SULPHATE REMOVAL BY NANOFILTRATION FROM WATER

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ASLI KARABACAK

IN PARTIAL FULFILLMENT OF THE REQUIREMENT
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

DECEMBER 2010

Approval of the thesis:

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ABSTRACT

SULPHATE REMOVAL BY NANOFILTRATION FROM WATER

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December 2010, 152 pages

Excess sulphate in drinking water poses a problem due to adverse effects on human health and also due to aesthetic reasons. This study examines the nanofiltration (NF) of sulphate in surface water using a laboratory cross-flow device in total recycle mode. In the study, three NF membranes, namely DK-NF, DL-NF and NF-270, are used. The influence of the main operating conditions (transmembrane pressure, tangential velocity and membrane type) on the steady-state permeates fluxes and the retention of sulphate are evaluated. Kızılırmak River water is used as the raw water sample. During the experimental studies, the performance of NF is assessed in terms of the parameters of UVA_{254}, sulphate, TOC and conductivity of the feed and permeates waters. Results indicated that NF could reduce sulphate levels in the surface water to a level below the guideline values, with a removal efficiency of around 98% with all three membranes. DK-NF and NF-270 membranes showed fouling when the surface water was fed directly to the system without any pre-treatment. MF was found to be an effective pretreatment option for the prevention of the membrane fouling, but no

further removal of sulphate was achieved. Parametric study was also conducted. No change in flux values and in the removal of sulphate was observed when the crossflow velocity was lowered. The flux values were decreased as the transmembrane pressure was lowered; however there were not any decrease in the sulphate removal efficiency.

Keywords: Drinking water; fouling; membranes; nanofiltration; sulphate removal

ÖZ

NANOFİLTRASYON İLE SUDA SÜLFAT GİDERİMİ

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Yüksek Lisans, Çevre Mühendisliği
Tez Danışmanı: Prof. Dr. Ülkü Yetiş
Ortak Tez Yöneticisi: Prof. Dr. Mehmet Kitiş

Aralık 2010, 152 sayfa

İçme sularındaki fazla sülfat, insan sağlığı üzerindeki olumsuz etkileri ve estetik nedenlerden ötürü problem teşkil etmektedir. Bu çalışma, yüzey sularında sülfat nanofiltrasyonunu (NF), laboratuar şartlarında ters-akışlı cihaz kullanılarak tam çevrim modunda incelemektedir. Çalışmada, 3 adet NF membranı, isimleriyle DK-NF, DL-NF ve NF-270, kullanılmaktadır. Ana işletim koşullarının (transmembran basıncı, teğetsel hızı ve membran çeşidi) denge durumu permeat akılarına ve sülfat giderimine etkisi değerlendirilmektedir. Ham su numunesi olarak Kızılırmak Nehri suyu kullanılmıştır. Deneysel çalışmalar sırasında, NF performansı, besleme suyu ve permeat suyunda UVA254, sülfat, TOK ve iletkenlik gibi parametrelerle değerlendirilmektedir. Sonuçlar, NF nun yüzey sularındaki sülfat seviyesini, her üç membranda da görülen %98 civarında sülfat arıtım verimiyle, yönergelerde yer alan limit değerlerin altına düşürebildiğini göstermiştir. Yüzey suyu herhangi bir ön işleme tabi tutulmadan sisteme direkt beslendiğinde, DK-NF ve NF-270 membranlarında tıkanma gözlemlenmiştir. Mikrofiltrasyon (MF) membran tıkanmasını engellemede etkili bir ön-arıtma

yöntemi olarak bulunmuş, fakat daha fazla bir sülfat giderimine ulaşılmamıştır. Ayrıca bir parametrik çalışma da yapılmıştır. Teğetsel hız düşürüldüğünde akı ve sülfat giderim değerleri değişmemiştir. Transmembran basıncı düşürüldüğünde akı değerleri de düşmüştür, fakat sülfat giderim veriminde herhangi bir düşüşe rastlanmamıştır.

Anahtar Kelimeler: İçme suyu, tıkanma, membran, nanofiltrasyon, sülfat giderimi

To a world where people drink safe water…

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my supervisor Prof. Dr. Ülkü Yetiş for her encouragement, patience, guidance and valuable advices from which I have learnt to look from a wider perspective to the problems and to life. I would also like to express my gratitude to my co-supervisor Prof. Dr. Mehmet Kitiş for his support and guidance throughout my research.

I gratefully thank the Supervising Committee members, Prof. Dr. Filiz B. Dilek who has added to my thesis with her valuable suggestions and constant support and Prof. Dr. Levent Yılmaz who has been a real driving force for me with his excitement and constructive criticisms.

I would like to thank Environmental Engineering Department staff Kemal Demirtaş and Mehmet Dumanoğulları for their help and support. My sincere thanks go to Gizem Uğurlu who has been a friend other than a staff in the department, for her help, patience and valuable moral support.

I would like to express my special thanks to Hasan Zerze for his kind support and guidance for the experiments.

Many thanks go to Fadime Kara, Çiğdem Moral, Mihriban Yılmaz, Nagehan Keskin and Büşra Keskin for their encouragement and moral support throughout my research.

I would like to thank Gözde Tezce for her valuable moral support.

I would also like to thank to AKER Family, Zülküf Aker, Fırat Aker and Murat Zeydanlı for being a family for me other than an employer and Hakan Damar for being a brother for me and I really appreciate their moral support throughout my research study.

I want to give my special thanks to Emre Çavdaroğlu for his endless valuable moral support.

I would like to express my very special thanks to Eda Çapa for her precious friendship, for being in my life and for her never ending positive attitude towards my research, calming me down whenever I worry, whenever I want to run away from the laboratory, for her endless support, for her cozy voice on the phone when I was at the laboratory.

Many thanks go to my little sister, Gülşah Korkmaz, just for being in my life and her endless support and enthusiasm towards my thesis.

My sincere thanks also go to my grandfather and grandmother, İbrahim and Necmiye Karabacak, who have always supported me towards my research activities and for their love.

Lastly, I also would like to express my endless thanks to my beloved mother and father Emine and Haluk Karabacak, also my brother Alp Karabacak who made everything possible for me and who always being there whenever I need and also to Meliha Karabacak for being a part of our family and Damla Karabacak for being in our lives.

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ABBREVIATIONS

CFV: Cross Flow Velocity

DDW: Distilled and Deionized Water

Jcw: Initial clean water flux

Jrw: Raw water flux

Jcws: Clean water flux after raw water

Jcwc: Clean water flux after cleaning

MF: Microfiltration

MWCO: Molecular Weight Cut-off

NF: Nanofiltration

PIP: Piperazine

RO: Reverse Osmosis

TFC: Thin-film Composite

THMFP: Trihalomethane Formation Potential

TMC: Trimesoyl Chloride

UF: Ultrafiltration

CHAPTER 1

INTRODUCTION

Sulphate, in drinking water resources, if present in excess amounts, is one of the important issues to consider due to the adverse health effects posed, as well as due to aesthetic reasons like odor and taste and economic effects resulting from corrosion of the structures.

The reasons of sulphate existence in drinking water are mainly because of oxidation of pyrite, dolomite layers and also due to the anthropogenic sources like industrial activities [14, 6].

Regarding the above-mentioned problems arising from excess sulphate in drinking water, national and international standards and guidelines have set certain limits for the sulphate levels in drinking waters.

World Health Organization (WHO) has recommended a limit of 250 mg/L for sulphate levels in drinking water in Guidelines for Drinking-Water Quality [15].

Environmental Protection Agency (EPA) has placed a limit of 250 mg/L and stated noticeable effects above this limit as salty taste in Secondary Drinking Water Regulations: Guidance for Nuisance Chemicals [16].

When Australian national guidelines namely Australian Drinking Water Guidelines 6, are considered, there are two kinds of limits as aesthetic and health limits. The limits are set as 250 mg/L for aesthetic reasons and as 500 mg/L for health reasons [41].

A Turkish national standard on drinking water quality (TS 266) has put a limit for the sulphate levels of 250 mg/L [42].

Following the drought occurrence in 2008, sulfate in drinking water supplies has been a concern in Turkey, especially in Ankara where a need for providing supplementary water from a new source, namely Kesikköprü Reservoir, did arise. This water source is characterized by high sulphate content and its possibility to be used in Ankara has brought serious discussions and debates both in the media and the public.

Since the regulations, standards and guidelines have put a limit for the sulphate levels in drinking water as discussed above; there is an important need for treatment of the water supplied to Ankara for drinking purposes from Kesikköprü Reservoir.

There are conventional methods for sulphate removal from drinking water. Examples of most popular methods are brine purge, chemical precipitation and ion exchange. However, there are many drawbacks in terms of applicability, efficiency and cost. Removal of sulphate by conventional drinking water treatment techniques is not reasonable and requires advanced techniques, such as reverse osmosis (RO). However, very high pressure application in reverse osmosis systems make this option unfeasible, especially in huge water demands, like in Ankara.

On the other hand, in recent years, nanofiltration (NF) has gained an importance over reverse osmosis as its application requires lower transmembrane pressure. In this respect, NF membranes are capable of removing charged particles from solutions through electrostatic and sieving mechanisms have been tested towards sulphate removal from surface waters, though very limited [9, 36]. For example, Košutić et al. [3] have shown that the NF membranes, especially NF-270, were able to remove sulphate from water at high retention.

However, different characteristics of raw water resources necessitate case specific tests due to possible different matrix effects. Therefore, in this study, NF tests were conducted to evaluate the performance of NF treatment process for sulphate removal from the above-mentioned surface water.

In the present study, removal efficiency of sulphate from Kesikköprü Reservoir Water was considered. The specific research objectives are to investigate the effects of:

- Membrane Type
- Pretreatment Effect
- Crossflow Velocity
- Transmembrane Pressure

The research is carried out in three parts; of which the first is the effect of membrane type for which three different membranes namely, DK-NF, DL-NF and NF-270, were tested. Second is the effect of pretreatment and as a pretreatment method microfiltration was selected and applied. Third part is the parametric study in which effects of crossflow velocity and transmembrane pressure were examined. During the tests, water samples collected from Kesikköprü Reservoir were utilized.

The overall motivation for the present study is to investigate the nanofiltration removal of sulphate from Kızılırmak River water of Ankara and optimize the process.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Membrane Processes

Membrane technology is a worldwide used technology today in many applications of water and wastewater treatment processes. There had been many efforts for the improvement of the membrane technology and the efforts are still continuing.

Developments in the membrane technology may be considered in two ways, which are scientific and commercial.

Scientific studies on membrane phenomena date back to eighteenth century. In 1748, Abbé Nolet [37] was the first to use the word “osmosis” for water permeation. During the nineteenth and early twentieth centuries’ theories were developed by laboratory works with membranes like Van’t Hoff equation and Maxwell.

The first production of commercial membranes dates back to 1920s [2]. The early workers for the first commercial membranes were Zsigmondy and Bachmann [38] and Ferry [39]. In Germany, Sartorius produced the first commercial Microfiltration (MF) membranes after World War I [1].

Also, first application of MF on water treatment was in Germany and it was one of the first large-scale productions done commercially. At the end of World War II, the drinking water was tested for safety by membranes since water supplies of drinking water was broken down [37].

For ultrafiltration membranes, the most important actions on the development of these membranes have started in 1960s. Reverse Osmosis (RO) were developed before ultrafiltration was taken into consideration. Ultrafiltration was derived from RO [2].

Developments in nanofiltration technology goes back to 1960s and between 1960s to early 1990s, NF technology has been brought to its current status. One of the very first applications of nanofiltration was the treatment of drinking water sources. In Florida, it was used for water softening in 1976 [9].

USA has also taken many efforts to develop the membrane separation technologies on water and wastewater treatment processes. Jacangelo et al. [3] stated the increasing use of membranes with some factors like environmental standards and regulations that become more stringent as the time passes and therefore reaching the water quality standards becomes difficult by conventional treatment processes. Also they added that freshwater supplies with high quality starts to be lessen, and therefore usage of brackish water and reuse of wastewater come into scene, better performance of the membranes and better technologies with the membranes are developed and technological developments provided the membrane technology to become cheaper day by day [3].

The materials of the membranes also started to develop from those days which leaded membrane technology to build up. Membrane material can be divided into three categories according to the structures and ways of functioning, which are synthetic products, modified natural products and inorganic products [4].

Ho and Sirkar [5] defined the process as two bulk phases physically separated by a third phase, namely membrane. Membrane phase controls the exchange of mass between the other two bulk phases. The membrane is stated to be selective to one of the species and one bulk phase is enriched with one of the species while the other bulk phase is depleted of it.

Membrane processes are performed as a selective transfer of the species between the two bulk phases. Two process modes are possible in membrane filtration processes, namely dead-end filtration and crossflow filtration. In conventional filtration processes, dead-end filtration occurs while in membrane filtration processes, other than microfiltration for which both are applicable, crossflow filtration is applied [1, 5].

In the dead-end filtration process, a membrane or a kind of filter medium is utilized to remove the suspended particles and the mechanism governs in the process is sieving mechanism of surface filtration [5]. Here, the solution flows perpendicular to the membrane or filter medium with the presence of pressure application and the particles simply build up on the membrane or filter paper surface. As the filtration continues, a cake layer develops by time on the membrane or filter paper. A schematic representation of dead-end filtration can be seen in Figure 1.

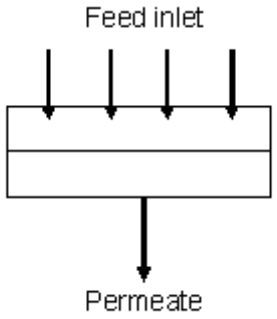

Figure 1 Dead-end filtration

Dead-end filtration happens to be with a constant imposed pressure drop which then results in permeate flux decline with time and buildup of cake layer. With a clean membrane, the permeate flux is at its initial value and with time it starts to decrease in a linear pattern for so short time because of the cake layer formation. With the drop of the flux values of the permeate, cake buildup ratio also decreases [5].

In dead-end filtration mode, the solution is forced via pressure perpendicular through the filter as shown in Figure 1. The particles remain on the filter. These retaining particles buildup a cake layer on the surface of the membrane or filter medium. The cake buildup results in the resistance to filtration which decreases the permeate flux at the same time if the pressure drop is constant. Therefore dead-end filtration is stopped in some periods and depending on the choice filter medium is changed or the particulates on the filter are cleaned [5].

In crossflow mode, solution to be filtered flows across the membrane parallel to the membrane surface. Some of the solids accumulate on the membrane surface [1, 5]. Figure 2 is the schematic representation of the cross-flow operation mode.

In crossflow filtration mode, sieving mechanism of surface filtration dominates. Solution flows tangential to the surface of the membrane as shown in Figure 2. In this mode, no cake layer formation occurs.

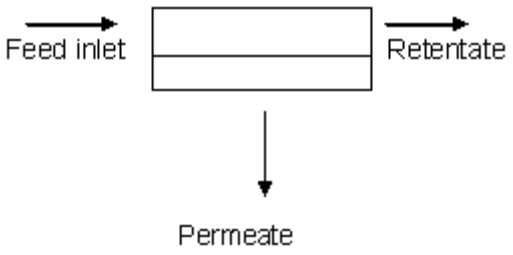

Figure 2 Crossflow Filtration

Main parameter to determine mass transfer ratio in the cross-flow operating mode is the cross-flow velocity [1].

In membrane processes, there is a driving force which acts on the feed components and permeation rate is proportional to the driving force. This proportionality is expressed by the formula given in (1).

$$J = - A \left(dX/dx\right) \quad (1)$$

where,

A: phenomenological coefficient

dX/dx : driving force (gradient of X, type of driving force)

Driving forces can be classified as pressure, concentration, electrical potential and temperature [1]. In this thesis, pressure driven membrane processes will be of concern.

The driving force for pressure-driven membrane processes is the transmembrane pressure (TMP) which is, in fact, a pressure gradient across the membrane. The TMP is defined by the average of the feed pressure and concentrate pressures minus the permeate pressure as shown in (2) [40].

$$TMP = [(Pf + Pc) / 2] - Pp \quad (2)$$

where;

TMP: Transmembrane pressure

Pf: Feed pressure

Pc: Concentrate Pressure

Pp: Filtrate pressure

There are two important concerns in membrane processes which are *flux and selectivity*. These two important parameters govern the efficiency of the

membrane [1]. Flux is also called as flow or permeation rate and is equivalent to the volume of the permeate per unit area and time. Also flux can be expressed as the mole flux or mass flux. The permeate flux can also be defined as the total flux of all the permeated components. Material flux can also be expressed in terms of volume or mass flow rate. Flux is expressed with the formula given in (3) [1].

$$J_v = (1/A)\ (dV/dt)\ [m^3/m^2s \text{ in SI units}] \quad (3)$$

where,

J_v : Volume flux ($L/m^2.h$)

A: Effective membrane area (m^2)

dV/dt : Permeate flowrate (L/h)

Selectivity can be defined by the retention (R) or the separation factor (α). Retention factor (R) is used to express the selectivity when dilute liquid mixtures, which are composed of solvent (that is mostly water) and solute, are of concern. Below formula (Eqn 4) is taken from [1].

$$R = (C_p - C_f) / (C_p) = 1 - (C_f / C_p) \quad (4)$$

where;

C_p : solute concentration in the permeate

C_f : solute concentration in the feed

Solvent molecules, which are water most of the time, goes through the membrane and the solute remains in the solution forming a concentrated solution which we name as a concentrate stream. The remaining part of the solute is calculated as the retention (R) given in (4).

Separation factor (α) is used to express selectivity when gas mixtures and organic liquid mixtures are of concern. Separation factor $\alpha_{A/B}$ is defined for a mixture with components A and B as given in (5) [1].

$$\alpha_{A/B} = (y_A / y_B) / (x_A / x_B) \quad (5)$$

where;

$\alpha_{A/B}$: Separation factor for a mixture with components A and B

y_A: concentration of component A in the permeate

y_B: concentration of component B in the permeate

x_A: concentration of component A in the feed

x_B: concentration of component B in the feed

For a given mixture and a component to be filtrated by a membrane, the rejection rate relates the characteristics of the membrane and the properties of the component in interest like solubility, affinity, wettability, electrical charges, membrane pore size and particle size, etc. [6].

Another important concept in the membrane processes is the *flux decline* with time which is explained by the *concentration polarisation* and *fouling*. Also gel layer formation, clogging of the membrane pores and adsorption are the other reasons for the flux through the membrane decrease [1]. All of these are very much related to which membrane process is applied and solution used to feed the system.

Flux decline is calculated by measuring the initial clean water flux (Jcw), raw water flux (Jrw), clean water flux after raw water passage from the system

(Jcws) and the clean water flux after cleaning of the membrane (Jcwc). Below calculations can be made to determine flux decline:

Total flux decline = Jcw- Jrw

Flux decline due to concentration polarization = Jcws – Jrw

Flux decline due to fouling = Jcw – Jcws

Membrane Fouling

In a normal separation process, the permeate flux decreases over time and this decline may be described by several reasons like concentration polarization, adsorption, gel layer formation and pore plugging.

Concentration polarization is accomplished by the retained solutes at the membrane surface where their concentration is gradually increased. This causes a diffusive flow back to the feed part, then steady-state conditions appear and in the boundary layer, a concentration profile is formed. This phenomenon is called concentration polarization [1].

Adsorption phenomenon is the resistance resulting from the adsorption of the solute molecules on and in the membrane.

The phenomenon of pore blocking is the blockage of the pores by the molecules of the solute. This is mostly due to solutions that contain proteins.

One of the important points in here is to distinguish between the concentration polarization and the fouling. They are not totally different from each other since concentration polarization is the reason for fouling phenomenon. However considerable issue is that concentration polarization is reversible while fouling is irreversible.

Concentration polarisation is the formation of a very concentrated solute layer near the membrane surface and here the concentration is increased

gradually. Figure 3 presents the concentration profile formed in the boundary layer [1].

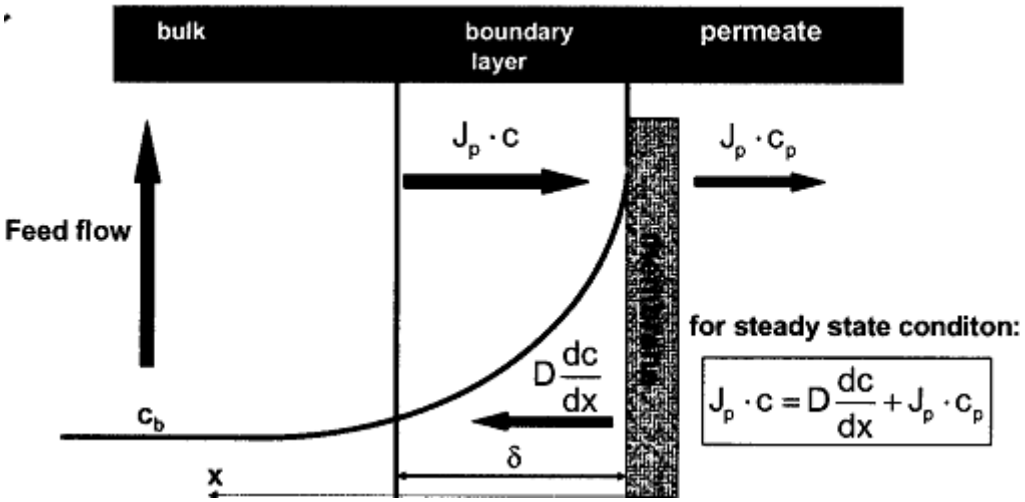

Figure 3 Concentration polarization, concentration profile under steady-state conditions [7].

c_b : bulk concentration;

$J_p.c$: convective flow of solutes towards the membrane;

$J_p.c_p$: solute flow through the membrane

Since fluxes are high and mass transfer coefficients are low in microfiltration and ultrafiltration, the influence of concentration polarization is high [1].

There are several reasons why fouling is of high importance such as cost and energy demand increase, labour increase for maintenance works, chemical cost increase for cleaning issues and decrease in the membrane life. Therefore especially for both nanofiltration and reverse osmosis taking actions against fouling is of high importance.

Possible origins of fouling are summarized below [9, 11]

- Dispersed colloidal material deposition

- Precipitation of substances exceeded their solubility product (scaling)
- At the membrane boundary layer, chemical reactions of solutes
- Chemical reactions of solutes with the membrane
- Irreversible gel formation of macromolecular substances
- Bacteria colonization

The phenomenon of gel layer formation is the accumulation of the solute molecules so that a gel layer is formed across the membrane.

It is also very important to control fouling; therefore appropriate control strategies are required. In Table 1, foulants and their control techniques in nanofiltration and reverse osmosis are listed [9,12].

Contaminants which reduce membrane productivity over time is called foulants [5].

Table 1 Foulants and control techniques in nanofiltration and reverse osmosis [9, 12]

Foulant	**Fouling Control**
General	Hydrodynamics/shear, operation below critical flux, chemical cleaning
Inorganic (scaling)	Operate below solubility limit, pretreatment, reduce pH to 4-6 (acid addition), low recovery, additives (antiscalants)
Organics	Pretreatment using biological processes, activated carbon, ion exchange, ozone, enhanced coagulation
Colloids(< 0.5 μm)	Pretreatment using coagulation and filtration, microfiltration, ultrafiltration
Biological solids	Pretreatment using disinfection, filtration, coagulation, microfiltration, ultrafiltration

Here, the important factors are feed pretreatment, mode of operation and module design, membrane selection and cleaning.

Feed pretreatment is required as the feed water contain foulants which would affect the performance and lifetime of the membrane process. The type and extent of the pretreatment would depend on type of membrane, feed water composition and the required performance of the system [5].

For a particular operation of membranes, there are some key factors for the membrane selection which are flux and rejection properties, fouling rate, bacteria adhesion properties, life time, stability to pH, temperature, chemical concentrations, etc [5].

Different module designs are available for both laboratory scale usage and commercial needs. For instance flat sheet membranes are prepared as spiral-wound or plate-frame modules while other modules are prepared as tubular or hollow-fiber type. Fouling characteristics and handling of the fouling problem, holdup volume and cost are the factors that affect the module design [5].

Cleaning of the membrane can be in two ways. One way is to apply physical cleaning methods in which mechanical forces are used to remove foulants. The other way is the chemical cleaning method in which bonds and cohesion forces between the membrane and foulants are broken by the chemical reactions [9].

Alkaline and acid cleaning are the most applied chemical cleaning methods. In alkaline cleaning, organic foulants from the surface of the membrane and from the pores of the membrane are removed. In acid cleaning, precipitated salts (scaling) from the surface of the membrane and from the pores are removed [9].

Pressure Driven Membrane Processes

The aims of the pressure-driven processes are to concentrate a dilute solution or to purify an aqueous solution [1].

In these membrane processes, pressure is applied and hence solvent and the solute molecules that are not rejected by the membrane go through the membrane as permeate stream. As the membrane pore size changes with

different types of membranes, the size of the solute molecules that are separated also changes.

Pressure-driven membrane processes may be operated in both crossflow mode and dead-end flow mode. In Figure 4 and Figure 5, there are schematic representations of both modes, in respective order [7].

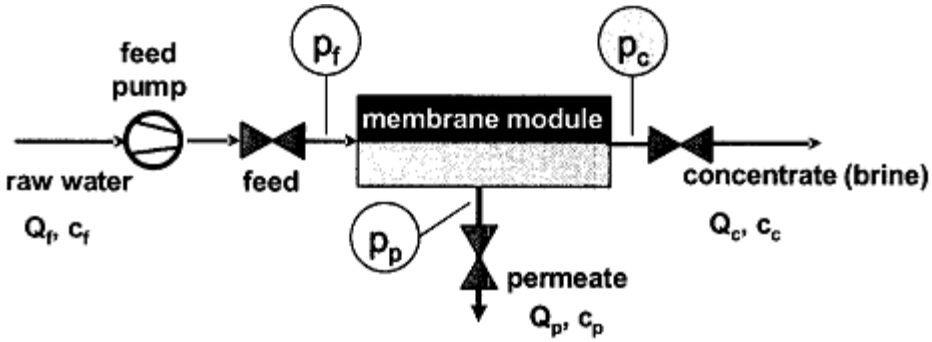

Figure 4 Scheme of a pressure-driven membrane crossflow process [7]

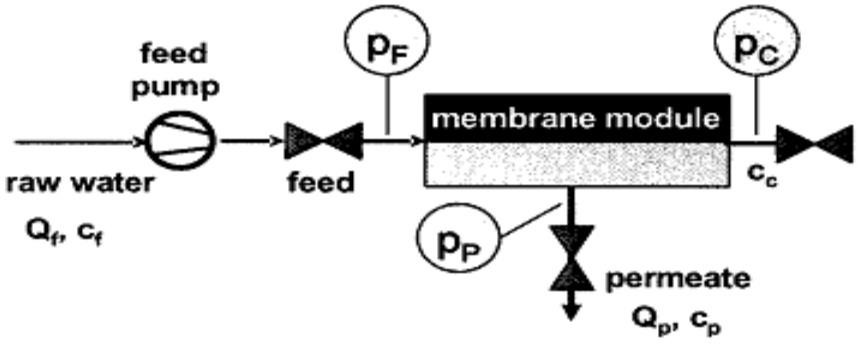

Figure 5 Scheme of a pressure-driven membrane dead-end process [7]

As the pore sizes of the membrane gets smaller then the mass transfer resistance of the membrane increases, therefore the need for the quantity of the applied pressure increases [1].

Pressure-driven membrane processes are categorized into four types according to their pore sizes and thus the pore sizes of the molecules they remove. They are classified from smallest pore size to bigger pore sizes as

reverse osmosis, *nanofiltration*, *ultrafiltration* and *microfiltration* [1, 5]. In Figure 6, approximate pore sizes of the four pressure-driven membrane processes, namely reverse osmosis, nanofiltration, ultrafiltration and microfiltration, are shown as well as the molecular weight of the molecules that the membranes may be able to remove [8].

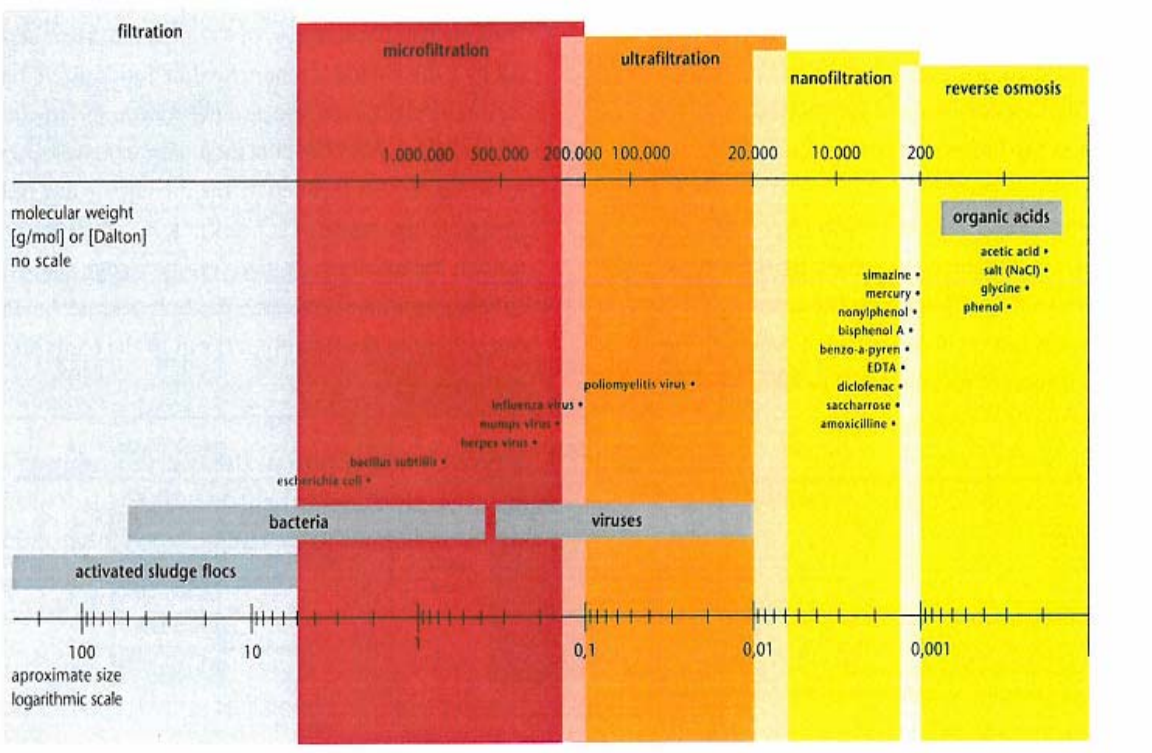

Figure 6 Size of the materials that retain on each type of membrane [8]

2.1.1 Microfiltration

Microfiltration (MF) process is pretty much alike conventional coarse filtration in which sieve mechanism is applied. Size of the particulates, that retain on the MF membrane or filter medium, ranges from 0.01 to 10 μm. The pressure applied during MF ranges from 0.5 to 2 bars. Separation of colloids, suspensions, microorganisms and emulsions is possible with MF [6].

As the pore size of MF membrane is larger than ultrafiltration, nanofiltration and reverse osmosis, then the permeate flux is also higher than other membrane processes. There are two kinds of configurations in MF process applications which are crossflow and dead-end.

In drinking water, desalination and wastewater applications, MF started to become a considerable pretreatment method so that the practices of MF pretreatment are increasing [6]. Water disinfection and the detection of microorganisms are the traditional applications of MF used over the years [6].

MF is also used in the industrial processes such as juice production, sugar and starch production, clarification of beer, whey sterilization, boiler feed water and etc [6].

2.1.2 Ultrafiltration

Ultrafiltration process lies between nanofiltration and microfiltration processes. The pressure applied during ultrafiltration process is between 1 to 10 bars. Separation of macromolecules such as proteins, polymers having a molecular weight of between 1000-1000 000 Da, polysaccharides as well as emulsions and micelles are enabled by ultrafiltration. Also microorganisms and colloidal particles can be removed by ultrafiltration. The pore sizes of the ultrafiltration membranes range from 0.05μm to 1 nm [1, 6].

In order to describe the ultrafiltration membranes, nominal molecular weight cutoff (MWCO) definition is made. Molecular weight cutoff concept can be defined as the smallest molecular weight species for which the membrane has more than 90% rejection. However, Mulder [1] pointed out in his book that molecular weight is not the only criterion that determines the selectivity; also occurrence of concentration polarisation has an important effect on cut-off measurements [1]. Also feed chemistries, molecular orientation, molecular configuration, operating conditions play an important role [1].

In ultrafiltration applications, membrane fouling and concentration polarization are more drastic. In UF processes, species separated have high molecular weights this causes the osmotic pressure differentials to be smaller which then causes lower diffusivities [5]. Therefore module and system design are very important concepts in ultrafiltration to reduce the fouling ratio at the possible minimum cost [1].

Ultrafiltration membranes do not reject salts; therefore osmotic pressure differentials are small compared to reverse osmosis [1].

Ultrafiltration process is mostly used for fractionation of solutes, feed clarification and concentration of rejected solutes. Ultrafiltration was developed for the treatment of wastewaters and sewage, water treatment in process and drinking water as well as other industrial applications. For instance, it has been widely used in food industry for sugar refining, vegetable oils, corn, fruit juices, wine and beer, etc. Ultrafiltration technology has also been used in pharmaceutical industry, paper and pulp production, textile industry, chemical industry, dairy industry, leather industry and etc [6].

2.1.3 Nanofiltration

Nanofiltration process lies between ultrafiltration and reverse osmosis processes. Nanofiltration processes has lower transmembrane pressures than reverse osmosis processes ranging from 3 to 20 bars and this means lower concentrations, larger molecules or multivalent ions to be separated. Nominal molecular weight cutoff (MWCO) of NF membranes ranges from 100 to 1000. Typical pore size range of nanofiltration membranes are between 0.5 nm to 5 nm [1, 6, 9].

On the other hand, at an average, NF membranes have pore sizes of 1.5 to 2.5 nm [9, 10]. NF applications have an advantage for reverse osmosis for the energy consumption issue since in nanofiltration less pressure is applied.

NF membranes show an important comparable attitude to reverse osmosis membranes to remove multivalent ions [9]. Monovalent ions are only rejected partly [1].

