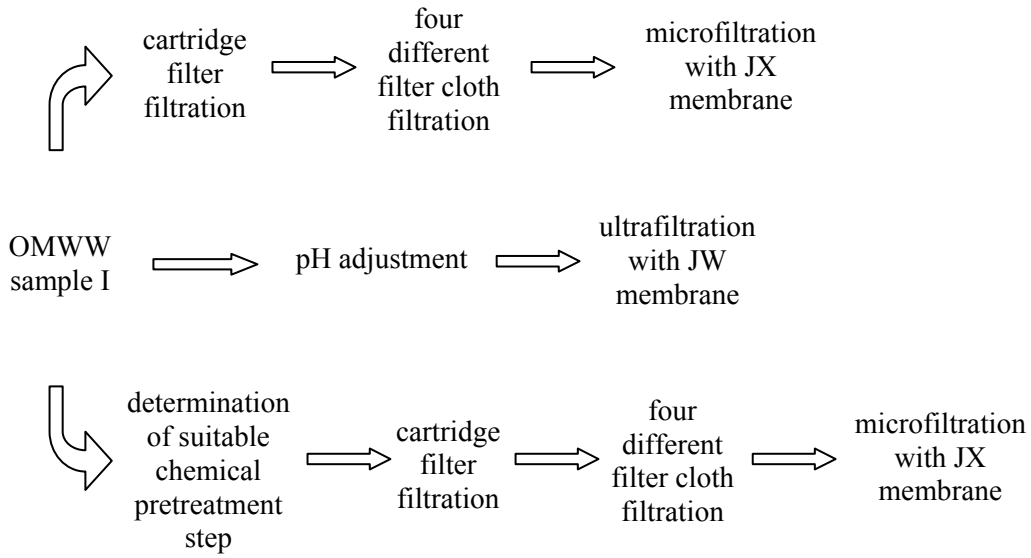


Figure 3.15 Schematic flow diagram of the treatment steps for OMWW sample I

3.2.1.1 Physical Pretreatment Experiments

Cartridge filter filtration and filter cloth filtration were applied before membrane processes. Sample I was used for the experimental studies given in this section.

3.2.1.1.1 Pretreatment with Cartridge Filter. 20 liter of OMWW was used during experimental studies. This wastewater was filtered from a 20-µm cartridge filter. Filtered wastewater was collected in a tank for using in following experiments. Treatment results of filtration from cartridge filter are given in Table 3.26. 23% COD and SS removal efficiencies were obtained after cartridge filter filtration. If the results were compared to effect of cartridge filter filtration on the pretreatment of cheese whey effluent, which were given in Section 3.1.1 (3% COD removal efficiency, 13% SS removal efficiency), higher removal efficiencies were obtained with OMWW. Solid content of OMWW could be more easily captured on the cartridge filter surface.

Table 3.26 Results of cartridge filter pre-treatment

Parameter	**Before Cartridge Filter**	**After Cartridge Filter**	**Removal Efficiency (%)**
COD (mg/L)	120000	93000	23
SS (mg/L)	18600	14320	23
Oil and Grease (mg/L)	2870	2715	5

3.2.1.1.2 Pretreatment with Different Filter Cloths. OMWW was filtered from four different filter cloths with different permeability, in membrane cell. Effluent form cartridge filter was used during experiments. Filter cloths were used successively from more permeable to less permeable filter cloth. Experiments were done at 100 L/h flowrate and open concentrate flow control valve (CFCV) condition. Characteristics of wastewater before and after filter cloth filtration experiments are given in Table 3.27. Maximum removal efficiency (50%) was obtained for SS parameter with the combination of cartridge filter and four different filter clothes.

Table 3.27 Results of four different filter cloth pretreatment

Parameter	Raw Water	Cart. Filter	Filter Cloth I	Filter Cloth II	Filter Cloth III	Filter Cloth IV
COD (mg/L)	120000	93000	87000	83200	81600	77700
COD removal efficiency (%)	-	23	28	31	32	35
SS (mg/L)	18600	14320	13050	12190	10900	9320
SS removal efficiency (%)	-	23	30	35	41	50
Oil-Grease (mg/L)	2870	2715	2415	2258	1912	1758
O-G removal efficiency (%)	-	5	16	21	33	39

3.2.1.2 Chemical Coagulation Experiments

In order to select the optimum coagulant for OMWW, the coagulation tests were conducted with different coagulants. The selection based on the COD concentration of supernatant after coagulation-flocculation and sedimentation. In chemical pretreatment experiments, $FeCl_3$, $FeSO_4$, chitosan, H_2SO_4, and $Ca(OH)_2$ were used.

3.2.1.2.1 Experimental Studies with $FeCl_3$. $FeCl_3$ was added to OMWW sample as a coagulant in different doses between 100-500 mg/L. No pH adjustment was done. Jar test procedure with rapid mixing at 225 rpm for 5 minutes, slow mixing at 25 rpm for 45 minutes, and sedimentation for 2 hours was applied. Supernatant of samples were taken and COD analyzes were done. COD concentrations and COD removal efficiencies are given in Table 3.28. Optimum $FeCl_3$ dosage for OMWW was found as 200 mg/L with 16% COD removal efficiency.

Table 3.28 COD removal efficiency of coagulation experiments with $FeCl_3$

$FeCl_3$ Dosage (mg/L)	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
-	120000	-
100	112500	6
200	101200	16
300	102100	15
400	105000	13
500	103800	14

3.2.1.2.2 Experimental Studies with $FeSO_4$. pH value of the raw OMWW was 4.4. For this reason, no pH adjustment was done during $FeSO_4$ experiments. $FeSO_4$ was added to sample in dosages of 100-500 mg/L and then jar test was applied. COD concentrations and removal efficiencies are given in Table 3.29. Optimum $FeSO_4$ dosage for OMWW was also found as 200 mg/L. Removal efficiencies of $FeCl_3$ and $FeSO_4$ were approximately same at the optimum dosage.

Table 3.29 COD removal efficiency of coagulation experiments with $FeSO_4$

$FeSO_4$ Dosage (mg/L)	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
-	120000	-
100	116600	3
200	101750	15
300	108000	10
400	107800	10
500	110600	8

3.2.1.2.3 Experimental Studies with Chitosan. Chitosan was also used during chemical pretreatment studies with no pH adjustment. This biological cationic polymer was added to wastewater in 10 different doses and then jar test was carried out. After precipitation, samples were taken and COD analyses were done. Experimental results are depicted in Table 3.30. Maximum COD removal efficiency was achieved with 300 mg/L chitosan dosage for the treatment of OMWW.

Table 3.30 COD removal efficiency of coagulation experiments with chitosan

Chitosan Dosage (mg/L)	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
-	120000	-
10	119000	1
20	120000	0
30	118000	2
40	112500	6
50	106800	11
100	105000	13
200	103100	14
300	100100	17
400	103500	14
500	105000	13

3.2.1.2.4 Experimental Studies with H_2SO_4. In order to see the effects of acidic condition on COD removal efficiency, pH value of the OMWW was adjusted to different pH values by using 98 % H_2SO_4 solution. Then jar test procedures were carried out and optimum dosage of H_2SO_4 was found. Results are given in Table 3.31. Optimum pH value of sample was found as pH=2 with 42% COD removal efficiency.

Table 3.31 COD removal efficiencies at different pH

pH	**COD Concentration of Effluent (mg/L)**	**COD Removal Efficiency (%)**
4.4	120000	-
4.0	118800	1
3.0	102000	15
2.0	70000	42
1.0	108000	10

3.2.1.2.5 Two Step Coagulation with H_2SO_4 and $Ca(OH)_2$. In another chemical pretreatment experiment, two steps coagulation was aimed. pH was adjusted from 4.4 to 2 by adding 98 % H_2SO_4 solution, then jar test was carried out and supernatant of sample was taken. COD concentration of supernatant was 70000 mg/L. Then, pH was adjusted to 7 by adding 10 % (w/v) $Ca(OH)_2$ in order to achieve neutral pH. After jar test, COD concentration of supernatant was measured as 61000 mg/L. COD, SS, and oil-grease concentrations of all coagulation studies are summarized in Table 3.32.

Table 3.32 Removal efficiencies of coagulation experiments

Treatment Chemicals	**COD (mg/L)**	**Rem. Eff. (%)**	**SS (mg/L)**	**Rem. Eff. (%)**	**Oil and Grease (mg/L)**	**Rem. Eff. (%)**
Raw wastewater	120000	-	18600	-	2870	-
$FeCl_3$	101200	16	10230	45	2560	11
$FeSO_4$	101750	15	14110	24	2520	12
Chitosan	100100	17	15605	16	2660	7
H_2SO_4	70000	42	9650	48	2240	22
H_2SO_4+$Ca(OH)_2$	61000	49	8040	57	2130	26

As a result of all coagulation experiments, two steps coagulation was selected as chemical pretreatment method. Before microfiltration process, pretreated OMWW with two steps coagulation was filtered from cartridge filter and four different filter cloths in order to prevent membrane fouling. Results are given in Table 3.33.

Instead of filter cloths, second finer cartridge filter usage may be more practical for the industrial applications. This kind of experiments is given in Section 3.2.3.

Table 3.33 Characteristics of OMWW after two steps coagulation + physical pretreatment

Parameter	Raw Water	2 Step Coag.	Cart. Filter	Filter Cloth I	Filter Cloth II	Filter Cloth III	Filter Cloth IV
COD (mg/L)	120000	61000	56100	52400	51200	49400	48000
COD removal efficiency (%)	-	49	53	56	57	59	60
SS (mg/L)	18600	8040	7012	6540	5980	4820	4020
SS removal efficiency (%)	-	57	62	65	68	74	78
Oil –Grease (mg/L)	2870	2130	1915	1845	1702	1453	1213
O-G removal efficiency (%)	-	26	33	36	41	49	58

3.2.1.3 Microfiltration Experiments

Microfiltration experiments were carried out with two different wastewater samples. Differences of samples were their pretreatment options. One of them was pretreated with only physical treatment methods, which were filtration from cartridge filter and filter cloths. The other sample was pretreated with two steps coagulation and physical pretreatment methods (2 SC+P). Different flowrate (100–150–200 L/h), and different pressure (open CFCV condition, 1-2 bar) were applied.

3.2.1.3.1 Permeate Flux Experiments. The influence of the pressure on the permeate flux at 100, 150, and 200 L/h flowrate during the 120 minutes for microfiltration of pretreated OMWW by physical treatment methods and two steps coagulation + physical pretreatment is shown in Figure 3.16, 3.17, and 3.18, respectively.

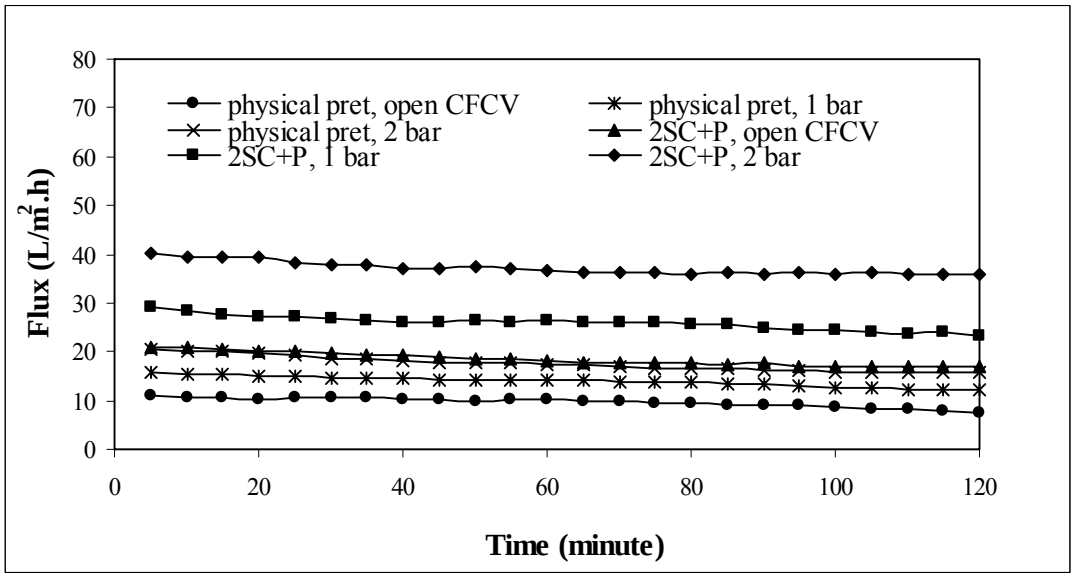


Figure 3.16 Permeate fluxes of pretreated OMWW at 100 L/h flowrate in different pressure after physical pretreatment and two steps coagulation + physical pretreatment (2 SC+P)

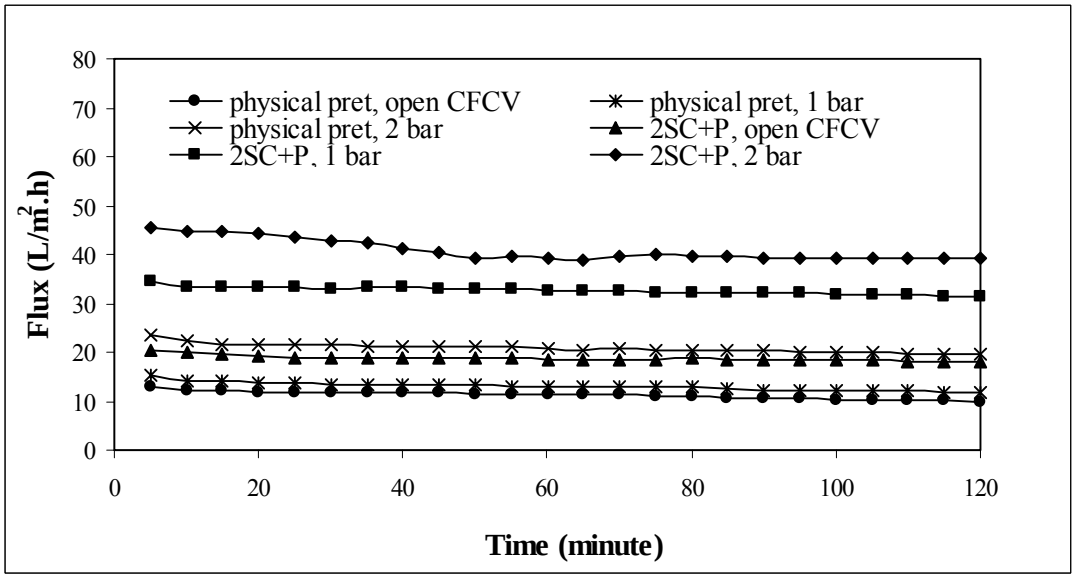


Figure 3.17 Permeate fluxes of pretreated OMWW at 150 L/h flowrate in different pressure after physical pretreatment and two steps coagulation + physical pretreatment (2 SC+P)

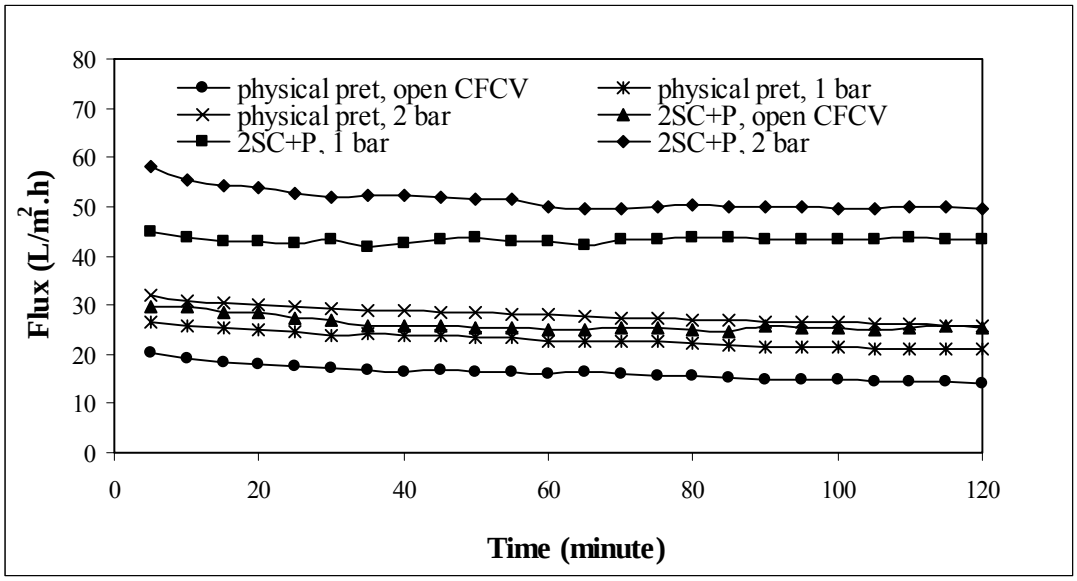


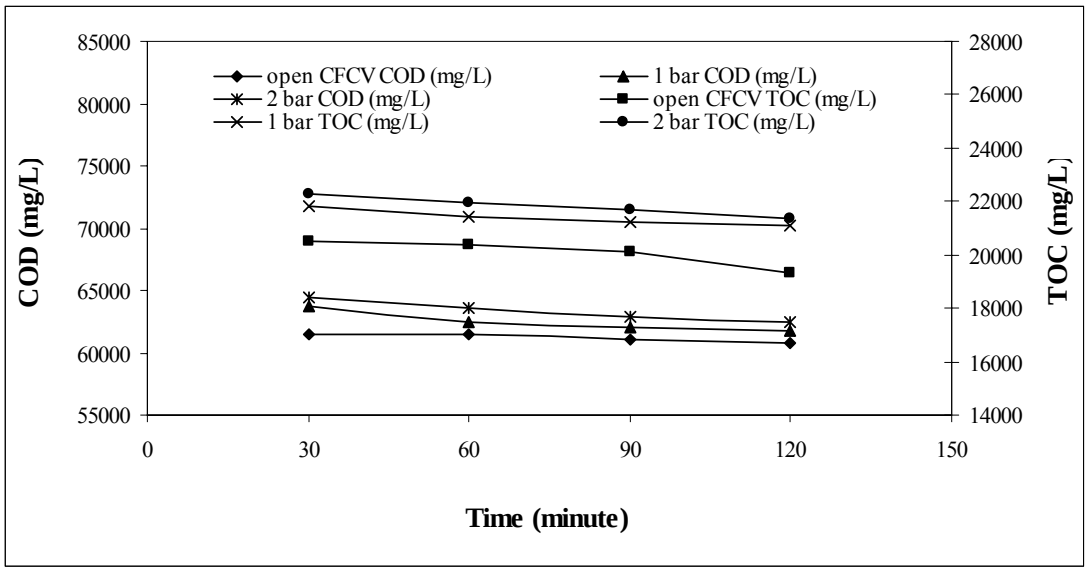
Figure 3.18 Permeate fluxes of pretreated OMWW at 200 L/h flowrate in different pressure after physical pretreatment and two steps coagulation + physical pretreatment (2 SC+P)

As it can be seen from figures, flux became independent of the time after 60 minutes for all flowrates and pressures. So, all flux experiments were finished after 120 minutes. For pretreated wastewater with 2 SC+P, permeate flux for 1 bar pressure and 100 L/h flowrate (Fig 3.16) was around 30 L/m^2.h at the beginning of the experiment and 25 L/m^2/h after two hours. The corresponding fluxes were around 45 L/m^2.h at the beginning and end of the experiment for the 200 L/h flowrate (Fig 3.18).

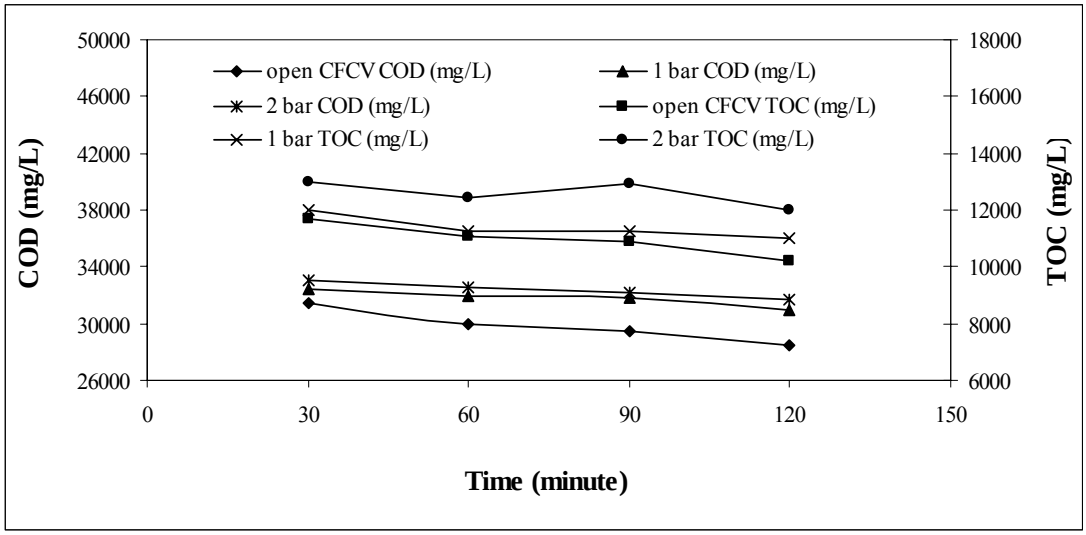
Maximum water fluxes were obtained at 200 L/h flowrate and 2 bar pressure. It can be clearly seen that, fluxes are bigger for the pretreated wastewater with 2 SC+P. Probably, the flock formation on membrane surface during the microfiltration might increase the flux like filter press filtration. The results illustrate that the increase in applied pressure led to an increase in both the initial and final flux values. These data are in agreement with the findings of Wu et. al. (2007) and Mohammadi & Esmaeelifar (2005). Based on Darcy's law, the increasing pressure gradient increases permeate flux. However, an increase in transmembrane pressure (TMP) could also attribute to the fouling layer compression (Ahmad et. al. 2005). The increase in feed flow rate results an increase in cross flow velocity. At the highest cross flow

velocity, precipitated mass on the membrane surface was swept away by the tangential flow. The high shear tangential flow to the membrane surface sweeps deposited particles away. So, permeate flux increases (Mourad &Martine, 2002).

