

Challenges in the chemical cleaning of UF membranes fouled at low temperatures

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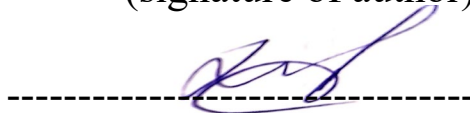
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DECLARATION

I hereby, declare that this manuscript, entitled “Challenges in the chemical cleaning of UF membranes fouled at low temperatures”, is the result of my own work except for quotations and citations which have been duly acknowledged.

I also declare that, to the best of my knowledge and belief, it has not been previously or concurrently submitted, in whole or in part, for any other degree or diploma at Nazarbayev University or any other national or international institution.

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Abstract

Membrane separation technology is widely applied in water treatment; nonetheless, currently, there is no any established protocol for filtration and cleaning processes. This research attempts to study the nature of membrane fouling at low temperatures and select optimal conditions for chemical cleaning based on the membrane fouling propensity. Due to the complex nature of membrane fouling, it is difficult to predict fouling intensity and mechanism. Optimal chemical cleaning conditions could be selected based on the fouling mechanism parameters and membrane reaction to cleaning agents at different temperatures.

From the literature review, it is clear that ultrafiltration process can successfully purify water from various contaminants through size exclusion mechanism and experiments were conducted with this process. In addition, the organic fouling remain as the major performance decline problem in membrane treatment processes. The protein fouling type (reversible or irreversible) and pattern is inquired through filtration experiments performed at different temperatures and chemical cleaning efficiency is investigated through membrane surface analysis. It was observed that, low filtration temperature affects membrane performance negatively by elevating fouling intensity, while high operation temperature demonstrated better water flux. Nonetheless, membrane surface investigation infers that high operation temperature affected membrane structure which can reduce membrane lifetime. These operation temperature influences must be considered in deciding convenient filtration process conditions based on preferred long-term operation or high water flux.

Keywords: *membrane, ultrafiltration, fouling, protein, organic fouling, chemical cleaning, operating temperature, zeta potential, FTIR, atomic force microscopy.*

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Chapter 1 - Introduction

1.1 General

Water is one of the most essential environmental resources of the planet. However, only 2.5 % of the global water resource is considered fresh and not easily accessible [1]. For the last hundred years, world-wide water use increased more than eight times as a natural result of global population growth and industrial boom [1]. The continuous trend will yield an increased water scarcity level among world population. Considering mentioned facts, finding solutions for wide scale water and wastewater treatment is very crucial.

1.2 Research Significance

One of the promising and efficient methods of water treatment is membrane separation technology. Nonetheless, wide application of membrane separation technology (MST) is significantly impeded by membrane fouling factor. The motivation of this research paper is formulated on the need for improvement of water treatment performance and reducing operational costs of MST by reusing cleaned membranes. Membrane performance could be improved by performing filtration at optimal conditions. This research aims to investigate temperature impact on filtration and chemical cleaning of UF membranes.

In order to mimic environmental conditions and to investigate nature and propensity of organic fouling, which is the major fouling problem in water treatment, protein is used as a foulant in this study. UF process operates through size exclusion mechanism to reject contaminants and rejection rate highly depends on size, shape of pollutants and the membrane pore size. Therefore, it is crucial to study how protein and the membrane react and change at different temperatures. Temperature impact on membrane cleaning efficiency was studied through cleaning experiments performed with four different cleaning agents – nitric acid, liquid bleach, caustic soda, and water. It has commonly been acknowledged that the membrane cleanliness level could be obtained by comparison of surface characteristics of pristine and cleaned membranes. Also, the water flux dissimilarity between fouled and cleaned membranes can provide information about cleaning efficiency. The application of water flux and recovery measurements, zeta potential analyzer, contact angle meter, Fourier Transform Infrared

Reflectance (FTIR) spectra, and Atomic Force Microscopy (AFM) will assist in gathering experimental data about the membrane fouling and chemical cleaning efficiency that could help in selection of optimal filtration conditions.

1.3 Research Aims and Objectives

The objectives of this research project are as follows:

1. Investigate membrane parameters including hydrophobicity, permeability, and surface charge.
2. Conduct membrane filtration and cleaning experiments at different temperatures.
3. Investigate membrane surface condition after the experiments including hydrophobicity, surface charge, cleanness, and surface roughness.
4. Inquire membrane fouling mechanism based on experimental data.
5. Study membrane cleaning efficiency at different temperatures.
6. Summarize temperature influence on membrane filtration and cleaning processes.

1.4 Thesis Structure

In order to achieve mentioned aims, research design was formulated and divided into three phases as illustrated in Figure 1.

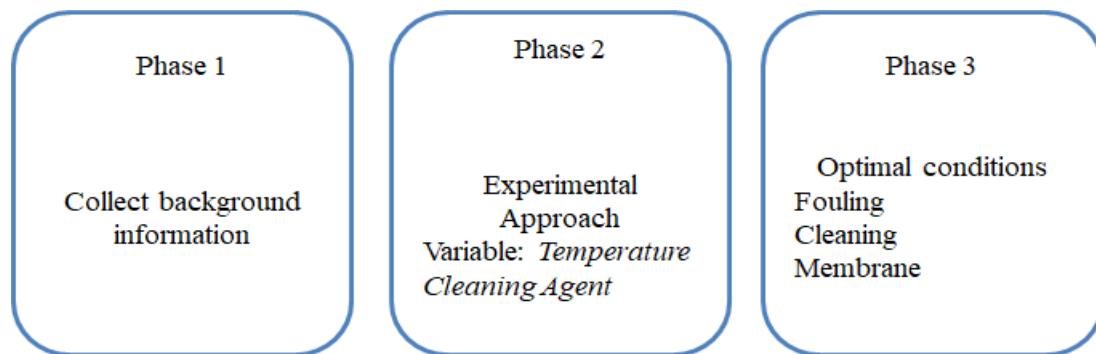


Figure 1.1: A concise illustration of research phases.

In phase 1, background information major topics related to the research that are membrane separation technology, conventional membrane separation processes, membrane parameters, permeation mechanisms, concentration polarization, fouling phenomena, temperature impact and challenges, and theoretical water flux models are collected and included

in Chapter 2. The theoretical models for predicting water flux are based on the different membrane fouling mechanisms. In phase 3, detailed information about experimental approach of research methodology is presented and included in Chapter 3. In order to understand complex nature of fouling phenomena, set of fouling and cleaning experiments are conducted with manipulating temperature and cleaning agent variables; other conditions of the experiments remains same. Chapter 4 includes and discusses experimental results of fouling and chemical cleaning experiments performed at different temperatures and membrane surface analysis. Chapter 5 sums up this research with a summary of fouling and cleaning temperature impact and optimal conditions for filtration process.

Chapter 2 - Literature Review

2.1 Membrane Separation Technology

The membrane separation technology is based on the application of the membrane that acts as a perm-selective filter between two phases that retains certain elements. The most important factor deciding the retaining mechanism of the MST process is membrane pores that come in various shape and sizes. The separation of the components is achieved through applying of the driving force. Components separation efficiency depends on the physicochemical properties of the membrane and components including shape, size, and chemical structure. The basic concept of MST process is presented in Figure 2.1.

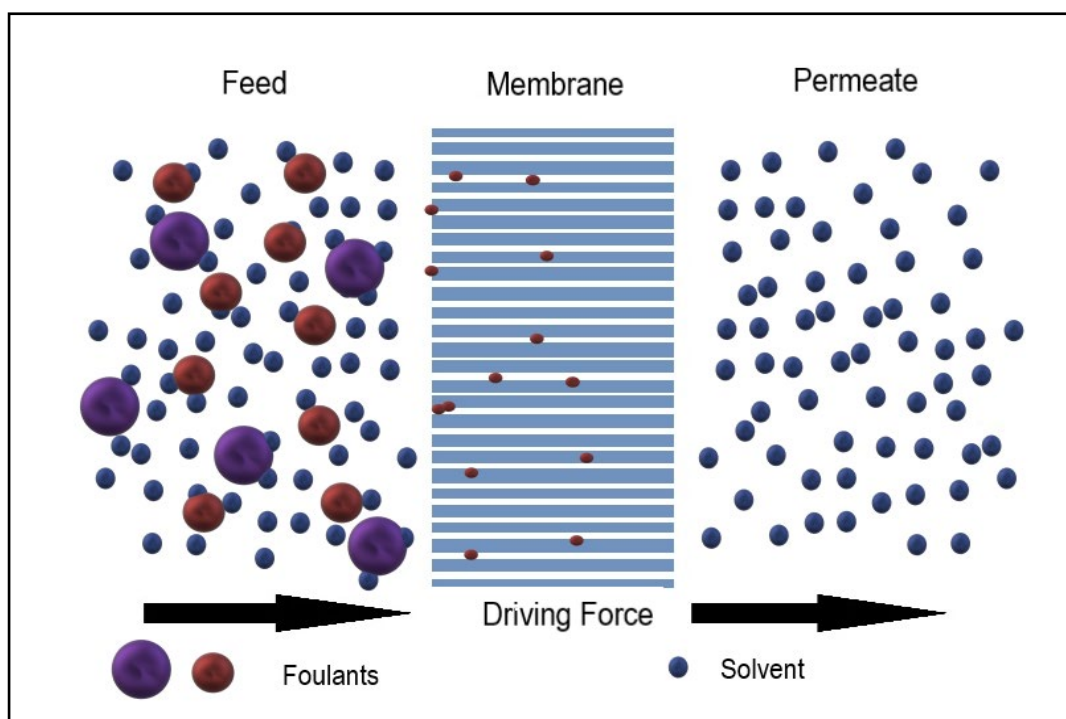


Figure 2.1: MST Process Schematic Diagram.

Today, MST is applied in different areas such as water and wastewater treatment, water desalination, beverage and food industries, pharmaceutical and healthcare industries, petrochemical industries, biotechnology, and production of ultra-pure water. MST application fields and its scale are increasing due to energy efficiency, high quality performance, and relatively simple operation process parameters. In addition, MST processes are environmentally

friendly with low environmental impact [2]. The other benefits of MST include continuous separation application, capability to combine different separation technologies, adjustable membrane properties, and no demand for additives. Nonetheless, MST application in water and wastewater treatment is limited on account of process disadvantages such as fouling and concentration polarization phenomenon, and high cost. Most of the conventional MST processes operate requiring relatively low energy; however, cost of the MST process is increased due to initial high cost of required equipment and membranes. For the purpose of treating contaminated water in large scales, selecting a convenient membrane with high rejection performance and at reasonable cost is crucial. The cost of the MST could be reduced by limiting fouling impact and reusing membranes after chemical cleaning. Also, finding the optimal MST conditions is important to obtain high contaminant rejection rate. The performance of the membrane separation can be affected by many factors such as operation conditions, the liquid mixture characteristics, the membrane properties, and reaction of contaminants to the membrane surface.

2.2 Conventional Membrane Separation Processes

The conventional membrane processes include microfiltration (MF), ultrafiltration, nanofiltration (NF), and reverse osmosis (RO). In order to achieve the required water quality from wastewater reclamation, MST frequently consists of multiple phases. MF and UF are generally applied as pre-treatment phase and NF and RO as post-treatment phase.

MF is the filtration process which is similar to conventional coarse filtration and frequently applied as the first phase of MST. In MF, the operating pressure ranges from 0.1 to 2 bars. MF membrane pore sizes range from 0.05 to 10 μm and thickness range from 10 to 150 μm . MF process can treat water from suspended solids, bacteria, and viruses and other components with size greater than membrane pore diameter [3]. The main advantages of the MF are the simplicity of the process and low operational cost due to the low energy requirement. However, MF application is very limited as process cannot retain particles smaller than 0.1 μm . Also, MF could allow passage of big particles due to the complex shape of the pollutants. For example, long and thin particle could pass through membrane. Permeation mechanism in MF process is convective flow. Water flux in MF is directly proportional to the applied driving pressure and calculated by Equation 2.1 [4].

$$J = A\Delta P \quad (2.1)$$

where,

J – theoretical water flux;

A – permeability constant depending on porosity, pore size, and viscosity;

ΔP – pressure difference.

UF is another filtration process similar to conventional coarse filtration in which hydrostatic pressure is applied as driving force to pass liquid through the membrane. In UF, the driving pressure ranges from 1 to 5 bars. UF process use membranes with more asymmetric structure compared to MF and usually consist of two layers: thin top layer and porous sublayer [4]. The typical pore diameter of UF membranes are within 1-100 nm range and thickness is approximately 150 μm . UF procedure can treat wastewater by retaining suspended solids, bacteria, and spherical viruses, and treat the effluents in chemical industry [5]. In municipal water treatment, application of UF as pre-treatment is favored as UF demonstrate improved results of membrane fouling prevention [6, 7]. Furthermore, UF can be used during or after the bio-treatment with or without application of further pretreatment processes [7-9]. The advantages of UF include relatively low pressure requirement and effective removal of colloids. Furthermore, the UF process has simple operation system. The main drawbacks of UF are inability to desalinate water and retain low molecular weight species. Permeation mechanism in UF process is also convective flow and water flux directly depends on driving pressure. With consideration of asymmetric membrane structure characteristics of UF membranes, the theoretical water flux of the UF process is calculated by Equation 2.2 [4].

$$J = K\Delta P \quad (2.2)$$

where,

J - theoretical water flux;

K - permeability constant depending on porosity, pore size, and viscosity.

NF process works with a “size exclusion” concept in which after applying driving force, ideally semipermeable membranes allow the flux of only solvent. In NF, the driving pressure ranges from 5 to 20 bars and process is characterized as a high-pressure process. NF process use composite membranes. The typical pore diameters of NF membranes are within 0.5-2 nm range

and have approximate thickness 150 μm for sublayer and 1 μm for toplayer [4]. NF process can successfully purify liquid mixture from contaminants such as suspended solids, viruses, bacteria, proteins, pathogens, salts, paints, multivalent ions, and other low molecular weight species. With capability to efficiently remove various types of elements, the main benefit of NF processes is wide range application sphere such as water and wastewater treatment and disinfection, beverage, dairy, and food industries, biotechnology, and pharmaceutical and healthcare industries. Nonetheless, NF processes require higher driving pressure and consequently have higher operating cost. Furthermore, treatment of highly contaminated wastewater treatment with NF requires additional pre-treatment process. The pore sizes of NF membranes are middle between UF (total microporous) and RO (solution-diffusion) membranes. The main permeation mechanism in NF is solution diffusion. The theoretical water flux of the NF process is calculated by Equation 2.3 [4].

$$J = A(\Delta P - \Delta \pi) \quad (2.3)$$

where,

J - theoretical water flux for NF;

$\Delta \pi$ - osmotic pressure difference;

A - permeability coefficient of water defined by Equation 2.4.

$$A = \frac{D_w c_w V_w}{RT \Delta x} \quad (2.4)$$

Where,

D_w - diffusion coefficient of water;

c_w - concentration of water;

V_w - volume of water;

R - universal gas constant;

T - temperature;

Δx - membrane thickness.

The schematic comparison of filtration spectrum of conventional membrane separation is illustrated in Figure 2.2.

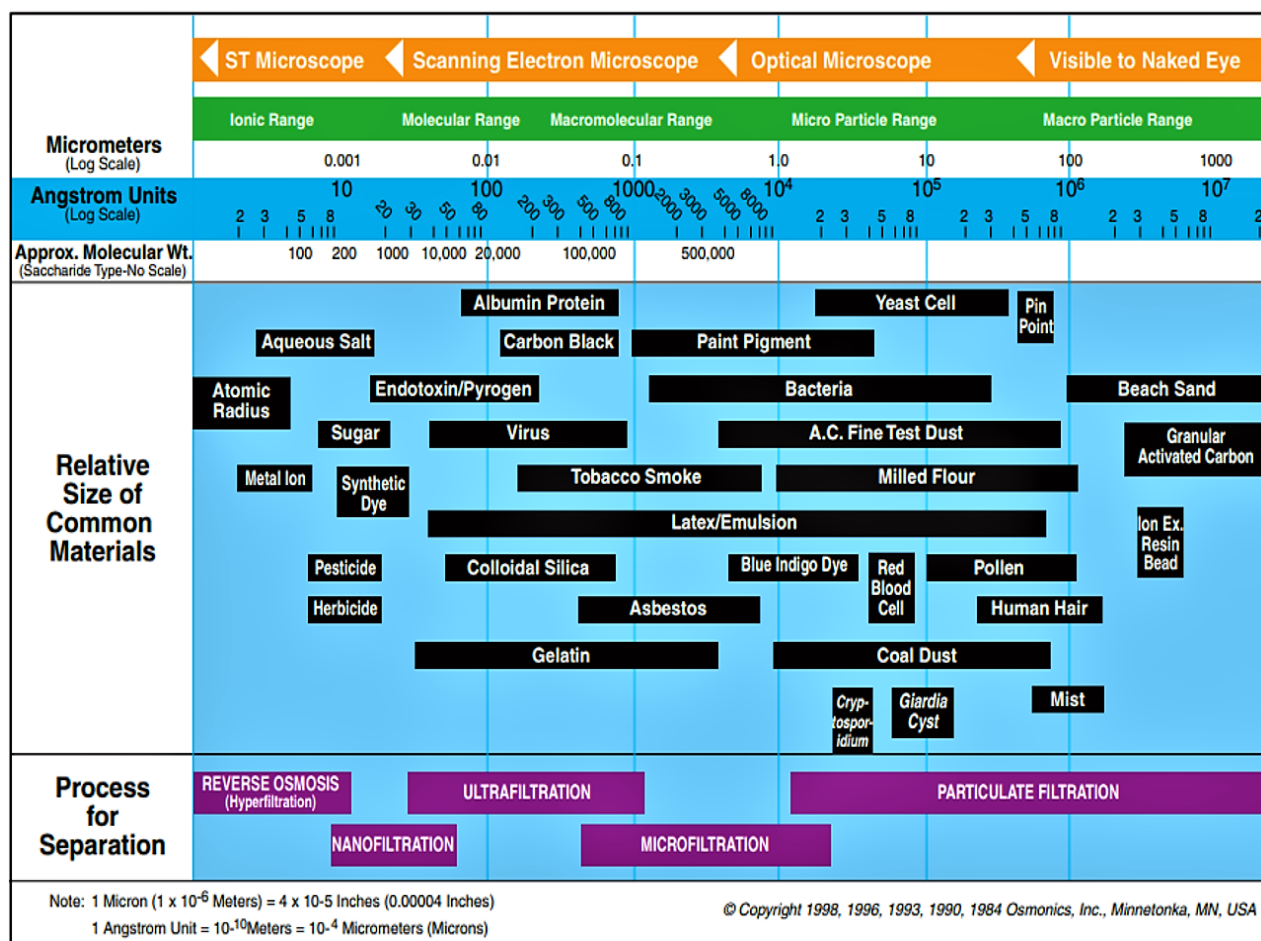


Figure 2.2: Filtration spectrum chart for MF, UF, NF, and RO processes [10].