There are two main principles said to govern the rejection of solutes in nanofiltration processes: neutral species rejection due to their size and rejection of inorganic ions due to their size and electrostatic interactions between the ion and the membrane [9].

Nanofiltration technology is utilized for both the separation processes and the treatment processes. Separation processes by nanofiltration membranes was first developed to separate lactose from monovalent salts in whey processing in the dairy industry and now it is widely used in industrial applications. The treatment processes may include water softening, treatment of wastewaters - originating from various industries such as metal finishing industry and textile industry , removal of sulphates from sea water, etc [9].

Nanofiltration is also applied in many industries other than water and wastewater treatment, such as separation of dyes and separation of surfactants in textile industries, removal of heavy metals in the industries dealing with heavy metals, sugar industries, dairy industries, pharmaceutical industries, paper industries, chemical industries and etc [6].

2.1.4 Reverse Osmosis

Osmosis is a natural phenomenon and described as the passage of water through a semipermeable membrane until the equilibrium of the chemical potential is reached [1]. The passage of water through the membrane is from lower solute concentration to higher solute concentration. Then, the pressures at each side of the membrane become equal to osmotic pressure difference. For the reverse osmosis application, the flow of water is reversed in a way that a pressure higher than the osmotic pressure is applied so that the separation of water from the solution is enabled. This is called *reverse*

osmosis or *hyperfiltration* in other words [1, 6]. Reverse osmosis rejects inorganics (95% to 99.9% NaCl rejection) and low molecular weight organics [5].

In reverse osmosis process, monovalent ions and molecules are separated on the dense membranes. The molecular size that retained, range from 1 to 10 Å. The transmembrane pressure applied in reverse osmosis applications are between 10 to 100 bars. Separation properties of organics are determined by several factors which are membrane structure, physicochemical properties of the membrane and organic molecules and organic solute and membrane material interaction [6].

There are some important operating parameters in reverse osmosis which are transmembrane pressure, feed flowrate, temperature, pH, dissolved solute concentration, solute type, etc [1].

Two streams are defined like other membrane processes, retentate (concentrate) and permeate. There are three important parameters of concern in reverse osmosis applications which are solute rejection, water flux and water recovery [1, 6]. Water recovery is defined as the fraction of the feed flow that passes through the membrane. Water flux is the volume flowing through the membrane per unit time and area. Water flux and solute rejection are related to each other [1].

There are two traditional applications of reverse osmosis, namely seawater and brackish water desalination processes. However today there are many other applications like wastewater treatment, water softening, food processing, ultrapure water production, etc [6].

CHAPTER 3

LITERATURE REVIEW

3.1 SULPHATE IN DRINKING WATER

Oxidation of pyrite (FeS_2) is one of the main reasons of sulphate in the drinking water and occurs as a result of microbial activity. Pyrite mainly originates in the ground levels [6, 13]. Schippers et al. [14] showed that more than 90% pyrite was oxidized to sulphate which was originated in mine waste.

Another source of sulphate in drinking water is the dolomite layers from which salts of sulphate are drained into water sources [6]. Anthropogenic sources like industrial activities and their point and nonpoint wastewater sources containing sulphate ions are also another reason for the existence of sulphate in drinking water.

Whatever the source is, excess of sulphate in drinking water causes some problems like health effects, economical effects resulting from corrosion of some structures and aesthetic effects like odor and taste [6].

In the drinking water guidelines of World Health Organization (WHO) high levels of sulphate is stated to cause laxative effects in unaccustomed customers [15]. Moreover, health effect of excess sulphate ions in drinking water is the acute (diarrhea) which is relatively short term and a substantial decrease of sulphate content in drinking water is recommendable [15,6].

Corrosion of water infrastructure by sulphate is of an important concern. For instance, for the drinking water transportation, iron pipes are used. Structural failure of the iron pipes is not common; however water quality problems may occur due to the corrosion of the iron pipes. The level of the sulphate concentration effects the corrosion of iron pipes [15].

For the concrete and cement structures, sulphate ions may cause attack which may lead to the structural failure of the concrete pipes [15]. Therefore treatment of drinking water in terms of sulphate may sometimes be necessary to protect the structures and prevent the associated water quality problems.

Other than corrosive effects of sulphate, it may cause noticeable taste problems. When there is excess of sulphate in drinking water, it makes the taste bitter or medicinal. Therefore it is unpleasant to drink water with high sulphate levels.

Regarding the above problems arising from the excess of sulphate in drinking water, national and international standards and guidelines have set some limits for the sulphate levels in drinking waters.

World Health Organization (WHO) has recommended in Guidelines for Drinking-water Quality, a limit of 250 mg/L for sulphate levels in drinking water.

Environmental Protection Agency (EPA), in Secondary Drinking Water Regulations: Guidance for Nuisance Chemicals has put a limit of 250 mg/L and stated the noticeable effects above this limit as salty taste [16].

When Australian national guidelines namely Australian Drinking Water Guidelines 6, are considered, there are two kinds of limits which are aesthetic and health limits. The limits are 250 mg/ L for aesthetic reasons and 500 mg/L for health reasons.

A Turkish national standard on drinking water quality (TS 266) has put a limit for the sulphate levels of 250 mg/L.

3.2 SULPHATE REMOVAL METHODS IN DRINKING WATER

Sulphate is naturally present in surface or drinking waters. However, sometimes it is found in high concentrations which are mainly due to anthropogenic sources like mining activities and industries. These all cause the natural sulphur cycle to overbalance [19, 20] and a necessity is raised to remove sulphate from high-sulphate containing surface waters or drinking waters.

Removal of sulphate is done by several methods. Chemical, physicochemical and thermal methods are applied in order to remove sulphate from drinking water. Below is some brief knowledge on most applied techniques of sulphate removal from water.

3.2.1 Brine Purge

Brine purge method is mostly used in coastal plants to reduce the sulphate levels. Sulphate ion contained brine is contacted with granular ion exchange resin and sulphate ions are adsorbed and removed from brine. There are some disadvantages of the process which are resulting effluent with high volumes and the high operating costs. High operating costs are due to the fact that valuable salt is lost during the brine purge [17].

3.2.2 Chemical Precipitation

The idea behind the chemical precipitation method is to remove sulphates by adding barium salt and re-precipitating the sulphate as barium sulphate. Since barium sulphate is insoluble in water, it is easy to separate and remove it from drinking water so that the sulphate in drinking water is reduced. The separation of the solid precipitate may be done by filtration; centrifuge or by other available methods [20]. The barium in the sludge, which is removed from the process, can be recycled back to the main stream.

There are some disadvantages of the barium sulphate precipitation method such as the cost of the barium reagents, disposal of the solid precipitate that contains barium and the handling of the barium compounds which are known to be carcinogenic [17].

For chemical precipitation applications to remove sulphates, lime addition is another method. However, the sulphate level in the water is important to be able to apply calcium sulphate precipitation. The sulphate level in the water should not be less than 1500mg/L to have an efficient precipitation of calcium sulphate [18]. If the sulphate level in the drinking water is above this specified level, it is an inexpensive method to apply.

3.2.3 Ion Exchange

If sulphate will be removed from large volumes of water, most commonly applied method is ion exchange. In ion exchange, the ion found in the solution is replaced with another similarly charged ion which is attached in the ion exchange resin.

Like water softening process, ion exchange resin, which is found in a unit, is used and as the water passes through this unit, the resin adsorbs the sulphate. The process continues until the resin is full with sulphate. At this point, the resin can no more adsorb any more sulphate. Then a process called *regeneration* is applied. The regeneration process is done with a salt (sodium chloride) so that the resin unit is able to process again to remove sulphate from water. In ion exchange method, basically a reversible and stoichiometric chemical reaction takes place. Ion exchange resin may be either natural (inorganic zeolites) or synthetic (organic resins).

Certain substances found in water may foul the resin, which is a drawback of ion exchange method. Iron fouling is the most common one that is seen in the application. Bacterial contamination is another disadvantage of the ion exchange resins. Moreover, organic matter found in the water may irreversibly attach anion beads and therefore reduce the exchange capacity

of the resin. This is another disadvantage and it affects the water quality negatively.

3.2.4 Membrane Processes

Many of the above mentioned techniques for the removal of sulphates from drinking water have certain disadvantages. Recently membrane processes to remove sulphate from drinking water is studied. Among membrane process types, nanofiltration and reverse osmosis are applied for sulphate removal. Košutić et al. [21] have conducted research for optimal water treatment process for sulphate removal from drinking water and they have applied both reverse osmosis and nanofiltration experiments with NF-270, NF (Filmtec Co.) and CPA2 (Hydranautics) thin-film polyamide membranes. The results of the study showed that all these membranes had very high sulphate retentions and NF-270 membrane presented high productivity.

Similarly, Bargeman et al. [22] have conducted a study using the membrane NF-270 for the production of permeate saturated in NaCl which is low in sulphate content. They produced retentate saturated in NaCl and supersaturated in Na_2SO_4. As a result of the experiments conducted, NF-270 was found to be superior than the other membranes, namely Desal DK (GE/Osmonics), Desal DL(GE/Osmonics), TS-80(TriSep) and MPF-34(Koch). Sulphate retention of NF-270 membrane was found to be 98% (CF=1.0, P=54bar). NF-270 membrane was found to be also effective for some other treatment processes. Hilal et al. [24] studied the pretreatment applications for the desalination process and they have used NF-270 membrane. They observed that the membrane showed lower rejections when the flux values were high.

Another study done by Meihong et al. [23] showed the sulphate removal rates from the concentrated brine of chloralkali industry with TFC nanofiltration membrane which was prepared with PIP and TMC by interfacial polymerization. The parametric study results showed that the rejection for

Na_2SO_4 decreased slightly with the increasing solute concentration, however it also remained more than 90% with a feed concentration of more than 30 g/L. High filtration efficiency and performance stability was observed for the selective sulphate removal with TFC NF membrane.

Other than sulphate removal efficiencies of nanofiltration process, many researchers studied the drinking or surface water treatment applications by nanofiltration till now.

In a study of Bruggen et al. [34], nanofiltration was implemented in drinking water and the capillary and flat sheet membranes were compared. The results of the study showed that capillary membrane has a higher water flux than the flat sheet membrane and this difference ranged from 3-15 times. During the nanofiltration from the capillary membrane, the surface water was fed directly to the system, however the water fed to the flat sheet membrane was microfiltrated. The fouling ratios were observed to be similar to each other even the capillary membrane was fed without pretreatment of the surface water. The rejection of ions was less than the flat sheet membranes.

Different mechanisms affect the transport phenomena during nanofiltration process which are convection, diffusion and charge effects. Convection is due to the pressure differences that are applied over the membrane. Diffusion exists due to the concentration gradient and charge effects are mainly resulted from electrostatic repulsion between the membrane and organic compound which are already charged [29, 30, 31].

During the transport of solute in nanofiltration, the dominant mechanism is the convection especially when the charge density of the membrane is low. However, when the membrane charge density is high, then diffusion contribution becomes high since electrostatic repulsion hinders the convection through the membrane [29, 30].

Influence of charge is also supported by the researches of Braeken et al. [29] who studied with the membranes UTC-20, Desal HL-51, NF-270, NTR-7450 and NF-PES-010. The effect of membrane and solute charges by increasing the pH in nanofiltration experiments were studied and they observed that pH increase resulted in a decrease of convective and diffusive transports for charged compounds due to increased repulsion between the membrane and the solute while large and uncharged compounds showed a slight increase in convective and diffusive transports due to an increase in the pore sizes resulting from the repulsive effects between the charged acidic groups.

Wang et al. [31] indicated that salt concentration is directly related with the charge density and their results with the experiments done with four different membranes, namely Desal-S, NF-40, NTR 7450 and G-20 showed that as the molecular weight of the solute becomes larger, then the real rejection becomes also higher.

The separation mechanism in nanofiltration processes are basically described by the charge and size effects. Schaep et al. [25] also studied the mechanisms for the retention of salt solutions using two negatively charged (Filmtec NF 40 and Nitto Denko NTR 7450) and one positively charged (Toray UTC 20) membrane. The results of the study showed that NF 40 and UTC 20 which has 0.42 nm and 0.41 nm pore radii, respectively had both high retentions for Na_2SO_4 and $MgCl_2$. Charge effects were found to be the determining factor of salt retention of the negatively charged NTR 7450 membrane which has larger pore as 0.80 nm [25]. In another study, Schaep and Vandecasteele [26] showed that membrane charge influenced the ion diffusion. For positively charged membranes, cation diffusion is more obstructed than anion diffusion and for negatively charged membranes; anion diffusion is more difficult than cation diffusion. In the same study, they have done the zeta potential measurements and they concluded that all the five membranes they studied had a negative surface charge at neutral pH.

It is known that nanofiltration can remove multivalent ions and relatively small organic molecules from liquid streams [27, 28]. Traditionally, performance of a membrane is evaluated by trial-and-error method. However, some models to predict the retention of the molecules have been developed. Bruggen and Vandecasteele [28] have derived a model for the evaluation of the retention of organic molecules by nanofiltration membranes at different pressures. They found that with this model MWC variations with pressure can be predicted which is very important for the selection of the operating pressure.

Since nanofiltration is very promising for the drinking water treatment applications, there are also some drawbacks of the system to be applied. Bruggen et al. [32] stated the most important ones as membrane fouling problem and the need for cleaning. These are all practical problems and there are several proposed options for the solution of these problems.

Bruggen et al. [33] also evaluated the flux decline in nanofiltration with the relation of adsorption process. Two different membranes were used for the experiments which are NF-70 and UTC-20. They found out that there is an important relationship between the drop of the water flux during nanofiltration and the adsorption of the organic molecules inside the membrane pores or on the membrane surface. If the component is hydrophobic then adsorption is higher. The results also showed that the effect of organic matter adsorption on the water flux is more for NF-70 than for UTC-20.

Lee et al. [35] studied the $CaSO_4$ scale formation mechanisms with the nanofiltration membranes and found out that with cross flow NF membranes, there was a flux decline problem due to both surface and bulk crystallization.

CHAPTER 4

MATERIALS AND METHODS

4.1 SOURCE WATER

In the experiments, Kızılırmak River water was used as the raw water resource. Kızılırmak River water was collected from Kesikköprü Dam which served as a supplementary surface water resource for the Ankara, between July 2008 and June 2009. Raw water samples were collected from Kesikköprü Dam Reservoir on a monthly basis throughout a year. These samples were analyzed for their sulphate content in order to determine the seasonal variation. The samples were collected with bottles of 35 liters and immediately transferred to the laboratory. Each sample was analyzed for sulphate, arsenic, dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), turbidity, conductivity and UVA_{254} contents and then kept in a refrigerator at $+4^{o}C$ to be used in membrane filtration tests.

Table 2 presents the typical characteristics for Kızılırmak River water that was collected from Kesikköprü Dam. The representative data belong to the raw water sample taken in different months of the year, namely July, January and April.

Table 2 Raw water characteristics

Parameters	Unit	July 2008	January 2009	April 2009
SO_4	mg/L	310	420	390
As	µg/L	13.01	9.78	10.12
THMFP	µg/L	67	40	49
DOC	mg/L	5.03	-	3.12
Turbidity	NTU	1.34	-	1.74
Conductivity	µS/cm	1910	-	1488
UVA_{254}	-	-	-	0.0151

4.2 MEMBRANE FILTRATION SYSTEM

The filtration unit used in all the experiments is a lab-scale cross flow type system (SEPA CF II Membrane Element Cell) in which a single piece of rectangular membrane is installed. The membrane used in the experiments is a flat sheet type membrane and effective area of these flat sheet membranes is 140 cm^2 (22-$inch^2$) with dimensions of 19 cm and 14 cm (7.5-inch x 5.5-inch).

The system basically consists of the following items: a high pressure pump which can adjust feed flow rate via a digital variable frequency drive, feed tank with a capacity of 35 liters, concentrate flow control valve, high pressure hose, cell body, cell holder, cell holder pressure gauge, concentrate pressure gauge, hydraulic hand pump and permeate collection vessel. Other than all these main items, throughout the system, there are several fittings and coupling pieces. The detailed schematic representation can be seen in Figure 7.

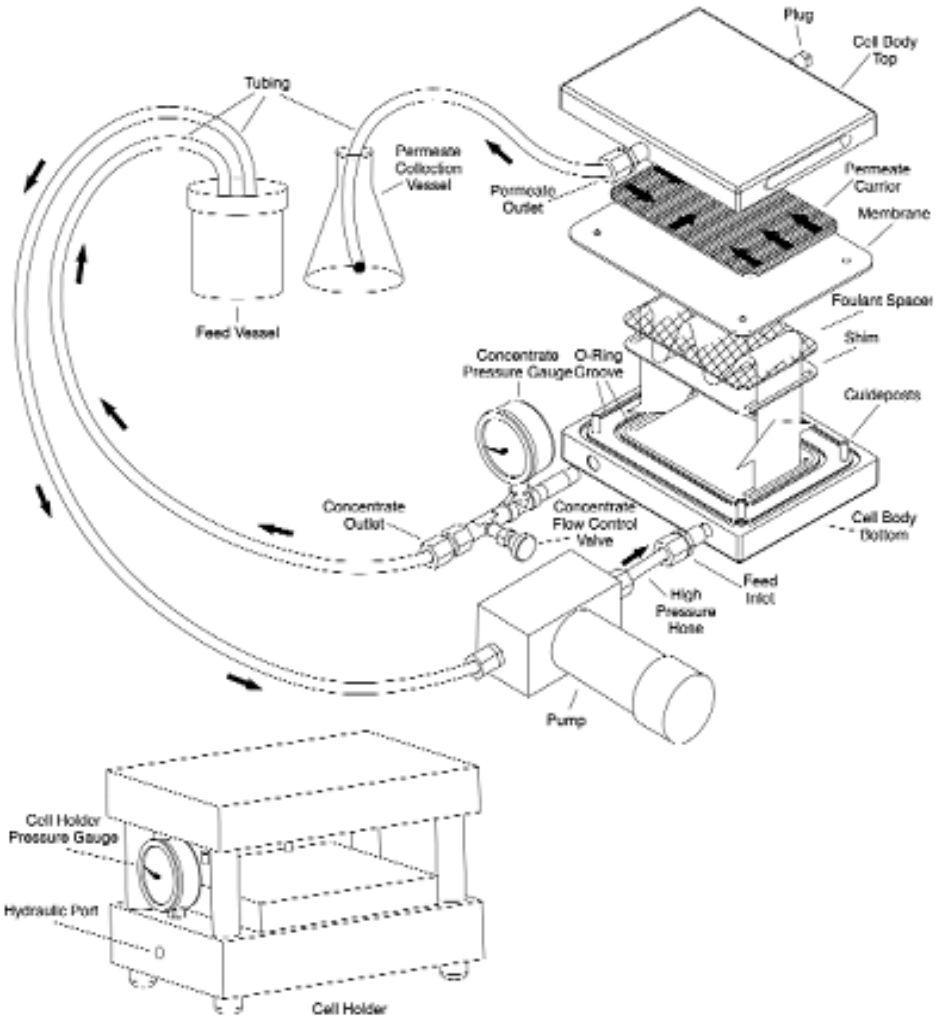

Figure 7 Schematic representation of the filtration set-up

The membrane, with above-mentioned features, is placed on top of the feed spacer. Here the membrane resides between the bottom and top cell bodies and the assembled cell body is inserted into the cell holder. Cell body is compressed via hydraulic pressure originating from a fitting found at the bottom of the cell holder. A hydraulic hand pump is used for pressurizing the cell holder. In the set-up, the high pressure pump is utilized for pumping the feed stream from the feed vessel to the feed inlet and provide the circulation of the permeate stream and reject stream in the system.

In order to feed the system, there exists a feed water tank which has a maximum capacity of 35 liters liquid. For controlling the temperature in the set-up during the system runs, feed water temperature was kept constant by cold tap water. To achieve this, there exists a jacket in which tap water can circulate at the outer walls of the feed tank. During the experiments, feed water temperature was set 20±2^{o}C by feeding the jacket with tap water continuously. In the set-up, there are mainly three connections which are feed, permeate and hydraulic port for piston.

The material of the cell body, concentrate flow control valve and concentrate pressure gauge is 316 Stainless Steel (SS316). The holder is made of high-grade anodized aluminum since it does not contact with the feed solution during normal operation. However, high-grade anodized aluminum will prevent corrosion of the holder if there are any spills.

Concentrate flow control valve which is made of stainless steel provides control of pressure and flow over the surface. The valve is placed on the concentrate outlet of the cell and by using this control valve, pressure in the membrane cell can be adjusted as well as the flow rates of the permeate streams and concentrate streams.

4.3 MICROFILTRATION

During the study, in certain experiments, Kızılırmak River water is fed to the system without any pre-treatments. However, in some other experiments, raw water is first microfiltrated and then fed to the system for further treatment with NF. MF is applied in dead-end mode using a conventional vacuum filtration apparatus (Millipore). The pore size of the filter media is 2,5 μm and the material of the filter media is ashless cellulose (Whatman 42). Effective area of the microfiltration membrane is 0,0014 m^2. The filtrate is analyzed for its pH, conductivity, UVA_{254} and sulphate content.

4.4 NANOFILTRATION

In this study, three different thin-film composite nanofiltration membranes, namely DK-NF, DL-NF and NF-270, are tested. The characteristics of the membranes given by their manufacturers, used in the experiments are presented in Table 3.

Table 3 Characteristics of the flat sheet membranes

Name of the Membrane	Polymer Structure	pH Range	Rejection Size	Typical Flux/psi GFD@PSI
DK-NF	Thin Film	2-11	98 -MgSO4	22/100
DL-NF	Thin Film	2-11	96 -MgSO4	31/100
NF-270	Thin Film	1-12	*	*

The filtration set-up allows for two kinds of operations during the experiments which are total recycle mode and concentrate mode. In this study, total recycle mode is run in which both permeate and concentrate streams are returned to the feed water tank so that the characteristics of the feed water are kept constant. Representation of the total recycle mode flow diagram can be seen in Figure 8.

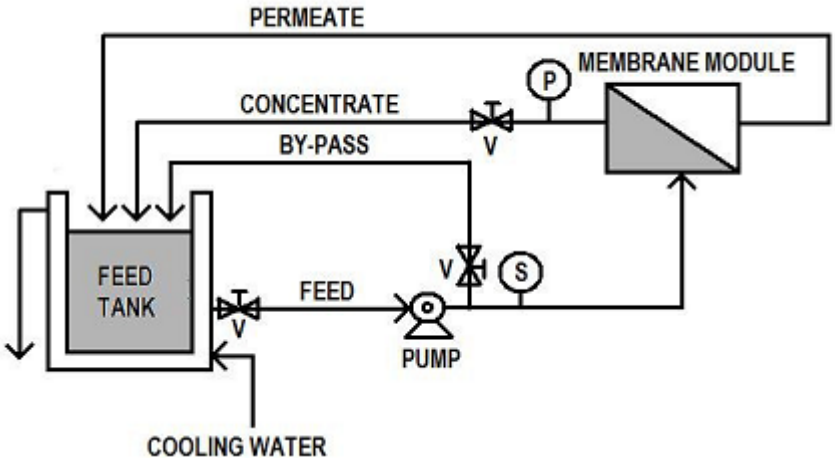

Figure 8 Total recycle mode flow diagram

(V: Valve, P: Pressure Gauge & S: suction Gauge)

As stated before, the temperature of the system is kept constant at 20±2^{o}C during the experiments and this is provided by cooling of feed water with the cold tap water.

The test duration ranged from 8 to 15 hours at each run for both clean and raw water passage through the system. The time period for each run changed according to the time needed to obtain steady-state. The steady-state condition is checked by measuring the permeate flux. When the permeate flux reaches steady-state, then the system said to come to steady-state or it is checked by the parameter analysis.

The nanofiltration experiments, which are conducted with the experimental set-up described above, are implemented in a stepwise manner. Experimental matrix related can be seen in Table 4. As can be seen from this Table, overall 13 sets of experiments are employed. First five sets (Set 1-Set 5) of experiments are conducted with DK-NF membrane at 6.9 bar pressure and 1.2 m/s cross flow velocity (CFV). NF-270 membrane is tested at the same operational conditions (6.9 bar pressure and 1.2 m/s cross flow velocity) through Set 6 and Set 8. Experimental set 9 is also conducted with

NF-270, but it is tested with microfiltrated raw water which is different than Set 6, Set 7 and Set 8. Then, as a third membrane type, DL-NF is selected and tested at 6.9 bar pressure and 1.2 m/s cross flow velocity (Set 10). Following this experiment, the same membrane is tested again with microfiltrated water at the same pressure and cross flow velocity (Set 11). Then, to see the effect of transmembrane pressure, in Set 12, DL-NF is tested at 3.5 bar, keeping the CFV same as the CFV of Set 10, using microfiltrated water. Finally, DL-NF is tested at 6.9 bar pressure and 0.7 m/s cross flow velocity with microfiltrated raw water in order to see the effect of CFV on the filtration performance (Set 13).

Table 4 Experimental Matrix

Experimental Sets	Membrane Type	Pressure (bar)	Cross Flow Velocity (m/s)	Microfiltration Pretreatment
Set 1	DK-NF	6.9	1.2	No pre-treatment
Set 2	DK-NF	6.9	1.2	No pre-treatment
Set 3	DK-NF	6.9	1.2	No pre-treatment
Set 4	DK-NF	6.9	1.2	No pre-treatment
Set 5	DK-NF	6.9	1.2	No pre-treatment
Set 6	NF-270	6.9	1.2	No pre-treatment
Set 7	NF-270	6.9	1.2	No pre-treatment
Set 8	NF-270	6.9	1.2	No pre-treatment
Set 9	NF-270	6.9	1.2	2.5µm pre-treatment
Set 10	DL-NF	6.9	1.2	No pre-treatment
Set 11	DL-NF	6.9	1.2	2.5µm pre-treatment
Set 12	DL-NF	3.5	1.2	2.5µm pre-treatment
Set 13	DL-NF	6.9	0.7	2.5µm pre-treatment

During the nanofiltration test runs, permeate samples are collected in certain periods and are analyzed for their sulphate content, temperature, pH, conductivity and UV absorbance levels.

In the nanofiltration experiments, membrane filtration protocol is applied in which there are seven steps to follow during the conduction of the experiments.

In Table 5, steps followed during the experimental study can be seen.

Table 5 Steps applied in the nanofiltration experiments

	Pressure (Bar)	Feed Water	Cross Flow Velocity (m/s)	Duration
Step 1: Compaction	13.8	DDW	0.7-1.2	24 hours
Step 2: Cleaning of Membrane	3.5	HNO_3 @ pH 3	0.5	1 hour
	3.5	DDW	0.5	1 hour
	3.5	NaOH @ pH 9	0.5	1 hour
	3.5	DDW	0.5	1 hour
Step 3: Clean Water Flux Before Raw Water	6.9	DDW	0.7-1.2	Until steady-state is reached
Step 4: Raw Water Flux	6.9	RawWater/ Microfiltrated Raw Water	0.7-1.2	Until steady-state is reached
Step 5: Clean Water Flux After Raw Water	6.9	DDW*	0.7-1.2	Until steady-state is reached
Step 6: Cleaning of Membrane	3.5	HNO_3 @ pH 3	0.5	1 hour
	3.5	DDW	0.5	1 hour
	3.5	NaOH @ pH 9	0.5	1 hour
	3.5	DDW	0.5	1 hour
Step 7: Clean Water Flux After Cleaning of the Membrane	6.9	DDW	0.7-1.2	Until steady-state is reached

In step 1, the membrane is compacted with a pressure which is much higher than the normal operating pressure, so that the expansion or compaction of the membrane in the further steps is minimized. The compaction duration is 24 hours.

Cleaning of the membrane is performed by feeding the system with an acidic solution of pH 3 and with an alkaline solution of pH 9. The pH values of the cleaning solutions are determined so that the acidity or alkalinity of the solutions would not harm the membranes. Between the acidic and alkaline solution passage from the set-up, DDW is passed through the system. Membrane cleaning procedure is applied with a pressure lower than the normal operating pressure; at 3.5 bars.

Cleaning procedure is applied before and after the clean water passage from the system. The purpose is to recover the membrane by removing the fouling at the membrane surface. Therefore, membrane fouling ratio and recovery of the flux are determined by the clean water flux data that are collected during the DDW passage through the system. Clean water is passed through the system before and after raw water is fed into the system. Clean water and raw water fluxes are measured until the system reaches steady-state conditions, which is determined by considering the flux values and permeate parameter analysis. In experiments, two kinds of raw water were used. One of them was taken from the Kızılırmak River water, which was directly fed to the system without any pre-treatment and the other one was also the Kızılırmak River water, but it was microfiltrated with a 2.5 μm MF filter. In most of the experiments, cross flow velocity was fixed at 1.2 m/s, but in certain experiments cross flow velocity of the system was changed to 0.7 m/s for the parametric study.

4.5 ANALYTICAL METHODS

Analytical methods used during the experiments are presented below:

4.5.1 UVA_{254}

Varian 100 Spectrophotometer was utilized to measure the UV absorbance at a wavelength of 254 nanometer. The spectrophotometer is connected to a computer from which the data can be read. The calibration of the spectrophometer is done by using water, which is distilled twice.

4.5.2 Sulphate

Analysis of sulphate was conducted with raw water; permeate samples and feed stream. Sulphate content of the samples was measured by Hach DR-2000 spectrophotometer device. Blank sample was prepared for all the measurements. The measurements were done by utilizing Hach sulphate kits, according to Hach Method no 8051 (USEPA approved). 25 mL samples were used for the measurement each time.

4.5.3 Conductivity

Conductivity and total dissolved solids (TDS) of the membranes measured directly by using a Hach Sension 378 conductivity meter. The device calibration is done by the calibration standards given by the manufacturer.

4.5.4 pH

pH of the samples were measured by Hach Sension 378. The device was calibrated by the standards given by the manufacturer at pH levels of 4, 7 and 10.

4.5.5 Temperature

Temperature was measured directly by using the Hach Sension 378 device.

4.5.6 Turbidity

Turbidity of samples was measured using Hach 2100 N model turbidimeter. Calibration of the turbidimeter was done by using standard solution.

4.5.7 DOC

For the analysis of DOC, TOC-5000A model TOC analyzer (Shimadzu) applying high temperature combustion method (APHA, AWWA, WEF, 1998) was used. Oxygen at a high purity level was used as a carrier gas, besides being used for sparging purposes. In order to ensure the accuracy of measurements, inorganic carbon has to be removed from the samples. To provide this, samples were sparged with dry air for 10 minutes. 0.05N HCl was used to adjust the pH of the samples to be measured in order to remove inorganic carbon from the samples through stripping via dry air sparging. The pH ranges of the samples and standards were between 2.5 and 3.0 for an efficient stripping of the inorganic carbon and thus for an efficient measurement of the DOC in the samples. The idea behind stripping of inorganic carbon is to eliminate the inorganic carbon concentration which may be larger than the organic carbon concentration in surface waters. Injection of the samples ranged between 3 and 5 times; depending on the standard deviations of the samples and it was automatically done by the device.

4.5.8 Trihalomethanes Formation Potential

Trihalomethanes Formation Potential (THMFP) was analyzed in raw waters. Raw water was chlorinated to simulate the average chlorination conditions in drinking water distribution systems. A contact time of 7 days was applied and a free chlorine residual of 1.0±0.4 mg/L residual free chlorine was provided. A stock solution of sodium hypochlorite solution with 13% free chlorine was used to spike chlorine to the bottles with gas tight glass syringes. After incubation at 20±2^{o}C in dark for 7 days, residual free chlorine was measured according to SM 4500 Cl G (APHA/AWWA/WEF, 1998). Then the samples were quenched with sodium sulfite before extraction for trihalomethanes analysis. Trihalomethanes (THM), namely chloroform, dibromochloroform, bromodichloroform and bromoform were analyzed by applying liquid-liquid extraction method by using pentane. After the extraction, the samples were

measured by gas chromatography (GC) device. The measurements were done according to SM 6232 B (APHA/AWWA/WEF, 1998). Supelco standard mixture was used to prepare the calibration standards and calibration curves were drawn for the calculation of the THMs concentrations of the samples. Calibration standards were prepared following the same procedure as done for the samples.

4.5.9 Arsenic

For the measurement of arsenic in the raw water, from standard methods, the manual hydride generation / atomic absorption spectrometric method (3114B) was used.

CHAPTER 5

RESULTS AND DISCUSSION

In this experimental study, the performances of three different NF membranes, namely DK-NF (GE/Osmonics), DL-NF (GE/Osmonics) and NF-270 (Filmtec Co.), were tested for the removal of sulphates from the studied raw water source. The related raw water characteristics data of Kesikköprü Reservoir is illustrated in Table 2, where high sulphate levels can be seen.

All three membranes were tested with raw Kesikköprü Reservoir water. NF-270 and DL-NF membranes were also tested with pretreated Kesikköprü Reservoir water to which microfiltration was applied as a pre-treatment method. The characteristics of raw surface water and microfiltrated raw Kesikköprü Reservoir water are shown in Table 6. Moreover, a parametric study was also conducted with DL-NF membrane with the pretreated Kesikköprü raw water by changing the transmembrane pressure and crossflow velocity.

Table 6 Raw surface water and microfiltrated water characteristics

Parameters	Unit	Raw Surface Water	Microfiltrated Water
Sulphate	mg/l	420	400
pH		8.5	8.5
Temperature	^{o}C	20	20
Conductivity	µS/cm	1651	1643
UVA_{254}		0.0166	0.0088

The performances of the membranes were monitored mainly by flux and sulphate removal efficiencies as well as some other parameters analyzed. The feed and permeate were sampled periodically.

5.1 EXPERIMENTS WITH "DK-NF" MEMBRANE

For the initial trial of NF, "DK-NF" membrane was employed, and its performance in removing sulphate from the Kesikköprü water was examined. Before its use, each membrane firstly compressed at 13.8 bar pressure with DDW for 24 hours.

Five sets of experiments were conducted with "DK-NF" membrane. The first two experimental sets were conducted with the same "DK-NF" membrane and the other three experimental sets were conducted with another new "DK-NF" membrane from the same batch.. All the five experiments were conducted at 6.9 bar pressure and 1.2 m/sec cross-flow velocity. The temperature of the feed water was kept at 20±2^{o}C.