3.2.1.3.2 Treatment Results of Microfiltration Experiments. COD and TOC concentration of the microfiltration membrane influent were 77700 mg/L, and 25064 mg/L for pretreated OMWW with physical treatment methods; 48000 mg/L and 16100 mg/L after two steps coagulation + physical pretreatment (2 SC+P), respectively. Maximum COD and TOC removal efficiencies for 100 L/h flowrate and open CFCV condition for pretreated OMWW with 2 SC+P were 49% COD, 58% TOC; and 77% COD and 78% TOC, respectively. In order to observe the effects of increasing pressure on the COD and TOC removal, pressure of the system was increased to 1 bar. In this case, COD and TOC removal efficiencies were 49% and 55 % for physical pretreatment; 74% and 76 % for 2 SC+P, sequentially. If the pressure of the system was raised to 2 bar, COD and TOC concentration of permeate also increased. Change of COD and TOC concentrations of permeate at 100 L/h flowrate after physical pretreatment and 2 SC+P are given in Figure 3.19.



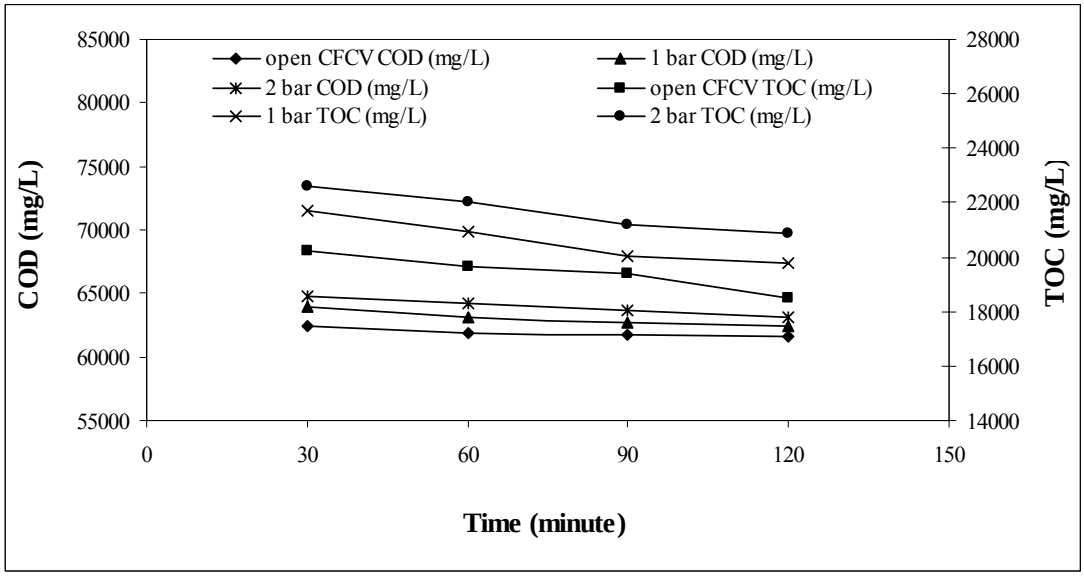
(a)



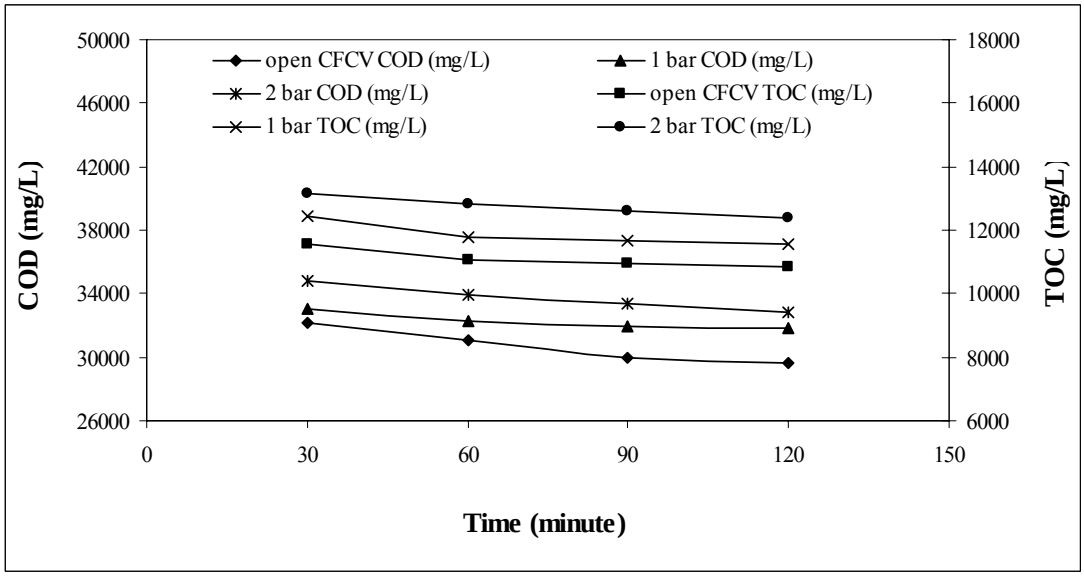
(b)

Figure 3.19 COD and TOC concentration of permeate after pretreatment at 100 L/h flowrate (a) physical pretreatment (b) two steps coagulation + physical pretreatment

In order to observe the effects of increasing flowrate on COD and TOC concentration and removal efficiency, flowrate was raised to 150 L/h. Maximum efficiency for all pressure was obtained for pretreated OMWW with 2 SC+P. In this case, COD removal efficiencies were 76%, 73%, 72%; TOC removal efficiencies were 77%, 76%, 74% for open CFCV condition, 1, and 2 bar, respectively. If the pressure of the system was increased, COD and TOC concentrations of permeate also increased. It is thought that, pollutant was forced to pass through the membrane into permeate with increasing pressure. So, final COD and TOC concentration of permeate increased by increasing pressure. COD and TOC concentration of experimental studies at open CFCV condition, 1 and 2 bar pressure are given in Figure 3.20.

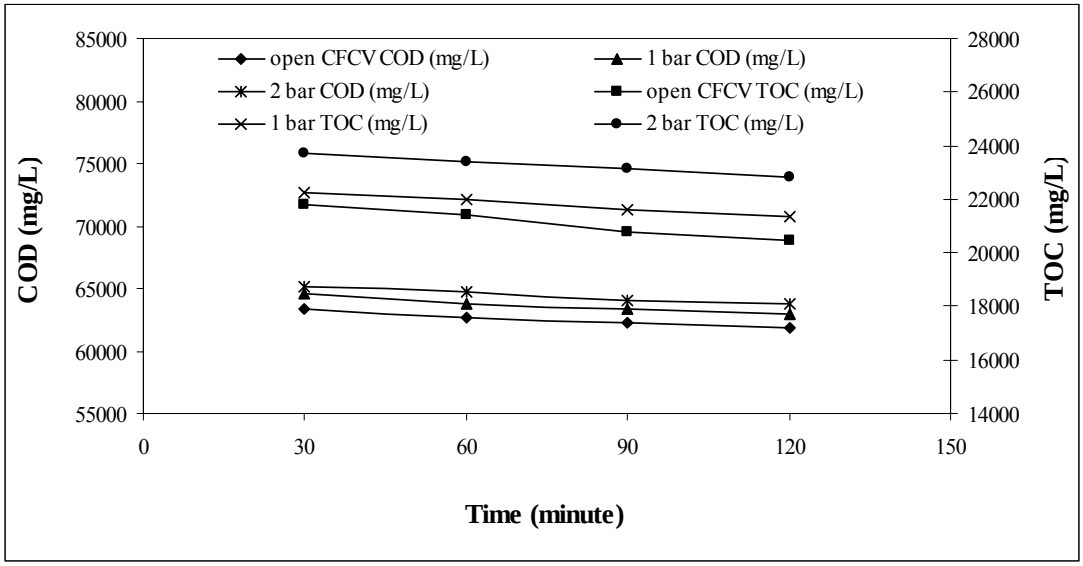


(a)

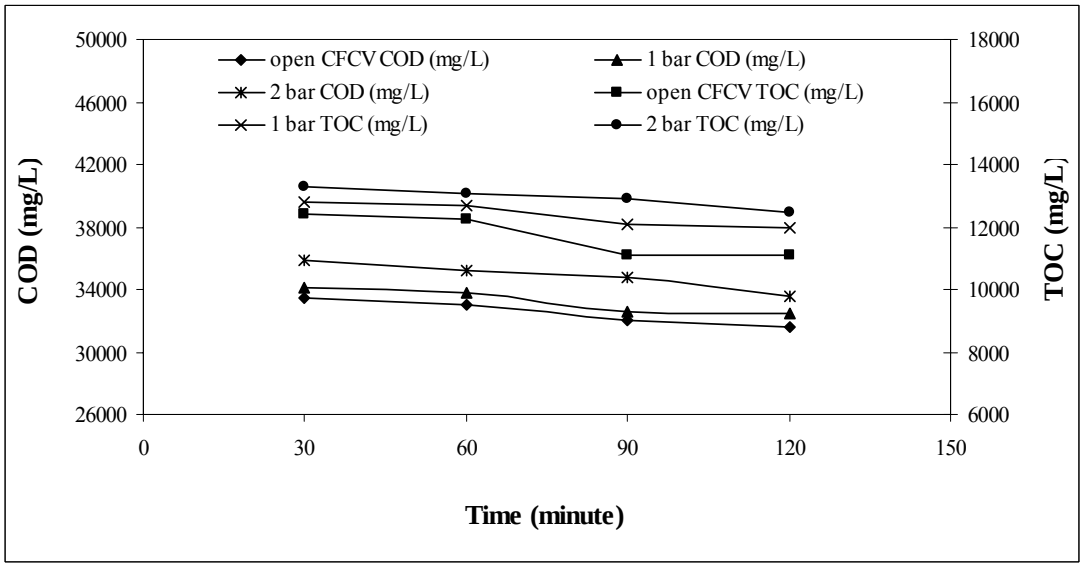


(b)

Figure 3.20 COD and TOC concentration of permeate after pretreatment at 150 L/h flowrate (a) physical pretreatment (b) two steps coagulation + physical pretreatment



(a)



(b)

Figure 3.21 COD and TOC concentration of permeate after pretreatment at 200 L/h flowrate (a) physical pretreatment (b) two steps coagulation + physical pretreatment

As a last treatment experiment, recycling flowrate of the system was increased to 200 L/h. COD and TOC concentration of permeate at the pressure of open CFCV condition, 1, and 2 bar are given in Figure 3.21. COD removal efficiencies of permeate after physical pretreatment were 48%, 48%, 47%; after two step coagulation + physical pretreatment were 74%, 73%, 72% for open CFCV

condition, 1 and 2 bar pressure, respectively. TOC removal efficiencies were 56%, 55%, 51% for physical pretreatment; 76%, 73%, 72% for 2 SC+P at open CFCV condition, 1 and 2 bar, respectively.

As it can be seen from all results, if the pressure of system was increased, COD and TOC concentration of samples also increased. In addition, increasing flowrate also resulted an increasing in COD and TOC concentration. Maximum removal efficiencies were achieved at 100 L/h flowrate and open CFCV condition. Pretreated OMWW with physical pretreatment methods was used in the experiments for 3 different flowrates and 3 different pressures. The COD and TOC concentrations obtained for all experiments were not significantly different from each other. The use of 2 bar pressure on 200 L/h flowrate is not changing the removal efficiency compared to open CFCV condition and 100 L/h flowrate. Therefore industrial usage of open CFCV condition may be more reasonable. In order to obtain representative sample for physical pretreatments nine pretreated effluent samples were mixed using equal volumes. For the two steps coagulation + physical pretreatment, that 9 experimental set described above were repeated and then these effluents were also mixed using equal volumes. It was representative of two steps coagulation + physical pretreatment. In order to compare the results of two set of 9 different experiments mentioned above, the same treatment options were repeated with the physical pretreatment and two steps coagulation + physical pretreatment effluent mixtures. The results are given in Table 3.34. Also the results were in accordance with the individual experiments. As it can be seen from Table 3.34, two steps coagulation + physical pretreatment (2SC+P) and then microfiltration alternative gave the best effluent qualities.

Table 3.34 Treatment results of pretreatment and membrane experiments

Treatment Options	COD (mg/L)	TOC (mg/L)	SS (mg/L)	Oil Grease (mg/L)
Raw wastewater	120000	46340	18600	2870
Physical pretreatment	77700	30500	3530	1110
Physical pretreatment + Microfiltration	62000	20560	2790	718
Two steps coagulation+ physical pretreatment	48000	18530	1590	500
Two steps coagulation+ physical pretreatment + Microfiltration	31000	11390	372	172

3.2.1.4 Ultrafiltration Process after Coagulation with H_2SO_4

For ultrafiltration experiments, pretreatment method was coagulation with H_2SO_4. pH of raw wastewater was adjusted from pH=4.4 to pH=2. The supernatant was subjected to ultrafiltration. Three different flowrate (100 – 150 – 200 L/h), and four different pressure (open CFCV condition, 1, 2, 3 bar) were applied.

3.2.1.4.1 Permeate Flux Experiments. Permeate fluxes of OMWW from ultrafiltration membrane at different flowrate are given in Figure 3.22, 3.23 and 3.24. The same conclusions were acquired with either microfiltration membrane or ultrafiltration membrane. The increase in both transmembrane pressure and feed flow rate resulted an increase in the permeate flux values. For the flow rate of 100 L/h, 2.7 L/m^2.h and 8.5 L/m^2.h permeate fluxes were obtained for the open CFCV condition and 3 bar pressure, respectively. If the flow rate of the system was increased to 200 L/h, permeate fluxes increased to 4.7 L/m^2.h, and 13.8 L/m^2.h for the same operation pressures. As a result, maximum permeate flux was achieved at 200 L/h flowrate and 3 bar pressure. In addition, no flux decline was observed during filtration period for all flow rates and pressures.

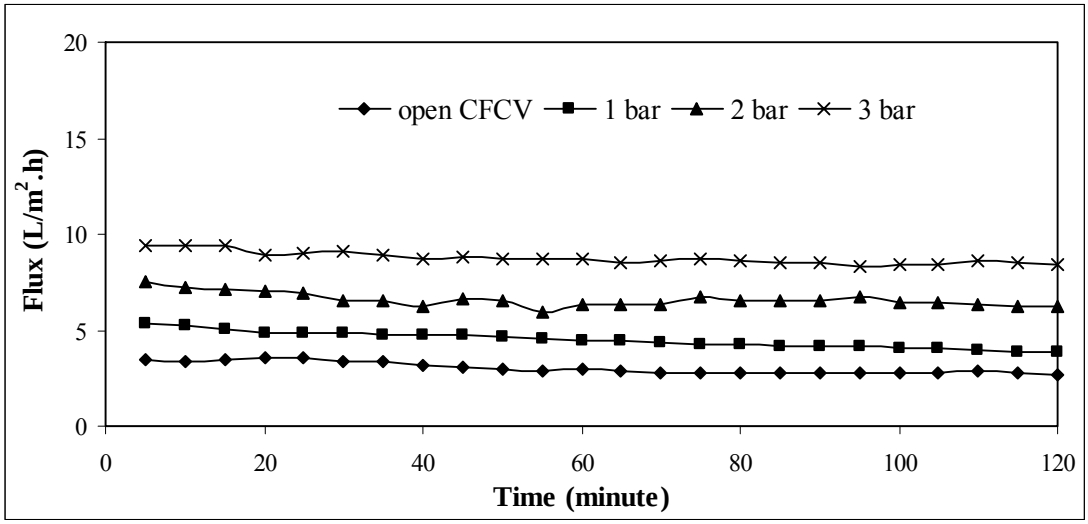


Figure 3.22 Permeate fluxes of OMWW at 100 L/h flowrate

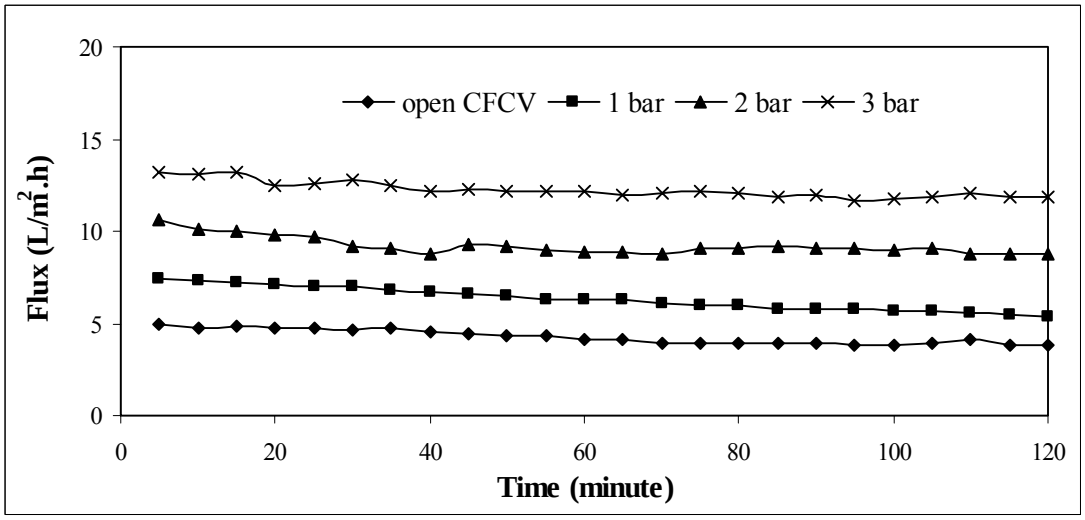


Figure 3.23 Permeate fluxes of OMWW at 150 L/h flowrate

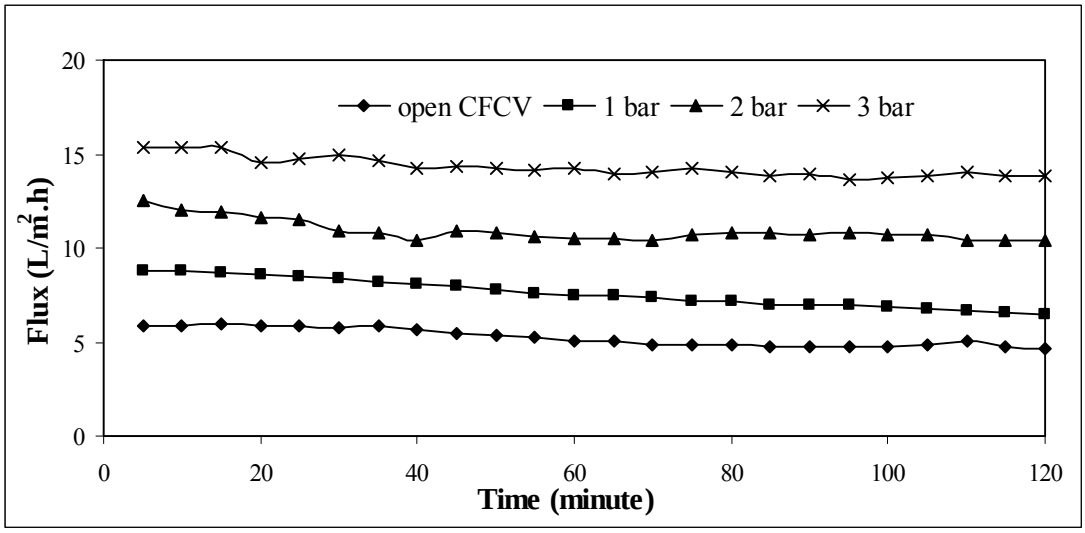


Figure 3.24 Permeate fluxes of OMWW at 200 L/h flowrate

3.2.1.4.2 Treatment Results of Ultrafiltration Experiments. OMWW samples were ultrafiltered at three different flowrate and four different pressures. pH value of permeate was around pH = 2 in all experiments. Temperature of sample was kept 22-24° C by cooling system. Permeates were also collected in 30 minutes interval for all experiments. Treatability results of ultrafiltration experiments at 100, 150, and 200 L/h flowrate are given in Figure 3.25, 3.26 and 3.27.