RO is a type of membrane separation in which a liquid mixture passes through a filter in opposite path to natural osmosis after application of hydrostatic driving pressure. In order to start separation process, the driving pressure must be higher than the osmotic pressure of the mixture. The typical driving pressure ranges from 15 to 80 bars and characterized as a high-pressure process. RO membranes are typically asymmetric or composite. RO membranes are not totally semipermeable and consists two layers with 150 μm thick sublayer and 1 μm thick toplayer [4]. RO membranes have pore size less than 2 nm. RO separation process can efficiently purify water from suspended solids, viruses, bacteria, proteins, pathogens, paints, multivalent ions, monovalent ions, and other low molecular weight species [11]. In addition, RO process demonstrate up to 99.8 % of salt rejection and mostly applied in desalination of seawater; also, RO process an completely reject pathogens [11]. The main advantages of RO are high treatment performance, removal of hardness, and wide range of application sphere. Nonetheless, before

RO treatment, raw water should undergo a pre-treatment process due to high operational cost of RO process. Another drawback of RO process is complexity of the system. RO membranes are classified as dense and main permeation mechanism in RO is solution-diffusion. The theoretical water flux of the RO process is calculated by Equation 2.3 [4].

2.3 Membrane Materials

Membrane material type is important parameter that significantly affects membrane fouling type and behavior. The suitable membrane selection based on the material properties, surface morphology and geometry (in consideration of the interaction between foulant and membrane) can seriously improve MST performance [12]. Important factors of convenient membrane selection include cost, pore size, porosity, fouling, chemical resistance factors, and mechanical strength. All factors mentioned have influence for membrane performance, concentration polarization, and fouling. Membranes fabricated from materials with little adhering property and good resistance to cleaning agents demonstrates higher fouling recovery after chemical cleaning [11]. Such membranes are very efficient in reuse and can significantly reduce MST operational cost. The membrane materials demonstrate different fouling tendency depending on membrane morphology, hydrophobicity, and pore size [13, 14]. Membranes are divided into different categories depending on their material composition and most common types are: *Organic*: polysulfone (PSU), polyvinylidene fluoride (PVDF); polyethersulfone (PES); polyvinyl chloride (PVC); cellulose acetate (CA); and *Inorganic*: ceramic membranes.

PSU membranes can be used for UF, NF, and RO processes. The main advantages of PSU membranes are improved permeation result, chemical resistance, mechanical strength, and improved hydrophilicity by addition of additives [15]. However, the application of PSU membranes in high pressure processes is limited due to accumulation of organic fouling on membrane surface which consequently negatively impacts the permeate quality.

PVDF membranes can be used for MF, UF, NF, and RO processes. It is the most common membrane type used in MF. PVDF membrane application in potable water treatment is increasing due to improved performance of polymeric membrane. The main benefits of PVDF membrane include relatively low cost, prolonged membrane life and chlorine resistant property which is favored for membrane chemical cleaning [16]. In addition, PVDF membranes have the strongest mechanical strength among polymer membranes [17]. Moreover, PVDF membranes

can go through surface modification methods such as non-solvent stimulated phase separation method and demonstrate improved performance on irreversible fouling prevention [15]. The main disadvantage of PVDF membranes is intrinsic hydrophobicity that increases membrane fouling level due to interaction between hydrophobic membrane and hydrophobic foulant types such as proteins and microorganisms.

PES membranes are generally used in UF, NF, and RO processes. PES membranes are one of the common membrane type used in UF process; in addition, PES membranes are used as additional substratum in NF and RO systems. The main benefits of PES membranes include improved permeation result, chemical resistance, and mechanical strength [15]. Also, increased pores of PES membranes can reduce membrane fouling. After surface modifications, PES membranes demonstrate enhanced thermal resistance. The major disadvantage of PES membranes is inherent hydrophobic characteristic.

PVC membranes are most frequently used polymer membranes in MF and UF processes. The main advantages of PVC membranes include relatively low cost, chemical stability, and strong mechanical strength [15]. In addition, after surface modifications, PVC membranes demonstrate enhanced antifouling characteristic. The major drawback of PVC membranes is hydrophobic nature.

CA membranes are used MF, UF, NF, and RO processes. The main advantages of CA membranes are low cost due to natural existence of CA polymer and hydrophilicity that causes high fouling resistance [15]. Also, CA membranes demonstrate high salt rejection and are chlorine resistant. However, chemical cleaning options for such membranes are very limited as CA membranes have tendency to deteriorate permeability property at high driving pressure as CA polymer is inclined to hydrolysis [11]. Moreover, CA polymer is biodegradable which makes the membrane not resistant to attack of bacteria and cannot be used to treat the feed with bacteria [17].

Ceramic membranes are mostly applied in MF and UF processes. Ceramic membranes are chemically inert, have high thermal resistance, and can operate at high temperatures in which organic membranes fail [3]. Furthermore, ceramic membranes can be reused several times after membrane fouling cleaning and can be used to treat solutions with high fouling rates [18]. Nonetheless, compared to polymeric material membranes, ceramic membranes demonstrate less

separation capability (range of contaminants that can be removed is limited due to large pore size), more expensive, fragile, and application area is limited.

Considering the facts mentioned above, it is very important to select membrane based on their material type and their properties. Overall, most of the polymer membranes have hydrophobic nature which results in a high membrane fouling propensity which consequently results in increased operational cost, reduced membrane lifetime, and reduced application range. Moreover, most of the polymer membranes' surface can be damaged in case of cleaning with specific chemicals. In order to improve chemical and/or thermal stability of polymer membranes, additional surface modification should be performed which leads to additional expenses. On the other hand, ceramic membranes can be easily cleaned with a variety of chemicals with no or little damage caused to membrane surface. Most of the available commercial ceramic membranes have limited range of pore size; however, chlorine resistance and tolerance to high concentration levels of oxidants and coagulants make ceramic membranes attractive for fouling prevention.

2.4 Membrane Morphology and Fabrication Methods

Membranes are divided into two main categories based on their morphology: isotropic (symmetric) membranes and anisotropic (asymmetric) membranes.

Anisotropic membranes are divided into two types based on structure composition: anisotropic asymmetric membranes and anisotropic composite membranes. Anisotropic asymmetric membranes (also named as Loeb-Sourirajan membrane) are composed of a single polymer: dense and thin top layer with 0.1-0.5 μm and microporous sublayers with 50-150 μm thickness range [17]. Anisotropic composite membranes are generally composed of different polymers with several layers with different pore size and porosity: very thin top layer (thickness range less than 0.1 mm) which acts as an active surface layer and thick microporous sublayers that work as mechanical support [17]. Anisotropic asymmetric membranes are mostly fabricated by The Loeb-Sourirajan process. This process involves four main steps: casting – polymer solvent is cast as a thin film; evaporation – the cast film is left stand for short period to allow evaporation of part of solvent; precipitation - the cast film is immersed into bath in order to precipitate polymer and form the membrane; annealing – formed membrane undergoes final post-treatment by hardening in bath [3].

The basic morphology of isotropic and anisotropic membranes is illustrated in Figure 2.3 [19].

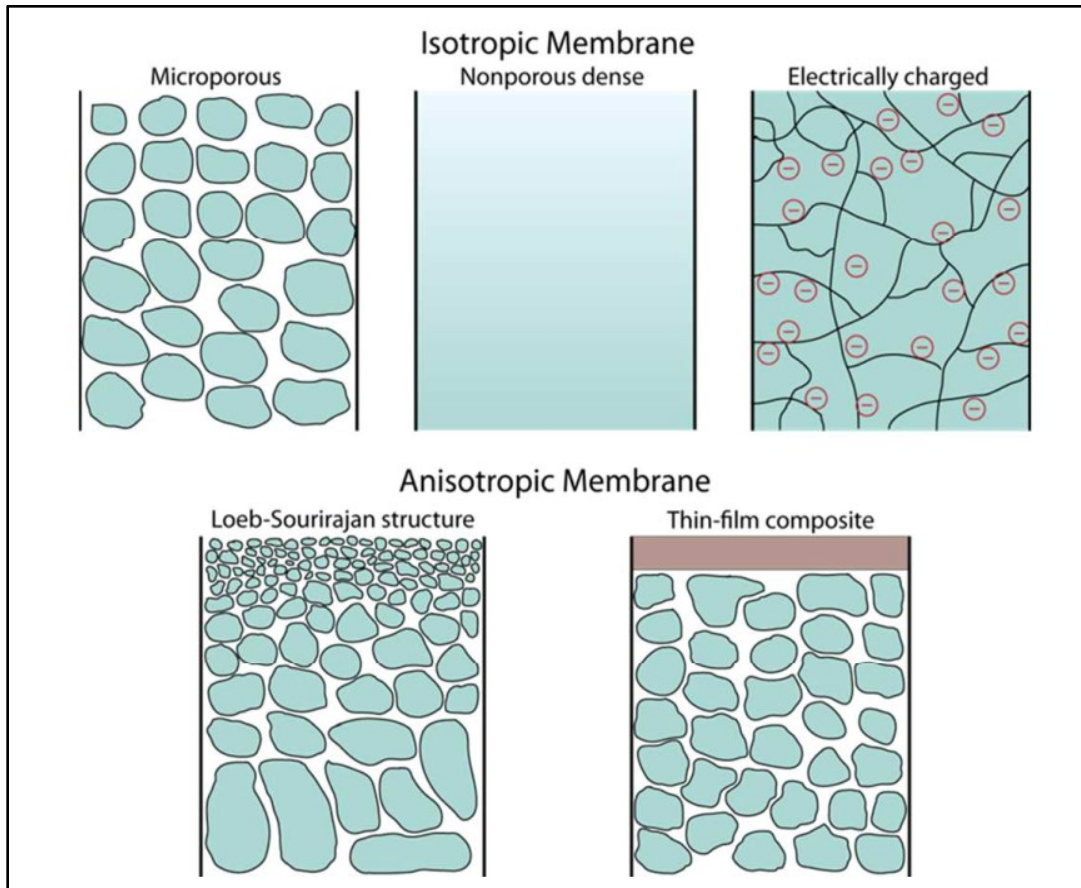


Figure 2.3: Schematic illustration of morphology of isotropic and anisotropic membranes [19].

In anisotropic composite membranes, water flux performance and separation properties are directly related to top layer. Such membranes are widely applied NF and RO due to high permeability and selectivity levels [17, 20]. Furthermore, permeability properties of thin film composite membranes do not decrease at high operating pressures due to high mechanical strength of support layer of the membrane [21]. Today, anisotropic composite membranes are mostly prepared by method proposed by Riley et al. in which dilute polymer solution is directly laid onto the clean and finely microporous support layer [3].

Isotropic membranes are divided into three types based on structure composition: microporous membranes, nonporous and/or dense membranes, and electrically charged membranes [17]. First, symmetric microporous membranes have a fixed, interconnected void

and pore structure with randomly distributed pores with 0.01-10 μm size. Such membranes are generally used in MF and UF process as it efficiently able to separate contaminants and solvent with significant size difference [17, 20]. Isotropic microporous membranes are usually fabricated through track-etching and template leaching methods. Track-etching method involves irradiation of polymer in which polymer surface is damaged and tracks are formed by breaking chains of molecule. After tracks formation, chemical solution hat etches the film and polymer pores appears in track places [3]. Template leaching technique uses a leachable component and insoluble polymers to produce microporous membrane: the film is formed after carefully mixing leachable component and polymer. After removal of leachable component, microspores appear on the film [3].

Next, symmetric nonporous and/or dense membranes are composed of a very dense film that allows transportation of permeates by diffusion mechanism. In such membranes, separation property is directly related to relative transport rate which is regulated by diffusivity and solubility characteristics of membrane material [17]. Isotropic nonporous membranes are usually prepared by solution casting method. In solution casting method, polymer film solution is spread evenly with a casting knife onto flat plate. Polymer film is left stand for short period to allow evaporation of part of solvent after which homogeneous thin membrane is formed [3].

Symmetric electrically charged membranes are dense or microporous membrane type with pore walls transporting uniformly distributed and fixed ions with positive or negative charge [3, 20]. The main factors affecting separation process in this type of membrane are ions' charge and concentration. Depending on a material of membrane, in order to achieve antifouling effect and improved membrane performance, membrane surface can be further modified with chemical and physical technologies including polymerization, hydrophilization treatment, hydrothermal synthesis, catalytic ozonation, and ion charge assisted deposition [11].

2.5 Membrane Geometry

Membranes are divided into four main categories based on their geometry: flat plate, spiral wound, tubular, and hollow fibers. As MST developed over time, a variety of membrane module types have been developed too with the aim that membrane application will not be limited by its module type. The basic illustration of main membrane module types is presented in Figure 2.4 [11].

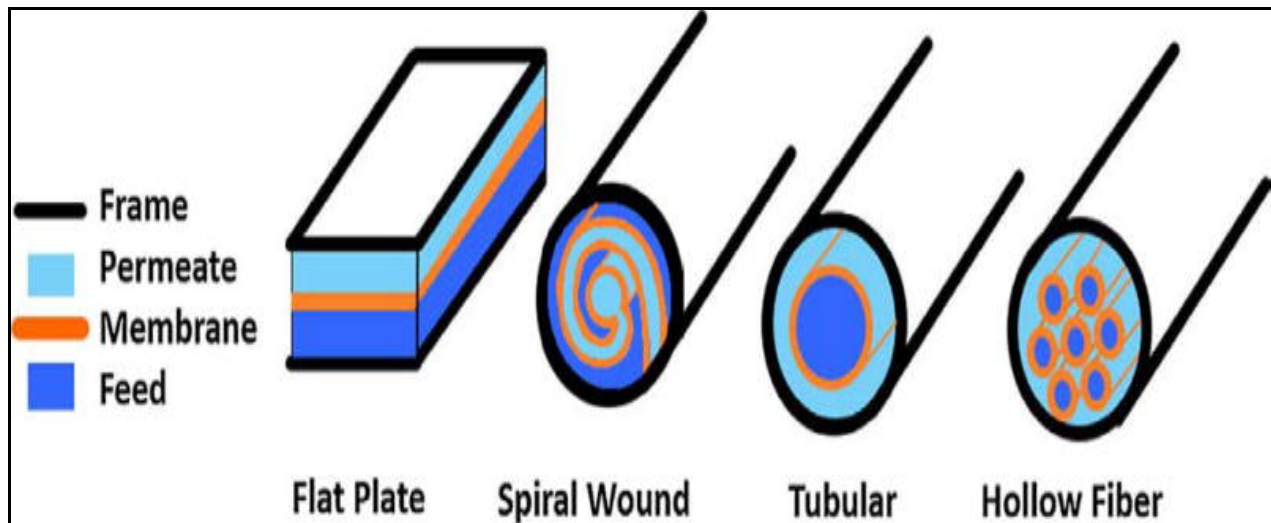


Figure 2.4: Schematic illustration of main types of membranes based on module [11].

The flat-plate membrane, also named as flat-sheet, module is often applied in MST where treatment of the feed containing big concentration of contaminants and have high viscosity. Most of the commercial flat-plate membranes are fabricated to support high operating pressures. This type of module is mostly applied in MF and UF processes. The flat-sheet membranes can be used in industrial wastewater treatment and landfill leachates treatment processes [22]. Also, hydraulic configuration of the flat-sheet membrane is preferred for wastewater treatment as they can be immersed into the feed. The main benefits of the flat-plate membrane module are simple and compact operation system. The drawback of the flat-plate membrane module includes limited application range on account of their low surface area. The main challenges present in flat-sheet membrane modules are low treatment performance associated with low available surface area to volume densities and high rate of membrane fouling [11].

The spiral-wound module refers to membranes organized between porous supports enclosed a central tube. The spiral-wound membrane module is relatively complex shaped and consists of different components such as the membrane, central and permeates tubes, mesh spacers, channels for feed and permeate, and the membrane housing [17]. This type of module is mostly applied in NF and RO processes. Unlike from the flat-sheet membrane, the spiral-wound membrane module has higher surface area available for a filtration and has wider application range in MST. The spiral-wound membrane can be used in treatment of both water and wastewater sources by successfully purifying water from traditional and hazardous contaminants [23, 24]. The main advantages of the spiral-wound module is high packing density, relatively

simple operation system, and low maintenance cost as module have cleaning-in-place systems. The main challenge present in this type of module is tendency to fouling which results in decreased membrane lifetime and membrane performance drop.

The hollow-fiber membrane module refers thousands of hollow membranes arranged into hollow fiber form and has circular cross section and has diameter of 50 to 3000 μm [20]. Hollow portions of hollow-fiber membrane come in different sizes and usually about 0.5-1.5 mm. Hollow-fiber module has the very high surface area per membrane volume and mostly applied in large scale MST processes. This type of module is mostly manufactured for MF and UF processes. For NF and RO process, hollow-fiber module offers optimal mass transfer coefficients and maximum packing density available; nonetheless, application of this module in RO and NF is still very limited due to fouling tendency and low pressure tolerance of module [25]. Most of the commercial hollow-fiber membranes cannot operate at pressures higher than 4 bar [16]. On the other hand, this module offers higher separation efficiency and out-inside and inside-out operation modes; therefore, such modules are widely applied in potable water reuse by treating water efficiently and removing foulant particles with backwashing technique. In addition, hollow fiber module application range in wastewater treatment and water desalination is increasing as such module has stronger resistance to fouling particles than the spiral-wound module. However, fouling in hollow-fiber membrane module remains as a crucial drawback with fouling impact increase with fiber clogging and limited chemical cleaning options due to module's small channel size.

The tubular membrane module refers to the membrane arranged into tubular form and has circular cross section. This type of module has advantage in membrane maintenance and replacement on account of module elements arrangement that allows the tube to be disconnected from module and can be separately cleaned or replaced. Diameter of the tubular membrane module is higher than the hollow-fiber module [20].

2.6 Membrane Hydraulic Configuration

Pressure driven perm selective membrane filtration processes have two types of hydraulic configuration modes: the dead-end filtration and the cross-flow filtration. The main difference between hydraulic configuration types is the number of streams. The basic schematic illustration of MST process with dead-end mode and cross-flow mode is presented in Figure 2.5.

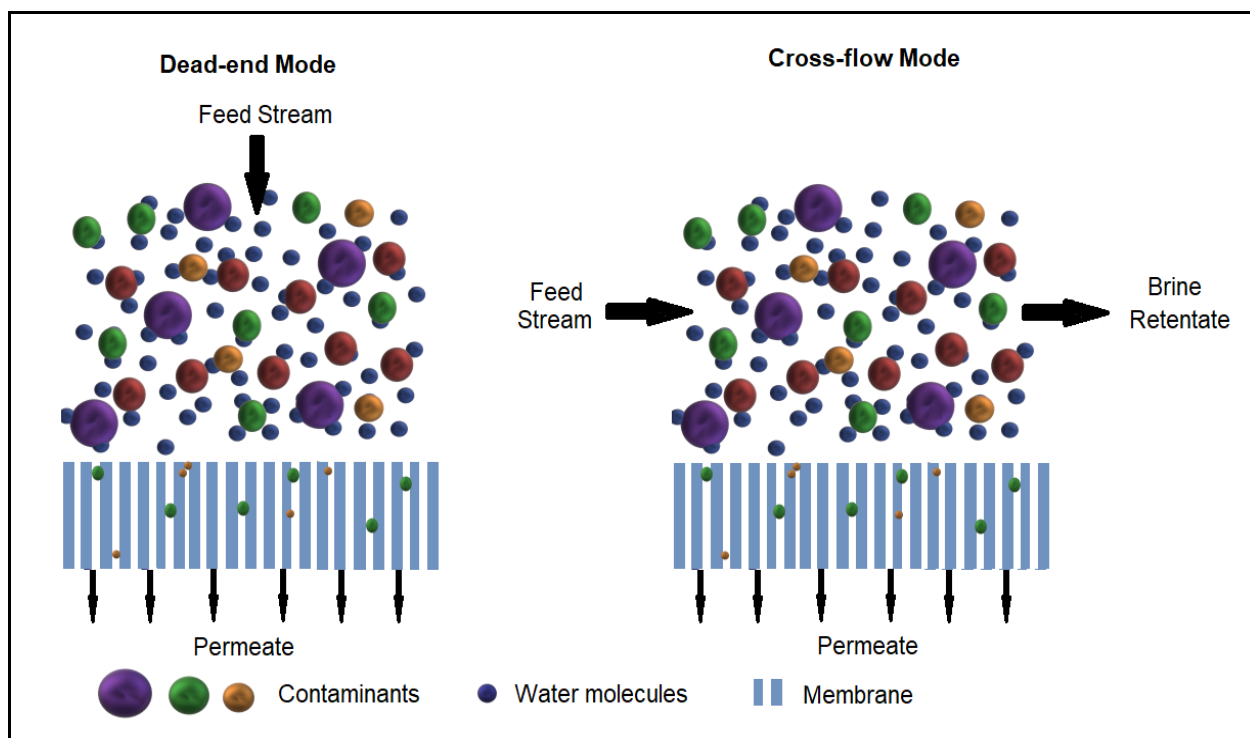


Figure 2.5: Schematic illustration of MST process with dead-end mode and cross-flow mode.