The sulphate level of the raw water fed to the system in the first set of experiment was 440 mg/L. Permeate samples were collected during the test and the sulphate and turbidity levels were monitored. Sulphate removal efficiency at around 98% was achieved (Figure 9) which is very promising for

the first trial. Even at the very start of the experimental run, removal percentage of sulphate became constant.

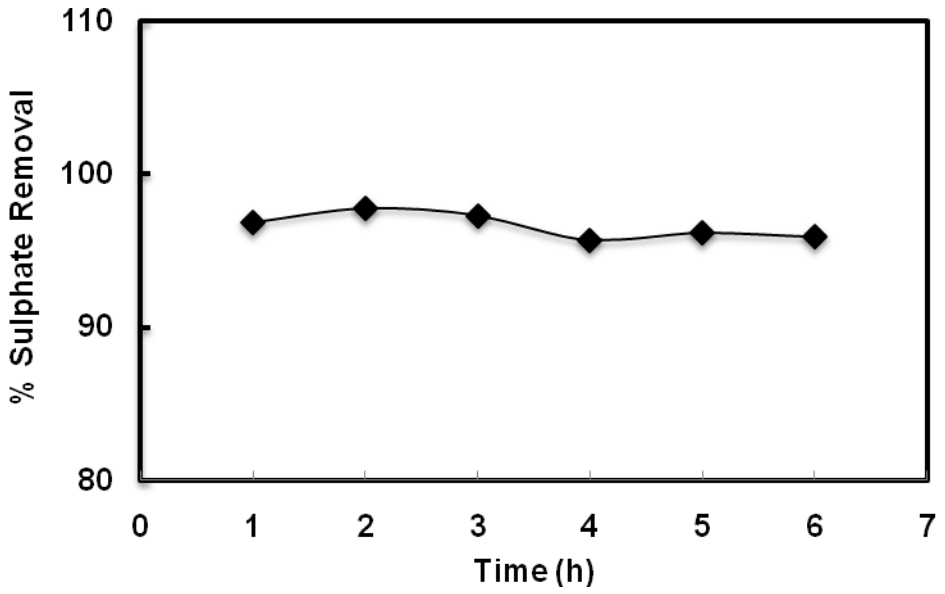

Figure 9 Sulphate Removal Efficiency for DK-NF membrane at 6.9 bar pressure (first trial)

Turbidity removal efficiencies were up to 67% as illustrated in Figure 10. After three hours the experimental run started, there is a considerable increase in the removal percentage of turbidity. When the removal efficiency of sulphate was compared with the removal efficiency of turbidity, sulphate removal percentages seem to become constant at the start of the experimental run. However for turbidity removal percentages, it starts to increase after four hours. The reason for this may be the bigger turbidity causing particles are rejected first and then a second layer is formed which cause higher rejection for smaller turbidity causing particles.

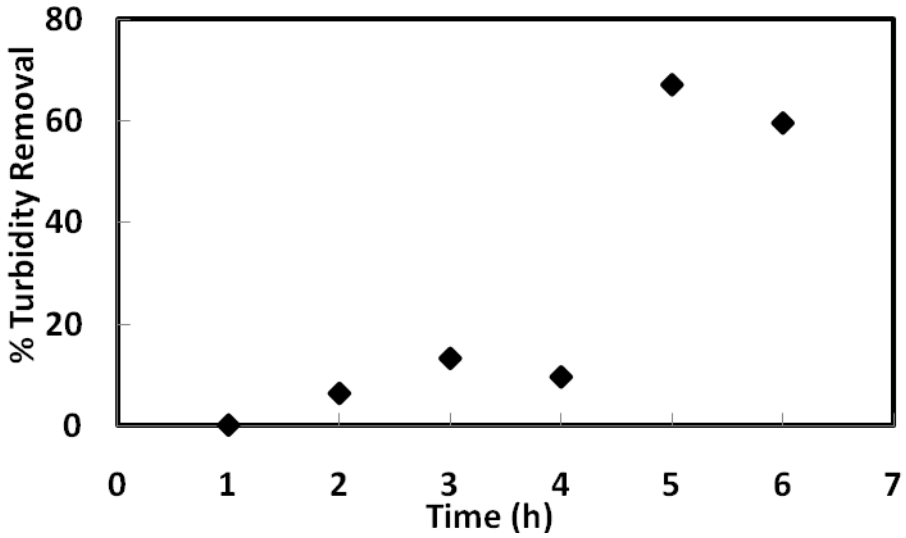

Figure 10 Turbidity removal efficiencies for DK-NF membrane at 6.9 bar pressure (first trial)

In the first trial, very promising removal efficiency of sulphate was achieved, which was around 98%. However the flux values are to be considered to detect if there occurs any fouling problem. If fouling problem exists, fouling type is to be investigated as reversible or irreversible. The flux values are shown in Figure 11.

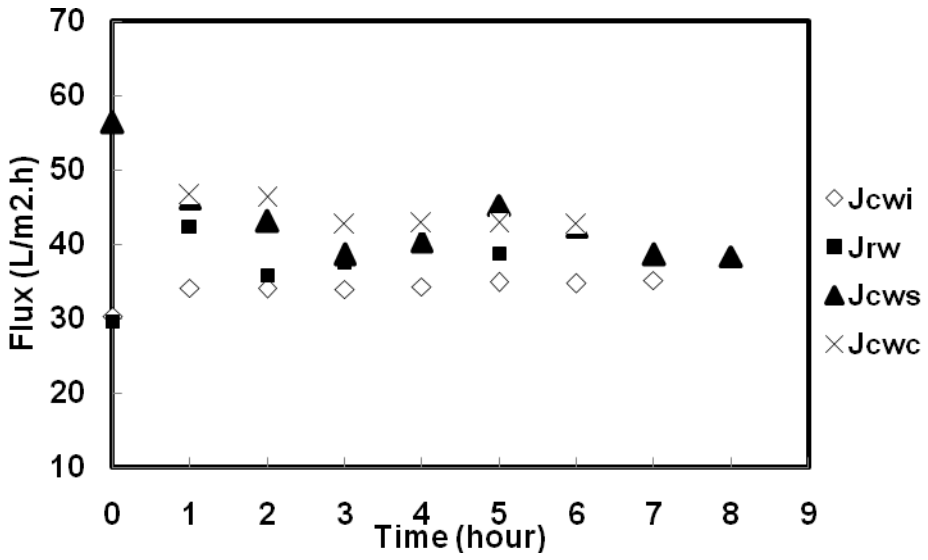

Figure 11 Time-dependent flux values for DK-NF membrane at 6.9 bar pressure and 1.2 m/sec crossflow velocity (first trial)

Steady-state flux values are 35.1 L/m^2.h, 38.7 L/m^2.h, 38.4 L/m^2.h and 42.7 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively. In Table 7 water flux, flux decline and total fouling values at steady-state are shown. Neither flux decline nor fouling was observed in this first trial with DK-NF membrane. Flux decline was only seen at the very start but then it reached steady-state at 38.7 L/m2.h which is higher than the clean water flux before raw water is passed. Therefore no flux decline was observed. Moreover, clean water flux after the cleaning is applied was also increased. The reason for the increase in the clean water flux after cleaning of the membrane may be the permanent swelling or expansion of the membrane pores.

Table 7 Water flux, flux decline and total fouling for DK-NF membrane (first trial) at 6.9 bar pressure, 1.2 m/sec crossflow velocity

*Clean Water Flux (L/m2.h)	35.1
Raw Water Flux (L/m2.h)	38.7
**Clean Water Flux (L/m2.h)	42.7
Flux Decline (%)	No flux decline
Irreversible Fouling (%)	No fouling

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

Since there was no fouling and flux decline, the same experiment was repeated. This time the flux values were 40.4 $L/m^2.h$, 33.3 $L/m^2.h$, 38.0 $L/m^2.h$ and 34.5 $L/m^2.h$ for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively. The flux values of the second DK-NF membrane set can be seen in the Figure 12. As it can be depicted from the figure, raw water flux values go nearly constant while clean water flux values decrease with time. Also raw water flux values are lower than the clean water flux values.

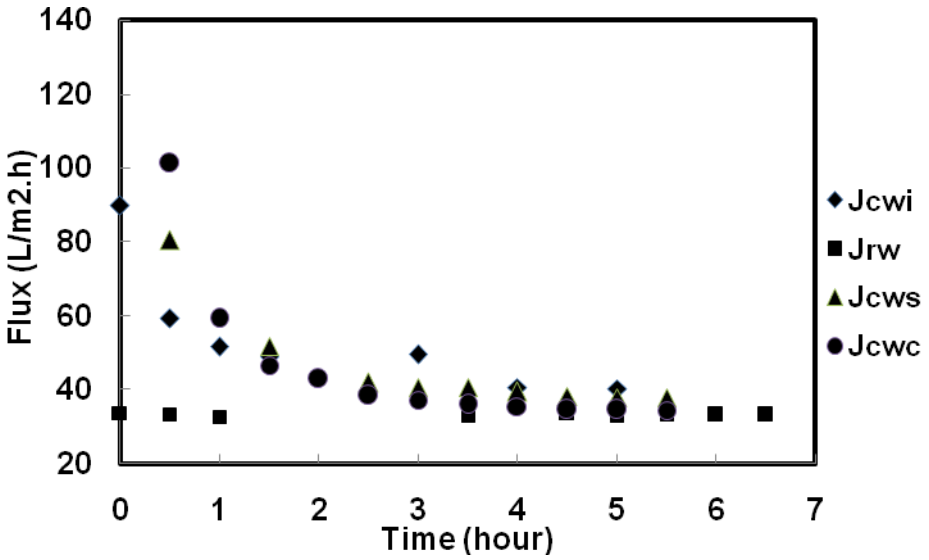

Figure 12 Time-dependent flux values for DK-NF membrane (second trial) at 6.9 bar pressure

Table 8 shows the water flux, flux decline and total fouling. Total flux decline was 18%. It is seen from the steady-state flux values that there is fouling. Total fouling is 15% and it is observed that this is irreversible fouling. Relative raw water flux behavior is presented in Figure 13. Normalized flux value at steady state conditions of DK-NF membrane for the second trial was 0.80.

Table 8 Water flux, flux decline and total fouling for DK-NF membrane (second trial) at 6.9 bar pressure, 1.2 m/sec crossflow velocity

*Clean Water Flux (L/m2.h)	40.4
Raw Water Flux (L/m2.h)	33.3
**Clean Water Flux (L/m2.h)	34.5
Flux Decline (%)	18.0
Irreversible Fouling (%)	15.0

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

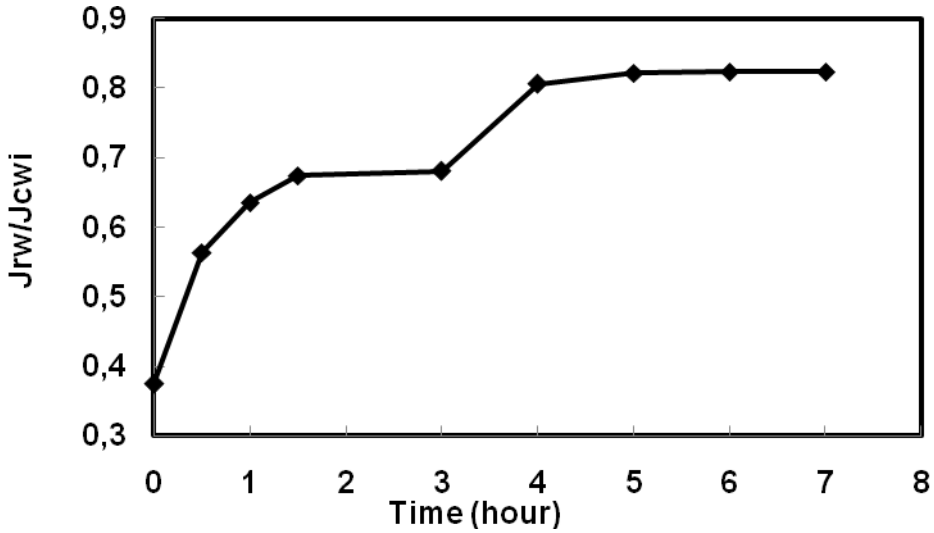

Figure 13 Change in relative flux for DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity (second trial)

Under 6.9 bar pressure and 1.2 m/sec crossflow velocity, 98% sulphate removal efficiency was achieved with DK-NF membrane. Turbidity removal efficiencies were up to 72%. Also conductivity measurements were performed and the removal efficiencies were around 83%.

The sulphate and turbidity removal efficiencies were observed to be nearly same with the first trial, but the membrane was observed to be fouled in the second trial.

The results of the third experiment with DK-NF membrane were not so accurate. Different sulphate removal efficiencies and flux values showed that the results were not good to continue with that membrane. Even the same operational conditions were supplied, the removal efficiency of sulphate, which was around 73%, was not satisfactory regarding the other two experiments done with the same membrane. The relevant data can be found in Appendix A. Also the flux values were not reasonable. The clean water flux values after the raw water fed to the system increases in a considerable amount. This may be due to the fouling of the membrane [9, 11].

Therefore with a new DK-NF membrane under the same operational conditions, the experimental set was re-operated twice. Before starting the experimental set, the new membrane was compressed at 13.8 bar pressure for 24 hours to prevent the possible expansion and contraction of the pores of the membrane during the experimental run. Two experimental runs were conducted. The flux values regarding all of these phases are shown in Figure 14.

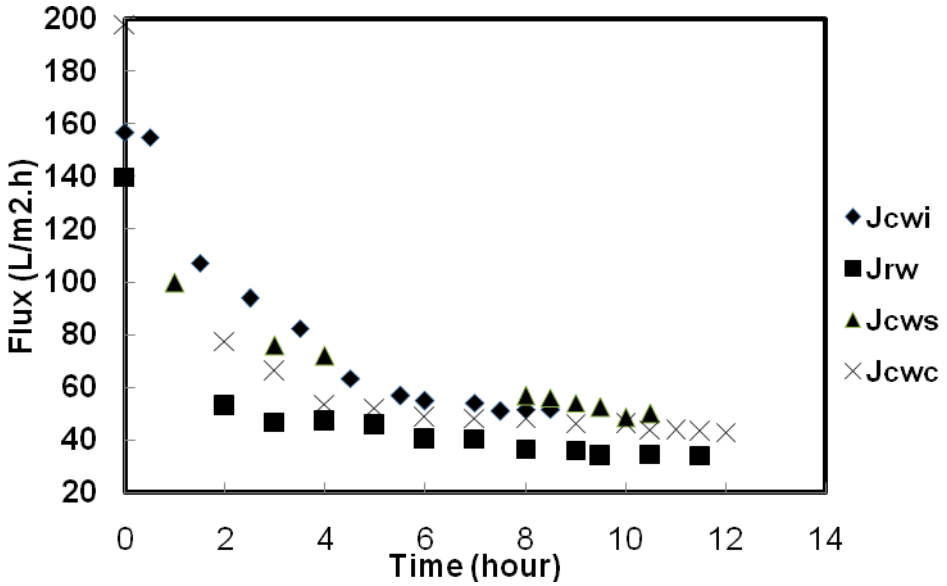

Figure 14 Time-dependent flux values for DK-NF membrane (with another new membrane) at 6.9 bar pressure (third trial)

As can be seen from the Figure 14 and Table 9, fouling percentage is low. Steady-state flux values were 51.6 L/m^2.h, 34.0 L/m^2.h, 49.8 L/m^2.h and 42.9 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively. The flux decline was found to be 34% and the total fouling was around 4%.

Table 9 Water flux, flux decline and total fouling for DK-NF membrane (third trial) at 6.9 bar pressure, 1.2 m/sec crossflow velocity

*Clean Water Flux (L/m2.h)	51.6
Raw Water Flux (L/m2.h)	34.0
**Clean Water Flux (L/m2.h)	42.9
Flux Decline (%)	34.0
Irreversible Fouling (%)	17.0

The sulphate removal was 84% which was lower than the first and second trials conducted with the first DK-NF membrane. Figure 15 shows the sulphate removal efficiencies versus time which is also satisfactory. However there is an unsteady behavior in sulphate removal efficiency. The reason for this may be the layer formation by time on the membrane surface and concentration polarization causes the sulphate removal efficiency to reach a steady-state level after some time is passed.

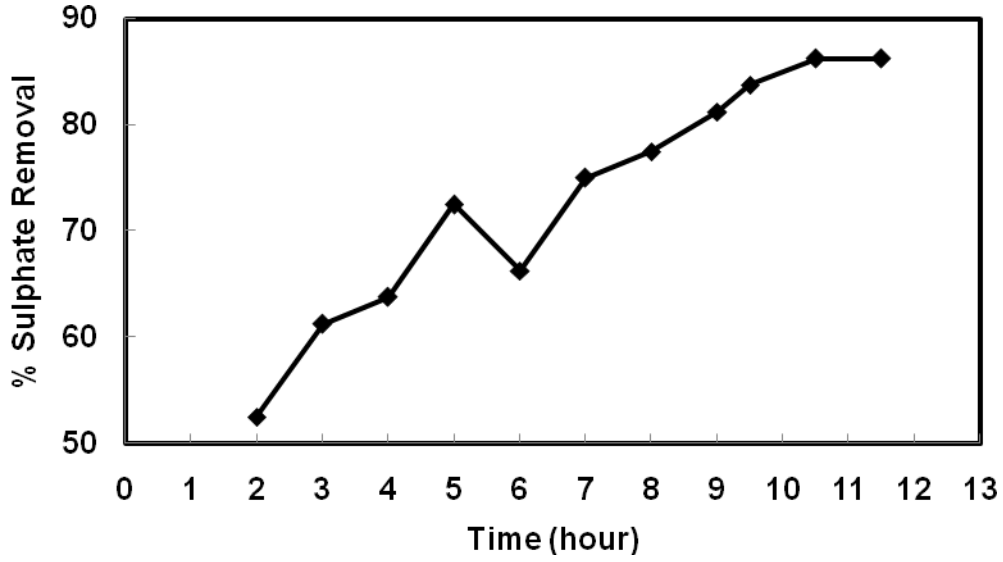

Figure 15 Sulphate removal efficiency values for DK-NF membrane (with another new membrane) at 6.9 bar pressure (third trial)

The removal rates of sulphate and UV_{254} absorbance with respect to the time periods in which permeate samples collected are shown in Table 10. There is a significant decrease in the UV_{254} absorbance levels which shows the organic matter removal from the raw water.

Table 10 Sulphate and UVA_{254} absorbance analysis results with the samples taken at different time periods with DK-NF membrane (with another new membrane) at 6.9 bar pressure

Time (h)	Sulphate (mg/L)	UV_{254}
0	350	0.0253
2	190	0.0147
3	155	0.0083
4	145	0.0066
5	110	0.0023
6	135	0
7	100	0
8	90	0
9	75	0
9.5	65	0
10.5	55	0
11.5	55	0

According to the results of the five experiments conducted with DK-NF, no consistent data was obtained from these experiments. Therefore, DK-NF is decided to be unsuitable for further experiments. The reason of this inconsistency may be the ionic interaction or different fouling mechanisms applied during the experimental run [32]. Also since the membrane is negatively charged, membrane surface may be modified by the chemicals used during cleaning of the membrane. This may cause permanent swelling. Scale formation also causes lower flux values.

5.2 EXPERIMENTS WITH "NF-270" MEMBRANE

There occurred a need for new membrane to conduct experiments with the same operating conditions. In order to meet this demand, "NF-270" (Filmtec Co.) membrane was selected to be used in the experiments. NF-270 membrane has been used in several researches, especially in drinking water treatment process studies [21, 24].

Firstly, compression was applied to the new membrane. Then three experimental runs were conducted in which surface water was fed directly as raw water. Afterwards, another experimental run was carried out in which surface water was first microfiltrated with 2.5 μm filter paper with dead-end filtration and then fed to the system. Therefore two kinds of experimental runs were conducted: experiments conducted with raw surface water and experiments conducted with pretreated surface water, respectively.

The operational conditions were kept the same as the operational conditions in experiments conducted with DK-NF. Transmembrane pressure was 6.9 bars and the cross-flow velocity was kept at 1.2 m/sec. The temperature of the feed water was kept at 20±2^{o}C.

5.2.1 Experiments without Pre-treatment

The first experiment was conducted with a new NF-270 membrane. Therefore the membrane was first compressed for 24 hours with DDW at 13.8 bars to maintain a consistent membrane in further runs.

In Figure 16, the flux values for the first run with NF-270 membrane are shown. Steady-state flux values were 99.7 L/m^2.h, 87.5 L/m^2.h, 97.4 L/m^2.h and 96.7 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively. In Table 9, water flux, flux decline and irreversible fouling can be seen.

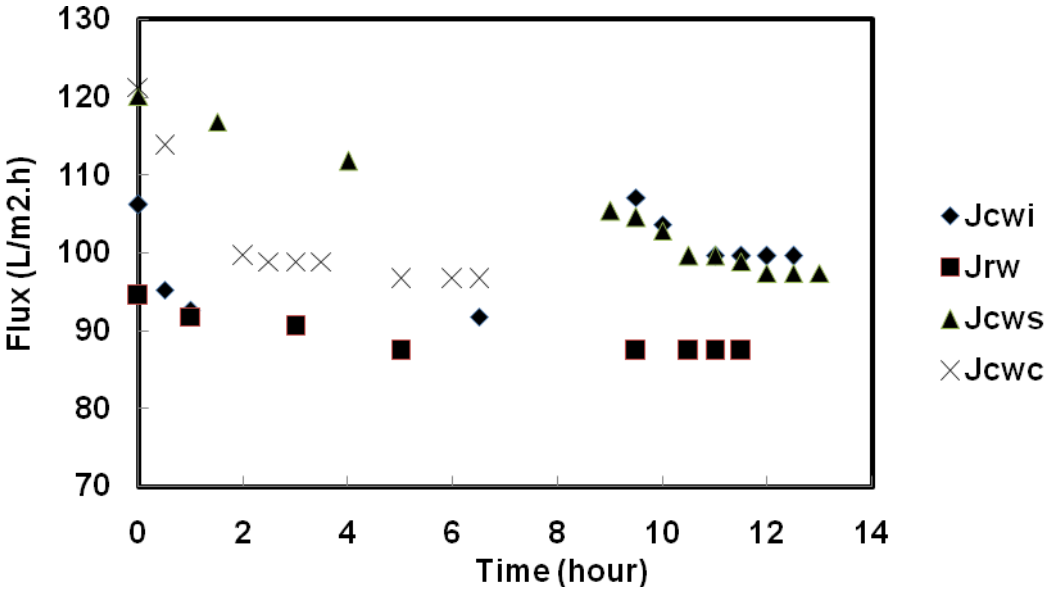

Figure 16 Time-dependent flux values for NF-270 membrane at 6.9 bar pressure and 1.2m/sec cross flow velocity (first trial)

Table 11 Water flux, flux decline and total fouling for NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity (first trial)

*Clean Water Flux (L/m2.h)	99.7
Raw Water Flux (L/m2.h)	87.5
**Clean Water Flux (L/m2.h)	96.7
Flux Decline (%)	12.0
Irreversible Fouling (%)	3.0

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

The flux decline observed in this experimental run was 12% and the fouling ratio was found to be 3.0%. Experimental results of the flux values show that fouling occurred in the membrane, however it is reversible fouling which is thought to result from concentration polarization. The normalized flux values of the permeate samples are shown in Figure 17. Flux decline cannot clearly be seen from this figure.

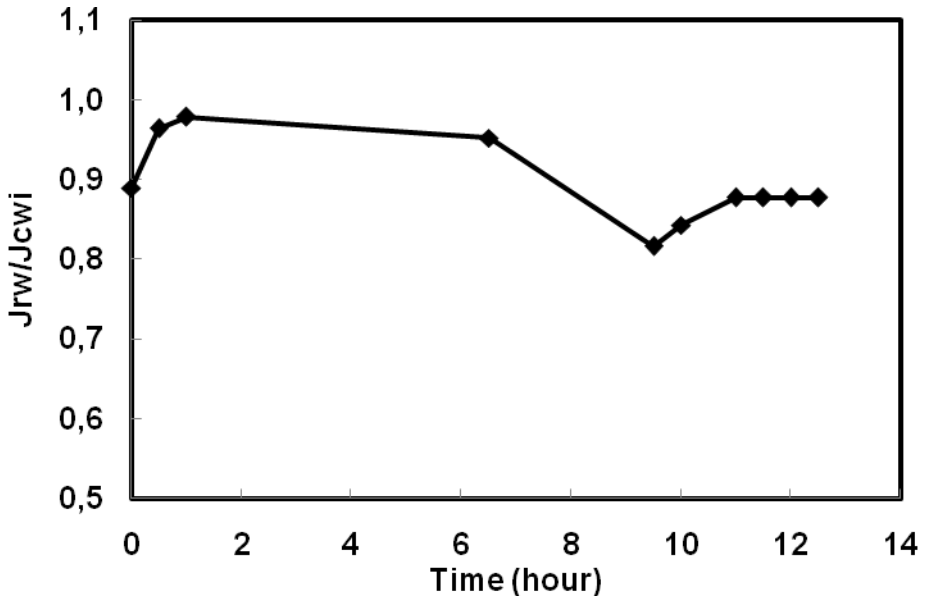

Figure 17 Normalized flux values of the permeate samples for NF-270 membrane at 6.9 bar pressure and 1.2m/sec cross flow velocity (first trial)

Certain parameters were analyzed in order to investigate the removals, and the removal efficiencies for conductivity and sulphate were calculated. The results are shown inTable 12 and Table 13 and characteristics of the permeate samples were evaluated. This evaluation showed a positive result as the UV_{254} absorbance levels are decreasing in great extent while the pH of the samples are maintained nearly the same as the pH of the raw water.

Table 12 Characteristics of raw water and permeate samples taken during NF-270 membrane experimental run at 6.9 bar pressure and 1.2m/sec cross flow velocity (first trial)

Time (hour)	Sulphate (mg/L)	Conductivity (µS/cm)	UVA_{254}	pH	Temp (^oC)	DOC (mg/L)
Raw Water	420	1473	0.0276	8.20	15.3	2.92
1.0	8	572	0.0072	8.22	14.6	
3.0	9	576	0	8.20	15.1	
5.0	8	572	0.0001	8.20	15	2.57
9.5	7	579	0.0001	8.20	16.5	
10.5	6	580	0.0015	8.18	17.1	
11.0	7	578	0	8.19	17.2	
11.5	7	581	0	8.19	17.5	

Table 13 Sulphate and conductivity removal efficiencies for NF-270 membrane experimental run at 6.9 bar pressure and 1.2m/sec cross flow velocity (first trial)

Time (hour)	Sulphate Removal (%)	Conductivity Removal (%)
0.0	98.1	61.1
1.0	98.1	61.2
3.0	97.9	60.9
5.0	98.1	61.2
9.5	98.3	60.7
10.5	98.6	60.6
11.0	98.3	60.8
11.5	98.3	60.6

When the sulphate removal efficiencies of NF-270 and DK-NF membrane are compared, it is seen that the efficiencies are very much similar to the first two experiments conducted with DK-NF membrane and the removal rates are promising. The extent of the conductivity removal efficiency is also high since it shows the removal of the dissolved solids that cause conductivity levels to increase, which is also very important in drinking water applications.

Since promising results were derived from the first experimental run under those operational conditions with NF-270 membrane, the second experiment conducted with the same membrane and the operational conditions were the same as the first experimental run. Transmembrane pressure was 6.9 bars and the cross-flow velocity was kept at 1.2 m/sec. The temperature of the feed water was kept at 20±2^{o}C.

In Figure 18 and Table 14, the flux values of all phases are shown. Steady-state flux values were 96.7 L/m^2.h, 85.7 L/m^2.h, 90.5 L/m^2.h and 90.5 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively.

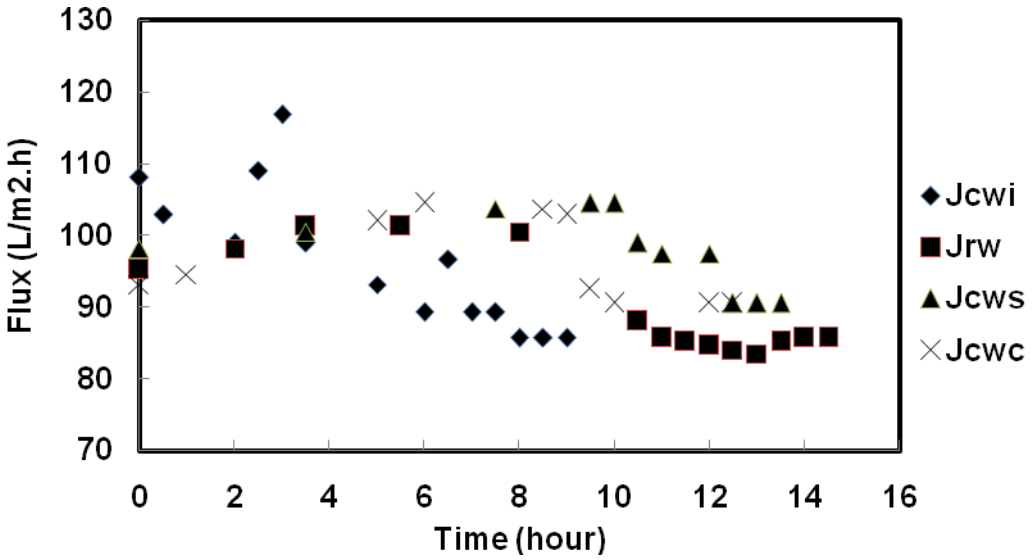

Figure 18 Time-dependent flux values for NF-270 membrane at 6.9 bar pressure (second trial)

In Table 14, steady-state flux values are shown and there is 6.4% fouling. Raw water flux decline is 11.4%. From the Figure 18 it is obvious that there is fouling problem, but it is reversible. No irreversible fouling is observed from the permeate flux values. The reasons for the fouling can be the ionic interaction, scale formation and pore blockage [9, 11].

Table 14 Water flux, flux decline and total fouling for NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity (second trial)

*Clean Water Flux (L/m2.h)	96.7
Raw Water Flux (L/m2.h)	85.7
**Clean Water Flux (L/m2.h)	90.5
Flux Decline (%)	11.4
Irreversible Fouling (%)	6.4

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

During the experimental run, permeate samples were collected and certain parameters were analyzed in order to notice when the steady-state conditions are reached and also to notice the sulphate and conductivity removal efficiencies. The parameters analyzed from the permeate samples were sulphate, conductivity, UV absorbance, pH and temperature. The results of the experimental analysis done on the permeate samples that were collected in certain time periods are shown in Table 15.

Table 15 Analysis results of the permeate and raw water samples taken during NF-270 membrane experimental run at 6.9 bar pressure (second trial)

	Time (hour)	Sulphate (mg/L)	Conductivity (µS/cm)	UVA	pH	Temp (^{o}C)
Raw Water		420	1521	0.0240	8.21	22.4
T0	0	8	592	0.0037	7.90	22.6
T1	2.0	8	535	0	7.92	22.7
T2	3.5	8	540	0	7.82	22.8
T3	5.5	8	537	0	7.75	22.6
T4	7.5	8	543	0	7.74	22.7
T5	10.5	8	533	0	7.77	22.8
T6	12.5	8	544	0	7.72	22.8
T7	14.0	8	536	0	7.70	22.8
T8	14.5	8	530	0	7.71	22.9

From the experimental results, it is seen that pH decreased slightly in the permeate samples compared to the pH values of the raw water. The reason for this may be the ionic interaction through the surface of the membrane due to the accumulation of anions at the membrane surface.

UV absorbance decreased drastically showing the efficient removal of organic matter. Moreover, sulphate and conductivity decreased as well. In Table 16, removal rates of sulphate and conductivity are shown.

Table 16 Sulphate and conductivity removal efficiencies for NF-270 membrane experimental run at 6.9 bar pressure (second trial)

Time (hour)	Sulphate Removal (%)	Conductivity Removal (%)
0	98.1	61.08
2	98.1	64.83
3.5	98.1	64.50
5.5	98.1	64.69
7.5	98.1	64.30
10.5	98.1	64.96
12.5	98.1	64.23
14	98.1	64.76
14.5	98.1	65.15

The removal of sulphate efficiency is promising; it is quite similar to the removal ratio of sulphate in the first experiment conducted with NF-270. In Figure 19 and Figure 20, the removals of sulphate and conductivity, can respectively be seen.

