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NANOFILTRATION MEMBRANES BASED ON NANOFIBROUS MATERIAL

Baturalp YALCINKAYA, M.Sc.

SUMMARY OF THESIS

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Author: Baturalp Yalcinkaya, M.Sc.

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Department: Department of Nonwovens and Nanofibrous materials

Supervisor: Ing. Jiří Chaloupek, Ph.D.

Committee for defense of the dissertation:

Chairman:	
prof. RNDr. Oldřich Jirsák, CSc.	FT TUL, Department of Nonwovens and Nanofibrous Materials
Vice-chairman:	
prof. Ing. Jakub Wiener, Ph.D.	FT TUL, Demartment of Material Engineering
prof. Ing. Jaromír Šňupárek, DrSc.	Univerzity of Pardubice, Faculty of Chemical Technology
prof. Ing. Ivan Stibor, CSc. (opponent)	FP TUL, Department of chemistry
doc. Ing. Luděk Jelínek, Ph.D. (oponent)	UCT Prague, Faculty of Environmental Technology
doc. Ing. Eva Kuželová Košťáková, Ph.D.	FT TUL, Department of Nonwovens and Nanofibrous Materials
Ing. Jakub Hrůza, Ph.D.	TUL, Department of Nanotechnology and Informatics

The third opponent who is not a member of the committee is: Assoc. Prof. F. Cangiz Callioglu ze Suleyman Demirel University, Textile Department, Turkey.

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Abstract

The primary goal of this dissertation was fabrication and optimization of thin film composite membranes based on laminated nanofibrous and nonwoven composite materials and investigation of their filtration performance against to mono and divalent salt solution. The best filtration (selectivity and flux) by the active barrier layer was achieved by optimizing four parameters: the monomer solution concentration, the reaction time for monomer polymerization, the drying time and the post-treatment temperature. At each step of the process, one of the optimum conditions, indicated by filtration performance, was selected, and the investigation proceeded to the next step. The filtration performance of the fabricated thin film nanofibrous composite (TFNC) membranes was compared to the performance of reference samples, including commercial ones. The TFNC (2) membrane based on *m*-phenylenediamine monomers showed a higher rejection of NaCl salt ions (93.57%) at a lower flux when compared to commercial NF90 membranes. The flux performances of the piperazine monomer-based TFNC (1) and (3) membranes, were about 10 and 100% higher, respectively, than that of a commercial NF270 membrane, while maintaining the same $MgSO_4$ salt rejection rate (95.6 and 93.5%, respectively).

Once, the optimization of thin film nanofibrous composite membrane was done for liquid filtration and salt separation, the enhancement of filtration performance carried out using additives. Surfactants were used to increase hydrophilicity and flux performance of TFNC membranes whereas acid acceptors were used to increase salt rejection performance. The filtration performance was performed using four different salt solutions with dead-end filtration cell in the second experimental part. Piperazine monomer-based membranes that were prepared by adding acid acceptor were able to reject 98.8 % $MgSO_4$ and 97.4% Na_2SO_4 with high flux 40.5 L m^{-2} h^{-1} and 23.2 L m^{-2} h^{-1} respectively. The rejection rates of monovalent salts were lower than divalent salts using PIP-based membranes such as 25.9 % $CaCl_2$ and 18.3 % NaCl. *M*-phenylenediamine monomer-based membranes, which were prepared by adding surfactants and acid acceptor, showed higher rejection performance in four kinds of salts solutions in comparison with PIP based membranes. The rejection rates of $MgSO_4$, Na_2SO_4, $CaCl_2$ and NaCl salts solution were 98.5 %, 98.3 %, 97.4 % and 96.3 % respectively while the flux performance was increased four times higher, than that of TFNC (2).

The filtration of real seawater showed that the combination of prepared PIP and MPD based TFNC membranes were performed good salt ions rejection from seawater. However, to retain the salt ions from the seawater was impossible all at once. The first filtration attempt was not able retained sufficient amount of salt ions from seawater. For this reason, filtered permeate seawater was used again as a feed water and circulated six times with same PIP-based membrane and two times with same MPD-based membrane. Finally, TFNC membranes were succeeded retain 80 % of salt ions from seawater.

All the laminated membranes were showed high tensile strength under the applied pressure, and there was no breakdown during the filtration process. Therefore, this study gave insight on the industrial role of nanofibrous and nonwoven fabric as a support membrane to fabricate high mechanical performance nanofiltration membranes.

Keywords: Nanofiltration, nanofibers, reverse osmosis, polyamide, lamination, desalination, thin film nanofibrous composite, interfacial polymerization.

Anotace

Tato práce se zabývá studiem procesů odsolování roztoků solí pomocí vodné filtrace. Konkrétně se zabývá konstrukcí a výrobou filtračních membrán s využitím nanovlákenných materiálů.

