Novel Polymeric Ultrafiltration Membranes – Performance, Retention, Fouling and Cleaning Analysis

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Thesis to obtain the Master of Science Degree in

Biological Engineering

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July 2020

Preface

The work presented in this thesis was developed at the Department of Chemical Engineering of Lund University (Lund, Sweden), under the supervision of Prof. Frank Lipnizki and Mikael Sjölin, between September/2019 and January/2020 and within the Erasmus programme. The thesis was co-supervised by Prof. Marília Mateus at Instituto Superior Técnico. Furthermore, this project was conducted in partnership with the Institute of Physical Organic Chemistry – National Academy of Sciences of Belarus.

Acknowledgements

First and foremost, I would like to show my deepest gratitude to Professor Frank for giving me the opportunity to be part of his research group and for all the sympathy, guidance and constant feedback throughout this thesis. I am very thankful for this enriching experience. Thank you to Mikael for all your time, assistance, patience, knowledge and for allowing me to work with you in this project.

A special thank you to Professor Marília for believing in me since the first day. Thank you for your kindness, for constantly reaching out to me to offer help and support and for your feedback in every stage of this experience.

Thank you to everyone in the Department of Chemical Engineering, specially to the people from the Membrane Group for welcoming me and for all the assistance provided during my 5 month journey in Sweden. I am also thankful to the Institute of Physical Organic Chemistry – National Academy of Sciences of Belarus, in particular Katerina and Tatsiana for their work and help in this project.

To Joana, Mariona, Miguel, Rubén, Ximo, Katarina, Lidia, Maria and Piotr, thank you all for your friendliness and for turning this experience into something unforgettable.

Last but not least, thank you to my family, particularly to my parents and my sister for all their support throughout this entire journey.

Declaration

I declare that this document is an original work of my own authorship and that it fulfils all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

Abstract

The implementation of the membrane process ultrafiltration systems for valorisation of by-products while reducing water and energy consumption has been reported for many worldwide industries including pulp and paper or food and beverages. Ultrafiltration enables the recovery of valuable compounds without diminishing their intrinsic qualities, but the general hydrophobicity of polysulfone (PS) and polyethersulfone (PES) membranes makes them prone to fouling. Fouling generally reduces fluxes and can, ultimately, affect the structure of the membranes permanently. In this work polyacrylic acid, poly(methyl vinyl ether-alt-maleic acid), a cationic charged polyelectrolyte Praestol 859 and an anionic charged polyelectrolyte Praestol 2540 were considered as modifying agents during membrane preparation via phase inversion to improve hydrophilicity and antifouling properties of PS and PES membranes.

Thus, novel flat sheet modified polymeric PS and PES membranes were evaluated for ultrafiltration of thermomechanical pulping (ThMP) process water based on permeate fluxes, impact of fouling and retention of hemicelluloses and lignin. A comparison between the effect of the different additives and concentrations on the membranes performance was established for the novel membranes and two commercial membranes. Furthermore, a similar study was conducted for recovery of protein from potato fruit water from a starch production plant.

Overall, the results were generally good, in particular for the ultrafiltration of ThMP process water. The key finding of this work is that membrane surface modification with Prestol 859 can improve both flux and hydrophilicity of PES based membranes and thus can lead to the development of low fouling membranes.

Keywords: UF; modification of polymeric membranes

Resumo

Sistemas de Ultrafiltração para valorização de subprodutos e redução do consumo energético ou água têm sido constantemente relatados em indústrias como da celulose ou alimentar, permitindo a recuperação de valiosos compostos e mantendo as suas qualidades intrínsecas. As propriedades hidrófobas da polissulfona e polietersulfona tornam as membranas propensas ao *fouling*, reduzindo os fluxos e, inclusive, afetando irreversivelmente a estrutura das membranas. Neste trabalho, tendo em vista o aumento do poder hidrófilo e resistência ao *fouling*, ácido poliacrílico, poli(metil vinil éter-alt-ácido málico), um polieletrólito catiónico Praestol 859 e um polieletrólito aniónico Praestol 2540 foram considerados como agentes modificadores durante a preparação das membranas por inversão de fase.

Assim, membranas poliméricas planas modificadas foram avaliadas baseado nos fluxos de permeado durante a ultrafiltração de uma corrente de processo de uma fábrica de produção termomecânica de pasta celulósica, o impacto do *fouling* e na retenção de hemiceluloses e lenhinas. Comparou-se de que forma cada aditivo e respetivas concentrações influenciam o desempenho das membranas e ainda os resultados obtidos com duas membranas comerciais. Semelhante estudo foi realizado para uma corrente de processo de uma fábrica de produção de amido de batata.

De um modo geral, os resultados foram bons, em particular para a ultrafiltração de corrente celulósica. A principal conclusão deste trabalho é que a modificação da superfície da membrana com Praestol 859 resulta num aumento dos fluxos e do poder hidrófilo de membranas de polietersulfona, podendo por isso produzir-se membranas com elevada resistência ao *fouling*.

Palavras-chave: UF; modificação de membranas poliméricas

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List of Abbreviations

A	Absorbance
AA	Acrylic acid
ATR	Attenuated total refraction
BL	Black liquor
BSA	Bovine serum albumin
CB	Coagulation bath
CFV	Crossflow velocity
COD	Chemical oxygen demand
DF	Diafiltration
DMAc	Dimethyl acetamide
DMF	Dimethylformamide
EBA	Expanded bed adsorption
EU	European Union
FRR_{clean}	Fouling recovery ratio after cleaning
FRR_{rinse}	Fouling recovery ratio after rinsing
FTIR	Fourier-transform infrared
FUSIONS	Food Use for Social Innovation by Optimising Waste Prevention Strategies
GGM	Galactoglucomannans
HEMA	2-hydroxyethylmethacrylate
HSA	Human serum albumin
IFB	Integrated forest biorefineries
MF	Microfiltration
M_n	Number average molecular weight
MW	Molecular weight
MWCO	Molecular weight *cut-off* (kDa)
NF	Nanofiltration
NIPS	Non-solvent Induced Phase Separation
NMP	N-methyl-2-pyrrolidone
NREL	National Renewable Energy Laboratory
PAA	Polyacrylic acid
PEG	Poly(ethylene glycol)
PEG-400	Poly(ethylene glycol) M_n=400 g/mol
PEG-600	Poly(ethylene glycol) M_n=600 g/mol
PEG-PPG-PEG	Poly(ethylene glycol) – b – poly(propylene glycol) – b – poly(ethylene glycol)
PEO	Polyethylene oxide
PEO-PPO-PEO	Polyethylene oxide-polypropylene oxide-polyethylene oxide
PES	Polyether sulfone
PFW	Potato fruit water
PMVEMA	Poly(methyl vinyl ether-alt-maleic acid)
PPG	Poly(propylene glycol)
PPO	Polypropylene oxide
Pr. 2540	Praestol 2540
Pr. 859	Praestol 859

PS	Polysulfone
PV	Pervaporation
PVP	Poly(vinyl pyrrolidone)
PWF	Pure water flux
RC	Regenerated cellulose
RO	Reverse osmosis
SDS	Sodyum dodecyl sulfate
Syn	Synperonic
Synperonic	Polyethelene glycol-polypropelene glycol-polyethelene glycol
TCD	Thermal conductivity detector
ThMP	Thermomechanical pulping
ThMPPW	Thermomechanical pulping process water
TIPS	Thermally induced phase separation
TN	Total Nitrogen
UF	Ultrafiltration

List of Variables

c	Concentration
J_0	Initial Flux [L/(m^2 h)]
J_{clean}	Flux after cleaning [L/(m^2 h)]
$J_{P,pure\ water}$	Permeate pure water flux [L/(m^2 h)]
J_{rinse}	Flux after rinsing [L/(m^2 h)]
l	Length
L_P	Hydraulic permeability [L/(m^2 h bar)]
TMP	Transmembrane pressure (bar)
X_{feed}	Feed concentration
$X_{permeate}$	Permeate concentration
ε	Absorptivity coefficient [L/(g cm)]

Introduction

Ultrafiltration (UF) has been widely established as a separation technique, mainly due to the advantages it presents when compared to the other separation techniques, both economically and regarding the quality of the recovered products. Applications of UF processes can be found in a wide variety of industries, such as in wastewater treatment or water production, as a concentration step in the food and beverage and pharmaceutical industries or for the removal of pollutants and recovery of by-products from the pulp and paper industry. One major concern with UF processes is how fouling, which severely affects the performance of membranes, can be reduced.

Fouling reduces fluxes, selectivity and the lifetime of the membranes, diminishing the quality of the UF process, increasing energy consumption, economical expenses and leading to a downfall in the possible environmental benefits of this technology. For these reasons, the vast majority of the researches on UF processes have been focused on the reduction of the influence of fouling on the membranes, which consequently improves the efficiency of the UF stage. Pre-treatment of the feed solutions, the development of new membranes materials, modules, cleaning products or cleaning procedures are amongst the many research areas connected to this topic. In addition, a significant amount of work has been devoted to identifying and characterize fouling agents and mechanisms. One different approach has been the introduction of modifying agents (polymers and polyelectrolytes) during the production of membranes via phase inversion with the goal of producing low fouling membranes.

In this work, polymeric UF membranes - modified to improve hydrophilicity and to reduce the impact of fouling - were compared based on their ability to filtrate thermomechanical pulping (ThMP) mill process water and potato fruit water (PFW) from a starch production factory. The membranes were evaluated regarding the pure water flux prior to the UF of the mentioned feed solutions, product flux during the UF of those feeds, influence of fouling interactions with the membrane and retention of hemicelluloses and lignin (for the process water from the pulp and paper industry) or retention of proteins (for the process stream from the food and beverage industry).

The novelty of this work lies in the test and evaluation of novel membranes using real life industrial process/waste streams, providing closer results to those observable if an UF setup was introduced in the actual sites of production.

Literature Review

2.1 Membrane Filtration Processes Principle

UF, microfiltration (MF), nanofiltration (NF) and reverse osmosis (RO) can be grouped as pressure-driven membrane processes, where a difference in pressure between the permeate and the feed side is the driving force for water and some particles to go through the membrane. Membrane processes have been used to separate particles that may be dissolved in a feed stream based on different properties such as size, charge or shape of the solutes found in the solution. In pressure-driven membrane processes, a solution passes through the membrane under the pressure difference applied and it is divided into two different streams, designated permeate and retentate. The permeate solution mostly contains solvent, small size and narrow particles that partially pass through the membrane pores. The retentate is a concentrated stream of the feed, containing the remaining large size and wider compounds that were retained by the membrane, and therefore, not able to pass to the permeate side. Overall, MF, NF, UF and RO are distinguished by pore size and consequently, by the size of the particles that are retained by the membranes. In addition, the required operation pressures for RO are much higher than for UF and chemical affinities of the solute molecules also play an important role in determining the degree of retention. Pore size of UF membranes is between the size of the pores of MF and NF/RO membranes. A more detailed characterization on the UF membranes is provided in 2.3. (Baker, 2004; Bungay *et al.*, 1983; de Pinho and Minhalma, 2018).

2.2 Ultrafiltration – History

Applications of membrane processes in large scale industrial plants reached a breakthrough when in 1963 Loeb and Sourirajan developed cellulose acetate asymmetric membranes. Less than ten years later, starting from 1969, the first industrial UF systems were installed to recover electrocoat paint from rinse water in automobile paint shops followed by the installations to recover proteins from cheese whey from 1970 (Baker, 2004).

The initial cellulose acetate membranes produced could only operate under strict and limited chemical conditions and the tubular or plate-and-frame modules installed in the early systems were very expensive. Besides, it was discovered that the asymmetric structure of the membranes was influenced by the production method, which lead to trails with other polymeric solutions and production techniques (Bungay *et al.*, 1983).

Since then and due to the increasing applications of membrane processes, new materials, such as inorganic materials and natural based or synthetic polymers, have been tested to meet the often challenging demands of membrane processes. Amongst the many polymers used, such as polyacrylonitrile copolymers or aromatic polyamides, polysulfone (PS) and polyether sulfone (PES) are still widely used to produce commercial UF membranes. As a result, commercial membranes are nowadays much more chemically stable and resistant to higher pressures and temperatures while providing high permeability and selectivity. Also, research has been focused on the development of membranes with different surface properties to minimize the influence of the fouling agents (Plisko *et al.*, 2018) (de Pinho and Minhalma, 2018).

However, not only membranes have evolved from the early days; but also modules and systems design, cleaning agents and protocols have been under continuous study to minimize the effect of fouling in industrial membrane systems (Rudolph *et al.*, 2018).

2.3 Characterization of Ultrafiltration Membranes

UF membranes consist of two layers: an active thin layer, responsible for the actual separation process and a more porous textile layer which provides mechanical strength and support to the active layer, containing asymmetric pores. This thin layer on top of the membrane allows the asymmetric membranes to retain the rejected material at the membrane surface, acting as a surface filter, preventing pore blocking. Overall, the active layer thickness is about 0.1 to 1 µm and the support layer is between 100 and 200 µm. UF membranes pores size is in the range of 10 to 1000 Å and these membranes are usually distinguished one from another by manufacturers based on their pure water flux (PWF) and molecular weight cut-off (MWCO) (Baker, 2004; Bungay *et al.*, 1983).

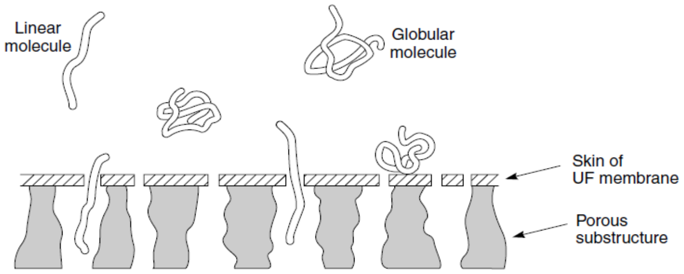
2.3.1 Hydraulic Permeability

A membrane is initially quantified by the flux of pure water that passes through the membrane for a given transmembrane pressure applied. This characterization parameter is called hydraulic permeability. To obtain its value, experimental procedures are conducted with pure water and graphical representation of the permeate water fluxes ($J_{P,pure\ water}$) in function of the transmembrane pressure (TMP) are produced. Ideally, the plot should represent a linear function where the slope is the hydraulic permeability L_P, represented according to the following equation (de Pinho and Minhalma, 2018):

$$J_{P,pure\ water} = L_P \times TMP \tag{1}$$

2.3.2 Molecular Weight Cut-Off

According to the IUPAC recommendations, the molecular weight cut-off (MWCO) of a membrane is defined as the molecular weight of solute which has a 90% rejection coefficient (Aptel *et al.*, 1996). However, it is important to state that MWCO measurements are very subjective as a variety of other factors influencing its determination, such as membrane module, composition of the feed solution or operational parameters etc. Membrane retention measurements are most of the times conducted using linear water soluble molecules, such as poly(ethylene glycol) or polydextran, in low concentration solutions, which may produce results relatively different from the ones obtained when using the same membranes for filtering real life aqueous solutions. The reason for the inconsistent results may be due to the fact that, when in solution, protein molecules exist in a globular configuration, held together by, for example, hydrogen bonds. In the end, it is believed that a linear and flexible molecule may be less retained because of its ability to pass through the membrane pores while the globular molecule may be rejected by the same membrane (Figure 1), even if both of them have the same molecular weight, just because of their special configuration. Not only that but pH values can also influence membrane selectivity and retention values, as the configuration of certain types of molecules, for example polyelectrolytes, changes according to pH levels. Furthermore, different salt concentrations can make the proteins either shrink or swell, also affecting its size. (Baker, 2004; Bungay *et al.*, 1983).



	Globular Proteins		Linear Polymer
Solute	Pepsin	Cytochrome *c*	Polydextran
MW (1000s)	35	13	100
Rejection (%)	90	70	0

Figure 1: Schematic representation of MWCO experiments and how molecule configuration may influence the results. Low molecular weight globular molecules are retained by the membrane while linear high molecular weight molecules may pass through the membrane pores. Adapted from (Baker, 2004).

2.4 Concentration Polarization

Concentration polarization is a phenomenon that can occur on both sides of the membranes as not all the components on the feed mixture flow at the same rate, which inevitably creates concentration gradients both on the feed side of the membrane and on the permeate side. In UF processes, macromolecular solutes and colloidal suspensions are part of the bulk feed solution whereas the permeate flux is only influenced by the rate at which the solvent and small solutes can pass through the membrane. This means that concentration polarization on UF membranes is only formed on the feed side of the membrane. As the permeability of the UF membranes nowadays is relatively high, the process is now limited by the rate of mass transfer at the membrane-solution interface, where the concentration of the accumulated solutes is higher. The rejection of macromolecules by the membrane and the subsequent accumulation of these molecules on the membrane surface may lead to the formation of a gel layer that will eventually become a secondary barrier and result in a decrease of the permeate fluxes. This layer of accumulated solutes on the membrane surface due to concentration polarization affects the linear correlation between pure water fluxes and pressure in the system. In Figure 2, below 0.5 × 10^{-5} Pa, pressure and permeate fluxes are linearly correlated. For pressure differences above the one mentioned, and as solute molecules accumulate on the membrane surface, increments in pressure result in smaller increases in permeate fluxes and, eventually, we reach a point known as limiting flux where the permeate flux remains constant over time (Figure 2) and where increasing the pressure only increases the thickness of the gel layer. Studies have shown that long term membrane processes nowadays should be conducted in sustainable flux, which is the region between the critical flux point and the limiting flux. (Baker, 2004; Bungay *et al.*, 1983).

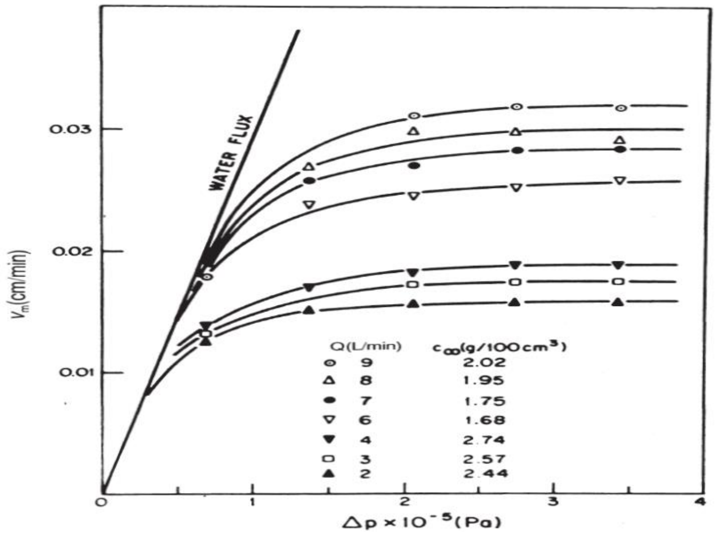


Figure 2: Influence of concentration polarization on the linearity of the correlation between pressure increase and permeate flux increase. Adapted from (Bungay et al., 1983).

2.5 Membrane Fouling

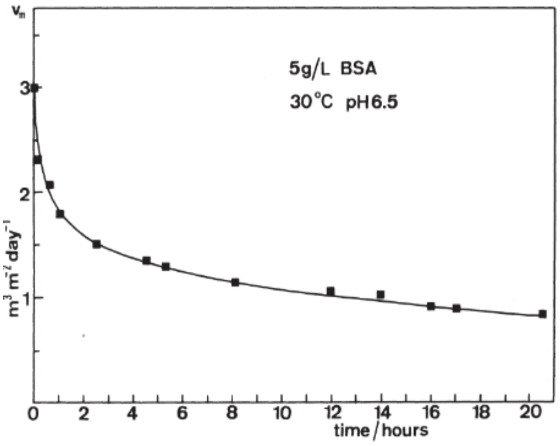


Figure 3: Schematic representation of flux decline over time due to membrane fouling when operating in the limiting flux region for long periods of time. Adapted from (Bungay et al., 1983).

In many industrial applications, when operating at pressures above the critical flux, permeate fluxes decrease gradually with time (Figure 3). The explanation for this phenomenon may be due to the formation of a secondary barrier on the membrane surface that modifies the membrane properties and results in flux losses – membrane fouling. For example, when filtering solutions containing proteins, the existence of a gel layer over time on the membrane surface (surface fouling) may lead to denaturation of proteins and consequential precipitation of these proteins.

Ideally, techniques such as backflushing or regular cleaning of the membrane should restore the initial flux (Figure 4) of the membrane and remove the gel layer that is formed on the membrane surface (reversible fouling – Figure 5). Researchers focus also on the development of new membranes containing certain additives which minimize fouling adhesion (Plisko *et al.*, 2019). In most of the cases, the initial flux is not restored, and permanent flux loss is visible. The permanent loss of permeate flux is due to irreversible fouling, usually associated to fouling agents attached to the internal structures of the membrane (internal membrane fouling – Figure 5) (Baker, 2004; Bungay *et al.*, 1983).

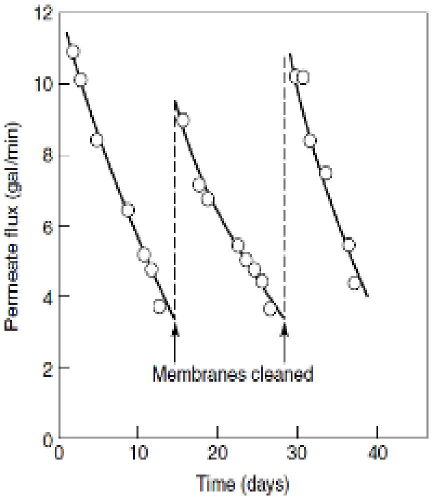


Figure 4: Schematic representation of flux decline due to fouling accumulation over time and flux recovery when the membrane is cleaned. Adapted from (Baker, 2004).

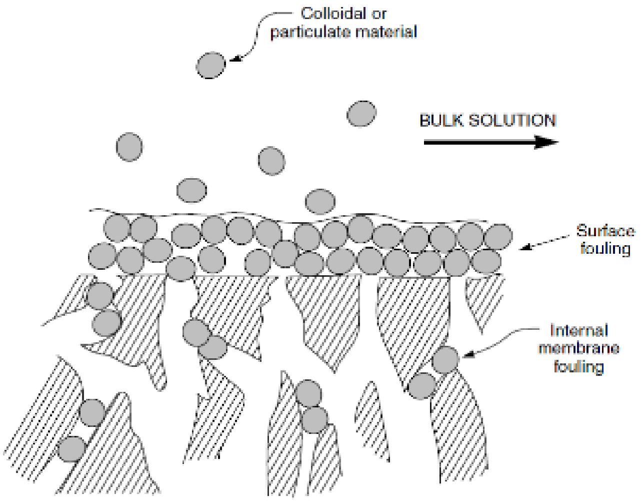


Figure 5: Schematic representation of surface fouling and internal fouling on an UF membrane. Adapted from (Baker, 2004).

2.6 Asymmetric membranes prepared by phase Inversion

Phase inversion (or phase separation) is the main process to produce commercial synthetic membranes for filtration processes available in the market. This process was first described by Kesting in 1971. A homogeneous solution (polymer) is transformed into a system with two phases where the porous structure is formed when the polymeric solution solidifies, and a liquid phase fills the pores. The liquid phase is poor in polymer and phase separation occurs due to the exchange between solvent and non-solvent in the polymeric solution (Bungay *et al.*, 1983).

To produce membranes by phase inversion, a system with three components is needed: a polymer and both a solvent and a non-solvent to the polymer. Solvent and the non-solvent may contain more than one component, but it is essential that they are miscible. Depending on what type of membrane are producing, the polymeric solution can either be cast on a solid support made of e.g. glass, polymer or metal, or it can be spun through a spinneret containing an extra outlet in the center of the opening for pressurized air or liquid. In the first case, the produced membranes will be either flat sheet or tubular and the latter case is used to produce hollow fiber membranes. The phase inversion process starts when solvent and non-solvent interact and mass transfer takes place, increasing the concentration of the non-solvent in the polymer. As the concentration of the non-solvent in the polymer region increases, the solution becomes thermodynamically unstable and precipitation occurs, inducing phase inversion (Bungay *et al.*, 1983).

Four different techniques can be used for phase inversion:

1. Precipitation by solvent evaporation: Polymer, solvent and non-solvent are mixed and cast in a solid surface. The solvent is volatile and, as it evaporates, the concentration of non-solvent in the casting solution increases, inducing precipitation (Baker, 2004).

2. Precipitation from the vapor phase: a vapor phase is saturated with the solvent, which prevents the outflow of solvent from the mixture while the non-solvent penetrates the polymer, inducing precipitation (Bungay *et al.*, 1983).

3. Non-Solvent Induced Phase Separation (NIPS): The polymer and the solvent are initially mixed in what is called the polymeric solution while the non-solvent is part of the coagulation bath (CB). When the polymeric solution is immersed in the CB, the solvent is lost to the CB and the penetration of the non-solvent into the polymer induces the precipitation. Also called immersion precipitation (Bungay *et al.*, 1983).