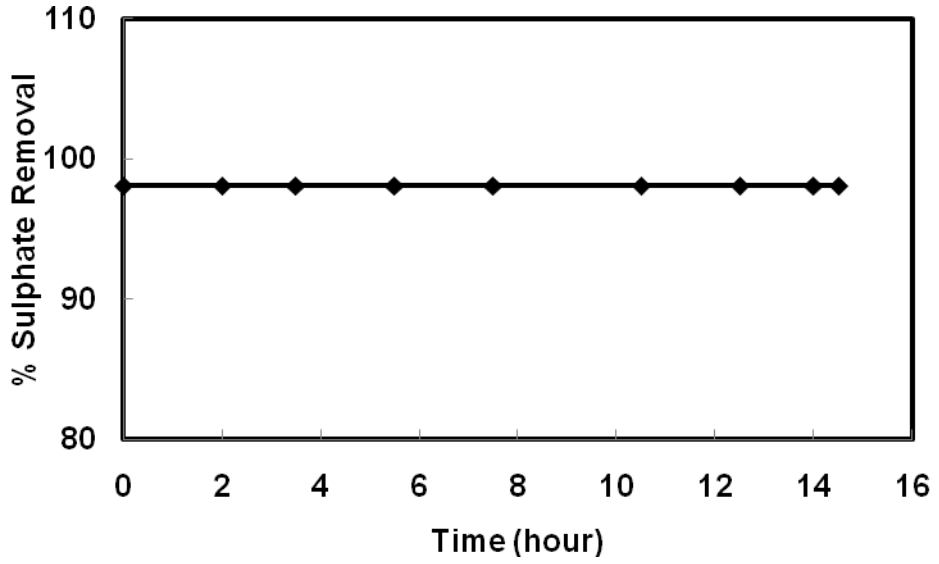

Figure 19 Sulphate removal efficiency values for NF-270 membrane (second trial) at 6.9 bar pressure

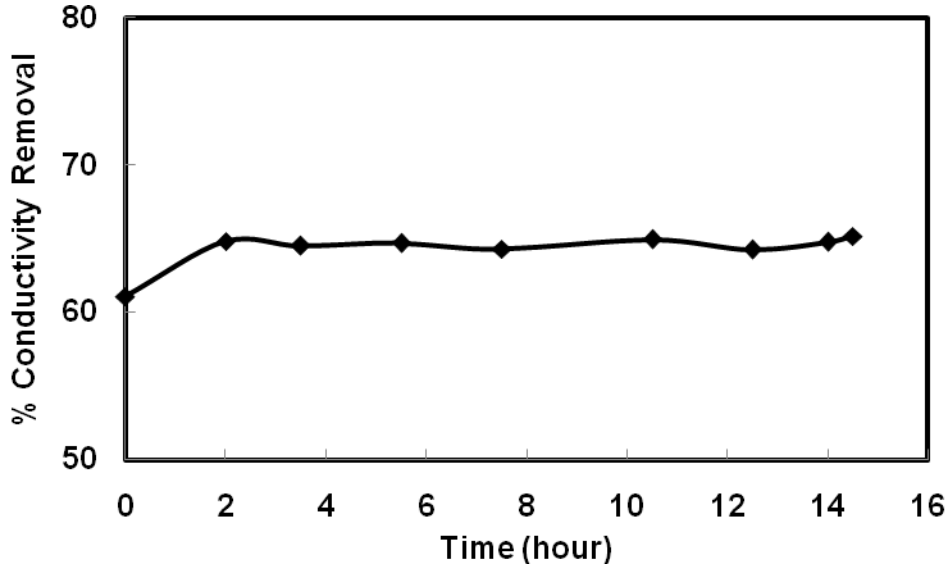

Figure 20 Conductivity removal efficiencies for NF-270 membrane (second trial) at 6.9 bar pressure

To be able to ensure the performance of the NF-270 membrane under the same operational conditions, another experiment with NF-270 membrane under the same operating conditions was carried out. Experimental conditions were fixed at a transmembrane pressure of 6.9 bars and a cross-flow velocity of 1.2 m/sec. The temperature of the feed water was kept at 20±2^{o}C by circulating the tap water and measurements of the feed water temperature was done periodically.

In Figure 21, changes in flux values of all phases with respect to time are shown. As can be seen from the graph, the related flux data was collected for more than 15 hours.

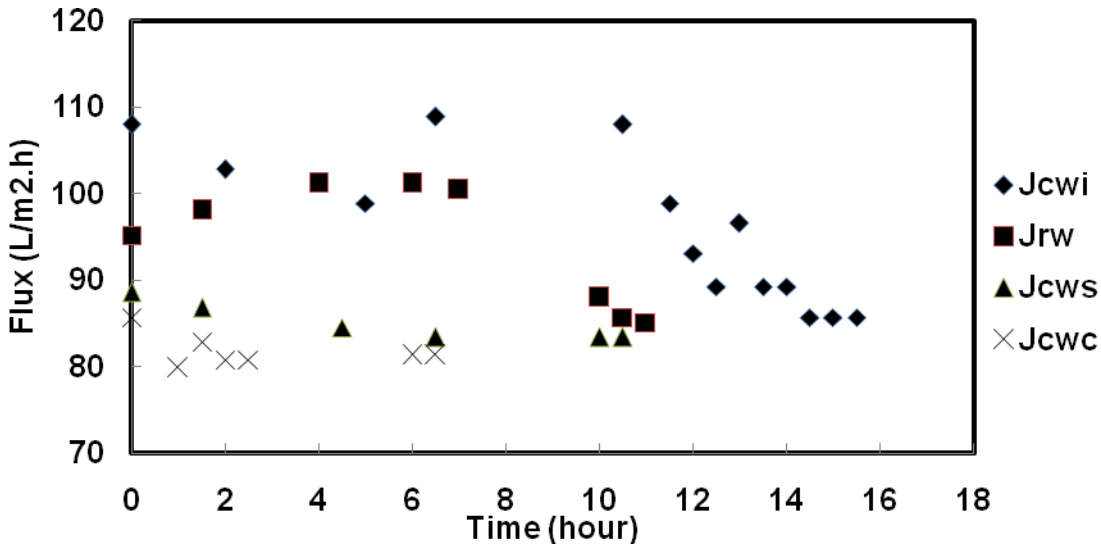

Figure 21 Time-dependent flux values for NF-270 membrane at 6.9 bar pressure (third trial)

Steady-state flux values were 85.7 L/m^2.h, 85.1 L/m^2.h, 83.5 L/m^2.h and 81.4 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively. In Table 17, steady-state flux values together with flux decline and fouling values are shown.

Table 17 Water flux, flux decline and total fouling for NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity (third trial)

*Clean Water Flux (L/m2.h)	85.7
Raw Water Flux (L/m2.h)	85.1
**Clean Water Flux (L/m2.h)	83.5
Flux Decline (%)	0.7
Irreversible Fouling (%)	2.6

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

Raw water flux decline was 0.7% and the fouling ratio was 5% in this experimental run. From the flux data graph, it can be seen that there is fouling, which is both reversible and irreversible and may be due to concentration polarization.

In Table 18, the results from the analysis conducted on the permeate samples are shown. The parameters analyzed in the permeate samples were sulphate, conductivity, UV absorbance, pH and temperature.

Table 18 Analysis results of the permeate and raw water samples taken during NF-270 membrane experimental run at 6.9 bar pressure (third trial)

	Time (hour)	Sulphate (mg/L)	Conductivity (µS/cm)	UVA	pH	Temp (^{o}C)
Raw Water		460	1662	0.0210	8.25	20.2
T0	0	10		0	8.01	21.0
T1	1.5	12	508	0	7.35	20.3
T2	4	12	512	0	7.37	20.3
T3	6	10	500	0	7.36	20.0
T4	7	12	507	0	7.34	20.0
T5	10.5	12	530	0	7.21	20.2

It can be seen from the experimental analysis of the raw water and permeate samples that pH also decreased, which may be due to the ionic interaction through the surface of the membrane or the accumulation of anions at the membrane surface. Furthermore, considering the UV absorbance, it could be seen that it becomes zero starting from the initiation of the experimental run, with the first permeate sample collected. There is also a satisfactory decrease in sulphate and conductivity levels. In Table 19, the efficiency of the removal of sulphate and conductivity are shown, regarding the permeate sample collection periods.

Table 19 Sulphate and conductivity removal efficiencies for NF-270 membrane experimental run at 6.9 bar pressure (third trial)

Time (hour)	Sulphate Removal (%)	Conductivity Removal (%)
0.0	97.8	
1.5	97.1	66.6
4.0	97.1	66.3
6.0	97.6	67.1
7.0	97.1	66.7
10.5	97.1	65.2

In Figure 22 and Figure 23, the removal rates of sulphate and conductivity, respectively can be seen. Sulphate removal efficiency is 97.1% which is nearly similar to the other first two trials done with NF-270 membrane. Also conductivity removal efficiency is 65.2% which is also comparable to the first two experimental runs with NF-270 membrane.

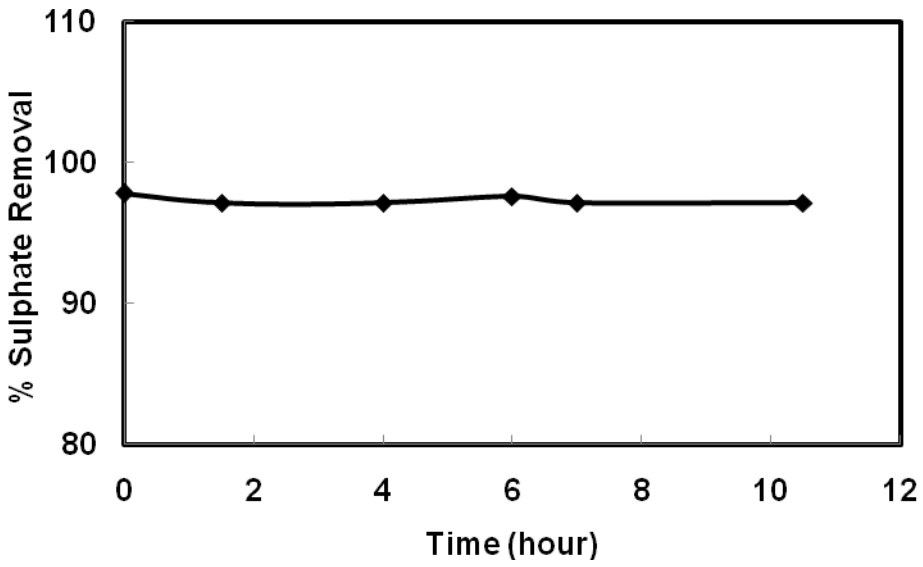

Figure 22 Sulphate removal efficiency values for NF-270 membrane (third trial) at 6.9 bar pressure

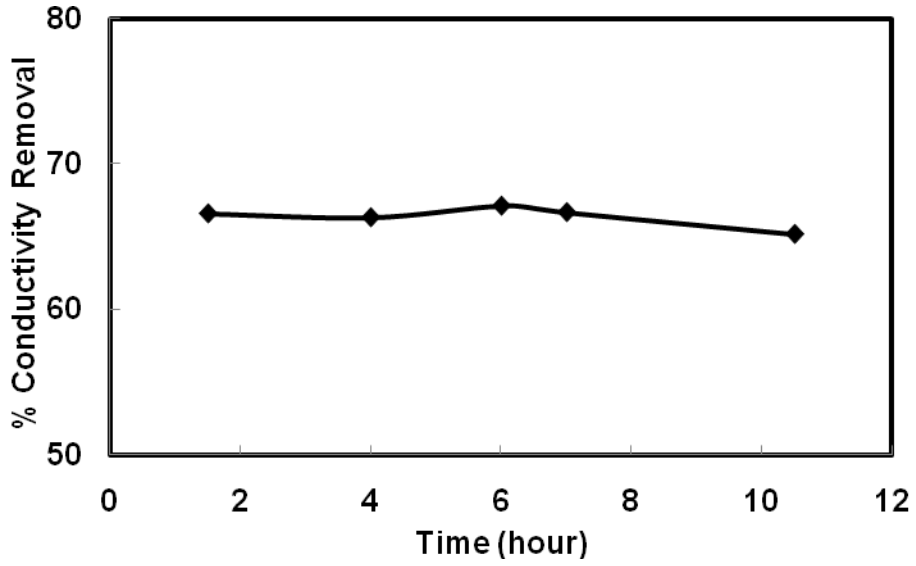

Figure 23 Conductivity removal efficiencies for NF-270 membrane (third trial) at 6.9 bar pressure

Considering all these data collected with NF-270 membrane, reversible flux decline may be because of the fouling of the membrane or the reason may be the osmotic pressure effect. If the osmotic pressure increases, then the flux declines and concentration polarization is responsible for the decline in water flux due to the increased osmotic pressure.

Since all those experimental runs were done by feeding the surface water directly to the system, a new approach was developed and applied. Therefore applying pre-treatment before nanofiltration run was decided since pretreatment is an effective way of solving fouling problem which is a common problem in membrane filtration treatment applications. Microfiltration before nanofiltration is applied for this purpose.

5.2.2 Experiments with Pre-treatment

For pre-treatment, microfiltration was selected. Filtration with 2.5 μm pore size was employed for the microfiltration in dead-end filtration mode. Then, the pretreated raw water was fed to the system as feed water for further treatment with nanofiltration. In Table 20, the characteristics of raw water before microfiltration and after microfiltration are given. The microfiltration pretreatment affected the UV_{254} absorbance levels which caused a decrease at nearly half amount. UV_{254} absorbance levels decreased due to the removal of the organic matter. Conductivity is mainly because of the ions like sulphate, etc. Since sulphate was decreased only a little, there is also no expectation of a decrease in the conductivity levels which is supported by the analysis results shown in Table 20.

Table 20 Analysis results of raw water before and after microfiltration with 2.5 µm filter paper

	pH	Temp (^oC)	Conductivity (µS/cm)	Sulphate (mg/L)	UVA_{254}
Before MF (2.5 µm)	8.5	20	1651	420	0.0166
After MF (2.5 µm)	8.5	20	1643	400	0.0088

The same procedure was applied for nanofiltration run. The only difference was the feed water which was microfiltrated with 2.5 µm filter paper in dead-end filtration. Experimental conditions were fixed at a transmembrane pressure of 6.9 bars and a cross-flow velocity of 1.2 m/sec. The temperature of the feed water was kept at 20±2^oC by circulating the tap water and measurements of the feed water temperature was done periodically.

In Figure 24, the flux changes versus time are shown for all phases together.

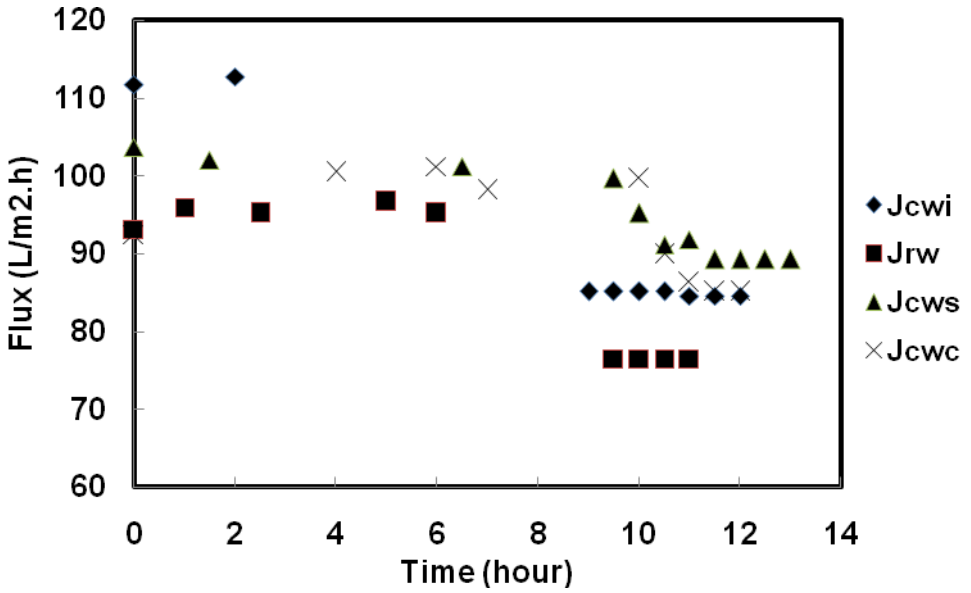

Figure 24 Time-dependent flux values for NF-270 membrane fed with microfiltrated raw water at 6.9 bar pressure, 1.2 m/sec crossflow velocity

Steady-state flux values were 84.6 L/m^2.h, 76.5 L/m^2.h, 89.3 L/m^2.h and 85.1 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively. In Table 21, water fluxes, flux decline and fouling is shown for both experiments conducted with and without microfiltrated raw water with NF-270 membrane at 6.9 bar pressure and 1.2 m/sec crossflow velocity.

Table 21 Water flux, flux decline and total fouling for NF-270 membrane with and without microfiltrated raw water at 6.9 bar pressure, 1.2 m/sec crossflow velocity

	With Microfiltrated Raw Water	**With Raw Water**
***Clean Water Flux (L/m2.h)**	84.6	96.7
Raw Water Flux (L/m2.h)	76.5	85.7
****Clean Water Flux (L/m2.h)**	85.1	90.5
Flux Decline (%)	9.6	11.4
Irreversible Fouling (%)	No fouling	6.4

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

Raw water flux decline is 9.6%. As seen from the flux values, no fouling is observed; neither reversible fouling nor irreversible fouling. There is a good evidence that when the system is fed with microfiltrated raw water, then no fouling was observed when compared with the experimental run fed with directly raw water. Therefore, it seems that MF pretreatment is meaningful in terms of resolving fouling problems. However, sulphate removal efficiencies and water characteristics of the permeate samples are also important for this research. In Table 22, raw water and permeate samples' characteristics are shown.

Table 22 Analysis results of the permeate and raw water samples taken during NF-270 membrane experimental run with microfiltrated raw water at 6.9 bar pressure

	Time (hour)	Sulphate (mg/L)	Conductivity (µS/cm)	UVA	pH	Temperature (^{o}C)
Raw Water		410	1545	0.0556	8.5	16.6
T0	0.0	5	77.8	0	7.4	19.7
T1	1.0	6	537	0	7.41	19.6
T2	2.5	6	538	0	7.6	19.6
T3	5.0	4	534	0	7.63	19.4
T4	6.0	3	534	0	7.63	19.4
T5	9.5	3	524	0	7.62	19.6
T6	11.0	3	555	0	7.67	19.7

From the Table 22, it is noticed that in permeate samples, UV absorbance levels could not be measured which shows a considerable decrease in organic matter content. pH is observed to decrease compared to the raw water and feed water pH data which may be due to ionic interaction or anion accumulation at the membrane surface. Therefore, there is no difference with the levels of UV absorbance and pH when compared to the results of the experimental set that was run by directly feeding with surface water without pretreatment.

In Table 23, sulphate and conductivity removal rates are given.

Table 23 Sulphate and conductivity removal efficiencies for NF-270 membrane experimental run with microfiltrated raw water at 6.9 bar pressure

Time (hour)	Sulphate Removal (%)	Conductivity Removal (%)
0.0	98.8	
1.0	98.5	65.2
2.5	98.5	65.2
5.0	99.0	65.4
6.0	99.3	65.4
9.5	99.3	66.1
11.0	99.3	64.1

As can be seen from Table 23, especially sulphate removal rates are affirmative, since it is around 99.3%. Conductivity removal rates are satisfactory, as well. Both sulphate and conductivity removal efficiencies are comparable to the experimental run results done with the raw surface water without microfiltration. Sulphate removal efficiency for the experimental run without microfiltration was 98.6% at most and was 99.3% for the experimental run with microfiltrated raw water. Both experimental runs were conducted with NF-270 membrane. For conductivity removal efficiencies, 61.2% removal was achieved with the experimental run without microfiltration while the experimental run with microfiltrated raw water reached 66.1% removal. Therefore very similar removal efficiencies were achieved in terms of sulphate and conductivity parameters. In Figure 25 and Figure 26, sulphate and conductivity removal rates are shown, respectively.

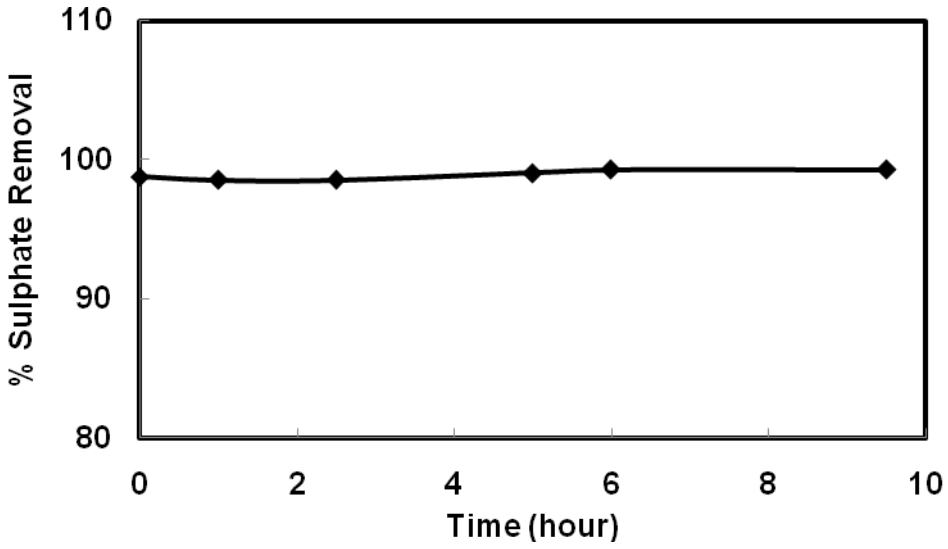

Figure 25 Sulphate removal efficiency values for NF-270 membrane experimental run with microfiltrated raw water at 6.9 bar pressure, 1.2 m/sec crossflow velocity

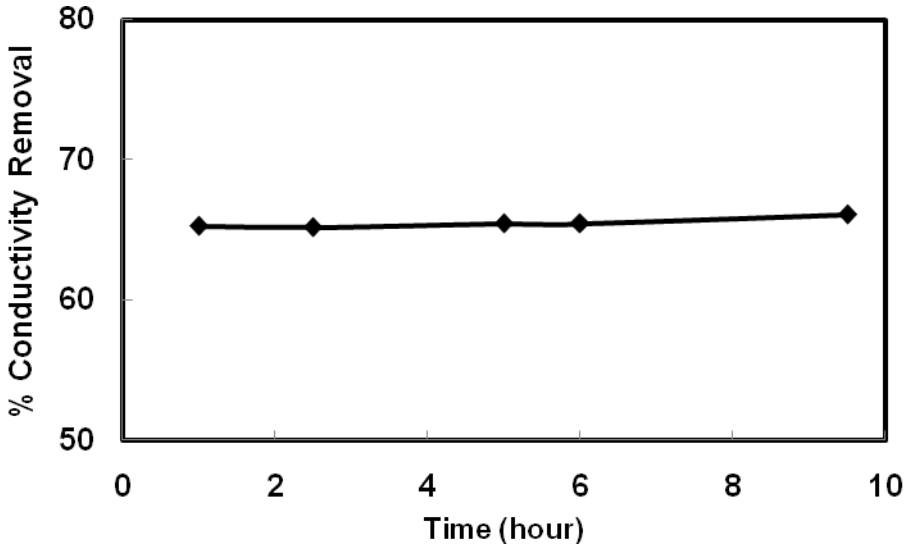

Figure 26 Conductivity removal efficiency values for NF-270 membrane experimental run with microfiltrated raw water at 6.9 bar pressure, 1.2 m/sec crossflow velocity

Microfiltration was decided to be effective (Table 23) in terms of preventing the fouling problem and achieving the satisfactory removal rates of sulphate and conductivity.

Parametric study was not conducted with NF-270 membrane, since microfiltration pretreatment was needed for NF-270 membrane to have a stable performance. Therefore, experimental sets with another nanofiltration membrane were conducted to search for a membrane which does not require pretreatment.

5.3 EXPERIMENTS WITH "DL-NF" MEMBRANE

A new membrane was selected to see as if it is effective when it is run without pretreatment. DL-NF membrane (GE/Osmonics) was preferred for this trial.

5.3.1 Experiments without Pretreatment

In this experimental run, DL-NF was selected and fed directly with surface water, without pretreatment.

The membrane was first compressed for 24 hours with DDW at 13.8 bars as it was done before for the membranes that were to be used for the first time in the experiments. The reason was for maintaining the consistency of experimental runs.

Experimental conditions were fixed at a transmembrane pressure of 6.9 bars and a cross-flow velocity of 1.2 m/sec. The temperature of the feed water was kept at 20±2^{o}C by circulating the tap water and measurements of the feed water temperature was done periodically. The flux changes versus time are illustrated in Figure 27.

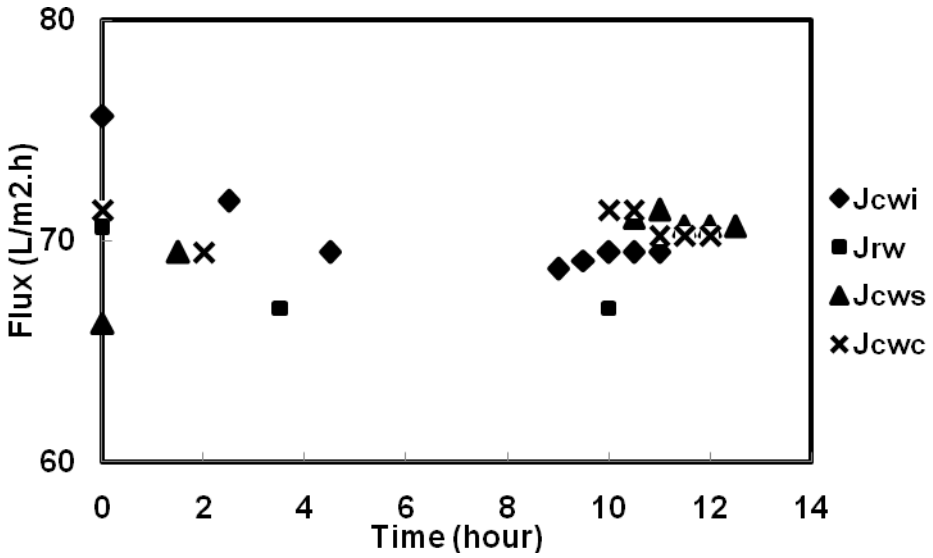

Figure 27 Time-dependent flux values for DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity with raw water

Steady-state flux values were 69.5 L/m^2.h, 67.0 L/m^2.h, 70.6 L/m^2.h and 70.3 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively. As can be seen from Table 24, there is no fouling in this experimental run and the raw water flux decline value is 3.6%.

Table 24 Water flux, flux decline and total fouling for DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity with raw water

*Clean Water Flux (L/m2.h)	69.5
Raw Water Flux (L/m2.h)	67.0
**Clean Water Flux (L/m2.h)	70.3
Flux Decline (%)	3.6
Irreversible Fouling (%)	No fouling

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

Table 25 shows the analysis results for the characteristics of permeate samples and raw water.

Table 25 Analysis results of the permeate and raw water samples taken during DL-NF membrane experimental run at 6.9 bar pressure

	Time (hour)	Sulphate (mg/L)	Conductivity (µS/cm)	UVA	pH	Temp (^{o}C)
Raw Water		380	1469	0.0374	8.02	18.2
T0	0.0	6	670	0.0088	7.83	18.2
T1	3.5	5	675	0.0061	7.7	18.2
T2	10.0	5	678	0.0072	7.69	18.4

As can be depicted from Table 17, there is a considerable decrease in sulphate, conductivity and UVA levels of the water when filtered with DL-NF membrane at 6.9 bar pressure. Also, the pH of the permeate from DL-NF membrane is lower than the pH of the raw water of the feed water which can be again explained by the anionic accumulation at the membrane surface. Decrease in UVA levels may be explained by the organic matter removal ability of NF membranes

Table 26 Sulphate and conductivity removal efficiencies for DL-NF membrane experimental run at 6.9 bar pressure

Time (hour)	Sulphate Removal (%)	Conductivity Removal (%)
0.0	98.4	
3.5	98.7	54.1
10.0	98.7	53.8

Sulphate and conductivity removals achieved are given in Table 26. As seen, favorable results were achieved for the removal of sulphate which are very much comparable to the NF-270 membrane performance. However, there is a slight decrease in conductivity removal efficiency of DL-NF membrane when compared with the removal efficiency of NF-270 membrane. This shows there is a slight decrease in the removal of organic matter. In Figure

28, the graph for the removal efficiency is shown. The removal efficiency of sulphate and conductivity was around 98.7% and 53.8%, respectively. The removal efficiencies became constant at the start of the experimental run as can be depicted from Figure 28.

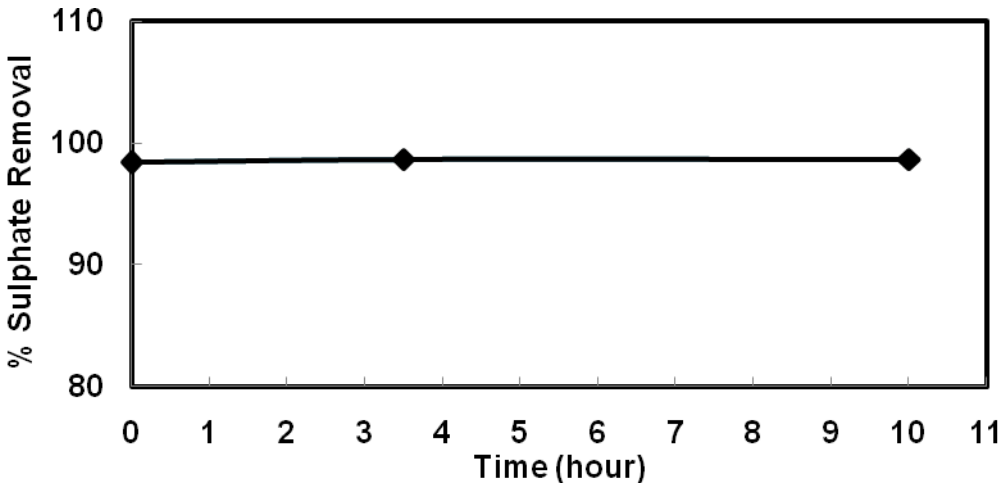

Figure 28 Sulphate removal efficiency values for DL-NF membrane experimental run at 6.9 bar pressure, 1.2 m/sec crossflow velocity with raw water

DL-NF membrane was found to be promising in terms of removal efficiencies and fouling problem. Therefore, a need to see the effects of microfiltration before nanofiltration was in consideration and a new set of experiment with a new DL-NF membrane was run with microfiltration pretreatment of surface water before it was fed into the system to see the effects of microfiltration on flux values and removal efficiencies of sulphate and conductivity.

5.3.2 Experiments with Pre-treatment

2,5 µm filters were employed for the MF. Dead-end filtration was done as a pre-treatment. Then, the pretreated raw water was fed to the system as feed water for further treatment with nanofiltration. The characteristics of raw water before microfiltration and after microfiltration could be seen in Table 20.

The same experimental conditions with the first experiment conducted with DL-NF membrane fed with raw surface water were provided. A transmembrane pressure of 6.9 bars and a cross-flow velocity of 1.2 m/sec were applied. The temperature of the feed water was kept at 20±2^{o}C by circulating the tap water and measurements of the feed water temperature was done periodically.

Flux values of all phases are shown in Figure 29. Steady-state flux values were 68.8 L/m^2.h, 60.6 L/m^2.h, 67.0 L/m^2.h and 68.0 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively.

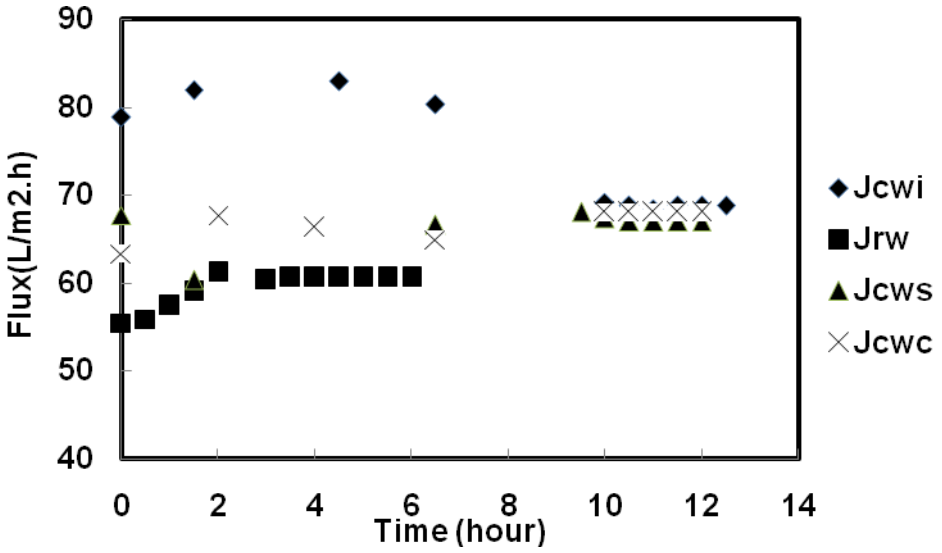

Figure 29 Time-dependent flux values for DL-NF membrane conducted with pretreated raw water at 6.9 bar pressure

From the flux values, it can be understood that microfiltration was effective and no fouling is observed. In terms of fouling, the experimental run was successful; however removal efficiencies are also important. Removal efficiencies of sulphate and conductivity were also determined.

The characteristics of permeate samples and microfiltrated raw water are given in the Table 27.

Table 27 Analysis results of the permeate and raw water samples taken during DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure

	Time (hour)	Sulfate (mg/L)	Conductivity (µS/cm)	UVA	PH	Temp (^{o}C)
Raw Water		400	1389	0.0294	8.02	12.7
T0	0.0	6	19.85	0.0045	8.02	12.7
T1	1.0	6	640	0	7.40	12.8
T2	3.0	7	652	0	7.35	12.6
T3	5.0	6	654	0	7.23	13.0
T4	6.0	6	654	0	7.26	12.9

It can be seen from the Table 27 that pH values is lower than the pH values of raw water and feed water. It may be explained by the anionic accumulation at the membrane surface. Also, an important sharp decrease is noticed in UV absorbance levels which mean a considerable removal in organic matter content. Conductivity and sulphate levels also decreased as can be seen from the Table 28.

Table 28 Sulphate and conductivity removal efficiencies for DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure

Time (hour)	Sulphate Removal (%)	Conductivity Removal (%)
0.0	98.5	
1.0	98.5	53.1
3.0	98.3	53.1
5.0	98.5	52.9
6.0	98.5	52.9

From the Figure 30 and Figure 31, the time dependent sulphate and conductivity removals, respectively can be seen. 98.5% sulphate removal efficiency is satisfactory and in terms of conductivity removal rate, 52.9% is also affirmative. These removal efficiencies are also very similar to the removal efficiencies achieved with the experimental run with DL-NF

membrane with non-pretreated surface water and NF-270 membrane both with and without pretreated surface water.