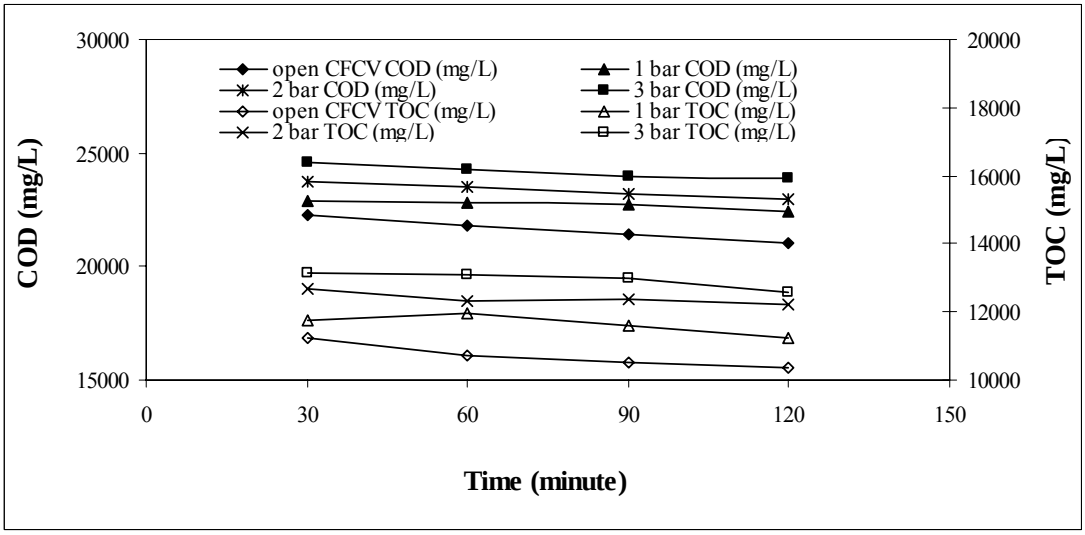


Figure 3.25 COD and TOC concentration of permeate at 100 L/h flowrate

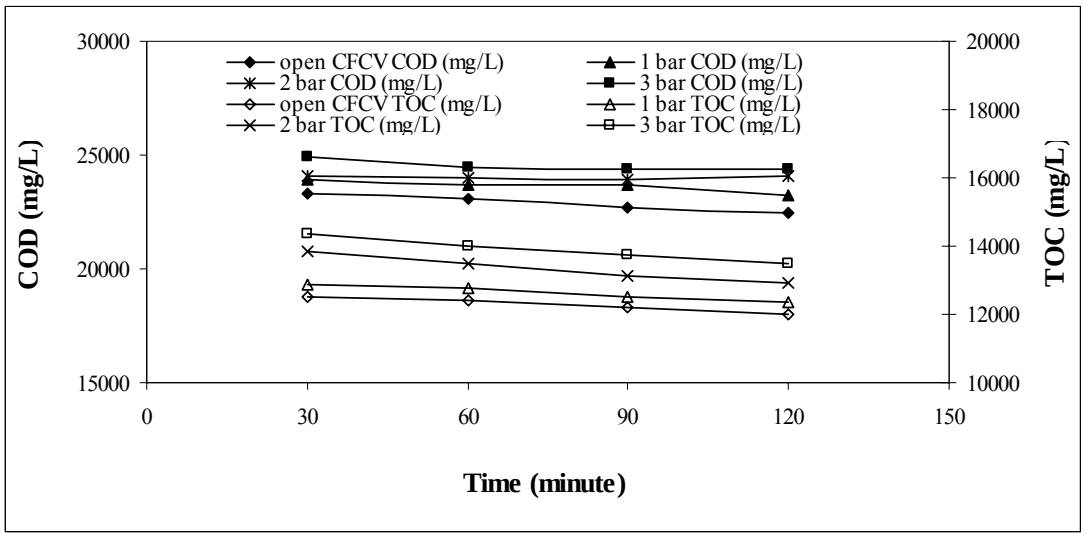


Figure 3.26 COD and TOC concentration of permeate at 150 L/h flowrate

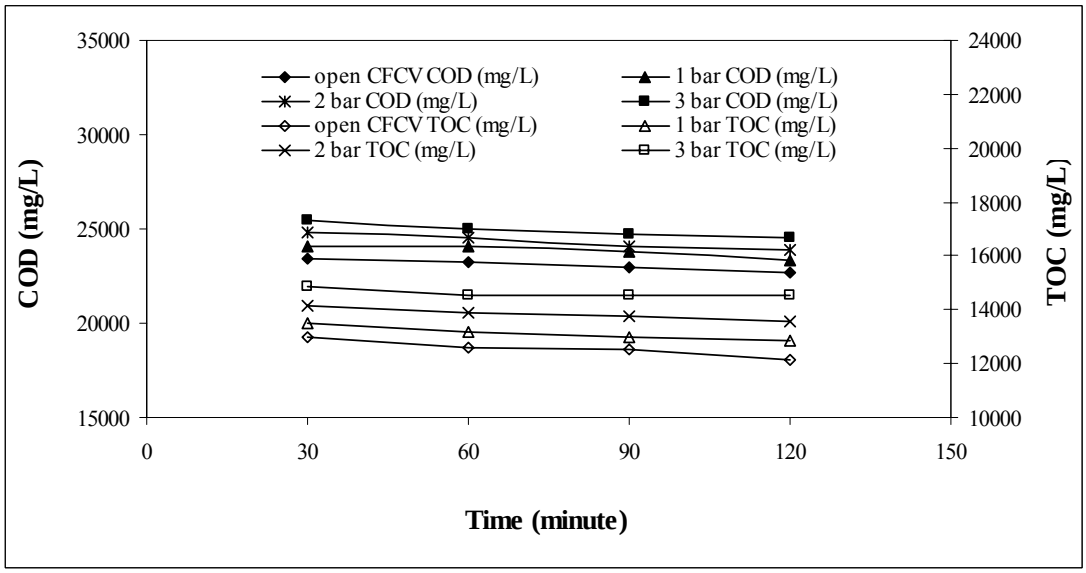


Figure 3.27 COD and TOC concentration of permeate at 200 L/h flowrate

The effect of pressure and feed flow rate on COD concentration was observed in this study. COD concentration increased with the increase in pressure and flow rate. This phenomenon might be influenced by the existence of fouling layer. At low flow rate and cross flow velocity, the growth of fouling layer was easily developed and natural organic matter can accumulate on this layer. The fouling layer acted as another filter layer that increased the resistance for organic matter to pass through. The adsorption or deposition of organic matter on the fouling layer lead to lower concentration of COD in permeates acting as cake layer. This phenomenon was also

observed in other studies (Mikulasek et. al., 2004; Alves & Pinho, 2000; Schafer et. al., 2000). At higher flow rate and cross flow velocity, the high shear tangential to the membrane surface allowed sweeping the deposited particles away. Therefore, the fouling layer on the surface of the membrane reduced. As a result, higher organic matter could pass through the membrane and COD concentration become higher.

As a result of ultrafiltration study, maximum removal efficiencies for both COD and TOC concentrations were achieved at minimum flowrate and minimum pressure, where the minimum permeate flux obtained. Optimum operation condition was found as 100 L/h flowrate and open CFCV condition for ultrafiltration process if maximum removal efficiencies were aimed. Treatment results of coagulation with H_2SO_4 and membrane process are given in Table 3.35. Generally, physical separation is the major removal mechanism in membrane filtration. 95% of suspended solids removal was achieved in this study. Ultrafiltration membrane is suitable to remove suspended solids content extensively but it was difficult to remove dissolved organic matters (Oe. et. al., 1996). So, the percentage removal of COD (88%) obtained was smaller than SS removal efficiency.

Table 3.35 Treatment results of chemical pretreatment and membrane process

Treatment Steps	**COD (mg/L)**	**COD Rem. Eff. (%)**	**SS (mg/L)**	**SS Rem. Eff. (%)**	**Oil and Grease (mg/L)**	**O-G Rem. Eff. (%)**
Raw wastewater	120000	-	18600	-	2870	-
Coagulation with H_2SO_4	70000	42	9650	48	2240	22
Coagulation with H_2SO_4 + Ultrafiltration	22500	81	930	95	140	95

3.2.2 Chemical Coagulation and Physical Pretreatment + Ultrafiltration + Nanofiltration Experiments

Ultrafiltration and then nanofiltration processes were applied on OMWW sample II, after pH adjustment and physical pretreatment. Schematic diagram of the treatment steps are given in Figure 3.28.

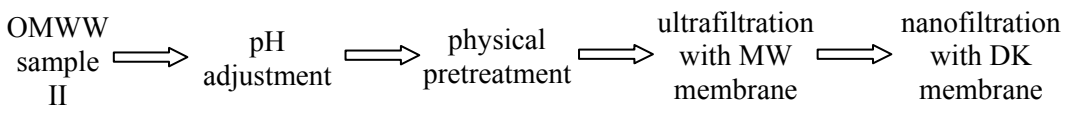


Figure 3.28 Schematic flow diagram of the treatment steps for OMWW sample II

3.2.2.1 Chemical Coagulation and Physical Pretreatment Experiments

The effective chemical coagulation method was found as pH adjustment to acidic value for OMWW in Section 3.2.1.2.4. Therefore this pretreatment method was repeated with another OMWW sample (sample II). In order to select the optimum dosage of H_2SO_4, different dosage of acid with 98% purity were used. Then jar tests were carried out. After settling period, the supernatant of sample was separated and analyzed. Results are given in Table 3.36.

Table 3.36 Effects of different dosage of H_2SO_4 on pretreatment of OMWW

H_2SO_4 volume (mL/L)	**pH**	**Volume of sludge (mL)**	**COD (mg/L)**	**TOC (mg/L)**
0	5.1	-	100000	21870
2	3.6	50	68000	14600
4	2.6	50	66000	14530
6	2.4	55	67000	14770
8	2.3	65	68000	15090
10	2.2	70	65000	14550

Maximum COD and TOC removal efficiencies were achieved as 65000 mg/L COD and 14550 mg/L TOC concentrations with 10 mL/L H_2SO_4 volume. However, in order to avoid too much acid consumption and considering the close treated COD values for different dosages, 4 mL/L H_2SO_4 dosage was selected for membrane studies. 20 liters of OMWW was taken and 4 mL/L acid was added to sample. After coagulation, flocculation and settling period, 10 L of supernatant was obtained. This wastewater was filtered through a 20-µm cartridge filter in order to avoid membrane fouling, during 30 minutes. Filtered wastewater was collected in a tank for using in following experiments.

OMWW was then filtered through two different filter cloths with 7.2 L/dm^2.h (filter cloth III) and 3.2 L/dm^2.h (filter cloth IV) air permeability, in membrane cell. Experiments were done at 100 L/h flowrate and open concentrate flow control valve (CFCV) condition. Characteristics of wastewater after cartridge filter and filter cloth filtration experiments are given in Table 3.37. Effluent of filter cloth IV was collected in a tank and used in ultrafiltration studies.

Table 3.37 Results of all pretreatment experiments

Parameter	**Raw Water**	**pH Adjustment**	**Cartridge Filter**	**Filter Cloth III**	**Filter Cloth IV**
COD (mg/L)	100000	66000	63000	60000	57000
COD removal efficiency (%)	-	34	37	40	43
SS (mg/L)	17600	15130	14320	13050	12190
SS removal efficiency (%)	-	14	19	26	31
Oil -Grease (mg/L)	3070	2760	2715	2415	2358
O-G removal efficiency (%)	-	10	12	21	23

It can be concluded that, only cartridge filter filtration is sufficient without filter cloth filtrations. Moreover instead of settling phase of coagulation, only cartridge filtration after rapid mixing is reasonable industrial application. This experimental study is given in Section 3.2.3.

3.2.2.2 Ultrafiltration Experiments

In this section, ultrafiltration experiments were applied after chemical and then physical pretreatment of OMWW. Performance of UF membrane was evaluated by measuring the permeate flux, COD and TOC concentration of permeate at different pressure and flowrate.

3.2.2.2.1 Permeate Flux Experiments. Permeate flux experiments were carried out with 100 L/h, 150 L/h and 200 L/h flowrates and 2, 3, 4 bar pressure for pretreated OMWW. The influences of the pressure on the permeate flux at 100 - 200 L/h flowrate during the 120 minutes for ultrafiltration of pretreated OMWW are shown in Figure 3.29, 3.30 and 3.31.

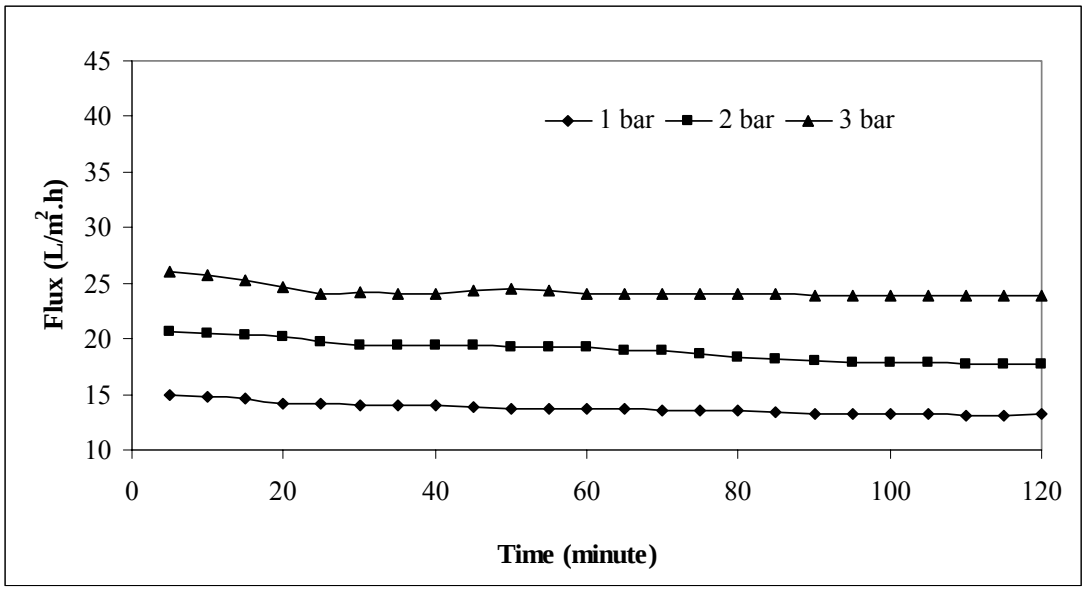


Figure 3.29 Permeate fluxes of pretreated OMWW at 100 L/h flowrate in different pressure

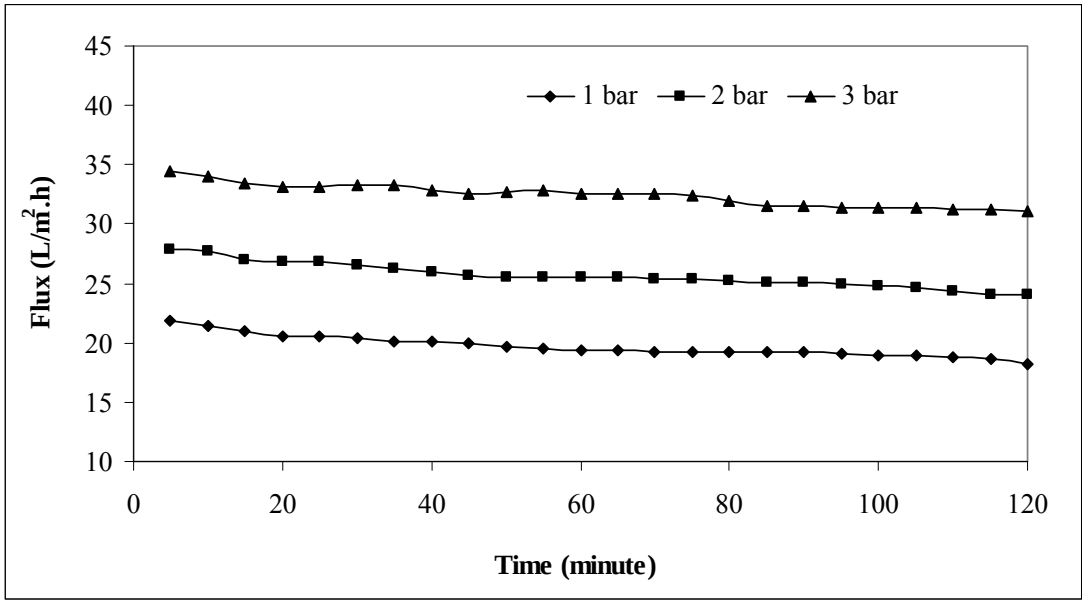


Figure 3.30 Permeate fluxes of pretreated OMWW at 150 L/h flowrate in different pressure

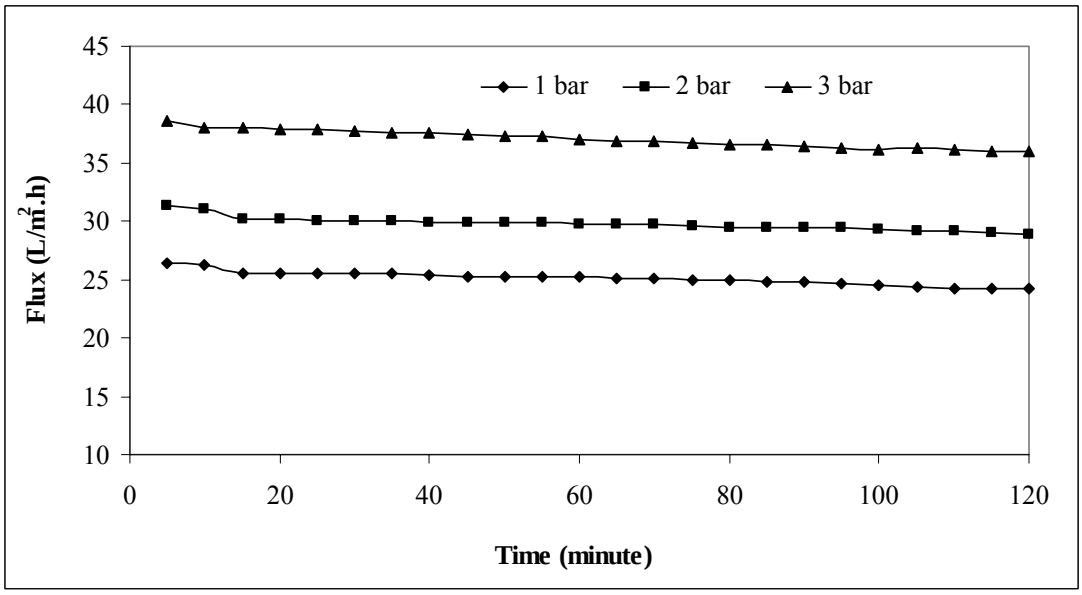


Figure 3.31 Permeate fluxes of pretreated OMWW at 200 L/h flowrate in different pressure

As it can be seen from all three figures, flux became independent of the time for all flowrate and pressure. So, all flux experiments were finished at the end of the 120 minutes. Pressure and recycle flowrate significantly influenced the permeate flux. Higher flowrate at the membrane surface is a very important factor in increasing the permeate flux. Using higher velocity the deposited molecules are continuously removed from the membrane surface and thus permeate flux increases. If the

pressure was kept as 1 bar, 14.9 L/m^2.h, 21.8 L/m^2.h, 26.4 L/m^2.h permeate fluxes were obtained for 100, 150 and 200 L/h, respectively. Increase in pressure also increased water fluxes for all flowrates. For 200 L/h flow rate, 26.4 L/m^2.h, 31.4 L/m^2.h and 38.6 L/m^2.h permeate fluxes were obtained for 1, 2 and 3 bar transmembrane pressures, respectively. Maximum water fluxes were obtained at 200 L/h flowrate and 3 bar pressure

3.2.2.2.2 Treatment Results of Ultrafiltration Experiments. Treatability results of OMWW were given in terms of COD and TOC removal. pH value of permeate was between 2.5 and 2.6 during all experiments. Temperature of wastewater in feed tank and permeate was kept 22-24°C by cooling system. Permeate was collected with 30 minutes interval in all experiments. Treatability results of ultrafiltration of pretreated wastewater at 100- 200 L/h flowrate are given in Figure 3.32, 3.33, 3.34.

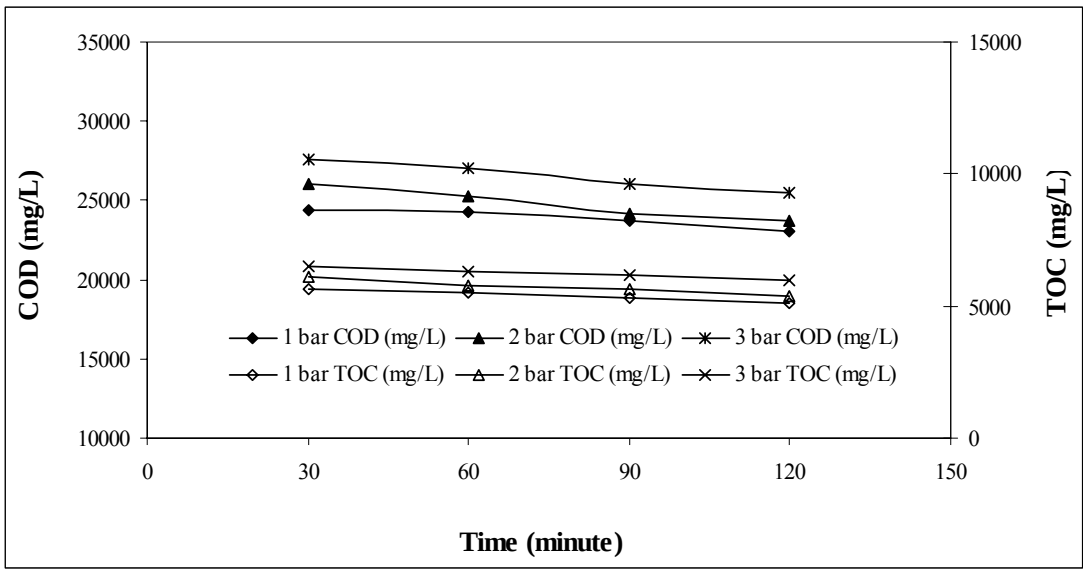


Figure 3.32 COD and TOC concentration of permeate at 100 L/h flowrate

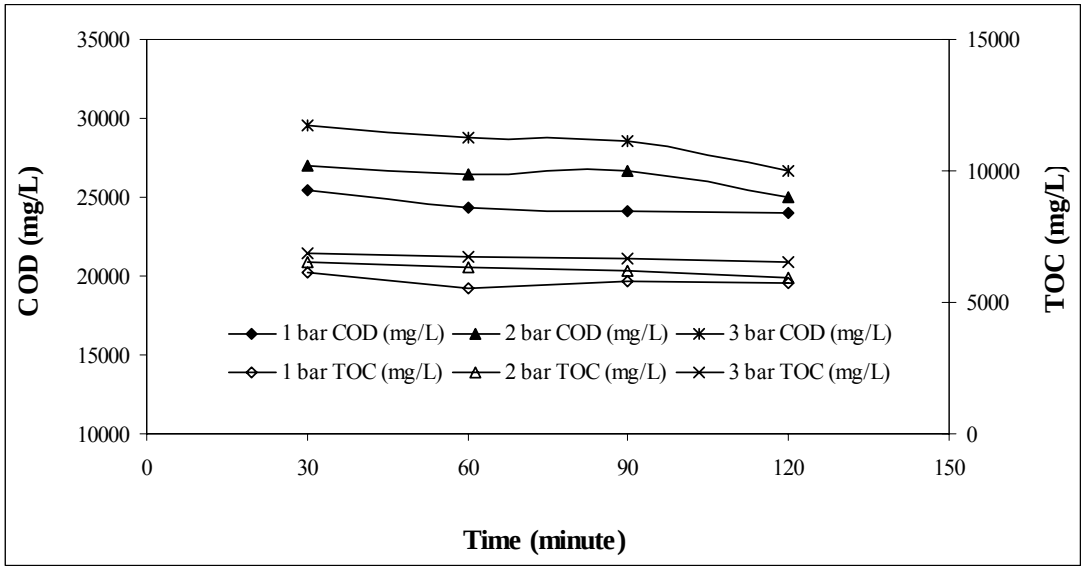


Figure 3 33 COD and TOC concentration of permeate at 150 L/h flowrate

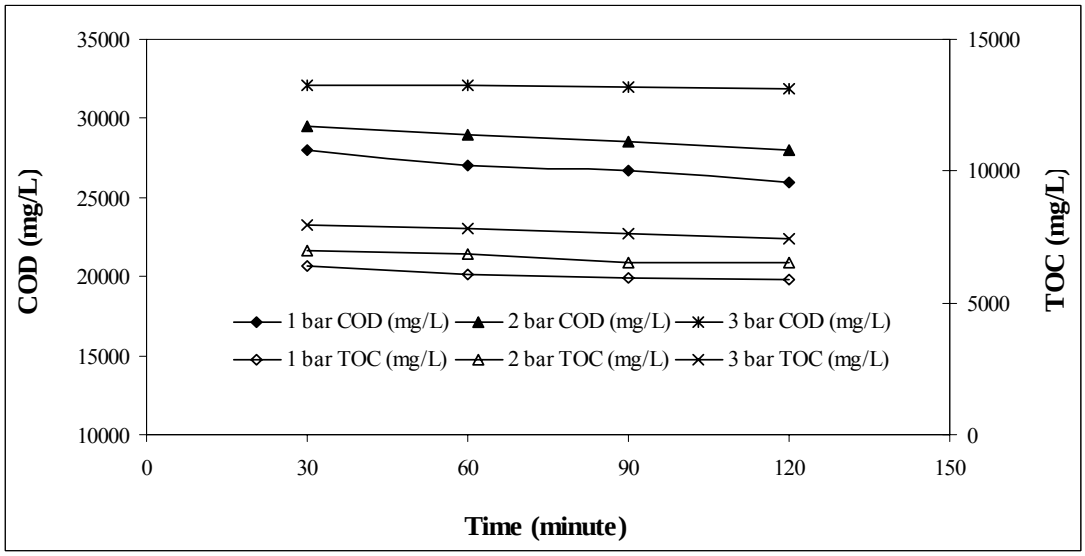


Figure 3.34 COD and TOC concentration of permeate at 200 L/h flowrate

As it can be seen from Figure 3.32-3.34, if the pressure of system was increased, COD and TOC concentration of permeate samples also increased. For 100 L/h recycling flow rate, COD concentration of permeate was 22000 mg/L for 1 bar pressure and 25500 mg/L for 3 bar pressure. In terms of TOC, 5100 mg/L and 6400 mg/L concentrations were obtained for 1 and 3 bar pressure, respectively. Increase in