There are two streams in dead-end filtration mode: the feed stream – raw liquid containing contaminants; permeate stream – purified liquid free from contaminants. The applied driving pressure forces the feed to pass through filter. This type of hydraulic configuration is often applied for small-scale MST processes. The main advantages of the dead-end filtration are relatively simple process and have high recovery of product [26]. However, this hydraulic configuration have tendency to fouling due to combination of driving pressure and permeate drag force: retained foulant particles concentrate on the membrane surface often in a cake layer [27]. Filtration performance is significantly reduces due to the formation of the cake fouling in a short time. While conduction of filtration in dead-end configuration, it is important to periodically perform backwashing to clean membrane if high permeate flux and improved permeability is needed.

There are three streams in cross-flow filtration: the feed stream – raw liquid containing contaminants; brine retentate – portion of the feed that failed to pass through filter; permeate stream – purified liquid free from contaminants. The tangential feed stream exerts shear force on the membrane surface which minimizes accumulation of foulants on the membrane surface. This

type of hydraulic configuration is often applied in wide-scale industrial MST processes. Compared to the dead-end hydraulic filtration, cross-flow mode demonstrates higher permeate flux. In addition, it is generally accepted that tangential flow in cross-flow mode assists in prevention of irreversible fouling which consequently increases membrane lifetime.

2.7 Membrane Removal Mechanisms

Depending on the membrane characteristics and solute properties, MST can treat feed solution with main four types of pollutant removal mechanisms. The basic concept of main membrane removal mechanisms is illustrated in Figure 2.6.

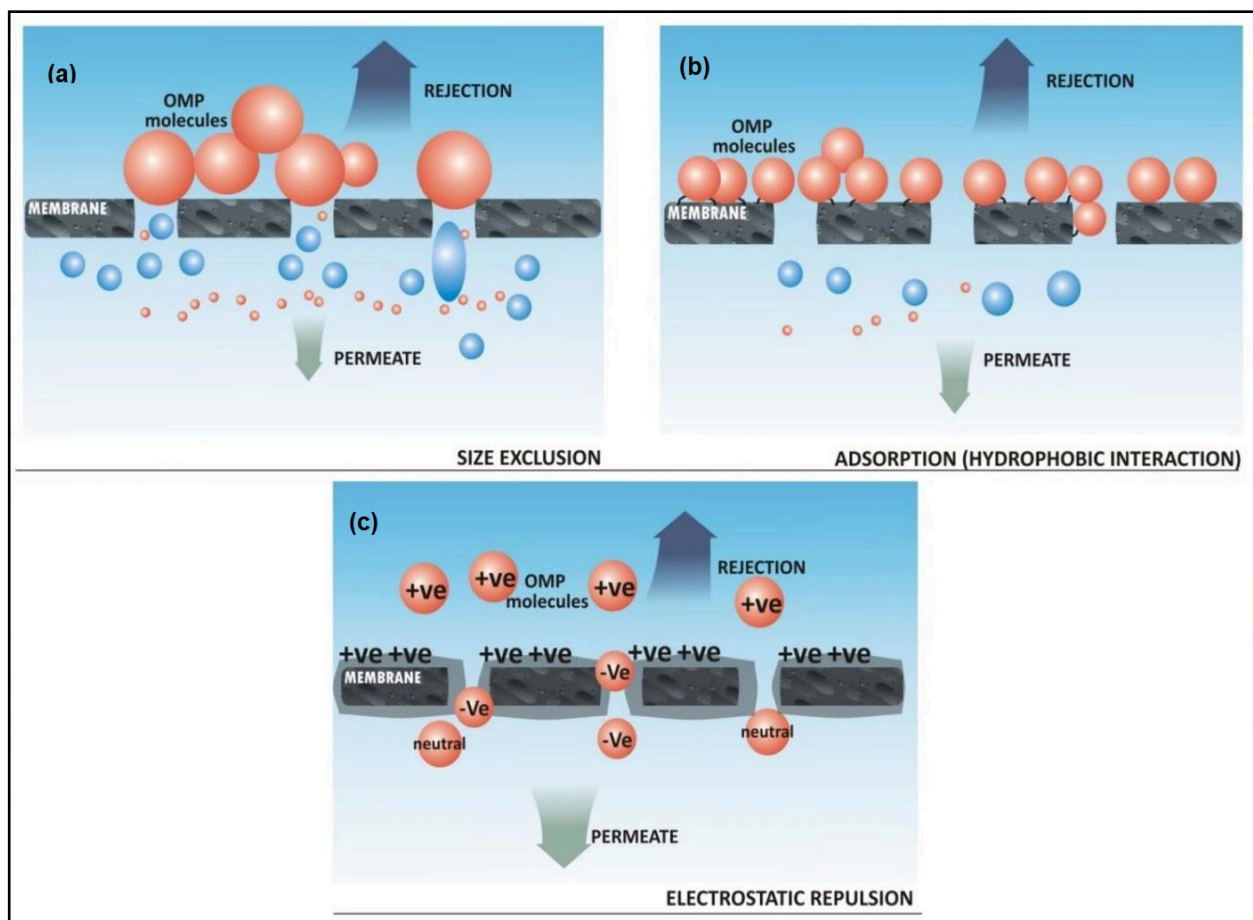


Figure 2.6: Types of micro pollutants removal mechanism: a) Size exclusion; (b) Adsorption by hydrophobic interaction; (c) Electrostatic interaction [28].

Contaminants present in feed solution have different chemical and physical characteristics such as solubility, surface charge, hydrophobicity/hydrophilicity, diffusivity, size, etc. based on the source of feed. In addition all the characteristics are not the same for all contaminants: the feed may contain a variety of pollutants. MST processes can operate in different removal mechanisms and/or mixed removal mechanism mode depending on the membrane properties, pollutant characteristics and operating conditions.

Size exclusion removal mechanism is the fundamental separation mechanism that rejects contaminants present in feed solution by the membrane due to smaller pore size of membrane in comparison to dimensions of pollutants. The removal process is very similar to conventional coarse filtration and often MF and UF processes operate with this mechanism removing large sized contaminants and suspended solids. However, removal efficiency of this mechanism is highly dependent of the membrane pore size and size of pollutants. Furthermore, some studies reported that rejection of contaminants with larger size than membrane pore was not very efficient [28]. This is due to assumption of spherical-homogenous shape of pollutants and considering only their molecular weight, while pollutants can come in different length and width. This type of removal mechanism is the dominant in rejecting uncharged pollutants.

Adsorption by hydrophobic interaction removal mechanism reject contaminants based on the interaction properties between water and low water soluble pollutants. This type of removal mechanism is the prevailing in removal of hydrophobic pollutants. Hydrophobicity of pollutants is measured by $\log K_{ow}$ values (octanol–water partition coefficient) and hydrophobicity of membrane surface is measured by contact angle [28]. Hydrophobic membrane application increases adsorption rate of hydrophobic pollutants onto membrane surface. Hydrophobic interaction between membrane surface and pollutants can be affected by pH level. Membrane surface hydrophobicity could be decreased at lower pH due to polymer hydrophobic core chains protrusion in acidic environment [17]. Also, higher rejection rate of hydrophobic pollutants is obtained at higher pH levels on account of polymer pore shrinkage [17]. In addition, adsorption removal mechanism performance is highly dependent on K_{ow} values, and molecular weight of the solutes [17, 29]. However, rejection of hydrophobic pollutants by adsorbing them onto membrane surface is not efficient in long-term removal process due to steadily decreased pollutants adsorption and rejection rates over time [17, 30]. Furthermore, membrane fouling is a natural result of adsorption by hydrophobic interaction removal mechanism. The presence of

adsorbent materials such as activated carbon fibers on the membrane surface can make adsorption process easier [28]. Adsorption process can be further improved by membrane fouling by organic matter and presence of humic acid. Several studies demonstrate that membrane adsorption properties are influenced by membrane properties such as surface morphology, pore size, and active layer parameters [28, 31, and 32]. For example, membranes with smaller pore sizes have fewer tendencies for pollutant adsorption onto membrane surface [31]. Pollutants can also be adsorbed within membrane internal pores; nonetheless, assessing this type of adsorption is very complex due to a variety of membrane morphology and materials. Contaminant adsorption rate gradually goes down over the time due to saturation of adsorbed contaminants [33]. Therefore, adsorption rate measured at the beginning of the MST process should not be considered as constant result for retention factor. Furthermore, pollutant adsorption rate can be influenced by other factors such as interaction of pollutant particle with other pollutants, pH of the feed solution, and operating conditions. This type of pollutant removal mechanism is considered as highly complex and it is difficult to predict pollutant rejection rates.

Electrostatic interaction (also named as van der Waals interaction) could be formed between charge of the membrane surface and charged pollutants. Removal mechanism based on electrostatic interaction rejects pollutants with repulsive force induced due to similar charge (in most of the cases negative charge) of membrane surface and charged pollutants. Several researches investigated on electrostatic interaction between membrane and pollutants and concluded that repulsion rate of pollutants did not change over time [28, 34]. Nonetheless, electrostatic interaction could be interfered with other chemical properties of solution. For example, at increased pH of the feed solution, sulfonic and carboxylic functional groups are affected and compounds dissociate more frequently. Such dissociation of compounds leads to more negative surface charge of the filter which consequently increases repulsive force between the filter and negatively charged pollutant particle [17].

2.8 Permeation Mechanisms

Permeability of membrane is highly dependent on the membrane properties. Based on the permeability characteristics of membrane and pollutants properties, there are main three types of

permeation mechanisms for solutes through porous membrane. The basic concept of permeation mechanisms is presented in Figure 2.7.

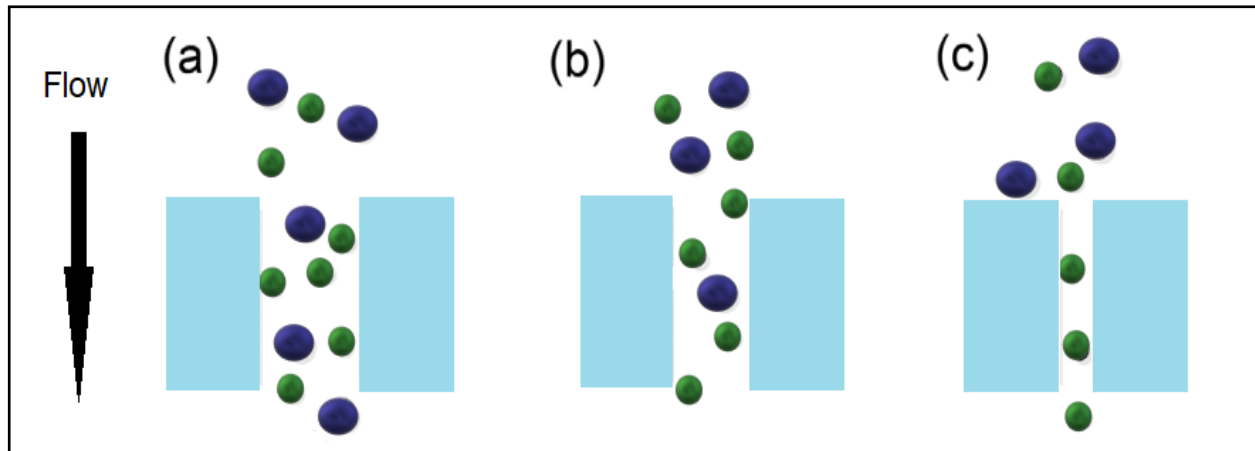


Figure 2.7: Permeation mechanisms for solutes through porous membrane: a) Convective flow (bulk flow); b) Knudsen diffusion; c) Restricted diffusion.

Convective flow refers to the transport of solute particles present in the feed between membrane boundary surface and a moving feed solution. This type of permeation mechanism is often present in MF and UF procedures. The main principle of the convection permeation mechanism is sieving process through porous membrane layer with application of bulk convective velocity parallel to the membrane surface. In addition, the performance of the convective permeation is directly related to the pressure-driven velocity of the flow [35]. Depending on the pore size, theoretical water flux of convective flow is calculated by Equation 2.5 for membranes with symmetric pore structure, and Equation 2.6 for asymmetric membrane structure characteristics [3].

$$J = \frac{\varepsilon r^2 \Delta P}{8 \eta \tau \Delta x} \quad (2.5)$$

where,

J - theoretical water flux;

ε - membrane porosity;

r - pore radius;

ΔP - pressure difference;

Δx - membrane thickness;

η - liquid viscosity;

τ – pore tortuosity.

$$J = \frac{\varepsilon^3}{K\eta S^2(1-\varepsilon)^2} \frac{\Delta P}{\Delta x} \quad (2.6)$$

where,

J - theoretical water flux;

S - membrane internal surface area;

K – Kozeny-Carman constant based on shape of pores and tortuosity of the membrane.

Knudsen diffusion permeation mechanism occurs when membrane pore size is smaller than size of solute particles. The membrane pore size in Knudsen diffusion permeation mechanism is smaller than in membranes which operate with convection permeation mechanism. The solute particles in the feed are separated due to different solubility rates and diffusion coefficients. This permeation mechanism is often occurs in RO and NF processes where large pressure is applied [36]. Knudsen diffusion permeation mechanism depends on both kinetic and equilibrium properties: diffusivity and solubility. The water flux for Knudsen diffusion permeation mechanism is calculated by Equation 2.7 [3]:

$$J_w = \frac{D_w c_w V_w}{RT\iota} (\Delta P - \Delta \pi) \quad (2.7)$$

where,

J_w - water flux;

D_w - diffusion coefficient of water;

c_w - concentration of water;

V_w - volume of water;

$\Delta \pi$ - osmotic pressure difference;

R – Universal gas constant;

T - temperature;

ι - membrane thickness;

In restricted diffusion permeation mechanism, the concentration of diffusing solute particles is dependent on the driving pressure and temperature. Restricted diffusion permeation mechanism generally occurs in RO and NF process [36]. The diffusion of the solutes becomes restricted when size of the membrane pore is similar with thermal displacements of the molecules as a result of occurred electrical interactions and collisions between membrane pore wall and solute molecules [35]. In addition, the available the active pore area for contaminant

permeation/transportation decreases. The water flux for restricted diffusion permeation mechanism is calculated by Equation 2.7 with modified diffusion coefficient factor [3].

2.9 Concentration Polarization Phenomena

Concentration polarization is a phenomenon that negatively affects the overall performance of the MST processes. Concentration polarization occurs as a result of increased accumulation of rejected solutes on the membrane surface due to selective membrane transport. The concentrations of solutes are steadily increases due to applied pressure force impact solute accumulation and eventually a concentration build-up will form. Concentration polarization causes membrane lifespan reduction and membrane performance decline.

As a result of retention of solute particles onto membrane, permeate solute concentration (C_p) is lower than the bulk concentration (C_b). Over the time, C_p will increase steadily. As it can be seen in Figure 2.8, C_b is lower than concentration at the membrane surface (C_m) and boundary layer is formed. Concentration polarization and fouling both causes continuous flux decline. Theoretically, flux decline due to concentration polarization is resulted from higher osmotic pressure in RO process [37]. In addition, in RO processes, concentration polarization impact is much higher than other conventional MST processes as in conventional processes influence of concentration polarization on membrane performance can be controlled [3]. In MF and UF processes concentration polarization is considered as part of fouling phenomena, while in NF and RO processes is not.

The schematic representation of concentration polarization for pressure-driven processes is illustrated in Figure 2.8.

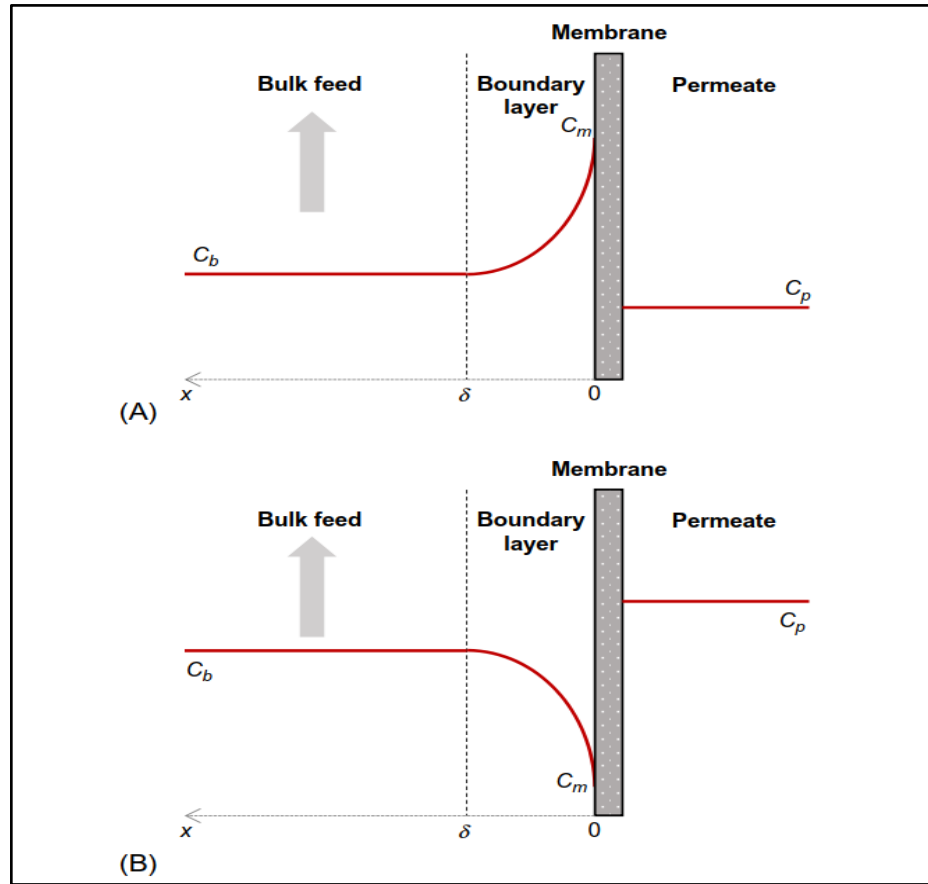


Figure 2.8: A schematic representation of concentration polarization: (A) mass transfer profile limited by the membrane; (B) mass transfer profile limited by the boundary layer [37].