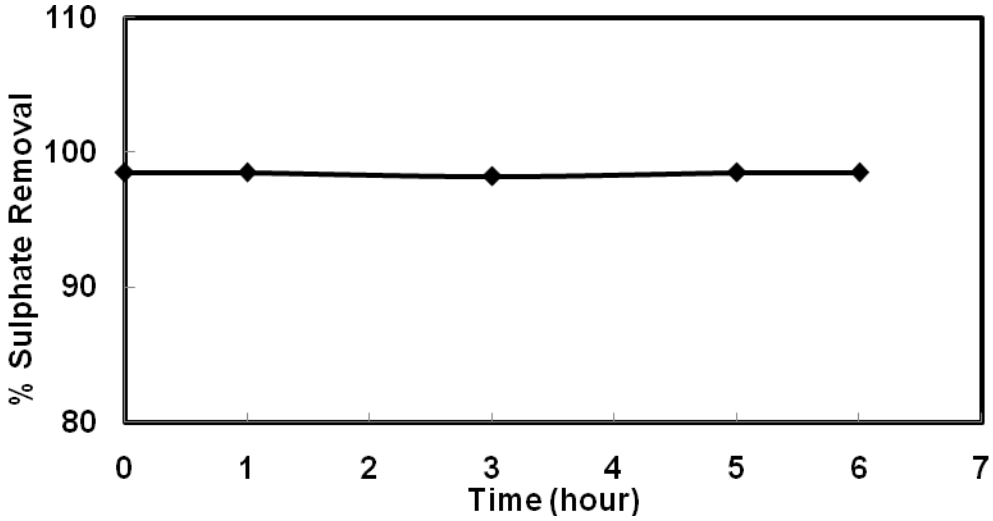

Figure 30 Sulphate removal efficiency values for DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure

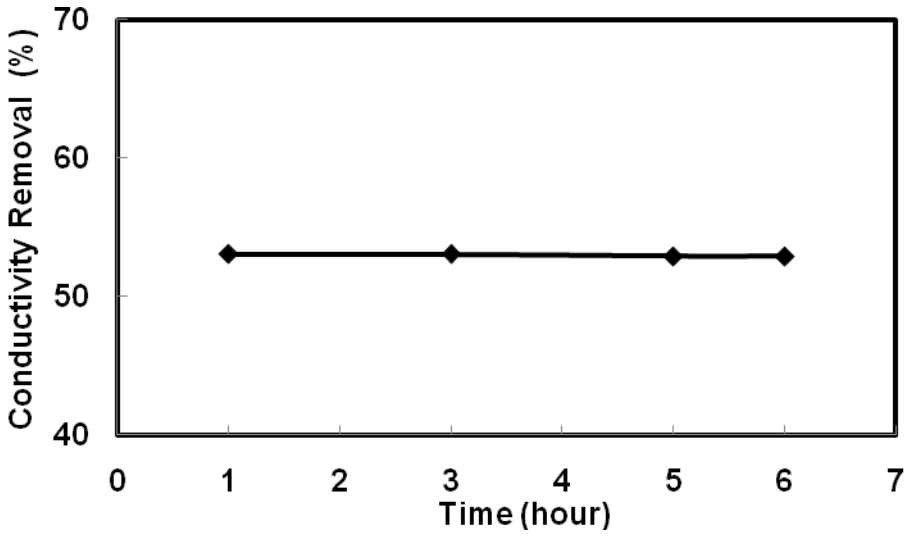

Figure 31 Conductivity removal efficiency values for DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure

In this experimental run with microfiltration pretreatment, no fouling is observed and high removal rates of sulphate and organic molecules were reached which is also promising in terms of both removal efficiencies and prevented fouling problem.

Table 29 Comparison of the results with raw and microfiltrated raw water at 6.9 bar pressure and 1.2 m/sec crossflow velocity

	DL-NF with Raw Water	**DL-NF with Microfiltrated Raw Water**
*Clean Water Flux (L/m2.h)	69.5	68.8
Raw Water Flux (L/m2.h)	67.0	60.6
**Clean Water Flux (L/m2.h)	70.3	68.0
Flux Decline (%)	3.6	11.9
Irreversible Fouling (%)	No fouling	No Fouling

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

As can be seen from the Table 29, there is no irreversible fouling for both runs conducted with raw and microfiltrated raw water. This shows the membrane is appropriate for further runs. However there is an interesting result with the flux decline values that flux decline was increased in the run conducted with microfiltrated raw water.

5.4 EFFECT OF OPERATING PARAMETERS

Since DL-NF membrane worked well with the pretreated surface water, a parametric study was decided to be done with the same DL-NF membrane. All the experimental runs done with DL-NF membrane were at the same operating conditions. The fixed operating conditions were 6.9 bar pressure,

1.2 m/sec cross-flow velocity and the temperature of the feed water was 20±2^{o}C.

In this part of the study, two different parametric analyses were done. Firstly, cross-flow velocity was changed and the other parameters were fixed. Secondly, transmembrane pressure was changed and the other parameters were fixed. In the next two sections, the results from the experiments conducted by changing transmembrane pressure and crossflow velocity are presented.

5.4.1 Effect of Cross Flow Velocity

Effect of cross-flow velocity was analyzed with this experimental set. The system was fed with pretreated surface water by dead-end microfiltration with Whatman 42 membrane which has a pore size of 2.5 μm. The other operating parameters were 6.9 bar pressure and 20±2^{o}C feed water temperature. Cross-flow velocity was decreased to 0.7 m/sec for this experimental run which was formerly kept at 1.2 m/sec for the other runs.

Steady-state flux values were 70.6 L/m^2.h, 69.1 L/m^2.h, 69.1 L/m^2.h and 69.5 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw water and clean water flux after cleaning is applied, respectively (Table 30).

Table 30 Water flux, flux decline and total fouling for DL-NF membrane with microfiltrated raw water at 6.9 bar pressure, 0.7 m/sec crossflow velocity

*Clean Water Flux (L/m2.h)	70.6
Raw Water Flux (L/m2.h)	69.1
**Clean Water Flux (L/m2.h)	69.5
Flux Decline (%)	2.1
Irreversible Fouling (%)	1.5

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

Flux decline of raw water was 2.1%. Compared to the experimental run conducted with the same membrane, but at 1.2 m/sec cross-flow rate: it is obvious that flux values and fouling ratio seem to be nearly the same. Also, removal efficiencies comparison is essential for a full-fledged comparison. Therefore essential analysis were done with the permeate samples collected during the experimental run.

In Table 31, characteristics of raw water and permeate samples collected periodically during the nanofiltration run is shown.

Table 31 Analysis results of the permeate and raw water samples taken during DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure, 0.7 m/sec cross-flow velocity

	Time (hour)	Sulphate (mg/L)	Conductivity (µS/cm)	UVA	pH	Temp (^{o}C)
Raw Water		360	1449	0.0385	8.03	14.8
T0	0	6	640	0.0138	7.90	15.3
T1	2	6	642	0	7.75	15.3
T2	5	5	640	0	7.64	15.3
T3	7	6	644	0	7.60	15.4
T4	10	6	641	0	7.59	15.7
T5	11	6	638	0	7.52	15.4

Removal efficiencies are not much different than the removal efficiencies of the experimental run done with 1.2 m/sec cross-flow rate (Table 19 and Table 20). pH also decreased in permeate samples with nanofiltration run. This may be due to the ionic interaction or anionic accumulation at the membrane surface. Also, UV absorbance decreased nearly to zero as it did in other experimental run showing effective removal of organic matter. Sulphate and conductivity removal efficiencies can be seen from the Table 33. In Table 32, water flux, flux decline and total fouling are given for both experimental runs conducted with 0.7m/sec and 1.2 m/sec crossflow velocity

at 6.9 bar pressure with DL-NF membrane. As can be depicted from the table, flux decline is lower with the experimental run conducted at 0.7 m/sec crossflow velocity. There is no important difference in the fouling percentages which is very low.

Table 32 Water flux, flux decline and total fouling for DL-NF membrane with microfiltrated raw water at 6.9 bar pressure for 1.2 m/sec and 0.7 m/sec crossflow velocity

	0.7 m/sec crossflow velocity	**1.2 m/sec crossflow velocity**
***Clean Water Flux (L/m2.h)**	70.6	68.8
Raw Water Flux (L/m2.h)	69.1	60.6
****Clean Water Flux (L/m2.h)**	69.5	68.0
Flux Decline (%)	2.1	11.9
Irreversible Fouling (%)	1.5	1.2

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

In Table 32, it is seen that there is lower flux for higher crossflow velocity which is an interesting result.

Table 33 Sulphate and conductivity removal efficiencies for DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure, 0.7 m/sec cross-flow velocity

Time (hour)	**Sulphate Removal (%)**	**Conductivity Removal (%)**
0.0	98.3	
2.0	98.3	55.7
5.0	98.6	55.8
7.0	98.3	55.6
10.0	98.3	55.8
11.0	98.3	56.0

From the Table 33, sulphate and conductivity removal efficiencies are 98.3% and 56%, respectively. It is seen that nearly the same removal efficiencies for sulphate and conductivity were achieved when compared with the trials done before at 1.2 m/sec crossflow velocity. Figure 32 and Figure 33 shows the removal efficiencies of sulphate and conductivity with respect to time in permeate samples.

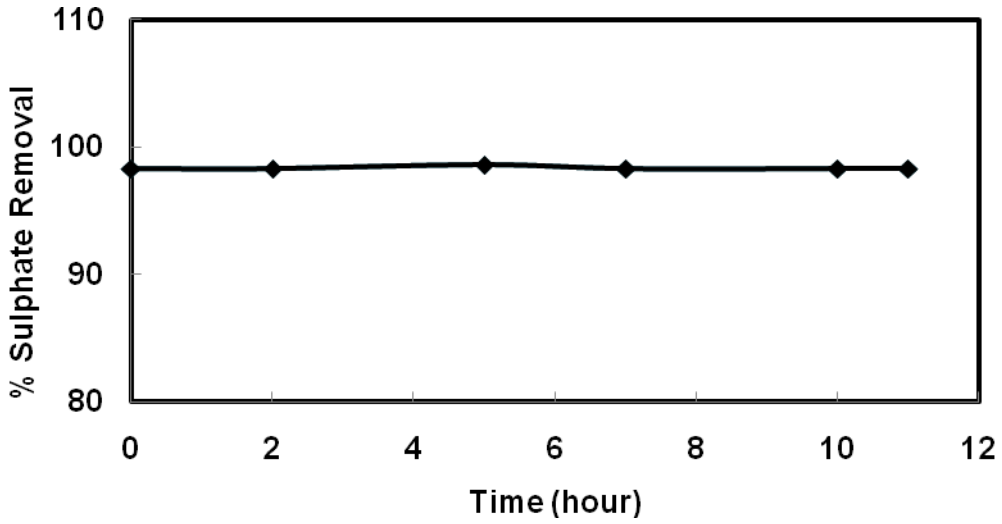

Figure 32 Sulphate removal efficiency values for DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure, 0.7 m/sec cross-flow velocity

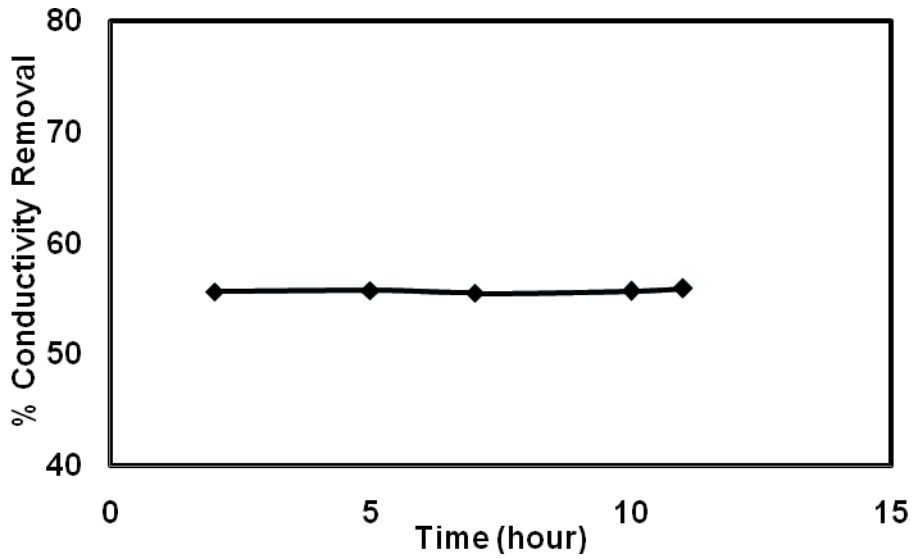

Figure 33 Conductivity removal efficiency values for DL-NF membrane experimental run with microfiltrated raw water at 6.9 bar pressure, 0.7 m/sec cross-flow velocity

As a result of the comparison of this experimental runs which were with 0.7 m/sec and the experimental run with 1.2 m/sec, it is obvious that there is not much difference in terms of flux values and fouling ratios and also the removal efficiencies of sulphate and conductivity. Therefore decrease in cross-flow rate was meaningful since desired fouling ratios and removal efficiencies were achieved with less velocity. Lower CFV provides a lower shear flow which then increases the concentration polarization. However, this effect was not observed in this experimental run.

5.4.2 Effect of Transmembrane Pressure

Effect of transmembrane pressure was assessed in this experimental run. The feed water is used as pretreated surface water with microfiltration. The operating conditions were 1.2 m/sec cross-flow velocity and 20±2^{o}C feed water temperature. The transmembrane pressure was decreased to 3.5 bars from 6.9 bars.

Steady-state flux values were 45.6 L/m^2.h, 42.6 L/m^2.h, 45.9 L/m^2.h and 45.3 L/m^2.h for initial clean water flux, raw water flux, clean water flux after raw

water and clean water flux after cleaning is applied, respectively. Raw water flux decline is 6.6%. The flux values decreased, when compared to the flux values of the experimental run conducted at 6.9 bar pressure. The decrease in flux values with decreasing transmembrane pressure is meaningful and correlates with the literature. Also no fouling is observed at the run applied at this pressure.

The characteristics of the pretreated raw water and permeate samples collected during the nanofiltration run are shown in Table 34.

Table 34 Analysis results of the permeate and raw water samples taken during DL-NF membrane experimental run with microfiltrated raw water at 3.5 bar pressure, 1.2 m/sec cross-flow velocity

	Time (hour)	Sulfate (mg/L)	Conductivity (µS/cm)	UVA	pH	Temp (^{o}C)
Raw Water		370	1350	0.0286	8.02	13.7
T0	0	8	27.6	0.0116	7.32	14.7
T1	1	8	744	0.0047	7.41	13.5
T2	2.5	7	745	0.0010	7.35	13.7
T3	4.5	7	746	0.0052	7.32	13.8
T4	9	7	750	0.0065	7.45	13.5
T5	10	7	747	0.0056	7.45	13.7
T6	11	7	745	0.0063	7.43	13.5

As can be seen from the table, UV absorbance decreased considerably explaining the removal of organic matter in the water. pH levels also decreased compared to the pH of the raw water. The reason of this decrease may be the ionic interaction or the anionic accumulation at the membrane surface. Sulphate and conductivity removal efficiencies can also be seen from the Table 35.

Table 35 Sulphate and conductivity removal efficiencies for DL-NF membrane experimental run with microfiltrated raw water at 3.5 bar pressure, 1.2 m/sec cross-flow velocity

Time (hour)	Sulphate Removal (%)	Conductivity Removal (%)
0	97.8	
1	97.8	44.9
2.5	98.1	44.8
4.5	98.1	44.7
9	98.1	44.4
10	98.1	44.7
11	98.1	44.8

The removal efficiencies of sulphate and conductivity are 98.1% and 44.8%, respectively. There is no change in the removal efficiency of sulphate, when the sulphate removal efficiency is compared to the experimental run done at 6.9 bar transmembrane pressure. However, there is a small decrease in the conductivity removal levels, which is directly related with the removal of organic molecules. In Figure 34 and Figure 35, removal efficiencies of sulphate and conductivity can be seen, respectively.

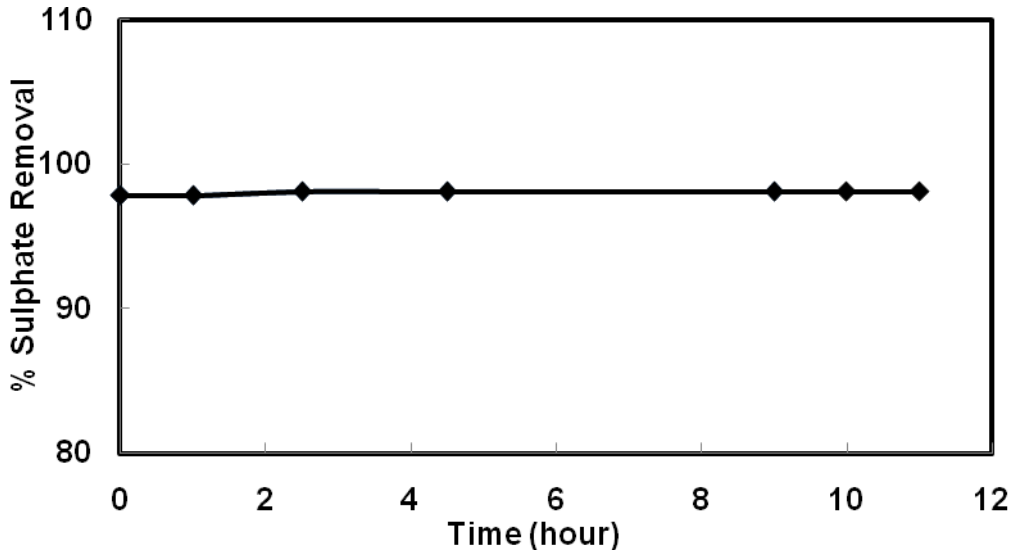

Figure 34 Sulphate removal efficiency values for DL-NF membrane experimental run with microfiltrated raw water at 3.5 bar pressure, 1.2 m/sec cross-flow velocity

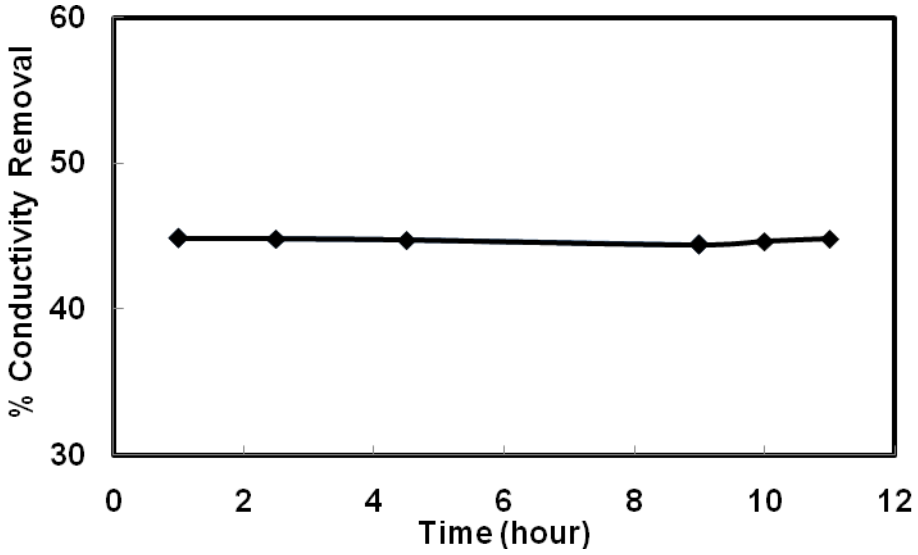

Figure 35 Conductivity removal efficiency values for DL-NF membrane experimental run with microfiltrated raw water at 3.5 bar pressure, 1.2 m/sec cross-flow velocity

Table 36 Water flux, flux decline and total fouling for DL-NF membrane with microfiltrated raw water at 1.2 m/sec crossflow velocity for 6.9 and 3.5 bar pressure

	6.9 bar transmembrane pressure	**3.5 bar transmembrane pressure**
*Clean Water Flux (L/m2.h)	68.8	45.6
Raw Water Flux (L/m2.h)	60.6	42.6
**Clean Water Flux (L/m2.h)	68.0	45.3
Flux Decline (%)	11.9	6.6
Irreversible Fouling (%)	No Fouling	No Fouling

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

When the experimental runs with transmembrane pressures of 6.9 bars and 3.5 bars are compared in Table 36, it is obvious that flux efficiency decreased, but again there is no fouling. Moreover, no change was observed in the removal efficiency of sulphate, but a small decrease was observed in conductivity removal levels.

In order to be able to make a comparison easier, the permeances were tabulated (Table 37) which were calculated by dividing the flux values by transmembrane pressure.

Table 37 Membrane permeances for DL-NF membrane with microfiltrated raw water at 1.2 m/sec crossflow velocity for 6.9 and 3.5 bar pressure

	6.9 bar transmembrane pressure	**3.5 bar transmembrane pressure**
*Clean Water Permeance(L/m2.h.bar)	9.97	13.03
Raw Water Permeance(L/m2.h.bar)	8.78	12.17
**Clean Water Permeance(L/m2.h.bar)	9.86	12.94

*Clean water flux before raw water is passed

** Clean water flux after the cleaning procedure is applied

When the membrane permeances are compared, it is obvious that there is a difference in the permeance values. The reason may be the expansion of the membrane.

Therefore, it seems reasonable to decrease transmembrane pressure since by decreasing the transmembrane pressure by half, no important change was observed in terms of flux decline and removal efficiencies. However a decrease of nearly half of the pressure means a reasonable decrease in the operational costs due to low energy cost which should also be dealt in further studies.

5.4.3 Comparison of the Membrane Types

Three different types of membranes, namely DK-NF, NF-270 and DL-NF were used in the experimental runs conducted. Different membranes showed different behaviors. In Table 38, it is seen that steady-state raw water flux values vary between 33 to 48.3 L/m2.h and sulphate removal efficiency between 99 to 73%.

Table 38 Steady-state raw water flux and sulphate removal efficiencies of DK-NF membrane

Pressure (bar)	6.9	6.9	6.9	6.9	6.9
Crossflow Velocity (m/sec)	1.2	1.2	1.2	1.2	1.2
Micron Pretreatment	no	no	no	no	no
Raw Water Flux (L/m2.h)	38.7	33.3	48.3	33.0	34.0
Sulphate Removal (%)	99	99	73	83	83

However in Table 39, it is obvious that at the same operational conditions NF-270 has showed better flux values than DK-NF membrane and also more consistent sulphate removal efficiencies.

Table 39 Steady-state raw water flux and sulphate removal efficiencies of NF-270 membrane

Pressure (bar)	6.9	6.9	6.9	6.9
Velocity (m/sec)	1.2	1.2	1.2	1.2
Pretreatment	no	no	no	pretreated
Raw Water Flux (L/m2.h)	87.5	85.7	85.1	76.5
Sulphate Removal (%)	98.30	98.10	97.10	99.30

In Table 40, steady-state raw water flux values of DL-NF membrane is not better than NF-270 membrane, however sulphate removal efficiencies are nearly the same.

Table 40 Steady-state raw water flux and sulphate removal efficiencies of DL-NF membrane

Pressure (bar)	6.9	3.5	6.9	6.9
Velocity (m/sec)	1.2	1.2	0.7	1.2
Pretreatment	pretreated	pretreated	pretreated	no
Raw Water Flux (L/m2.h)	60.6	42.6	69.1	67
Sulphate Removal (%)	98.50	98.10	98.30	98.70

When we compare the membranes in terms of steady-state raw water flux values and sulphate removal efficiencies, it seems that the best membrane throughout all the membranes used is NF-270 membrane.

CHAPTER 6

CONCLUSION

This study was performed to investigate the performance of NF treatment processes for the removal of sulphates from Kesikköprü Reservoir which is one of the drinking water supplies of Ankara and shows high levels of sulphate content.

Three different thin-film nanofiltration membranes which were commercially available, namely DK-NF, DL-NF and NF-270, were tested during the experimental study. A parametric study was also carried out investigating the effect of transmembrane pressure and cross-flow velocity on the performance of nanofiltration using DK-NF.

All three membranes tested resulted in high rejections of sulphate over 98 % from Kesikköprü Reservoir water. However, DK-NF and NF-270 membranes showed fouling when the surface water was fed directly to the system without any pre-treatment. MF with 2.5 μm pore size Whatman 42 membrane was found to be an effective pretreatment option for the prevention of the membrane fouling and swelling. But, as expected, MF provided no further treatment of sulphate and conductivity.

NF-270 membrane was found to be the best membrane among the three membranes tested as it resulted in high levels of sulphate removal and as it was consistent in the experimental runs.

When the effect of cross-flow velocity on NF performance was investigated, it appeared that flux, conductivity and sulphate removal efficiencies did not

change as it was decreased nearly to half (from 1.2 m/sec to 0.7 m/sec) in order to do a parametric study by changing the cross-flow velocity. There were no further treatments of sulphate and conductivity as well as there was no change in flux values.

Also effect of transmembrane pressure on the performance of NF was evaluated. Transmembrane pressure was decreased nearly to half (from 6.9 bar transmembrane pressure to 3.5 bar transmembrane pressure) for another parametric study. Decreasing the transmembrane pressure caused the flux values to decrease, which was already an expected result. However, there was no decrease in the sulphate removal efficiency.

It is very promising that decrease in the transmembrane pressure did not result in a decrease in sulphate removal efficiency. As a result of this fact, the energy costs will diminish significantly, when applied in real scale.

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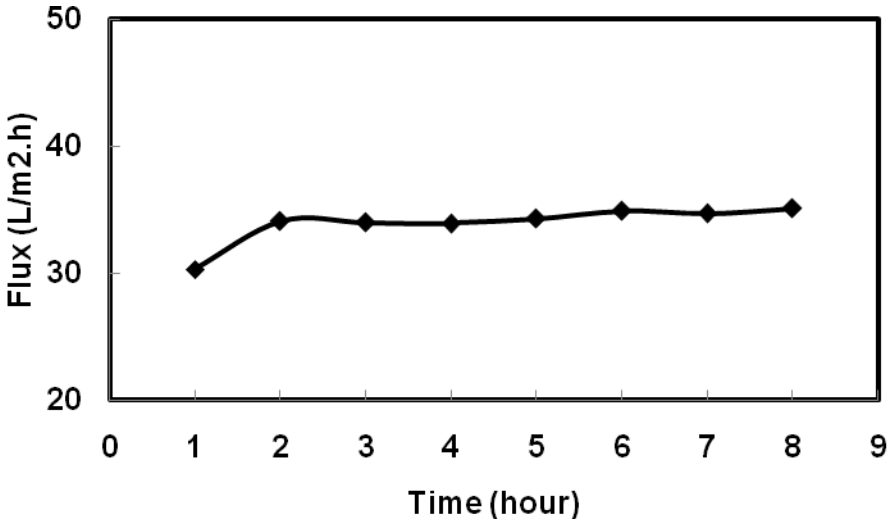
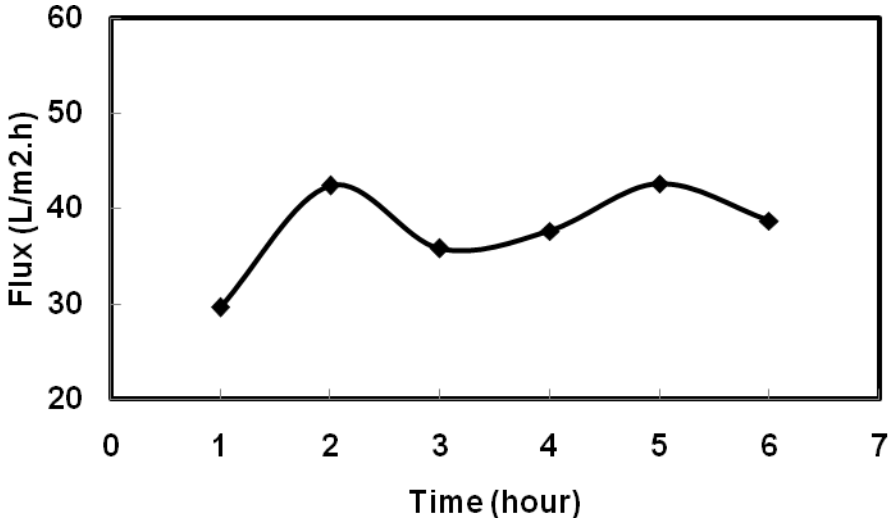
APPENDIX A

EXPERIMENTAL RESULTS OF THE NANOFILTRATION RUNS

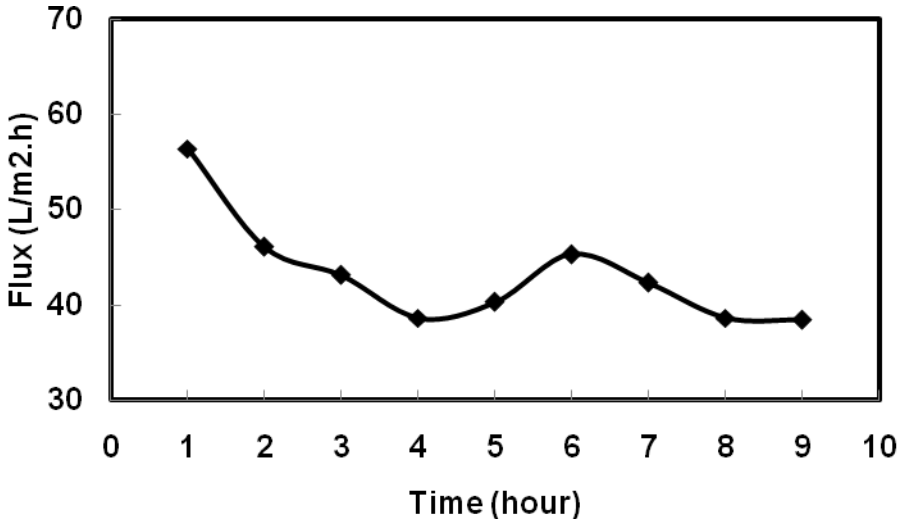
1. First Experimental Data with DK-NF at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



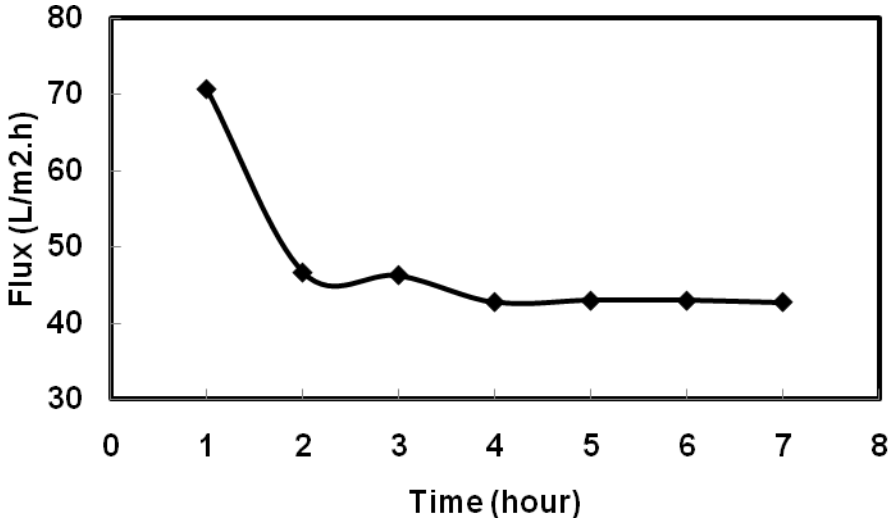
a)


60
50
40
30
20
Flux (L/m2.h)
0
1
2
3
4
5
6
7
Time (hour)

b)


70
60
50
40
30
Flux (L/m2.h)
0
1
2
3
4
5
6
7
8
9
10
Time (hour)

c)



d)

Figure A. 1. Flux changes with time a) Initial clean water flux b) Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

Table A. 1 Clean water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	1	30.3
T1	2	34.1
T2	3	34
T3	4	33.9
T4	5	34.3
T5	6	34.9
T6	7	34.7
T7	8	35.1

Table A. 2 Raw water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	1	29.6
T1	2	42.4
T2	3	35.8
T3	4	37.6
T4	5	42.6
T5	6	38.7

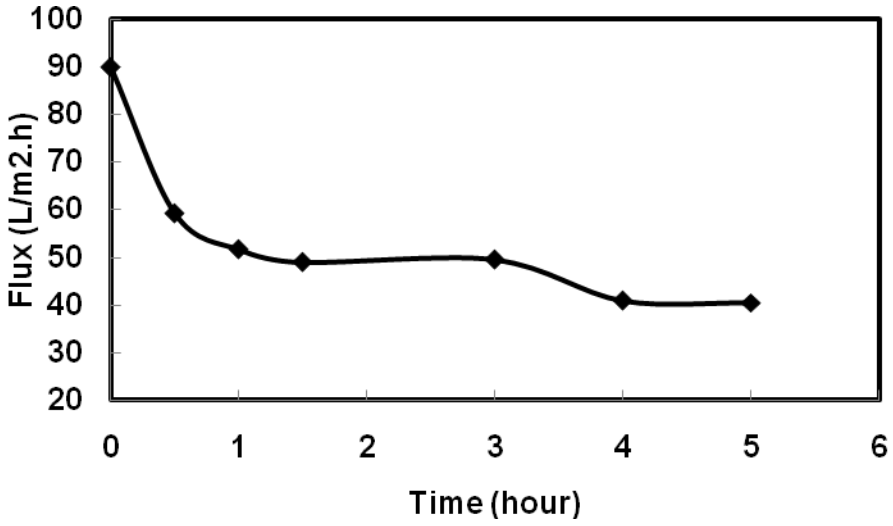
Table A. 3 Clean water flux values after raw water passage with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	1	56.4
T1	2	46.1
T2	3	43.1
T3	4	38.6
T4	5	40.3
T5	6	45.3
T6	7	42.3
T7	8	38.6
T8	9	38.4

Table A. 4 Clean water flux after cleaning values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	1	70.6
T1	2	46.6
T2	3	46.2
T3	4	42.7
T4	5	42.9
T5	6	42.9
T6	7	42.7