flowrate also resulted in increase in COD and TOC concentration. Maximum removal efficiencies were achieved at 100 L/h flowrate and 1 bar pressure with 22000 mg/L COD and 5100 mg/L TOC concentration. So, this operation conditions were selected as optimum conditions. COD, TOC, SS, and oil and grease concentrations of permeate at 100 L/h flowrate and 1 bar pressure are given in Table 3.38. Maximum removal efficiency was achieved with SS parameter as 98%.

Table 3.38 Treatment results of pretreatment and ultrafiltration process

Parameter	**Raw OMWW**	**Pre-treatment**	**Efficiency (%)**	**UF Effluent**	**Efficiency (%)**
pH	5.1	2.6	-	2.6	-
COD (mg/L)	100000	57000	43	22000	78
TOC (mg/L)	21870	11376	48	5100	77
SS (mg/L)	17600	12190	31	370	98
Oil and grease (mg/L)	3070	2358	23	400	87

3.2.2.3 Nanofiltration Experiments of Ultrafiltration Effluent

The second membrane experiment of this section was nanofiltration of OMWW. Effluent of ultrafiltration process was collected in a tank and used in nanofiltration experiments. Samples were filtered from nanofiltration membrane at 100, 150, and 200 L/h flowrate; 10, 15, 18, 20, 25 bar pressure.

3.2.2.3.1 Permeate Flux Experiments. Effects of pressure on the permeate flux at 100-150-200 L/h flowrate are given in Figure 3.35, 3.36, 3.37, respectively.

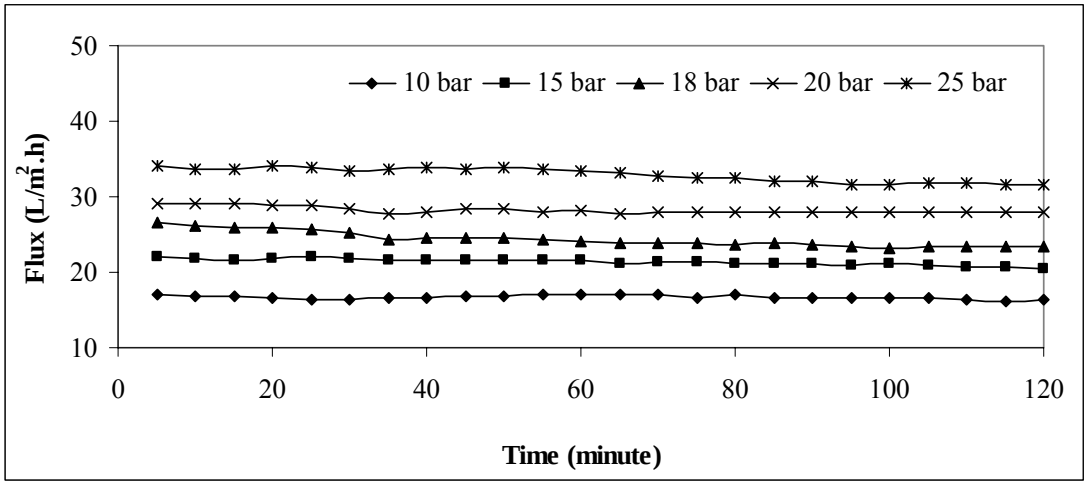


Figure 3.35 Permeate flux experiments for NF of UF effluent at 100 L/h flowrate

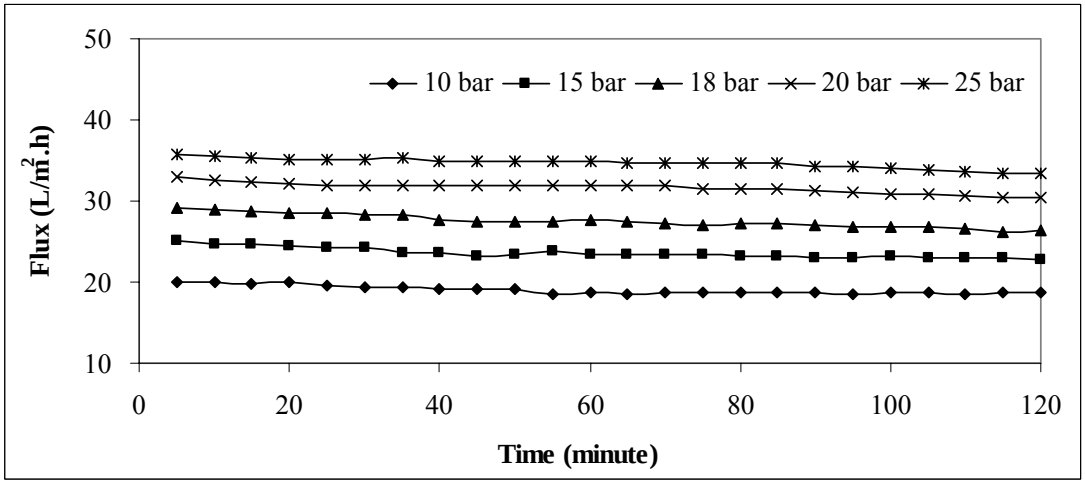


Figure 3.36 Permeate flux experiments for NF of UF effluent at 150 L/h flowrate

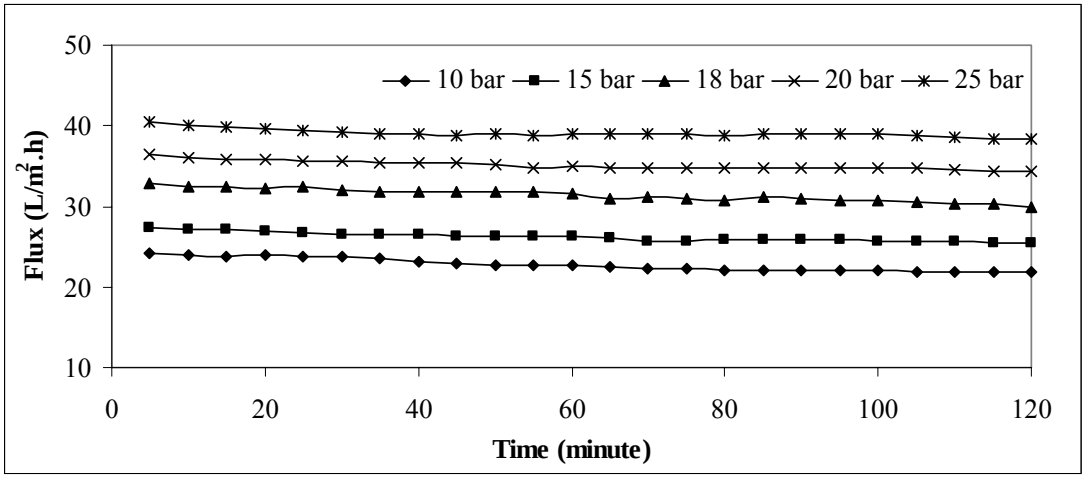


Figure 3.37 Permeate flux experiments for NF of UF effluent at 200 L/h flowrate

Pressure and the recycle flowrate significantly influenced the permeate flux for nanofiltration membrane. Maximum flux values were achieved at 25 bar pressure for each flowrate. About 41 $l/m^2.h$ permeate flux was obtained at 200 L/h flowrate and 25 bar pressure as maximum permeate flux during nanofiltration experiments.

3.2.2.3.2 Treatment Results of Nanofiltration of Ultrafiltration Effluents. Permeates of nanofiltration membrane were taken with 30 minutes interval and analyzed. Treatment results of nanofiltration experiments were also given in terms of COD and TOC and depicted in Figure 3.38, 3.39 and 3.40.

If COD and TOC concentration of permeate for all flowrate and pressure was investigated, it can be concluded that increasing in flowrate and pressure also increased COD and TOC concentration of permeate for nanofiltration of pretreated OMWW, same as the ultrafiltration results. Maximum removal efficiencies were achieved at 100 L/h flowrate and 10 bar pressure. In this case, COD, TOC, SS and oil-grease analysis were done and results are given in Table 3.39.

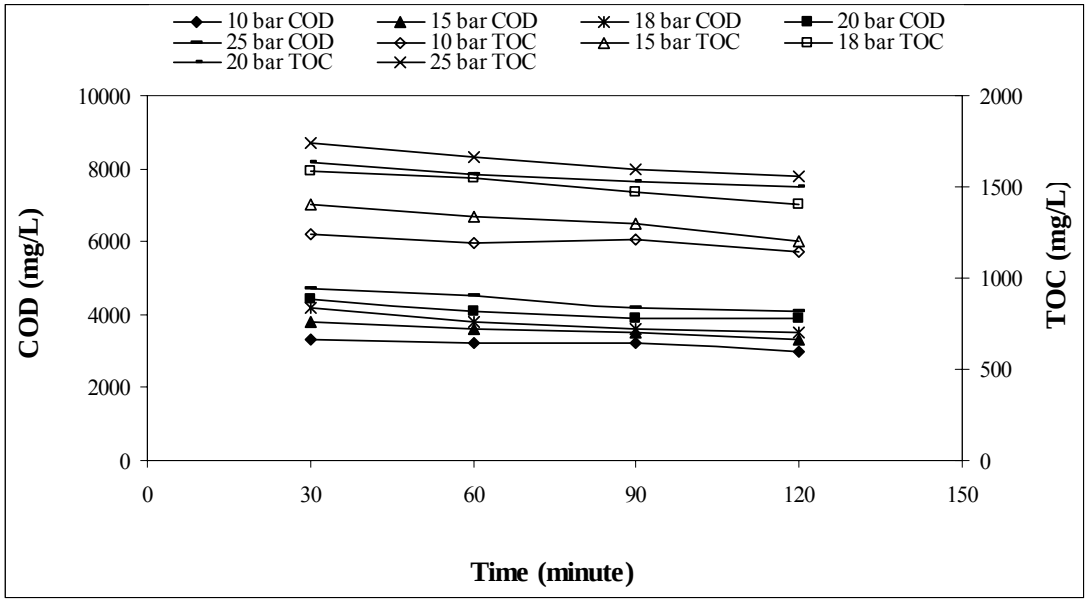


Figure 3.38 COD and TOC concentration of permeate at 100 L/h flowrate

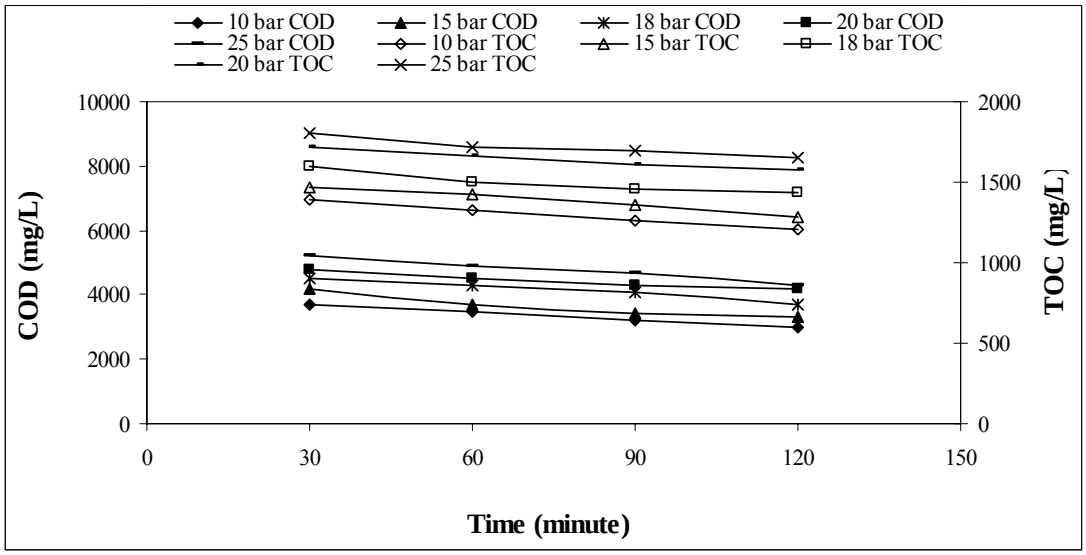


Figure 3.39 COD and TOC concentration of permeate at 150 L/h flowrate

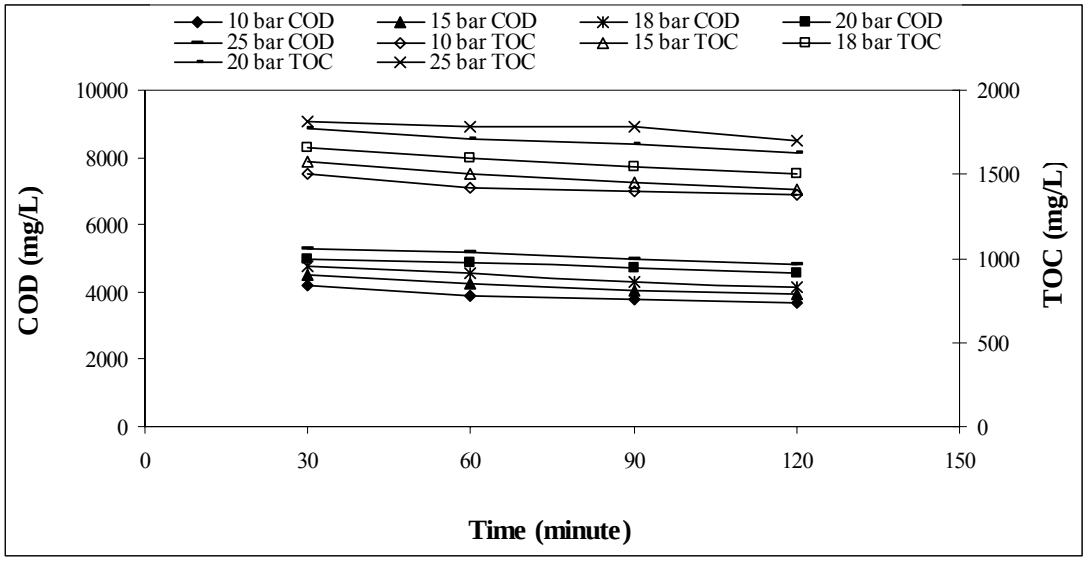


Figure 3.40 COD and TOC concentration of permeate at 200 L/h flowrate

Table 3.39 Treatment results of pretreatment, ultrafiltration and then nanofiltration process

Parameter	**Raw wastewater**	**UF effluent**	**Effic. (%)**	**NF effluent**	**Effic. (%)**
pH	5.1	2.6	-	2.6	-
COD (mg/L)	100000	22000	78	3700	96
TOC (mg/L)	21870	5100	77	1083	96
SS (mg/L)	17600	370	98	30	99
Oil and grease (mg/L)	3070	400	87	40	99

Maximum removal efficiencies for OMWW treatment was achieved by the combination of pH adjustment and physical pretreatment, ultrafiltration and nanofiltration processes. 99% total removal efficiencies were obtained for both SS and oil and grease parameters. COD and TOC removal efficiencies were 96% with 3700 and 1083 mg/L concentrations. It should be noticed that the pressures applied in nanofiltration is too high compared to ultrafiltration. In order to see the effect of using smaller pressures, new experiments for nanofiltration under pressure of 4-10 bar were done and results are given in Section 3.2.4.

3.2.3 pH Adjustment + Cartridge Filtration + Ultrafiltration or Nanofiltration Experiments

Ultrafiltration or nanofiltration processes were applied after pretreatment steps for OMWW sample III. Schematic flow diagram of the treatment steps are given in Figure 3.41.

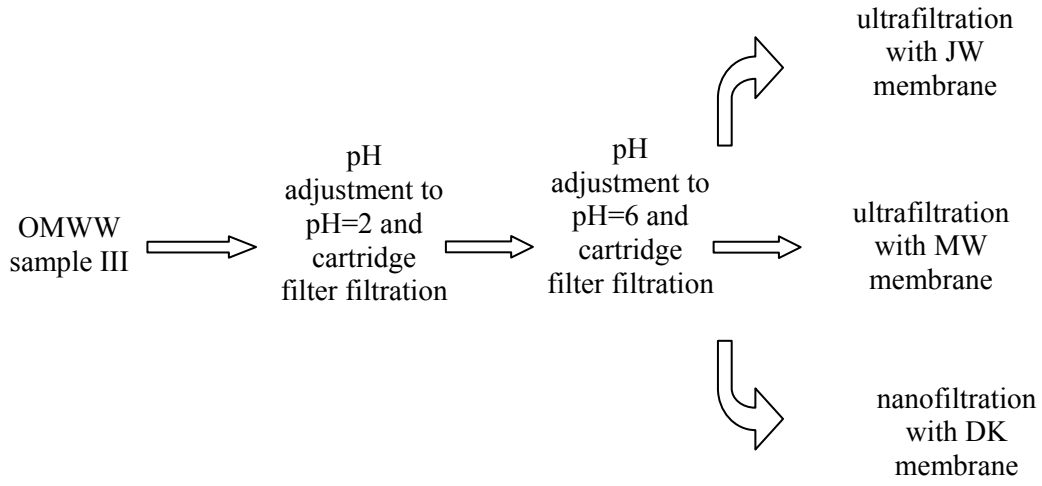


Figure 3.41 Schematic flow diagram of the treatment steps for OMWW sample III

3.2.3.1 pH Adjustment and Cartridge Filtration Experiments

Pretreatment steps were pH adjustments and cartridge filter filtration of OMWW sample III. The COD and TOC concentrations of sample at all steps were measured and given in Table 3.40. As a result of all pretreatment experiments, COD and TOC concentrations of OMWW were 31000 mg/L, and 8172 mg/L, respectively.

Table 3.40 Pretreatment results of OMWW

Treatment Steps	COD (mg/L)	Rem. Eff. (%)	TOC (mg/L)	Rem. Eff. (%)
Raw wastewater	84000	-	35542	-
pH adjustment to pH= 2 and cartridge filter filtration	35000	58	9309	74
pH adjustment to pH = 6 and cartridge filter filtration	31000	63	8172	77

COD removal efficiency was 63% by only pH adjustment and cartridge filtration. This efficiency is better than the efficiency obtained from acidification + cartridge filter filtration + two filter cloth filtration, which is given in Table 3.36. This result can also be evaluated as quite satisfactory compared to 49% COD removal by two step coagulation (Oktav & Ozer, 2003). It can be concluded that, after acidification the time elapsed during the sedimentation decreases the removal efficiency of cartridge filtration. The volume of captured particulate matter was too small compared to settled sludge during the two step coagulation. Total volume of settled sludge was approximately 750 mL during the two step coagulation of 1 L OMWW. On the other hand, the volume of total captured particulate matter was 50 mL for the two step cartridge filtration of 1 L OMWW. Adjustment of pH to 6 and cartridge filter filtration is useful to get bigger fluxes during the ultrafiltration than that of without pH=6 adjustment. Moreover pH=6 adjustment of effluent is necessary to satisfy discharge standards.

In addition to COD removal, olive oil was collected on the pretreated wastewater. Recovery of olive oil is done by second decanter in olive oil production process. For decanter separation, sometimes hot water addition is necessary. However, hot water addition causes increase in wastewater volume for the same amount of olive oil production without water addition (Niaunakis & Halvadakis, 2004).