2.10 Fouling Phenomena

Fouling is the phenomena in the membrane separation process in which particles of solution lies up on the membrane surface or inside its pores. As a result of fouling, MST performance is reduced with continuous flux decline. The nature of the fouling process is very complex. During the separation process, suspended particles, emulsions, colloids, salts macromolecules or components of solutions that are unable to dissolve deposits within membrane pores. Fouling in membranes is dependent on physical and chemical parameters such as concentration, particle size, temperature, pH, ionic strength and some atomic interactions as hydrogen bonding, dipole-dipole interactions [4, 38]. Microorganisms can sediment on membrane surface and are able to degrade polymer membranes [39]. Colloidal particles deposit on the membrane surface or clog within membrane internal pores resulting in interruption of the

separation system by causing hydraulic resistance to the flow [40-43]. In order to limit the effect of the fouling process, it is important to distinguish a fouling mechanism type. Typically there are four types of fouling mechanisms: complete pore blockage, internal pore blockage, partial pore blockage, and cake formation [44]. Mechanisms of fouling are presented in Figure 2.9.

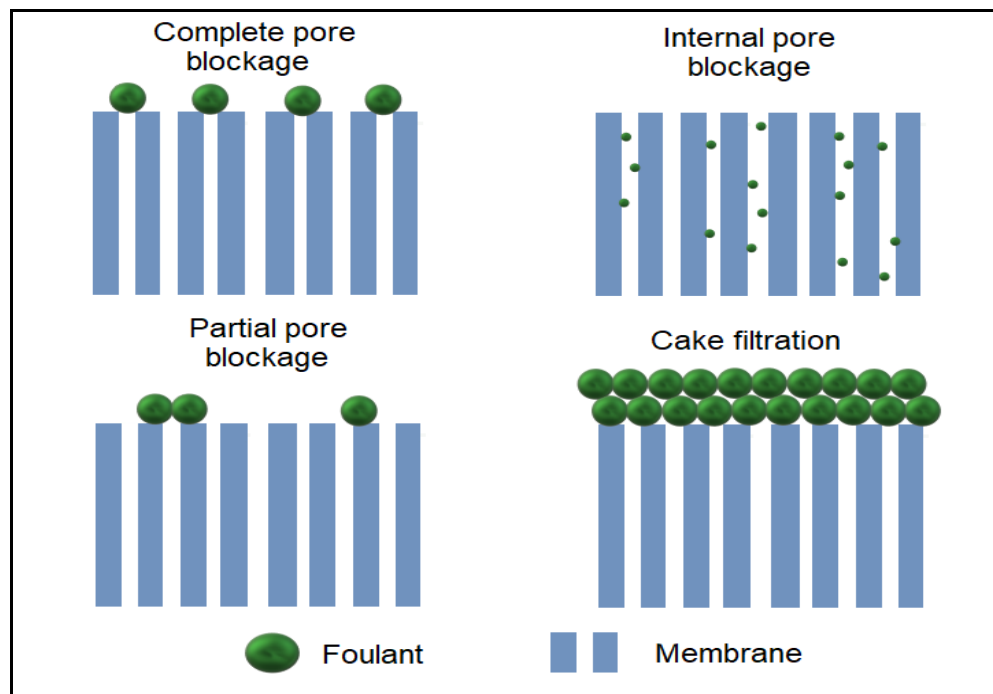


Figure 2.9: Fundamental fouling mechanisms.

In complete pore blockage mechanism, membrane pores are completely blocked by particles of bigger size. In internal pore blockage mechanism, particles not rejected by the pore entrance are adsorbed or trapped on the pore wall. This type of fouling restricts the permeate flow as the internal volume of the pores decreases due to deposition/adsorption of microsolutes on the pore walls. In partial pore blockage mechanism, particles might seal or partially block pores or be attached on inactive regions. In cake formation mechanism, contaminants accumulate on the membrane surface as a cake layer: particles do not enter or seal the pores.

Fouling accumulation on membrane surface can be reversible or irreversible types. In reversible fouling, the membrane selective performance can be recovered with application of chemical cleaning or backwashing processes. However, in irreversible fouling, application of different cleaning methods cannot recover initial performance of the membrane due to the strong

connection between foulants and the membrane. Therefore, it is very important to prevent formation of irreversible fouling.

Based on the nature of foulants, fouling is divided into four categories: colloidal fouling; organic fouling; inorganic fouling or scaling; biofouling. In colloidal fouling, inorganic or organic colloidal contaminants physically cover the surface of the filter and prevent liquid passage through filter pores [45]. Colloidal contaminants of similar size with the filter pores often cause fouling with pore blockage mechanism; whereas, smaller colloids causes fouling by formation of cake layer. In organic fouling, organic pollutants (such as acids and proteins) present in the feed dissolve and attaches to the filter or adsorb within the pores [45]. Organic pollutants causes pore blockage fouling by narrowing pore area after attaching within the pores and can cause cake fouling by formation of gel layer on the membrane surface. In inorganic fouling, inorganic pollutants (such as metal, metal oxides and coagulants) present in the feed dissolve and precipitates onto the filter surface as a result of oxidation for metal oxides and change in pH for the rest inorganic pollutants [45]. Precipitation of inorganic pollutants onto the filter surface usually happens as a result of hydrolysis and oxidation processes. In biofouling, microorganisms (such as bacteria and algae) adhere on the membrane surface [45]. The serious issue with biofouling is that adhered microorganisms can grow over time and increase fouling intensity.

2.11 Effect of Temperature

2.11.1. Fouling as a function of temperature

The temperature of the feed has direct influence on fouling. The changes in permeate flux can be attributed to feed temperature as liquid viscosity and resistance are temperature-dependent parameters [46]. At low processing temperature, poor experimental permeate flux results occur due to increased viscosity [47-50]. Furthermore, the pressure should be higher at low feed temperature to achieve higher water flux. However, higher working pressure results in accumulation of more stable and denser fouling layer that is difficult to remove by cleaning [48, 49, and 51]. Low feed temperature promotes growth of microbial community which amplifies membrane fouling [49, 52]. At low temperatures, increased water viscosity elevates rate of fouling that appeared due to increase of hydraulic resistance [53]. In addition, the nature of

contaminants tends to be more solid at low temperatures resulting in increase of cake formation (pollutant particle block pore entrance).

At higher feed temperature, fouling process appears faster due to the feed viscosity change that decreased as a result improved diffusion of foulant particles within the filter pores [54-56]. Moreover, decreased viscosity weakens permeate drag force and detachment of pollutant particles that adsorbed into the membrane proceeds more difficultly [52, 54, and 55]. Higher temperature results in higher irreversible fouling rate owing to the change in the membrane polymer chains [48, 51, and 56]. At high operating temperature, water flux recovery rate decreased on account of the more compact and resistant pollutant crystallization on filter surface that consequently increased fouling resistance [50]. Also, at elevated temperature formation of by-products occur more frequently [47]. Processing temperature higher than 50 °C promotes growth of microbial community which accelerates membrane fouling and its intensity [52].

2.11.2. Cleaning as a function of temperature

Chemical cleaning temperature of the membrane has direct influence on cleaning efficiency. Generally, magnifying cleaning temperature increases the cleaning efficiency; however, increased temperature has several drawbacks. Higher temperature of cleaning agent results in higher cleaning efficiency due to increased contaminant solubility on membrane surface [57-60], and due to increased chemical oxidation kinetics and faster distribution of oxidized functional groups of foulants in the membrane matrix [61].

Nonetheless, increasing temperature during cleaning leads to an increase of halogenated by-products formation when the membrane was cleaned with NaOCl [56]. In addition, temperature affects membrane itself: some of the UF membrane such as Polyacrylonitrile flat sheet membrane has a lower contact angle at increased temperature which means higher wettability and could influence fouling removal efficiency [62]. Flux recovery rate increased with cleaning temperature increase; however, for PSU membrane, at cleaning temperature > 50 °C flux recovery rate dropped which can be the evidence of membrane structure disturbance at extreme cleaning temperatures [61]. At higher cleaning temperature, more gel layer was removed that consequently increased contaminant concentration in the filter pool and increased contaminant concentration induces increased fouling rate in the following cleaning cycles [51].

2.12 Theoretical Water Flux

Theoretical flux of the four types of fouling mechanisms will be calculated with different mass transport equations in absence of cross-flow. Fouling with complete pore blockage mechanism is calculated by Equation 2.8 [63].

$$J = J_0 \times (1 + \frac{1}{2} \times K_s \times (A \times J_0)^{0.5} \times t)^{-2} \quad (2.8)$$

where,

J - theoretical water flux for complete pore blockage;

J_0 - flux through a pristine membrane;

K_s - phenomenological coefficients dependent on the fouling mechanism and is fitted parameter;

t - time.

In complete pore blockage fouling mechanism, mass transport effect reduces active membrane area and reduction of available area for solute transportation causes flux decline.

Next, Equation 2.9 is used to calculate theoretical water flux with internal pore blockage mechanism [64].

$$\frac{J}{J_0} = (1 + \frac{J_0 \beta t}{\varepsilon \lambda})^{-2} \quad (2.9)$$

where,

J - theoretical water flux for pore blockage;

β - dimensionless parameter that determines the solution potential to provoke an internal fouling;

ε - membrane porosity;

λ - the membrane thickness.

In internal pore blockage fouling mechanism, mass transport effect increases membrane resistance caused by pore size reduction.

Next, Equation 2.10 is for theoretical water flux with particle pore blockage mechanism [63].

$$J = J_0 \times (1 + K_i \times (A \times J_0) \times t)^{-1} \quad (2.10)$$

where,

J - theoretical water flux for pore blockage;

K_i - phenomenological coefficients dependent on the fouling mechanism is fitted parameter;

A - active membrane surface area.

In particle pore blockage fouling mechanism, mass transport effect works in similar manner as in complete pore blockage mechanism but with less intensity.

Final, Equation 2.11 is for calculation of theoretical water flux with cake formation mechanism [63].

$$\frac{J}{J_0} = \left(1 + \frac{2\alpha St}{\mu R_M^2} TMP\right)^{-0.5} \quad (2.11)$$

where,

J - theoretical water flux for cake formation;

α - parameter characterizing the fouling potential of the solution;

S - active membrane surface area;

μ - dynamic viscosity of water;

R_M - intrinsic membrane resistance calculated by Equation 2.12 [65].

$$R_M = \frac{TMP}{\mu J_0} \quad (2.12)$$

where,

TMP - transmembrane pressure (TMP).

In cake formation fouling mechanism, pollutants accumulate on the membrane surface as a cake layer: particles do not enter or seal the pores. In cake formation fouling mechanism, overall resistance becomes combination of the resistance of the cake membrane resistance causing gradual water flux decline.

Chapter 3 - Materials and Methods

3.1 Materials

Commercial YMLX3001 flat sheet UF membrane was used with following characteristics (Sterlitech Corporation, USA):

- Polymer: PES
- Pore size: 0.01 micron
- Thickness: 24 microns
- Operating pH range: 1-11
- Flux range: 429-451 LMH
- MWCO: 300,000 Da

3.2 Cleaning Agents

Three commercial chemical cleaning agents were used, HNO₃ (Sigma Aldrich, Germany), NaOCl (Sigma Aldrich, Germany), and NaOH (Sigma Aldrich, Germany) along with Milli-Q water (MerckMillipore, USA).

3.3 Filtration Set-Up

Filtration experiments at different temperatures were conducted in CF016 cross-flow cell (Sterlitech Corporation, USA) with a 16 cm² internal filtration area and MasterFlex peristaltic pump (Sigma-Aldrich Chemie GmbH, Germany) was used to apply driving pressure. Feed solution was placed on the stirrer plate (Sigma-Aldrich Chemie GmbH, Germany) to ensure homogeneous liquid solution throughout the filtration experiment. The permeate tank was placed on digital balance (Sigma-Aldrich Chemie GmbH, Germany) and accurate volume of permeate was automatically collected every minute. The feed liquid was prepared by mixing 1.2 g of Similac 1 (Abbott Laboratories, USA) baby powder with 2 litres of Milli-Q water. Organic powder was selected in order to mimic organic fouling which is the most common fouling type. Prior to the filtration experiment, membrane sheet was put into shaker with Milli-Q water for 1 hour at 37 °C temperature in order to remove chemical preservatives that were added by manufacturer to protect the membrane. Chemical cleaning solutions were prepared by mixing 10

mg of chemicals with 1 liter of Milli-Q water and final chemical cleaning solutions was obtained with 10 ppm concentration. Lab scale membrane filtration set-up is illustrated in Figure 3.1.

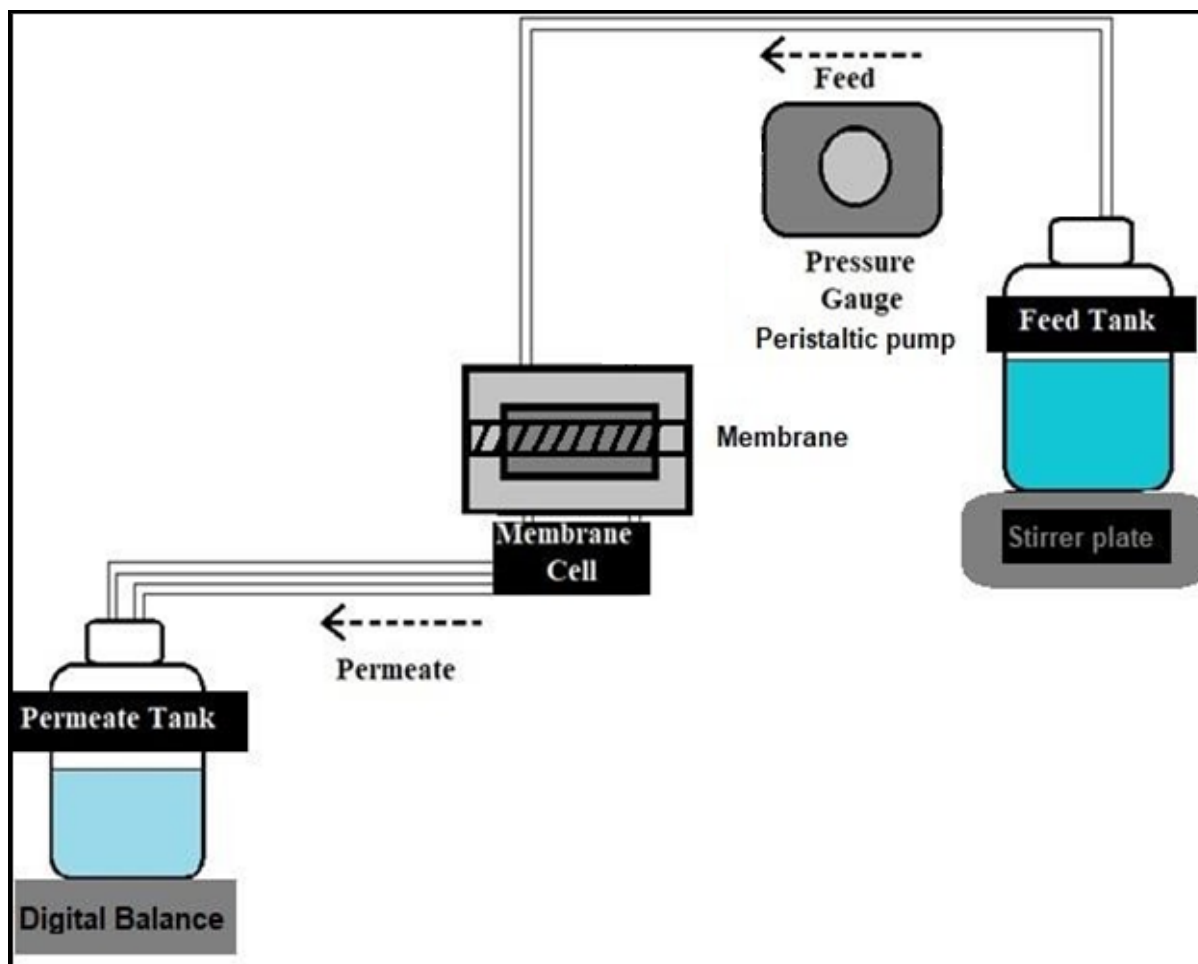


Figure 3.1: Lab Scale Membrane Filtration Set-Up.

The experiment conditions are as following:

- Feed solution: 0,6 g/L Similac 1
- Dead-end mode
- Pump velocity: 120 rpm
- Duration: 360 min
- Run: 6 run of 1 hour each
- Temperatures: 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C

Experimental water flux is calculated with Equation 3.1.

$$J = \frac{\Delta m}{\rho S t} \quad (3.1)$$

where,

J - experimental water flux;

Δm - permeate weight difference;

Δt - frequency interval;

S - active membrane surface area;

ρ - permeate density.

3.4 Chemical Cleaning Conditions

Chemical cleaning experiments of fouled membranes with 10 ppm of HNO₃, NaOH, NaOCl cleaning agents, and Milli-Q water were conducted with same protocol and by varying one parameter - temperature of cleaning solution (5 °C, 10 °C, 20 °C, 30 °C, 40°C, and 50 °C). The duration of chemical cleaning for mentioned temperature variation was 10 minutes. Fouled membranes were backwashed with mentioned chemical solutions and Milli-Q water after every run at 120 rpm pump velocity.

3.5 Membrane Surface Zeta Potential

Membrane surface charge was measured using a solid-surface zeta potential instrument - SurPass zetasizer (Anton Paar GmbH, Austria). The zeta potential values of pristine, fouled and cleaned membranes were collected. Small quantities of analytical grade chemicals were used for regulating zetasizer after every measurement. Ionic strength was regulated using KCl solution. Basic KOH solution and acidic HCl solution with 0.05 mol/L concentration each was used to perform pH titration. The zeta potential values were automatically collected with Ag/AgCl electrodes (Metrohm Ltd., Switzerland) within 2-10 pH range.

3.6 Membrane Surface Analysis

3.6.1. Contact angle

Membrane contact angle was measured with OCA 25 (DataPhysics Instruments GmbH, Germany) contact angle meter using the sessile drops (10 μL) of Milli-Q water at ambient temperature. The contact angle measurements have been done in triplicates. The reported values are the average of three contact angle measurements. Contact angle value indicates hydrophilicity/hydrophobicity of membranes and higher degree indicates membrane's hydrophobicity.

3.6.2. FTIR

Pristine, fouled, and cleaned membranes were analyzed by a Cary 660 FTIR spectrometer (Agilent, USA). All spectra were recorded at ambient temperature. Prior to analysis, all membranes were dried for 24 h in a desiccator to remove excess water residue. The records have been taken at 400 cm^{-1} - 4000 cm^{-1} wavelength range with a 4 cm^{-1} resolution.