2. Second Experimental Data with DK-NF at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



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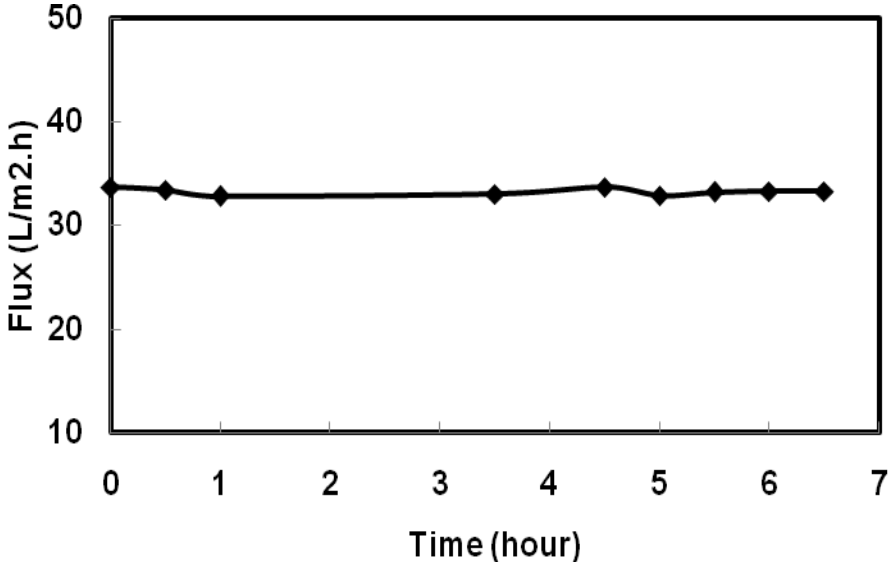
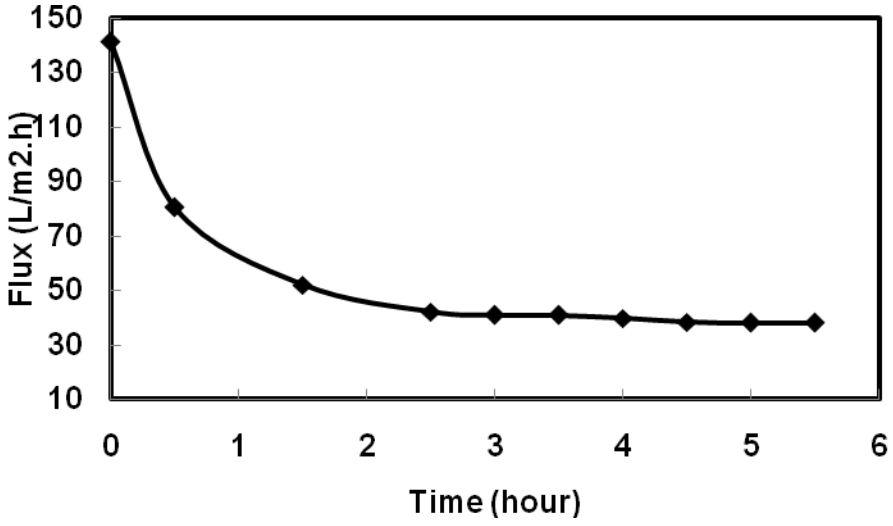
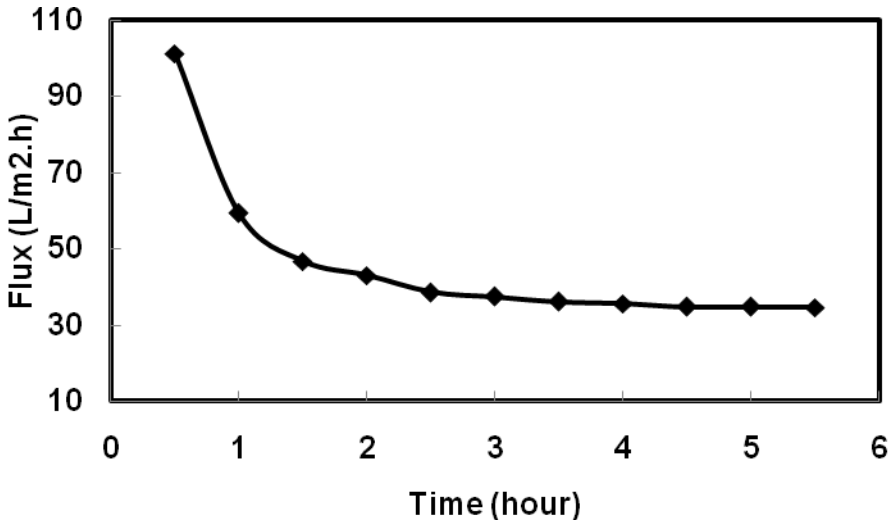


b)

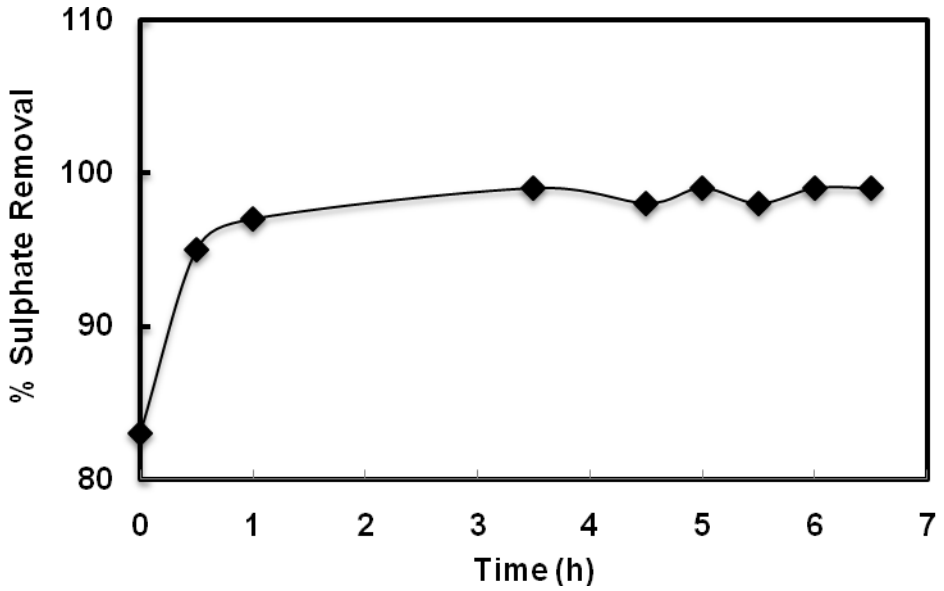


c)

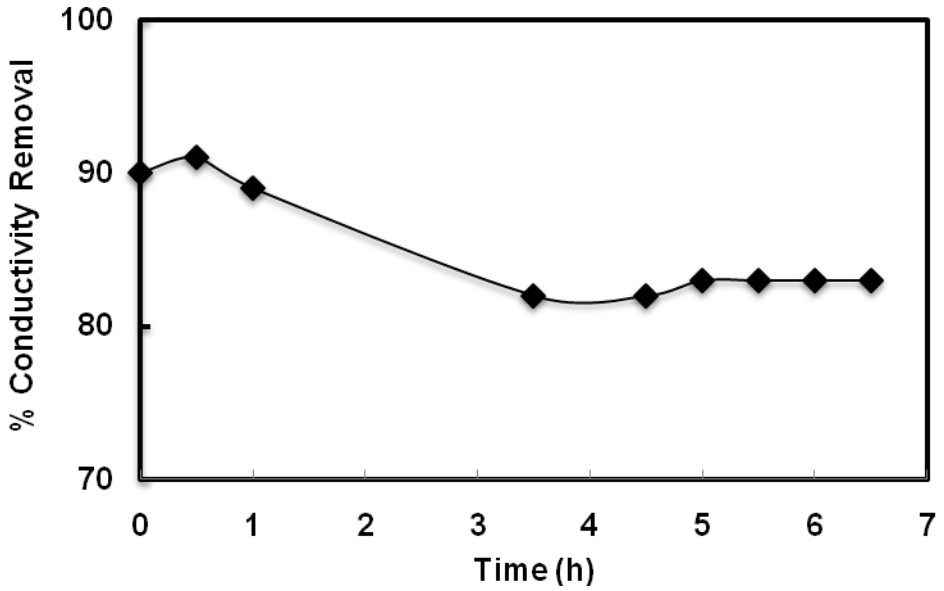


d)

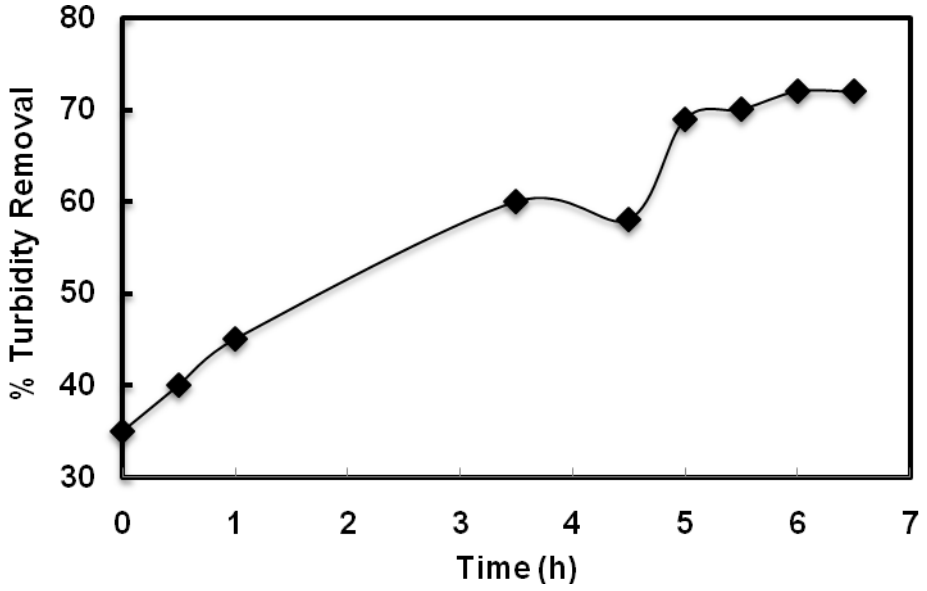
Figure A. 2. Flux changes with time a) Initial clean water flux b) Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied


% Sulphate Removal
110
100
90
80
0
1
2
3
4
5
6
7
Time (h)

a)


% Conductivity Removal
100
90
80
70
0
1
2
3
4
5
6
7
Time (h)

b)



c)

Figure A. 3. Removal efficiencies of a) Sulphate b) Conductivity c) Turbidity

Table A. 5 Clean water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	89.9
T1	0.5	59.2
T2	1	51.6
T3	1.5	48.9
T4	3	49.5
T5	4	40.8
T6	5	40.4

Table A. 6 Raw water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	33.7
T1	0.5	33.4
T2	1	32.8
T3	3.5	33
T4	4.5	33.7
T5	5	32.9
T6	5.5	33.2
T7	6	33.3
T8	6.5	33.3

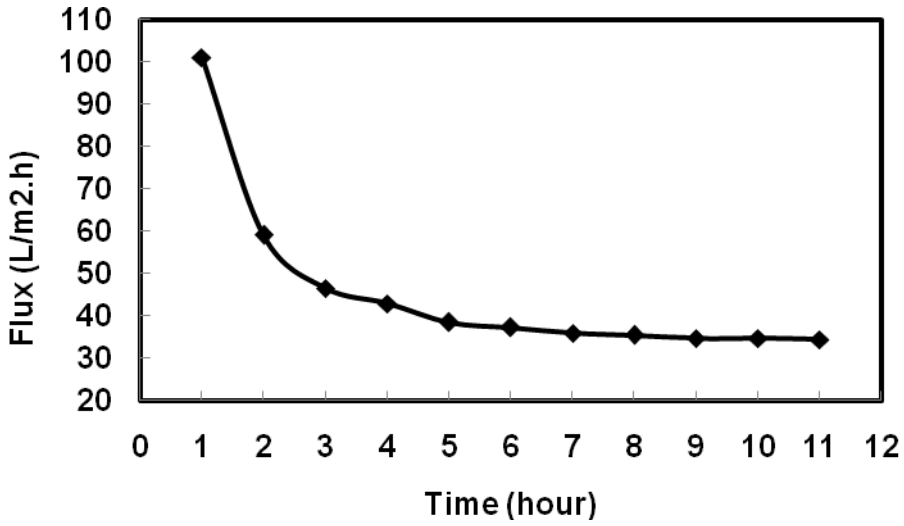
Table A. 7 Clean water flux values after raw water passage with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	141.3
T1	0.5	80.4
T2	1.5	51.8
T3	2.5	41.9
T4	3	40.7
T5	3.5	40.7
T6	4	39.6
T7	4.5	38.3
T8	5	38
T9	5.5	38

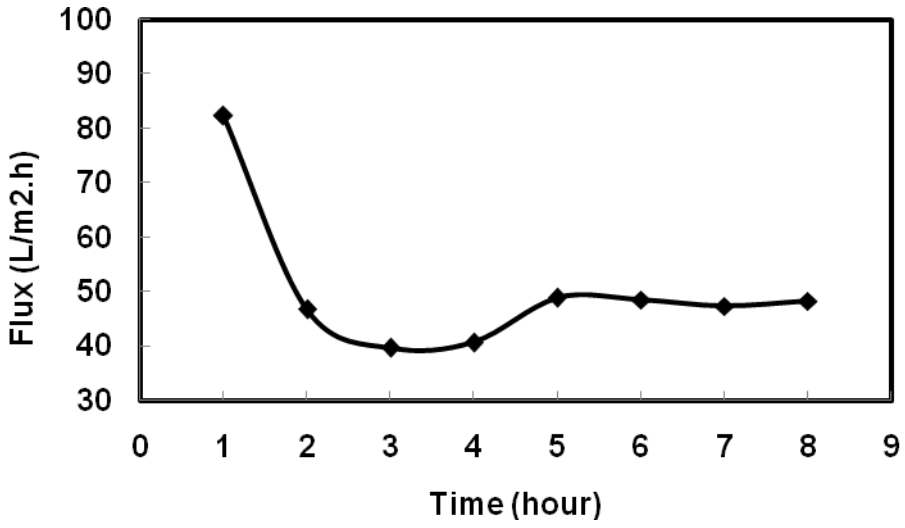
Table A. 8 Clean water flux after cleaning values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	189.1
T1	0.5	101.2
T2	1	59.2
T3	1.5	46.6
T4	2	42.9
T5	2.5	38.5
T6	3	37.3
T7	3.5	36
T8	4	35.5
T9	4.5	34.7
T10	5	34.7
T11	5.5	34.5

3. Third Experimental Data with DK-NF at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



a)



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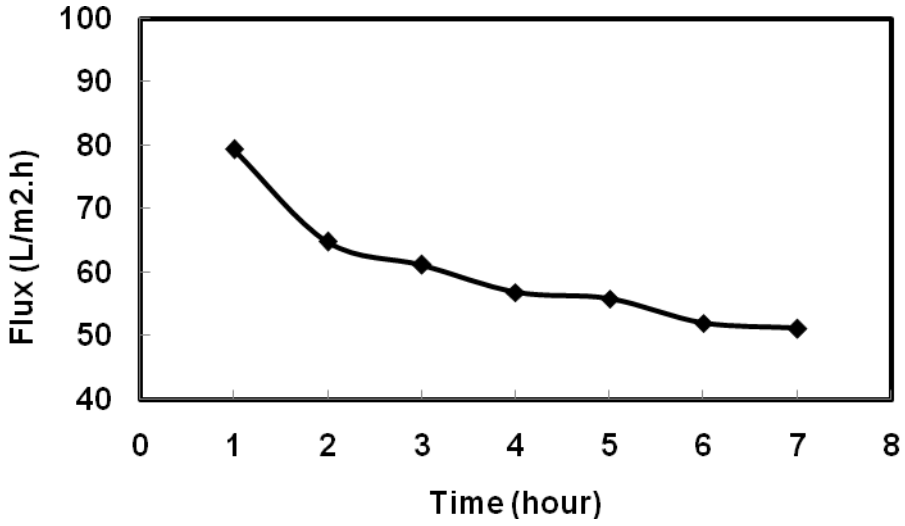
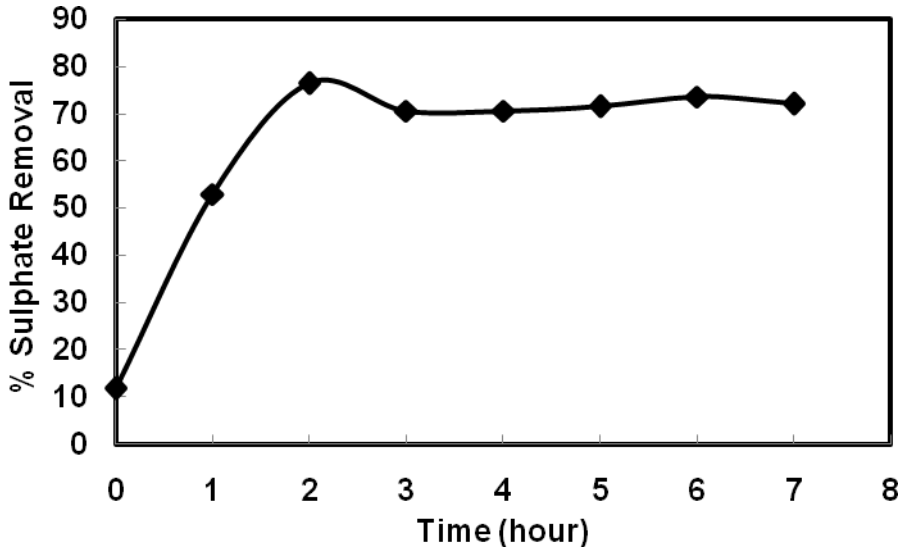
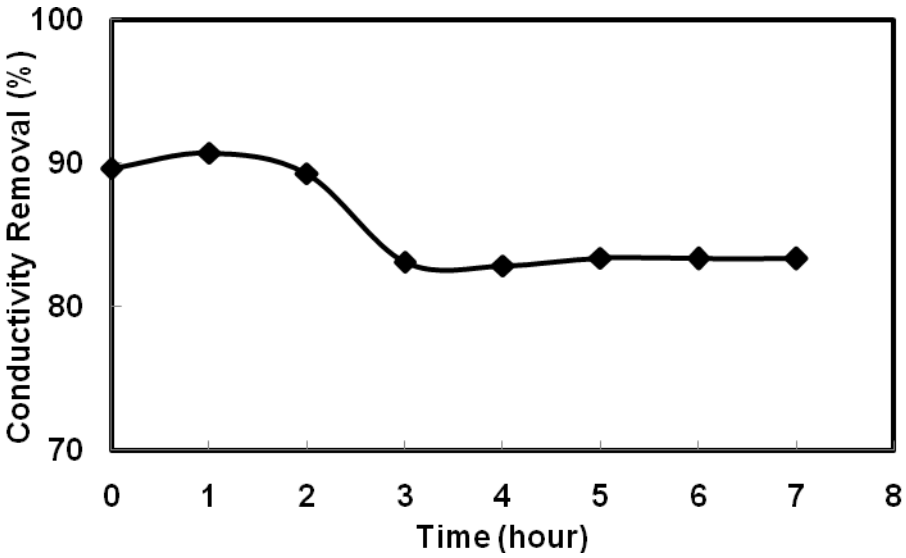


c)

Figure A. 4. Flux changes with time a) Initial clean water flux b) Raw water flux c) Clean water flux after raw water



a)



b)

Figure A. 5. Removal efficiencies of a) Sulphate b) Conductivity

Table A. 9 Clean water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (third trial)

	Time (hour)	Flux (L/m2.h)
T0	0	189.1
T1	1	101.2
T2	2	59.2
T3	3	46.6
T4	4	42.9
T5	5	38.5
T6	6	37.3
T7	7	36
T8	8	35.5
T9	9	34.7
T10	10	34.7
T11	11	34.5

Table A. 10 Raw water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (third trial)

	Time (hour)	Flux (L/m2.h)
T0	1	82.4
T1	2	46.8
T2	3	39.7
T3	4	40.7
T4	5	48.9
T5	6	48.5
T6	7	47.4
T7	8	48.3

Table A. 11 Clean water flux values after raw water passage with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (third trial)

	Time (hour)	Flux (L/m2.h)
T0	0	238.1
T1	1	79.4
T2	2	64.9
T3	3	61.2
T4	4	56.9
T5	5	55.9
T6	6	52.1
T7	7	51.2

4. Fourth Experimental Data with DK-NF at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment

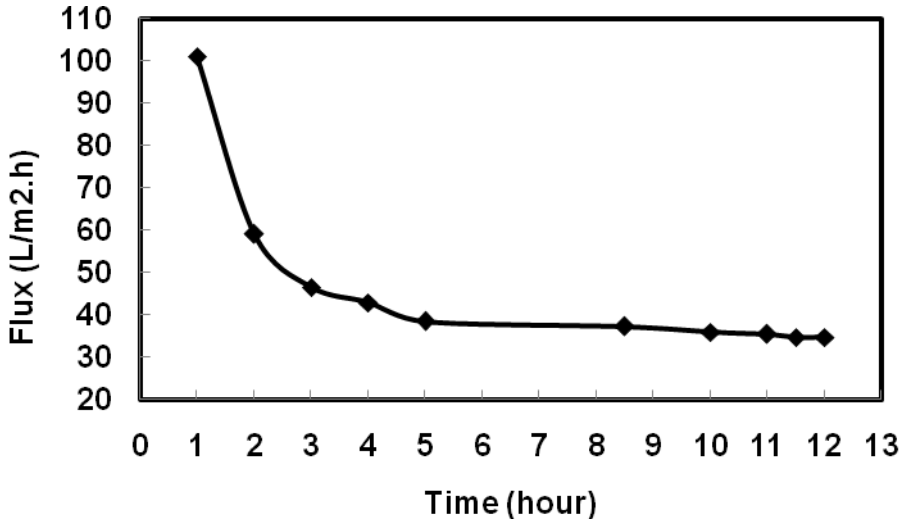


Figure A. 6. Flux changes with time of raw water flux

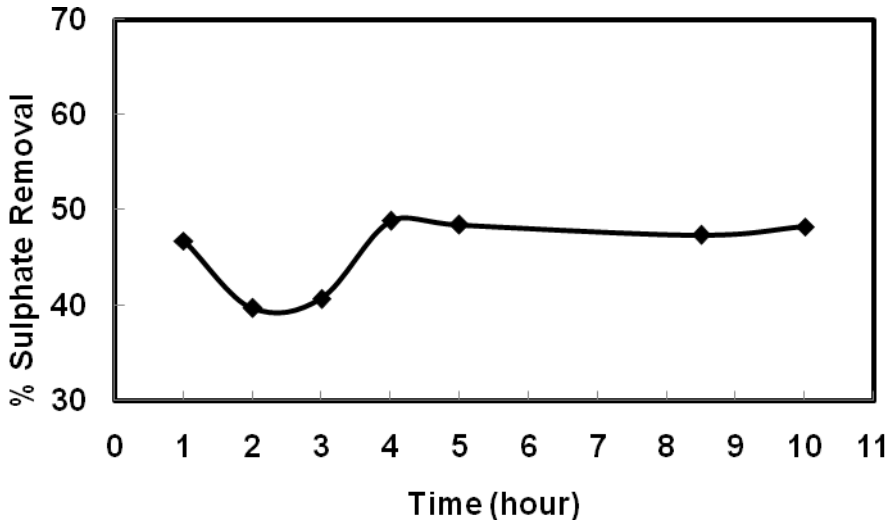
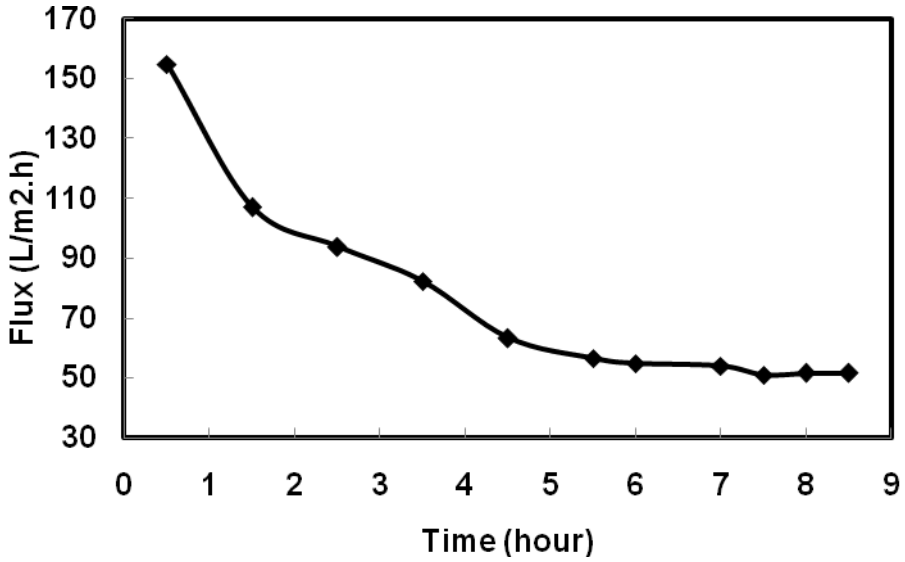


Figure A. 7. Removal efficiencies of sulphate

Table A. 12 Raw water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (fourth trial)

	Time (hour)	Flux (L/m2.h)
T0	0	129.9
T1	1	61.2
T2	2	54.2
T3	3	51.2
T4	4	47.3
T5	5	47.6
T6	8.5	39.1
T7	10	34.7
T8	11	33
T9	11.5	33.1
T10	12	33

5. Fifth Experimental Data with DK-NF at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



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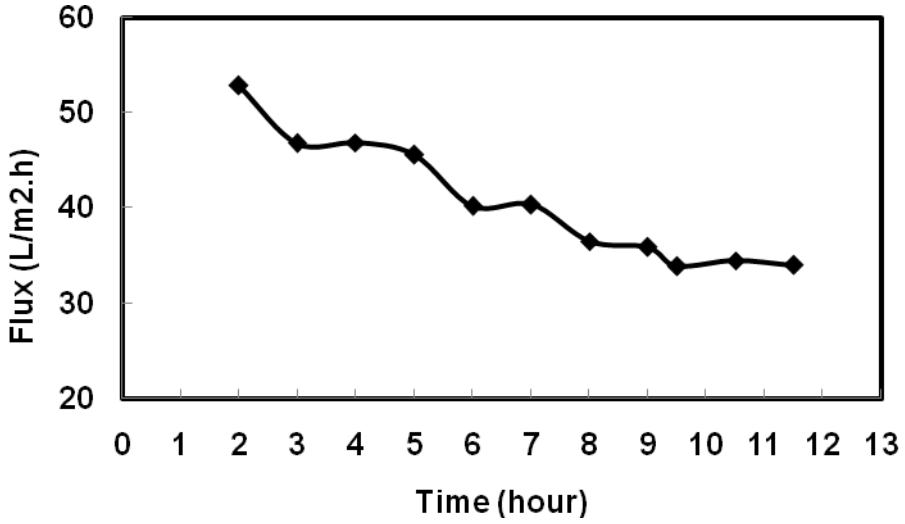
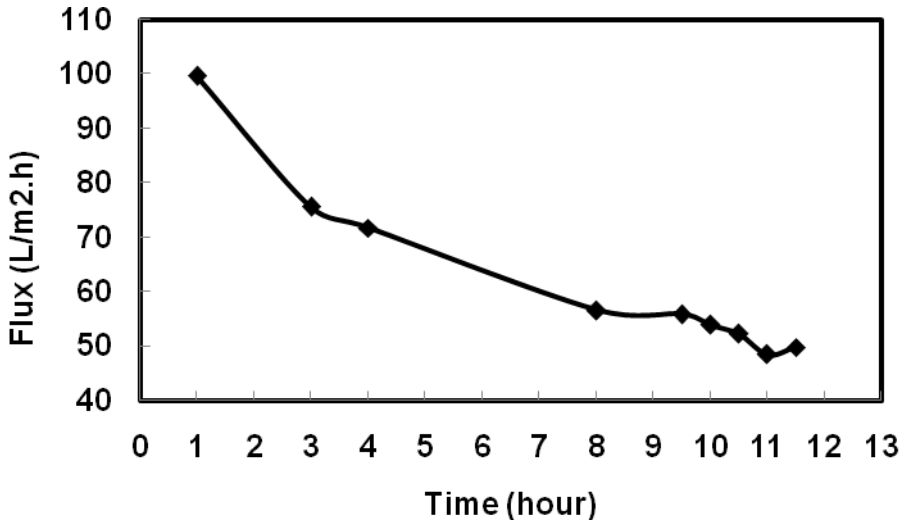
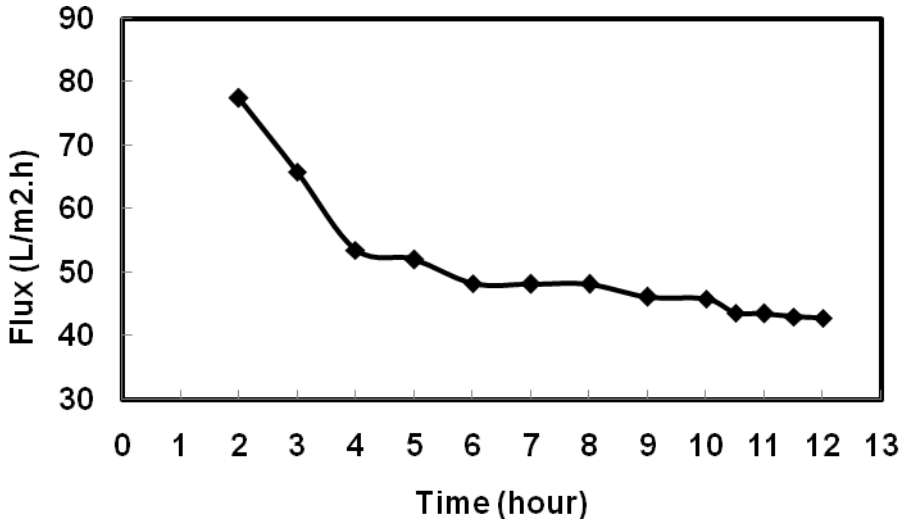


b)



c)



d)

Figure A. 8. Flux changes with time a) Initial clean water flux b)Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

Table A. 13 Clean water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (fifth trial)

	Time (hour)	Flux (L/m2.h)
T0	0	156.8
T1	0.5	154.9
T2	1.5	107.1
T3	2.5	93.8
T4	3.5	82.4
T5	4.5	63.3
T6	5.5	56.6
T7	6	54.9
T8	7	54
T9	7.5	51
T10	8	51.6
T11	8.5	51.6

Table A. 14 Raw water flux values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (fifth trial)

	Time (hour)	Flux (L/m2.h)
T0	0	139.8
T1	2	52.9
T2	3	46.8
T3	4	46.9
T4	5	45.6
T5	6	40.2
T6	7	40.4
T7	8	36.5
T8	9	35.9
T9	9.5	33.9
T10	10.5	34.5
T11	11.5	34

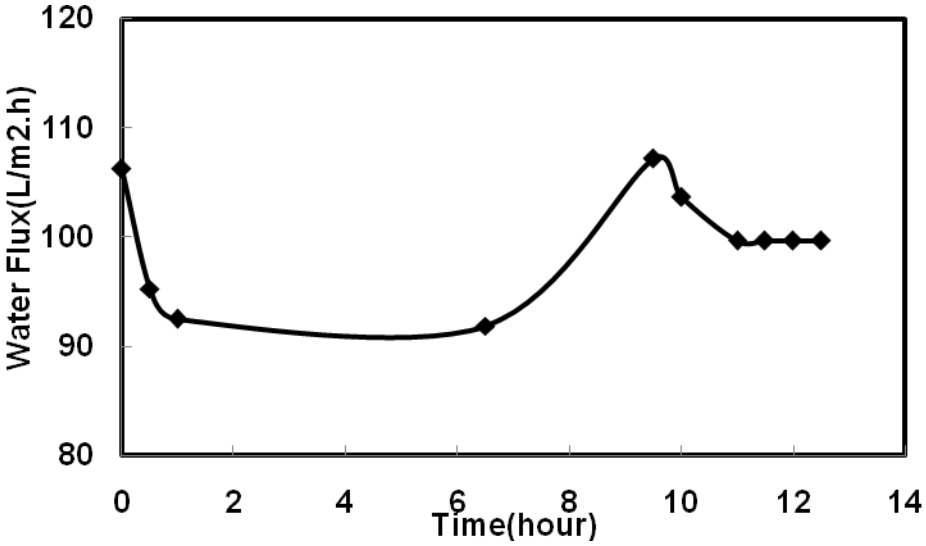
Table A. 15 Clean water flux values after raw water passage with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (fifth trial)

	Time (hour)	Flux (L/m2.h)
T0	0	207.4
T1	1	99.7
T2	3	75.6
T3	4	71.8
T4	8	56.6
T5	8.5	55.9
T6	9	54
T7	9.5	52.3
T8	10	48.5
T9	10.5	49.8

Table A. 16 Clean water flux after cleaning values with DK-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (fifth trial)

	Time (hour)	Flux (L/m2.h)
T0	0	197.8
T1	2	77.5
T2	3	65.9
T3	4	53.6
T4	5	52.1
T5	6	48.3
T6	7	48.2
T7	8	48.2
T8	9	46.2
T9	10	45.9
T10	10.5	43.7
T11	11	43.6
T12	11.5	43.1
T13	12	42.9

6. First Experimental Data with NF-270 at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



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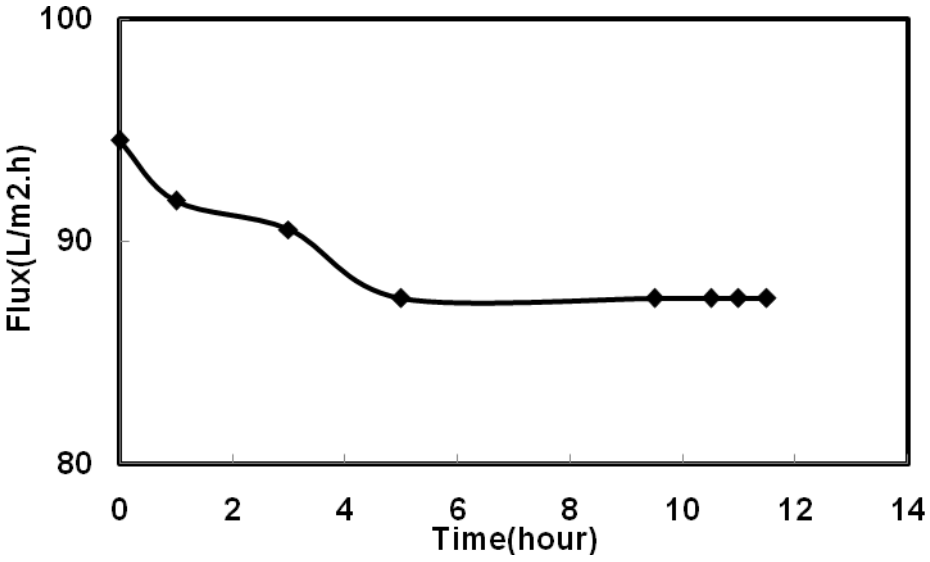