3.2.3.2 Membrane Experiments

One of the most important parameters in the membrane filtration is permeate flux, Jv, which is influenced by several operating conditions such as the transmembrane pressure (TMP), feed flowrate, pH and nature of the membrane. In order to examine these influences, cross flow operation mode and three membranes were used.

The efficiency of the membranes used in this study was assessed on the bases of the COD and TOC removal. Thus, retention coefficient of COD and TOC can be defined by the equations:

$$R_{COD} = \frac{(COD_F - COD_P)}{COD_F} \times 100 \tag{3.2}$$

$$R_{TOC} = \frac{(TOC_F - TOC_P)}{TOC_F} \times 100 \tag{3.3}$$

Where COD_F and COD_P represent the COD values measured in the feed and permeate streams; TOC_F and TOC_P represent the TOC values measured in the feed and permeate respectively.

The retention coefficients are affected by the operating conditions, such as feed flowrate or cross-flow velocity, the transmembrane pressure, retention time. Certainly the type of membrane determines the removal efficiencies.

3.2.3.2.1 Pressure- Permeate Flux-Removal Efficiency Relations. Increasing pressure increases permeate flux, but higher pressure causes the formation of cake layer on the membrane surface. In order to observe this phenomena and determine the optimum pressure, the variation of the permeate flux with the increasing transmembrane pressures at three different feed flowrates (100, 150, 200 L\h) for the

MW ultrafiltration membrane are given in Figure 3.42. As it can be seen, the permeate flux increases with the increasing transmembrane pressure up to 1 or 2 bar. At higher pressures, almost a constant value of flux is reached. This effect is caused by the formation of cake layer on the membrane surface, which accelerates the membrane fouling (Koltuniewicz & Field, 1996). This cake layer is one of the main causes that promote the fouling of membranes. Therefore, at optimum pressure, permeation flux must be high and tendency to cake layer formation is low. Optimum pressure seems to be 2 bars for this filtration experiments.

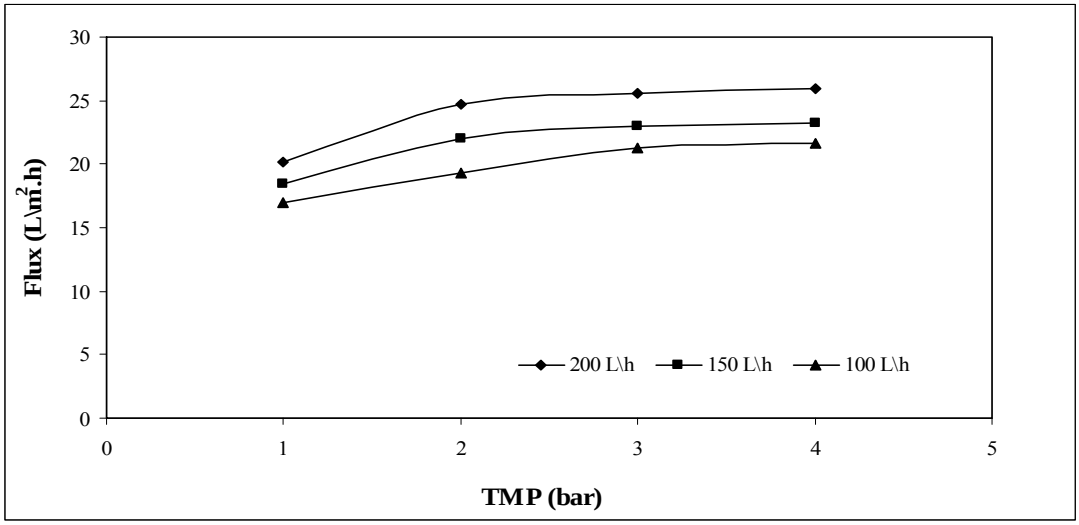
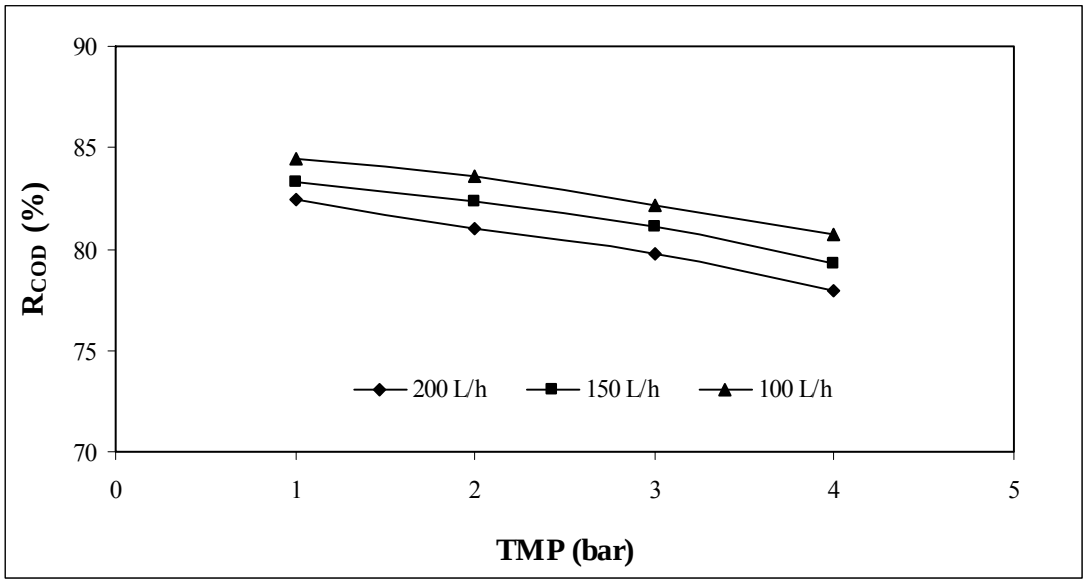
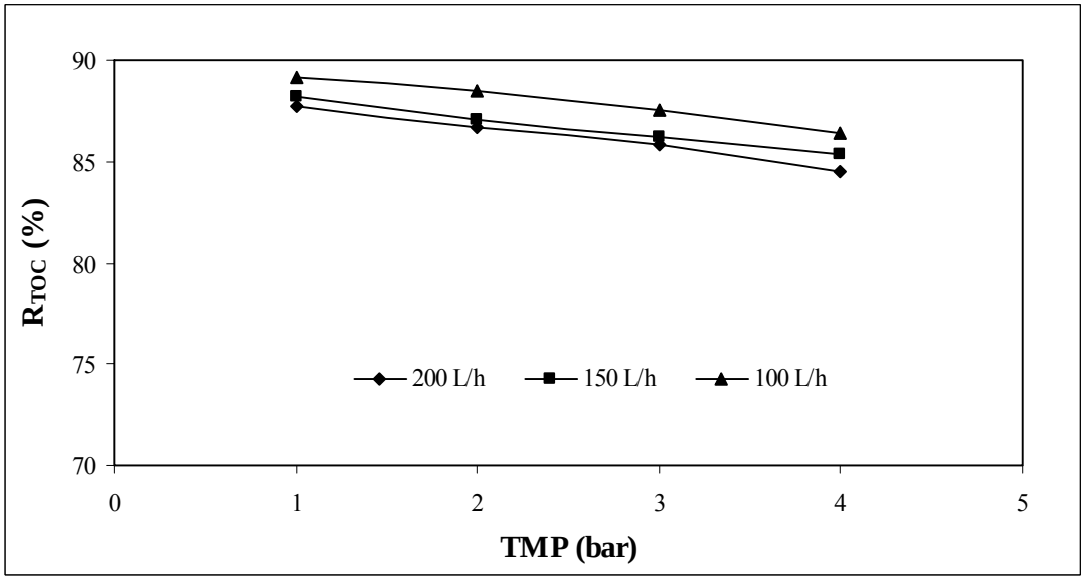


Figure 3.42 Influence of transmembrane pressure on the permeate flux for MW membrane

The influence of the pressure on the COD and TOC retention coefficients is depicted in Figure 3.43. As shown, increasing transmembrane pressure decreases COD and TOC retention coefficients. These results are in agreement with results from other authors (Mohammadi & Esmaeelifar, 2004; Mohammadi & Esmaeelifar, 2005). It is due to the fact that, at higher pressures, effect of pressure predominates over effect of pore size, and as a result, more organic compounds pass through the membrane. It must be mentioned that COD and TOC reduction is not significant at all pressures. The use of smaller pressures gives better removal efficiencies and decreases energy requirement.



(a)



(b)

Figure 3.43 Influence of transmembrane pressure on the apparent rejection coefficients for MW membrane, (a) R_{COD} (b) R_{TOC}

3.2.3.2.2 Feed Flowrate - Permeate Flux-Removal Efficiency Relations. The effect of the feed flowrate on the permeate flux for the MW membrane at three different transmembrane pressure is given in Figure 3.44. The feed flowrate parameter affects the tangential cross flow velocity. An increase in the cross flow velocity increases turbulence, and as a result permeation flux increases. The main

mechanism is reduction of the concentration polarization effect. Turbulence and shear stress on the membrane surface increase by increasing velocity. Therefore, accumulated particles on the membrane surface are carried into the bulk of the fluid, and the concentration polarization effect decreases. This causes osmotic pressure to decrease and therefore, the permeate flux increases (Mohammadi & Esmaeelifar, 2005). In this experiment, flux increases are moderate with increasing flowrate. Therefore minimum flowrate seems to be optimum.

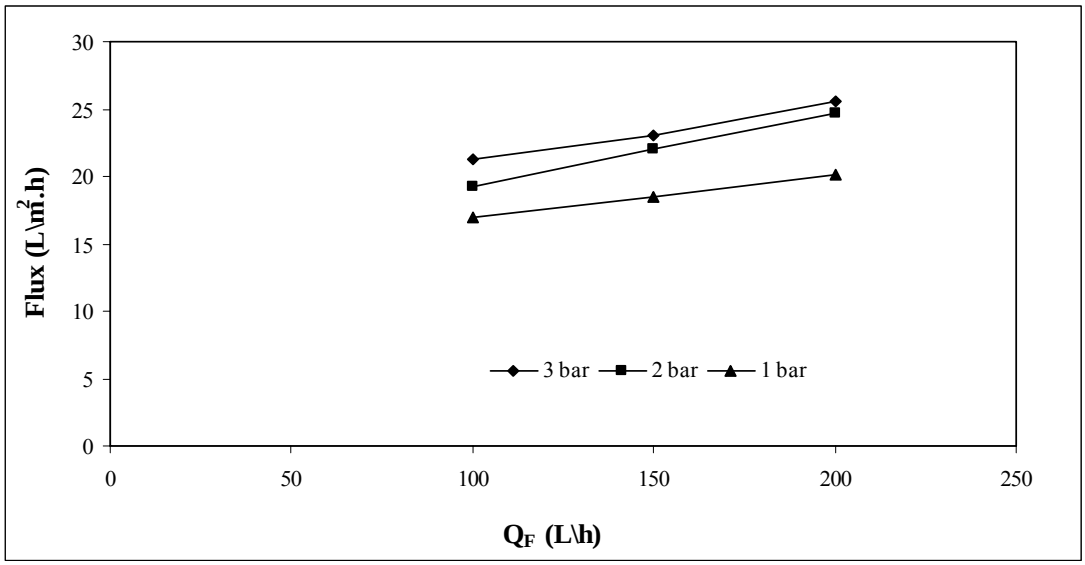
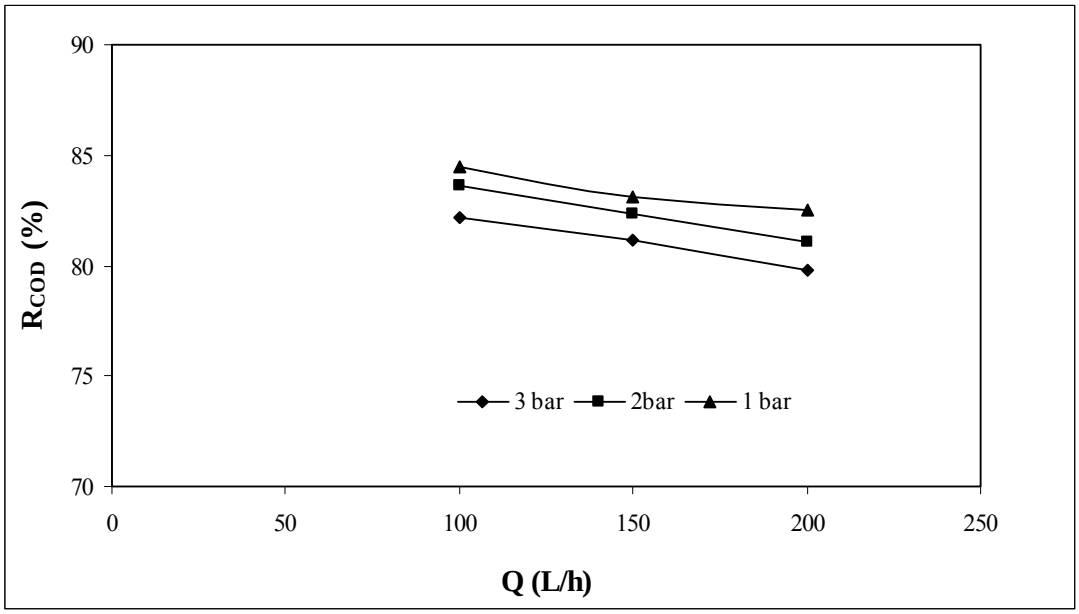
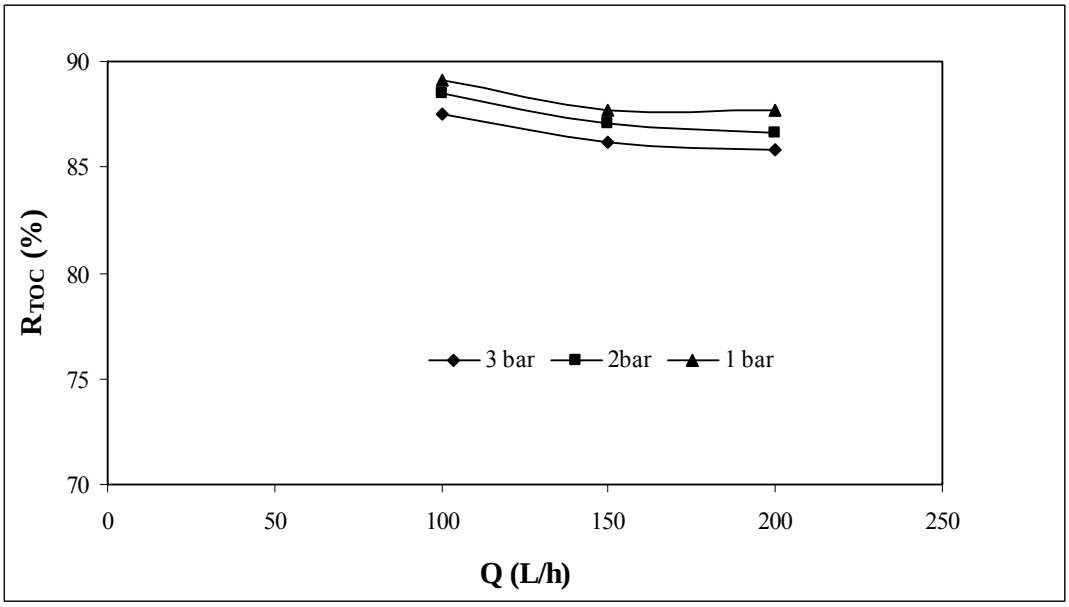


Figure 3.44 Influence of the feed flowrate on the permeate flux for the MW membrane

The effects of the flowrate on the COD and TOC retention coefficients are depicted in Figure 3.45. These coefficients decrease with increasing flowrate. This effect was also concluded by other authors (Minhalma et. al., 2000). It is suggested a change in the structure of the membrane active layer during the filtration process with the increase in the cross flow velocity and feed flowrate. An increase in the crossflow velocity resulted as a greater turbulence, which reduces the membrane fouling. Lower fouling enhances the permeation flux through the membrane and reduces the retention coefficients.



(a)



(b)

Figure 3.45 Influence of the feed flowrate on the rejection coefficients for MW membrane (a) R_{COD} (b) R_{TOC}

3.2.3.2.3 pH-Permeate Flux Relations. In order to see the effect of the pH on the permeate flux, pretreated effluent pH was adjusted to three different pH values as 2, 6, and 9. The better dissolution of fatty acids is observed at alkali solutions. Fatty acids are weak acids and their dissolution is expressed by equilibrium reaction. This reaction is given in Eq. (3.4).

$$HA^- + H_2O \leftrightarrow H_3O + A^- \quad (3.4)$$

Increasing pH pushes the equilibrium to the right side. Therefore, fatty acid molecules are converted into ions and their accumulation on the membrane surface are reduced. As a result, permeation flux increases (Brinck et. al., 2000). It was observed that as pH increases to pH=9, the permeation flux increases considerably. Effect of pH on the permeate flux for MW ultrafiltration membrane is given in Figure 3.46.

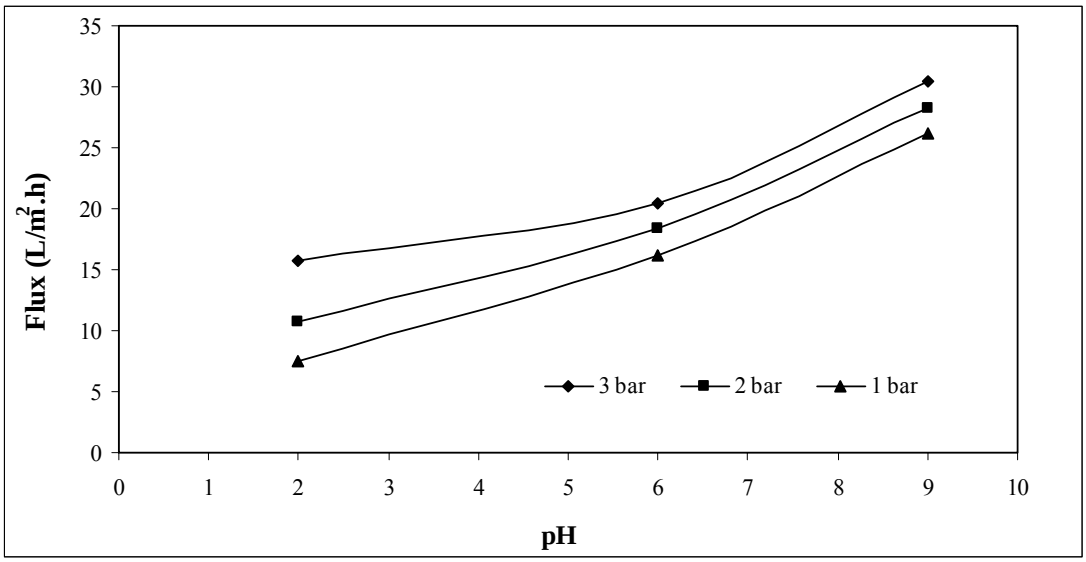


Figure 3.46 Influence of pH on the permeate flux for the MW membrane, T=22º C, Co constant, Q=100 L/h

Although flux at pH=9 is considerable higher than pH=6, an effluent at pH=9 is very close to hazardous waste characteristic. Therefore pH=6 may be better operation parameter value. On the other hand removal efficiencies are decreasing with increasing flux values.

3.2.3.2.4 Membrane Type - Permeate Flux Relations. The effect of the different types of membrane used in this study with different transmembrane pressure is shown in Figure 3.47 at pH=6. In case of MW ultrafiltration membrane, flux reached constant value at small TMP such as 2 bars. In DK nanofiltration membrane filtration, flux increasing rate has a critical value at 5 bars TMP. Flux increasing rate is very high for smaller TMP values than 5 bars and sharply declines for higher pressures than 5 bars. Therefore for DK nanofiltration membrane filtration, advantage of flux increment should be compared for the range of 5 to 25 bars. Optimum value may be considered as 5 bars.

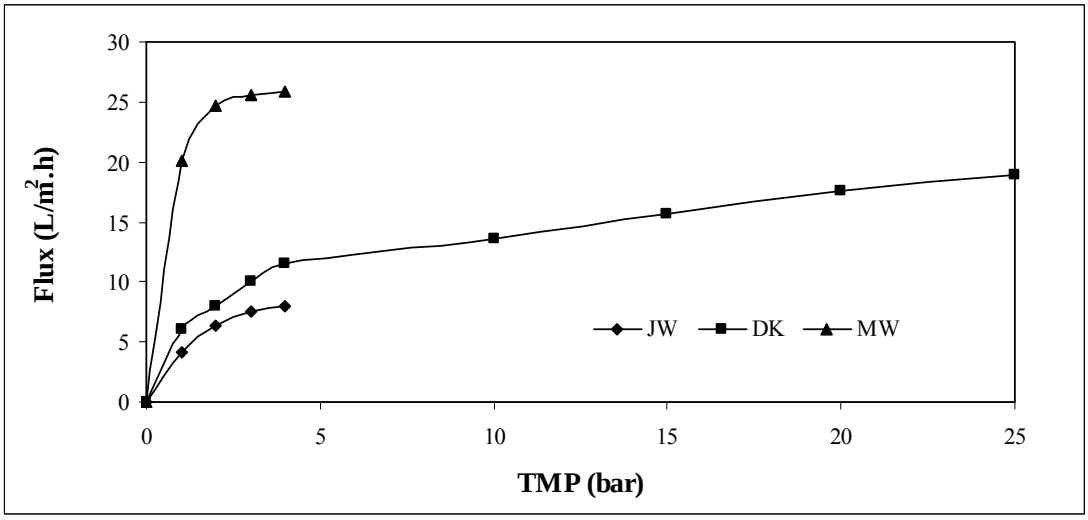


Figure 3.47 Influence of the type of membrane on the permeate flux, T=22º C, Co constant, Q=200 L/h

3.2.3.2.5 Pressure - Membrane Performance Relations. Membrane performance experiments were carried out at different pressures and the results are shown in Figure 3.48. Investigations of permeation flux as a function of time at different pressures show that trend of variations at all pressures is almost same. In all cases,

after a definite time, permeation flux reaches to a constant value depending on operating pressures. It seems effect of pressure on membrane fouling with time is not very prominent. Declining rate of flux is not significant during the whole filtration period. As expected, it tends to reach constant value after a definite time. According to the Figure 3.48, at each pressure after about 60 min, flux reaches to a constant value. It is because, after this time, the cake layer reaches to equilibrium and its growth ceases. So, the cake layer resistance and subsequently permeation flux remain constant (Mohammadi & Esmaeelifar, 2004). Considering Figure 3.42 and 3.48 it can be concluded that at a given feed flowrate and after a certain filtration time, flux has a tendency to take a constant value for all pressures.