4. Thermally Induced Phase Separation (TIPS): The porous structure is formed when the temperature of the mixture polymer, solvent and non-solvent is lowered. The initial mixture of the three components takes place at high temperatures and it is the cooling that induces the phase separation. The mass transfer solvent – non-solvent is only possible due to evaporation (Liu *et al.*, 2017).

Nowadays, other processes which combine two of the techniques have been used to produce membranes, for example, with NIPS and TIPS (Tan and Rodrigue, 2019).

2.6.1 Non-Solvent Induced Phase Separation

In this work, the membranes were produced by immersion precipitation (NIPS) since most of the asymmetric membranes are produced using this process. Special attention will be given to the variables that influence the overall performance and characteristics of the membranes. During membrane production via NIPS, the polymeric solution containing the solvent and the main polymer is casted on a solid surface using, for example, a casting knife, creating a very thin film. Next, the casted dope together with the casting surface is introduced in a CB (immersion) which contains the non-solvent – commonly water is used as a non-solvent for economic and environmental reasons. The immersion defines the structure and characteristics of the membrane as the mass transfer process will begin with the removal of the solvent the polymer surface into the CB. As a result, the concentration of polymer at the exposed membrane surface is going to increase and it is of the utmost importance that the polymer is evenly distributed all over the membrane to ensure the same morphological and performance characteristics. Casting on a solid support can either be automatic or manual but preferably it is done with the help of a machine to ensure that the speed, pressure and especially polymer thickness are homogenously applied resulting in a uniform membrane. More selective membranes can be produce if certain factors are taken into consideration – the overall composition of the polymeric solution, polymer concentration, solvents and other additives in the solution, the support material used for the casting; the temperature of not only the CB but also of the polymeric solution and the environment where the process is conducted; and finally the non-solvent or mixture of non-solvents used and the tendency of those to induce liquid-liquid separation (Bungay *et al.*, 1983).

2.6.2 Membrane Modification

Since Loeb's and Sourirajan's development of cellulose acetate asymmetric membranes and as a consequence of the increasing applications of membrane processes, new materials, such as inorganic materials and natural based or synthetic polymers were developed and constantly tested to maximize the lifespan and performance of the membranes. In this work, flat sheet polysulfone (PS) and polyethersulfone (PES) membranes were tested. These polymers are amongst the most used nowadays when producing commercial polymeric membranes due to their resistance to heat or pH range but also because of their solubility in conventional solvents like dimethyl acetamide (DMAc), N-methyl-2-pyrrolidone (NMP) or dimethylformamide (DMF). These solvents are highly soluble in water, which is the number one non-solvent used in the CB for economic and environmental reasons. The main problem concerning PS and PES in membrane production is related to the fact that these polymers have highly hydrophobic characteristics, therefore making them prone to fouling. Fouling results in flux decline, unpredictable separation of the solutions and increases energy demand, shortening the lifespan of the membranes. For that reason, a considerable amount of research has been directed to improving membrane hydrophilicity as it is believed that more hydrophilic membranes are less susceptible to interact with fouling agents.

Improving the surface hydrophilicity and charge as well as reducing the membranes roughness are techniques used to modify the membrane surface properties with the goal of reducing the energy demand of UF processes. Surface modification methods can be either physical or chemical modifications. Physical modifications include blending, coating or the production of composite membranes while chemical modification methods include functionalization, chemical or photochemical grafting and plasma grafting. Amongst all these techniques, blending has been most widely considered due to various advantages: it is an excellent technique when it comes to simplicity and versatility, has low associated costs, easy to reproduce and has low environmental impacts (Ayyavoo *et al.*, 2016).

A different procedure to modify membranes interactions with fouling agents is to introduce hydrophilic polymers in the CB which will be transferred and attach to the membrane during the phase inversion. Not many studies have been published regarding adding polymers to the CB, but the few results suggest that surface roughness and pore size may reduce while retention values and hydrophilicity are improved (Alsari *et al.*, 2001; Bildyukevich *et al.*, 2017; Plisko *et al.*, 2020; Rahimpour *et al.*, 2010).

2.6.2.1 Blending

The standard polymeric solution composition has a main polymer – in our case PS or PES – and a solvent such as DMAc or NMP. Blending consists on modifying the polymeric solution by adding an agent, usually hydrophilic polymers altering the membranes structure and properties during the phase separation. The modified membranes may exhibit increased pore size and porosity but also reduced macrovoids formation (Liu *et al.*, 2003). More recently, block copolymers have also been used to modify the properties of the membranes surface due to their amphiphilic nature.

Several reports on the addition of hydrophilic polymers such as poly(ethylene glycol) (PEG) or poly(vinyl pyrrolidone) (PVP) to the casting solution have been published. Kim and Lee tested how different molecular weight PEG additives and changed ratios of PEG/NMP(solvent) in the casting solution would affect the specific characteristics and performance capacities of PS membranes produce via NIPS. Their conclusion was that higher molecular weight PEG and larger PEG/NMP ratios increase both pore size and porosity, and thus pure water fluxes increased too. However retention values seem to diminish as a consequence of the increased pore size at the top surface as well as the increased porosity (Kim and Lee, 1998). Chakrabarty *et al.* compared the effect of the different molecular weights of PEG on PS/DMAc membranes functional properties and morphology. It was suggested that a more porous membrane may be related to a more viscous and less miscible casting solution in water (non-solvent) when high molecular weight PEG solutions are part of the casting solution (Chakrabarty *et al.*, 2008). Idris *et al.* performed the similar research with the polymeric mixture of PES/DMF. The results relevant to this thesis are that higher fluxes and lower solute retention values can be obtained for higher percentages of PEG-400 and PEG-600 in the polymeric solution. In conclusion, higher molecular weight PEG seems to act as a pore forming agent, but retention losses are inevitable when producing membranes with enhanced flux capacities. The experiments of Idris *et al.* imply that there is an optimal PEG molecular weight and concentration allowing the production of more efficient membranes (higher flux with minimal loss on retention). Ideally, concentrations of PEG-400 and PEG-600 should be kept bellow 15 % (w/w). One other reason for keeping PEG concentrations in production of polymeric membranes relatively low can be related to the mechanical strength of the membranes. Scanning Electron Microscopy (SEM) tests provide an image on the cross section and surface morphology of the membranes. The images from Idris *et al.* show that both molecular weight and concentration of the additive play an important role in the formation and configuration of macrovoids. For higher PEG concentrations it seems that the mechanical strength of the membrane is affected (Idris *et al.*, 2007). Ma *et al.* produced PS/DMAc membranes with different concentrations of PEG-400 and summarized that with higher concentrations of PEG-400 in the polymeric solution both PWF and pepsin rejection increased while no obvious changes in the rejection of bovine serum albumin (BSA) was reported. With regard to hydrophilicity, the contact angle decreases with an increase in the dosage of PEG-400 which suggests an entrapment of PEG-400 in the membrane (Ma *et al.*, 2011).

The interest in using block copolymers as modifying agents has been rising due to their amphiphilic nature. The reason why they have become more popular has to do with the doubts regarding whether or not the hydrophilic agents are able to retain on the membrane surface permanently. Triblock copolymers like polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO) or poly(ethylene glycol)-b-poly(propylene glycol)–b–poly(ethylene glycol) (PEG-PPG-PEG), also called Pluronic, have both hydrophilic groups (PEO or PEG) and hydrophobic groups (PPO or PPG). While the hydrophobic groups are firmly fixed to the membranes polymeric matrix, the hydrophilic groups form a highly hydrated layer at the membrane surface, preventing interactions between protein molecules and the surface of the membrane. Hence, fouling molecules that are deposited in this water layer can be easily removed (Wang *et al.*, 2006). The results published from different projects on PS or PES membranes with block copolymers as modifying agents in the polymeric solution showed that fouling can be decreased significantly and that flux recovery was higher in membranes with additives compared to the control membranes (Plisko *et al.*, 2019; Wang *et al.*, 2006; Wang *et al.*, 2005; Wang *et al.*, 2006a); Zhao *et al.*, 2008). Plisko, *et al.* compared membranes with different concentration of Pluronic F127 (PEG to PPG ratio of 70:30) with commercial PS membranes. In summary, pore size and hydrophilicity of the selective layer of the membranes with Pluronic increase compared to the commercial membrane leading to higher water fluxes and lower rejections. Furthermore, the antifouling performance of membranes with high Pluronic concentrations was found to be less than for lower concentrations of Pluronic due to increased pore sizes and surface roughness which enables foulants to penetrate in the membrane and prevent their removal (Plisko *et al.*, 2019).

2.6.2.2 Additives in the Coagulation bath

A relatively new technique for membrane modification consists on changing the composition of the CB by adding hydrophilic polymers. During precipitation, the interaction between the water-soluble polyectrolyte molecules, present in the CB, and the polymeric solution promotes changes in the precipitation conditions and in the matrix of the membrane. The polyeletrolyte molecules attach to the membrane and thus improve its hydrophilicity and anti-fouling properties. The influence of different concentrations of the surfactant sodium dodecyl sulfate (SDS) at the temperatures between 4 °C and 20 °C was studied by Alsari *et al*.. For concentrations below the critical micelle concentration, the mean pore size of the PES membranes decreased while it increased for concentrations of SDS in the CB above this critical concentration. As the pore size increased, the membranes surface became rougher and the influence of SDS concentration on the membranes morphology was more pronounced at lower temperatures (Alsari *et al.*, 2001).

After successfully manufacturing membranes with hydrophilic monomers in the polymeric solution with similar results as the ones presented in the section 2.6.2.1 (Rahimpour and Madaeni, 2010), a new study led by Rahimpour focused on the effect of hydrophilic monomers on the CB. For that, different percentages of either acrylic acid (AA) or 2-hydroxyethylmethacrylate (HEMA) hydrophilic monomers were introduced in the CB. The properties of these membranes were compared with a reference membrane produce without any AA or HEMA concentration. The same polymeric solution, containing 16 % PES, 2 % PVP and 82 % DMAc, was used for all the membranes, and the conditions were kept constant during the formation of each membrane. Membranes surface pore size decreased with the addition of both hydrophilic agents, which in theory could indicate a reduction on the PWF. In reality, the presented results in the article report an increase in PWF as the concentration of AA (Figure 6.A – black columns) or HEMA (Figure 6.A – grey columns) increased. Furthermore, compared to the reference membrane (Figure 6.A – pink column), the PWF were also higher in membranes with additives in the CB. Contrary to the reduction in pore size, the porosity of the membranes increased, resulting in higher PWF. In the same study, the novel membranes were used for UF of non-skim milk and a comparison between permeate fluxes and protein rejection was established. Once more, similarly to PWF measurements, permeate fluxes improved when in presence of higher concentrations of additives in the CB, most likely due to the increased porosity and hydrophilicity of the membranes surface. Membranes with smaller pore size on the surface may form a layer of rejected particles from the feed while membranes with larger pores are exposed to pore blockage, reducing permeation due to the additional resistance to the passage of the liquid through the membrane. Moreover, the improved hydrophilicity of the membranes surface was confirmed by attenuated total refraction (ATR) Fourier-transform infrared (FTIR) spectra (Figure 6.B) Hydrophilicity can reduce membrane fouling by milk proteins. In terms of protein rejection, the presence of AA and HEMA proved to enhance the results, probably due to the formation of membranes with smaller pore size on the active layer. As a general example of the changes in membranes structure and morphology, figure 6.C is presented. (Rahimpour *et al.*, 2010).

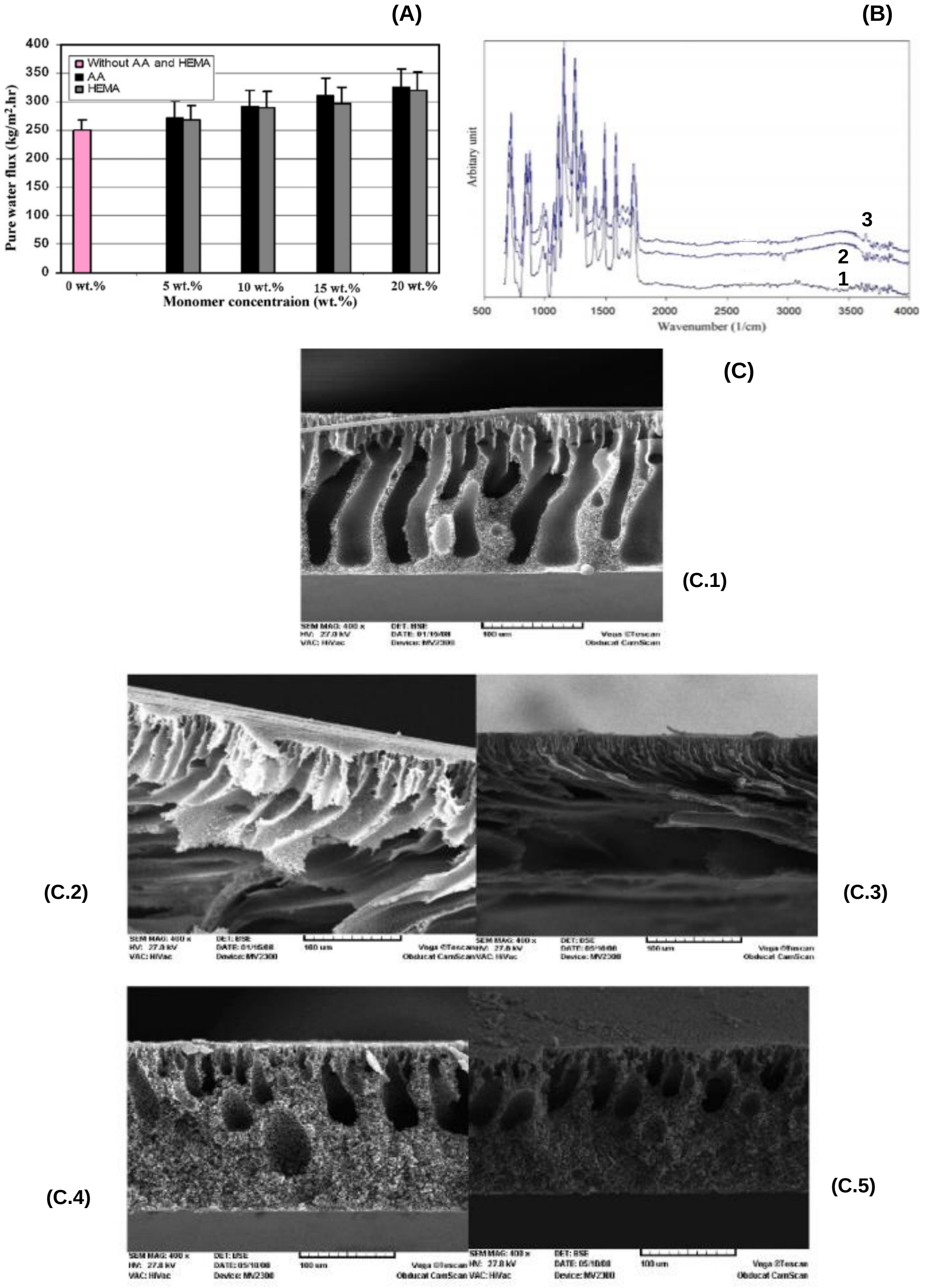


Figure 6: Influence of additives in the CB on membranes structure and performance. Polyether sulfone membranes were modified with acrylic acid (AA) or 2-hydroxyethylmethacrylate (HEMA). ***(A)*** *pure water fluxes of the reference membrane (pink column), membranes with AA (black columns) and membranes with HEMA (grey columns).* ***(B)*** *ATR-FTIR spectra illustrating the improved hydrophilicity of the membranes with additives compared to the reference. (1) reference; (2) 15 % (w/w) AA; (3) 15 % (w/w) HEMA.* ***(C)*** *General representation of the differences in the structure and morphology of the membranes with the introduction of different concentrations of AA and HEMA. (C.1) reference; (C-2) 5 % (w/w) AA; (C-3) 5 % (w/w) HEMA; (C-4) 20 % (w/w) AA; (C-5) 20 % (w/w) HEMA. Adapted from (Rahimpour* et al.*, 2010).*

More recently, it was reported the introduction of PVP in the CB, in this case bore fluid, as a modifying agent of PS hollow fiber membranes. When a high molecular hydrophilic compound such as PVP is attached to the inner membrane surface of the PS hollow fiber membranes, it increases the overall hydrophilicity of the membrane, most likely due to the hydrogen bonds formed between the C=O and C–N groups of the PVP and water molecules. The results were confirmed both by FTIR spectra and the decrease of the contact angle. The addition of PVP to the bore fluid resulted in a decrease of the nominal MWCO of the membranes from 100 to 20 kDa. A significant increase of the rejection coefficient – from 29 % to 85 % – consequence of the nominal MWCO was reported. The rejection coefficient was measured using a 0.3 g/L solution of PVP K-30 (M_n =40 000 g/mol). Although the PWF decreased when PVP was present in the membranes composition, the antifouling properties were enhanced due to the increased hydrophilicity and surface roughness of the membranes produced with higher concentrations of PVP (Bildyukevich et al., 2017). Overall, the results similar to previously presented by Rahimpour *et al.* support the relevance and interest of introducing additives in the CB.

Lastly, Praestol 859 in concentrations between 0.05 % and 0.3 % was introduced in the CB during the preparation of flat sheet PS membranes. Praestol 859 is a commercial cationic polyacrylamide-based floculant and polyelectrolyte with a content in charged groups of 90 %. Floculants are widely used, for example, in municipal waste water treatment (Kängsepp et al., 2020). The work performed by Plisko et al. via NIPS (Figure 7) was based on the hypothesis that charged polyetrolites immobilized in the membrane matrix increase both charge and hydrophilicity of the membranes selective layer, resulting in enhanced antifouling properties. As the CB composition and temperature can influence the membranes properties, the authors foccused not only on understanding the impact of different concentrations of Praestol 859 but also distinctive temperatures (25 °C, 40 °C, 60 °C and 70 °C). In addition, two different support materials – glass plates – for the casting of the polymeric solution and different coagulation times were also considered. Compared to smooth glass, a rough glass plate prevents coagulation from the back side and increases the time for membrane formation under all concentrations of Praestol 859, due to improved adherence of the polymeric to the surface irregularities) (Plisko et al., 2020).

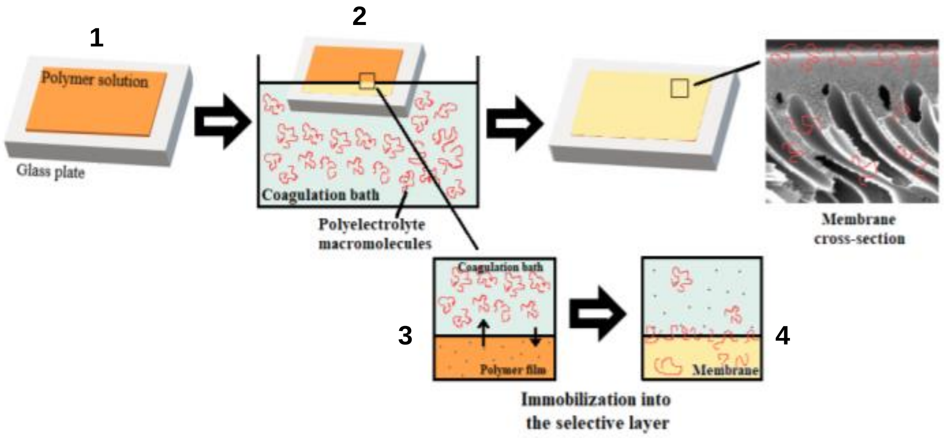


Figure 7: Non-induced phase separation – Immobilization of Polyectrolytes. ***(1)*** *polymeric solution cast on the solid surface;* ***(2)*** *Immersion in the CB;* ***(3)*** *exchange between solvent and non-solvent. Additive in the CB;* ***(4)*** *membrane formation. Additive immobilized in the selective layer. Adapted from (Plisko et al., 2020).*

In the same work, structure and performance of the UF polymeric membranes were directly affected by the viscosity and temperature of the CB. When low concentrations of high molecular weight polyelectrolytes, such as Praestol 859, were introduced in the CB, the overall viscosity dramatically increased compared to the reference membrane. Plus, at 25 °C, the viscosity of the CB containing 0.5 % Praestol 859 (in concentration) was 33.5 times higher than the viscosity of the CB containing 0.05 % Praestol 859. As the kinetics of the membrane formation is affected by the viscosity, the introduction of additives in the CB changes the membrane structure. According to SEM images, concentration of the additive, characteristics of the support and temperature of the CB indeed influenced the structure of the membranes. Compared to the reference membrane, the roughness of the membranes surface increased when in presence of additives due to increased coagulant viscosity and decreased exchange rate between solvent and non-solvent. Regarding the immobilization site of the Praestol 859, FTIR spectroscopy results indicate that polyelectrolyte macromolecules were immobilized on the selective layer, particularly on the surface (Plisko *et al.*, 2020). The overall hydrophilicity of the membranes was once more measured considering the contact angle. The reference membrane presented a contact angle of 54°–55° while the contact angle of all the membranes with additives (from 0.05 % to 0.3 % Praestol 859) was below 51° (minimum was 36° for the membrane produced with 0.3 % Praestol 859 in the CB, at the temperature of 70 °C). Generally, the introduction of Praestol 859 in the CB may result in more hydrophilic membranes because of the NH_2 groups from the Praestol 859 involved in the formation of hydrogen bonds. The temperature of the CB proved to have no significant impact on the contact angle. When in presence of Praestol 859, a less porous, ticker and denser selective layer was obtained, diminishing the pure water fluxes. During the filtration of human serum albumin (HSA) solutions, with pHs ranging from 3.2 to 9.5, the presence of Praestol 859 proved to improve fouling recovery ratio. The improved antifouling performance is attributed to the selective layer enhanced hydrophilicity and a more negative zeta-potential of the surface, resultant from the presence of the cationic polyelectrolyte.

The findings from this last discussed article were pretty relevant for the present study as Praestol 859 was also used as an additive in the CB and specially since no analysis (such as FTIR, structure studies or measurement of contact angles) were conducted in the present research. It is also my belief that the work of Plisko *et al.* is of the utmost importance to what is reported in this thesis, as a vast majority of the findings in the mentioned article were developed by the researchers from the Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus. Part of the team from the article (Plisko *et al.*, 2020) kindly produced and provided the novel membranes tested in this thesis and was also part of this project.

2.7 Pulp and Paper Industry

2.7.1 Integrated Forest Biorefineries

Sustainable growth has led to the development of alternative processes to the consumption of fossil and non-renewable resources like petroleum, coal or natural gas. Biobased products and bioenergy result from replacing petroleum-based refineries into biorefineries. Biological raw materials from forestry are widely used in the paper and cardboard industry, where physical and chemical treatments are performed and, as a result, biobased products are produced (Kamm and Kamm, 2004). Woods can be separated in two categories: hardwoods or softwoods. Although the three main organic polymers based on carbon backbones (cellulose, hemicellulose and lignin) are the same for both types of lignocellulosic materials, softwoods and hardwoods present different proportions of these polymers as the first contain higher percentages of lignin and the later have more cellulose, hemicelluloses and extractives (Fatih Demirbas, 2009). Cellulose provides strength to the wood and is made of long chains of glucose linearly connected. Lignin is a natural phenolic glue that holds the cellulose fibers together while hemicellulose is two dimensional polymer of pentoses (arabinose, xylose), hexoses (glucose, galactose, mannose) and sugar acids that can be converted in products and chemicals currently made from petroleum (Amidon *et al.*, 2008). Softwoods are one of the main sources of lignocellulosic materials, containing between 43 and 45 % of cellulose, 28 % lignin and 20 to 23 % of hemicelluloses. Galactoglucomannans (GGM) are the main hemicelluloses in softwoods and they are divided in two groups, one rich and one poor fraction on galactose. The main monomeric sugar in GGM is mannose and if we just consider mannose for the production of ethanol then, in theory, per each metric ton of dry raw material, we can produce 410 L of ethanol. An additional 45 L of ethanol can be produced if all carbohydrates are taken into consideration (Galbe and Zacchi, 2002). The concept of integrated forest biorefineries (IFB) was established when the pulp and paper industry global competition in the market raised, which forced these industries to find new sources of revenue in order to remain in business. Nonetheless, the existence of internet and e-mail also posed as a huge threat to the pulp and paper industry. In an IFB, pre-treatment stages enable the recovery of the diverse components in the lignocellulosic biomass and use them to produce value added products. At first, in conventional kraft pulping processes, cellulose fibers were used to produce paper while the degraded hemicelluloses, lignin and other pulping chemicals were dissolved in black liquor (BL), which was thereafter combusted to generate electricity and steam. Lignin is mainly used for applications related to heat and electricity generation. However, the low heating value of hemicelluloses results in an uneconomical use of resources. Hemicelluloses extraction prior to pulping generates new and multiple streams of income. Amongst the many applications is the production of ethanol. (Huang *et al.*, 2008). Further examples on lignin and hemicelluloses applications can be found in the next chapter.