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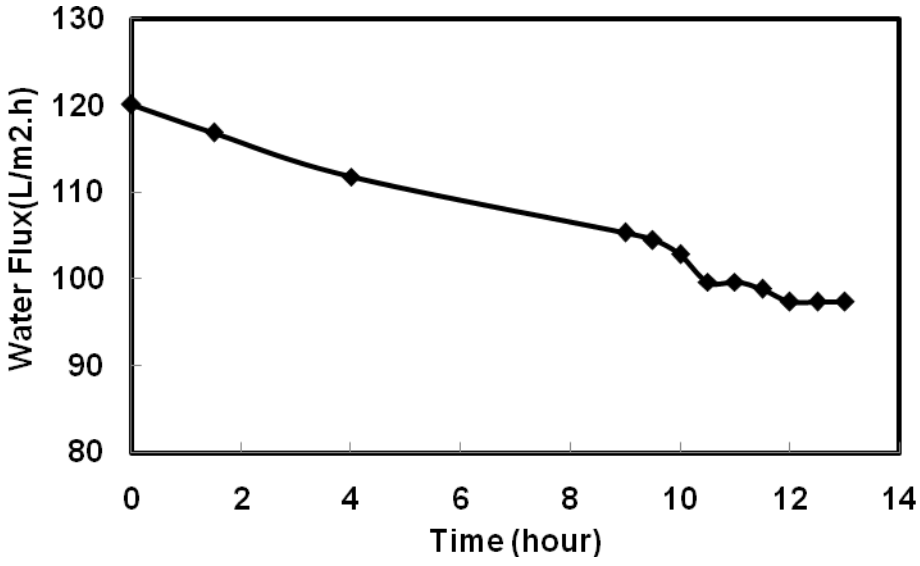

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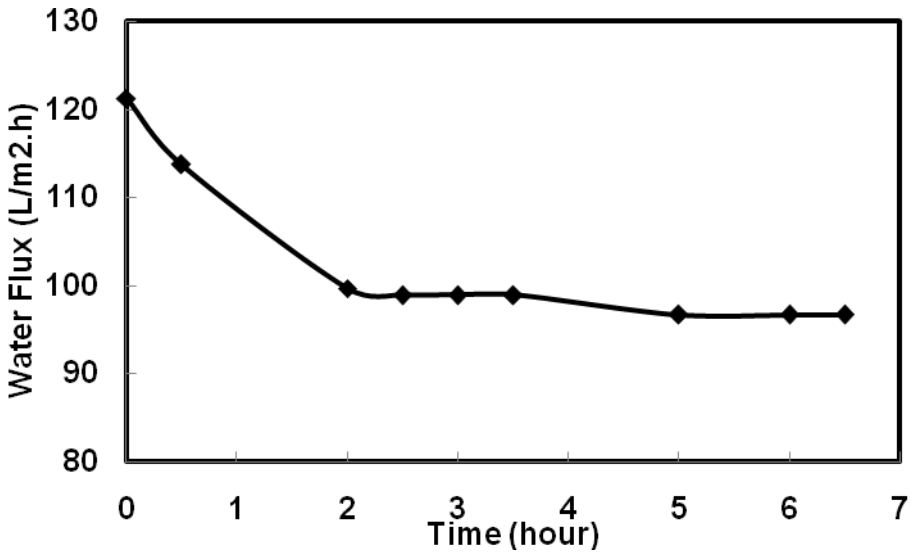
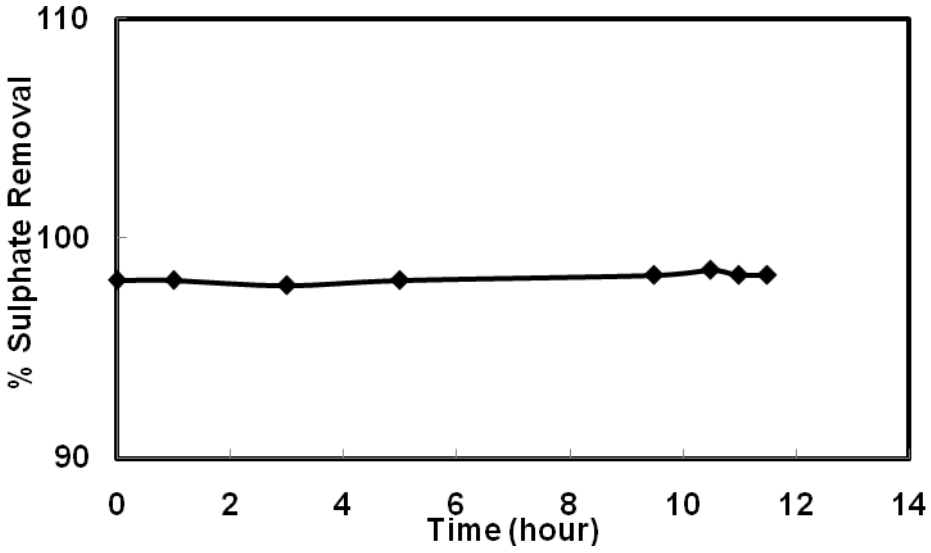
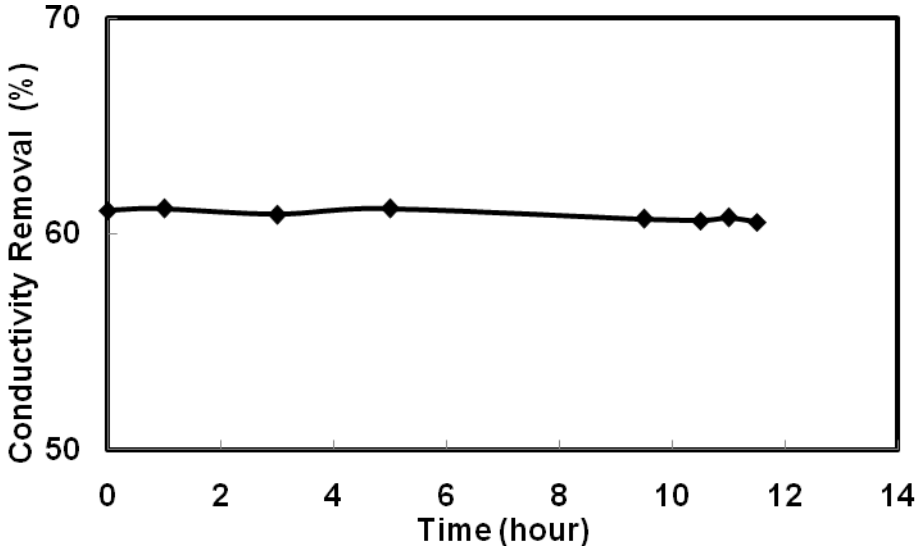


d)

Figure A. 9. Flux changes with time a) Initial clean water flux b) Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied



a)



b)

Figure A. 10. Removal efficiencies of a) Sulphate b) Conductivity

Table A. 17 Clean water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	0	106.3
T1	0.5	95.2
T2	1	92.5
T3	6.5	91.8
T4	9.5	107.1
T5	10	103.7
T6	11	99.7
T7	11.5	99.7
T8	12	99.7
T9	12.5	99.7

Table A. 18 Raw water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	0	94.5
T1	1	91.8
T2	3	90.5
T3	5	87.5
T4	9.5	87.5
T5	10.5	87.5
T6	11	87.5
T7	11.5	87.5

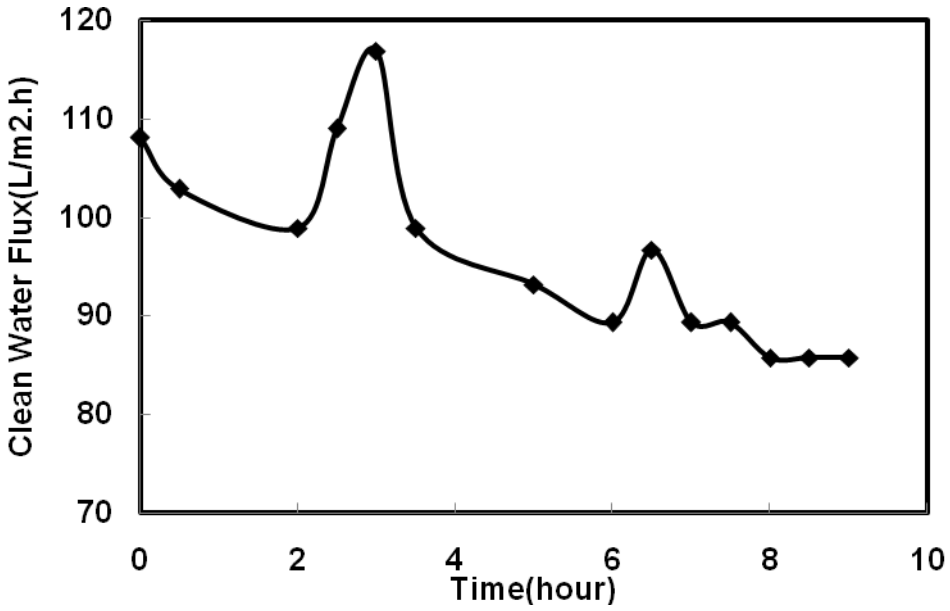
Table A. 19 Clean water flux values after raw water passage with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	0	120.2
T1	1.5	116.9
T2	4	111.8
T3	9	105.4
T4	9.5	104.5
T5	10	102.9
T6	10.5	99.7
T7	11	99.7
T8	11.5	98.9
T9	12	97.4
T10	12.5	97.4
T11	13	97.4

Table A. 20 Clean water flux after cleaning values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (first trial)

	Time (hour)	Flux (L/m2.h)
T0	0	121.3
T1	0.5	113.8
T2	2	99.7
T3	2.5	98.9
T4	3	98.9
T5	3.5	98.9
T6	5	96.7
T7	6	96.7
T8	6.5	96.7

7. Second Experimental Data with NF-270 at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



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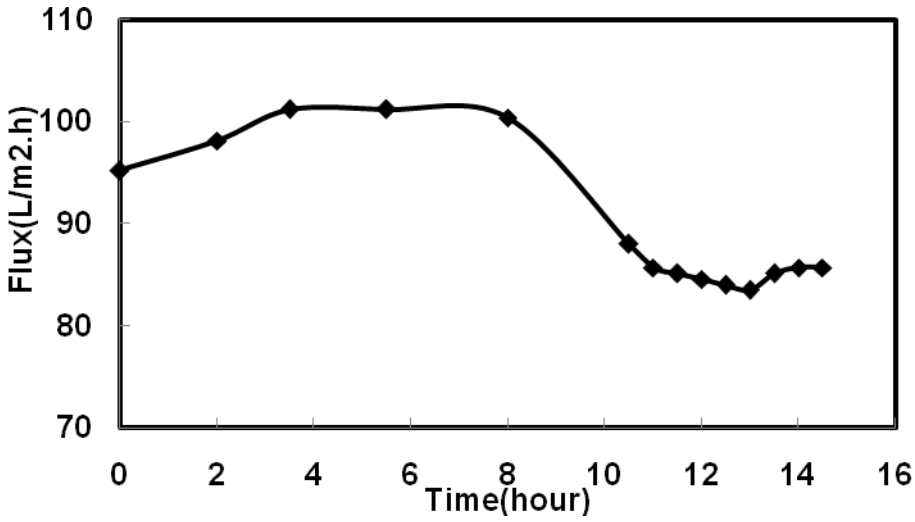
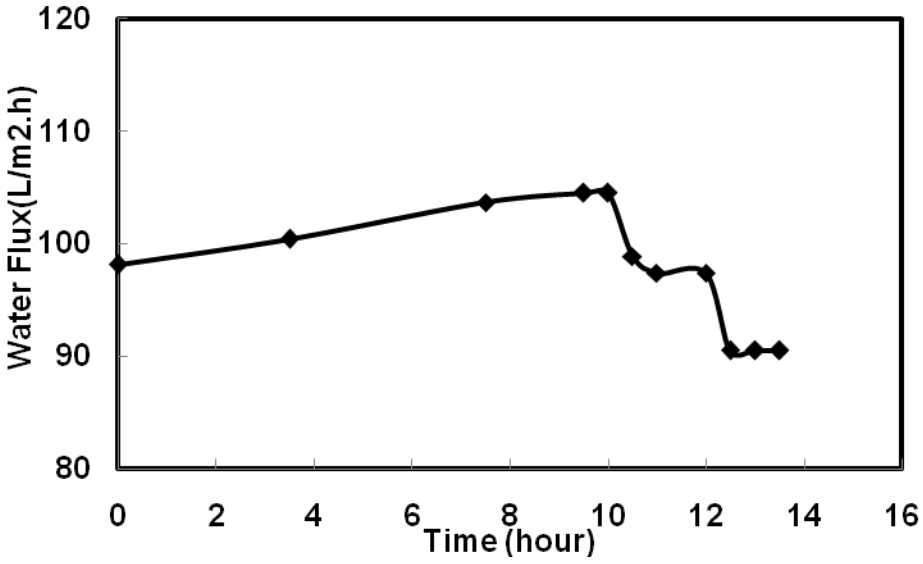
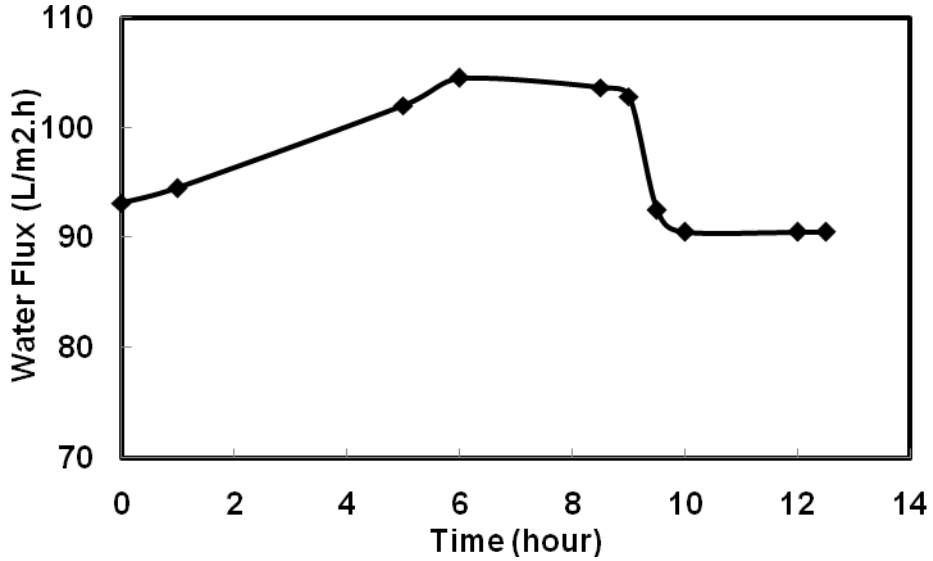


b)



c)



d)

Figure A. 11. Flux changes with time a) Initial clean water flux b) Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

Table A. 21 Clean water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	108.0
T1	0.5	102.9
T2	2	98.9
T3	2.5	109.0
T4	3	116.9
T5	3.5	98.9
T6	5	93.2
T7	6	89.3
T8	6.5	96.7
T9	7	89.3
T10	7.5	89.3
T11	8	85.7
T12	8.5	85.7
T13	9	85.7

Table A. 22 Raw water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	95.2
T1	2	98.1
T2	3.5	101.2
T3	5.5	101.2
T4	8	100.4
T5	10.5	88.1
T6	11	85.7
T7	11.5	85.1
T8	12	84.6
T9	12.5	84.0
T10	13	83.5
T11	13.5	85.1
T12	14	85.7
T13	14.5	85.7

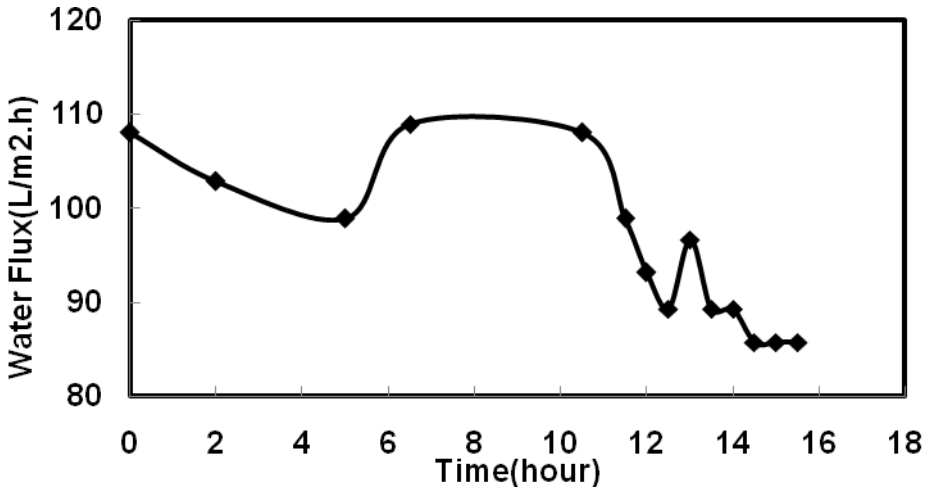
Table A. 23 Clean water flux values after raw water passage with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	98.1
T1	3.5	100.4
T2	7.5	103.7
T3	9.5	104.5
T4	10	104.5
T5	10.5	98.9
T6	11	97.4
T7	12	97.4
T8	12.5	90.5
T9	13	90.5
T10	13.5	90.5

Table A. 24 Clean water flux after cleaning values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (second trial)

	Time (hour)	Flux (L/m2.h)
T0	0	93.2
T1	1	94.5
T2	5	102.0
T3	6	104.5
T4	8.5	103.7
T5	9	102.9
T6	9.5	92.5
T7	10	90.5
T8	12	90.5
T9	12.5	90.5

8. Third Experimental Data with NF-270 at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



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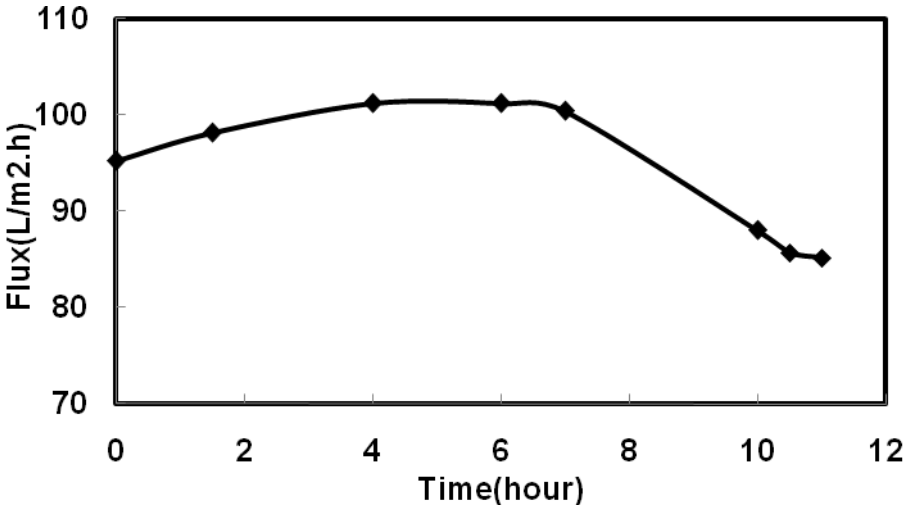

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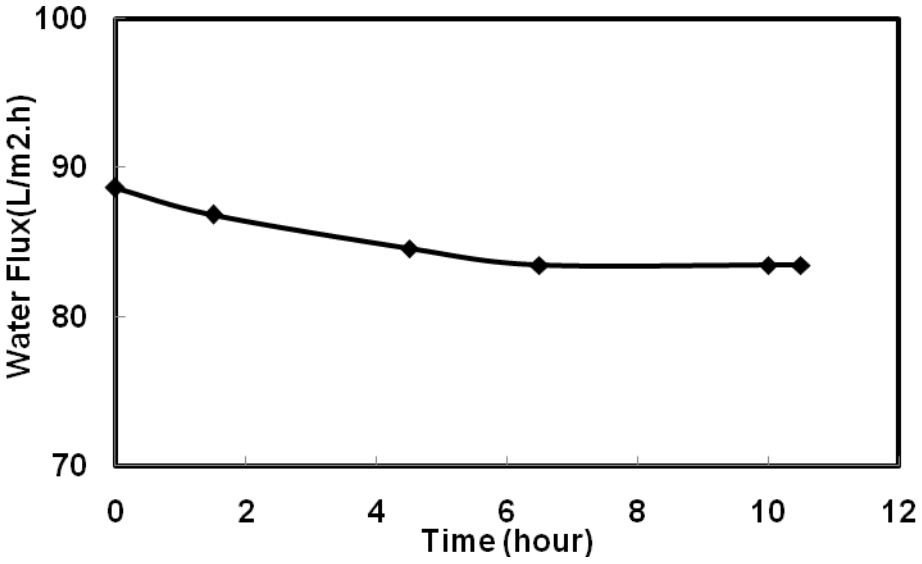

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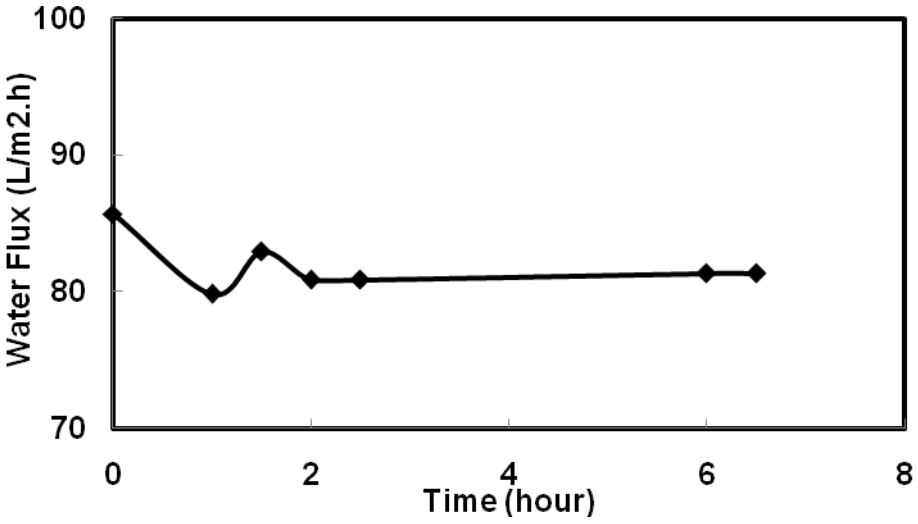


d)

Figure A. 12. Flux changes with time a) Initial clean water flux b) Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

Table A. 25 Clean water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (third trial)

	Time (hour)	Flux (L/m2.h)
T0	0	108.0
T1	2	102.9
T2	5	98.9
T3	6.5	109.0
T4	10.5	108.0
T5	11.5	98.9
T6	12	93.2
T7	12.5	89.3
T8	13	96.7
T9	13.5	89.3
T10	14	89.3
T11	14.5	85.7
T12	15	85.7
T13	15.5	85.7

Table A. 26 Raw water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (third trial)

	Time (hour)	Flux (L/m2.h)
T0	0	95.2
T1	1.5	98.1
T2	4	101.2
T3	6	101.2
T4	7	100.4
T5	10	88.1
T6	10.5	85.7
T7	11	85.1

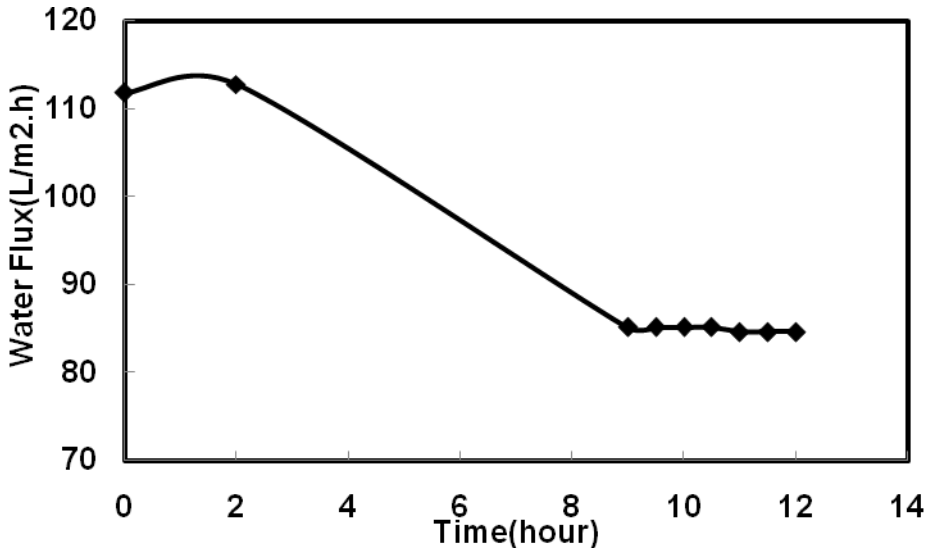
Table A. 27 Clean water flux values after raw water passage with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (third trial)

	Time (hour)	Flux (L/m2.h)
T0	0	88.7
T1	1.5	86.9
T2	4.5	84.6
T3	6.5	83.5
T4	10	83.5
T5	10.5	83.5

Table A. 28 Clean water flux after cleaning values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment (third trial)

	Time (hour)	Flux (L/m2.h)
T0	0	85.7
T1	1	79.9
T2	1.5	82.9
T3	2	80.9
T4	2.5	80.9
T5	6	81.4
T6	6.5	81.4

9. Experimental Data with NF-270 at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, with pre-treatment



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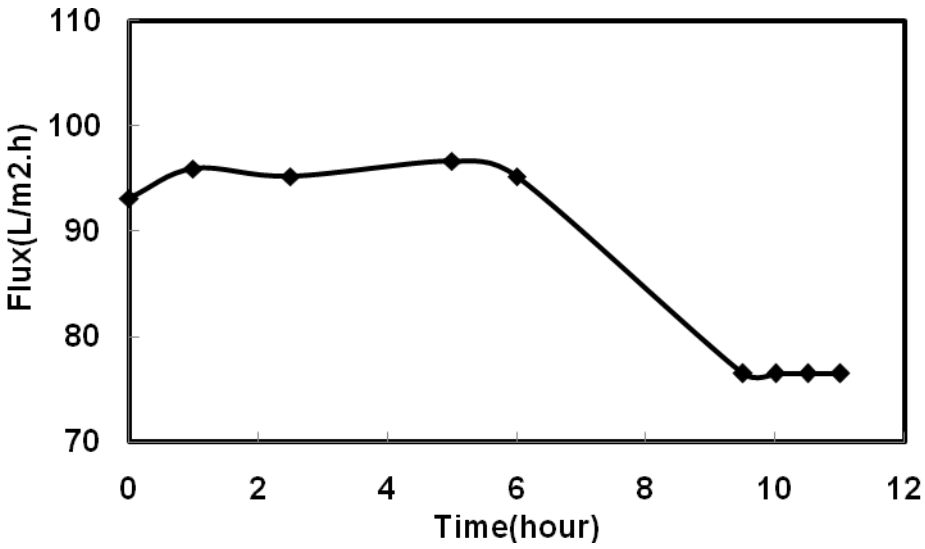

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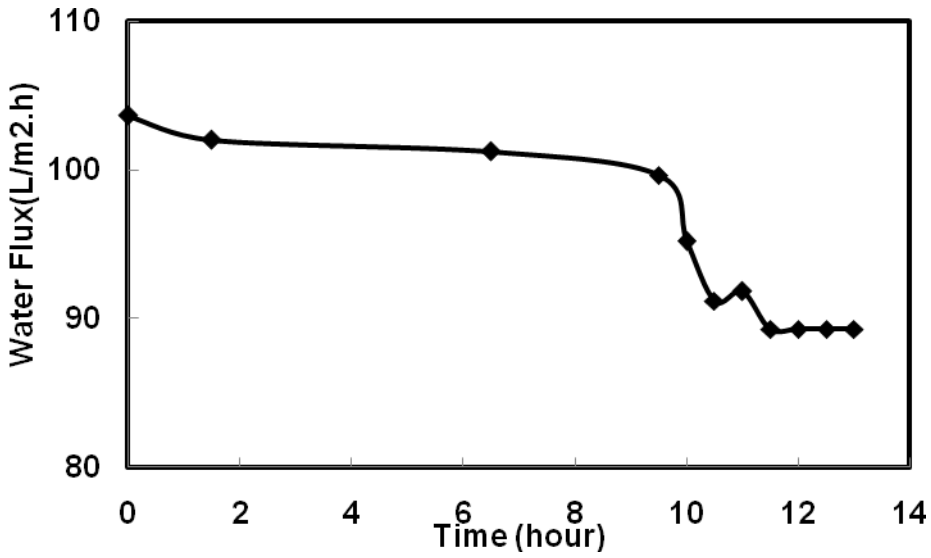

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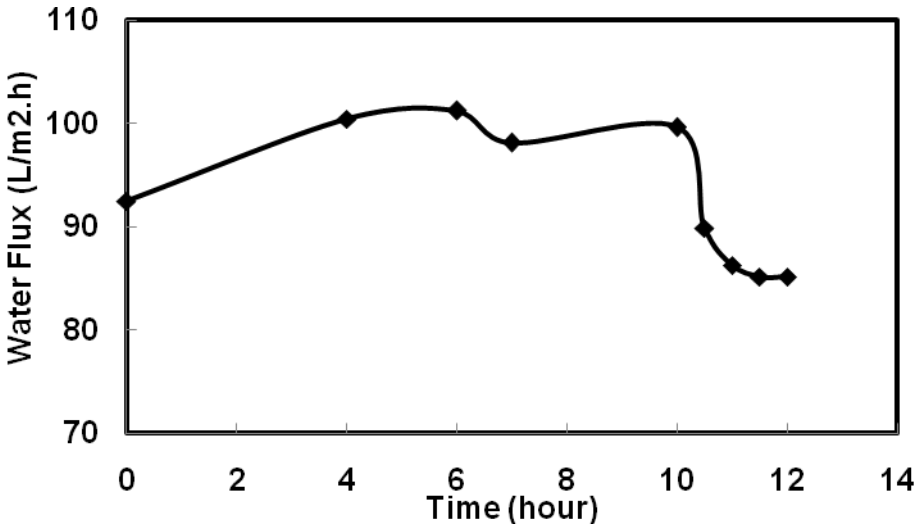


d)

Figure A. 13. Flux changes with time a) Initial clean water flux b)Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

Table A. 29 Clean water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	111.8
T1	2	112.8
T2	9	85.1
T3	9.5	85.1
T4	10	85.1
T5	10.5	85.1
T6	11	84.6
T7	11.5	84.6
T8	12	84.6

Table A. 30 Raw water flux values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	93.2
T1	1	95.9
T2	2.5	95.2
T3	5	96.7
T4	6	95.2
T5	9.5	76.5
T6	10	76.5
T7	10.5	76.5
T8	11	76.5

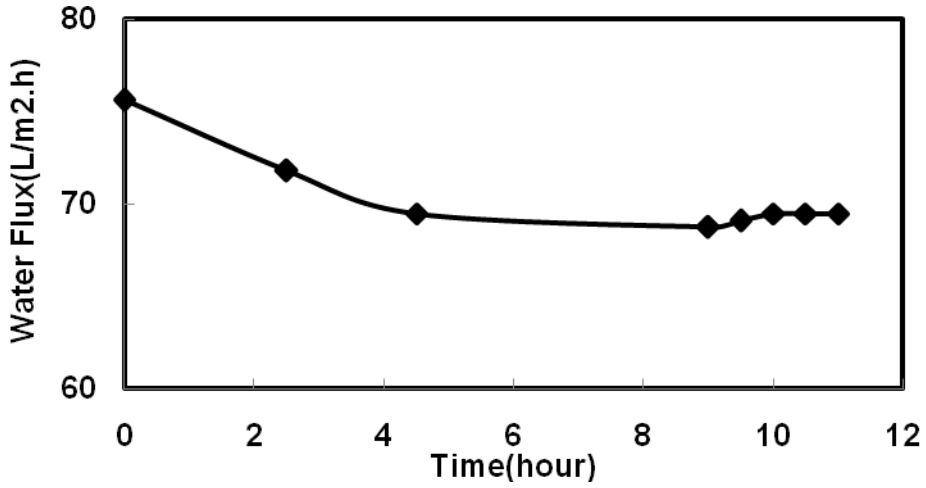
Table A. 31 Clean water flux values after raw water passage with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	103.7
T1	1.5	102.0
T2	6.5	101.2
T3	9.5	99.7
T4	10	95.2
T5	10.5	91.2
T6	11	91.8
T7	11.5	89.3
T8	12	89.3
T9	12.5	89.3
T10	13	89.3

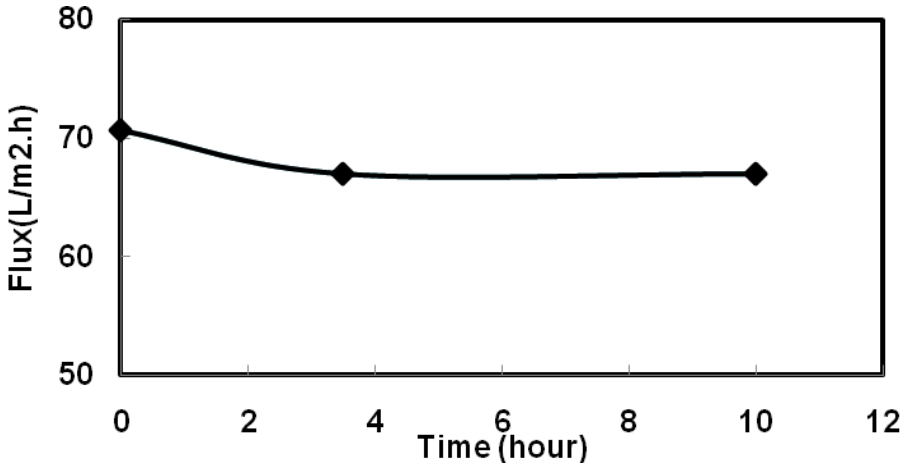
Table A. 32 Clean water flux after cleaning values with NF-270 membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	92.5
T1	4	100.4
T2	6	101.2
T3	7	98.1
T4	10	99.7
T5	10.5	89.9
T6	11	86.3
T7	11.5	85.1
T8	12	85.1