3.6.3. AFM

Membranes surface was analyzed with AFM SartSPM 1000 (AIST-NT Inc., USA). Imaging was performed in tapping mode with an etched silicon probe to obtain 3D visualization of the membrane surface. Pristine membrane was put into shaker with Milli-Q water for 1 hour at $37\text{ }^{\circ}\text{C}$ temperature to avoid manufacturer prints and was dried prior to visual analysis. The membrane images were obtained with $10\text{ }\mu\text{m}\times 10\text{ }\mu\text{m}\times 200\text{ nm}$ dimensions.

Chapter 4 - Results and Discussion

4.1 Cleaning and Fouling as a Function of Temperature

Two sets of fouling experiments were performed: (1) filtration experiments with 0.6g/L Similac 1 as feed solution at room and cleaned at different temperatures; (2) filtration experiments with 0.6g/L Similac 1 as feed solution at different temperatures, and cleaned at room temperature. Theoretical water flux values were calculated using Equations 2.8 (complete pore blockage), 2.9 (internal pore blockage), 2.10 (partial pore blockage), and 2.11 (cake fouling). The comparison of experimental and theoretical water flux results is illustrated in Figures 4.1-4.6.

Figure 4.1 contains the results of six filtration experiments and theoretical fouling model calculations for the membranes fouled at room temperature and cleaned with water at 5 °C-50 °C. The curves that lie in 0-60 minute range are results of the first run; the curves that lie in 61-120 minute range are results of the second run and so on. As it can be seen in Figure 4.1, the first runs of each experiment have the highest water flux results and flux gradually decreases. For example, initial water flux at 20 °C is 72 LMH and final water flux is 19.1 LMH. In addition, flux recovery can be observed after each run due to performance of the backwashing cleaning of membrane with water. It can be seen that efficiency of the cleaning is not the same for the different temperatures and overall water flux recovery increases with temperature increase. The flux recovery is not always achieved after each run regardless the cleaning temperature. For example at 5 °C, there is no water flux recovery at fourth and at 20 °C water flux was not recovered at third run. Overall, good water flux recovery could be seen in experiments that performed membrane cleaning with water at 20 °C.

Figure 4.2 contains the result of six filtration experiments and theoretical fouling model calculations for fouled at room temperature and cleaned with 10 ppm NaOH solution at 5 °C-50 °C after each run. Membrane water flux recovery is good at 5 °C and 10 °C cleaning temperatures; nonetheless, overall membrane performance is low with initial 30.2 LMH and 48 LMH water flux values for respective temperatures. Filtration experiments with chemical

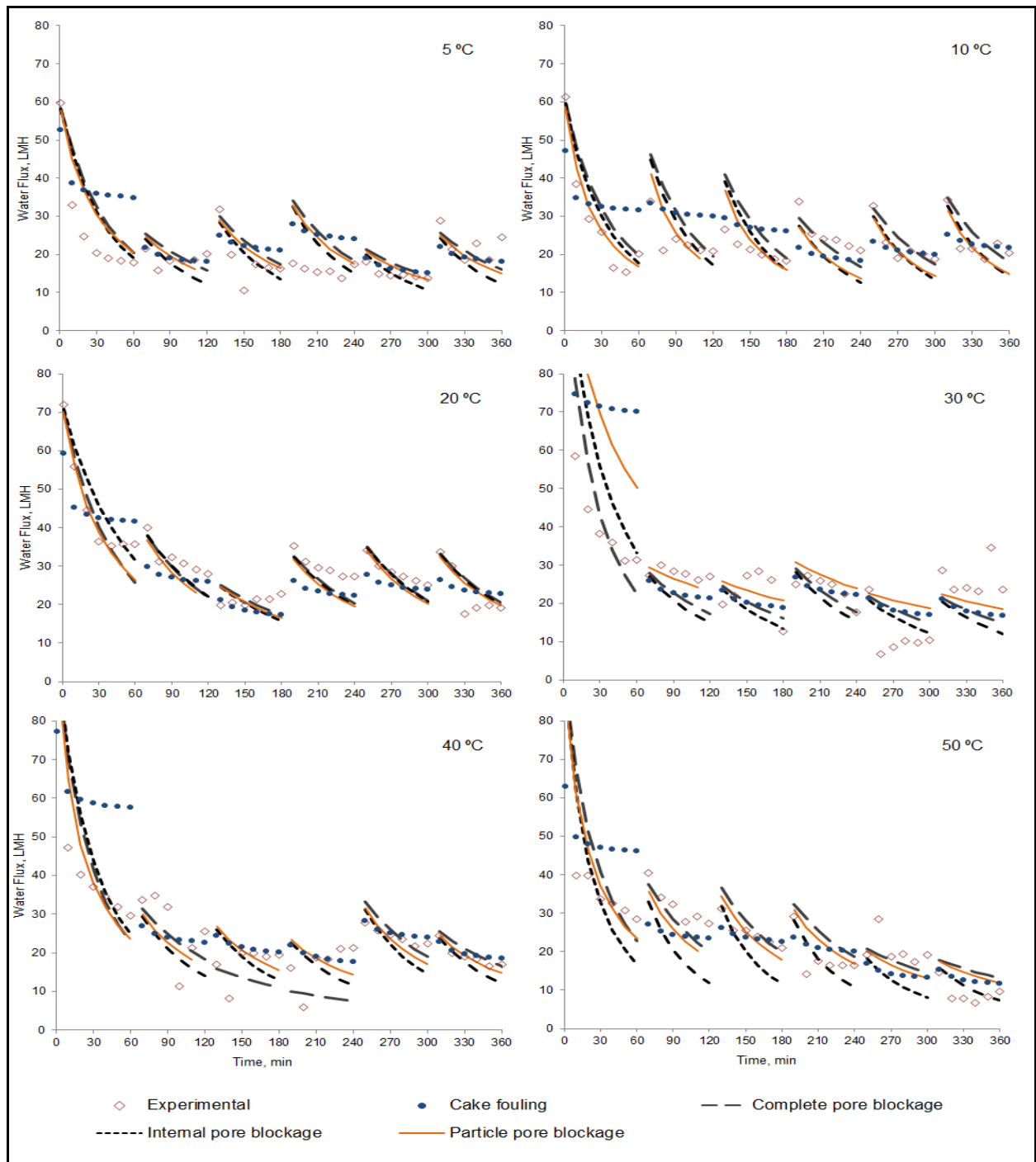


Figure 4.1: Experimental and theoretical water flux results: fouling experiments with 0.6 g/L Similac 1 solution at room temperature, cleaning experiments with water at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C. Theoretical curves were calculated with the best-fit approximation of flux behaviour due to complete pore blockage, internal pore blockage, partial pore blockage, and cake fouling (Equations 2.8, 2.9, 2.10, and 2.11 respectively).

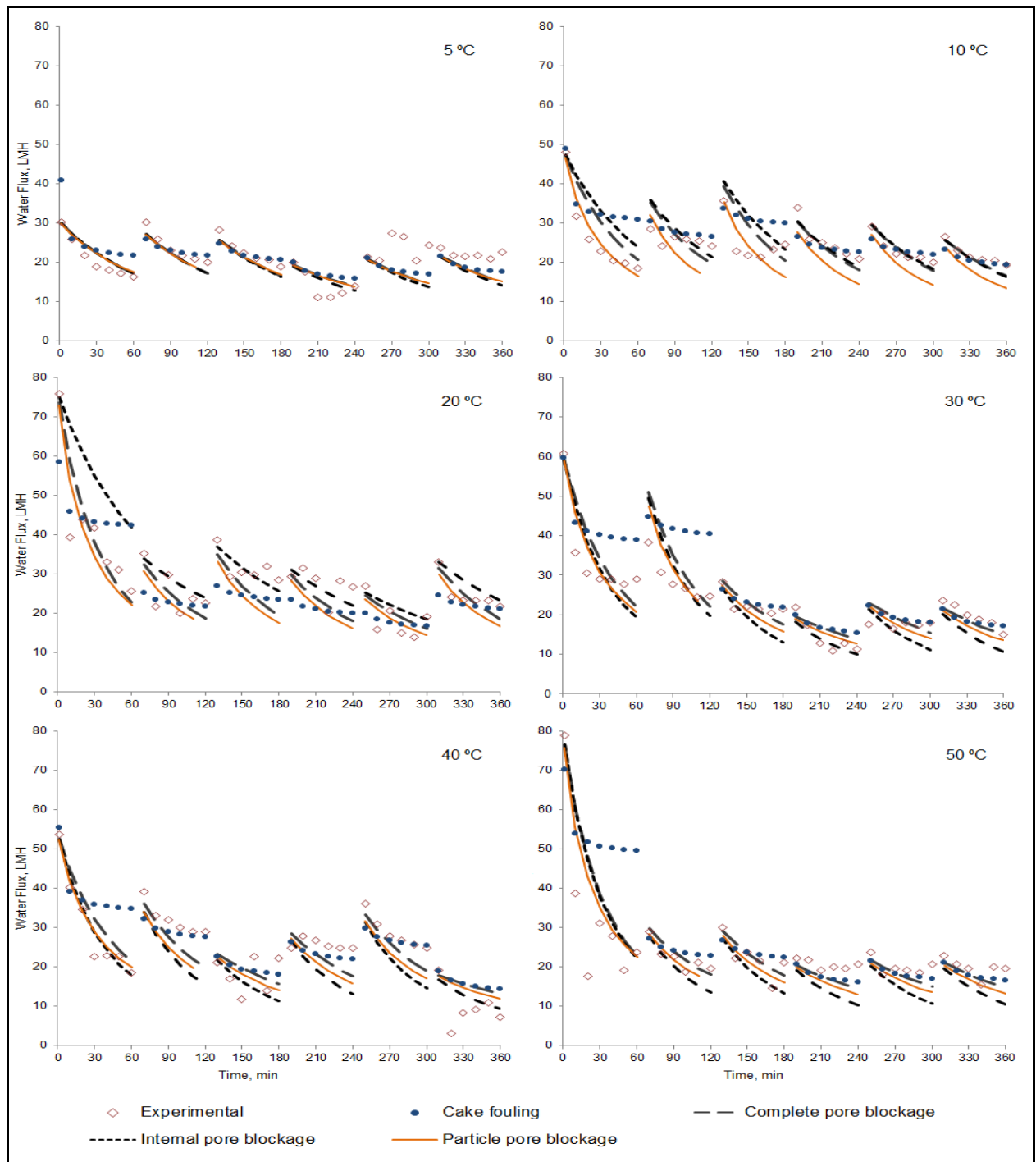


Figure 4.2: Experimental and theoretical water flux results: fouling experiments with 0.6 g/L Similac 1 solution at room temperature, cleaning experiments with 10 ppm NaOH at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C. Theoretical curves were calculated with the best-fit approximation of flux behaviour due to complete pore blockage, internal pore blockage, partial pore blockage, and cake fouling (Equations 2.8, 2.9, 2.10, and 2.11 respectively).

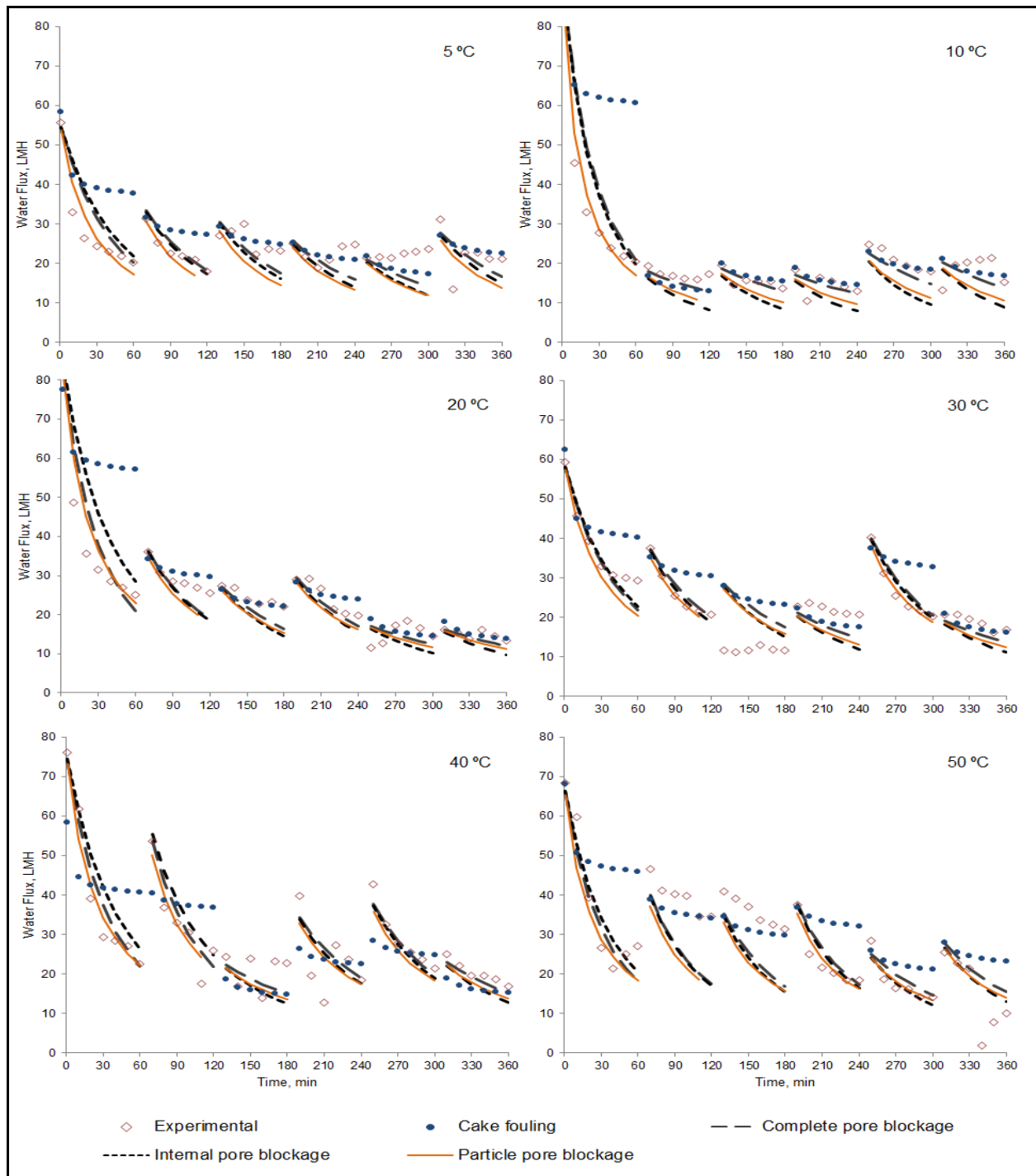


Figure 4.3: Experimental and theoretical water flux results: fouling experiments with 0.6 g/L Similac 1 solution at room temperature, cleaning experiments with 10 ppm HNO_3 at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C. Theoretical curves were calculated with the best-fit approximation of flux behaviour due to complete pore blockage, internal pore blockage, partial pore blockage, and cake fouling (Equations 2.8, 2.9, 2.10, and 2.11 respectively).

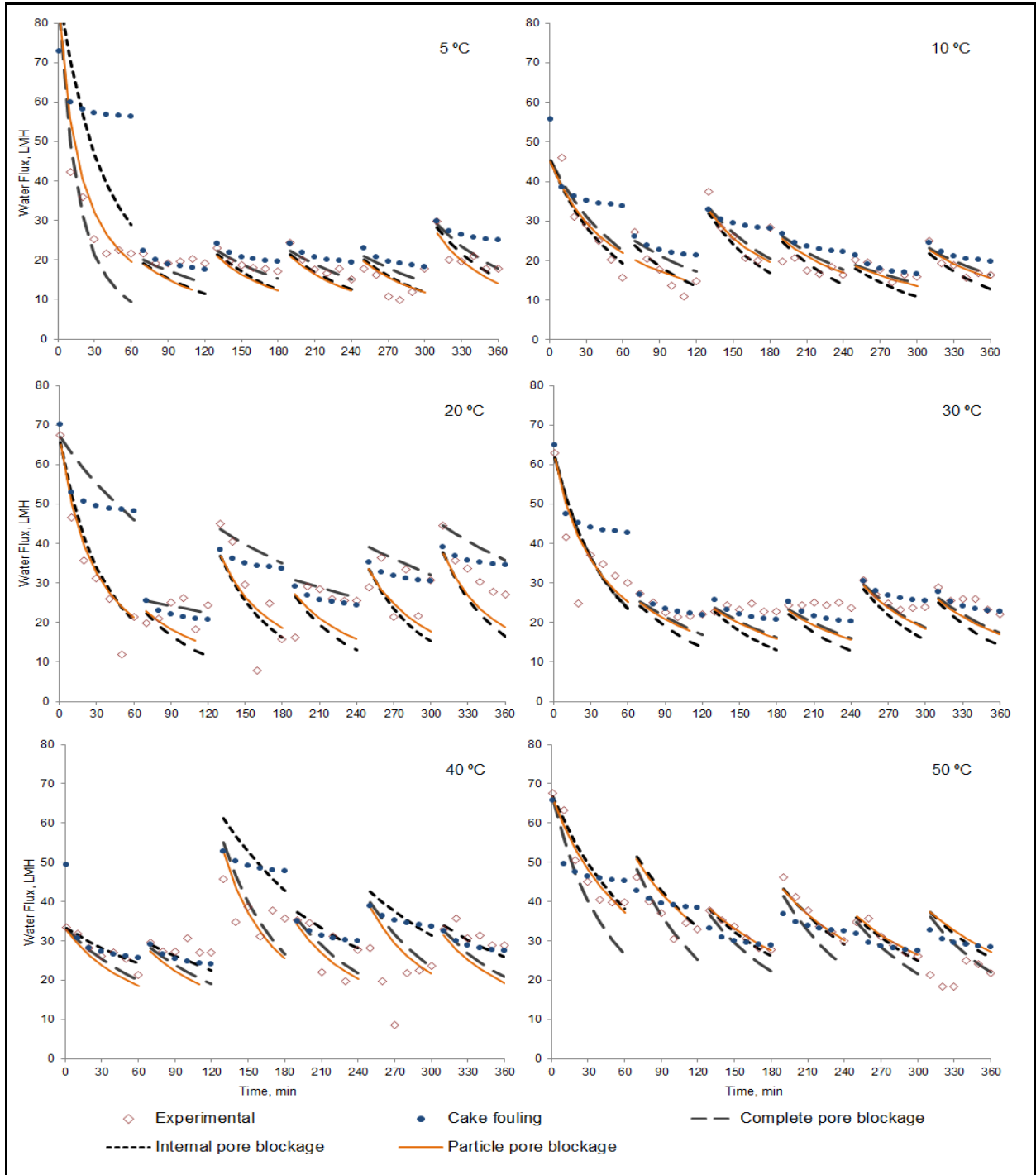


Figure 4.4: Experimental and theoretical water flux results: fouling experiments with 0.6 g/L Similac 1 solution at room temperature, cleaning experiments with 10 ppm NaOCl at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C. Theoretical curves were calculated with the best-fit approximation of flux behaviour due to complete pore blockage, internal pore blockage, partial pore blockage, and cake fouling (Equations 2.8, 2.9, 2.10, and 2.11 respectively).