Výroba a použití nanovlákenných materiálů se stala díky svým vlastnostem, jako je například porózita, zájmem vědců v mnoha oblastech. Během poslední doby je jednou z oblastí zájmu také problematika úpravy vlastností vody. Avšak, do této doby hlavním problémem použití nanovlákenných materiálů pro filtraci vody, jsou špatné mechanické vlastnosti zmíněných materiálů. Proto motivací této práce bylo zlepšení mechanických vlastností nanovlákenných materiálů a příprava nanovlákenných membrán vhodných pro filtraci vody, konkrétně pro odsolování vody.

Hlavním cílem práce byla příprava a optimalizace kompozitních membrán, složených z nanovlákenných materiálů, netkané textilie a tenkého polymerního filmu. U takto připravených filtračních membrán byla studována a sledována schopnost filtrovat jednomocné a dvojmocné soli z vodního roztoku. Nejlepších filtračních vlastností připravovaných membrán, bylo dosaženo optimalizací vlastností polymerního filmu, který lze nazvat jako aktivní bariérová vrstva. Toho bylo dosaženo optimalizací čtyř základních parametrů: koncentrací roztoků monomerů, reakčním časem polymerizace, časem sušení a teplotou, které jsou membrány vystaveny po sušení. Každý z těchto parametrů měl vliv na konečné vlastnosti membrány a optimální parametry byly stanovovány krok po kroku.

Vlastnosti všech připravených membrán, nanovlákenných kompozitů s tenkým polymerním filmem (TFNC), byly porovnány s komerčně dostupnými membránami, které sloužily jako referenční vzorky. Jako solné roztoky byly použity roztoky Mg SO_4, Na_2SO_4, $CaCl_2$, NaCl.

TFNC membrána vyrobená za použití monomerů m- fenyl diaminu vykazovala vyšší efektivitu záchytu NaCl iontů a vyšší průtok než komerční membrána NF90. Dosažený průtok membrán s polymerním filmem připraveným z monomerů piperazinu byl o 10-100% vyšší než u komerční membrány NF 270 při zachování podobné efektivity záchytu soli Mg SO4.

Pro dosažení ještě lepších výsledků, zvýšení efektivity záchytu a většího průtoku, bylo přidáváno několik typů aditiv do roztoků monomerů před mezifázovou polymerizací. Touto úpravou je dosaženo až 96 % záchytů iontů NaCl. Výsledky jsou uvedeny v práci.

V experimentální části se práce dále zabývá problematikou odsolováním skutečné mořské vody. Výsledkem je membrána TFNC, která je schopna odstranit 80 % iontů soli z mořské vody. Práce se také zabývá opakovaným použitím membrán a jejich mechanickými vlastnostmi.

Klíčová slova:

Nanofiltrace, Nanovlákna, reversní osmóza, polyamid, laminace, odsolování vody, kompozit, mezifázová polymerizace

CONTENT

1. Introduction

Essential nutrient for all living being is water. Living things are made up 50% to 95% water, and it covers more than 70% of Earth's surface that 96.5% of it found in oceans and seas, 1.7% in groundwater, 1.7% in ice caps and glaciers, rest of it in the air as the vapor or clouds. Only 3% of the Earth's water is freshwater, and 1% of freshwater is drinkable (Wikipedia 2015). Regrettably, the ratio of potable water is decreased day by day because of intense industrialization, increasing of population, over-urbanization.

Many countries or regions are under threat of water scarcity. The effects of water scarcity have been prompted to many governments to search for new drinkable water alternatives. However, alternatives are not always available for some countries, and therefore, desalination has been the center of interest for them.

Desalination refers to a water treatment process that separates salty water into a high salt concentration and a fresh water stream of low concentration and is one of the principal alternative sources for potable water available today. In the early 1970s, semipermeable membranes which are permeable to water but which reject salts and suspended solid that are located in the heart of the desalination process (Ribeiro 1996).

Last four decades, filter medias based on artificial polymers have been proved themselves on liquid filtration, especially reverse osmosis membranes with hi-performance (99.5% - 99.8% of salt ions rejection). Fibrous materials have been considered as a filter media in recent years of the twentieth century. Especially, nonwoven materials are used for air and liquid filtration such as car filter, medical filtration process and swimming pool filters.

Nonwoven filter media are ideal for filtration applications due to highly internal surface area and porosity that provides high liquid flux and dirt load capacity. Usage of nonwovens in water treatment is one of the fastest growing segment in the filtration industry. Nowadays, they are mainly used as pre-filter or supporting material and replaced other forms of media such as paper, glass, and carbon due to low cost and increased efficiency. However, the nonwoven filter media is remained incapable against the submicron particle due to the large pore size.