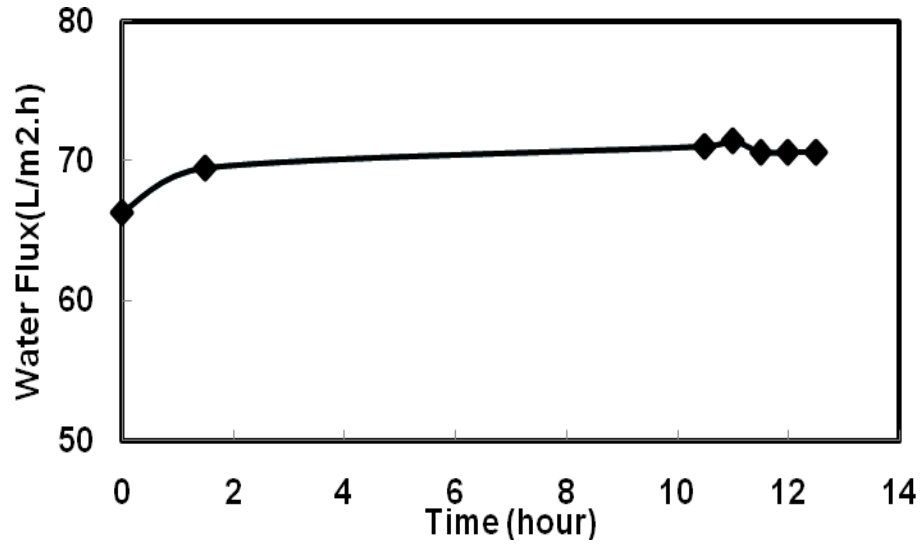
10. Experimental Data with DL-NF at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, without pre-treatment



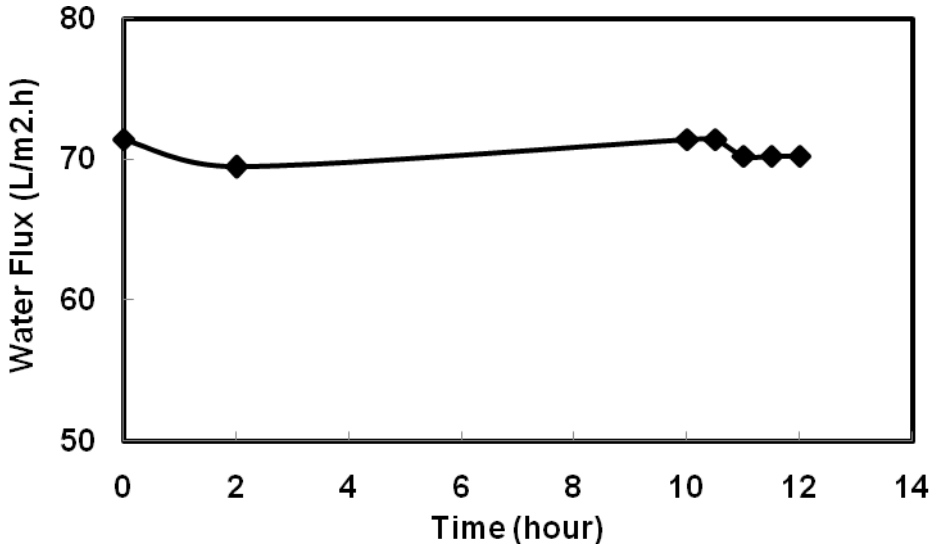
a)



b)



c)



d)

Figure A. 14. Flux changes with time a) Initial clean water flux b)Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

Table A. 33 Clean water flux values with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	75.6
T1	2.5	71.8
T2	4.5	69.5
T3	9	68.8
T4	9.5	69.1
T5	10	69.5
T6	10.5	69.5
T7	11	69.5

Table A. 34 Raw water flux values with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	70.6
T1	3.5	67.0
T2	10	67.0

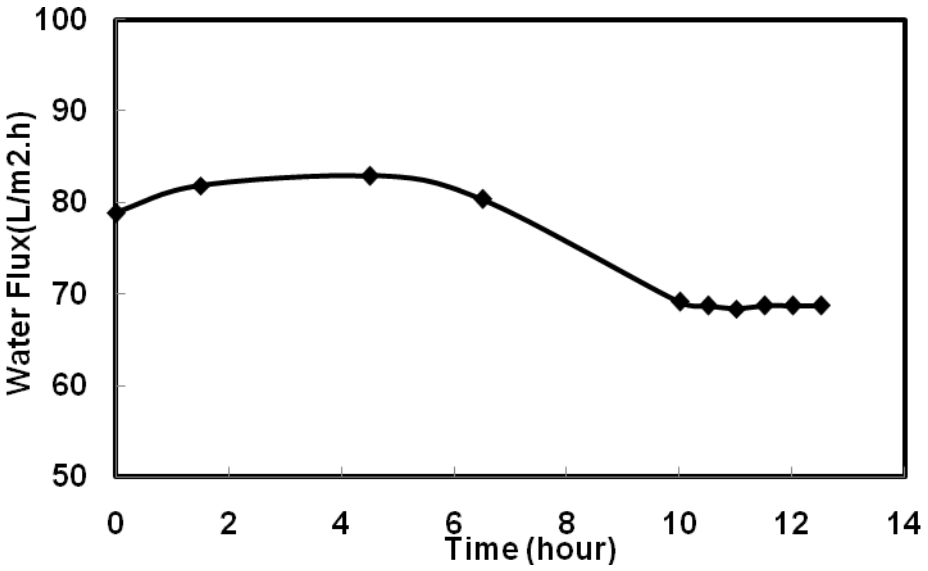
Table A. 35 Clean water flux values after raw water passage with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	66.3
T1	1.5	69.5
T2	10.5	71.0
T3	11	71.4
T4	11.5	70.6
T5	12	70.6
T6	12.5	70.6

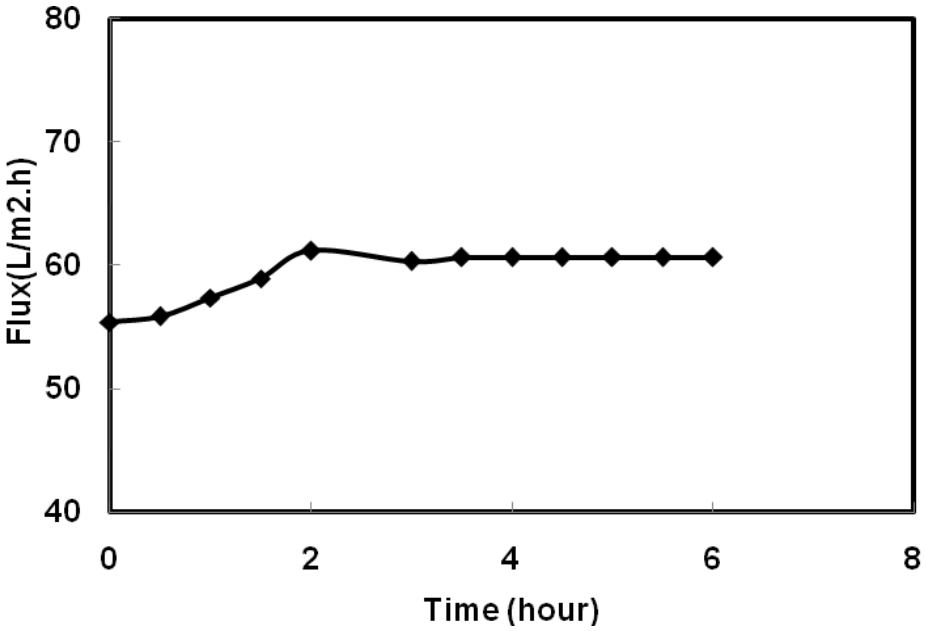
Table A. 36 Clean water flux after cleaning values with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, without pre-treatment

	Time (hour)	Flux (L/m2.h)
T0	0	71.4
T1	2	69.5
T2	10	71.4
T3	10.5	71.4
T4	11	70.3
T5	11.5	70.3
T6	12	70.3

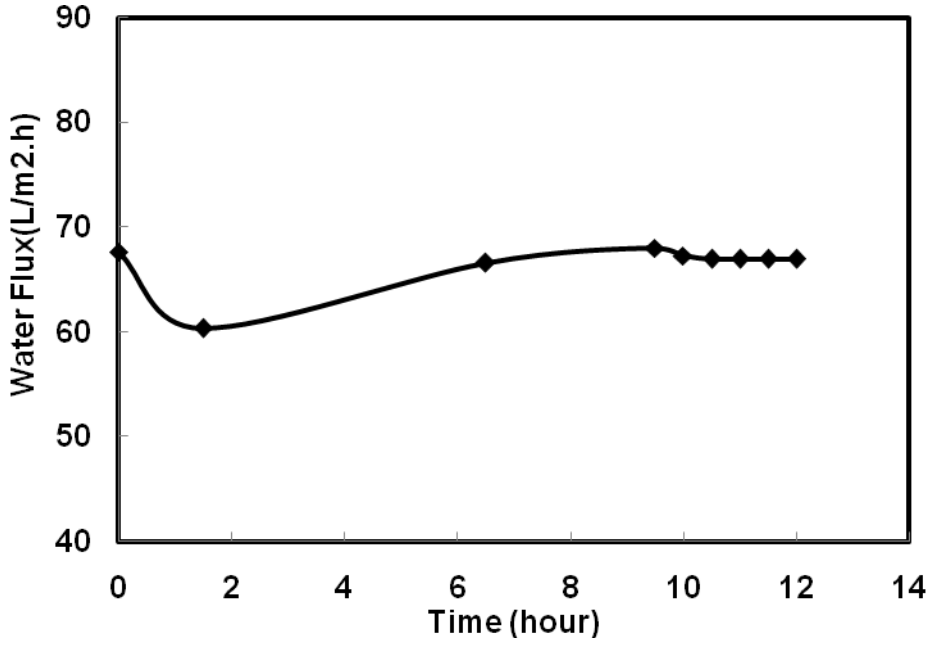
11. Experimental Data with DL-NF at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity, with pre-treatment



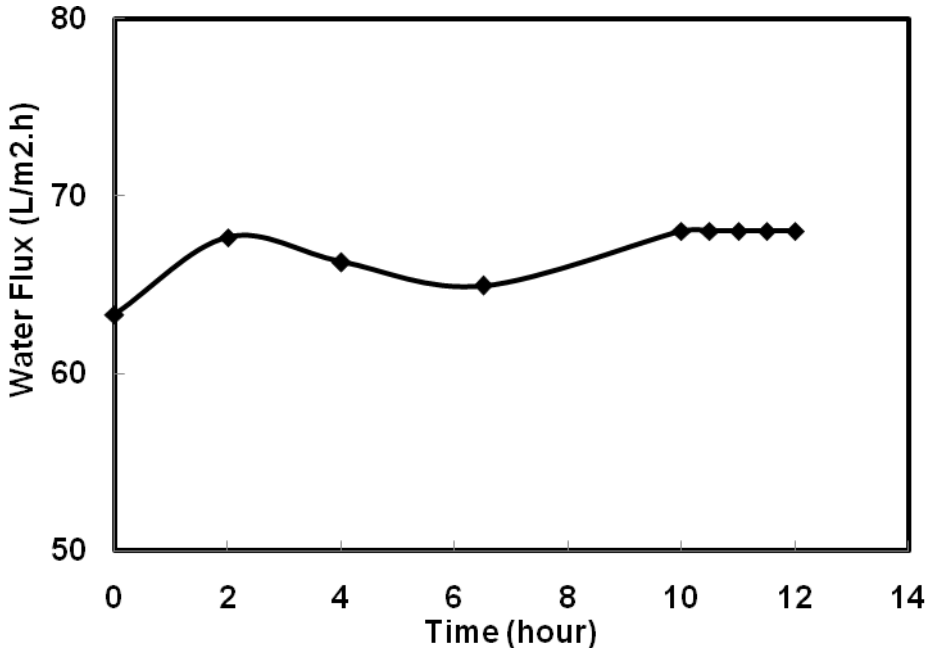
a)


80
70
60
50
40
Flux(L/m2.h)
0
2
4
6
8
Time (hour)

b)


90
80
70
60
50
40
Water Flux(L/m2.h)
0
2
4
6
8
10
12
14
Time (hour)

c)



d)

Figure A. 15. Flux changes with time a) Initial clean water flux b)Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

Table A. 37 Clean water flux values with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pretreated raw water

	Time (hour)	Flux (L/m2.h)
T0	0	78.9
T1	1.5	81.9
T2	4.5	82.9
T3	6.5	80.4
T4	10	69.1
T5	10.5	68.8
T6	11	68.4
T7	11.5	68.8
T8	12	68.8
T9	12.5	68.8

Table A. 38 Raw water flux values with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pretreated raw water

	Time (hour)	Flux (L/m2.h)
T0	0	55.4
T1	0.5	55.9
T2	1	57.4
T3	1.5	59.0
T4	2	61.2
T5	3	60.4
T6	3.5	60.6
T7	4	60.6
T8	4.5	60.6
T9	5	60.6
T10	5.5	60.6
T11	6	60.6

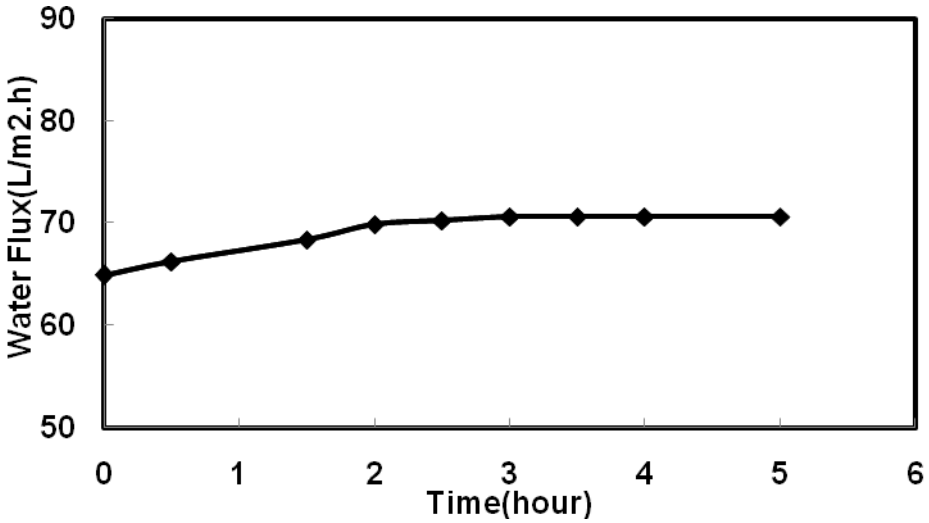
Table A. 39 Clean water flux values after raw water passage with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pretreated raw water

	Time (hour)	Flux (L/m2.h)
T0	0	67.7
T1	1.5	60.4
T2	6.5	66.6
T3	9.5	68.0
T4	10	67.3
T5	10.5	67.0
T6	11	67.0
T7	11.5	67.0
T8	12	67.0

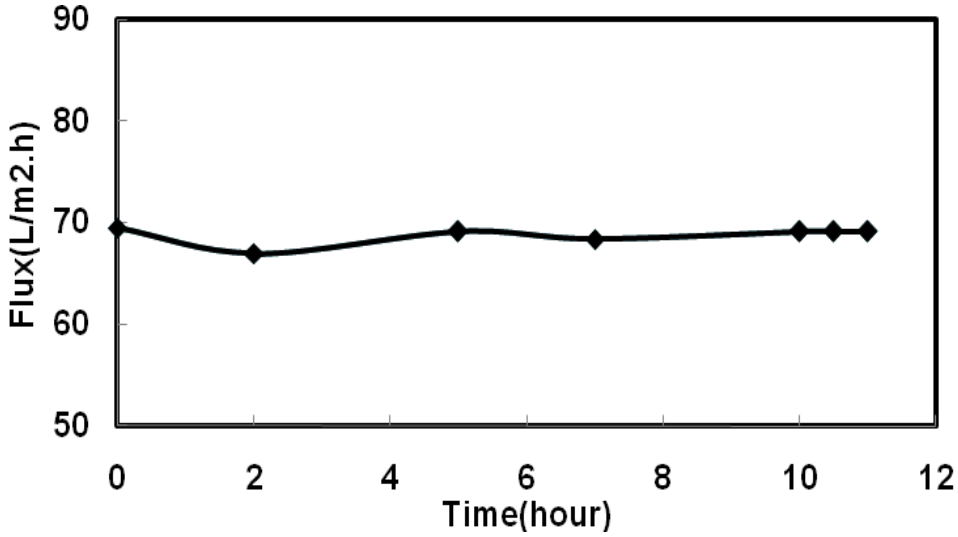
Table A. 40 Clean water flux after cleaning values with DL-NF membrane at 6.9 bar pressure, 1.2 m/sec crossflow velocity, with pretreated raw water

	Time (hour)	Flux (L/m2.h)
T0	0	63.3
T1	2	67.7
T2	4	66.3
T3	6.5	64.9
T4	10	68.0
T5	10.5	68.0
T6	11	68.0
T7	11.5	68.0
T8	12	68.0

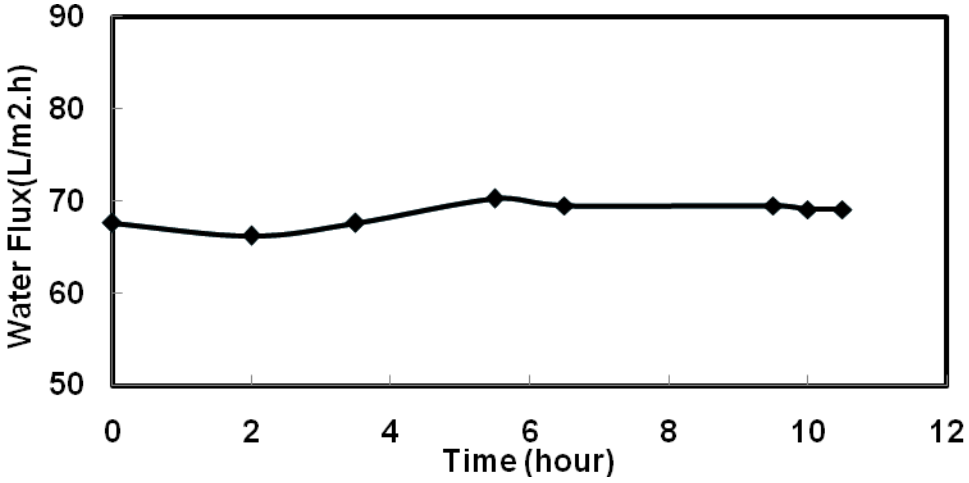
12. Experimental Data with DL-NF at 6.9 bar transmembrane pressure, 0.7m/s cross-flow velocity, with pre-treatment



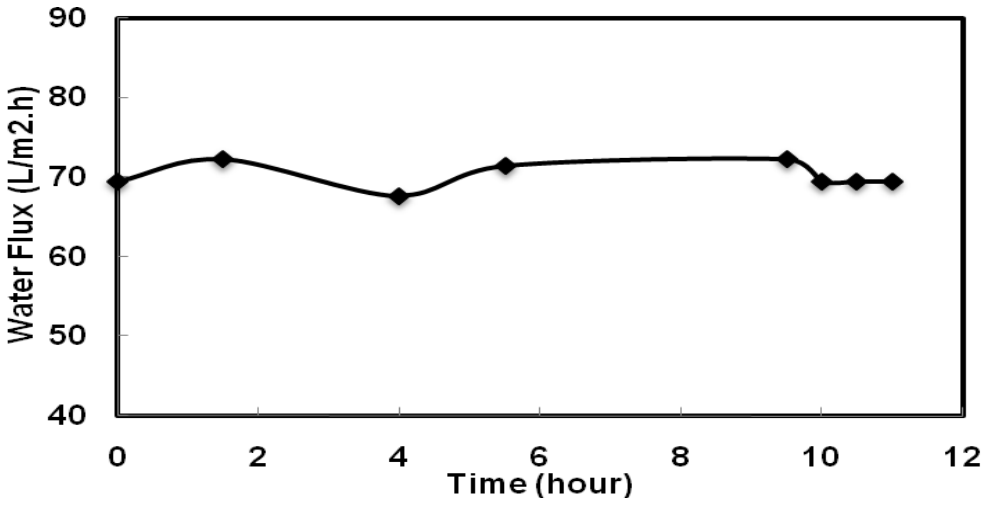
a)


90
80
70
60
50
Flux(L/m2.h)
0
2
4
6
8
10
12
Time(hour)

b)


90
80
70
60
50
Water Flux(L/m2.h)
0
2
4
6
8
10
12
Time (hour)

c)



d)

Figure A. 16. Flux changes with time a) Initial clean water flux b)Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

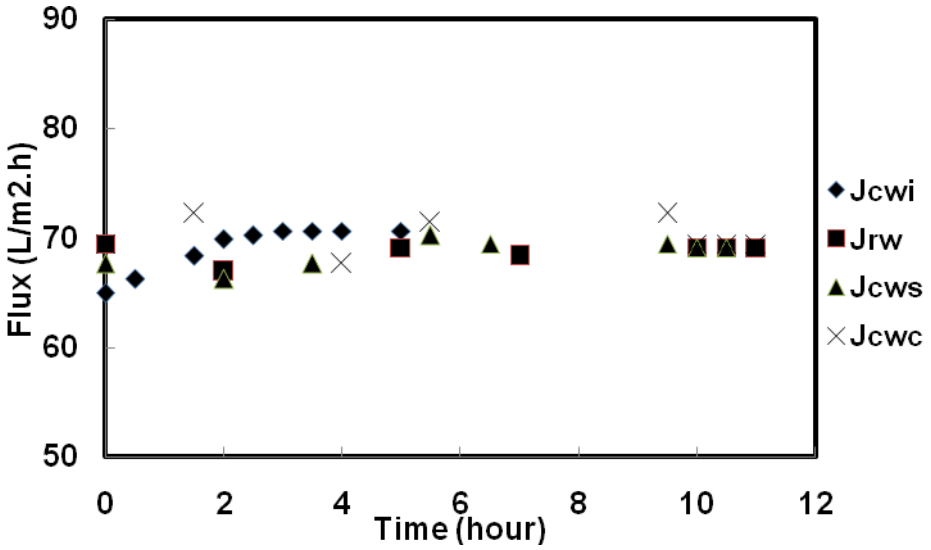


Figure A. 17 Time-dependent flux values for DL-NF membrane conducted with pretreated raw water at 6.9 bar pressure, 0.7 m/sec cross-flow velocity

Table A. 41 Clean water flux values with DL-NF membrane at 6.9 bar pressure, 0.7 m/sec crossflow velocity

	Time (hour)	Flux (L/m2.h)
T0	0	64.9
T1	0.5	66.3
T2	1.5	68.4
T3	2	69.9
T4	2.5	70.3
T5	3	70.6
T6	3.5	70.6
T7	4	70.6
T8	5	70.6

Table A. 42 Raw water flux values with DL-NF membrane at 6.9 bar pressure, 0.7 m/sec crossflow velocity

	Time (hour)	Flux(L/m2.h)
T0	0	69.5
T1	2	67.0
T2	5	69.1
T3	7	68.4
T4	10	69.1
T5	10.5	69.1
T6	11	69.1

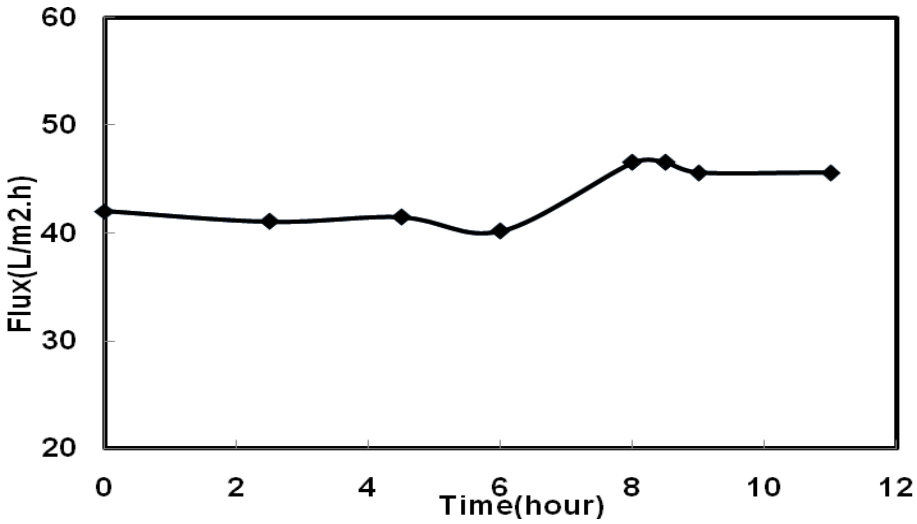
Table A. 43 Clean water flux values after raw water passage with DL-NF membrane at 6.9 bar pressure, 0.7 m/sec crossflow velocity

	Time (hour)	Flux (L/m2.h)
T0	0	67.7
T1	2	66.3
T2	3.5	67.7
T3	5.5	70.3
T4	6.5	69.5
T5	9.5	69.5
T6	10	69.1
T7	10.5	69.1

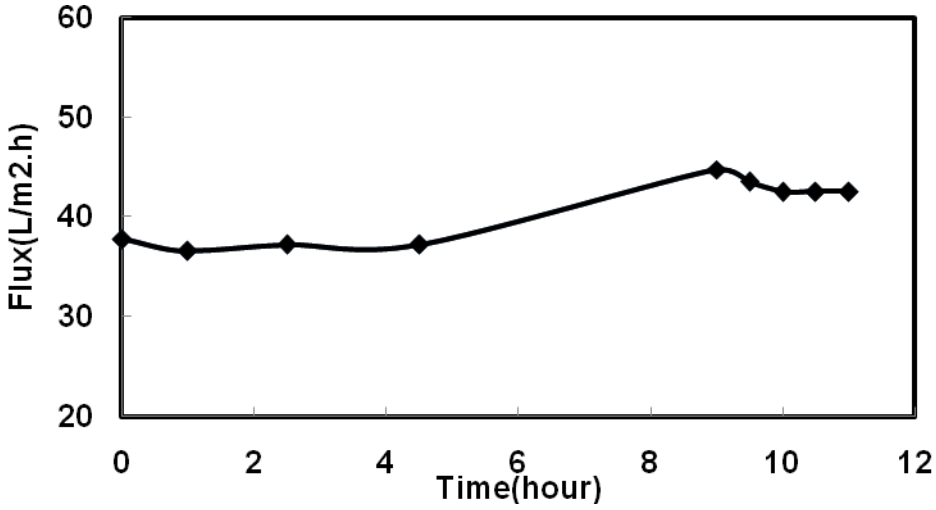
Table A. 44 Clean water flux after cleaning values with DL-NF membrane at 6.9 bar pressure, 0.7 m/sec crossflow velocity

	Time (hour)	Flux (L/m2.h)
T0	0	69.5
T1	1.5	72.2
T2	4	67.7
T3	5.5	71.4
T4	9.5	72.2
T5	10	69.5
T6	10.5	69.5
T7	11	69.5

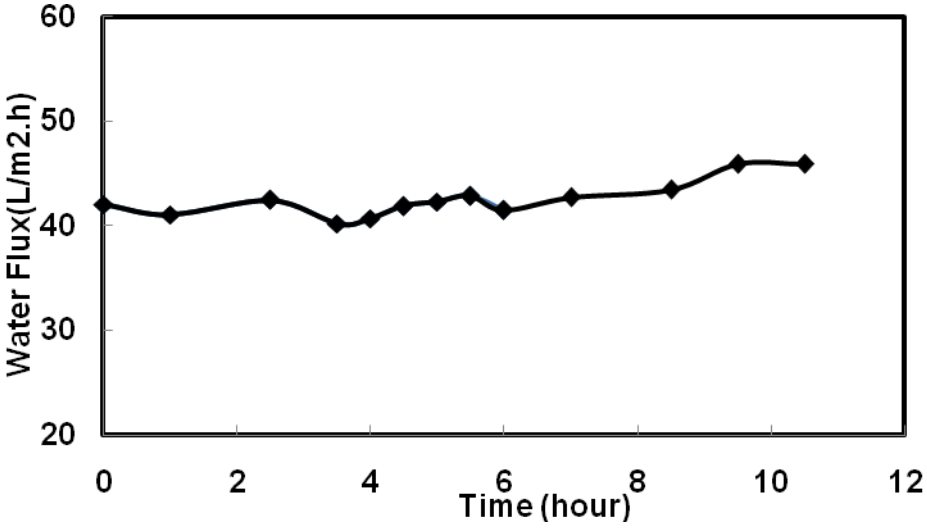
13. Experimental Data with DL-NF at 3.5 bar transmembrane pressure, 1.2 m/s cross-flow velocity, with pre-treatment



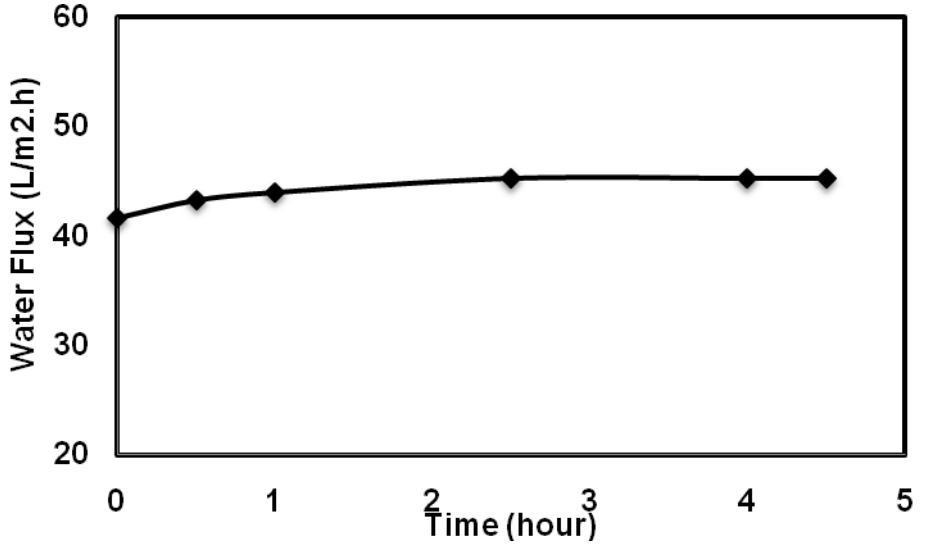
a)



b)


60
50
40
30
20
Water Flux(L/m2.h)
0
2
4
6
8
10
12
Time (hour)

c)


60
50
40
30
20
Water Flux (L/m2.h)
0
1
2
3
4
5
Time (hour)

d)

Figure A. 18. Flux changes with time a) Initial clean water flux b)Raw water flux c) Clean water flux after raw water d) Clean water flux after cleaning is applied

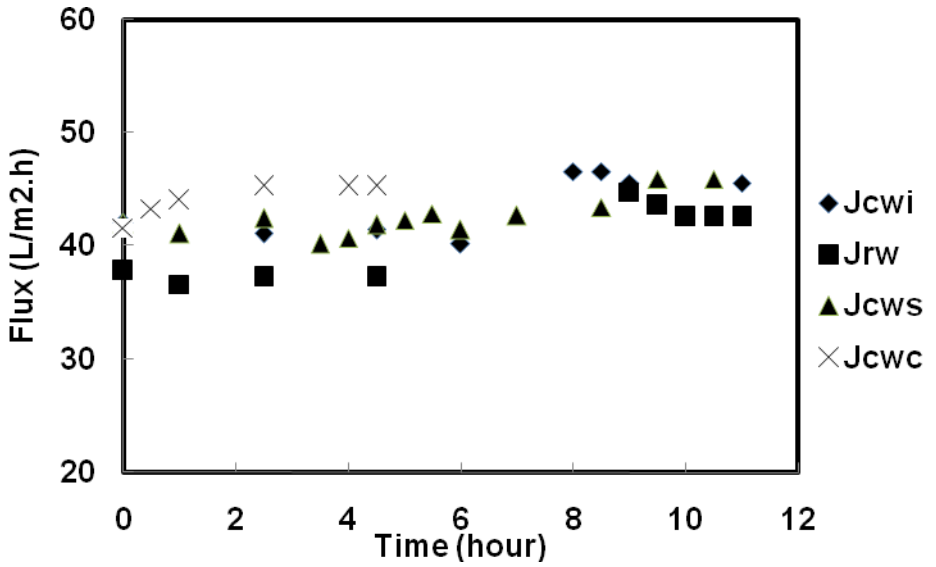


Figure A. 19 Time-dependent flux values for DL-NF membrane conducted with pretreated raw water at 3.5 bar pressure, 1.2 m/sec cross-flow velocity

Table A. 45 Clean water flux values with DL-NF membrane at 3.5 bar pressure, 1.2 m/sec crossflow velocity

	Time (hour)	Flux (L/m2.h)
T0	0	42.0
T1	2.5	41.1
T2	4.5	41.5
T3	6	40.2
T4	8	46.6
T5	8.5	46.6
T6	9	45.6
T7	11	45.6

Table A. 46 Raw water flux values with DL-NF membrane at 3.5 bar pressure, 1.2 m/sec crossflow velocity

	Time (hour)	Flux (L/m2.h)
T0	0	37.8
T1	1	36.6
T2	2.5	37.3
T3	4.5	37.3
T4	9	44.8
T5	9.5	43.6
T6	10	42.6
T7	10.5	42.6
T8	11	42.6

Table A. 47 Clean water flux values after raw water passage with DL-NF membrane at 3.5 bar pressure, 1.2 m/sec crossflow velocity

	Time (hour)	Flux (L/m2.h)
T0	0	42.0
T1	1	41.1
T2	2.5	42.4
T3	3.5	40.2
T4	4	40.7
T5	4.5	41.9
T6	5	42.3
T7	5.5	42.9
T8	6	41.5
T9	7	42.7
T10	8.5	43.4
T11	9.5	45.9
T12	10.5	45.9

Table A. 48 Clean water flux after cleaning values with DL-NF membrane at 3.5 bar pressure, 1.2 m/sec crossflow velocity

	Time (hour)	Flux (L/m2.h)
T0	0	41.6
T1	0.5	43.3
T2	1	44.0
T3	2.5	45.3
T4	4	45.3
T5	4.5	45.3