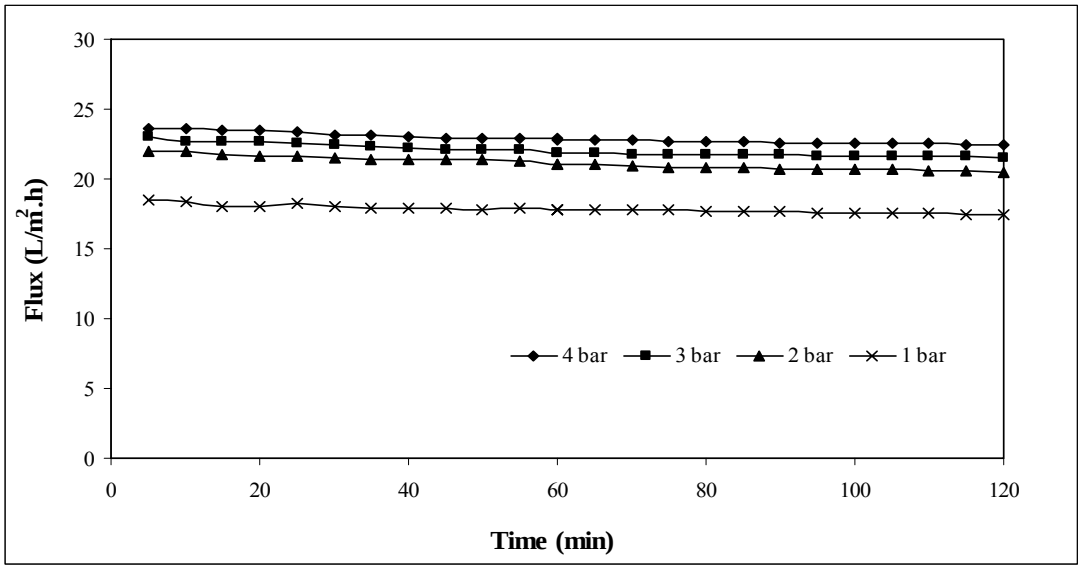


Figure 3.48 Effect of transmembrane pressure on membrane performance for MW membrane, Q=150 L/h

3.2.3.2.6 Feed Flowrate - Membrane Performance Relations. Effect of feed flow rate on membrane performance at three different flow rates is given in Figure 3.49. As it can be seen from figure, permeate flux more or less increases linearly with feed flow rate after 60 minutes filtration. Permeate flux decline rate decreased gradually in the first 60 minutes. The decrease of permeate flux between 60 and 120 minutes is less than 1.5% for all pressures. This percentage of decrease seems to get lower after 120 minutes. Therefore it can be accepted that steady state conditions were achieved after 60 minutes filtration.

Critical flux concept is a permeate flux below which fouling is not observed (Field et. al., 1995). However some authors introduced concept of sustainable flux at which only minimizing but not eliminating fouling entirely. Because critical flux may not be sufficient to avoid long term fouling (Stoller et. al., 2006; Cho et. al., 2002). Optimum permeate flux value can be determined by long term experiments for OMWW. Because more or less constant permeate flux values are obtained for all TMP indicating weak fouling of membrane. Moreover retention coefficients are not changing considerably. It is thought that characteristics of olive or other fruit particles and their sizes are giving these observed relations.

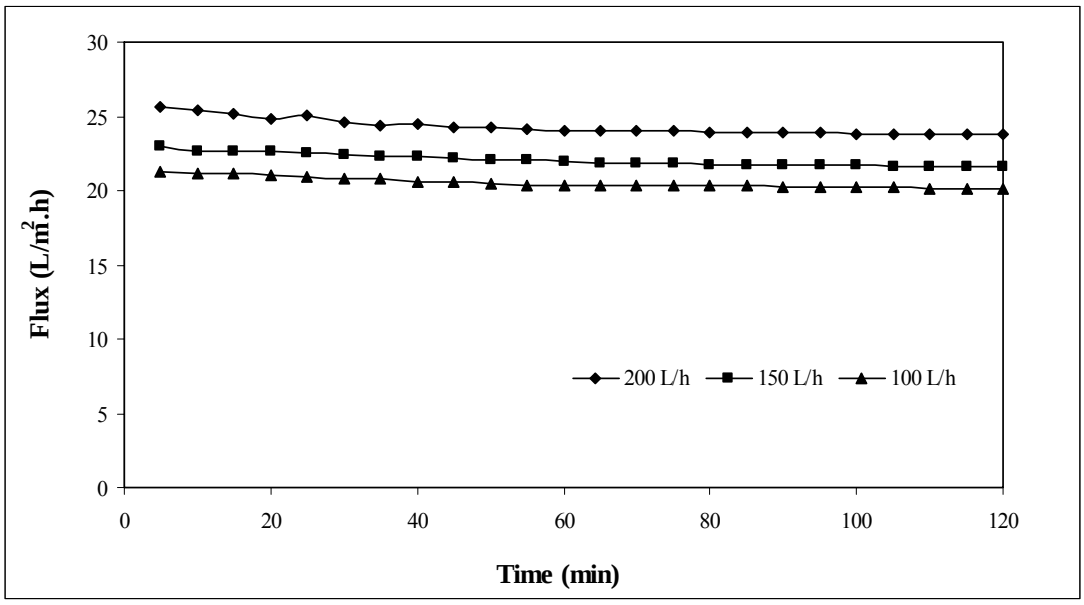


Figure 3.49 Effect of feed flowrate on membrane performance for MW membrane, TMP=3 bar

3.2.3.2.7 pH - Membrane Performance Relations. Membrane performance experiments were carried out at different pH values and results are given in Figure 3.50. Permeate flux increased with increasing pH. For all pH values, fluxes reached constant values in 60 minutes. These constant fluxes were higher for higher pH values. The main reason is that there is more hydrolysis of fatty acids at alkali solutions and subsequent removal of the molecules from the membrane surface. Thus, at higher pH, the layer formed was thinner, so permeation flux was higher (Brinck et. al., 2000). As fatty acid concentration increases, the effect of pH on permeate flux becomes greater.

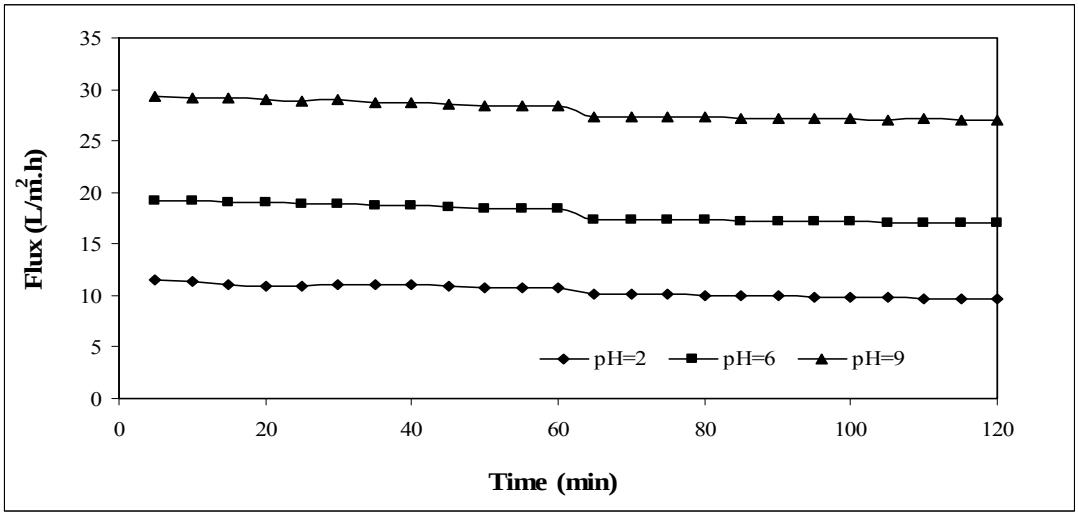


Figure 3.50 Effect of pH on fouling for MW membrane, TMP=2 bar, Qf=150 L/h

3.2.3.2.8 Membrane Type - Membrane Performance - Removal Efficiency Relations. The effects of the membrane type on the membrane performance are given in Figure 3.51. As expected, MW ultrafiltration membrane provided higher flux value, while lower values were obtained with the JW ultrafiltration membrane and DK nanofiltration membrane. It is interesting that nanofiltration with DK membrane (molecular weight cut-off of 150-300 Da) gave more flux values than that of ultrafiltration with JW membrane (molecular weight cut-off of 30000 Da). Cake layer characteristics are basically determined by the characteristics of wastewater. Therefore for some wastewaters like OMWW, the pore size of membrane may be less effective on fluxes than formed cake characteristics. The other explanation may be higher surface permeability of DK nanofiltration membrane than JW ultrafiltration membrane (Benitez et. al., 2006).

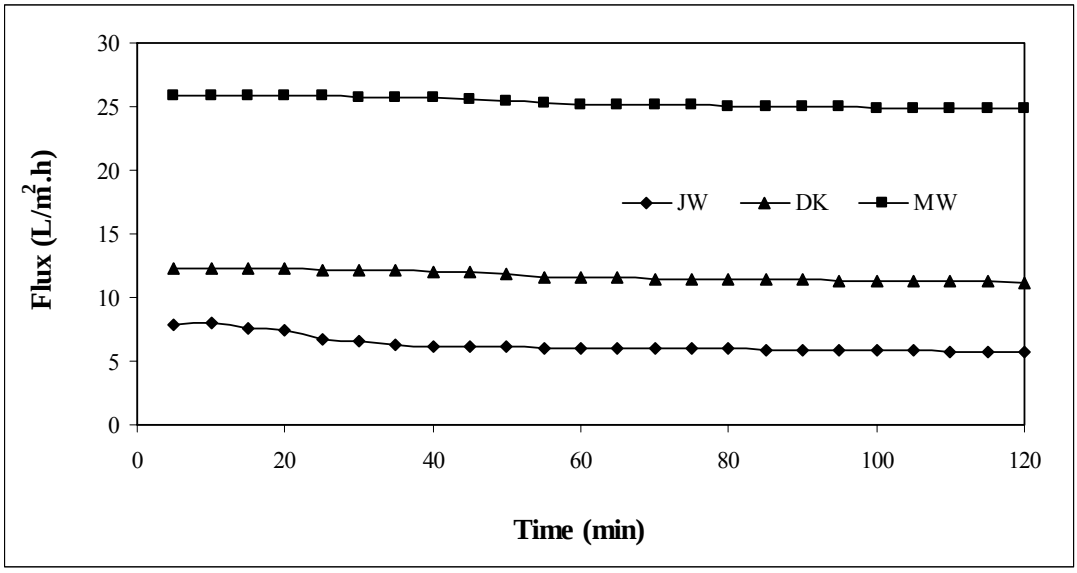
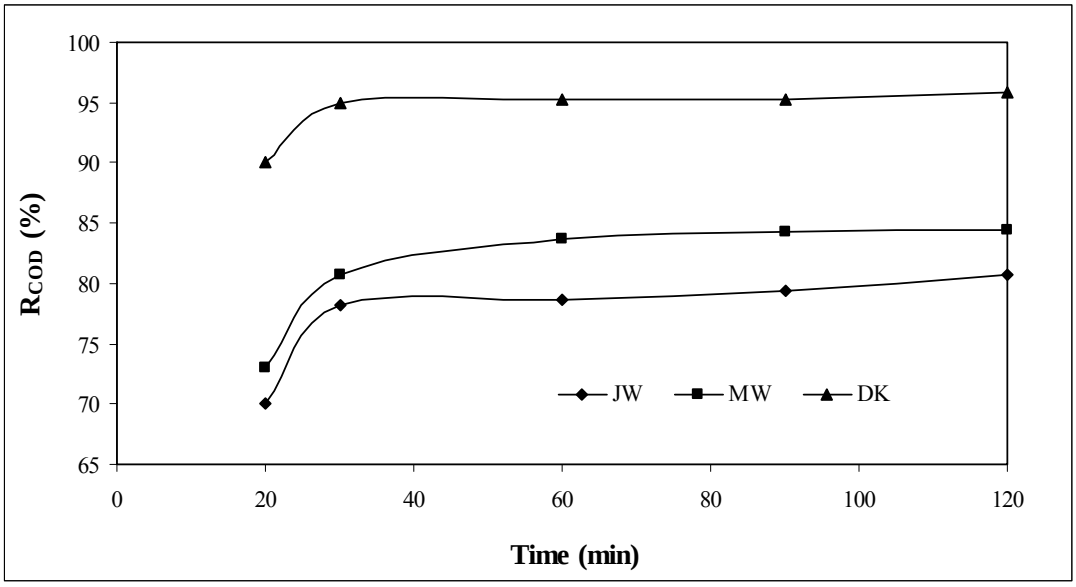
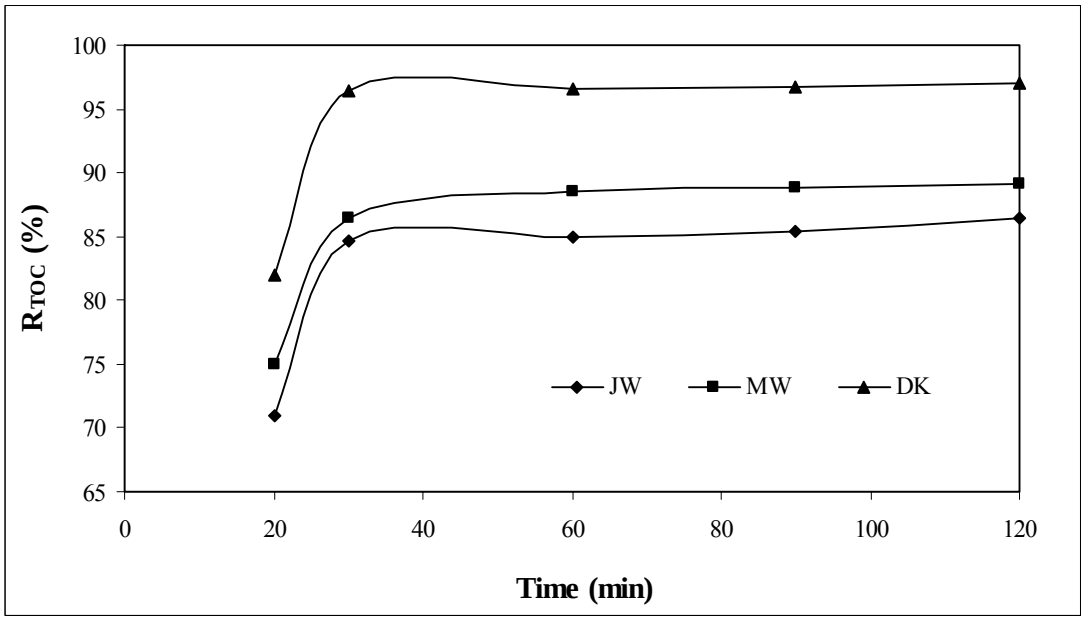


Figure 3.51 Influence of the type of membrane on the permeate flux, Q=200 L/h, TMP=4 bar

In order to see the effect of operation time on COD and TOC removal, all types of membranes were used. It is interesting to note that similar trends followed by the two rejection coefficients in the three membranes. Figure 3.52 shows the plot of the rejection coefficients for membranes JW, MW and DK. Similar behaviors were found for the retention coefficients for three membranes. In all cases, an important increase of the retention coefficients took place in the first minutes of the process, and after a time, steady-state conditions were reached with a maximum value approximately in 30 minutes. These results confirm the formation of a cake layer on the membrane surface or pore blocking, which causes of the membrane fouling. It can be concluded that the retention capacity of the membranes become constant after a time around 30 minutes and its maximum effectiveness is reached. This result shows that 30 minutes can be used as standard time because it is enough time for obtaining the steady-state conditions in the filtration process of the olive oil mill wastewater with these membranes.



(a)



(b)

Figure 3.52 Influence of the operation time on the rejection coefficients, Q=200 L/h, TMP=4 bar, (a) R_{COD} (b) R_{TOC}

Figure 3.52 is showing very important information about the differences of removal efficiencies of different membrane types under the same conditions (200 L/h flow rate and 4 bar pressure). It should be noticed that COD removal efficiencies of ultrafiltration with MW membrane and nanofiltration with DK membrane after same pretreatment steps (pH adjustment to pH=2 + cartridge filtration + pH adjustment to pH=6 + cartridge filtration) are 85% and 95%, respectively. Under same conditions, removal efficiency of nanofiltration is 10% higher than that of ultrafiltration. On the other hand, flux values of nanofiltration with DK membrane and ultrafiltration with MW membrane are 13 $L/m^2.h$ and 25 $L/m^2.h$, respectively. Selection should be based on economic comparison. However selection of ultrafiltration seems to be more reasonable because it will need less filtration module resulting in cheaper investment cost.

3.2.3.2.9 Treatment Results of the Membrane Processes. Table 3.41 shows the treatment results of the ultrafiltration and nanofiltration processes. As shown, considerable reductions of parameters were achieved. However, the results obtained by ultrafiltration membranes (membrane JW and MW) did not achieve environmental standards for wastewater discharge to sewer. Therefore, nanofiltration process can be applied for the treatment of olive oil mill wastewaters. It is worthwhile to examine other types of ultrafiltration membranes to achieve effluent standards for sewer discharge.

Table 3.41 Treatment results of pretreatment and membrane processes

Parameter	**Raw OMWW**	**JW Membrane**	**MW Membrane**	**DK Membrane**
COD (mg/L)	84000	11200	6400	1600
COD removal efficiency (%)	-	87	92	98
TOC (mg/L)	35542	2534	2592	948
TOC removal efficiency (%)	-	93	93	97
SS (mg/L)	11200	290	320	40
SS removal efficiency (%)	-	97	97	99
Oil-grease (mg/L)	2510	370	270	80
O-G removal efficiency (%)	-	85	89	97

3.2.4 pH adjustment + Cartridge Filter Filtration + Nanofiltration Experiments

In the last treatment experiments with OMWW, sample IV was used. Three different pretreatment steps were applied before nanofiltration process. Schematic flow diagram of these experiments is given in Figure 3.53.

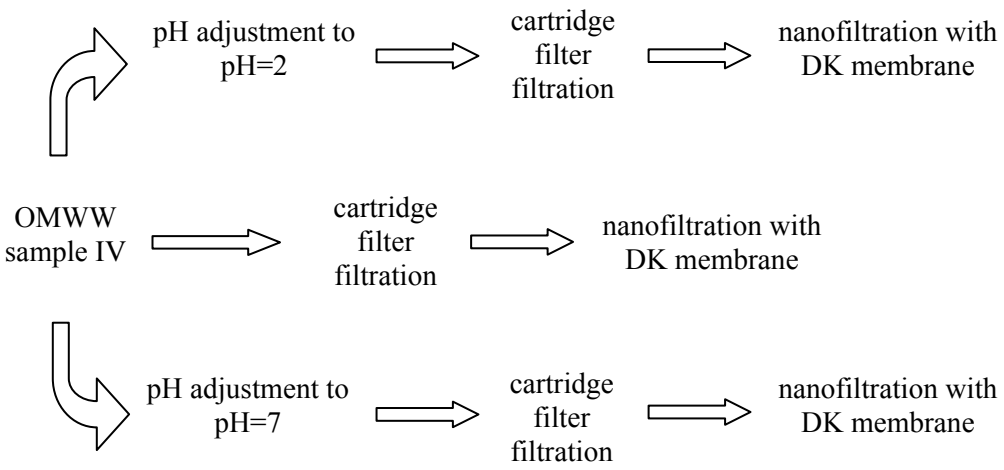


Figure 3.53 Schematic flow diagram of the treatment steps for OMWW sample IV

3.2.4.1 Pretreatment Experiments

Three different pretreatment steps were applied before nanofiltration process for the treatment of OMWW sample IV. pH of raw OMWW was adjusted from pH=5 to pH=2 and pH=7. Raw OMWW and pH adjusted OMWW were filtered from cartridge filters with two different pore sizes.

3.2.4.1.1 Cartridge Filter Filtration at pH=5 (Raw OMWW). 20 liter of raw OMWW was poured into feed tank and it was filtered from first cartridge filter with 20 μm pore size and then with 5 μm pore size. Effluent sample was taken with 15 minutes interval. COD and SS concentration of these samples were carried out and

given in Table 3.42. Usage of 5 μm cartridge filter resulted in higher removal efficiencies such as 40% COD removal efficiency and 50% SS removal efficiency.

Table 3.42 COD and TOC concentrations of raw OMWW after filtration through cartridge filter with 20 μm and then 5 μm pore size

Time (minute)	**COD (mg/L)**	**COD Removal Efficiency (%)**	**SS (mg/L)**	**SS Removal Efficiency (%)**
Cartridge filter filtration with 20 μm pore size				
0	120000	-	33200	-
15	96000	20	25600	23
30	94000	22	24500	26
45	92000	23	23700	29
60	90000	25	22100	33
Cartridge filter filtration with 5 μm pore size				
0	90000	25	22100	33
15	80000	33	18500	44
30	76000	37	17100	49
45	74000	38	16900	49
60	72000	40	16500	50

3.2.4.1.2 Cartridge Filter Filtration at pH=2. In the second cartridge filtration experiment, pH of OMWW was adjusted to pH=2 by using 10 ml/l H_2SO_4 with 98% purity. After pH adjustment, OMWW was also filtered through 20 μm and 5 μm cartridge filter, respectively during 60 minutes. Results are given in Table 3.43. Maximum COD and SS removal efficiencies were obtained as 64% and 57% with 5 μm cartridge filter, after 60 minutes filtration time.