With the new era in material science so-called nanotechnology, the finer fibers which have lower diameter than any conventional fiber and higher porosity of fabrics are possible to produce from polymeric materials. Nanofibers became a popular term in past decades and is rapidly growing in the application of filtration technology. Donaldson Company, USA has already commercialized nanofiber filter media consisted of 10μm size cellulose fibers and 250 nm size nanofibers, so-called Ultra-Web (Timothy H. and Kristine M. 2003). Usage of nanofibrous materials is still a big challenge in liquid filtration. They have been exhibited good filtration performance in micro dimension particles. However, when it comes to nano or sub-nano dimension, unaided nanofibrous layers are failed to satisfy. It will take to next decade or two to realize if nanofibrous filter materials are the serious rescuer of drought in the world.

2. Purpose and the aim of the thesis

The primary objective of this study is to fabricate a composite membrane by forming active barrier layer onto a fibrous material such as nonwoven and nanofiber layers. The nonwoven and nanofibrous fabrics are gathered by lamination method to achieve excellent adhesion. The optimization of the active barrier layer which is produced by the interfacial polymerization (IP) method is involved four different step. For instance, various concentration of monomer solutions, reaction or contact time of monomer solutions, determination of drying time and method, and determination of curing temperature are that to achieve best filtration performance (selectivity and flux). Characterization of membranes was done to evaluate their properties such as morphology, mechanical strength, contact angle. The filtration performance of TFNC membranes was compared with commercial membranes (i.e., NF90 and NF270). The nanofiltration test was carried out using monovalent and divalent salt solutions (NaCl and $MgSO_4$, 2000ppm) and a dead-end filtration cell. Moreover, the filtration performance (rejection and flux) was tried to increase by adding acid acceptor or surfactants (e.g. TEA, NaOH, Na_3PO_4, Synferol-AH, Triton-X 100). Extended period filtration performance of enhanced membranes was evaluated by dead-end filtration using deionized water and NaCl, $MgSO_4$, $CaCl_2$ and Na_2SO_4 as feed solutions. Finally, the filtration process was carried out using real seawater which was obtained from the mediterranean sea.

The impact of this study is filling the gap that weakness of nanofibrous materials in liquid filtration. For example, the major problems in the nanofibrous material are that weak mechanical properties, and irregular adhesion between nonwoven and nanofibrous scaffold were troubleshot by lamination of individually produced nonwoven and nanofibrous layer. The creation of active layer is breezed through step by step which will prove insights to the further research in liquid filtration.

3. Overview of the current state of the problem

The nanofibrous scaffold itself cannot function to use in nanofiltration processes. Either mechanical properties to withstand applied high pressure or selectivity properties against to smaller particles of nanofibrous scaffolds are not capable. In this reason, the plenty of researchers have functionalized the surface of nanofibrous scaffolds using interfacial polymerization (IP). One of the first studies about the usage of electrospun nanofibrous scaffolds as a porous layer on nanofiltration process is taken place by electrospinning of polyacrylonitrile (PAN) nanofibers. Nanofibrous mid-layer was used as a support in a high flux thin film nanofibrous composite (TFNC) membranes. Then the active barrier layer was produced by IP of piperazine, trimesoylchloride and some additives. The membrane performance was evaluated for nanofiltration using divalent salts ($MgSO_4$). They indicated that the concentration of piperazine was played a critical role in IP to optimize the flux and rejection performance. The TFNC membrane was showed higher permeate fluxes (21-42%) as well as higher rejection rates (2-22%) than those of TFC membranes (Yoon, Hsiao and Chu 2009b). Also, TFNC membrane was exhibited 38 % permeate flux increase while maintaining rejection to that NF270 at 70 psi.

One of the most important studies about electrospun nanofibrous composite membrane was carried out by Kaur et al. They were observed that the effect of nanofibrous structure on the thin film composite membrane and their performance in the nanofiltration process. In the first study, they have investigated the influence of fiber diameter on the filtration performance. Thus, various concentration of PAN solution was electrospun onto the nonwoven scaffold. The separation performance was done using dead-end filtration cell with 2000ppm $MgSO_4$ feed solution. The result showed that as the fiber size decreased, the pore-size also decreased, and the separation of salts increased, while at the expense of flux. When the cross-sectional thickness of the electrospun layer was decreased together with smaller pore-size, it resulted in the increased flux with high salt rejection (Kaur et al. 2012b). The same author was observed the hot pressing effect on the electrospun PAN nanofibrous membrane properties and the separation of salt after interfacial polymerization. The reason for applying hot press is the increase the mechanical properties and adhesion between nanofibrous and nonwoven scaffolds. The nanofiltration result showed that the higher applied hot pressure membrane was exhibited higher rejection and lower flux than that those of TFNC membranes (Kaur et al. 2011).