2.7.2 Membrane Separation Processes for Integrated Forest Biorefineries– Recovery of Value-added chemicals

Membrane separation processes are valuable for bioenergy and biomaterials production. MF, UF or NF are widely used to produce biodiesel or acetic acid and to recover enzymes, hemicelluloses or lignin. In addition, non-porous membrane techniques driven by a chemical potential gradient, like pervaporation (PV), or membrane processes driven by a thermal gradient (membrane distillation) can also be considered for bioethanol production (He *et al.*, 2012). PS, PES or regenerated cellulose (RC) polymeric membranes are preferentially suitable for hemicellulose recovery, whereas for lignin recovery from BL, ceramic membranes are the primary choice. BL presents extremely harsh physical and chemical properties, with a temperature of about 150 °C and pH levels slightly below pH 14, (Wallberg *et al.*, 2003). The fact that membrane processes allow the recovery and purification of hemicelluloses without diminishing their intrinsic properties is the major advantage compared to other techniques. Hemicelluloses have interesting applications in distinctive fields: production of hydrogels because of their gel-forming properties and biodegradability; food packaging, to produce oxygen barrier films or coatings, due to the mechanical strength and low oxygen permeability of hemicelluloses (Hansen and Plackett, 2008). Much of the lignin compounds are burned – for heat production. Besides, a considerable amount of research has been focused on lignin as a biofuel and in other fields, e. g. in phenol-formaldehyde resins as a substitute for part of the phenol (Tejado *et al.*, 2007) or in the production of lignin-based carbon fibers (Kadla *et al.*, 2002).

The quality of the final product as well as the amount of spent energy and resources to achieve that required quality is of great influence on the profitability of lignin and hemicelluloses separation. So, a large number of studies has been focused on this topic, for both BL (Jönsson *et al.*, 2008; Jönsson and Wallberg, 2009) and other waste streams of the pulp and paper industry (Persson *et al.*, 2007). Furthermore, the major challenge researchers have been facing when trying to recover lignocellulosic materials with membranes is fouling. Membrane fouling reduces the overall quality of the process, increasing the costs. Various and very different approaches have been conducted to avoid this phenomena, including pretreatment steps, the development of new cleaning protocols and, the investigation on new membranes to reduce the interactions between fouling agents and the membranes.

2.7.3 Membrane processes for thermomechanical pulp mill process water

Cellulose fibers are used to produce paper and the removal of hemicelluloses, lignin and other extractives or chemicals from the cellulose fibers present in wood is called pulping. These processes are used in the paper industry and one possible process to achieve this separation is using thermomechanical pulping (ThMP). The biggest advantages to the development and market introduction of the thermomechanical pulping processes were: 1) it limits the need to use other chemicals during the pulp production stage, reducing the potential environmental impact of these chemicals when discharged; 2) previous processes were reaching their limit potential in terms of product quality and production capacity; 3) hydroelectric power is relatively inexpensive in countries were wood is abundant (Jones and Pila, 1984); 4) the pulp mills do not have to invest in and build the chemicall recovery process, which for the Kraft process is a large part of the plant. In thermomechanical pulping, wood chips are placed inside the ThMP mill and heated with steam and hot water. Thereafter, the wood chips are ground in a first refiner at about 150 °C and 3 to 5 bar pressures, between two metal discs rotating at a speed of 1500 to 1800 rpm. The pulp is then refined a second time in similar conditions to the first process before a screening step is conducted to ensure that the quality of the product is according to the specifications. If not, it may be refined in a reject refiner before being dewatered and stored until pulp production. Overall, 10-30 m^3 of water are consumed per tonne of pulp produced. The process water usually contains less than 1 % (w/w) of total solids, where mainly hemicelluloses are contained, but also lignin, fibers, salts and extractives (Persson, 2009; Rudolph *et al.*, 2018; Thuvander, 2018), with a pH of approximately 4.6 (Persson *et al.*, 2007). According to (Persson and Jönsson, 2010) and (Thuvander and Jönsson, 2016), the majority of the hemicelluloses found in the ThMP were below the molecular mass of 100 kDa, specially below 20 kDa. As for lignin, the MW distribution was in between 1 and 10 kDa – Figure 8. Also found in ThMP process water are lignin carbohydrate complexes (LCC), which are basically resultant from the crosslink of the hemicelluloses by lignin in the native lignocellulosic materials. LCC have been reported and characterized previously by (Lawoko *et al.*, 2006), where the authors suggested that some small MW lignin compounds may be retained because of their bonds to higher MW hemicelluloses.

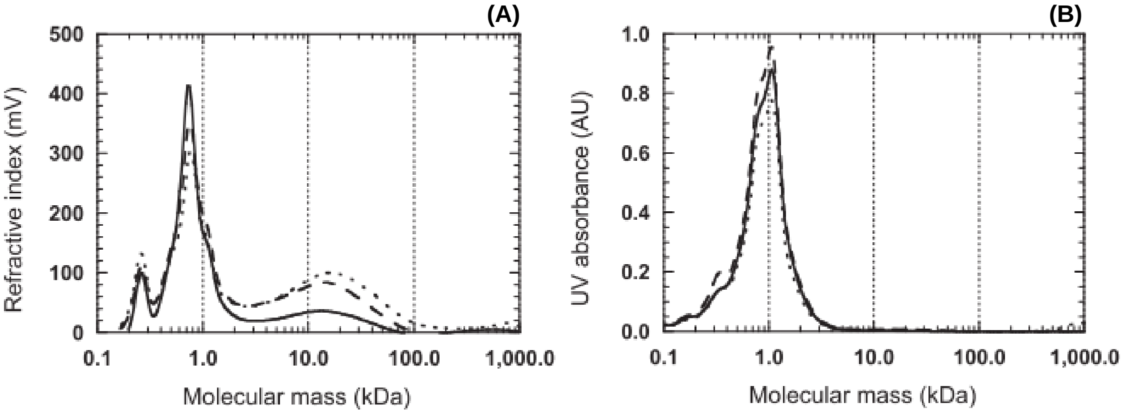


Figure 8: Molecular weight distribution of ***(A)*** *Sugars (Hemicelluloses) and* ***(B)*** *Lignin on three different MF permeates from ThMP process water filtration. The figures show the molecular mass of hemicelluloses is below 100 kDa and the distribution of lignin is below 10 kDa. Adapted from (Thuvander and Jönsson, 2016).*

ThMP process water has proven to be an excellent resource for the recovery of lignocellulosic compounds, in particular hemicelluloses (Persson *et al.*, 2010, 2007; Persson and Jönsson, 2010; Thuvander and Jönsson, 2016). Persson *et al.,* published an economical evaluation study of a laboratory scale membrane process to recover and purify hemicelluloses from ThMP process water. Based on their previous investigation, a two steps process involving a MF pretreatment to remove solids and a UF/diafiltration (DF) stage to concentrate and purify the hemicelluloses was performed. In the end of the study, the estimated costs to produce 1 tonne of hemicellulose proved to be promising for further studies. (Persson *et al.*, 2007). The recovery and purification of hemicelluloses – GGM in the case of ThMP process water – is highly dependent on the efficiency of the UF process. Both fluxes and retention capacities are of the utmost importance when choosing a membrane. Other than those, the ability to isolate GGM from other compounds present in the feed solution (specially lignin), cleaning frequency and the impact of fouling agents on the membranes performance are also important (Persson *et al.*, 2010). In 2009, Persson compared the fluxes achieved by membranes with MWCO of 1, 5 and 10 kDa, concluding that the membrane with the lowest cut-off could not be operated at fluxes so high as the others. Even though more susceptible to fouling, the 5 kDa membrane retained more GGM and sustained higher temperatures than the 10 kDa membrane. (Persson, 2009). Prior to the UF, the ThMP process water was pretreated to remove suspended matter and soluble wood extractives. The initial filtration stages included a 10 µm microscreen drum filtration first and a 0.2 µm MF. In the end, Persson *et al.* were able to recover 95 % hemicelluloses and 25 % lignin in the UF retentate using a 5 kDa spiral wound membrane, with a purity level of 60 %. Persson *et al.* also report a decrease in flux, probably due to fouling, and that alkaline cleaning [0.5 % (w/w) Ultrasil 10, for 1 h at 50°C] was unable to restore the PWF of the pristine membrane. However, the severe fouling and the unexpected results regarding the cleaning protocol could be related to a higher volume reduction in this study when compared to previous studies, as fouling degree and cleaning ineffectiveness are closely related (Persson *et al*., 2010).

In a different project, Persson and Jönsson studied the influence of the MF pore size on the UF performance. Particularly, the focus was on how the pretreatment with different pore size membranes may affect the flux during the UF and the recovery of GGM. According to their results, GGM retention is not influenced by the membrane used during the MF stage. On the other hand, improved UF fluxes and higher hemicelluloses purity can be achieved if a MF membrane with a pore size smaller than 0.2 µm is considered prior to the UF (Jönsson and Persson, 2009). Overall, the pretreatment of ThMP process water played a very important role in the efficiency of the UF as major foulants were retained during the MF (Jönsson and Persson, 2009). Fouling studies performed by Puro *et al.* concluded that dissolved and colloidal extractives fouled the membranes, suggesting hydrophobic membranes as more prone to fouling than hydrophilic membranes (Puro *et al*., 2011). More recently, Thuvander *et al.* characterized the irreversible fouling on UF membranes, after filtration of ThMP process water and chemical cleaning, comparing a pristine membrane with membranes exposed to process water. Two types of ThMP process water were used in this study: untreated water from a ThMP mill and MF permeate. Upon pressure increase to 2 bar, the flux increased for the MF permeate each time the pressure was increased while for the untreated process water, critical flux was reached at 1 bar. At the constant pressure of 1 bar for the untreated feed and 0.4 bar for the MF permeate, the initial flux for both feed solutions was identical, and so, these conditions were chosen to study how the flux evolved over time. Permeate flux decreased over time for the raw process water (until 500 g of permeate were collected, corresponding to a volume reduction of 12.5 %) while it was almost constant for the MF permeate (until 1000 g of permeate were collected, representing a VR of 25 %). It was not possible to restore the initial pure water flux of the membrane used during the filtration of the untreated process water even after rinsing with deionized water, two alkaline cleaning [0.25 % (w/w) and 0.5 % (w/w) Ultrasil 10 for 1 h at 1 bar, 50 °C and CFV of 0.2 m/s] and one acid cleaning [0.5 % Ultrasil 73 under the same conditions as the alkaline cleaning rounds] steps. As for the membrane fouled with the MF permeate, alkaline cleaning with the less concentrated Ultrasil 10 solution proved to be efficient for the removal of the foulants. SEM images confirmed the initial conclusions provided by the flux recovery results. The images from the pristine membrane and the membrane exposed to the MF permeate were very similar while the image from the UF membrane after filtration of untreated process water showed that the deposited material was not removed. The colloidal material removed during the MF was indeed responsible for the major fouling of the UF membranes. Further analysis on the membrane surface allowed Thuvander *et al.* to conclude that compounds predominantly responsible for irreversible fouling were polysaccharides with higher percentages of glucan (cellulose, starch or laricinan) and less common in ThMP process water than GGM (Thuvander *et al*., 2018). In the studies of Rudolph *et al.* on cleaning of UF membranes fouled by ThMP process water, alkaline cleaning [with 1.0 % (w/v) Ultrasil 10 at 50 °C, first for 1 h at ambient pressure and then at 2 bar until a 50 % volume reduction of the cleaning solution was achieved] proved to be efficient in restoring pure water fluxes of fouled membranes (Rudolph *et al*., 2018).

The novelty of the work developed in this thesis regarding UF of ThMP process water is that, despite minor reports that hydrophilic membranes could be less susceptible to fouling than hydrophobic membranes (Puro *et al*., 2011), this has not yet been the main focus of an investigation. Membranes produced to be more hydrophilic were tested according to the experiments previously discussed by the majority of these authors. It is expected that rather hydrophobic membranes (PS and PES), modified for hydrophilization, perform better than reference membranes without additives.

2.8 Food Industry

2.8.1 Processing and Valorization of Bio-Waste – Potato

Food waste is a very serious concern nowadays for public health as it impacts directly the health and equality of the societies and populations. Apart from the individual and direct implications in human life, food waste is also very important when considering environmental and economical factors. In 2012, Food Use for Social Innovation by Optimising Waste Prevention Strategies (FUSIONS) report estimated food waste in the European Union (EU) 28 countries (now 27 as United Kingdom in no longer part of the EU) to be of 88 million tonnes. This amount included the sectors of primary production, processing, wholesale and retail, food service and households.

A different report suggested about the same 90 million tonnes per year of food waste and that the food processing industry could be accounted for 39 % of those residues (European Commission and Report, 2010). Although there are some uncertainties regarding the official numbers when it comes to waste in the food processing industry because animal feed and by-products may or may not be considered waste, it is obvious that these numbers are extremely high and therefore, the problem should be addressed.

The EU directives on waste management suggest that industries should in first place collect the bio-wastes for composting and digestion; secondly, introduce bio-waste treatment procedures and processes to ensure the minimal impact on both human life and environment; thirdly, focus on developing new processes using the bio-waste to produce environmentally safe materials from bio-waste (European Parliament and Council, 2008).

In 2018, according to the Food and Agriculture Organization of the United Nations, more than 105 million tonnes of potatoes were produced in Europe. Starch production is one of the main processing industries where potatoes are used as raw material. The potato tuber main composition contains 72-75 % water, 16-20 % starch and 1-2.5 % soluble proteins. The remaining composition containing sugars, acids and fibers (Strætkvern and Schwarz, 2011; Waglay *et al.*, 2014). It is then obvious that when producing starch from potatoes, only a small part of the total composition is actually desired as final product with the rest being considered waste. The production of potato fruit water (PFW) from the starch industry in Europe is of about 2 million tonnes per year. PFW is a stream of water generated from the starch production which contains proteins, amino acids and sugars. These streams have a high chemical oxygen demand (COD) and their treatments involve high costs (Zwijnenberg *et al.*, 2002). Until this point, in an attempt to generate some value from these wastes while reducing the environmental impact, precipitation steps with high temperatures could be conducted to collect the protein content of the PFW and use them as animal feed. The recovered proteins were only suitable for animal use and not for human consumption as processes involving high temperatures and harsh pH conditions were used, denaturating the proteins (Cheng *et al.*, 2010). Reports suggest that these proteins have a very high nutritional value. In addition, the potato proteins are considered to be better in terms of nutritional value than those from other vegetables or cereals because they possess a higher percentage of lysine (Waglay *et al*., 2014).

Potato proteins are usually divided in three groups, according to their molecular weight (MW): protease inhibitors (5<MW(kDa)<25), patatin (40<MW(kDa)<45) and other MW proteins. Patatins, which are about 50 % of the total soluble proteins of the potatoes, possess an antioxidative activity (Kudoh *et al*., 2003), could be used as a foaming agent (Deveaux-Gobert, 2008) and protein fractions rich in patatin have been reported suitable as a food emulsifying agent (Van Koningsveld *et al*., 2006). Protease inhibitors, the second largest group of soluble proteins proteins (≈ 40 %), could be used in treatments against obesity as they may influence our appetite (Deveaux-Gobert, 2008), or may have other pharmaceutical and medical applications as anti-carcinogenic (Blanco-Aparicio *et al*., 1998) or anti-microbial agents (Kim *et al*., 2005). For all of the reason stated above, the recovery of the potato proteins maintaining all of their properties can be of great value for companies economically.

2.8.2 Membrane Processes in Food Industry

Membrane processes in the food industry have been largely growing over the past decades and food industry is now one of the main markets for membrane processes apart from water and wastewater treatment. Pressure driven membrane processes are the main technologies used in this market while other membrane processes such as pervaporation, electrodialysis or membrane contactors share smaller sections of the market. Major applications on the food market are related to the dairy industry, fermented food products such as beer vinegar and wine or fruit-juices clarification or concentration. The reasons behind why the importance of membrane processes has been growing are mostly related to energy savings and waste product valorization, which ultimately results in less costs. Nevertheless, membrane processes are also very important for environmental reasons as they eliminate polluting materials (Mohammad *et al*., 2012).

Alfa Laval developed the first MF system to reduce bacteria from the milk in 1986 without diminishing the properties of the final product, enhancing its shelf-life. Other applications of MF systems for bacteria and spores removal in the dairy products industry, such as in cheese production, banish the need of adding nitrate to ensure the quality of the final product. Besides bacteria and spore’s removal, membrane processes have been introduced in the dairy industry to facilitate the recovery and purification of weight protein concentrates and isolates from waste streams of cheese production factories. These proteins were, until this point, only suitable as feed for animals or disposed on fields. Using membrane processes enables the recovery of weight proteins for human consumption. In addition, weight proteins may be used in the production of gelling, emulsifying and foaming agents (Lipnizki, 2010).

In the fermented foods industry, the first small applications were related to the production steps using dead-end filtration or clarification of beer, wine or vinegar using crossflow filtration. Industrial applications started using a RO process for the dealcoholizing of beer. Similar applications can be found in the fruit-juice industry as clarification or pre-concentration steps are often carried out with membranes (Lipnizki, 2010).

2.8.3 Ultrafiltration Applications in Food Industry

UF processes are usually related to three major sectors related to food industry: the dairy industry, beverage industry and poultry industry. In the dairy industry, UF processes are used basically for the same purpose as described before for the general membrane processes and was the starting point for the development of other UF systems to be applied in the different industries. In the beverage industry, introducing UF processes in fruit and vegetables juice clarification, allowed the separation of these juice streams into two separate streams: the retentate stream containing all the fibers in a pulp; and a permeate stream, containing a clarified and sterile juice. By separating the whole juice fruit into two streams and by containing all the microorganisms in one of these streams, it meant the thermal treatment could be applied to one of the juice fractions (retentate) while all the original qualities and characteristics of the juice were kept intact by not submitting the permeate to unnecessary high temperature treatments. In the end, the final product presents a higher quality, once both streams were re-joined (Mohammad *et al.*, 2012). The permeate fraction of the fruit or vegetable juices also presents advantages for companies producing final products where the fibers or suspended solids may decrease the quality of the product, such as in clear juice blends or carbonated soft drinks (Vaillant *et al.*, 1999). UF systems in the fish processing industry have been used for the recovery of valuable protein from waste streams that were, until this point, discharged into the sea. Not only that but membrane processes in this industry can be vital in terms of environmental protection as the wastewaters contain a gigantic organic load. The oxygen demand can be reduced with a concentration step, resulting in less polluted permeate waters that are afterwards discharged into the sea. Finally, the concentration steps can also be used to reduce water consumption as the cleaner waters can be used in other parts of the fish processing industry (Afonso and Bórquez, 2002).

2.8.4 Ultrafiltration for Potato Fruit Water (PFW)

The first studies regarding UF industrial processes in the potato starch industry were reported in 1976. The goal was to concentrate the process water from a potato starch factory in Sweden, reducing the environmental impact associated to the discharge of the waste streams. Overall, they produced a permeate stream containing water, salts and other small compounds which could be discharged with less concerns in terms of biological oxygen demand. The concentrated retentate containing the majority of the proteins could then be purified and potentially used as an additional income source for the company. Major conclusions from these tests were that a high velocity process is desired for solutions with a low solid content and that fouling and cleaning of the membranes were the most severe problem (Eriksson and Sivik, 1976).

Zwijnenberg *et al.*, suggested using an UF process to recover proteins from the PFW. Their main motivation to start this project was that, up until that point, low quality proteins were being recovered from the existing processes installed in large starch industrial plants in Germany and Netherlands. Lower quality of the product diminished the potential profits. Amongst the major concerns were the possibility that the proteins could denature during the filtration step as they are very sensitive to heat and shear. Also, the authors concluded that a pre-concentration step was needed in order to remove fibers and minimize foaming formation. In the end, the influence of pore size and membrane material on the retention levels were insignificant, probably due to the very high protein concentration on the feed stream which also limited the fluxes. Moreover, additional steps (DF and spray drying) were needed to achieve functional products with equal or higher quality than those already available in the food market (Zwijnenberg *et al.*, 2002).

An UF+DF set-up was compared to an expanded bed adsorption (EBA) chromatography regarding the treatment of lab prepared PFW (Strætkvern and Schwarz, 2012). Focusing on the UF set-up, the flux tended to decrease gradually as the TMP increased, probably due to the higher solid concentration on the retentate. Process productivity and yield of recovered proteins were higher using the UF system. Although the yields are higher for the UF process, the final product collected from the EBA may offer advantages in food applications (Strætkvern and Schwarz, 2012).

As for any studies on cleaning agents and cleaning protocols used during the UF of streams from the potato industry, there are up to this point very few studies on the subject. Alkaline cleaning agents proved to be successful in restoring the initial pure water flux of the membranes (Dabestani *et al.*, 2017; Li *et al.*, 2020). Both studies were conducted using relatively diluted feed solutions and using experimental set-ups quite different from the one used in this work so little comparison can be made between the results in here reported and the mentioned articles. In conclusion, this work is very relevant and novel to the topic of membrane cleaning from UF of PFW.

Materials and Methods

3.1 Materials

3.1.1 Feed solutions

ThMP process water used in the filtration test was provided by Stora Enso (Kvarnsveden Mill, Sweden). This waste stream contains less than 1% (w/w) of total solids, mainly hemicelluloses and lignin. Other components such as salts, fibers and extractives are also present. Prior to the test, the process water was stored in a freezer at -18 °C, and a biocide was added to the ThMP water as a preservative, with a 0.1 % (w/w). The product used was FennoCide BZ26 (Kemira, Helsinki, Finland).

PFW solution was provided by Lyckeby Starch AB (Kristianstad, Sweden) stored in a freezer room at -18 °C and thawed at room temperature prior to the tests.

3.1.2 Polysulfone membranes

Two polymeric solution of the PS membranes prepared via non-induced phase inversion were prepared. Both solutions had in common dimethyl acetamide (DMAc, BASF, Germany) as solvent and glycerol (QREC) as non-solvent. The difference between them was the second non-solvent considered: polyethelene glycol <Mn> = 400 g/mol (PEG-400, BASF, Germany) or a block co-polymer of ethylene glycol and propylene glycol with a ratio EG/PG of 80/20 (Synperonic F-108). The casting of the polymeric solution on the support surface was performed manually and different concentrations of additives were introduced in the water-based CB for each of the polymeric solutions.

The PS membranes and their molecular weight cut-offs were kindly provided by the Institute of Physical Organic Chemistry – National Academy of Sciences of Belarus. Polymeric solution and CB composition as well as estimated MWCO for the PS membranes are summarized in Table 1.

3.1.2.1 Polyacrylic acid

Polyacrylic acid (PAA, Sigma Aldrich), MW = 250 kDa, was used as additive in the CB in concentrations between 0.175 % and 1.5 % (w/w) to compare the influence of different concentrations of PAA (Figure 9) in the CB on the membranes performance capacities.

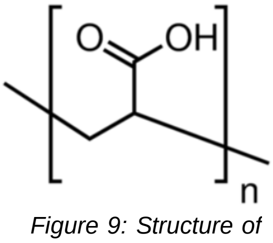


Figure 9: Structure of polyacrylic acid.

3.1.2.2 Poly(methyl vinyl ether-alt-maleic acid)

Poly(methyl vinyl ether-alt-maleic acid) (PMVEMA, Sigma Aldrich), MW = 216 kDa, was used as additive in the CB in concentrations between 0.5 % and 2.0 % (w/w) to compare the influence of different concentrations of PMVEMA (Figure 10) in the CB on the membranes performance capacities.

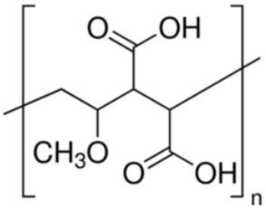


Figure 10: Structure of poly(methyl vinyl ether-alt-maleic acid).

Table 1: Composition of polymeric solutions and concentration of additives in the CB as well as MWCO of the PS membranes tested for the filtration of ThMP process water. Provided by the Institute of Physical Organic Chemistry - National Academy of Sciences of Belarus.

Polymer solution	**Type of additive in coagulation bath**	**Additive concentration (%)**	**MWCO (kDa)**
20 % Polysulfone 10 % PEG-400 DMAc	distilled water		10
	PAA (MW=250 kDa)	0.175	10
		0.4	10
		0.7	5
		1.0	5
		1.5	5
20 % Polysulfone 7 % Synperonic DMAc	distilled water		100
	PAA (MW=250 kDa)	0.175	50
		0.35	20
		0.5	20
		0.7	20
20 % Polysulfone 10 % PEG-400 DMAc	PMVEMA (MW=216 kDa)	0.5	*
		1.0	*
		1.5	*
		2.0	*
20 % Polysulfone 7 % Synperonic DMAc	PMVEMA (MW=216 kDa)	1.0	*
		1.5	*
		2.0	*

* not determined.

3.1.3 PES membranes

The polymeric solution of the PES (Ultrason E 6020P, BASF, Germany) membranes prepared via non-induced phase inversion included dimethyl acetamide (DMAc, BASF, Germany) as solvent and polyethelene glycol <Mn> = 400 g/mol (PEG-400, BASF, Germany) and glycerol (QREC) as non-solvents. The casting of the polymeric solution on the support surface was performed manually and different concentrations of additives were introduced in the water-based CB.