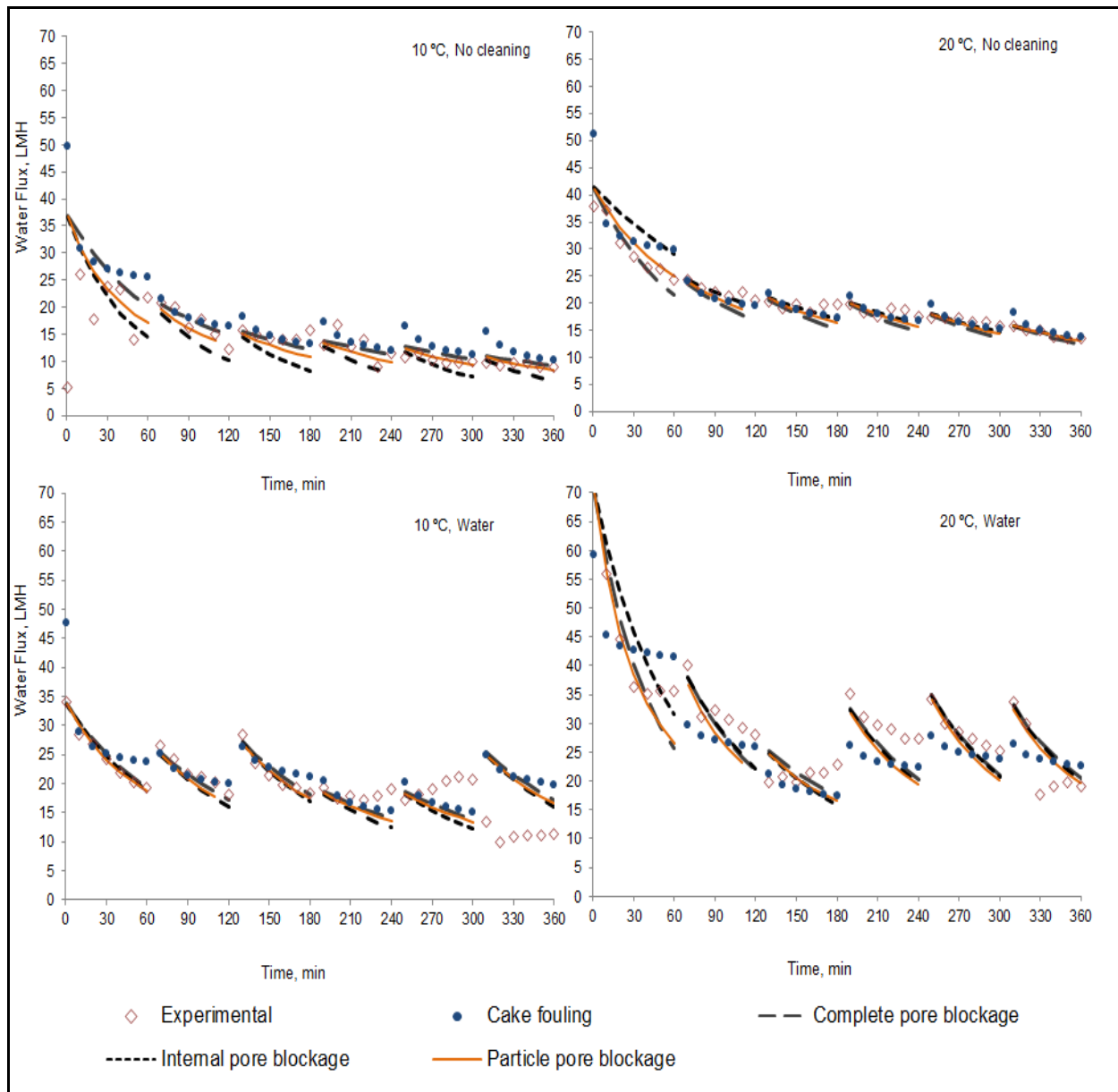


Figure 4.5: Experimental and theoretical water flux results: fouling experiments with 0.6 g/L Similac 1 solution at 10 °C and 20 °C, cleaning experiments with water at 20 °C. Theoretical curves were calculated with the best-fit approximation of flux behaviour due to complete pore blockage, internal pore blockage, partial pore blockage, and cake fouling (Equations 2.8, 2.9, 2.10, and 2.11 respectively)..

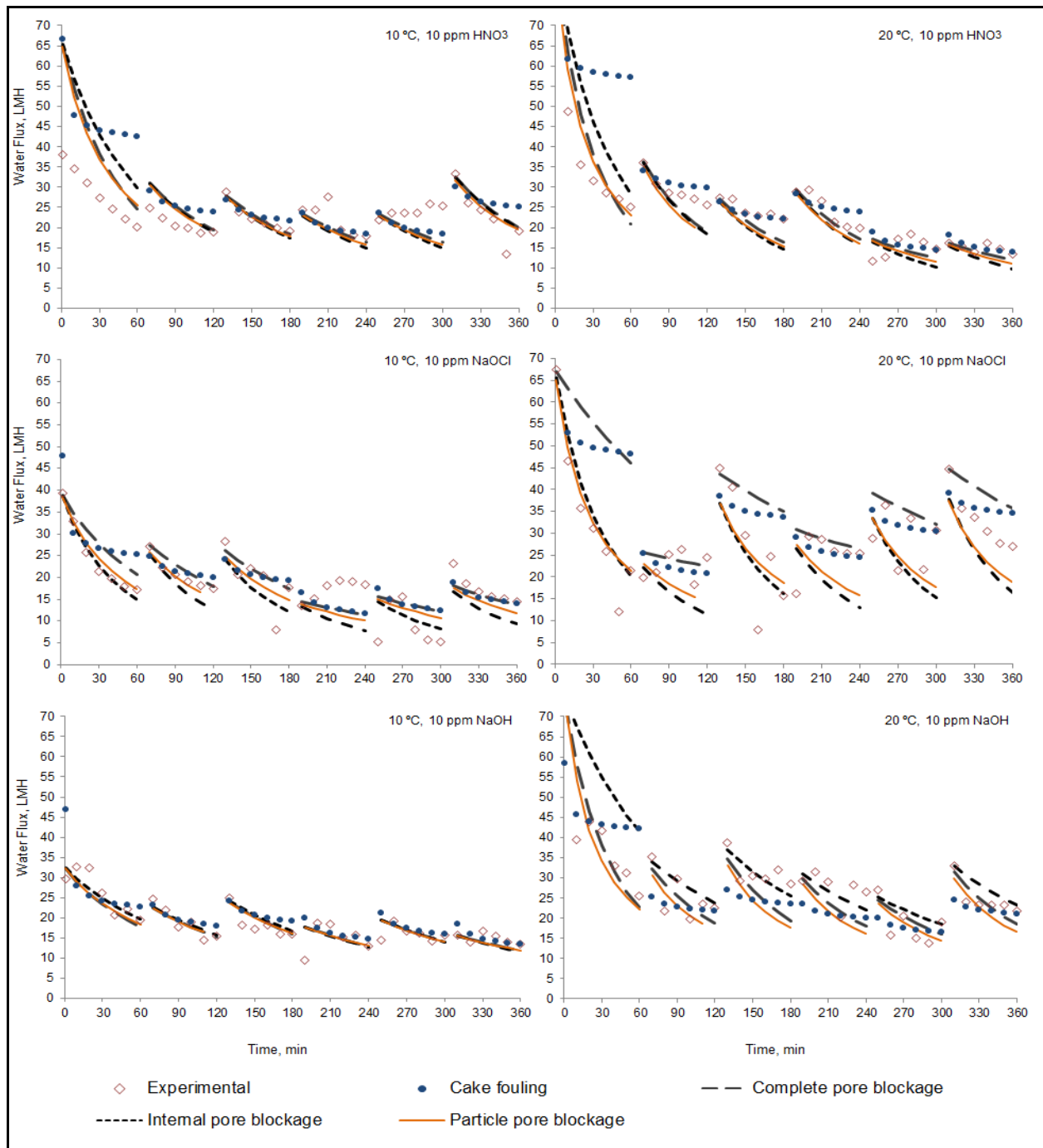


Figure 4.6: Experimental and theoretical water flux results: fouling experiments with 0.6 g/L Similac 1 solution at 10 °C and 20 °C, cleaning experiments with NaOH, HNO₃, NaOCl solutions with 10 ppm concentration at 20 °C. Theoretical curves were calculated with the best-fit approximation of flux behaviour due to complete pore blockage, internal pore blockage, partial pore blockage, and cake fouling (Equations 2.8, 2.9, 2.10, and 2.11 respectively).

cleaning at 20 °C and 30 °C demonstrate good results for both water flux and water flux recovery.

Figure 4.3 contains the result of six filtration experiments and theoretical fouling model calculations for the membranes fouled at room temperature and cleaned with 10 ppm HNO₃ solution at 5 °C-50 °C after each runs. Overall water flux results and flux recovery results are good in experiments with chemical cleaning at 40 °C and 50 °C: at first run, 76.125 LMH and 68.25 LMH and at last run, 25.125 LMH and 31.875 LMH respectively. Similar to cleaning with NaOH, first and second runs of water flux results mostly correlate with pore mechanisms for all temperatures.

Figure 4.4 contains the result of six filtration experiments and theoretical fouling model calculations for the filters fouled at room temperature and cleaned with 10 ppm NaOCl solution at 5 °C-50 °C after each runs. Overall water flux results and flux recovery results are good in experiments with chemical cleaning performed at 40 °C and 50 °C: at first run, 33.375 LMH and 67.5 LMH and at last run, 36 LMH and 40.5 LMH respectively.

Figure 4.5 contains the result of four filtration experiments and theoretical fouling model calculations for the membranes fouled at 10 °C and 20 °C with no cleaning and cleaned at room temperature with water. From the figure, it is clear that reduced fouling temperature results in decreased membrane performance: overall water flux results in fouled at 10 °C experiments are lower than fouled at 20 °C experiments. No water flux recovery can be observed in experiments without cleaning: water flux gradually decreases over the time. While cleaning with water experimental results demonstrate slight water recovery for both temperatures. In filtration experiments without cleaning, experimental curves are mostly scattered for both temperatures. Fouling mechanism behavior is also mostly scattered for fouled at 10 °C and water cleaning experiments. In experiments fouled at 10 °C and cleaned with water, the overall membrane performance is significantly lower than in experiments fouled at 20 °C: 34.1 LMH vs. 72 LMH initial water flux results respectively. Water flux values in experiments fouled at 20 °C is 72 LMH in the first run and 37.125 LMH in the second run. These results show that cleaning with water at room temperature is capable of partial removal of formed fouling.

Figure 4.6 contains the result of the filtration experiments and theoretical fouling model calculations for fouled at 10 °C and 20 °C and cleaning with HNO₃, NaOH, and NaOCl cleaning

agents with 10 ppm concentration each. From Figure 4.6, it is clear that overall water flux results in fouled at 10 °C experiments are distinctively lower than fouled at 20 °C experiments. For example, cleaning with HNO₃, fouling at 10 °C has 66.37 LMH initial water flux and fouling at 20 °C has 86.675 LMH initial water flux value. Water flux recovery can be observed in both fouling temperatures; nonetheless, in experiments fouled at 20 °C water flux is recovered with much stronger intensity in all cleaning agents. This trend indicates that chemical cleaning agents are more efficient than water cleaning; also, they can remove contaminants from membrane surface.

Progressive transition of water flux curves from pore blocking mechanism to cake formation indicates recovery of the initial filtration path which shows high efficiency of cleaning [66]. The absence of a progressive transition from pore blockage fouling to cake fouling is a sign of uninterrupted membrane fouling indicating that cleaning process had zero or insignificant impact. Table 4.1 contains fouling mechanisms of cleaned membranes obtained from comparison of experimental water flux with theoretical flux behaviors in Figures 4.1-4.4.

Table 4.1: Fouling mechanisms of filtration experiments cleaned at different temperatures.

Cleaning Experiments	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Water at 5 °C	Scattered	Cake	Pore	Scattered	Cake	Cake
Water at 10 °C	Pore	Pore	Pore	Pore	Pore	Scattered
Water at 20 °C	Pore	Pore	Pore	Scattered	Scattered	Pore
Water at 30 °C	Pore	Pore	Pore	Pore	Scattered	Scattered
Water at 40 °C	Pore	Scattered	Cake	Cake	Cake	Cake
Water at 50 °C	Pore	Pore	Cake	Cake	Cake	Cake
NaOH at 5 °C	Pore	Pore	Pore	Pore	Scattered	Scattered
NaOH at 10 °C	Pore	Pore	Pore	Cake	Cake	Cake
NaOH at 20 °C	Pore	Pore	Pore	Pore	Cake	Cake

NaOH at 30 °C	Pore	Pore	Cake	Cake	Cake	Cake
NaOH at 40 °C	Pore	Cake	Cake	Cake	Cake	Cake
NaOH at 50 °C	Pore	Cake	Cake	Cake	Cake	Cake
HNO ₃ at 5 °C	Pore	Pore	Pore	Pore	Pore	Cake
HNO ₃ at 10 °C	Pore	Scattered	Scattered	Cake	Cake	Cake
HNO ₃ at 20 °C	Pore	Cake	Cake	Cake	Cake	Cake
HNO ₃ at 30 °C	Pore	Pore	Scattered	Scattered	Scattered	Cake
HNO ₃ at 40 °C	Pore	Scattered	Scattered	Scattered	Scattered	Scattered
HNO ₃ at 50 °C	Pore	Cake	Cake	Pore	Pore	Pore
NaOCl at 5 °C	Pore	Cake	Scattered	Scattered	Scattered	Scattered
NaOCl at 10 °C	Pore	Pore	Pore	Pore	Cake	Pore
NaOCl at 20 °C	Pore	Pore	Pore	Cake	Cake	Cake
NaOCl at 30 °C	Pore	Cake	Cake	Cake	Cake	Cake
NaOCl at 40 °C	Scattered	Scattered	Scattered	Scattered	Scattered	Scattered
NaOCl at 50 °C	Pore	Pore	Pore	Pore	Scattered	Scattered
Total for 5 °C	11 pore, 8 scattered, and 5 cake					
Total for 10 °C	14 pore, 3 scattered, and 7 cake					
Total for 20 °C	12 pore, 2 scattered, and 10 cake					
Total for 30 °C	9 pore, 5 scattered, and 10 cake					
Total for 40 °C	3 pore, 12 scattered, and 9 cake					
Total for 50 °C	11 pore, 2 scattered, and 11 cake					

From Table 4.1, it is clear that chemical cleaning efficiency of filter occurs at 20 °C and 50 °C as for mentioned temperatures flux curves followed progressive transition from pore blockage to cake fouling. While poor chemical cleaning efficiency was observed at 5 °C and 40 °C temperatures as no transition stage was discovered.

Cleaning temperature impact on membrane performance can be assessed through comparison of total permeate volume passed through the filter. Table 4.2 contains the results of

the volume of the permeate that passed through the membrane for the all cleaning experiments conducted at 5 °C-50 °C temperatures.

Table 4.2: Volume of permeate that passed through membrane during filtration experiments cleaned at different temperatures.

	HNO₃ (ml)	NaOCl (ml)	NaOH (ml)	Water (ml)	Total volume for each temperature (ml)
5 °C	220.06	202.98	180.27	187.69	791.00
10 °C	182.88	183.74	216.40	227.42	810.44
20 °C	223.11	228.39	262.09	247.59	961.18
30 °C	212.88	240.09	200.07	241.30	894.34
40 °C	257.54	257.46	226.90	221.64	963.54
50 °C	253.25	285.26	199.95	218.77	957.23

From Table 4.2 it can be observed that lower cleaning temperatures (5 °C and 10 °C) result in reduced membrane performance; while, at elevated cleaning temperatures (40 °C and 50 °C) the membranes demonstrate better performance.

Table 4.3 includes fouling mechanisms of cleaning of fouled membranes at low temperatures obtained from comparison of experimental water flux with theoretical flux behaviors in Figures 4.5 and 4.6.

Table 4.3: Fouling mechanisms of filtration experiments fouled at different temperatures.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
10 °C, No clean	Pore	Scattered	Scattered	Scattered	Scattered	Scattered
20 °C, No clean	Pore	Pore	Scattered	Scattered	Scattered	Scattered
10 °C, Water	Pore	Pore	Scattered	Scattered	Scattered	Scattered
20 °C, Water	Pore	Pore	Pore	Scattered	Scattered	Pore
10 °C, HNO ₃	Pore	Scattered	Scattered	Scattered	Scattered	Scattered

20 °C, HNO ₃	Pore	Cake	Cake	Cake	Cake	Cake
10 °C, NaOCl	Pore	Scattered	Scattered	Scattered	Scattered	Scattered
20 °C, NaOCl	Pore	Pore	Pore	Cake	Cake	Cake
10 °C, NaOH	Scattered	Scattered	Scattered	Scattered	Scattered	Scattered
20 °C, NaOH	Pore	Pore	Pore	Pore	Cake	Cake
Total for 10 °C,	4 pore, 20 scattered, and 0 cake					
Total for 20 °C	12 pore, 2 scattered, and 10 cake					

From analysis of fouling behavior in cleaning experiments, it can be observed that fouling at 10 °C demonstrated very high scattered fouling behavior which indicates irreversible fouling formation. This might be accounted for increased adhesion characteristic of protein foulant (Similac 1) in lowered temperatures [67].

Table 4.4 shows the total volume of the permeate that passed through the membrane for filtration experiments conducted at 10 °C and 20 °C.

Table 4.4: Volume of permeate that passed through membrane during filtration experiments at different temperatures and cleaned at room temperature.

	HNO₃ (ml)	NaOCl (ml)	NaOH (ml)	Water (ml)	Total volume for each temperature (ml)
10 °C	219.93	155.97	168.14	182.52	726.55
20 °C	223.11	228.39	262.09	247.59	961.18

From Table 4.4, it is clear that lower feed temperature results in decreased membrane performance: 726.6 ml permeate volume at 10 °C vs. 961.2 ml 20 °C. Increased operating temperature gives higher filter performance.

Another factor indicating cleaning efficiency is relative dissimilarity of water flux values after each run. Kolmogorov-Smirnov test was used to calculate dissimilarity between water flux values after every run: differences between first and consequent runs were calculated and

maximum difference value was for every cleaning experiment [66, 68]. It is generally accepted in efficient cleaning, water flux of consecutive runs should follow pattern water flux of first run. Significant dissimilarity between water flux values implies that water flux is not recovered and cleaning efficiency is low. Table 4.5 includes total relative dissimilarity of water flux values of each run of filtration experiments cleaned at 5 °C-50 °C temperatures. Table 4.6 includes total relative dissimilarity of water flux values of each run of filtration experiments fouled at room and cleaned at 10 °C-20 °C temperatures (More detailed results are presented in Appendices A and B).

Table 4.5: Total dissimilarity of water flux values of each run of filtration experiments cleaned at different temperatures.

	Runs 1-3	Runs 1-3	Runs 1-4	Runs 1-5	Runs 1-6	Total dissimilarity for each temperature
5 °C	38.37	38.52	49.04	59.41	41.78	227.11
10 °C	58.84	56.44	63.56	56.15	66.37	301.36
20 °C	77.25	90.00	83.63	104.63	90.36	445.88
30 °C	58.88	100.50	91.50	77.25	81.50	409.63
40 °C	48.75	102.75	78.00	62.50	98.63	390.63
50 °C	51.00	67.13	81.34	95.25	123.75	418.50

Table 4.6: Total dissimilarity of water flux values of each run of filtration experiments cleaned at different temperatures.