The weak mechanical properties of nanofibers and their low adhesion to nonwoven supporting layer have always been a stumbling block to prepare nanofibrous liquid filter. In many studies, the researchers have been trying to solve the mechanical problem of nanofibers.

Some of the studies were focused on increasing inter-fiber adhesion to improve the mechanical properties of membranes. The mixed solvent system (Dimethylformamide (DMF) and N-methyl-pyrrolidinone (NMP) were used to prepare a solution of PES, then the PES polymer solution was electrospun using needle electrospinning. The different solvent mixed system contains various vapor pressure of solvents. Therefore, the nanoweb on the supporting material was still partly wetted because of the high vapor pressure of NMP, and this may lead the adhesion between fibers. The mechanical properties of PES membranes were improved significantly. However, the average fiber diameter was increased directly proportional to mechanical strength. The flux of the electrospun PES membrane was performed microfiltration performance (Yoon et al. 2009a). The same mixed solvent systems for electrospun PES membranes were mentioned above to prepare nanofiltration filter (Yung, Ma, Wang, Yoon, Wang, Hsiao and Chu 2010).

Instead of the mixed solvent system, the vapor of solvents was exposed to electrospun membranes to improve the mechanical strength. PAN and PSf in DMF solutions were spun via needle electrospinning method. Once spun, the PAN and PSf nanofibers were exposed to solvent vapor for a different period. This approach yielded smaller pore size and fiber fusion at junction points due to fiber swelling. Hence, the mechanical strength of nanofibers webs increased while the treated membranes showed lower permeability than untreated ones (Huang et al. 2013). In further studies of authors are investigated the effect of chemical modification on the improvement of mechanical properties of PAN and PSf electrospun web. The chemical modification involves coating of polydopamine (PDA) that is a hydrophilic polymer. The PDA-modified electrospun web was performed higher strength and improved hydrophilicity (Huang et al. 2014).

4. Used Materials and Methods

4.1 Materials used

The TFNC bottom substrate was a polypropylene/polyethylene (80/20,18g/m^2) bi-component spunbond nonwoven fabric (Pegatex S BICO) from Pegas Nonwovens s.r.o. (Czech Republic). The solution used to produce the porous nanofiber layer by electrospinning consisted of polyamide 6 (PA6) (BASF B24) dissolved in acetic acid/formic acid. The selective layer of the TFNC membrane was prepared by interfacial polymerization of two immiscible phases on the porous nanofiber layer. Piperazine (PIP) and *m*-phenylenediamine (MPD) were purchased from Sigma-Aldrich and prepared in deionised water as aqueous phases, while the organic phase was prepared by dissolving trimesoyl chloride (TMC) (Sigma-Aldrich) in hexane at 40 °C Triethylamine (TEA) from Sigma-Aldrich, sodium hydroxide (NaOH) and sodium phosphate (Na_3PO_4) were chosen for acid acceptor materials. Triton-X (Sigma-Aldrich) was used as non-ionic surfactants, and Synferol AH 1241 was used as an anionic surfactant. $MgSO_4$, NaCl, $CaCl_2$ salts as feed solutions were provided from Penta s.r.o. (CZE) moreover, Na_2SO_4 from Lachema, Brno (Chemapol).

4.2 Preparation of thin film nanofibrous composite membranes

A solution of polyamide 6 (8 wt.%) was dissolved in acetic acid/formic acid at a ratio of 2/1 at 80 °C for 4 hours to produce a nanofiber layer using wire electrode electrospinning equipment (NS 1WS500U, Elmarco s.r.o, Czech Republic). A solution carriage feeds polymer solution around a moving stainless steel wire (Fig. 1).

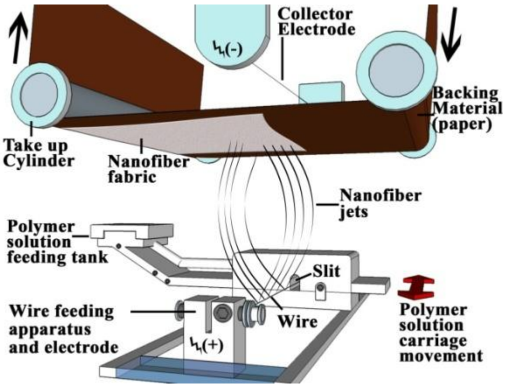

Figure 1. Electrospinning of PA6 nanofibers using Nanospider™ Production Line NS 1WS500U

The speed of the carriage is 245 mm/s and the rotation speed of the wire is 40.5 cm/h. High voltage suppliers are connected to the wire electrode (55 kV) and the collector electrode (–10 kV). When the applied voltage exceeds a critical value, many Taylor cones are created on the surface of the wire. Polymer solution jets move toward the collector, the solvent evaporates, and the PA6 nanofibrous layer is collected on a baking paper moving in front of the collector electrode. The speed of the baking paper was 9 cm/min.