Table 3.43 COD and TOC concentrations of OMWW at pH=2 after filtration through cartridge filter with 20 μm and then 5 μm pore size

Time (minute)	**COD (mg/L)**	**COD Removal Efficiency (%)**	**SS (mg/L)**	**SS Removal Efficiency (%)**
Cartridge filter filtration with 20 μm pore size				
0	120000	-	33200	-
15	54000	55	21300	36
30	54000	55	20000	40
45	53000	56	18100	46
60	53000	56	16500	50
Cartridge filter filtration with 5 μm pore size				
0	53000	56	16500	50
15	48000	60	16000	52
30	47000	61	15400	54
45	46000	62	14800	55
60	43000	64	14200	57

3.2.4.1.3 Cartridge Filter Filtration at pH=7. The last filtration step was cartridge filter filtration of OMWW at pH=7. The same treatment steps were applied and maximum removal efficiencies were also obtained with 5 μm cartridge filter after 60 minutes. In this case, COD and SS removal efficiencies were 43% and 50%, respectively. Obtained results are given in Table 3.44.

Table 3.44 COD and TOC concentrations of OMWW at pH=7 after filtration through cartridge filter with 20 μm and then 5 μm pore size

Time (minute)	**COD (mg/L)**	**COD Removal Efficiency (%)**	**SS (mg/L)**	**SS Removal Efficiency (%)**
Cartridge filter filtration with 20 μm pore size				
0	120000	-	33200	-
15	77000	36	23500	29
30	77000	36	22200	33
45	75000	38	21400	36
60	74000	38	20100	40
Cartridge filter filtration with 5 μm pore size				
0	74000	38	20100	40
15	72000	40	19650	41
30	71000	41	18700	44
45	69000	43	17500	47
60	68000	43	16700	50

3.2.4.2 Nanofiltration Membrane Experiments

Nanofiltration membrane process was applied to cartridge filter effluent in different operating condition. Nanofiltration experiments were carried out at low transmembrane pressures such as 4 – 10 bar, and 200 – 400 L/h flowrate.

3.2.4.2.1 Effect of Transmembrane Pressure on the Permeate Flux. Effects of transmembrane pressure on the permeate flux at different flowrates are given in Figure 3.54. Increasing pressure increases permeate flux. The initial permeate fluxes were about 13.2, 16.7, 18.7, 20.0 $l/m^2.h$ at the 4, 6, 8 and 10 bar pressures for 400 L/h flowrate, respectively.

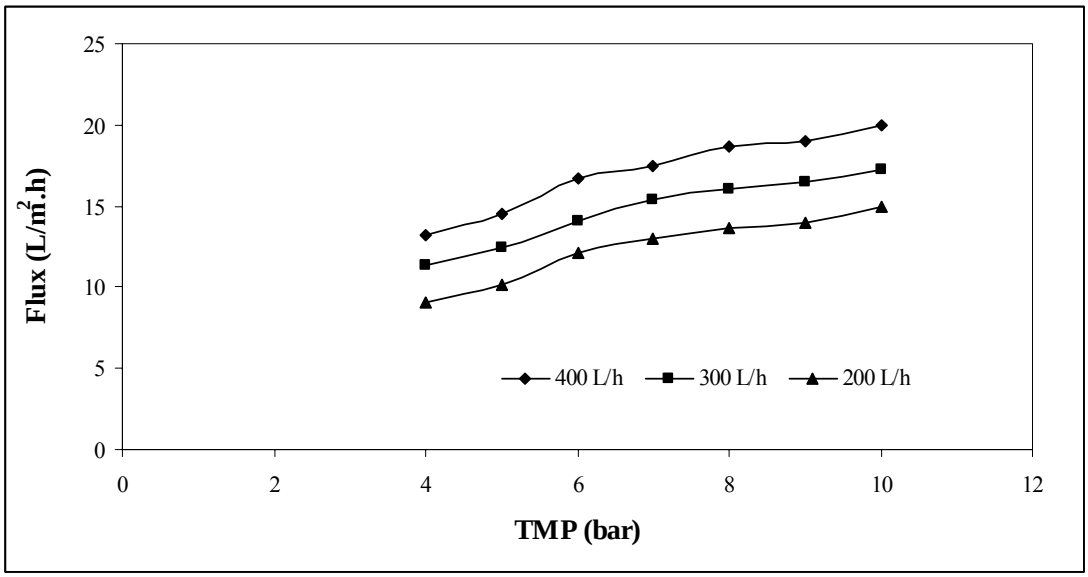


Figure 3.54 Influence of transmembrane pressure on the permeate flux, pH=5

As it shown in Figure 3.54 and 3.55, flux increased during the runs and not reached to constant value. Therefore no membrane fouling has occurred for this pressure range. Successive batch runs had shown that serious membrane fouling appeared not to be a problem. During the each run, pressure ranged from 4 to 10 bar, while flux values ranged from 13 to 20 $l/m^2.h$. Test results can be described by the straight line equation: $y=1.1214x+9.2357$, $R^2=0.9551$.

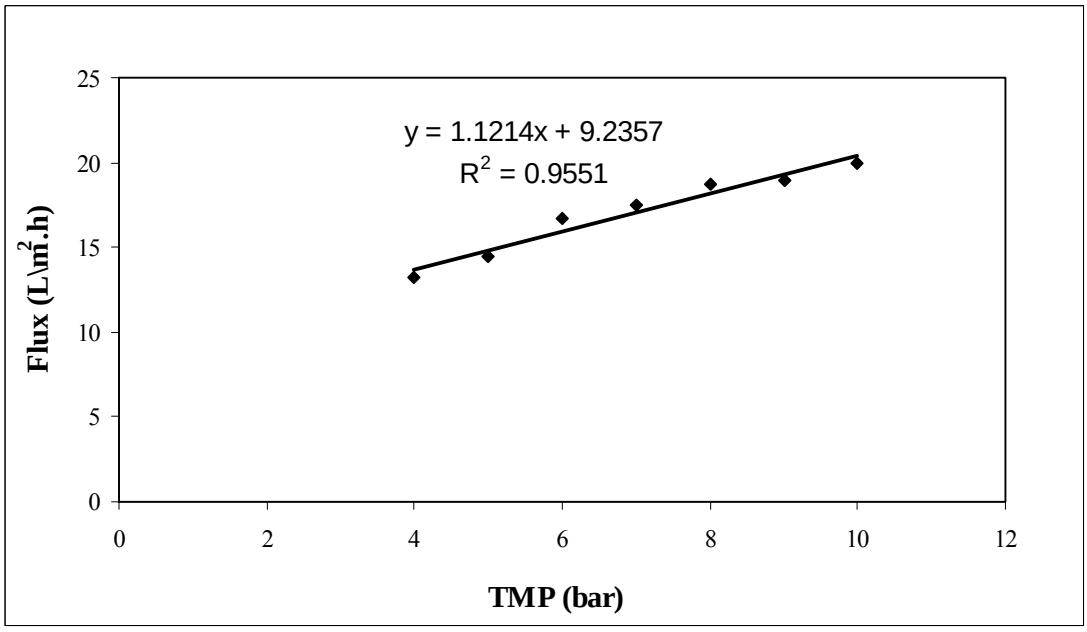


Figure 3.55 Relationship between flux and pressure, Q = 400 L/h, pH=5.

3.2.4.2.2 Effect of Feed Flowrate on the Permeate Flux. In Figure 3.56, the effect of feed flowrates on the permeate flux is shown. Permeate flux linearly increased when the feed flow rate was increased because of the turbulence on the membrane surface as a result of higher flow rate or cross flow velocity. At 7 bar of pressure, permeate fluxes were measured as 13 L/m^2.h at the flowrate of 200 L/h and 19 L/m^2.h at the flowrate of 400 L/h.

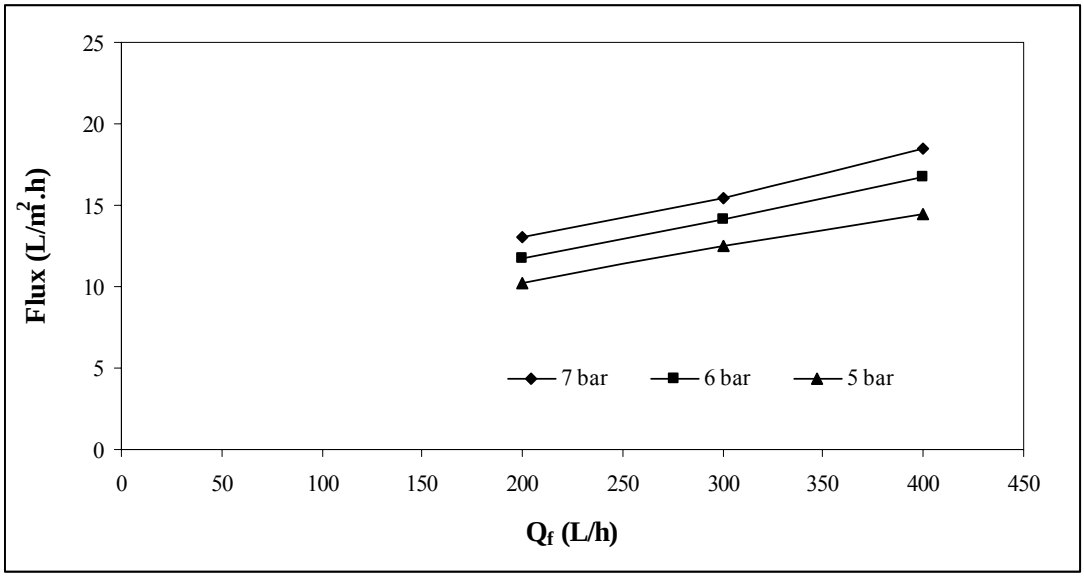


Figure 3.56 Influence of the feed flowrate on the permeate flux for raw OMWW, pH=5

3.2.4.2.3 Effect of pH on the Permeate Flux. In order to see the effect of the pH on the permeate flux; pH was adjusted to 2 and 7, while pH of raw wastewater was 5. Experimental results show that, increasing pH resulted an increase in the permeate flux. It was observed that as pH increases to pH=7, the permeation flux increases considerably. Effect of pH on the permeate flux at different pressures is given in Figure 3.57.

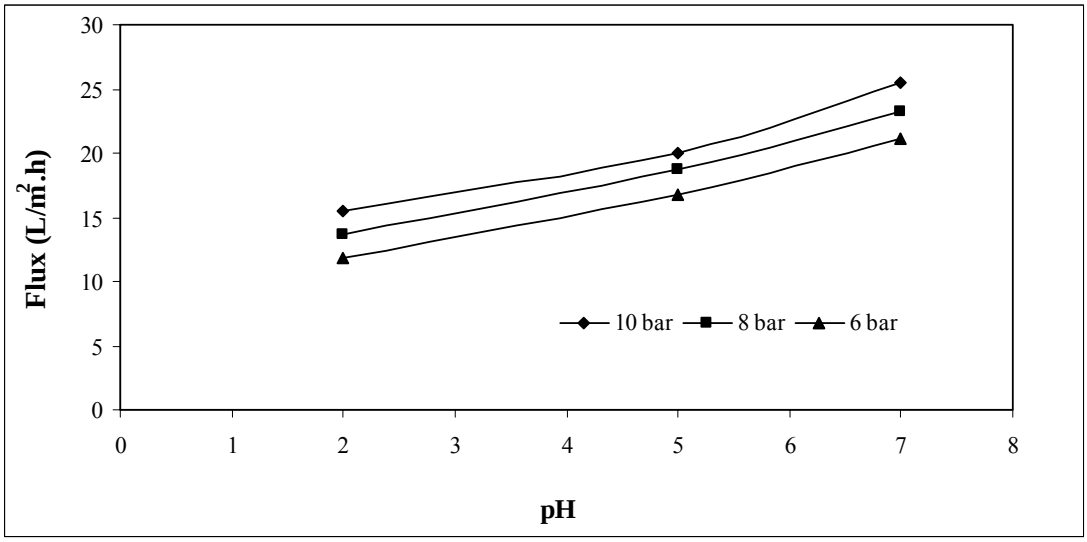


Figure 3.57 Influence of pH on the permeate flux, Q=400 L/h

3.2.4.2.4 Effect of Pressure on Membrane Performance. Membrane performance experiments were carried out at pH=5, 300 L/h flowrate and the results are shown in Figure 3.58. Results show that after 60 minute operation time, permeation flux reaches to a constant value; 22 L/m^2.h for pressure of 10 bar, 18 L/m^2.h for pressure of 7 bar, 12 L/m^2.h for pressure of 4 bar. Declining rate of flux is not significant during the whole filtration period.

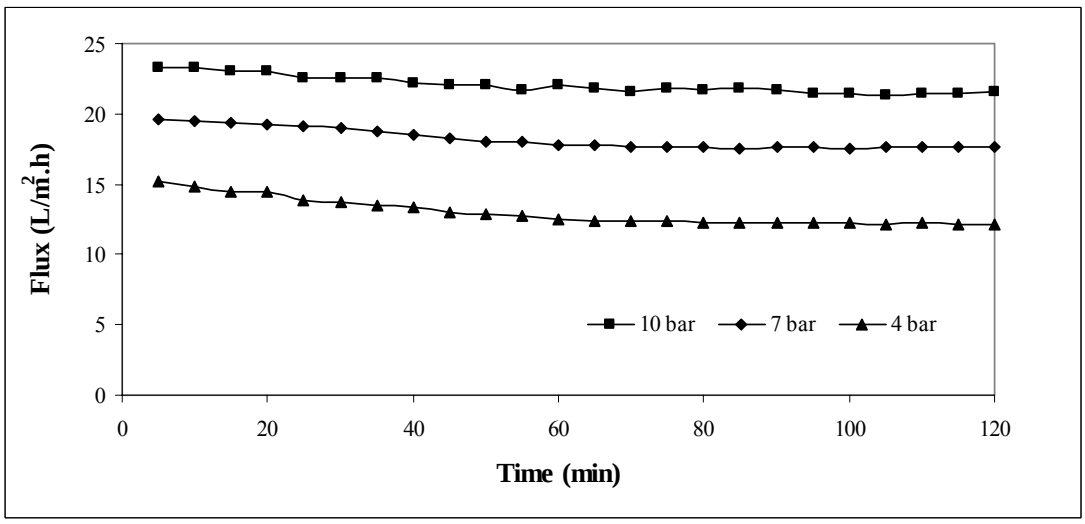


Figure 3.58 Effect of transmembrane pressure on membrane performance, Q=300 L/h, pH=5

In another filtration experiment with the same membrane at TMP=7 bar and Q=300 L/s, filtration time was increased to 12 hours and observed permeate flux values are given in Figure 3.59. As it can be seen from figure, the flux value remained constant for 12 hours. It indicates that, the effect of pressure on membrane fouling with time is not very prominent.

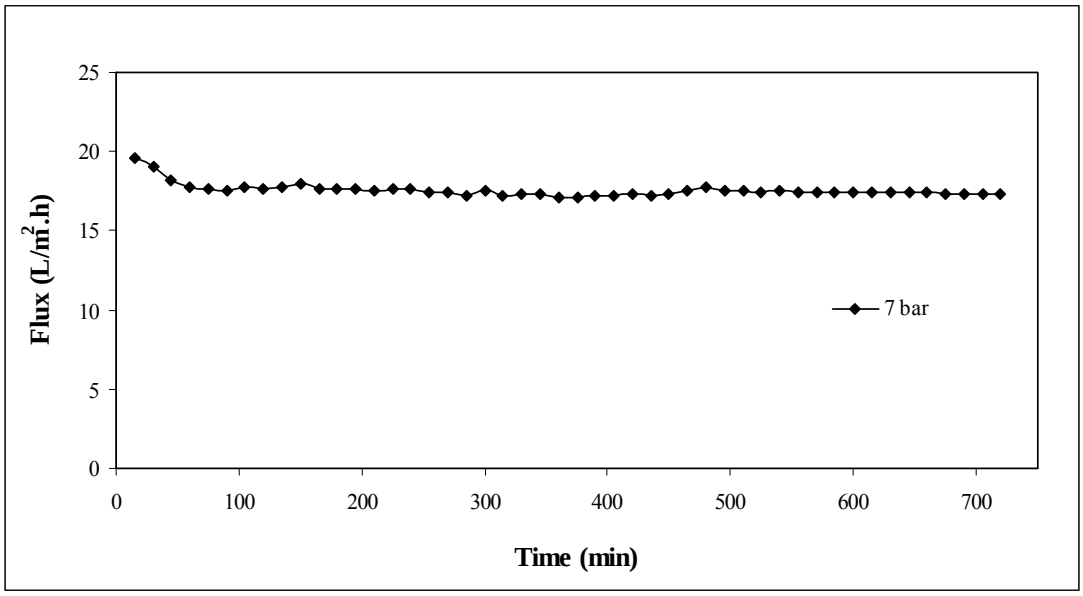


Figure 3.59 Effect of transmembrane pressure on membrane performance, Q=300 L/h, pH=5, TMP=7 bar.

3.2.4.2.5 Effect of Feed Flowrate on Membrane Performance. The effects of feed flowrate on membrane performance are given in Figure 3.60. As shown in figure, an increase of feed flowrate approximately linearly increased permeation flux, but for all flowrate used, there was a flux decline at the beginning of the filtration period. As with other results, permeation flux reached a constant value, after approximately 60 minutes. At higher velocities, because of greater turbulence, parts of the formed layer were removed from the membrane surface by hydro-dynamical forces and were returned into the bulk of the liquid. Thus, at higher velocities, the layer formed was thinner and permeation flux was higher (Mohammadi & Esmaeelifar, 2004).

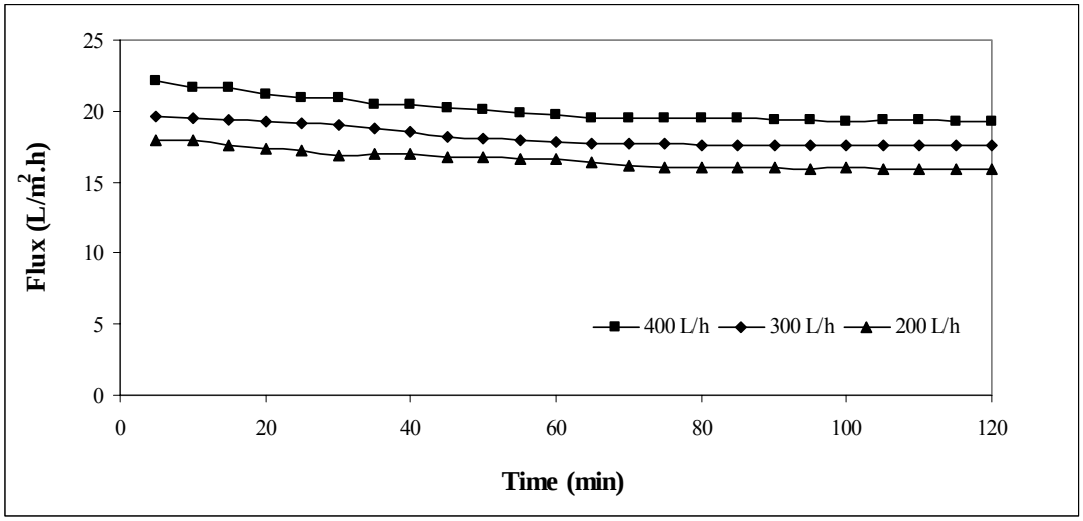


Figure 3.60 Effect of feed flowrate on membrane performance, TMP=7 bar, pH=5

3.2.4.2.6 Effect of pH on Membrane Performance. Effects of pH on membrane performance are given in Figure 3.61. Permeate flux increased with increasing pH. For all pH values, fluxes reached constant values. These constant fluxes were higher for higher pH values. No flux decline was observed during filtration period.

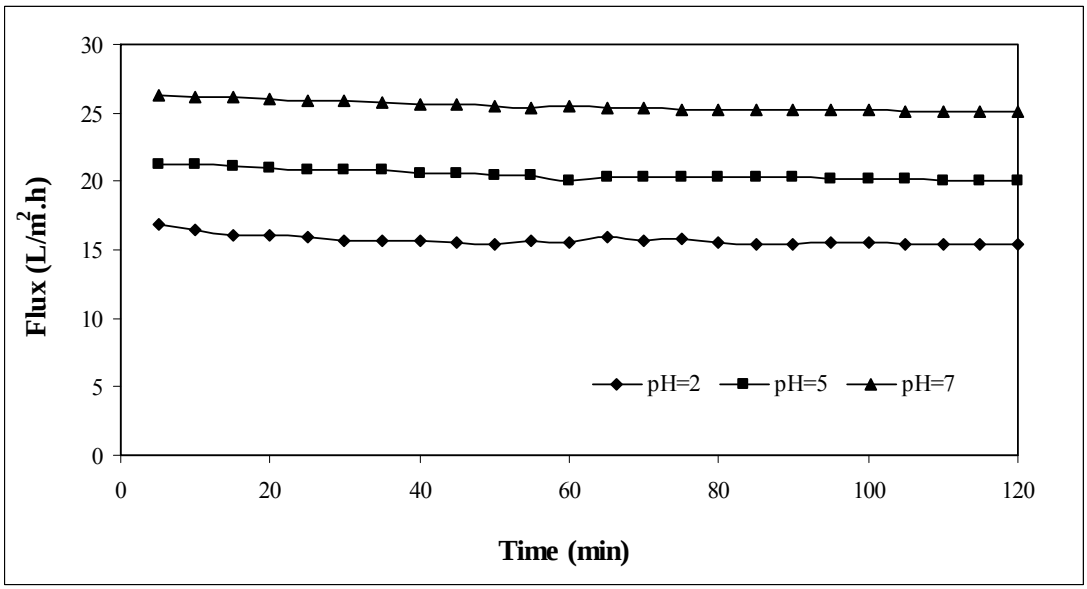


Figure 3.61 Effect of pH on membrane performance, Q=300 L/h, TMP=7 bar

3.2.4.2.7 Effect of Pressure on COD Removal. The influence of the pressure on the COD retention coefficient is depicted in Figure 3.62. As shown, retention coefficients decreased with increasing transmembrane pressure. More organic compound forced to pass through the membrane with increasing pressure.