The polyether sulfone membranes and their molecular weight cut-offs were kindly provided by the Institute of Physical Organic Chemistry – National Academy of Sciences of Belarus. Polymeric solution and CB composition as well as MWCO for the PES membranes are summarized in Table 2.

3.1.3.1 Polyacrylic acid

Polyacrylic acid (PAA, Sigma Aldrich), MW = 250 kDa, was used as additive in the CB in concentrations between 0.5 % and 1.5 % (w/w) to compare the influence of different concentrations of PAA (Figure 9) in the membranes performance capacities.

3.1.3.2 Praestol 2540

Praestol 2540 (Ashland Inc., USA), $10 < M_n$ (10^6 Da) < 14, is an anionic charged polyelectrolyte, containing about 40 % of charged groups and based on acrylamide. Two membranes were prepared with Praestol 2540 (Figure 11) in the CB, in concentrations of 0.1 % and 0.2 % (w/w).

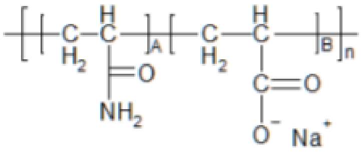


Figure 11: Structure of Praestol 2540.

3.1.3.3 Praestol 859

Praestol 859 (Ashland Inc., USA), $10 < M_n$ (10^6 Da) < 14, is a cationic charged polyelectrolyte, containing about 90 % of charged groups and based on polyacrylamide. Concentrations of Praestol 859 (Figure 12) in the CB varied between 0.1 % and 0.3 % (w/w).

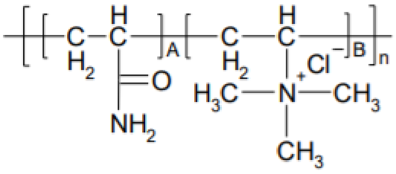


Figure 12: Structure of Praestol 859.

Table 2: Composition of polymeric solutions and concentration of additives in the CB as *well as MWCO of the PES membranes tested for the filtration of ThMP process water. Provided by the Institute of Physical Organic Chemistry - National Academy of Sciences of Belarus*

Polymer solution	**Type of additive in coagulation bath**	**Additive concentration (%)**	**MWCO (kDa)**
22% Polyether sulfone 10% PEG-400 10% Glycerol DMAc	distilled water		5
	PAA (MW=250 kDa)	0.5	20
		1.0	20
		1.5	20
	Praestol 2540 (10<Mn (10^6 Da)<14)	0.1	10
		0.2	10
	Praestol 859 (10<Mn (10^6 Da)<14)	0.1	5
		0.2	10
		0.3	10

3.1.4 Commercial membranes – UFX5 and UFX10

Flat sheet PS membranes UFX5 pHt (Alfa Laval AB, Naksov, Denmark) and UFX10 pHt, (Alfa Laval AB, Naksov, Denmark), with hydrophilic properties and, with molecular weight cut-offs of 5 kDa and 10 kDa, respectively were used for UF of ThMP process water and PFW. Both membranes present high temperature resistant and can be operated under a broad range of pH.The pristine membranes used for each UF experimental procedure were from the same commercial batch.

3.2 Ultrafiltration experiment

3.2.1 Experimental Setup

Schematic representation of the experimental setup is presented in Figure 13. The system used to study the performance and fouling and cleaning properties of each membrane consisted on a 15 L tank plus an immersion heater (Baker, Elektro-Varme, Sosdala, Sweden) containing the feed solution, where temperature was regulated by a control unit (Model MCM, Shinko, Technos Co., Ltd, Osaka, Japan). Three parallel circular flat sheet UF cells, with an effective membrane filtration area of 19.6 cm^2 were operated under cross flow. The pressure on the system was controlled using two digital pressure valves (DCS40.0AR, Trafag AG, Bubikon, Switzerland) placed on the feed and on the retentate sides. Adjusting the pressure was possible due to a needle valve placed on the retentate side and the flow was set with a positive displacement pump (Hydra-cell D25XL, Wanner, Minneapolis, USA) that was regulated by a frequency converter (ELEX 4000, Bergkvist & Co., AB, Gothenburg, Sweden). The crossflow velocity over the membranes was measured using a flowmeter (FCH-34-PP-Chemica, B.I.O-TECH e.K., Vilshofen, Germany) placed on the retentate side of the equipment and the permeate fluxes were measured with a scale (PL6001-1, Mettler Toledo Inc., Ohio, USA), which was recording weight changes in permeate mass underneath each one of the three parallelly connected flat-sheet modules. The average of the difference in pressure between the retentate and the feed sides is assumed to be the transmembrane pressure (TMP), since the permeate side is at atmospheric pressure.

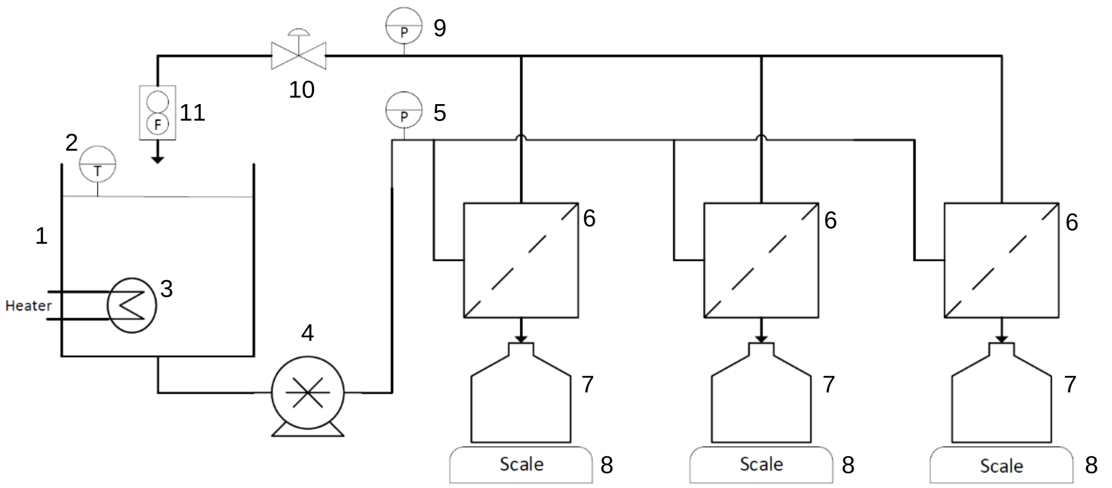


*Figure 13: Schematic representation of the experimental setup used in the performance studies. Feed tank (**1**), temperature control (**2**), immersion heater (**3**), pump (**4**), feed pressure gauge (**5**), UF cells (**6**), flasks for collecting permeate samples (**7**), scales (**8**), retentate pressure gauge (**9**), needle valve (**10**), flowmeter (**11**).*

3.2.2 Ultrafiltration performance experiment – ThMP process water

The steps during the UF of ThMP process water are presented in Figure 14 and the operational conditions of each step can be found on Table 3. Before the initial PWF (Figure 14 – J_0) measurements, a pre-cleaning step with an alkaline agent (Ultrasil 10, Ecolab, Sweden) was performed to ensure all remaining preservative chemicals that could be attached to the membranes were removed prior to the performance test. Pre-cleaning was conducted at 2.0 bar transmembrane pressure (TMP), 50 °C, crossflow velocity (CFV) of 0.5 m/s, for 1 h and 1 % (w/w) Ultrasil10 solution. After the pre-cleaning step was finished, the cleaning solution was discharged, and the system was rinsed with deionized water to ensure that all the cleaning agent was clearly removed. Initial measurements of Pure Water Flux (PWF) with deionized water at 30 °C and CFV of 0.3 m/s for the pressures of 1, 2 and 3 bar were conducted in between pre-cleaning and UF of ThMP process water [Figure 14 – Initial PWF (J_0)]. After a stationary state was ensured for each TMP, data points were recorded for 5 min (also for each TMP). Once the initial PWF (J_0) measurement was finished, deionized water was flushed from the system and 6 L of ThMP process water were added. The operating conditions during the UF of ThMP process water were 70 °C temperature, CFV of 0.3 m/s and TMP of 1, 3 and 5 bar. In this case, after the stabilization period, logging was set for 15 min per pressure point. Samples from the 3 permeates were collected while logging for each membrane sample and 100 mL of feed sample was collected after logging. Samples were collected for each pressure point. After ThMP UF, the industrial solution was replaced by deionized water. Once more, the system was carefully rinsed with deionized water before PWF (J_{rinse}) measurements were conducted under the same conditions as presented in PWF before the ThMP test (J_0). Following the PWF assessment, a cleaning step with Ultrasil 10 was performed as the one described for the pre-cleaning (1 h cycle, 2.0 bar TMP, 50 °C, CFV of 0.5 m/s and 1 % (w/w) Ultrasil10 solution). Finally, the effects of fouling on the membranes were evaluated through measurement of the PWF after the alkaline cleaning (J_{clean}). The procedure was once more the same as the one performed both before and after filtering the ThMP process water. The cleaning ptocedure was defined based on the reports of (Rudolph *et al.*, 2018)

After the study, membranes were rinsed with deionized water, left in a Petri Dish with deionized water for 24 h and dried overnight in a 50 °C oven before being stored in a desiccator and shipped to the Institute of Physical Organic Chemistry – National Academy of Sciences of Belarus for further analysis.

3.2.3 Ultrafiltration performance experiment – PFW

The steps performed during the UF of PFW are presented in Figure 14 and the conditions of each step can be found on Table 3. PFW UF tests were performed using the same experimental setup that was used for the UF of ThMP process water. The differences between the conditions of operation chosen for each feed solution were highlighted in Table 3.

The day before the UF experiment, a 15 min centrifugation at 4000 rpm was executed with the supernatant being collected and stored in a fridge room overnight at a temperature of 4 °C. Immediately prior to the UF of PFW, this supernatant was sieved with openings of 45 µm and then used as the initial feed solution for the UF.

Both pre-cleaning and assessment of the initial PWF (Figure 14 – J_0) were carried out as for the UF of ThMP process water. Later, during the UF of 5 L sieved centrifuged PFW, the temperature of the feed solution was 20 °C, and the effect of TMP on the membranes flux was operated at the same CFV and for the same TMP values as the ones used during the UF of ThMP process water (1, 3, 5 bar of TMP and CFV = 0,3 m/s). Due to the low fluxes spotted in the UF of PFW, logging periods were of 30 min, once a steady state was reached (15 minutes more than the logging periods for UF of ThMP process water). Samples from the 3 permeates and 100 mL of feed sample were collected for further analysis. Once finished the UF of PFW, the solution in the tank was discharged and the system was rinsed with deionized water. Next, evaluation on the impact of the fouling on the membranes was executed based on PWF (J_{rinse}), under the same conditions as the one performed initially for J_0, but for logging periods of 15 min instead of 5 min (due to low fluxes). Cleaning with Ultrasil 10 after the UF of PFW was performed under the same conditions as the ones used in the pre-cleaning step. The test ended with a PWF evaluation (J_{clean}) to understand whether the initial PWF (J_0) was restored. The conditions of this last PWF (J_{clean}) measurements were the same as for the other PWF and the logging period was 5 min.

After the study, membranes were rinsed with deionized water, left in a Petri Dish with deionized water for 24 h and dried overnight in a 50 °C oven before being stored in a desiccator and shipped to the Institute of Physical Organic Chemistry – National Academy of Sciences of Belarus for further analysis.

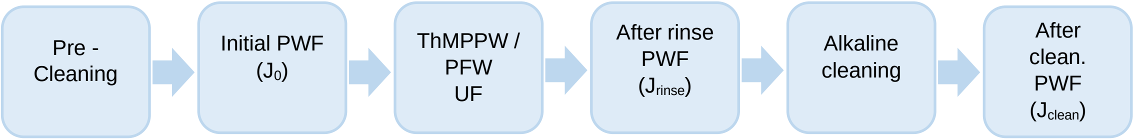


Figure 14: Flowchart of the several steps conducted during the experimental trials to evaluate membranes performance during the UF of ThMP process water and PFW.

Table 3: conditions of operation during the several stages of the UF of ThMP process water and PFW.

	ThMP process water	**PFW**
Pre - Cleaning	1h, 50 °C, TMP = 2 bar, CFV = 0.5 m/s 30 gata points	
PWF (J_0)	30 °C, TMP = 1, 2, 3 bar, CFV = 0.3 m/s 30 data points / TMP	
UF	70 °C, TMP = 1, 3, 5 bar, CFV = 0.3 m/s 90 data points / TMP	20 °C, TMP = 1, 3, 5 bar, CFV = 0.3 m/s 60 – 90 data points / TMP
PWF (J_{rinse})	30 °C, TMP = 1, 2, 3 bar, CFV = 0.3 m/s 30 data points / TMP	
Cleaning	1h, 50 °C, TMP = 2 bar, CFV = 0.5 m/s	
PWF (J_{clean})	30 °C, TMP = 1, 2, 3 bar, CFV = 0.3 m/s 30 data points / TMP	

3.2.4 Fouling and Cleaning Efficiency

Flux recovery ratio after rinsing membranes with deionized water (FRR_{rinse}) and flux recovery ratio after cleaning membranes with Ultrasil 10 (FRR_{clean}) were calculated as a percentage of the initial PWF (J_0) using the following equation:

$$FRR_{rinse} = \frac{J_{rinse}}{J_0} \times 100 \qquad (3)$$

$$FRR_{clean} = \frac{J_{clean}}{J_0} \times 100 \quad (4)$$

3.2.5 Retention / Rejection Coefficient

Retention or rejection values for each membrane were measured based on the following mathematical model:

$$Retention\ (\%) = \frac{X_{Feed} - X_{Permeate}}{X_{Feed}} \times 100 \quad (2)$$

which basically states that the retention or rejection value, in percentage, for a specific analysis is the observed concentration on the retentate side. It considers the difference between what is found in the feed and the permeate, divided by the value of the same compound that can be found on the feed.

3.3 Analytical Methods

The analysis relative to the UF of ThMP process water were performed in accordance to the standardized National Renewable Energy Laboratory (NREL) procedures (Sluiter *et al.*, 2012, 2008).

3.3.1 Hemicelluloses

To characterize hemicellulose composition in each sample and quantifying the hemicelluloses retention for each membrane, an acid hydrolysis step was performed to fractionate polymeric carbohydrates into the monomeric forms. The monomeric carbohydrates are soluble in the hydrolysis liquid.

Initially, glass vials were weighted, and 20 mL of each sample was introduced in each vial. Thereafter, to prevent pipetting failures, the vials were weighed once more before introducing 1.5 mL of 72 % sulphuric acidic in each vial, for a concentration of 0.054 mL of sulphuric acid per mL of sample. After a gently stir, the vials were placed inside the autoclave (Systec DX-150, Germany) and heated for 1 h at 121 °C, initiating the hydrolysis process. The hydrolysates were then cooled down to room temperature after an additional 45 min in the autoclave before continuing the NREL analysis. During the hydrolysis, lignin materials are also degraded, generating soluble and insoluble forms of lignin. The separate the monomeric forms of carbohydrates present in the soluble fraction of the hydrolysates from the insoluble forms of lignin, a vacuum filtration was performed using ceramic filters. After vacuum filtration, the liquid fraction of the hydrolysates was diluted in deionized water and analyzed by high-performance anion exchange chromatography in an ICS-3000 (Dionex Corp., USA) chromatography system, equipped with Carbo PA1 analytical column and a pulsed amperometric system. The analysis temperature was 30 °C and the injection loop volume was of 10 µL. The eluent solution composed of deionized water at a flow rate of 1.0 mL/min and the post column eluent addition was of 200 mM NaOH at a flow rate of 0.5 mL/min. The wash eluent solution used was 200 mM NaOH and 170 mM Sodium Acetate. Well-defined sugar solutions of D-Glucose, D-Galactose, D-Arabinose, D-Mannose and D-Xylose were used as calibration standards. The concentration of each of the five standards was of 0.1 g/L, 0.8 g/L, 0.05 g/L, 0.025 g/L and 0.005 g/L.

3.3.2 Total Lignin

A UV spectrophotometer (Shimadzu UV spectrophotometer UV-1800, Japan) was used to measure the soluble lignin. The wavelength used for these measurements was 280 nm and the samples were diluted to absorbance levels between 0.5 and 1.0 to ensure the linearity of the results. Prior to each test, the system was baselined using deionized water. Each sample was measured 3 times and in between the measurements the plastic vial was rinsed with deionized water. The spectrophotometer measurements follow the Beer-Lambert Law:

$$A = \varepsilon \times l \times c \tag{5}$$

A is absorbance, ε the absorptivity coefficient, l the length of the cell (set as 1 cm) and c is in this case the concentration of total lignin in the sample. The absorptivity value used was 17.8 L/ (g cm), according to (Örså *et al.*, 1997).

3.3.3 Total Nitrogen – Dumas Method

Total Nitrogen (TN) measurements according to the *Dumas* method were performed on an N/Protein Analyzer (Flash EA 1112 Serues, Thermo Electron S.p.A., Rodano, Italy) equipped with a water trap (silica gel), carbon trap (soda lime), catalysts of CuO and Pt/Al_2O_3, a thermal conductivity detector (TCD) and a separation column of Teflon and activated carbon. This test was conducted at the temperature of 900 °C using aspartic acid as a calibration standard (Standard 1 = 25.9 mg and Standard 2 = 51.3 mg). Samples were dried using a Gallenkamp vacuum oven OVA03100 (Fistreem International Ltd., Leicestershire, UK) overnight at the temperature of 70 °C and 150 mbar. No duplicate tests were performed.

3.3.4 Total Nitrogen – Spectrophotometric Method

Total Nitrogen (TN) content in the samples collected from the PFW tests were analyzed using a spectrophotometric method with Laton Total Nitrogen cuvette tests 20-100 mg/L TN LCK 338 (Hach Lange GmbH, Dusseldorf, Germany). Absorbance levels were measured on a DR2800 spectrophotometer (Hach Lange GmbH, Dusseldorf, Germany). No duplicate tests were performed.

Results and Discussion

4.1 ThMP process water – PWF, ThMP fluxes, Fouling and Cleaning

A group of membranes with different composition in both polymeric solution and CB were tested to better understand if the incorporation of additives was able to improve membranes' performance and if the concentration and type of additives in the CB allows modulation of permeability characteristic.

With that in mind, all the membranes were tested according to the procedure stated previously in 3.2.2, and both feed and permeate samples were collected and analyzed as described in 3.3. Since the experimental setup detailed in 3.2.1 holds 3 different UF cells in parallel, the membranes were tested in groups of 3, in no particular order and no duplicate tests were performed.

4.1.1 PS + PEG-400 + PAA

To a polymeric solution containing PS and PEG-400, different concentrations of PAA were introduced in the CB. Figure 15 represents the fluxes during the UF of ThMP process water and the permeability of the membranes based on PWF during the different parts of the test. The introduction of additives during membrane formation should lead to an increase in the hydrophilicity of the membrane surface, reducing the interactions between fouling agents and the membrane. With that in mind and compared to the reference membrane, it should be expected higher fluxes during UF of ThMP process water in membranes containing PAA. In addition, the PWF achieved in the end of the study – after the cleaning cycle – should be closer to the verified in the beginning of the test as a result from the reduced interactions between foulants and the membrane.

The MWCO from Table 1 suggest that pore size may decrease when higher concentrations of PAA are introduced in the CB as it decreases from 10 kDa to around 5 kDa. For the membranes with larger cut-offs, the initial water permeability increased when compared to the reference membrane (Figure 15.B – Initial). The enhanced permeability can be related to an increase in hydrophilicity or a decrease in thickness and density of the selective layer due to the presence of PAA, as suggested by (Plisko *et al.*, 2020). In contrast, the water permeability reduction perceived for membranes with higher percentages of PAA and lower MWCO, suggests that PAA may reduce pore size. In the latest case, membranes morphology (pore size) may be more influential on PWF than hydrophilicity, as reported by (Rahimpour and Madaeni, 2010).

During the UF of ThMP process water, higher fluxes were noticed for the majority of the membranes containing PAA, indicating that PAA may be efficient in reducing fouling accumulation in the membrane (Figure 15.A). The fact that membranes with more percentage of PAA in its composition were able to achieve higher fluxes when compared to membranes with low concentrations of PAA could also indicate the existence of an optimal concentration of PAA. At least between 0. 7 % PAA and 1.0 % PAA, something significant seems to happen. Further studies with additional concentrations of PAA could be useful to validate this hypothesis.

The slight decrease in the absolute flux value between the TMP of 3 and 5 bar for the membrane with 0.7 % PAA should not be considered relevant for the overall evaluation of the results when compared to the remaining data.

Considering the results presented in Table 4, the FRR suggest that specially for membranes with higher concentrations of PAA, less irreversible interactions between fouling compounds on the feed solution and the membrane surface may be happening. Overall, the improved hydrophilicity of the membranes 1.0 % PAA and 1.5 % PAA not only improved ThMP process water filtration fluxes but also reduced membrane-fouling interactions.

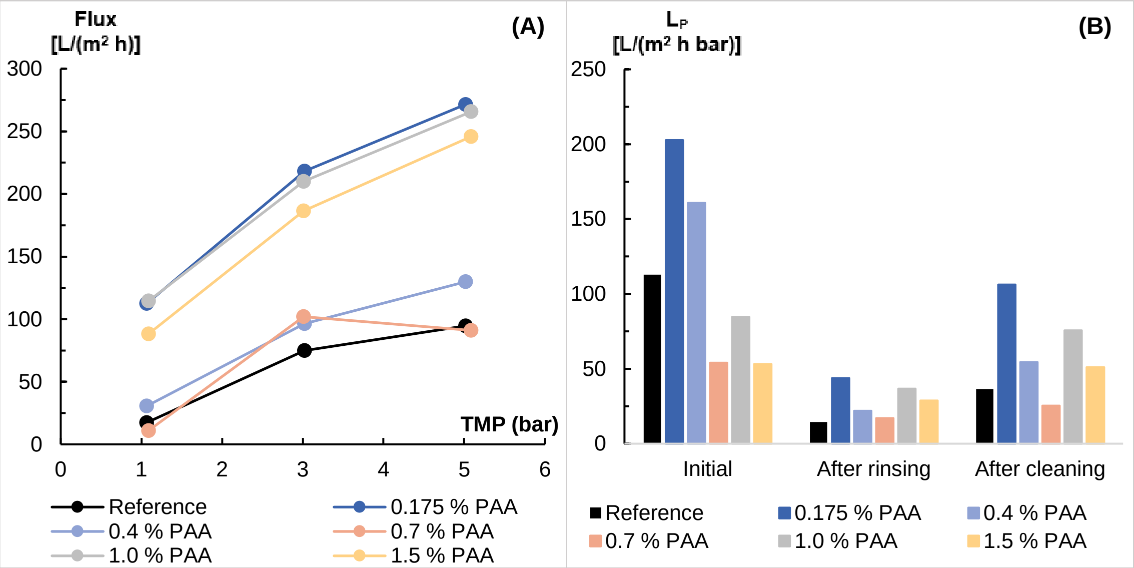


Figure 15: Performance of the PS + PEG-400 + PAA membranes on UF of ThMP process water – ***(A)*** *influence of TMP and PAA concentration on flux: concentrations of PAA in the CB between 0.175 % and 1.5 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 ºC and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of PAA in the hydraulic permeability (L_P) of PS + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 ºC and CFV of 0.3 m/s.*

Table 4: FRR of the PS + PEG-400 + PAA after UF of ThMP process water and rinsing with deionized water (FRR$_{rinse}$) and FRR after cleaning with Ultrasil 10 (FRRc$_{lean}$). Comparison between membranes of PS and PEG-400 produced with different concentrations of PAA on the CB

Coagulation bath additive	**FRR$_{rinse}$ (%)**	**FRR$_{clean}$ (%)**
PS + PEG-400	13	31
0.175 % PAA	22	52
0.4 % PAA	14	34
0.7 % PAA	33	49
1.0 % PAA	44	90
1.5 % PAA	54	96

4.1.2 PS + Synperonic F-108 + PAA

To prepare this group of PS membranes, Synperonic F-108 was added to the polymeric solution and different concentrations of PAA to the CB. Their performances are presented in Figure 16. Just like in the previous section, PAA seems to lead to a reduction in the MWCO of the membranes, resulting in the overall reduction of the initial permeability of the membranes with lower pore size (Figure 16.B). The fluxes during the filtration of ThMP process water (Figure 16.A) were higher when using membranes with additives when compared to the reference membrane. Once more, the results are similar to what was presented in the PS + PEG-400 + PAA group of membranes. In the case of the membrane with 0.5 % PAA, very low fluxes were achieved during the UF of ThMP process water.

The FRR for these membranes presented some interesting results (Table 5). For membranes with 0.35 % and 0.7 % of PAA in the CB, water fluxes after alkaline cleaning were very similar to the initial PWF, suggesting all the fouling accumulated in these membranes during the ThMP filtration was successfully removed (reversible fouling). Since for the reference membrane the PWF after the alkaline cleaning was 59 % of the initial flux, it is possible that fouling agents affected more severely the reference membrane. As the MWCO of the reference membrane was much bigger than the remaining membranes it is wise to assume that this membrane is more expose to internal membrane fouling (Figure 5) which is widely associated to permeant flux losses (Baker, 2004).