Bi-component spunbond nonwoven and PA6 nanofibrous fabrics were laminated using RPS-Mini fusing lamination equipment (Meyer-Germany). This process was carried out tenuously to avoid damaging the structure of the nanofibers such as the fiber diameter and pore size.

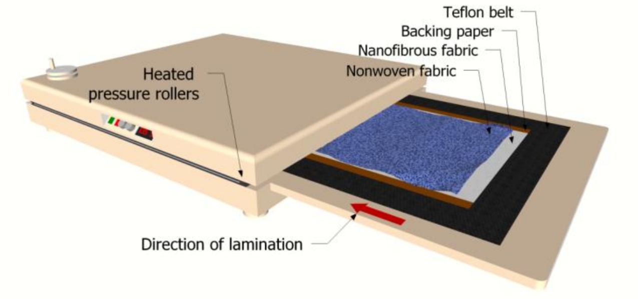

Figure 2. Lamination method and equipment.

PA6 nanofibrous layer was put onto PP/PE bi-component nonwoven fabric and inserted between two Teflon belts moving at 2 m/min in the lamination equipment. The temperature was set at 135 °C because of the melting point of PE (120–130 ^{o}C). The nanofibrous layer was adhered to the nonwoven fabric at the pressure of 15 N/cm while the PE fibers are partly melted, and the resulting product was called the nonwoven-nanofibrous composite (NNC) scaffold (Fig. 2).

In the first experimental part of the thesis, interfacial polymerization was carried out to form a polyamide active barrier layer on the NNC scaffolds. The aqueous phases were prepared by dissolving PIP and MPD in the DI water while the organic phase was prepared by dissolving TMC in the hexane. As a first step in the optimization of the barrier layer, different concentrations of monomers, 0.25, 0.5, 1.0, 2.0, and 4.0 % (w/v) were chosen to prepare aqueous phases while concentrations of 0.1, 0.2, and 0.4 % (w/v) were selected for the organic phase. In the second step of optimization, different reaction times for the formation of the polyamide layer were investigated. NNC scaffolds were immersed in the aqueous phase for 1, 3, or 5 min and immersed in organic phase for 10 s, 30 s, 1 min, 3 min, or 5 min. The third step of optimization was the investigation of the crucial drying time between two phases. After immersing the NNC scaffolds in the aqueous phase, the wetted scaffolds were left in air for 2.5, 5, 7.5, or 10 min. As a last step of optimization of the barrier layer, further processes were applied to complete the crosslinking of the polyamide layer. After the organic solution was drained out, the thin layered NNC scaffolds (TFNC) were cured at ≈21(at room temperature), 65, 70, 90, or 110 °C for 10 min each. Finally, the TFNC membranes were washed and stored in DI water before the tests.

In the second experimental part of the thesis, to prepare PIP-based TFNC membranes, different concentration of TEA [0.25, 0.5, 1.0, 2.0, 4.0 % (w/v)] were added in certain amount of PIP [2.0 %. (w/v)] aqueous solution while the concentration of TMC were kept constant [0.2 % (w/v)]. When the concentration of TEA determined according to best filtration performance, the certain amount of NaOH and Na_3PO_4 [1.0 % (w/v)] were added into [2.0% (w/v) PIP + TEA] aqueous solution and filtration performance were tested again. The reaction times for aqueous and organic solutions were chosen 1 min and 5min-45sec, respectively. The drying time between the solutions was determined 5 min. Curing temperature and time were 110 °C and 10 min in the incubator.

MPD-based membranes were prepared using acid acceptor [TEA, 2.0% (w/v)] and surfactants [non-ionic – anionic liquid, 0.2% (w/v)]. The concentrations of MPD [2.0% (w/v)] and TMC [0.2 % (w/v)] were kept constant in all aqueous and organic solutions. The IP reaction for MPD-based membranes was carried out under the same condition such as the drying, curing time and curing temperature that was mentioned above for PIP-based membranes except the reaction times. The reaction time for MPD aqueous solution was decided 1 min whereas the reaction time for an organic solution was decided 30 sec.

4.3 Evaluation of membrane performances

A dead-end solvent-resistant stirred cell (Millipore-XUF 047 01) with an active filtration area of 15 cm^2 and capacity of 0.05 L was used for evaluation of the membrane performance (Fig. 3). The feed chamber was pressurized by nitrogen gas and tests were conducted at room temperature (≈21 °C) at an applied pressure of 4.8 bar. The sufficient volume of DI water was passed through the TFNC membrane to ensure stable membrane performance before testing. The conductivity of permeates was measured using a digital conductivity meter. The rejection was calculated by Eq.1.