	Runs 1-3	Runs 1-3	Runs 1-4	Runs 1-5	Runs 1-6	Total dissimilarity for each temperature
10 °C	28.59	34.52	62.08	69.49	53.48	248.15
20 °C	77.25	90.00	83.63	104.63	90.38	445.88

Total relative dissimilarity values of water flux suggest that the best cleaning was conducted at 5 °C temperature and cleaning efficiency was very low at 20 °C. Also, from Table 4.6, cleaning was more efficient at 10 °C temperature. Nonetheless, it is very difficult to conclude cleaning efficiency only based on the water flux fouling behavior and relative dissimilarity values due to the chance that membrane surface can be damaged by chemicals that could distort results. Therefore, it is necessary to consider surface analysis of pristine, fouled, and cleaned membranes. Zeta potential, contact angle, AFM, and FTIR measurements will provide information about condition of the membrane surface.

4.2 Membrane Zeta Potential

The zeta potential results of membranes cleaned at different temperatures are illustrated in Figure 4.7. The zeta potential values of membranes were measured in 1.5-9.5 pH range. Surface charge of pristine membrane has maximum 1.41 mV and minimum -14.012 mV values and mostly lie in negatively charged zone starting from 2.36 pH level. Surface charge of fouled membrane ranges from -20.063 mV to 13.424 mV values and surface charge becomes negative starting from 3.66 pH level. From Figure 4.7, it is clear that chemical cleaning of fouled membrane at 20 °C with NaOCl cleaning agent was highly efficient; nonetheless, excessive agent concentration resulted in high deviation of zeta potential values between virgin and cleaned membranes. Table 4.7 contains the classification of cleaned membranes in regards to pristine membrane: membranes located below pristine membrane are considered as successfully cleaned.

Table 4.7: Zeta Potential results cleaned membranes.

	Above pristine membrane	Below pristine membrane
HNO₃	Cleaned at 5 °C-50 °C	None
NaOH	Cleaned at 5 °C- 50 °C	None
NaOCl	Cleaned at 5 °C, 10 °C, 30 °C-50 °C	Cleaned at 20°C
Water	Cleaned at 5 °C-50 °C	None

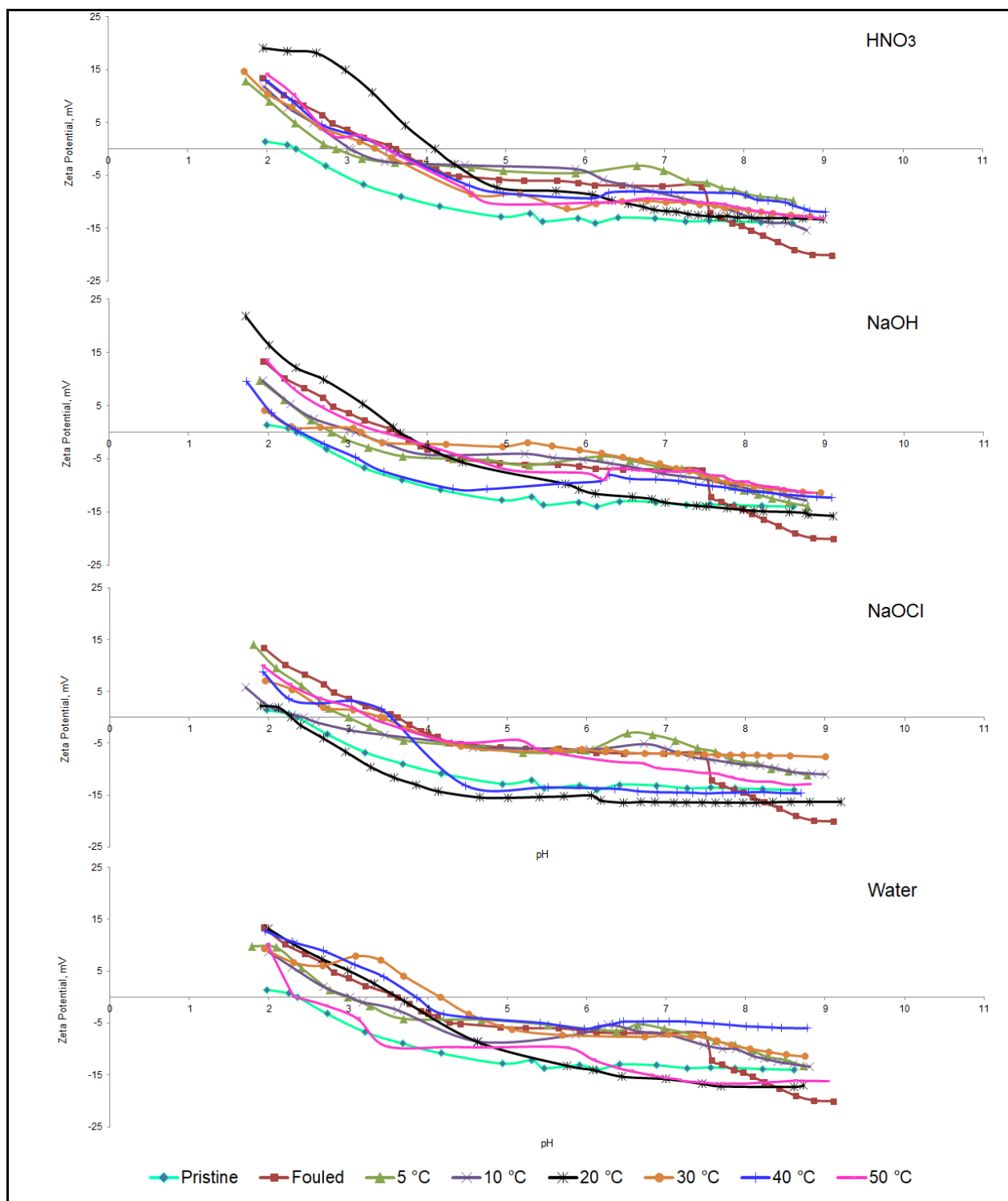


Figure 4.7: Zeta potential results of membranes: pristine, fouled with 0.6 g/L Similac 1 solution at room temperature and cleaned with 10 ppm HNO_3 , NaOH , NaOCl , and water at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C.

Kolmogorov-Smirnov test was used to calculate dissimilarity between zeta potential results of the virgin membrane and cleaned membranes. Increased dissimilarity between zeta potential values of the pristine and cleaned membranes demonstrate that cleaning process was not efficient or membrane was subjected to over cleaning. Membrane is considered as sufficiently cleaned if zeta potential values of cleaned membrane highly correlate with results of pristine membrane. Dissimilarity of zeta potential values of filtration experiments cleaned at 5 °C-50 °C temperatures is presented in Table 4.8.

Table 4.8: Total dissimilarity of zeta potential values of filtration experiments cleaned at different temperatures.

	HNO₃	NaOH	NaOCl	Water	Total for each temperature
5 °C	9.84	9.41	9.92	8.83	37.99
10 °C	10.38	8.86	7.98	8.56	35.78
20 °C	21.37	14.96	3.47	11.72	51.52
30 °C	9.61	11.03	8.78	14.63	44.05
40 °C	11.55	4.78	9.96	12.98	39.27
50 °C	12.81	12.18	8.65	8.81	42.44

From comparison of total relative dissimilarity of zeta potential values for each temperature, it can be noticed that the best membrane cleaning was performed at 5 °C, 10 °C, and 40 °C. While cleaning at 20 °C demonstrates poor cleaning efficiency.

4.3 Contact Angle Measurements and AFM Analysis

Figure 4.8 illustrates results of contact angle measurements membranes fouled and cleaned with water at different temperatures. The contact angle value of pristine membrane is 68° and fouled membrane is 83°.

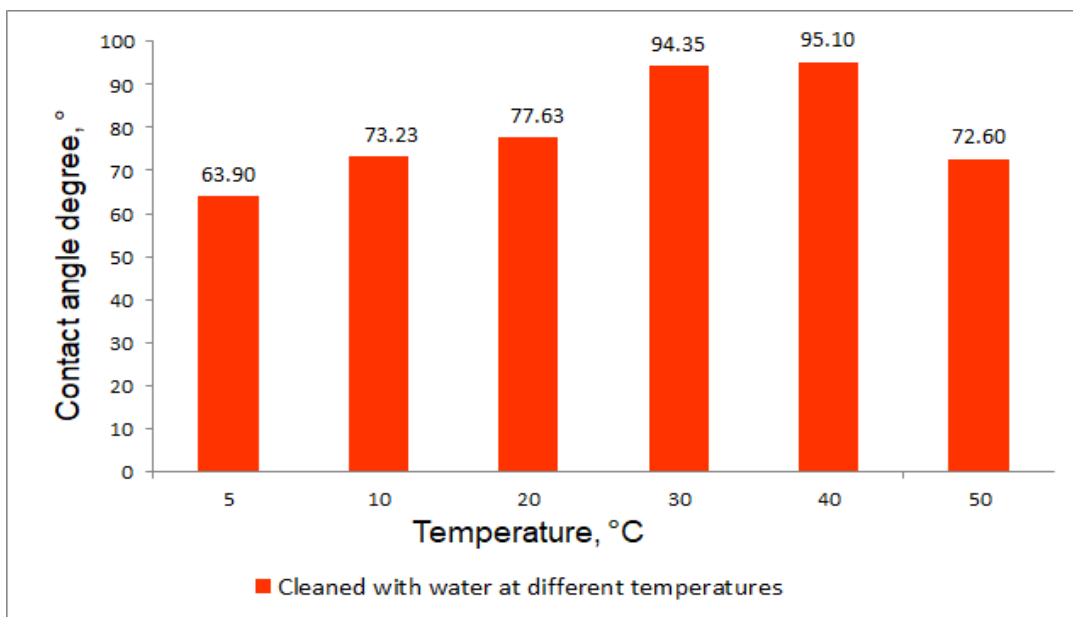


Figure 4.8: Contact angle degree results of membranes fouled with 0.6 g/L Similac 1 solution at room temperature and cleaned with water at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C.

From Figure 4.8, is clear that increase of cleaning temperature from 5 °C to 40 °C resulted in increase in contact angle values. Furthermore, membrane surface become more hydrophobic when cleaned with water at 30 °C and 40 °C with contact angle results higher than pristine membrane values. However, cleaning at 50 °C resulted in contact angle degree drop to 72.6 ° which indicates that at 50 °C protein denaturation occurred. Similar values to contact angle of pristine membrane indicate successful cleaning. Based only on contact angle degree results, the most optimal temperatures for cleaning are 10 °C and 20 °C.

Figure 4.9, illustrates the membrane surface conditions after the fouling. Virgin membrane has smooth surface and fouled membranes has rough surface as a result of foulant accumulation. Fouling at 20 °C temperature demonstrates less fouling and membrane surface is relatively flat that indicate foulants size is less than colloidal fouling. At elevated temperatures membrane surface has high level of roughness. At 50 °C, suggesting formations of irreversible fouling most probably as a result protein structure change at high temperatures [67]. Membrane surface fouled at 5 °C and 10 °C also have high level of foulant accumulation.

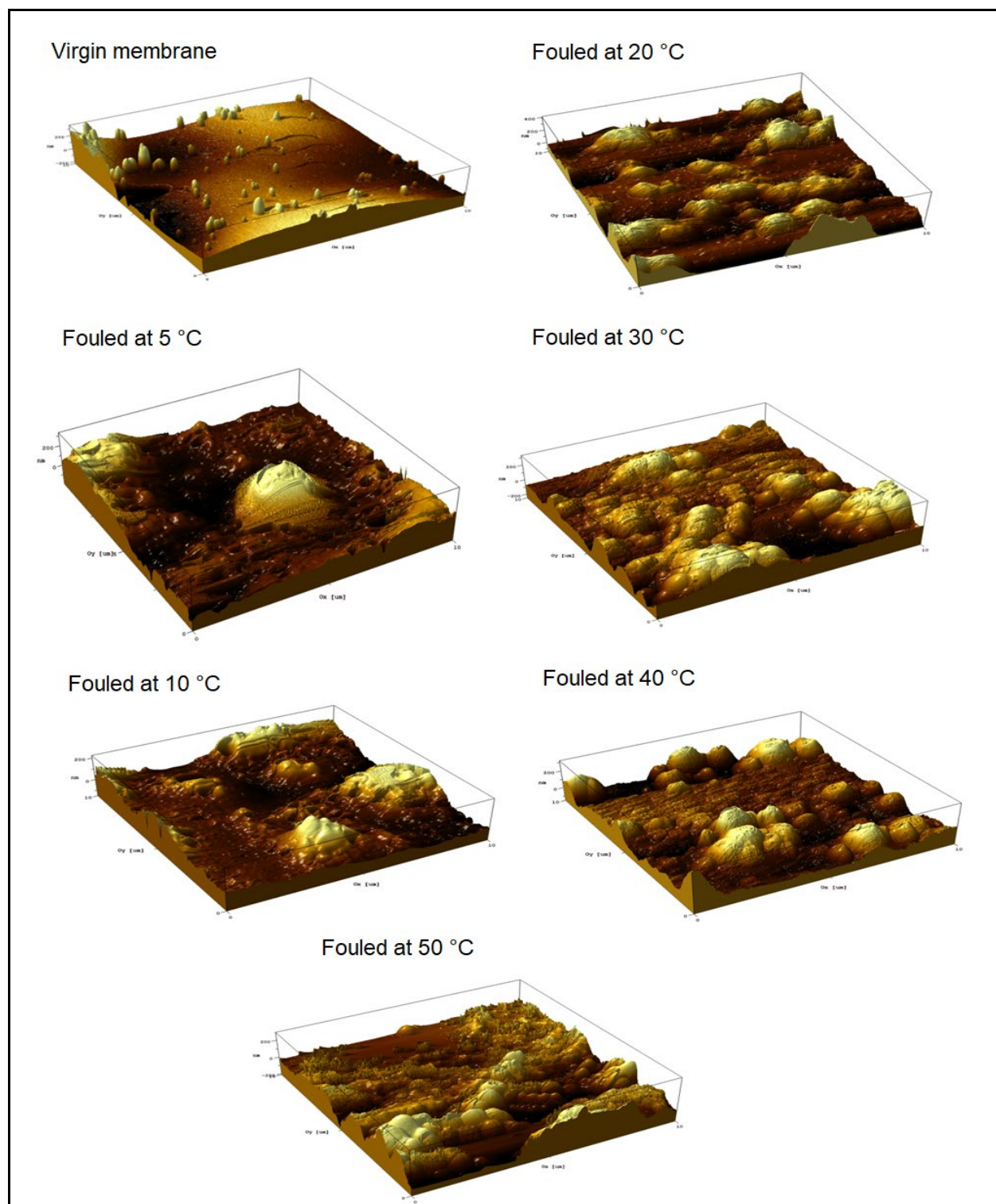


Figure 4.9: AFM results of membranes fouled with 0.6 g/L Similac 1 solution at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C.

4.4 The FTIR Spectra

The FTIR spectra of pristine, fouled membranes and membranes cleaned with water and with cleaning agents (HNO_3 , NaOH , and NaOCl) at different temperatures are presented in Figures 4.10-4.12. The absorbance of membranes ranges in -0.012-0.072 and wavelength is measured in $500\text{-}2500\text{ cm}^{-1}$ range. Most of the peaks of pristine membrane appear also in fouled and cleaned membranes but some of them disappears or changes the form. Disappearance or change of the peaks could give additional information about cleaning efficiency. Different ranges of IR absorption bands are responsible for polymer structure and protein bands [69, 70] (Detailed information about IR absorption bands assignment is presented in Appendices E and F). From the analysis of FTIR spectra in Figures 4.10-4.12, it can be observed that at elevated temperatures ($40\text{ }^{\circ}\text{C}$ and $50\text{ }^{\circ}\text{C}$.) peaks at 972 cm^{-1} disappeared or changed the form indicating that benzene rings of PES were affected by cleaning [70]. Moreover, at elevated temperatures 1714 cm^{-1} peak has been affected; this could be a result of protein removal as mentioned peak corresponds to Amide I $\text{C}=\text{O}$ stretching range [69]. Also, 1714 cm^{-1} peak disturbance could be related to $\text{C}=\text{C}$ stretching vibration of membrane polymer [70]. The peaks located in 2270 cm^{-1} - 2340 cm^{-1} and 3400 cm^{-1} range generally assigned to membrane surface preservatives and absence of these peaks in FTIR spectra of cleaned membranes demonstrate preservatives removal [69]. Table 4.9 includes FTIR spectra peaks of pristine membrane and their absence or change in cleaned membranes collected from data in Figures 4.10-4.12. FTIR spectra results of cleaned membranes suggest that effective cleaning temperatures are $5\text{ }^{\circ}\text{C}$ - $30\text{ }^{\circ}\text{C}$, while elevated temperatures result in membrane structure disturbance.

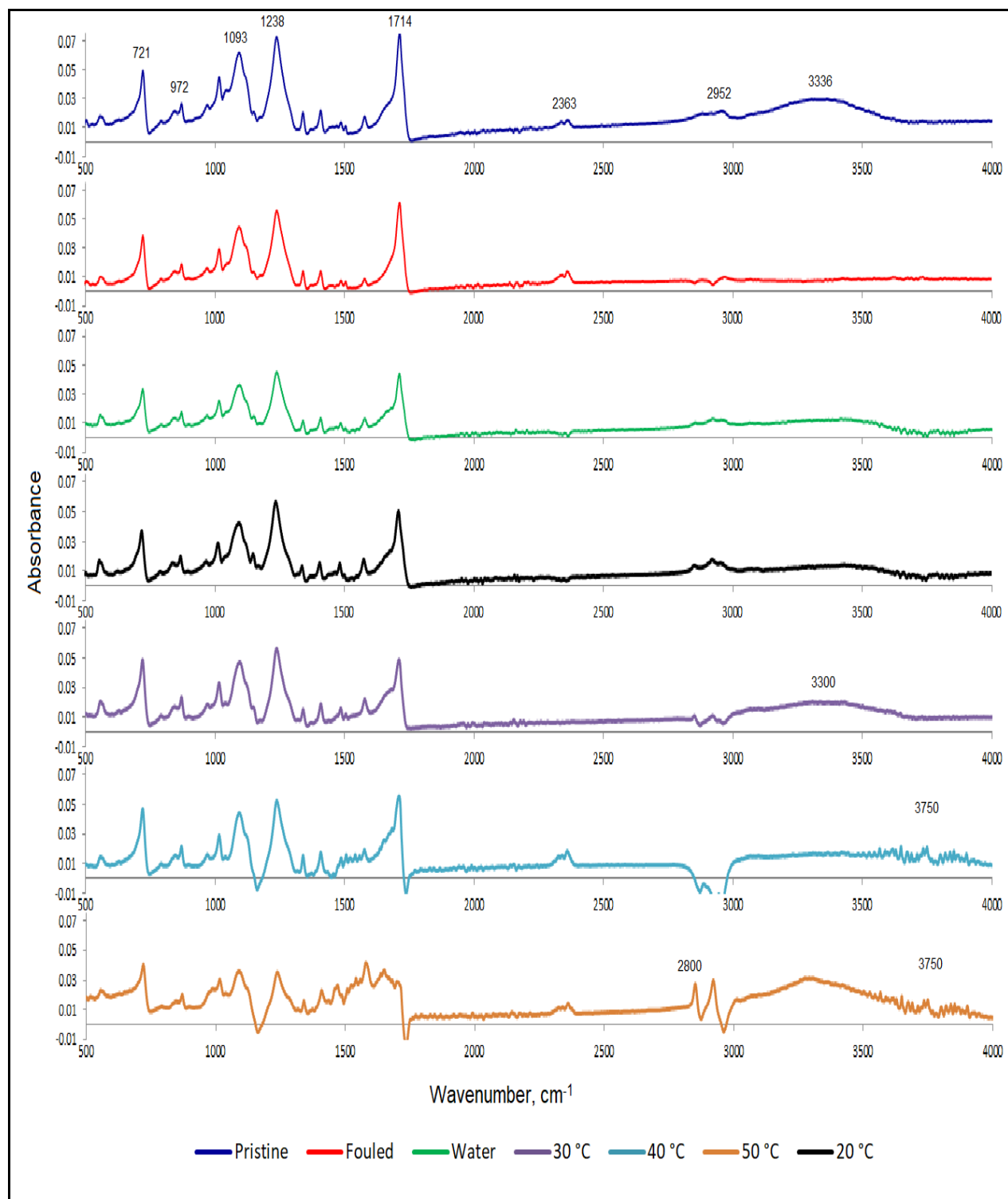


Figure 4.10: FTIR spectra of pristine, fouled with 0.6 g/L Similac 1 solution at room temperature, and cleaned membranes with water at 20 °C and 10 ppm HNO_3 solution at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C.