For the membranes with 0.175 % and 0.5 % of PAA, very different results were obtained. For the first, the permeability after the cleaning was about 1.41 times the initial permeability and for the second, the permeability in the last part of the study was about 8 % of the initial. The results may have different explanations. For the 0.175 % PAA membrane, some detachment of the membrane surface could have happened during the test. As for the 0.5 % PAA membrane, low fluxes in the end of the parameter study were most likely caused by irreversible fouling pore blocking, which is in line with the low fluxes obtain during the ThMP filtering (Figure 16). The reason behind the not so promising results may be due to the formation process of the membranes, specially the casting of the polymeric solution in the thin solid surface and the time of duration of the CB. As presented in the 2.6.1, these two parameters are of great importance and influence in a large way the characteristics and performance of the membranes.

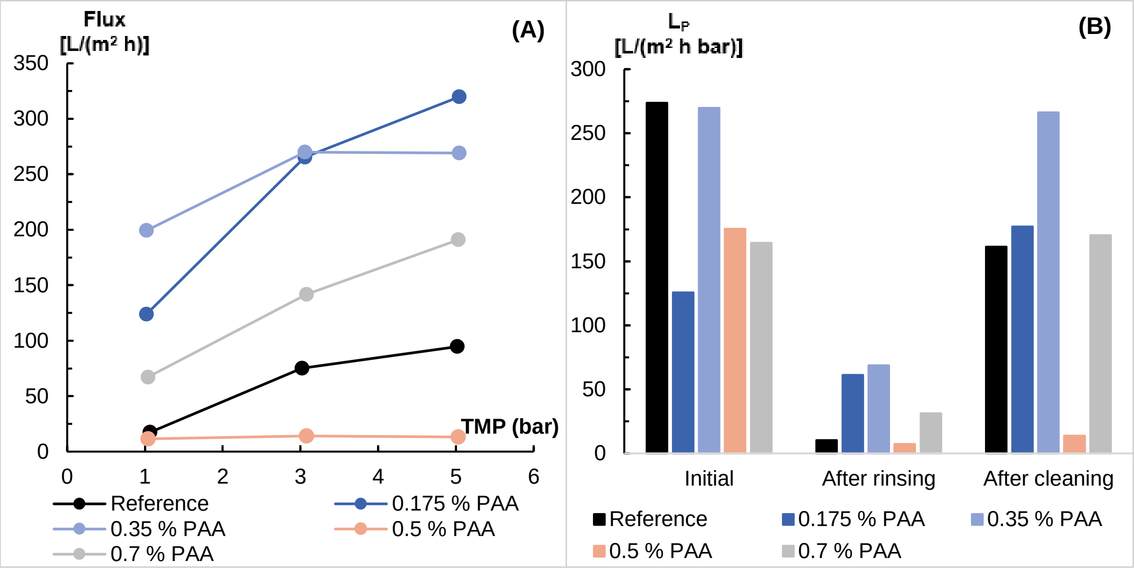


*Figure 16: Performance of the PS + Synperonic F-108 + PAA membranes on UF of ThMP process water – **(A)** influence of TMP and PAA concentration on flux: concentrations of PAA in the CB between 0.175 % and 0.7 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 ºC and 0.3 m/s, respectively **(B)** comparison between the influence of different concentrations of PAA in the hydraulic permeability (L_P) of PS + Synperonic F-108 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 ºC and CFV of 0.3 m/s.*

Table 5: FRR of the PS + Synperonic F-108+ PAA after UF of ThMP process water and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$). Comparison between membranes of PS and Synperonic F-108 produced with different concentrations of PAA on the CB

Coagulation bath additive	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
PS + Synperonic F-108	4	59
0.175 % PAA	49	141
0.35 % PAA	25	99
0.5 % PAA	4	8
0.7 % PAA	29	104

4.1.3 PS + PEG-400 + PMVEMA

Membranes produced with PS and PEG-400 as main components in the polymeric solution were introduced in the CB containing different concentrations of PMVEMA. Overall, the results from Figure 17 show that the pristine membrane proved to be more permeable to pure water and ThMP process water than the membranes with additives, meaning that PMVEMA could act as a hydrophobic agent in polymeric membranes. During the filtration of ThMP process water, the flux increase (when TMP changed from 3 bar to 5 bar) for the membrane 1.0 % PMVEMA must be considered an experimental error.

The difference between water permeability in the beginning of the test and after the alkaline cleaning (evaluated based on the fouling recovery ratios presented in Table 6) were very distinctive for membranes with additives. For membranes with 0.5 % and 2.0 % PMVEMA, the fluxes in the beginning and end of the test were equal while for the 1.0 % and 1.5 % PMVEMA, the flux in the end was about half of the initial. Nevertheless, all the FRR of the membranes with additives were higher than the non-modified membrane, which indicates that the percentage of reversible fouling in the membranes with the additives may be higher than the membrane without additive. The high FRR are practically irrelevant as the fluxes were very low in the first place.

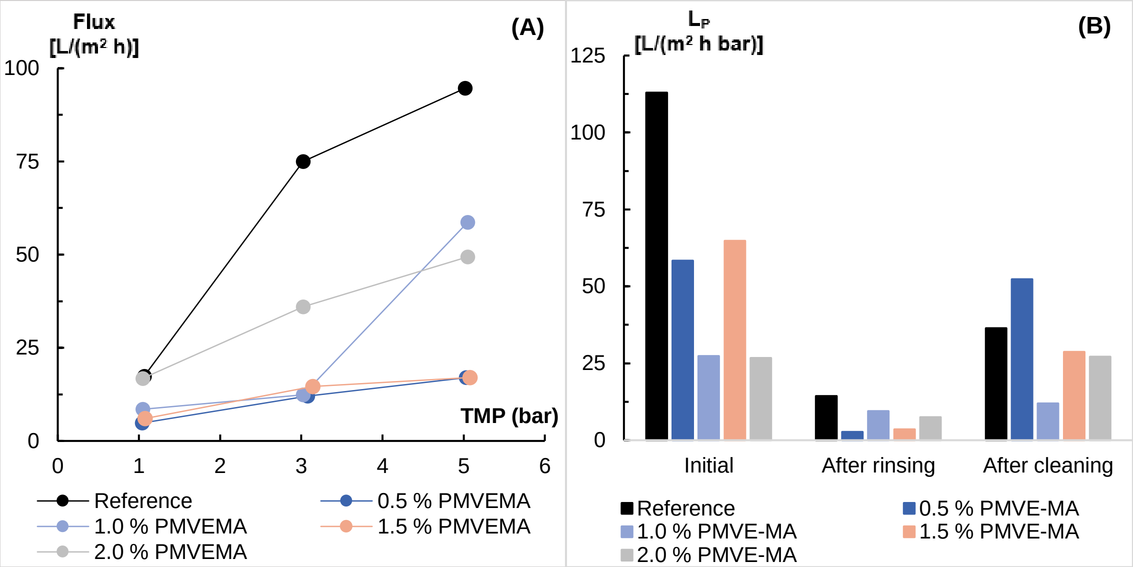


Figure 17: Performance of the PS + PEG-400 + PMVEMA membranes on UF of ThMP process water – ***(A)*** *influence of TMP and PMVEMA concentration on flux: concentrations of PMVEMA in the CB between 0.5 % and 2.0 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 °C and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of PMVEMA in the hydraulic permeability (L_P) of PS + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 °C and CFV of 0.3 m/s.*

Table 6: FRR of the PS + PEG-400 + PMVEMA after UF of ThMP process water and rinsing with deionized water (FRR$_{rinse}$) and FRR after cleaning with Ultrasil 10 (FRR$_{clean}$). Comparison between membranes of PS and PEG-400 produced with different concentrations of PMVEMA on the CB.

Coagulation bath additive	**FRR$_{rinse}$ (%)**	**FRR$_{clean}$ (%)**
PS + PEG-400	13	31
0.5 % PMVEMA	5	90
1.0 % PMVEMA	34	44
1.5 % PMVEMA	7	56
2.0 % PMVEMA	28	100

4.1.4 PS + Synperonic F-108 + PMVEMA

In the polymeric solution for this group of membranes, the main components were PS and Synperonic F-108. To the deionized water CB, different concentrations of PMVEMA were added. Results from the experimental trial on the UF of ThMP process water are presented in Figure 18 and recovery ratios in Table 6

Based on the initial permeability data, PMVEMA decreases the hydrophilicity of the membranes as the PWF's decrease with an increase in the percentage of PMVEMA.

The UF of ThMP process water presented some promising results as membranes with 1.0 % and 1.5 % PMVEMA achieved higher fluxes than the reference membrane. As for the 2.0 % PMVEMA membrane, the flux is similar to the reference membrane for 1 bar and it gradually becomes lower than the reference as pressure increases, indicating that with such high concentrations of PMVEMA the membrane may be more prone to fouling. With the increase in pressure, all the membranes seem to behave in similar conditions considered the profile of the flux curves, entering the region of critical flux

Although the ThMP process water fluxes seemed promising (Figure 18.A), the differences between the permeability from the start of the test and after the cleaning step resulted in FRR$_{clean}$ above 130 %. This percentages for FRR show that detachment probably took place during the test. The retention results for hemicelluloses and lignin presented further down in 4.2 were not significantly different from the remaining membranes to validate the idea of membrane detachment. A cleaning round with a different agent could be useful to better understand if the chosen protocol was harmful to the membranes.

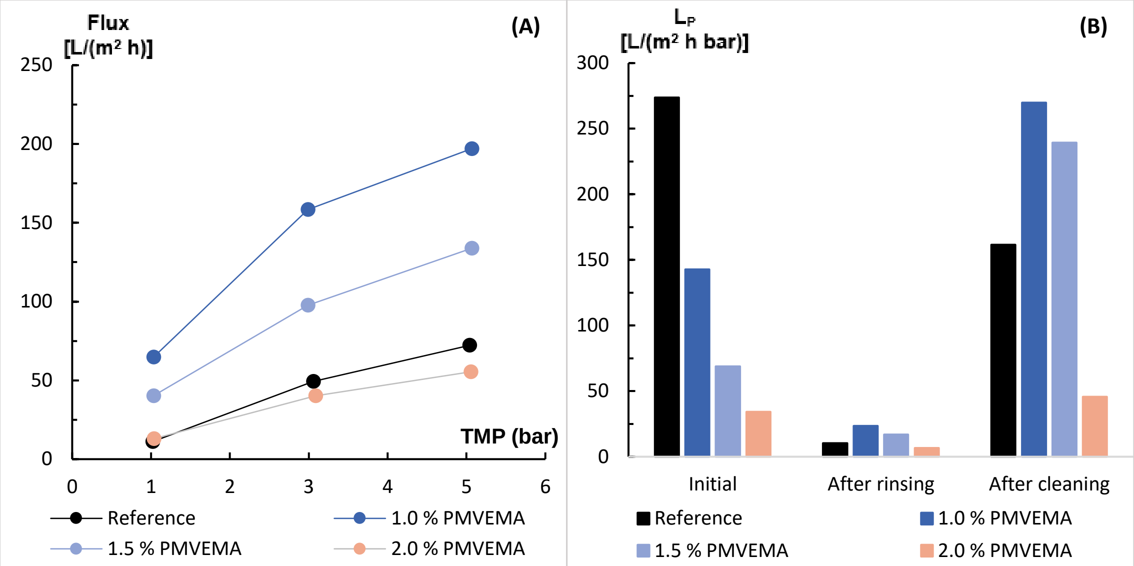


Figure 18: Performance of the PS + Synperonic F-108 + PMVEMA membranes on UF of ThMP process water – ***(A)*** *influence of TMP and PMVEMA concentration on flux: concentrations of PMVEMA in the CB between 1.0 % and 2.0 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 ºC and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of PMVEMA in the hydraulic permeability (L_P) of PS + Synperonic F-108 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 ºC and CFV of 0.3 m/s.*

Table 7: FRR of the PS + Synperonic F-108 + PMVEMA after UF of ThMP process water and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 (FRR_{clean}). Comparison between membranes of PS and Synperonic F-108 produced with different concentrations of PMVEMA on the CB.

Coagulation bath additive	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
PS + Synperonic F-108	4	59
1.0 % PMVEMA	16	189
1.5 % PMVEMA	24	348
2.0 % PMVEMA	19	133

4.1.5 PES + PEG-400 + PAA

The results for the membranes produced with a polymeric solution of PES and PEG-400 and a CB containing different concentrations of PAA are presented in Figure 19.

Contrary to what was believed in 4.1.1 and 4.1.2, the MWCO of the membranes was not reduced due to the addition of PAA to the CB. Overall, the fluxes obtained during the filtration of ThMP process water suggest that the membranes with additives could perform better at higher TMP values. For the reference membrane at 5 bar, the membrane seems to be performing close to the limiting flux region where irreversible fouling may start to appear (Figure 19.A). Considering that this combination of polymeric solution and PAA as an additive in the CB could allow working at higher pressures than the reference membrane, the results seem to be promising.

The FRR after rinsing with deionized presented in Table 8 showed some interesting results. It is possible to say that membranes with additives achieved permeabilities similar or even better than the ones from beginning of the test. On the other hand, it is not entirely certain that all fouling agents were removed from the membrane surface. Furthermore, these results could indicate some type of loss of additive or detachment happened during the test. Another possible situation of what may have caused such FRR is of inefficient cleaning prior to the measurements of the initial PWF, as reported by (Rudolph *et al.*, 2018). Inefficient removal of preservatives and consequent permeability after cleaning higher than in the beginning. Obviously, the concerns with the cleaning agent and cleaning cycle, as well as some type of loss of additive from the membranes surface is a valid hypothesis for all the membranes presented in this thesis. The reason why these hypotheses are stated in this section and not in the remaining has to do with the fact that the FRR verified for this group of membranes is above 100 % but not high enough to ensure that the membranes were damaged during the UF. Still, the results seem to be promising for further studies.

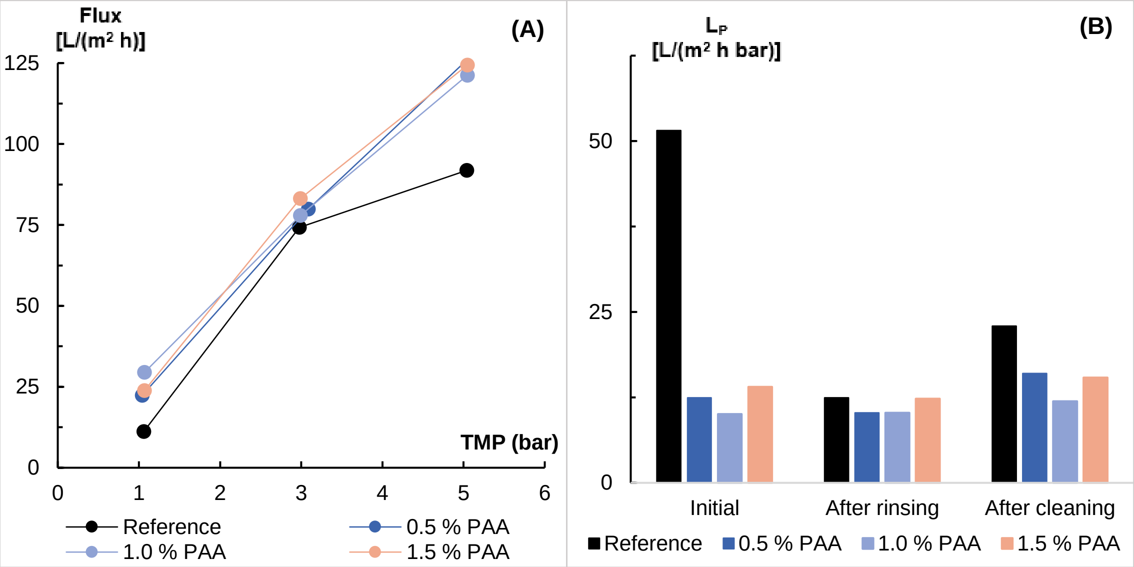


Figure 19: Performance of the PES + PEG-400 + PAA membranes on UF of ThMP process water – ***(A)*** *influence of TMP and PAA concentration on flux: concentrations of PAA in the CB between 0.5 % and 1.5 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 ºC and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of PAA in the hydraulic permeability (L_P) of PES + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 ºC and CFV of 0.3 m/s.*

Table 8: FRR of the PES + PEG-400 + PAA after UF of ThMP process water and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$). Comparison between membranes of PES and PEG-400 produced with different concentrations of PAA on the CB.

Coagulation bath additive	FRR_{rinse} (%)	FRR_{clean} (%)
PES + PEG-400	24	44
0.5 % PAA	82	129
1.0 % PAA	102	119
1.5 % PAA	88	111

4.1.6 PES + PEG-400 + Praestol 2540

This group of polyether sulfone membranes was produced using the same polymeric solution as the previous group (PES + PEG-400). The additive used in the CB was Praestol 2540.

The results regarding the UF of ThMP process water and the effects of fouling are presented in Figure 20. Adding this polyelectrolyte to the CB could potentially lead to a slight increase in MWCO, according to the values presented in Table 2 (10 kDa for both membranes compared to the 5 kDa of the reference membrane). Even tough pore size seems to increase upon the presence of Praestol 2540, the membrane containing 0.2 % of this additive registered lower water permeability values than the reference membrane during all stages of the trial as well as lower fluxes during UF of ThMP process water. The opposite results were verified for the membrane with the lowest concentration of Praestol 2540. The opposite results may demonstrate that the characteristics of the membranes could be quite different in terms of surface roughness, porosity and thickness. The membrane with 0.1 % Praestol 2540 may present very high porosity and surface roughness compared to the 0.2 % Praestol 2540 membrane. The 0.2 % Praestol 2540 membrane may also be thicker than the 0.1 % Praestol 2540, resulting in different fluxes.

Fouling recovery ratios (Table 9) after rinsing and after alkaline cleaning indicate that Praestol 2540 may reduce the interactions between fouling agents and the membrane structure, as a higher recovery of permeability was detected for the membranes with the additive when compared to the reference membrane (Table 9). Nevertheless, it is only desired to achieve high flux recoveries for membranes that present relevant flux improvements compared to the reference membrane, such as for 0.1 % Praestol 2540. And so, even tough the membrane containing 0.2 % Praestol 2540 presented a significant FRR, the extremely low flux during the UF of ThMP water prevents such membrane from being considered preferable to the reference membrane.

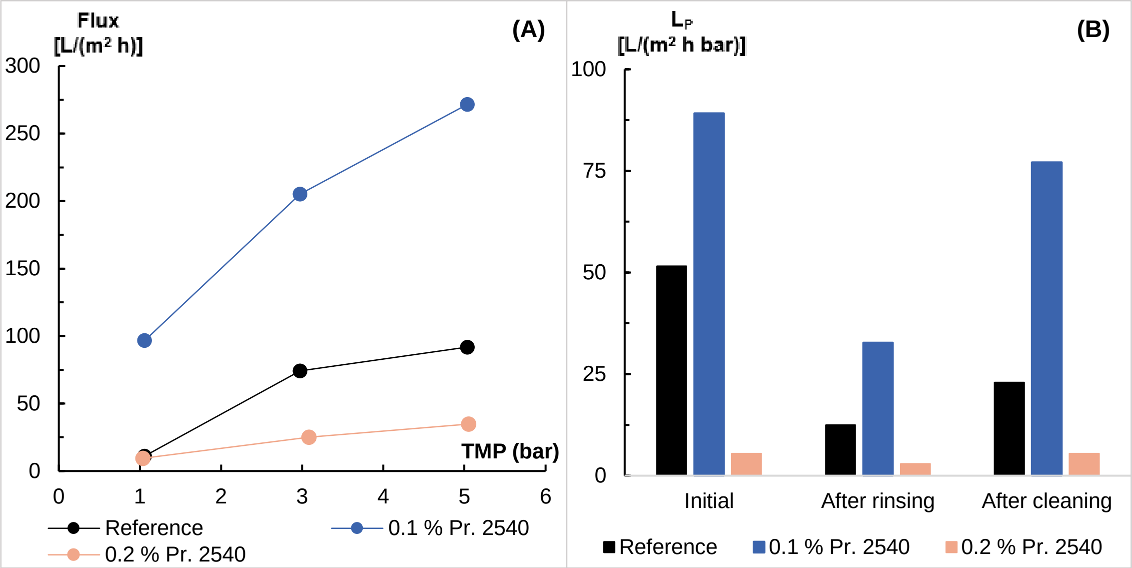


Figure 20: Performance of the PES + PEG-400 + Pr. 2540 membranes on UF of ThMP process water – ***(A)*** *influence of TMP and Pr. 2540 concentration on flux: concentrations of Pr. 2540 in the CB were 0.1 % and 0.2 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 ºC and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of Pr. 2540 in the hydraulic permeability (L_P) of PES + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 ºC and CFV of 0.3 m/s.*

Table 9: FRR of the PES + PEG-400 + Pr. 2540 after UF of ThMP process water and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$). Comparison between membranes of PES and PEG-400 produced with different concentrations of Pr. 2540 on the CB-

Coagulation bath additive	**FRR$_{rinse}$ (%)**	**FRR$_{clean}$ (%)**
PES + PEG-400	24	44
0.1 % Praestol 2540	37	86
0.2 % Praestol 2540	53	99

4.1.7 PES + PEG-400 + Praestol 859

The results regarding the effect of different concentrations of Praestol 859 on the membranes ThMP water permeation fluxes are illustrated in Figure 21.A. When comparing hydraulic permeability before the filtration with ThMP process water (Figure 21.B), modified membranes achieve higher permeabilities compared to the reference membrane. A trendline is even detectable, except for the membrane with 0.2 % Praestol 859. This indicates a general increase in PWF of the modified membranes. The lower initial permeability may be resultant from the formation of a low porosity membranes with a denser selective layer (Plisko *et al.*, 2020).

After the filtration of ThMP process water and rinsing with deionized water, the FRR_{rinse} of the modified membranes were higher than the FRR of the reference membrane, probably a result of the more hydrophilicity conceded by the Praestol 859.

When focusing only on the membrane containing 0.2 wt.% Praestol 859 solution and considering the fact that the permeability before the filtration of ThMP (Figure 20.B – Initial) for this membrane was more than three times lower than the reference membrane, it is reasonable to say that adding Praestol 859 to the CB improves the filtration of ThMP process water for all membranes and not only for the ones where the permeability values were higher than the non-modified membrane. This improved performance of the modified membranes is probably due to their enhanced hydrophilicity, which may result in less fouling of these membranes.

ThMP process water fluxes of the modified membranes were superior to the flux of the unmodified membrane. As the pressure increased, the difference between the fluxes of the initial and modified membranes increased as well (see Figure 21.A). The profile of the curve flux vs.TMP for the reference membrane indicates that critical flux was achieved, and soon irreversible fouling may appear. On the other hand, no significant deviation from linearity was observed for the modified membranes indicating that these membranes may be more resistant to fouling.