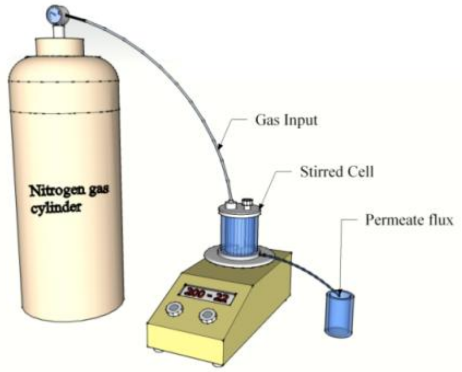

Figure 3. Schematic of dead-end filtration unit

$$\text{Rejection (\%)} = \frac{Cf - Cp}{Cf} \times 100 \qquad \text{Eq. (1)}$$

where Cf and Cp are the conductivity of the feed and permeate concentrations.

5. Summary of the results achieved

5.1 Summary of the first experimental part of thesis

In this part, production of PA6 nanofibers was carried out by Nanospider electrospinning machine onto backing paper substrate. Then the PA6 nanofibrous layer was transferred onto PP/PE spunbond nonwoven by a lamination method. Figure 4 illustrates the top-viewed and cross-sectioned SEM image of the NNC scaffolds. The average fiber diameter of NNC scaffolds top layer was 126 ± 29.1 nm and mean flow pore size was 0.739 µm. Further features of the NNC scaffold are listed in Table 1.

Table 1. Properties of NNC scaffold

	Smallest Pore Size (μm)	Bubble Point Pore Size (μm)	Mean Flow Pore Size (μm)	Fiber Diameter (nm)
NNC scaffold	0.469	1.064	0.739	126 ± 29.1

The tensile strength test of the nonwoven, nanofibrous scaffold and NNC scaffold were measured individually. The nanofibrous layer showed weak mechanical properties of 4.33 N/25mm (machine direction) and 4.12 N/25mm (counter-direction) while the tensile strength of the bi-component spunbond nonwoven was 14.95 N/25mm (machine direction) and 6.14 N/25mm (counter-direction). When the lamination method was applied, the tensile strength of the NNC scaffold was increased to 29.17 N/25mm (machine direction) and 14.42 N/25mm (counter-direction). The thicknesses of the nanofibrous scaffold and spunbonded bi-component nonwoven were 38 ± 0.5 μm and 75 ± 1 μm, respectively. After lamination of fabrics, the total scaffold thickness was 105 ± 5 μm.

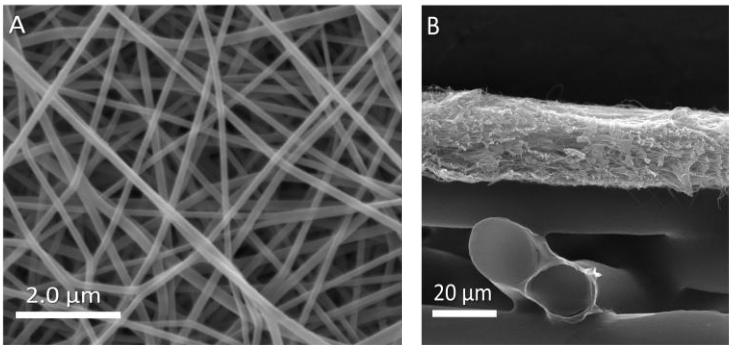

Figure 4. SEM images of (A) top view (nanofibers) and (B) cross-sectioned NNC scaffolds

Interfacial polymerization was carried out to form a barrier layer by introducing an organic solution on top of the NNC (PP-PE/PA6) scaffold containing the aqueous solution. The most important reaction parameters for the optimization of the barrier layer were investigated, such as various concentrations of monomer solutions, the reaction time in solutions (contact time), drying time after immersion of scaffolds in the aqueous solution, and curing type. According to the membrane performance (flux and rejection), in each step, one of the optimum conditions was chosen, and then the investigation proceeded to the next step. All experiments were carried out without extra additive (e.g., surfactant, ionic liquid, nanoparticles) in the monomer solutions or surface modification to enhance the performance of the membranes.