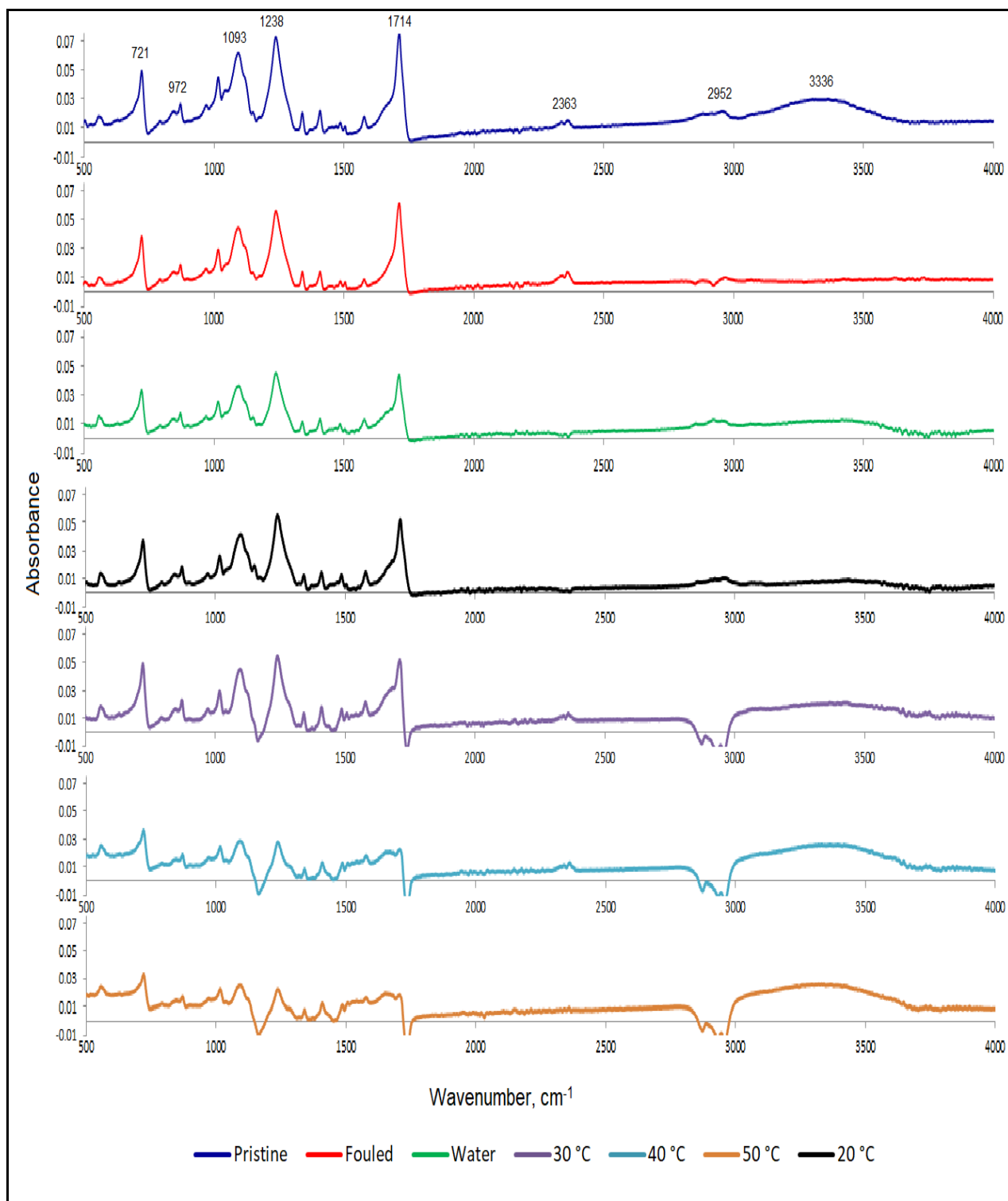


Figure 4.11: FTIR spectra of pristine, fouled with 0.6 g/L Similac 1 solution at room temperature, and cleaned membranes with water at 20 °C and 10 ppm NaOH solution at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C.

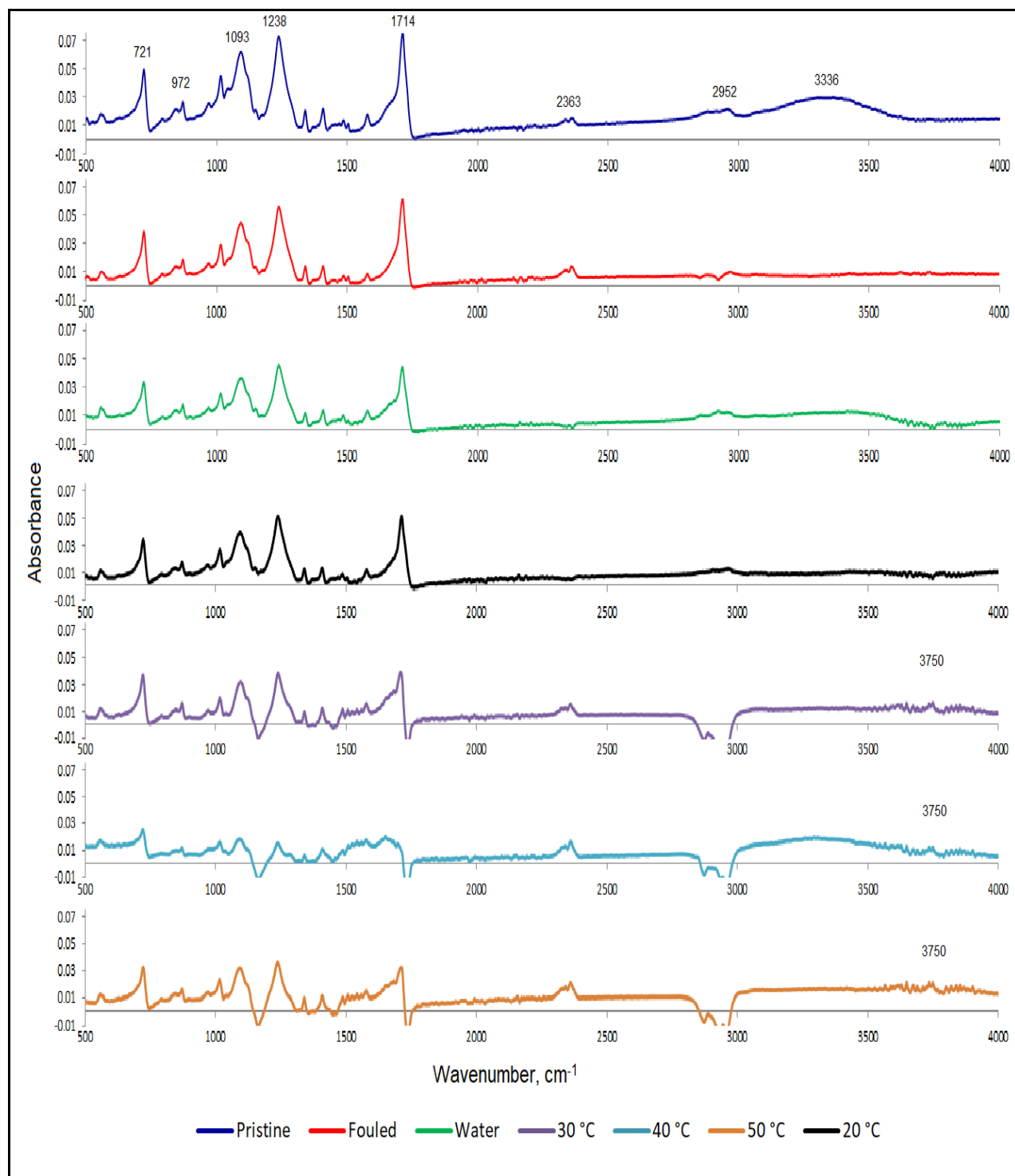


Figure 4.12: FTIR spectra of pristine, fouled with 0.6 g/L Similac 1 solution at room temperature, and cleaned membranes with water at 20 °C and 10 ppm NaOCl solution at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, and 50 °C.

Table 4.9: The peaks of FTIR spectra of pristine and cleaned membranes.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	New
Pristine	972	1714	2363	2952	3336	NA
Fouled				No	No	
Water cleaned			No		No	
HNO ₃ at 20 °C			No			
HNO ₃ at 30 °C			No	No	No	3300
HNO ₃ at 40 °C				No	No	3750
HNO ₃ at 50 °C	Change of the from	No				2800; 3750
NaOH at 20 °C			No		No	
NaOH at 30 °C				No	No	3750
NaOH at 40 °C	No	No		No	No	3750
NaOH at 50 °C	No			No	No	3750
NaOCl at 20 °C			No		No	
NaOCl at 30 °C				No		
NaOCl at 40 °C	No	No		No		
NaOCl at 50 °C		No	No	No		

Chapter 5 - Conclusions

Most of the studies related to MST suggest that membrane demonstrates different types of fouling mechanism and different cleaning performance. Nonetheless, there is no protocol for MST filtration and cleaning processes and information provided by manufacturers are for ambient temperature. The motivation of this research paper is formulated on the need of determining optimal operating conditions of MST. The investigation of the temperature impact on membrane fouling and cleaning from water flux and membrane surface analysis, several conclusions are formed:

- At low operation temperature, water flux and membrane performance is negatively affected. At 10 °C feed temperature, irreversible fouling is formed. Membrane surface investigation infers that low operation temperature has less influence on membrane structure which consequently increases membrane lifespan.
- At increased operation temperature, filtration experiment results demonstrate that membrane have higher water flux. However, high operation temperature affects membrane structure which can reduce membrane lifetime. Membrane structure disturbance can negatively influence permeate quality and could lead to decline of the membrane performance. High operation temperature requires more energy thus more expensive.

Considering the issues present in low and high operation temperatures, low operation temperature is considered as more sustainable. The low water flux problem can be solved by increasing membrane surface area. The initial cost for low operation temperature could be higher but on account of prolonged membrane lifespan, overall cost of MST at low temperatures will be less than operation at high temperatures. Membrane structure disturbance at high operating temperature can only be solved by replacing the membrane that comes as additional expenses. Mentioned temperature impacts must be considered in deciding convenient filtration process conditions based on preferred long-term operation or immediate high water flux.

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Appendices

Appendix A

The dissimilarity of water flux values of cleaning at different temperatures after every run.

	Runs 1-2					Runs 1-3					Runs 1-4			
	HNO3	NaOCl	NaOH	Water		HNO3	NaOCl	NaOH	Water		HNO3	NaOCl	NaOH	Water
5	2.222	20.592	4.148	11.41		5.926	19.259	3.555	9.777		8	17.926	7.852	15.259
10	26.222	18.6963	5.629	8.296		25.925	12.7407	5.925	11.85		27.111	26.074	3.26	7.111
20	12.75	26.625	22.125	15.75		21.375	18	14.625	36		19.875	30.375	12.75	20.625
30	9	14.625	4.125	31.13		34.125	18.75	9	38.63		22.875	17.25	18	33.375
40	9.375	5.625	10.5	23.25		37.5	14.25	19.125	31.88		22.125	6.375	15.375	34.125
50	18.375	17.25	9.75	5.625		18.75	25.5	8.625	14.25		22.125	17.25	16.5	25.5
	Runs 1-5					Runs 1-6								
	HNO3	NaOCl	NaOH	Water		HNO3	NaOCl	NaOH	Water					
5	11.556	24.444	8.592	14.82		12.889	15.852	6.371	6.666					
10	20.74	25.7778	2.667	6.963		32.296	21.037	5.334	7.703					
20	37.125	17.625	28.125	21.75		32.625	15.75	19.875	22.13					
30	9	12.375	18	37.88		25.125	12.75	13.875	29.75					
40	19.125	17.625	6.375	19.38		36.75	7.5	31.5	22.88					
50	31.125	28.5	15	20.63		34.125	42	15.75	31.88					
10	12.741	27.556	18.074	11.11		8.593	9.778	18.37	16.74					
20	37.125	17.625	28.125	21.75		32.625	15.75	19.875	22.13					

Appendix B

The dissimilarity of water flux values of fouling at different temperatures after every run.

	Runs 1-2					Runs 1-3					Runs 1-4			
	HNO3	NaOCl	NaOH	Water		HNO3	NaOCl	NaOH	Water		HNO3	NaOCl	NaOH	Water
10	9.926	5.778	10.37	2.519		7.259	9.926	14.222	3.111		10.223	19.408	23.111	9.334
20	12.75	26.625	22.125	15.75		21.375	18	14.625	36		19.875	30.375	12.75	20.625
	Runs 1-5					Runs 1-6								
	HNO3	NaOCl	NaOH	Water		HNO3	NaOCl	NaOH	Water					
10	12.741	27.556	18.074	11.11		8.593	9.778	18.37	16.74					
20	37.125	17.625	28.125	21.75		32.625	15.75	19.875	22.13					

Appendix C

Water flux recovery of filtration experiments cleaned at different temperatures.

Cleaning Experiments	Run 2	Run 3	Run 4	Run 5	Run 6
Water at 5 °C	6.2 %	54.49 %	4.19 %	3.36 %	82.79 %
Water at 10 °C	22.22 %	17.54 %	58.33 %	34.65 %	47.51 %
Water at 20 °C	6.25 %	-20.56 %	62.26 %	19.15 %	25.23 %
Water at 30 °C	-3.62 %	-26.07 %	62.26 %	23.88 %	77.24 %
Water at 40 °C	4.2 %	-25.56 %	-20 %	40.31 %	6.73 %
Water at 50 °C	13.33 %	9.26 %	26.19 %	9.01 %	-23.53 %
NaOH at 5 °C	45.59 %	27.59 %	3.69 %	37.04 %	-3.47 %
NaOH at 10 °C	20.68 %	41.15 %	25.55 %	24.45 %	21.94 %
NaOH at 20 °C	12.87 %	45.74 %	1.94 %	1.28 %	52.85 %
NaOH at 30 °C	15.43 %	9.48 %	1.32 %	29.31 %	31.92 %
NaOH at 40 °C	38.46 %	-20.19 %	12.5 %	45.45 %	-15.63 %
NaOH at 50 °C	6.67 %	36.36 %	3.75 %	13.56 %	9.52 %
HNO ₃ at 5 °C	19.95 %	28.77 %	6.56 %	-13.61 %	35.17 %
HNO ₃ at 10 °C	-1.28 %	11.54 %	23.48 %	63.71 %	-19.16 %
HNO ₃ at 20 °C	12.56 %	5.21 %	24.66 %	-28.57 %	12.9 %
HNO ₃ at 30 °C	13.92 %	-24 %	96.77 %	85.24 %	0.94 %
HNO ₃ at 40 °C	40.89 %	-2.8 %	69.23 %	61.32 %	87.72 %
HNO ₃ at 50 °C	28.57 %	13.71 %	14.68 %	27 %	39.47 %
NaOCl at 5 °C	0	17.12 %	30.97 %	10.98 %	66.67 %
NaOCl at 10 °C	12.2 %	82.7 %	-23.02 %	19.4 %	44.12 %
NaOCl at 20 °C	-2.22 %	103.77 %	0.83 %	20.93 %	48.05 %
NaOCl at 30 °C	-4.17 %	2.74 %	6.55 %	29.23 %	15.85 %
NaOCl at 40 °C	24.72 %	63.29 %	-0.82 %	1.06 %	33.33 %
NaOCl at 50 °C	9.44 %	10.57 %	48.51 %	10.57 %	-13.98 %

Appendix D

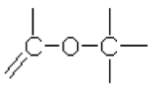
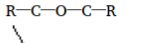
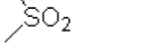
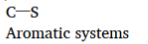
Water flux recovery of filtration experiments fouled at different temperatures.

Cleaning Experiments	Run 2	Run 3	Run 4	Run 5	Run 6
10 °C, No clean	NA	NA	NA	NA	NA
20 °C, No clean	NA	NA	NA	NA	NA
10 °C, Water	21.31 %	39.1 %	3.13 %	-4.62 %	-43.11 %
20 °C, Water	6.25 %	-20.56 %	62.26 %	19.15 %	25.23 %
10 °C, HNO ₃	12.11 %	40.71 %	18.46 %	16.36 %	36.49 %
20 °C, HNO ₃	12.56 %	5.21 %	24.66 %	-28.57 %	12.9 %
10 °C, NaOCl	24.81 %	39.89 %	-15.19 %	-96.7 %	336.13 %
20 °C, NaOCl	-2.22 %	103.77 %	0.83 %	20.93 %	48.05 %
10 °C, NaOH	17.6 %	38.56 %	-26.19 %	15.63 %	0
20 °C, NaOH	12.87 %	45.74 %	1.94 %	1.28 %	52.85 %

Appendix E

Assignment of relevant IR absorption bands to PES-300.

Table 1
Assignment of relevant IR absorption bands to PES-300.

IR band, cm ⁻¹	Range given in the literature [49], cm ⁻¹	Assignment
555, 620, 915, 942, 990, 1000	1000≥	Benzene rings
1030	About 1030	Benzene ring
1100	1085–1125	C-O stretching vibration
1150	1150 up to 1225	O-H deformation and C-O stretching vibration interaction
1250	1275–1200	
1290		
1320	1300–1050 1310–1350	
1485		
1575	1460–1550	C-S
1650	About 1580	Aromatic systems
	1580 up to 1660	C=C stretching vibration

Appendix F

Characteristics IR bands of proteins.

Table 2
Characteristics IR bands of proteins.

IR band, cm^{-1}	Designation	Description
200	Amide VII	Skeletal torsion
537–606	Amide VI	Out-of-plane C=O bending
625–767	Amide IV	OCN bending
640–800	Amide V	Out-of-plane NH bending
1229–1301	Amide III	CN stretching, NH bending
1480–1575	Amide II	CN stretching, NH bending
1600–1690	Amide I	C=O stretching
3100	Amide B	NH stretching
3300	Amide A	NH stretching