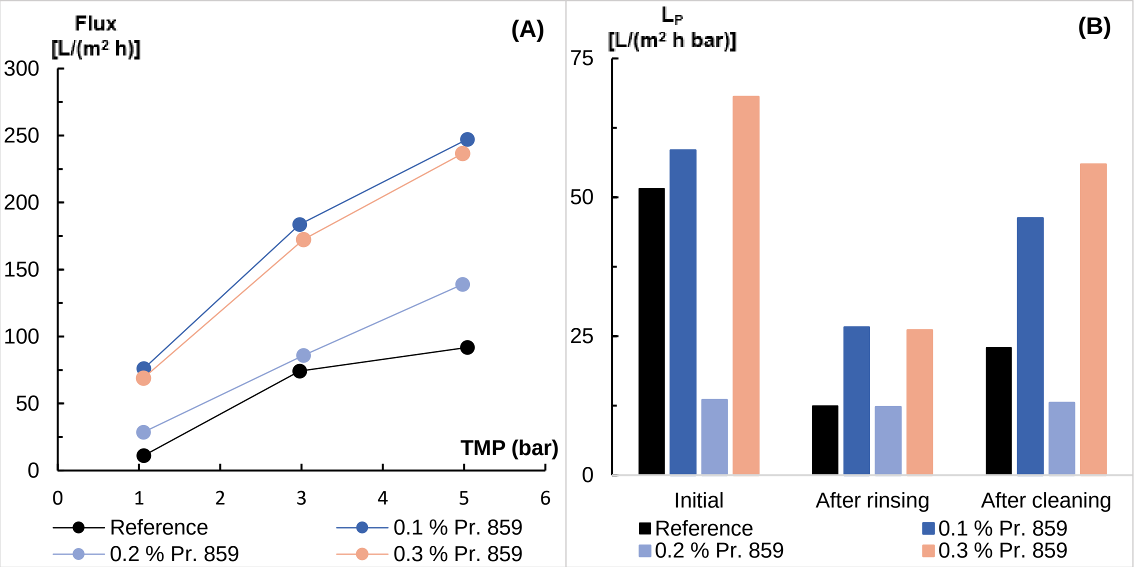


Figure 21: Performance of the PS + PEG-400 + Pr- 859 membranes on UF of ThMP process water – ***(A)*** *influence of TMP and Pr. 859 concentration on flux: concentrations of Pr. 859 in the coagulation bath between 0.1 % and 0.3 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 °C and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of Pr. 859 in the hydraulic permeability (L_P) of PES + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 °C and CFV of 0.3 m/s.*

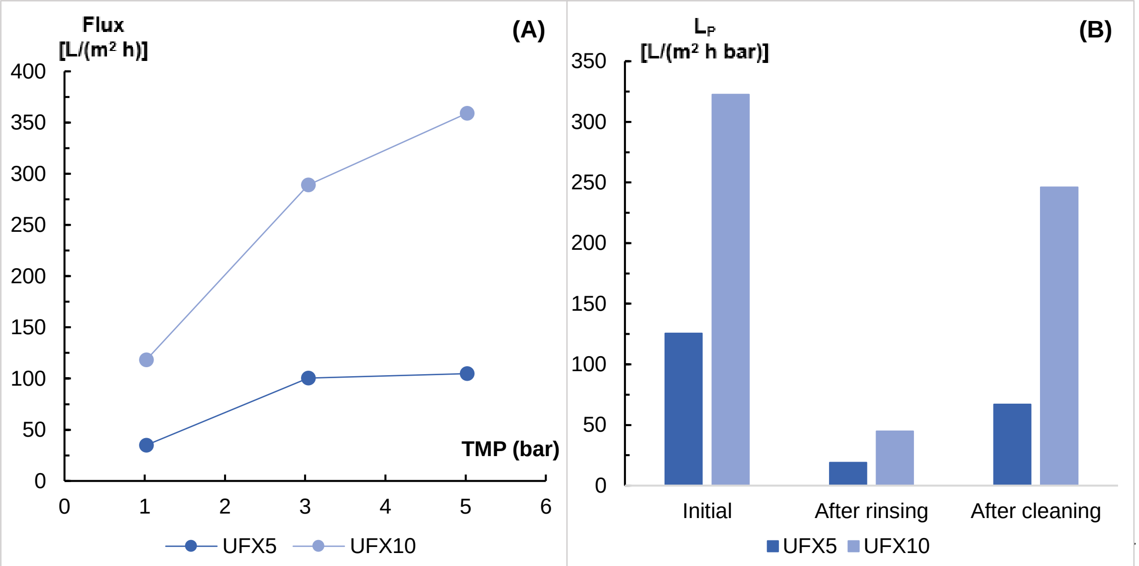
Table 10: FRR of the PES + PEG-400 + Pr. 859 after UF of ThMP process water and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$). Comparison between membranes of PES and PEG-400 produced with different concentrations of Pr. 2540 on the CB.

Coagulation bath additive	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
PES + PEG-400	24	44
0.1 % Praestol 859	46	79
0.2 % Praestol 859	90	96
0.3 % Praestol 859	38	82

4.1.8 Commercial Membranes – UFX5, UFX10

Two different commercial membranes widely used in industrial applications were tested to compare the results with the novel membranes. As expected, the fluxes when filtering ThMP process water with UFX5 were much lower than the fluxes of UFX10 (Figure 22.A). These is mainly due to the fact that the nominal MWCO of the UFX5 membrane is 5 kDa while the cut-off of UFX10 is 10 kDa. It is also interesting to state that, at 5 bar, the UFX5 membrane begins to enter the limiting flux region.

The PWF tests allowed the conclusion that the UFX5 pure water flux after the alkaline cleaning step was 53 % of the initial flux and the fluxes for the membrane with the cut-off of 10 kDa was 78 % (Table 11). The lower recovery in permeability of UFX5 is in line with the idea of irreversible fouling (Bungay *et al.*, 1983).



*– **(A)** influence of TMP on the flux of commercial membranes; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 °C and 0.3 m/s, respectively **(B)** hydraulic permeability (L_P) of UFX5 and UFX10 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of ThMP process water and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 °C and CFV of 0.3 m/s.*

Table 11: FRR of the commercial membranes UFX5 and UFX10 after UF of ThMP process water and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$).

Membrane	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
UFX5	15	54
UFX10	15	79

Compared to the commercial membrane, the novel membranes performed quite differently. The reference membranes initial water permeabilities were 113 L/(m^2 h bar) for PS + PEG-400 (10 kDa MWCO), 274 L/(m^2 h bar) for PS + Synperonic F-108 (100 kDa MWCO) and 56 L/(m^2 h bar) for the PES + PEG-400 (5 kDa MWCO). The permeability of UFX5 was 126 L/ (m^2 h bar) and UFX10 achieved 323 L/ (m^2 h bar).

It is safe to say that the introduction of additives in the CB seems to influence the molecular weight cut-off of the membranes. Based on the initial permeability for pure water, three novel membranes stood out as rather hydrophilic and with permeabilities closer the commercial membranes: PS + PEG-400 + 0.175 % PAA, PS + PEG-400 + 0.4 % PAA and PS + Synperonic F-108 + 0.35 % PAA. The initial water permeability of the mentioned membranes were 203 L/(m^2 h bar), 161 L/(m^2 h bar) and 270 L/(m^2 h bar), respectively.

During the UF of ThMP process water, the reference membranes were never able to surpass the 100 L/ (m^2 h) flux while both commercial membranes performed above this value for higher TMP. The most promising modified membranes in this aspect were:

- PS + PEG-400 + PAA – where the 0.175 %, 1.0 % and 1.5 % concentrations of PAA resulted in flux enhancements until at least 246 L/(m^2 h) at 5 bar TMP.
- PS + Synperonic F-108 + 0.175 % PAA – with a flux of 320 L/(m^2 h) at 5 bar TMP. It may be related to the high MWCO of this membrane – 50 kDa.
- PES + PEG-400 + 0.1 % Praestol 2540 – MWCO of 10 kDa and ThMP process water UF flux of 242 L/(m^2 h) at 5 bar TMP.
- Two of the three membranes of PES + PEG-400 + Praestol 859 – 0.1 % Praestol 859, 5 kDa MWCO, and 0.3 % Praestol 859, 10 kDa MWCO, with fluxes of 247 L/(m^2 h) and 237 L/(m^2 h), respectively.

At the TMP of 5 bar, the flux for UF of ThMP process water with the UFX5 was 105 L/(m^2 h), operating in the limiting region, and the flux of the UFX10 was 327 L/(m^2 h). Overall, based on the UF fluxes of ThMP process water, the most promising membrane was the PES + PEG-400 + 0.1 % Praestol 859 as it was the only one to outperform the commercial membrane with similar characteristics (UFX5).

Although the FRR of the commercial membranes values are in the range of the majority of the results obtained for the membranes produced by the National Academy of Sciences of Belarus, in some of the novel membranes tested in this thesis, the percentage of reversible fouling could be higher. Therefore, the additives used in the coagulation bath may lead to an increase in the hydrophilicity of the surface and reduce the percentage of irreversible fouling. In particular, the FRR_{clean} of 141 % for the PS + Synperonic F-108 + 0.175 % PAA (Table 5) raises concerns regarding the quality and properties of this membrane. The FRR_{clean} of the PES + PEG-400 + 0.1 % Praestol 859 (Table 10) demonstrates that indeed this may be a successful alternative to the UFX5 (Table 11).

In previous studies, the influence of TMP on the flux during the UF of ThMP process water was investigated using an UFX5 spiral UF membrane (Persson and Jönsson, 2010; Thuvander *et al.*, 2018). Reference to these studies was made previously in 2.7.3 but considered that more information is known at this point of the work than when the articles were first mentioned, further discussion is relevant. Despite the fact that neither the operational conditions nor the membranes used on those trials were the same as in this test, an analysis and comparison between the results is still valid just as an indicator on the relevance of this work regarding UF of ThMP process water. The differences between the UF experimental procedure and cleaning cycle used in each research can be consulted in Table 12 and some experimental results of the previous works are in Figure 23.

The ThMP fluxes described by Persson and Jönsson (Figure 23.A) were in the same order of magnitude of the ones detailed in this work (Figure 22.A) while the results of Thuvander *et al.* (Figure 23.B) were quite different. According to the authors, it was resultant from the accelerated fouling due to very low CFV (Thuvander *et al.*, 2018).

As for the FRR, all the cleaning cycles were distinctive. In particular, the concentration of the solution that was used was distinctive (Table 12). The fouling conditions chosen by the researchers were also quite different from the one in this study. The hemicelluloses concentration on the feed used by Persson and Jönsson for the fouling test was of 1 g/L and the membrane was fouled for 3 days at 2 bar TMP and 75 °C. Nevertheless, the pure water flux was completely restored after the cleaning cycle (Persson and Jönsson, 2010). In the case of Thuvander *et al.*, after the experiments of the influence of TMP on the flux, a trial at constant pressure was performed before the cleaning stage. After the rinsing and cleaning, only about 60 % of the initial PWF was restored. More informations on the concentration stage and aditional cleaning steps studied by Thuvander *et al.* were provided in 2.7.3.

Experiments on the successful fouling removal, with complete flux recovery, from the UFX5 flat sheet membrane using a stirred dead end module after filtration of ThMP, by (Rudolph et al., 2018) were the guidelines for the definition of the cleaning cycle used in this work.

Table 12: Comparison between the performance of the UFX5 membranes in this study and the work developed by (Persson and Jönsson, 2010) and (Thuvander et al., 2018) in relation two initial hemicelluloses concentration, operating conditions of the study of TMP influence on flux during UF of ThMP and cleaning cycle.

Membrane	**Initial Hemicelluloses concentration (g/L)**	**Filtration of ThMP**	**Cleaning cycle**
UFX5 flat sheet	2.5	70.0 °C, TMP = 1.0, 3.0, 5.0 bar, CFV = 0.3 m/s	Rinsing + 1.0 % (w/w) Ultrasil 10, 1 h, 50 °C, TMP = 2 bar, CFV =0.5 m/s
UFX5 spiral (Persson and Jönsson, 2010)	2.0	75.0 °C, TMP = 2.0, 4.0, 6.0 bar, Crossflow = 1.3 m/s	0.5 % (w/w) Ultrasil 10, 45 min, 60 °C
UFX5 spiral (Thuvander *et al.*, 2018)		75 °C, TMP = 0.5, 1.0, 1.5, 2.0 bar, CFV = 0.05 m/s	Rinsing + 0.25 % (w/w) Ultrasil 10, 1 h, 50 °C, TMP = 1 bar, CFV =0.2 m/s

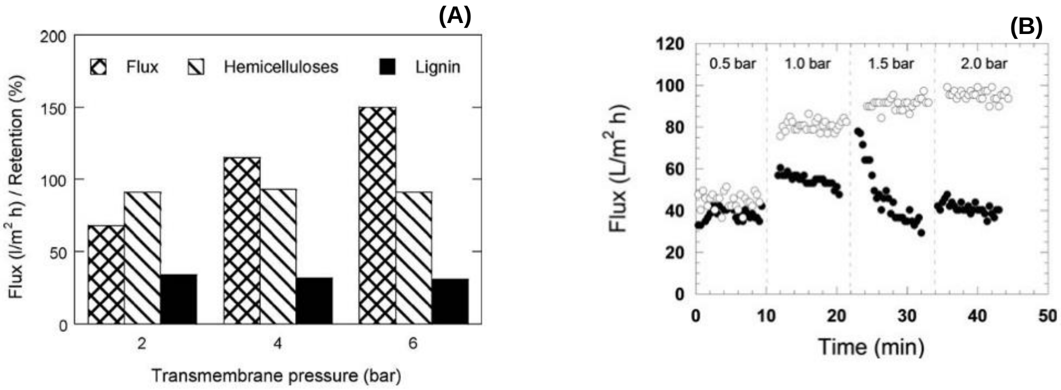


Figure 23: ***(A)*** *influence of TMP on UF ThMP process water fluxes, hemicelluloses and lignin retention. Adapted from* (Persson and Jönsson, 2010). ***(B)*** *influence of TMP on UF fluxes of pre-treated (by MF) (○) and untreated ThMP process water (●). Adapted from (Thuvander et al., 2018).*

4.2 ThMP process water – Retentions

Modified and unmodified membranes were compared based on the retention values for the two major lignocellulosic compounds found in ThMP process water: hemicelluloses and lignin. The volume of permeate samples collected during the performance tests for 1 and 3 bar was not enough to run analysis on all membranes. For that reason, the discussion presented in this section focuses on feed and permeate samples collected at the constant pressure of 5 bar. Furthermore, the retention of both hemicelluloses and lignin does not seem to be influenced by the difference in TMP, which means no major difference in compressibility – Figure23.A (Persson and Jönsson, 2010).

4.2.1 Hemicelluloses

Figure 24 summarizes the results of hemicellulose retentions observed during the UF with the diverse polysulfone membranes. In general, the values of retention for the PS membranes were between 84 % and 97 %. The most significant difference was identified for membranes with PEG-400 in the polymeric solution and membranes with Synperonic. The retentions were higher for the membranes with PEG-400. Indeed, MWCO of the PS membranes (presented in Table 1) support the results, as membranes with larger cut-offs should be more permeable to hemicelluloses. The MWCO of the PS + PEG - 400 + PAA membranes were in the range 5 to 10 kDa while the values of MWCO for the PS + Synperonic + PAA were 20 to 100 kDa. In addition, hemicelluloses rejection of the PS + Synperonic membrane (MWCO = 100 kDa) was 90 % and higher than the retentions for the membranes with the same polymeric solution (PS + Synperonic) and in which PAA was part of the CB composition (the MWCO of the membranes PS + Synperonic + PAA was 20 kDa). For membranes bellow 100 kDa MWCO, it was expected that the differences in the cut-offs would influence the rejection of hemicelluloses found in ThMP (which are mainly bellow the molecular mass of 100 kDa, according to (Thuvander and Jönsson, 2016) – Figure 8). As no analysis were performed e.g. on possible interactions between any of the additives and the feed solution or on the influence of pH, the retention results could be influenced by other parameters more than just MWCO. Also, MWCO are dependent on many factors – type of compound, conditions of the test, etc. – which means that the presented values in Table 1 and Table 2 may not be that sharp.

- PS + PEG + PAA: the range in retention of hemicelluloses for these membranes was between 89 % for the 0.7 % PAA and 97 % for 0.4 % and 1.5 % PAA. PAA does not seem to affect the retention of hemicellulose.
- PS + PEG + PMVEMA: The lowest retention was identified for 1.0 % PAA. Samples with the lowest and highest concentration of PMVEMA retained the same as the reference membrane.
- PS + Syn + PAA: retention of hemicelluloses decreases with an increase in PAA concentration, even though the differences are below 5 %.
- PS + Syn + PMVEMA: a slight decrease in retention is distinguished when PMVEMA is present.

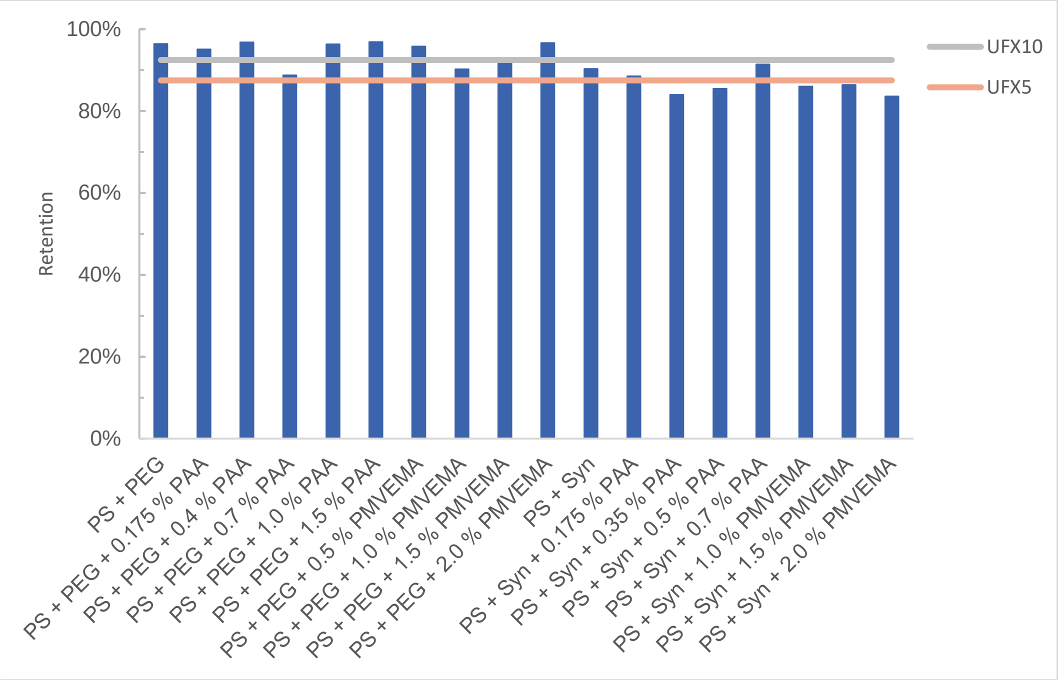


Figure 24: Hemicellulose retention results for the UF of ThMP process water with polysulfone (PS) membranes at 5 bar TMP.

The rejection results of hemicelluloses by the PES membranes are presented in Figure 25. The membrane PES + PEG + 0.2 Praestol 2540 seems to be an outlier as it retained 74 % of the hemicelluloses. Compared to the commercial membranes, hemicelluloses retention of the different tested membranes was similar, although it was interesting to note that the commercial membrane with the lowest MWCO (UFX5) presented lower retention values than the UFX10 (93 % of the hemicelluloses were retained by the UFX10 membrane). (Persson and Jönsson, 2010) report retention of hemicelluloses with the UFX5 spiral UF membrane above 90 % (Figure 23.A), which was higher than the 88 % obtained in here. The membrane PES + PEG-400 + 0.1 % Praestol 859 retained 94 % of the hemicelluloses, reinforcing its position as a suitable candidate for further studies as an alternative to UFX5. Furthermore, the retention of hemicelluloses by the membrane with 100 kDa MWCO (PS + Synperonic F-108) was also higher than UFX5 but lower than UFX10, even though the values were not that different. Additives in the CB do not seem to have influenced the retention properties of the membranes.

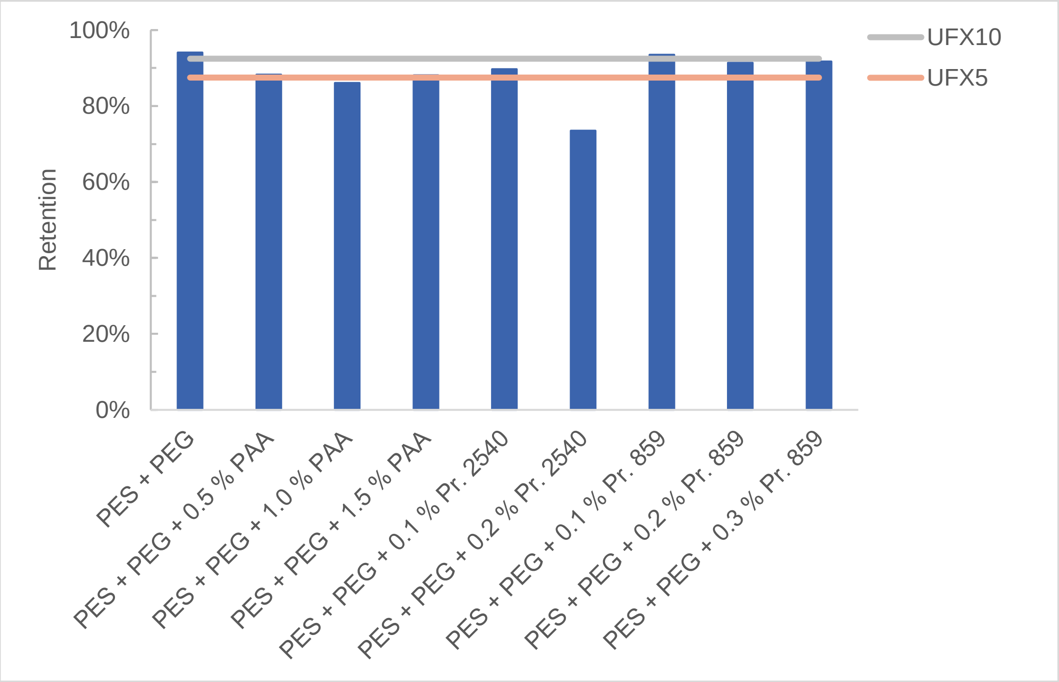


Figure 25: Hemicellulose retention results for the UF of ThMP process water with the polyether sulfone (PES) membranes at 5 bar TMP.

4.2.2 Total Lignin

Results of the lignin retention for the PS membranes are presented in Figure 26. The absolute values of retention were much lower (16 – 36 %) but profile of the results is very similar to that of Figure 24. The interesting part about these results was that, on average, the commercial membranes retained more lignin than the novel membranes. The explanation for the differences regarding the PS + Synperonic F-108 + PAA (including the reference membrane) may be the MWCO of this group of membranes (> 10 kDa), which is above the value for the molecular weight distribution of lignin in ThMP (<10 kDa) – Figure 8. When recovering hemicelluloses from ThMP process water, the purification value of the recovered compounds is important for further application. As lignin is the second major compound found on ThMP process water, the purification of hemicelluloses is largely affected by the lignin content on the retentate. With that in mind, the fact that the novel membranes retain lower percentages of lignin may be an advantage when compared to the membranes available in the market.

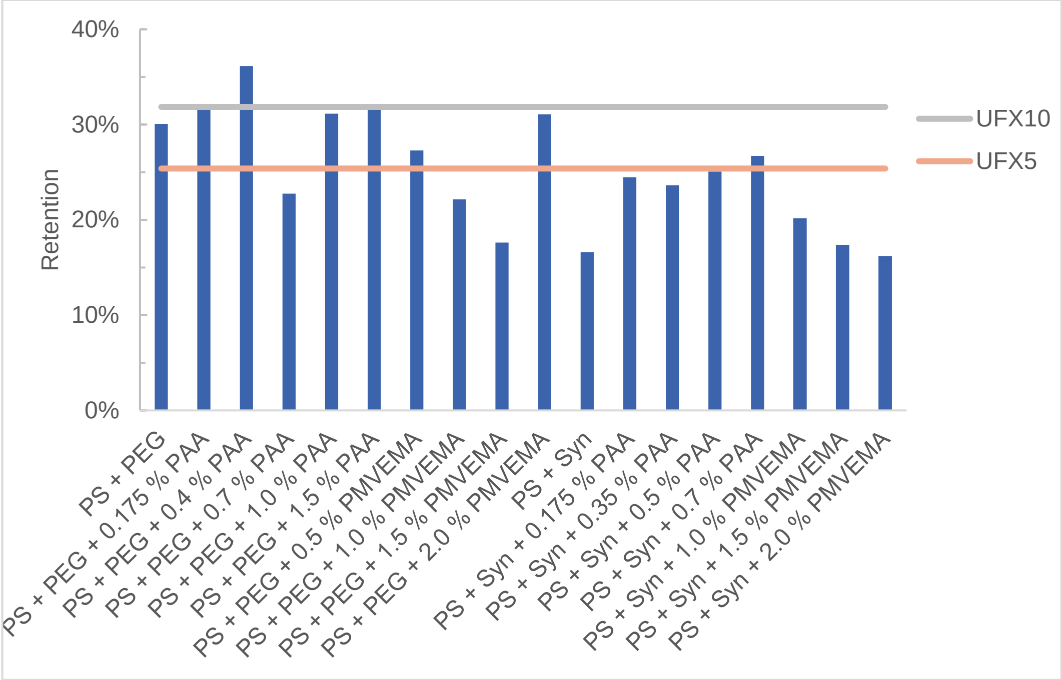


Figure 26: Total lignin retention results for the UF of ThMP process water with polysulfone (PS) membranes at 5 bar TMP.

The data regarding total lignin retention of the PES membranes at 5 bar TMP is reported in Figure 27. The retentions were between 17 % and 29 %. Just like for the retention of hemicelluloses, the membrane PES + Praestol + 0.2 % Praestol 2540 was the one with the lowest retention of lignin. During the permeability studies and the UF of ThMP process water (Figure 20), the fluxes achieved by this membrane were very low. The reduced fluxes to pure water and ThMP water, together with the lower retention values for both hemicelluloses and lignin could mean that higher concentrations of Praestol 2540 may be decreasing the hydrophilicity of the membrane instead of enhancing it. It is interesting that Praestol 859 seems to be a hydrophilic agent (see 4.1.5) while the opposite is verified for Praestol 2540 since the first is a cationic polyelectrolyte and the later anionic. The charge of the groups could therefore play an important role in the overall hydrophilicity of the membranes.

All the additives in the CB seem to induce lower retention values of lignin, not only compared to the reference membrane but also when compared to the commercial membranes – specially with UFX10. Once more, the retention of total lignin for the UFX5 membrane was not only lower than the retention verified by the UFX10, which was in contrary to the expected, but also lower to the values reported by (Persson and Jönsson, 2010) – Figure 23.A, meaning much better separation ability.