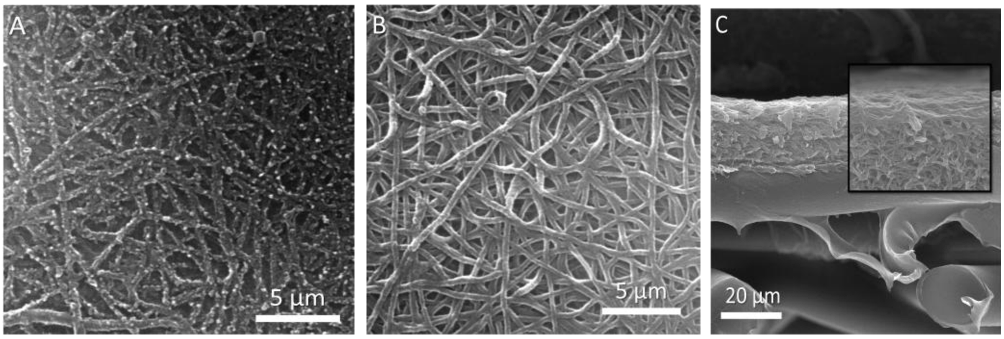

Figure 5. SEM images of TFNC membranes (A) 2.0–0.2 (w/v)% MPD–TMC, (B) 2.0–0.2 (w/v)% PIP–TMC, (C) cross-sectioned 2.0–0.2 (w/v)% PIP–TMC.

Although the pattern of the nanofibers layer was visible from the surface of the SEM images of TFNC membranes, it is clear that the PIP-based TFNC membrane formed a defect-free barrier layer while the MPD-based TFNC membrane formed a spotted (dotted) barrier layer (Fig. 5).

The fabrication and optimization of TFNC membranes were done in four different steps. Three different TFNC membranes were determined as optimum filter samples for the separation of NaCl and $MgSO_4$ in feed solution and were compared with commercial Dow Filmtec membranes NF 270 and NF 90. The combination of 2.0 % (w/v) MPD in DI water and 0.2 % (w/v) TMC in hexane solution with 110 ^{o}C annealing exhibited the highest NaCl separation, and this membrane was named TFNC (2). Two membranes were chosen for the separation of $MgSO_4$. In the second step, the various reaction times of PIP and TMC were investigated. The reaction times of 1 min in PIP and 5 min in TMC solutions exhibited the highest $MgSO_4$ separation with reasonable flux and named TFNC (1). Finally, in the last step, the TFNC membrane that was annealed at 110 ^{o}C in the oven was chosen as the last sample and was named TFNC (3).

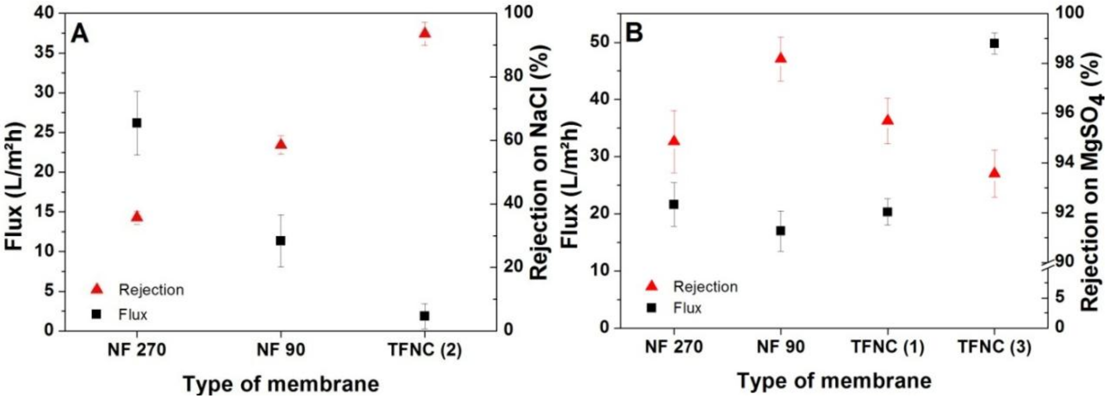

Figure 6. Comparison of filtration performance (A-NaCl, B-$MgSO_4$) between TFNC and commercial membranes at 2000ppm and 4.8 bar with dead-end filtration cell

According to Dow Filmtec sources, the NF 270 commercial membrane has a rejection capability of more than 97% for 2000 ppm $MgSO_4$ and a flux of around 52 L $m^{-2}h^{-1}$, while NF 90 has a rejection capability of more than 97% for 2000 ppm $MgSO_4$ and a flux of around 41 L $m^{-2}h^{-1}$. However, despite choosing the same process conditions in the filtration method (4.8 bar applied pressure, room temperature, stirring at 350 rpm, and 2000 ppm feed solutions in the dead-end filtration cell), NF 270 and 90 exhibited a lower flux performance than expected without showing a problem in the rejection performance (see in Figure 6.B). Figure 6.(A) illustrates that TFNC (2) exhibited higher NaCl rejection performance (93.57%) than the NF 270 and NF 90 commercial membranes (35.6 and 58.5%,respectively, NaCl) while the flux performance of TFNC (2) (1.84 L $m^{-2}h^{-1}$) was significantly lower than the others (26.1 and 11.3 L $m^{-2}h^{-1}$, respectively). Figure 6.(B) illustrates that TFNC (1) exhibited a slightly higher $MgSO_4$ rejection performance (95.6%) than NF 270 (94.8%) and lower rejection performance than NF 90 (98.1%) while the flux performance was competitive (20.2, 21.6, and 16.9 L $m^{-2}h^{-1}$, respectively). In the case of TFNC (3), the $MgSO_4$ rejection performance (93.5%) was slightly lower than that of NF 270 and explicitly lower than that of NF 90, while the flux performance of TFNC (3) was twice as high (49.7 L $m^{-2}h^{-1}$) as the others.