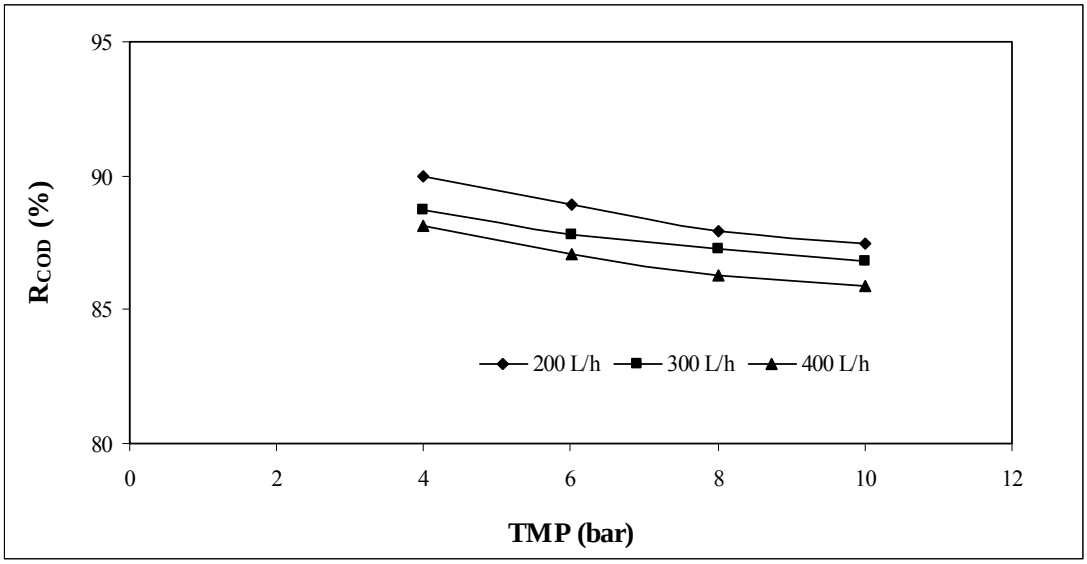


Figure 3.62 Influence of transmembrane pressure on COD rejection coefficients, pH=5

3.2.4.2.8 Effect of Feed Flowrate on COD Removal. The feed flowrate is another operating condition affects the retention coefficient. The effects of the flowrate on the COD retention coefficients are depicted in Figure 3.63. These coefficients decrease with increasing flowrate. This effect was also concluded by other authors (Mohammadi & Esmaeelifar, 2005). It is suggested a change in the structure of the membrane active layer during the filtration process with the increase in the cross flow velocity and feed flowrate. An increase in the cross flow velocity resulted as a greater turbulence, which reduces the membrane fouling. Lower fouling enhances the permeation flux through the membrane and reduces the retention coefficients.

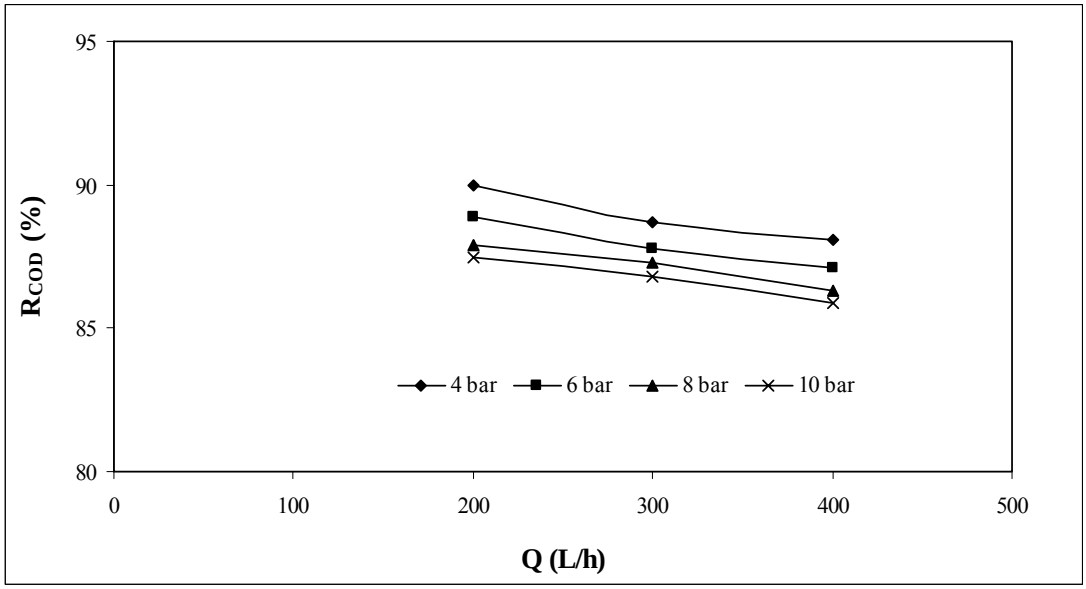


Figure 3.63 Influence of the feed flowrate on the COD rejection coefficients, pH=5

3.2.4.2.9 Effect of Operation Time on COD Removal. Figure 3.56 shows the plot of the retention coefficient for three different transmembrane pressures. Similar behaviors were found for the retention coefficients for all pressure. In all cases, retention coefficients were not changed considerably. As it can be seen from Figure 3.64, COD retention coefficient was 85% after 30 minutes, and 85.2% after 120 minutes operation time at 9 bar transmembrane pressure.

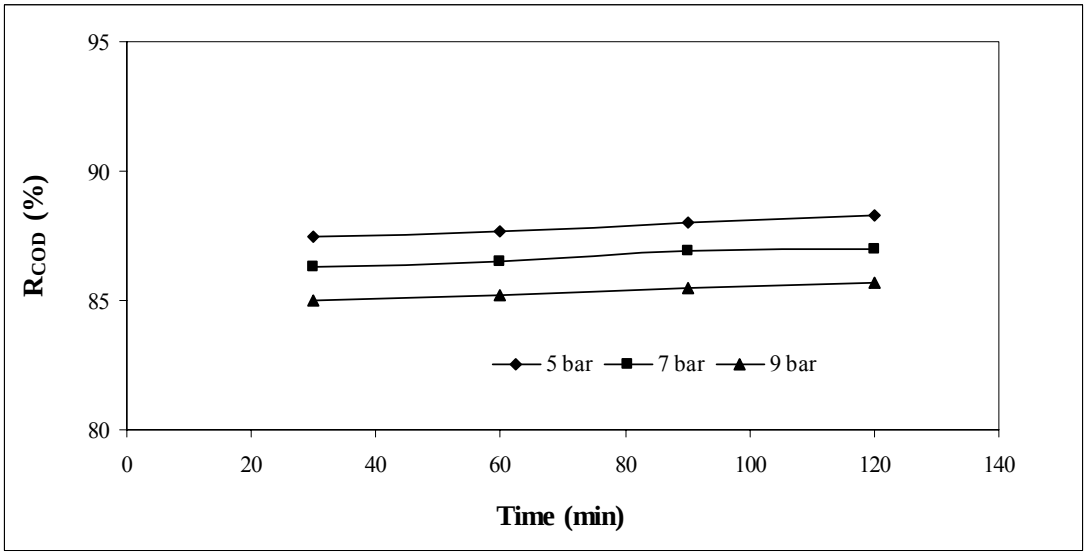


Figure 3.64 Influence of the operation time on the COD rejection coefficient, pH=5

3.2.4.2.10 Treatment Results of the Nanofiltration Process. The treatment results and efficiencies for low pressure nanofiltration membrane application of raw OMWW sample after cartridge filtration are given in Table 3.45. Maximum removal was achieved in SS parameter with 97% removal efficiency. However, COD and TOC removal efficiencies were not satisfactory for obtain discharge standards.

Table 3.45 Treatment results of raw OMWW at pH=5 after cartridge filter and low pressure nanofiltration

Treatment Steps	**COD (mg/L)**	**COD Rem. (%)**	**TOC (mg/L)**	**TOC Rem. (%)**	**SS (mg/L)**	**SS Rem. (%)**
Raw wastewater	120000	-	31650	-	33200	-
Two step cartridge filter filtration	72000	40	18300	42	16500	50
Two step cartridge filter filtration + Nanofiltration	14000	88	3778	85	1110	97

CHAPTER FOUR
CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

The aim of this thesis was application of membrane processes (microfiltration, ultrafiltration and nanofiltration) for treatment of high strength wastewaters such as cheese whey effluent and olive oil mill wastewater. Different physical and chemical pretreatment experiments were done before all membrane applications to find the most suitable treatment method for cheese whey effluent and olive oil mill wastewater. COD, TOC, SS, oil and grease concentrations were measured throughout the study as the performance indicators.

In the first part of the experimental studies, treatability of cheese whey effluent with physical, chemical treatment methods and membrane processes was investigated. The combination of cartridge filter and filter cloths were used first time as the physical pretreatment of cheese whey effluent. The removal efficiencies were 29%, 45%, and 64% for COD, SS, oil and grease, respectively for the cheese whey effluent.

Chemical coagulation with ferric chloride, alum, CMC and chitosan were applied to the cheese whey effluents. Chemical treatment of dairy wastewater was a common method but it was a new method for cheese whey effluent pretreatment. Especially chitosan and CMC were tested first time in the literature for the pretreatment of cheese whey effluent before membrane filtration. Chitosan and $FeCl_3$ combination was the most effective method with 59 % COD removal efficiency for the pretreatment of cheese whey effluent. It was determined that, chemical treatment is not sufficient to meet effluent standards into the sewerage or to the receiving water media as a full treatment method. It can be used as a pretreatment stage before biological and/or advanced treatment.

Pretreated samples with physical and chemical treatment methods were microfiltrated in the membrane module, separately. Approximately the same removal efficiencies were obtained for both pretreatment options. So, microfiltration effluent after physical pretreatment was done before ultrafiltration because it was cheaper and easier than chemical processes. Combination of physical pretreatment, microfiltration and ultrafiltration is not sufficient enough in terms of COD concentration because it was still 22000 mg/L. But this combination is very successful at the removal of other parameters, especially 99 % of SS reduction and 98 % of oil and grease reduction.

In the second part of experimental studies with cheese whey effluent, the Steffen process and centrifugation or sedimentation and cartridge filtration unit operations were applied before microfiltration membrane. 71% COD removal efficiency and 71% TOC removal efficiency were achieved with the combination of pretreatment and microfiltration process. By using the Steffen process and microfiltration, less removal efficiencies and less permeate fluxes were obtained compared cartridge filter filtration after coagulation with chitosan and $FeCl_3$. The Steffen process is also not suitable due to its huge sludge production. Its application can only be considered if sludge is sent to cement production plant.

Treatment results of all pre-treatment and membrane experiments for cheese whey effluents are given in Table 4.1. Maximum removal efficiencies for both COD and TOC parameters were achieved at minimum flowrate and minimum pressure, where the minimum permeate flux obtained. Optimum operation condition was found as 100 L/h flowrate and 1 bar pressure for microfiltration and ultrafiltration processes. Ultrafiltration can not be as full treatment either sewer or surface water discharge even with comprehensive pretreatment. Moreover usage of several treatment steps possibly will result in unfeasible solution. For the separation of sugar compounds in the whey, reverse osmosis is necessary. In this thesis, chitosan or the Steffen process was thought to be effective pretreatment which may result in full treatment with membrane filtration. Unfortunately, this hypothesis has not been proven.

Table 4.1 Results of all treatment experiments with cheese whey effluents

Wastewater Type	**Treatment Options**	**COD Concentrations (mg/L)**	**COD Removal Efficiency (%)**
Cheese whey sample I	Raw cheese whey	65600	-
	Physical pretreatment	46400	29
	Physical pretreatment + Microfiltration	30400	54
	Physical pretreatment + Microfiltration + Ultrafiltration	22000	66
	Chemical coagulation+ Physical pretreatment	23500	64
	Chemical coagulation+ Physical pretreatment + Microfiltration	21000	68
Cheese whey sample II	Raw cheese whey	60000	-
	The Steffen process + Sedimentation	25000	53
	The Steffen process + Sedimentation + Cartridge filter filtration	22500	58
	The Steffen process + Sedimentation + Cartridge filter filtration + Microfiltration	17000	72

Olive oil mill wastewater was another strong wastewater which was investigated in the content of this thesis. Four different treatment schemes were used for OMWW treatment. In the first experiment, physical pretreatment (cartridge filter and filter cloth filtration), two step coagulation and cartridge filter filtration, and then microfiltration or ultrafiltration processes were applied. Obtained water flux and removal efficiencies of pretreated OMWW with two step coagulation and cartridge filter filtration were higher than pretreated OMWW with physical pretreatment methods for all flow rate and pressure. However, solid content of sludge after coagulation with lime in the second step of coagulation was very high. NaOH may be used in the second step of coagulation in order to prevent high sludge production. If the ultrafiltration process was applied on the same OMWW sample without microfiltration step at pH=2, very close treatment efficiencies were obtained with microfiltration after two step coagulation. Therefore two step coagulation and microfiltration should be preferred by considering the simplicity and economics of microfiltration.

Ultrafiltration and then nanofiltration experiments were applied on OMWW at different flow rates and different pressures after pH adjustment and filtration through cartridge filter and two different filter cloths. Filtration through two filter clothes was done under open CFCV condition. Filter cloth filtrations are not worthwhile compared to their operational difficulties and costs. Maximum removal efficiencies were achieved at 100 L/h flow rate and 1 bar pressure for ultrafiltration experiments. In this case, COD, TOC, SS, oil and grease concentrations were 22000 mg/L, 5100 mg/L, 370 mg/L, and 400 mg/L, respectively. Nanofiltration membrane was used after ultrafiltration process. Maximum permeate flux was obtained at 200 L/h flow rate and 25 bar pressure. However, maximum removal efficiencies were achieved at minimum flow rate and pressure, such as 100 L/h flow rate and 10 bar pressure. In this case, COD, TOC, SS, oil and grease concentrations were 3700 mg/L, 1083 mg/L, 30 mg/L, and 40 mg/L, respectively. Although these removal efficiencies are very satisfactory, there are many treatment steps. So, further studies were done to decrease the number of treatment steps with another OMWW sample.

In the third part of the experimental studies with OMWW, the variation of COD and TOC removal efficiencies together with permeate fluxes for ultrafiltration or nanofiltration processes was investigated. Before the membrane processes, pH adjustment and physical pretreatment steps were applied. First step of pretreatment is 20-μm cartridge filtration of OMWW after pH adjustment to pH=2. Then effluent pH was adjusted to pH=6 and filtered through the same cartridge filter again. Each steps of cartridge filter filtration was done by recycling the cartridge filter effluent back to the OMWW tank. Pretreated OMWW was sent to ultrafiltration and nanofiltration membranes. Two step cartridge filtration after pH adjustment gave better COD removal efficiency (63%) than that of two step coagulation (49%). It can be concluded that after acidification, the time elapsed during the sedimentation decreases the removal efficiency of cartridge filtration. Furthermore the volume of residue was considerably smaller compared to coagulation can result in. After pretreatment steps, olive oil in the raw OMWW was recovered by collecting it from the top of the tank. This process is both production and treatment work.

The removal of the COD and TOC is determined by the retention coefficients. Increasing transmembrane pressure (TMP) and feed flow rate decreases COD and TOC retention coefficients. The treatment results obtained by ultrafiltration membranes (membrane JW and MW) did not achieve effluent standards for wastewater discharge to sewer. However, COD, TOC, SS, oil and grease concentrations nanofiltration effluent were 1600 mg/L, 948 mg/L, 40 mg/L, 80 mg/L, respectively. The results obtained showed that NF treatment is a possible and acceptable method for treatment of olive oil mill wastewater. Two step pH adjustment and cartridge filter filtration is most promising pretreatment method for ultrafiltration and nanofiltration processes.

Although discharge effluent standards are not obtained with MW ultrafiltration membrane, COD, TOC, SS, oil-grease removal efficiencies were 92%, 93%, 97%, 89%, respectively. Further treatment steps using cartridge filters with finer pore size and then ultrafiltration with several different membranes which can be determined by experimental or pilot plant studies should be considered.

With the treatment steps of pH adjustment (pH=2) + cartridge filtration + two filter clothes + ultrafiltration + nanofiltration, COD removal efficiency was 96%. On the other hand, two step pH adjustment + cartridge filtration + (ultrafiltration or nanofiltration) steps gave more reasonable COD removal efficiencies. 92% COD removal efficiency was achieved with the combination of two step pH adjustment + cartridge filtration + ultrafiltration and 98 % COD removal efficiency was obtained with the combination of two step pH adjustment + cartridge filtration + nanofiltration. Therefore two step pH adjustment is more reasonable and feasible for field application.

In the all membrane filtration experiments, the permeate flux increased with increase in the transmembrane pressure until a limiting value of transmembrane pressure was reached. The increase in the feed flow rate and pH resulted in increase of the permeate flux. MW ultrafiltration membrane provided higher flux value, while lower values were obtained with the JW ultrafiltration and DK nanofiltration membranes. It should be noticed that increasing flux values always resulted in decreasing COD removal efficiency.

The change of permeate flux with time was also examined in this thesis. In these experiments, effect of pressure, flow rate, pH and type of membrane were evaluated. An increase of the pressure, feed flow rate and pH increased permeation flux. Naturally for all pressure, flow rate and pH used, there was a little flux decline in the beginning of the filtration period. More or less steady state conditions were achieved after 60 minutes and remained constant indicating the weak fouling conditions

In the last membrane experiment with OMWW, low pressures (4-10 bar) were applied on nanofiltration membrane. Permeate flux has not reached a constant value during the runs and no membrane fouling has occurred for this pressure range. However, permeate fluxes (13 $L/m^2.h$ for 400 L/h flow rate and 4 pressure) were smaller than high pressure applications (40 $L/m^2.h$ for 200 L/h flow rate and 25 bar pressure).

Results of all physical, chemical pre-treatment experiments and then membrane processes for OMWW treatment are given in Table 4.2. Under the light of results obtained from this PhD thesis, it can be concluded that combination of pretreatment unit with pH adjustment and cartridge filter filtration and then application of ultrafiltration or nanofiltration membranes provided the best available treatment efficiency for treatment of OMWW.

Table 4.2 Results of all treatment experiments with olive oil mill wastewaters

Wastewater Type	Treatment Options	COD Concentrations (mg/L)	COD Removal Efficiency (%)
OMWW sample I	Raw OMWW	120000	-
	Physical pretreatment	77700	35
	Physical pretreatment + Microfiltration	62000	48
	Two steps coagulation+ Physical pretreatment	48000	60
	Two steps coagulation+ Physical pretreatment + Microfiltration	31000	74
	Coagulation with H_2SO_4	70000	42
	Coagulation with H_2SO_4 + Ultrafiltration	22500	81
OMWW sample II	Raw OMWW	100000	-
	pH adjustment	66000	34
	pH adjustment + Physical pretreatment	57000	43
	pH adjustment + Physical pretreatment+ Ultrafiltration	22000	78
	pH adjustment + Physical pretreatment+ Ultrafiltration + Nanofiltration	3700	96

Table 4.2 Results of all treatment experiments with olive oil mill wastewaters (continued)

Wastewater Type	**Treatment Options**	**COD Concentrations (mg/L)**	**COD Removal Efficiency (%)**
OMWW sample III	Raw OMWW	84000	-
	pH adjustment to pH= 2 + Cartridge filter filtration	35000	58
	pH adjustment to pH= 2 + Cartridge filter filtration + pH adjustment to pH = 6 + Cartridge filter filtration	31000	63
	Pretreatment + Ultrafiltration with JW membrane	11200	87
	Pretreatment + Ultrafiltration with MW membrane	6400	92
	Pretreatment + Nanofiltration with DK membrane	1600	98
OMWW sample IV	Raw OMWW	120000	-
	Two step cartridge filter filtration	72000	40
	Two step cartridge filter filtration + Nanofiltration	14000	88

4.2 Recommendations

Cheese whey production is sequencing batch process. An equalization tank has to be used as the first unit of the treatment plant. For chemical and physical pretreatment, as in membrane bioreactors, immersed membranes made of filter clothes can be constructed in equalization tank. Equalization tank can be operated similar to sequencing batch membrane bioreactors. So, the filtered water from immersed filter cloth will be pretreated by chemical and physical methods.

At the literature survey, it was seen that biological treatment is suitable for the treatment of cheese whey effluent because of having treatment efficiency of 85-95 % in terms of COD. So, biological treatment methods and membrane processes may be applied together as membrane bioreactor for the treatment of cheese whey effluent.

Turano et.al. (2002) used centrifugation and ultrafiltration system for treatment of olive oil mill wastewater with 90 % COD removal efficiency. In this study, 80% removal efficiency was achieved by precipitation of OMWW at pH=2 and then microfiltration at minimum pressure. This wastewater may be used as influent of anaerobic biological treatment system, after neutralization. Energy consumption and operation costs of this process will be less than ultrafiltration process. Using different filter cloths is not increasing removal efficiencies significantly.

In this thesis, membrane experiments were not carried out at the combination of microfiltration, ultrafiltration and nanofiltration membranes. A further experiment may be designed by considering this combination after pretreatment.

Chemical oxidation of OMWW especially with Fenton's reagent gives alone removal efficiency as high as 50-60% (Oktav, 2001). As an untested study, cartridge filter filtration may be used instead of sedimentation step of Fenton oxidation. Membrane processes such as ultrafiltration and nanofiltration may be applied after oxidation and filtration steps.

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NOMENCLATURE

2 SC+P : Two step coagulation and physical treatment methods

CFCV : Concentrate flow control valve

COD : Chemical oxygen demand, mg/L

MF : Microfiltration

MWCO : Molecular weight cut off

NF : Nanofiltration

OMWW : Olive oil mill wastewater

PVDF : Polyvinylidene difluorie

RO : Reverse osmosis

SS : Suspended solid, mg/L

TMP : Transmembrane pressure

TOC : Total organic carbon, mg/L

UF : Ultrafiltration