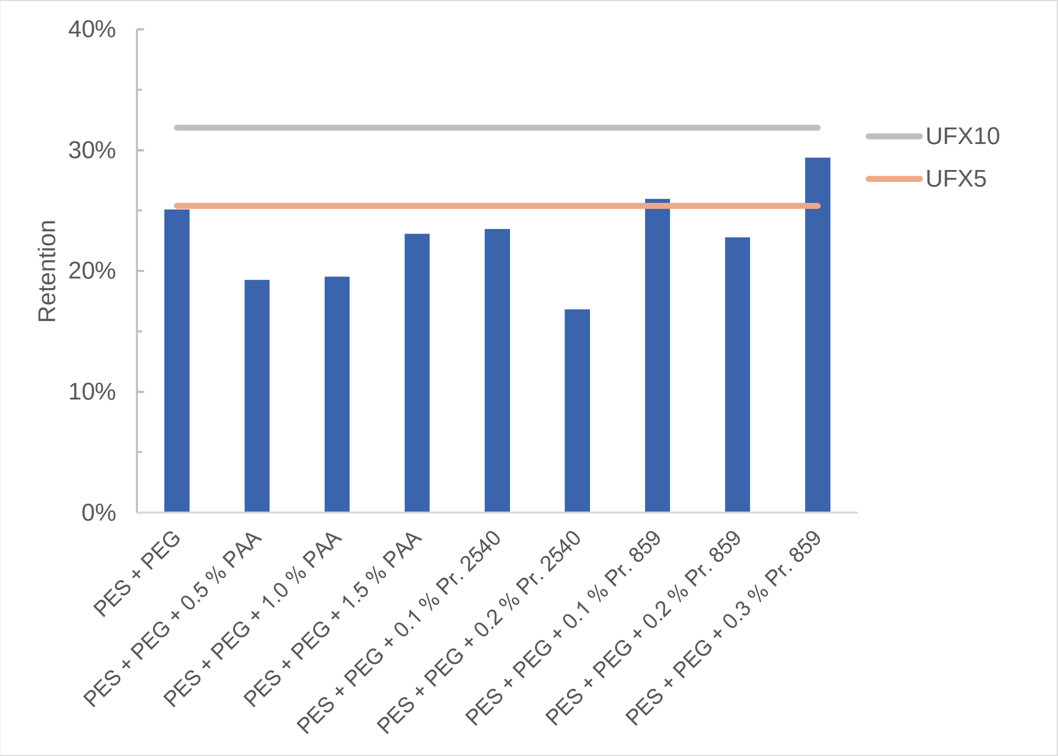


Figure 27: Total lignin retention results for the UF of ThMP process water with polyether sulfone (PES) membranes at 5 bar TMP.

4.3 Potato Fruit Water – PWF, PFW fluxes, Fouling and Cleaning

From all the membranes tested for UF of ThMP, a restrict group was selected for the second part of the work. The two feed solutions used in this study – ThMP process water and PFW – present very distinctive properties. For that reason, it is not wise to assume that a membrane suitable for the filtration of ThMP could perform identically for PFW filtration. In fact, it is very unlikely that such scenario is verified. Indeed, the characteristics of the feeds and operational conditions influence the filtration process and, in this case, some of the parameters were very different. For example, 1) ThMP and PFW composition differs, which means that the the compounds found in each feed and possible fouling agents are different. While for ThMP, major foulants were colloidal particles and polysaccharides (Puro *et al.*, 2011; Thuvander *et al.*, 2018), in the case of PFW, performance may be affected by proteins (Dabestani *et al.*, 2017); 2) the temperature at which the UF experiments were conducted was distinctive, directly impacting the viscosity of the solution and subsequently the fluxes achieved during UF; 3) pH of the feed solution and charge of the molecules affects the interactions between the feed solution and the membrane.

The fact that not all the membranes were tested in this second part of the experimental trials was never related to the criteria that *if a membrane is no good for UF of ThMP then it is no good for UF of PFW*. As the time was limited in this second part of the work, we considered membranes that, according to the ThMP process water filtration tests seemed to present better structure and mechanical strength. In addition, it was also evaluated the initial PWF of the pristine membranes, FRR and whether the membranes were degraded by the cleaning agent or other compounds.
In total, twenty-nine membranes were successfully tested during the filtration of ThMP water, including two commercial membranes (UFX5 and UFX10). Of those, fifteen were tested for PFW. All the membrane samples used for UF of PFW belonged to the same production batch of the ones tested with ThMP process water. No membrane was re-used for any of the performance tests and these were tested in groups of 3, one per each UF cell (Figure 13), according to following order:

- PS + PEG-400; PS + PEG-400 + 1.0 % PAA; PS + PEG-400 + 1.5 % PAA.
- PS + Synperonic F-108; PS + Synperonic F-108 + 0.35 % PAA; PS + Synperonic F-108 + 0.7 % PAA.
- PES + PEG-400; PES + PEG-400 + 0.1 % Praestol 2540; PES + PEG-400 + 0.1 % Praestol 859.
- PES + PEG-400 + 1.0 % PAA; PES + PEG-400 + 0.2 % Praestol 859; PES + PEG-400 + 0.3 % Praestol 859.
- PES + PEG-400 + 1.5 % PAA; 2 randomly selected membranes not relevant for the study.

The list of PS and PES membranes tested for UF of PFW can be found in Table 13 and Table 14.

Table 13: Composition of polymeric solutions and concentration of additives in the CB as well as MWCO of the PS membranes tested for the filtration of PFW. Provided by the Institute of Physical Organic Chemistry - National Academy of Sciences of Belarus-

Polymer solution	**Type of additive in coagulation bath**	**Additive concentration (%)**
20 % Polysulfone 10 % PEG-400 DMAc	distilled water	
	PAA (M_w=250 000)	1.0
		1.5
20 % Polysulfone 7 % Synperonic DMAc	distilled water	
	PAA (M_w=250 000)	0.35
		0.7

Table 14: Composition of polymeric solutions and concentration of additives in the CB as well as MWCO of the PES membranes tested for the filtration of PFW. Provided by the Institute of Physical Organic Chemistry - National Academy of Sciences of Belarus.

Polymer solution	**Type of additive in coagulation bath**	**Additive concentration (%)**
22% Polyether sulfone 10% PEG-400 10% Glycerol DMAc	distilled water	
	PAA (M_w=250 000)	1.0
		1.5
	Praestol 2540 (10<Mn (10^6 Da)<14)	0.1
	Praestol 859 (10<Mn (10^6 Da)<14)	0.1
		0.2
		0.3

4.3.1 PS + PEG-400 + PAA

The results for the filtration of PFW with membranes of PS, PEG-400 and different concentrations of PAA in the CB are presented in Figure 28. The influence of fouling in the membranes can be assessed by the FRR in Table 15. The addition of PAA in the CB seems to increase the fluxes during the filtration of PFW although the critical flux region was achieved not only for the reference membrane but also for the 1.5 % PAA.

Based on the FRR_{rinse}, the hydraulic permeability of the membranes with additives after rinsing seemed to be closer to the initial value when compared to the reference membrane. These two results combined support the conclusion that the interactions between fouling agents in the PFW and the membrane may be reduced by the addition of PAA to the CB. In contrast, cleaning agent and cleaning procedure seem to be less efficient in the membranes with additives as the FRR_{clean} of the membrane with no PAA is higher. If a different cleaning agent or cleaning procedure was considered, the membranes with this composition could be suitable for the filtration of PFW, at least based on the flux results.

At this point, two tests were performed with these three membranes: first with ThMP process water as a feed solution and now with PFW. One part of both tests was performed in identical conditions: initial PWF measurements, allowing comparisons between the results. In Figure 15.B, just by looking at the permeability of the membrane where 1.0 % PAA was added to the CB, the initial pure water permeability of the membrane is lower than the reference membrane while in Figure 28.B, the same permeability is higher than the membrane with no additive.

Since the conditions of operation were the same, the reason for this difference is most likely due to the low fluxes and problems in measuring the exact fluxes.

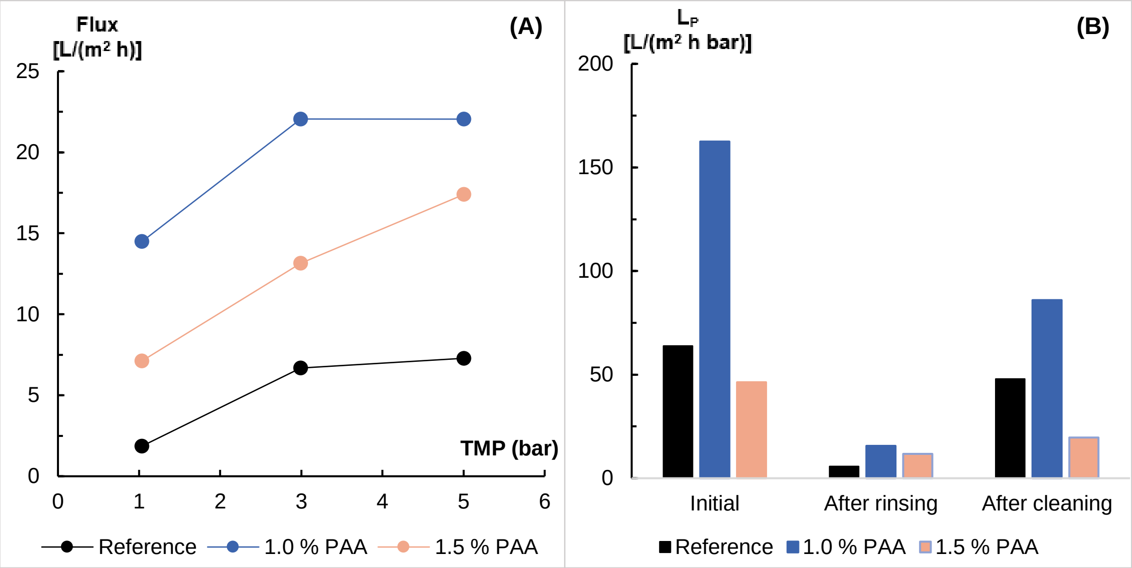


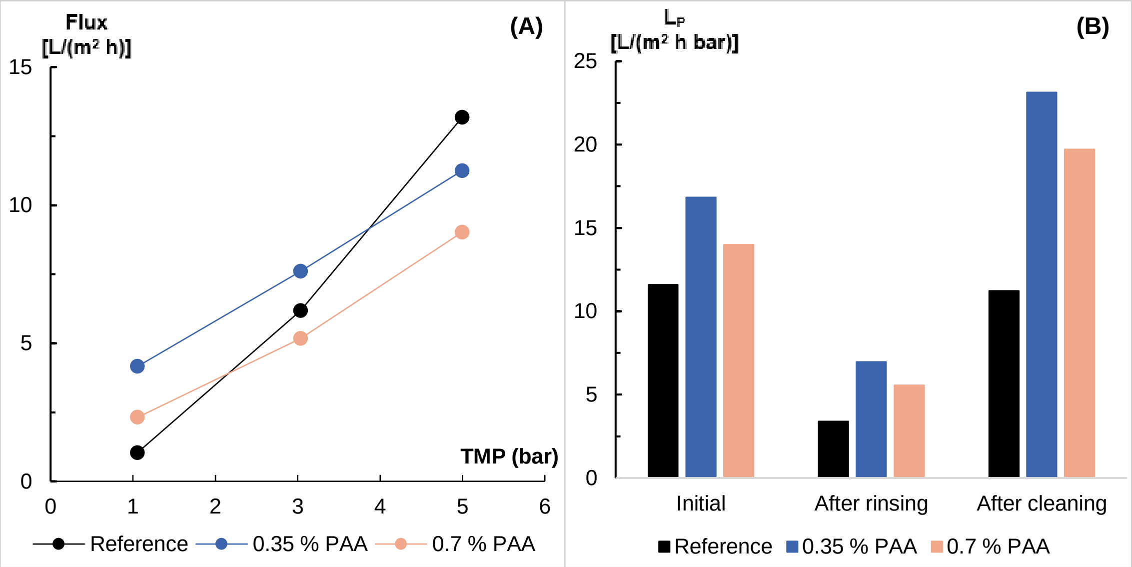
Figure 28: Performance of the PS + PEG-400 + PAA membranes on UF of potato juice– ***(A)*** *influence of TMP and PAA concentration on flux: concentrations of PAA in the coagulation bath were 1.0 % and 1.5 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 °C and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of PAA in the hydraulic permeability (L_P) of PS + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of potato juice and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 °C and CFV of 0.3 m/s.*

Table 15: FRR of the PS + PEG-400 + PAA after UF of PFW and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 (FRR_{clean}). Comparison between membranes of PS and PEG-400 produced with different concentrations of PAA on the CB.

Coagulation bath additive	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
PS + PEG-400	9	75
1.0 % PAA	10	53
1.5 % PAA	25	43

4.3.2 PS + Synperonic + PAA

Figure 29 presents the influence of TMP in the flux during the filtration of PFW and pure water permeability across the experimental trial of PS and Synperonic membranes with different concentrations of PAA in the CB. Compared to the reference membrane, the initial water permeability values of membranes with PAA support the theory that this additive increases the hydrophilicity of the membrane. Nevertheless, all the permeabilities were much lower than the values registered during the filtration test for the ThMP process water in 4.2.2, Figure 16.B. During the filtration of PFW, an increase in pressure proved to be more favorable for the reference membrane. Ideally, if the additive enhanced the performance properties of the membrane, expected results were that the flux of the membranes with additives was higher than the flux of the reference membrane. This would be a result of more hydrophilic membranes and less interactions between the membrane and the compounds from the feed solution. The fact that the flux of the reference membrane increases more than the flux of the membranes with additives could be a sign that the presence of PAA induces fouling accumulation on the membrane, although there is no knowledge regarding the mechanism of such fouling. It may also be the result of more impact of concentration polarization due to a rougher surface. After filtration of the PFW and rinsing with deionized water, the FRR of the membrane with additives were higher (Table 16) than the unmodified membrane. PAA may possibly increase the fraction of reversible fouling that can be removed without additional cleaning agents. After the cleaning step, FRR's of the modified membranes were very high. Even though additive loss may be happening, it is wise not to forget experimental errors associated to the low fluxes.



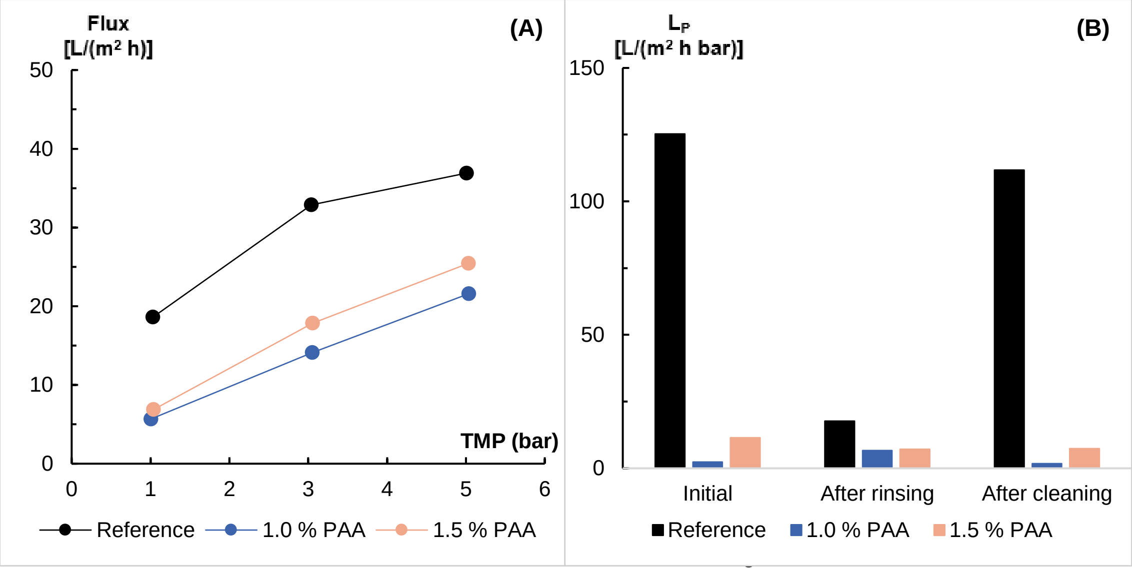
influence of TMP and PAA concentration on flux: concentrations of PAA in the coagulation bath were 0.35 % and 0.7 %; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 °C and 0.3 m/s, respectively ***(B)*** *comparison between the influence of different concentrations of PAA in the hydraulic permeability (L_P) of PS + Synperonic membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of potato juice and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 °C and CFV of 0.3 m/s.*

Table 16: FRR of the PS + Synperonic F-108 + PAA after UF of PFW and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 (FRR_{clean}). Comparison between membranes of PS and Synperonic F-108 produced with different concentrations of PAA on the CB.

Coagulation bath additive	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
PS + Synperonic F-108	29	97
0.35 % PAA	41	137
0.7 % PAA	40	141

4.3.3 PES + PEG-400 + PAA

PES polymeric membranes with PEG-400 and 1.0 % and 1.5 % PAA were tested and compared to a reference membrane regarding UF of PFW. Figure 30 and Table 17 show the results of this test. The initial PWF of the reference membrane is much higher than the PWF of the membranes with PAA and so the effect of the additive is contrary of the desired. Similar results were noticed in Figure 19.B (Initial Permeability). Regarding the UF of PFW, in Figure 30.A, the fluxes of the membranes with the additive were lower than the fluxes of the reference membrane. The reference membrane seems to be already operating in the critical flux region while the modified membranes graphical representation is closer linear form. FRR were inconclusive according to values reported in Table 17. While the cleaning agent decreased the level of fouling significantly, it proved to be ineffective for the membrane with 1.5 % PAA. Also, an experimental error during the measurements of the PWF after rinsing (Figure 30.B) invalidated the results regarding cleaning effectiveness on the 1.0 % PAA membrane. Once again, it is extremely difficult to draw any conclusions from such low fluxes.



TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 °C and 0.3 m/s, respectively ***(B)*** *comparison between the influence of different concentrations of PAA in the hydraulic permeability (L_P) of PES + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of potato juice and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 °C and CFV of 0.3 m/s.*

Table 17: FRR of the PES + PEG-400 + PAA after UF of PFW and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$). Comparison between membranes of PES and PEG-400 produced with different concentrations of PAA on the CB.

Coagulation bath additive	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
PES + PEG-400	14	89
1.0 % PAA	346*	90
1.5 % PAA	63	65

* experimental error during the experimental trial.

4.3.4 PES + PEG-400 + Praestol 2540 & Praestol 859

Figure 31 shows the results of the experimental performance tests for the PES membranes with PEG-400 as an additive in the polymeric solution and different concentrations of Praestol electrolytes in the CB. Initial water permeabilities of the membranes with Praestol 859 were lower than the reference membrane whilst the same parameter for the membrane with Praestol 2540 was the highest of the test. In Figure 21.B, for the membranes with Praestol 859, the reference membrane initial water permeability was much lower than the recorded in this test.

When filtering PFW, the fluxes of the reference membrane were higher than the fluxes of the membranes with Praestol. In addition, the expectations were that with the rising in the transmembrane pressure, fluxes would increase as well. A slight decrease in flux was registered for the 0.1 % Praestol 859 and 0.1 % Praestol 2540, probably due to low fluxes and sensitivity errors.

The results in here reported contradict the idea that Praestol 859 enhances the hydrophilicity while, in contrats, Praestol 2540 contributes to a reduction. Although there was no real confirmation regarding the referred hypothesis, the test of UF of ThMP process water was more reliable than the UF of PFW.

Rinsing with deionized water was more efficient for the membranes with Praestol 859 and the cleaning protocol with Ultrasil 10 proved to be efficient for all the membranes regarding the recovery of the initial PWF (Table 18).

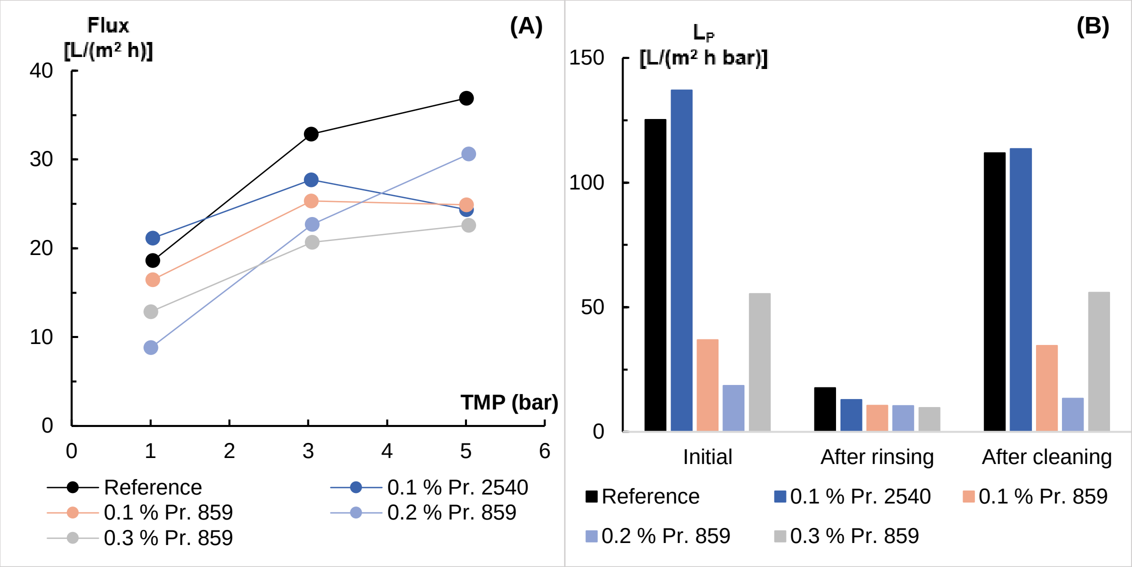


Figure 31: Performance of the PS + PEG-400 + Pr. 2540 & Pr- 859 membranes on UF of PFW– ***(A)*** *influence of TMP and Pr.2540 or Pr- 859 concentration on flux: concentration of Pr.2540 was 0.1 % and concentrations of Pr- 859 were between 0.1 % and 0.3 % in the coagulation bath; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 ᵒC and 0.3 m/s, respectively* ***(B)*** *comparison between the influence of different concentrations of Pr. 2540 and Pr. 859 in the hydraulic permeability (L_P) of PS + PEG-400 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of potato juice and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 ᵒC and CFV of 0.3 m/s.*

Table 18: FRR of the PES + PEG-400 + Pr. 2540 & Pr. 859 after UF of PFW and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$). Comparison between membranes of PES and PEG-400 produced with different concentrations of Pr. 2540 & Pr. 859 on the CB.

Coagulation bath additive	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
PES + PEG-400	14	89
0.1 % Praestol 2540	9	83
0.1 % Praestol 859	29	94
0.2 % Praestol 859	57	72
0.3 % Praestol 859	18	102

4.3.5 Commercial Membranes – UFX5, UFX10

Commercial membranes UFX5 and UFX10 were tested for protein recovery from PFW and the results are presented in Figure 32. Overall, the novel membranes flux profiles were similar to the commercial membranes and the fluxes for the PFW filtration were in the same magnitude order. Although the limiting flux region was reached for UFX10 and critical flux for UFX5, permeability of the membrane with the larger MWCO (UFX10) was bigger than the permeability of UFX5, just as expected.

After rinsing with deionized water, the membranes were heavily fouled and after cleaning with Ultrasil 10, the recovery of the initial permeability was higher for UFX10 (Table 19).

In comparison to the commercial membranes, most of the membranes tested in this thesis under these conditions proved to be viable alternatives to the filtration of PFW but no significant improvements were perceived when additives were part of the CB.

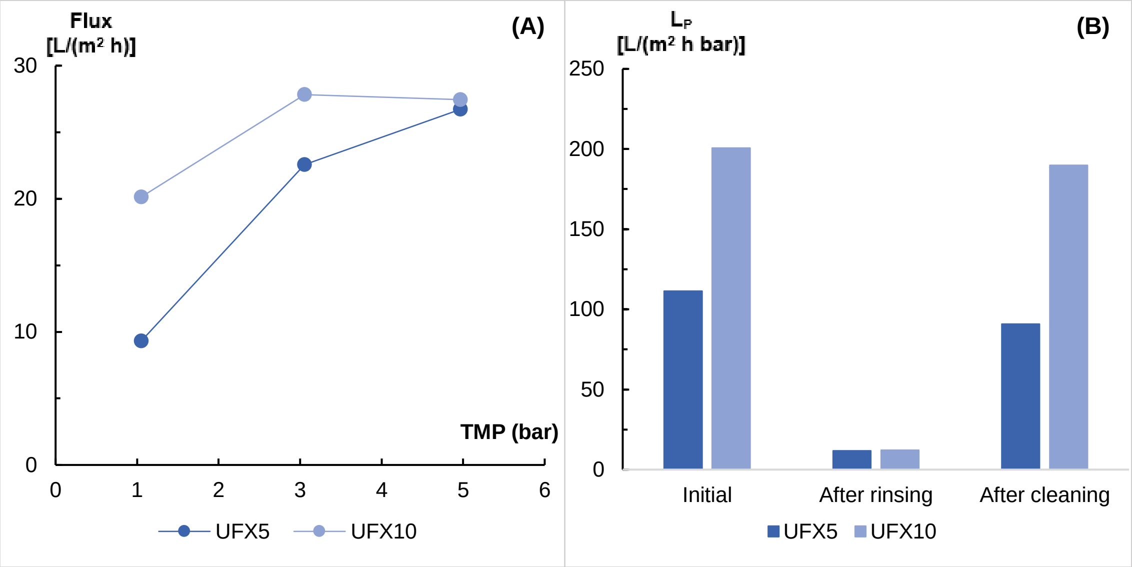


*Figure 32: Performance of the commercial membranes UFX5 and UFX10 on UF of PFW – **(A)** influence of TMP on the flux of commercial membranes; TMP 1, 3, 5 bar; constant temperature and cross flow velocity (CFV) of 70 ºC and 0.3 m/s, respectively **(B)** hydraulic permeability (L_P) of UFX5 and UFX10 membranes, based on the pure water flux (PWF) measurements conducted in the beginning of the test (Initial), after the filtration of potato juice and rinsing with deionized water (After rinsing) and after cleaning with Ultrasil 10 (After cleaning); the presented results consider an average of the logg data for 1, 2 and 3 bar TMP, at 30 ºC and CFV of 0.3 m/s.*

Table 19: FRR of the commercial membranes UFX5 and UFX10 after UF of PFW and rinsing with deionized water (FRR_{rinse}) and FRR after cleaning with Ultrasil 10 ($FRRc_{lean}$).

Membrane	**FRR_{rinse} (%)**	**FRR_{clean} (%)**
UFX5	10	81
UFX10	6	92

The comparison between tests regarding the ultrafiltration of PFW and ultimately conclusions on whether the novel membranes performed better than the commercial membranes was very difficult based on the low fluxes. As stated in 3.2.1, permeate fluxes were calculated based on the difference of permeate weight over a certain time gap. For the UF of ThMP, this interval of time was kept constant for all the tests, because the fluxes were quite high and constant, as well as the influence of fouling on the membranes performance was very low. The same was not possible for the UF of PFW. The number of flux points recorded for each TMP varied from trial to trial according to the outward perception of the flux. It is true that, according to the information reported in 4.3, not all the membranes from the same group (each group contains the same polymeric solution plus additive in the CB, as well as reference membrane) were tested in the same trial and a comparison was still presented between them. The reason for that was because the goal of this work was to compare the effect of the additives in the membranes performance. Now, comparing all the membranes with each other and even with the commercial membranes would represent an additional error and quite possibly provide false results, reason why the comparison was not realized. Instead, and since both commercial membranes were tested under the same conditions, this section may be relevant for further studies regarding the comparison of UFX5 and UFX10 for the UF of PFW, a novel topic that, to the best of my knowledge, is yet to be reported.

4.4 Potato Fruit Water – Protein Retention

UF membranes protein retention values were determined according to total nitrogen measurements. The nitrogen to protein content on the PFW is directly correlated according to the Jones' factor (6.25) (Jones, 1941).

In food technology research, protein analysis tests are usually performed according to the Dumas method while spectrophotometric measurements are more common in wastewater applications. The apparatus available to perform the analysis according to the Dumas method, requires considerable amounts of volume per sample. The volumes of permeate collected during the PFW UF tests were very low due to the low fluxes. For that reason, it was not possible to measure TN for all the membranes according to the Dumas method. Instead, the samples collected during the experiments of UFX5 and UFX10 membranes were analyzed via both methodologies and a comparison between the retention results is presented in Table 20.

The results show that, although the spectrophotometric procedure was not the most adequate for this type of samples, it provided reliable results. The difference was therefore irrelevant for the study in question because as the membranes retained about 60 % of the proteins in the PFW.

Table 20: Comparison between protein retention by the Dumas' and Spectrophotometric methods.

Membrane	TMP (bar)	Dumas Method (%)	Spectrophotometric Method (%)
UFX5	1	59	61
	3	60	63
	5	62	58
UFX10	1	56	60
	3	59	54
	5	60	59

In line with what was done during the analysis of retention results for the UF of ThMP process water, the comparison on protein rejection of the PFW stream discussed in this section was considered for permeate and feed samples collected during the log time at 5 bar. The remaining retention results can be consulted in the Appendix – Table 26. Figure 33 shows the results of protein retention for the membranes tested in this thesis in comparison to the commercial membranes.

In general, the membranes tested retained between 53 % and 60 % of the the proteins in the PFW. The commercial membranes UFX5 and UFX10 retained 58 % and 59 %, respectively. It was not possible to identify which type of proteins were retained from the different proteins that can be found on the potato as no analysis was performed on the composition of the PFW both prior and after centrifugation. Considering the range in MWCO of the membranes and the fact that about half of the total amount of proteins present in the potato are patatins, these should account for a vast majority of the retained proteins. Four membranes retained lower amounts of proteins:

- PS + Synperonic – 25 % protein retention.
- PES + PEG + 1.0 % PAA – 33 % protein retention.
- PES + PEG + 0.2 % Praestol 859 – 35 % protein retention.
- PES + PEG + 0.3 % Praestol 859 – 35 % protein retention.

The PS + Synperonic reference membrane sample was broken when it was removed from the module after the test. It is unknown whether the PFW filtration experiment was the reason why the membrane broke, but the lower retention of proteins was almost certainly a consequence of proteins not being retained in the regions where the membrane was broken. For the remaining membranes where the retention was lower, the values were influenced by the TMP as the retention decreased with an increase in the TMP (values presented in Appendix – Table 26). Compressibility may play an important role.

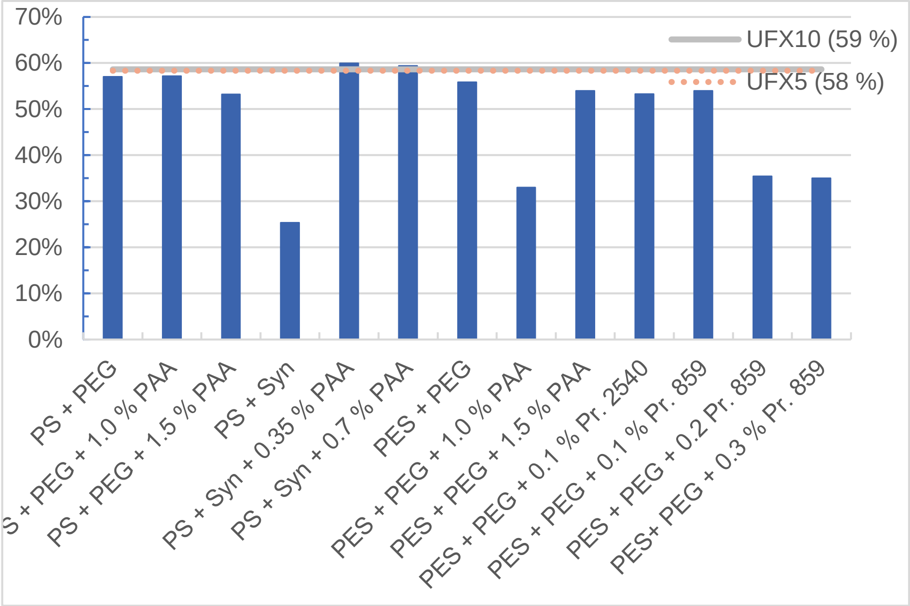


Figure 33: Protein retention results for the UF of PFW with polysulfone (PS) and polyether sulfone (PES) membranes at 5 bar TMP.

Conclusions

In the literature review presented in this work, it was demonstrated the value in treating waste and process streams from the pulp and paper and food and beverage industries using membrane processes. In addition, a broad part of the discussion was centred on membrane fouling and how it affects the performance of the membranes, diminishing the quality of the filtration process. A recently new concept was introduced – production of membranes with enhanced performance capacities and antifouling properties through the addition of hydrophilic agents in the CB. So, this work summarizes the results of the UF of process water from a ThMP mill and PFW from a starch production plant with PS and PES flat sheet membranes, modified with either PEG-400 or Synperonic F-108 and different concentrations of the following polyelectrolytes: PAA, PMVEMA, Praestol 859 and Praestol 2540.

The novel modified membranes were studied in regard to their performance during UF of ThMP process water, the influence of fouling on the membranes and the capacities to retain hemicelluloses and lignin.

The results suggest that PAA may essentially improve the hydrophilicity of the membrane and reduce the foulants interactions with the membrane for both PS and PES membranes. Higher fluxes were achieved for during the UF of ThMP process water. A limited amount of membranes where PAA was introduced in the CB contradict these conclusions possibly because of the formation of a more dense and thicker selective layer during phase inversion. The FRR for the membranes with PAA in the CB were inconclusive. If for the membranes PS + PEG + PAA, they all recorded FRR at least equal if not much better than the reference membrane, the values for the PES + PEG-400 + PAA membranes were between 111 % and 129 %. Such high values raise concerns regarding changes on the membranes structure and morphology. The same can be said in one of the membranes of PS + Synperonic F-108 + PAA and, on the contrary, a recovery of 8 % on a different membrane indicated the possibility of pore blockage.

As for the PS membranes modified with PMVEMA, fluxes during UF of ThMP process water of the membranes PS + PEG decreased, in comparison to the reference, suggesting an hydrophobic effect. Some of the FRR of the membranes PS + Synperonic + PMVEMA were above 300 %, which clearly indicates some damage of the membranes.

Praestol 859 proved to be very promising as a modifying agent of PES membranes for the UF of ThMP process water as the reference membrane recorded the lowest flux during the UF of this process stream. Furthermore, FRR also increased in the modified membranes.

As for Praestol 2540, the results were inconclusive regarding fluxes during ThMP filtration because only two concentrations of this additive were considered during membranes preparation and compared to the reference, one of them achieved higher fluxes and the other lower.

In the retention results of hemicelluloses and lignin, no major trendlines were distinguished. Apart from the lower retention by the membrane PES + PEG-400 + 0.2 % Praestol 2540 (74 %), all the remaining membranes retained more than 80 % of the hemicelluloses (84 % to 97 %). Lignin retention was between 16 % and 36 %. It is not clear the reason for the difference in the results amongst all the membranes.

Compared to the commercial membranes, none of the novel membranes was able to achieve a flux during the filtration of ThMP process water as high as the UFX10 – 359 L/(m^2 h) at 5 bar TMP. Compared to the UFX5, the opposite result was observed for quite a lot of the novel membranes. The lower MWCO of UFX5 (5 kDa) may justify the differences. The membrane PES + PEG-400 + 0.1 % Praestol 859 could pose as a viable alternative to UFX5, not only because of the higher flux [247 L/(m^2 h) at 5 bar TMP, compared to UFX5 105 L/(m^2 h) at 5 bar TMP] but also due to the higher FRR (79 % compared to 54 %). For the UFX10, 93 % of the hemicelluloses and 32 % of the lignin were retained while the values for the UFX5 were 88 % and 25 %. A special note to the unpredictable result of higher retention by the UFX10 (10 kDa MWCO) than the UFX5 (5 kDa MWCO).

For the UF of PFW, ten of the twenty-four membranes with additives were considered, as well as the three reference membranes and both commercial membranes. The quality of the results was highly affected by the very low fluxes which made it difficult to compare how type and concentration of the additives may influence fluxes during the UF of PFW and FRR. As for the protein retention results, most of the novel membranes retained between 53 % and 60 %, which was similar to the percentages reported for UFX5 and UFX10 (58 % and 59 %, respectively).

The major conclusion from this work was that improved hydrophilicity and flux enhancement was achieved by surface modification of a PES and PEG-400 based membrane with Praestol 859.

Future Considerations

Quite a few different approaches can be conducted in line with the work here presented.

First and foremost, the membranes not tested for the UF of PFW should be tested in order to provide a full comparison between all the membranes and different concentrations of additives in the CB.

Apart from that, instead of using so complex feed solutions like ThMP process water and PFW for the UF experiments, more simple solutions such as BSA could provide more simple and understandable results. The complex ThMP process water and PFW made it very difficult to understand which compounds present in solution may have interacted with the membranes.. It is also difficult to ensure that the initial composition of the feed is the same in every study with ThMP water and PFW. A more controlled and standard feed composition could provide more comparable results.

One other different scenario that could be considered was a concentration study. All the tests were performed with the retentate and permeate being recirculated into the feed tank (apart from when samples were collected).

For the ThMP process water, several different operational conditions could be considered. This work was focused on testing the same CFV and different TMP. Obviously, different CFV could be considered, which could lead to very different results. One other option was to work at constant pressure and crossflow velocity but increase the time of ultrafiltration, which was very short for this study.

The influence of pH and how it may affect the stability of the additives in the membrane as well as how it may influence fouling was never considered in this test. For that reason, pH measurements should be conducted. For the PFW, the charge of the proteins according to the pH level and their isoelectric point may increase the interactions between membrane-solute. Besides, Praestol 2540 and Praestol 859 present different charges.

For the PFW, the temperature at which the tests were performed was very low. Although it was important to keep this temperature of 20 °C as it is the temperature used in the plant that provided the potato juice, viscosity is highly dependent on the temperature and that was most likely the reason for the low fluxes. So, one single test of PFW filtration at a higher temperature could be relevant to understand the influence of the low temperature in the UF process. If the productivity (fluxes) go up considerably, it might be worth the investment cost for the heating of the feed.

Finally, different cleaning agents and protocols may be considered. For some of the membranes, the permeability levels after the cleaning with the alkaline agent proved to be intriguing. For those cases in particular, an additional cleaning cycle could be helpful to understand whether or not the cleaning agent may be influencing the membranes structure. Not only that but also longer times of cleaning or several consecutive cleaning rounds without ThMP water or PFW filtration, followed by measurements of PWF could indicate if the considered cleaning agent was changing the properties of the membranes.

All the suggestions presented before focus on the same experimental set-up and in the idea of a single UF operation. If a MF pre-treatment stage was introduced, the results of the UF would most likely improve. Not only that but a DF stage after the UF would also be beneficial for the quality of the recovered product.

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Appendix

Table 21:Permeability of pure water during the UF of ThMP process water – average values from the data points recorded for 1, 2 and 3 bar of TMP, at a CFV of 0.3 m/s and 30 °C of temperature.

Membrane	**Initial L_P [L/(m2 h bar)]**	**After rinsing L_P [L/(m2 h bar)]**	**After cleaning L_P [L/(m2 h bar)]**
PS + PEG	113	14	36
PS + PEG + 0.175 % PAA	203	44	106
PS + PEG + 0.4 % PAA	161	22	55
PS + PEG + 0.7 % PAA	54	17	25
PS + PEG + 1.0 % PAA	85	37	76
PS + PEG + 1.5 % PAA	53	29	51
PS + Syn	274	10	161
PS + Syn + 0.175 % PAA	126	61	177
PS + Syn + 0.35 % PAA	270	69	266
PS + Syn + 0.5 % PAA	175	7	14
PS + Syn + 0.7 % PAA	164	31	171
PS + PEG + 0.5 % PMVEMA	58	3	52
PS + PEG + 1.0 % PMVEMA	27	9	12
PS + PEG + 1.5 % PMVEMA	65	4	29
PS + PEG + 2.0 % PMVEMA	27	7	27
PS + Syn + 1.0 % PMVEMA	143	23	270
PS + Syn + 1.5 % PMVEMA	69	17	239
PS + Syn + 2.0 % PMVEMA	34	7	46
PES + PEG	52	12	23
PES + PEG + 0.5 % PAA	12	10	16
PES + PEG + 1.0 % PAA	10	10	12
PES + PEG + 1.5 % PAA	14	12	15
PES + PEG + 0.1 % Pr. 2540	89	33	77
PES + PEG + 0.2 % Pr. 2540	6	4	5
PES + PEG + 0.1 % Pr. 859	58	27	46
PES + PEG + 0.2 % Pr. 859	14	12	13
PES + PEG + 0.3 % Pr. 859	68	26	56

Membrane	Initial L_P [L/(m2 h bar)]	After rinsing L_P [L/(m2 h bar)]	After cleaning L_P [L/(m2 h bar)]
UFX5	126	19	67
UFX10	323	45	246

Table 22: ThMP process water flux for each membrane at each TMP – average TMP and flux values from the data points recorded at 70 °C and CFV of 0.3 m/s.

Membrane	TMP (bar)	Flux [L/(m2 h)]
PS + PEG	1,07	17
	3,02	75
	5,02	95
PS + PEG + 0.175 % PAA	1,07	112
	3,02	218
	5,02	272
PS + PEG + 0.4 % PAA	1,07	31
	3,02	96
	5,02	130
PS + PEG + 0.7 % PAA	1,09	11
	3,01	102
	5,09	91
PS + PEG + 1.0 % PAA	1,09	115
	3,01	210
	5,09	266
PS + PEG + 1.5 % PAA	1,09	88
	3,01	187
	5,09	246
PS + Syn	1,02	11
	3,06	49
	5,04	72
PS + Syn + 0.175 % PAA	1,02	124
	3,06	265
	5,04	320

Membrane	TMP (bar)	Flux [L/(m2 h)]
PS + Syn + 0.35 % PAA	1,02	199
	3,06	270
	5,04	269
PS + Syn + 0.5 % PAA	1,04	12
	3,08	14
	5,03	13
PS + Syn + 0.7 % PAA	1,04	67
	3,08	142
	5,03	191
PS + PEG + 0.5 % PMVEMA	1,04	5
	3,08	12
	5,03	17
PS + PEG + 1.0 % PMVEMA	1,05	11
	3,02	12
	5,05	59
PS + PEG + 1.5 % PMVEMA	1,08	6
	3,14	15
	5,08	17
PS + PEG + 2.0 % PMVEMA	1,05	17
	3,02	36
	5,05	49
PS + Syn + 1.0 % PMVEMA	1,03	65
	2,99	158
	5,07	197

Membrane	TMP (bar)	Flux [L/(m2 h)]
PS + Syn + 1.5 % PMVEMA	1,03	40
	2,99	98
	5,07	134
PS + Syn + 2.0 % PMVEMA	1,04	13
	3,09	40
	5,05	55
PES + PEG	1,06	11
	2,98	74
	5,04	92
PES + PEG + 0.5 % PAA	1,04	22
	3,09	80
	5,05	126
PES + PEG + 1.0 % PAA	1,07	29
	2,99	78
	5,05	121
PES + PEG + 1.5 % PAA	1,07	24
	2,99	83
	5,05	124
PES + PEG + 0.1 % Pr. 2540	1,06	97
	2,98	205
	5,04	272

Membrane	TMP (bar)	Flux [L/(m2 h)]
PES + PEG + 0.2 % Pr. 2540	1,05	2
	3,02	8
	4,98	18
PES + PEG + 0.1 % Pr. 859	1,06	76
	2,98	184
	5,04	247
PES + PEG + 0.2 % Pr. 859	1,05	29
	3,02	86
	4,98	139
PES + PEG + 0.3 % Pr. 859	1,05	69
	3,02	172
	4,98	237
UFX5	1,02	35
	3,04	101
	5,02	105
UFX10	1,02	118
	3,04	289
	5,02	359

Table 23:Retention of hemicelluloses and lignin for ach membrane at each TMP during UF of ThMP process water.

Membrane	**Hemicelluloses Retention (%)**			**Total Lignin Retention (%)**		
TMP (bar)	**1**	**3**	**5**	**1**	**3**	**5**
PS + PEG	-	97	96	-	27	30
PS + PEG + 0.175 % PAA	95	95	95	24	25	32
PS + PEG + 0.4 % PAA	-	97	97	-	27	36
PS + PEG + 0.7 % PAA	85	87	89	15	20	23
PS + PEG + 1.0 % PAA	95	97	96	20	28	31
PS + PEG + 1.5 % PAA	96	97	97	22	28	32
PS + Syn	-	83	90	17	14	17
PS + Syn + 0.175 % PAA	94	91	89	16	21	24
PS + Syn + 0.35 % PAA	83	78	84	16	21	24
PS + Syn + 0.5 % PAA	-	-	86	-	-	25
PS + Syn + 0.7 % PAA	89	89	91	13	19	27
PS + PEG + 0.5 % PMVEMA	-	-	96	-	-	27
PS + PEG + 1.0 % PMVEMA	-	-	90	-	18	22
PS + PEG + 1.5 % PMVEMA	90	89	92	16	15	18
PS + PEG + 2.0 % PMVEMA	95	96	97	23	26	31
PS + Syn + 1.0 % PMVEMA	92	87	86	13	17	20
PS + Syn + 1.5 % PMVEMA	-	87	86	-	14	17
PS + Syn + 2.0 % PMVEMA	-	87	84	-	14	16
PES + PEG	92	93	94	18	21	25
PES + PEG + 0.5 % PAA	80	87	88	14	17	19
PES + PEG + 1.0 % PAA	-	84	86	-	18	20
PES + PEG + 1.5 % PAA	-	87	88	-	20	23
PES + PEG + 0.1 % Pr. 2540	88	89	90	17	19	23
PES + PEG + 0.2 % Pr. 2540	-	-	74	-	-	17
PES + PEG + 0.1 % Pr. 859	91	93	94	17	24	26
PES + PEG + 0.2 % Pr. 859	87	91	91	20	20	23
PES + PEG + 0.3 % Pr. 859	90	92	92	22	25	29

Membrane	**Hemicelluloses Retention (%)**			**Total Lignin Retention (%)**		
TMP (bar)	**1**	**3**	**5**	**1**	**3**	**5**
UFX5	87	88	-	9	20	25
UFX10	91	92	92	18	27	32

Table 24: Permeability of pure water during the UF of PFW – average values from the data points recorded for 1, 2 and 3 bar of TMP, at a CFV of 0.3 m/s and 30 ºC of temperature.

Membrane	**Initial L_P [L/(m2 h bar)]**	**After rinsing L_P [L/(m2 h bar)]**	**After cleaning L_P [L/(m2 h bar)]**
PS + PEG	64	6	48
PS + PEG + 1.0 % PAA	162	16	86
PS + PEG + 1.5 % PAA	46	12	20
PS + Syn	12	3	11
PS + Syn + 0.35 % PAA	17	7	23
PS + Syn + 0.7 % PAA	14	6	20
PES + PEG	125	18	112
PES + PEG + 1.0 % PAA	2	7	2
PES + PEG + 1.5 % PAA	11	7	7
PES + PEG + 0.1 % Pr. 2540	137	13	114
PES + PEG + 0.1 % Pr. 859	37	11	35
PES + PEG + 0.2 % Pr. 859	18	10	13
PES + PEG + 0.3 % Pr. 859	55	10	56
UFX5	111	12	91
UFX10	201	12	190

Table 25: PFW flux for each membrane at each TMP – average TMP and flux values from the data points recorded at 20 °C and CFV of 0.3 m/s.

Membrane	**TMP (bar)**	**Flux [L/(m2 h)]**
PS + PEG	1,04	2
	2,99	7
	5,01	7
PS + PEG + 1.0 % PAA	1,04	14
	2,99	22
	5,01	22
PS + PEG + 1.5 % PAA	1,04	7
	2,99	13
	5,01	17
PS + Syn	1,06	1
	3,03	6
	5,00	13
PS + Syn + 0.35 % PAA	1,06	4
	3,03	8
	5,00	11
PS + Syn + 0.7 % PAA	1,06	2
	3,03	5
	5,00	9
PES + PEG	1,03	19
	3,04	33
	5,01	37
PES + PEG + 1.0 % PAA	1,01	6
	3,05	14
	5,04	22

Membrane	**TMP (bar)**	**Flux [L/(m2 h)]**
PES + PEG + 1.5 % PAA	1,04	7
	3,05	18
	5,03	25
PES + PEG + 0.1 % Pr. 2540	1,03	21
	3,04	28
	5,01	24
PES + PEG + 0.1 % Pr. 859	1,03	16
	3,04	25
	5,01	25
PES + PEG + 0.2 % Pr. 859	1,01	9
	3,05	23
	5,04	31
PES + PEG + 0.3 % Pr. 859	1,01	13
	3,05	21
	5,04	23
UFX5	1,05	9
	3,06	23
	4,97	27
UFX10	1,05	20
	3,06	28
	4,97	27

Table 26: Retention of hemicelluloses and lignin for ach membrane at each TMP during UF of PFW.

Membrane	**Total Nitrogen Retention (%)**		
TMP (bar)	**1**	**3**	**5**
PS + PEG	49	53	57
PS + PEG + 1.0 % PAA	56	48	57
PS + PEG + 1.5 % PAA	48	48	53
PS + Syn	41	27	25
PS + Syn + 0.35 % PAA	53	58	60
PS + Syn + 0.7 % PAA	64	54	59
PES + PEG	53	58	56
PES + PEG + 1.0 % PAA	49	47	33
PES + PEG + 1.5 % PAA	52	52	54
PES + PEG + 0.1 % Pr. 2540	47	53	53
PES + PEG + 0.1 % Pr. 859	50	55	54
PES + PEG + 0.2 % Pr. 859	42	50	35
PES + PEG + 0.3 % Pr. 859	49	48	35
UFX5	61	63	58
UFX10	60	54	59