These preliminary results indicated that the optimized active barrier layer based on a well-designed nanofibrous supporting surface is suitable for use in NF membranes for separation of salt (monovalent or divalent) ions without any extra additives or modification processes.

5.2 Summary of the second experimental part of thesis

In this part, the PIP and MPD based TFNC membranes were prepared by adding various additives to the aqueous solutions. The addition of acid acceptors such as TEA, NaOH and Na_3PO_4 to the aqueous solution has a significant effect on the surface morphology of the PIP-based TFNC membranes (Fig. 7).

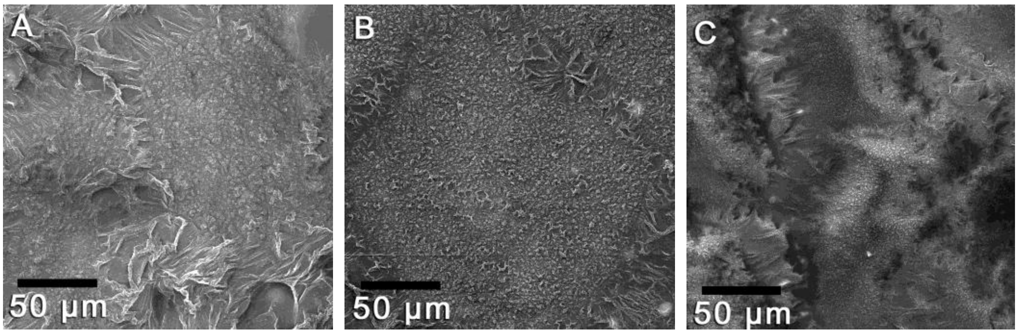

Figure 7. Surface images of PIP-based membranes which were prepared (A) 4 % w/v TEA, (B) TEA+NaOH and (C) TEA+ Na_3PO_4 in aqueous solutions.

It is obvious from the SEM images in Figure 7 that the fibrous pattern of top active film disappeared and formed typical ridge and valley PA structure on the NNC scaffold. It was the proof that the reactivity of PIP monomer increased towards the TMC monomer due to the presence of TEA. Hence, more PIP molecules reacted with TMC molecules and created thicker PA active layer. Surface morphology of the MPD-based membranes that were prepared with the addition of acid acceptor and surfactant to the aqueous solution were illustrated in Figure 8.

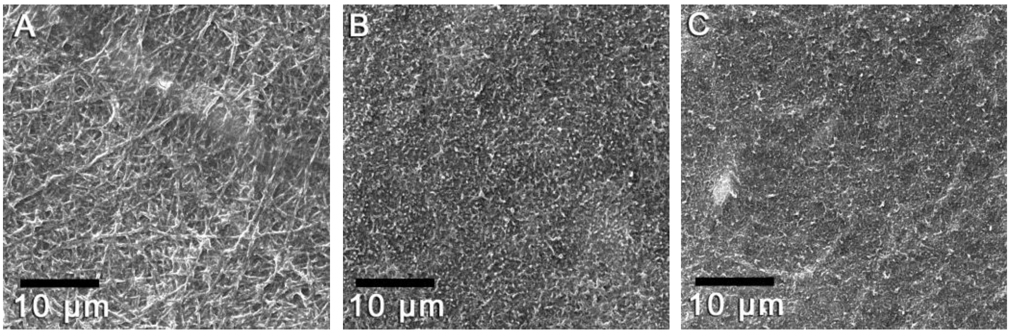

Figure 8. Surface images of MPD-based membranes which were prepared (A) 2 % w/v TEA, (B) TEA+Synferol AH and (C) TEA+Triton-X in aqueous solutions.

The addition of only TEA in the aqueous solution did not affect the surface morphology of MPD-based membranes (Fig.8.A). The fibrous pattern is clearly visible. However, the addition of ionic liquids (surfactants) in the aqueous solution was affected the active layer and formed ridge and valley structure (Fig. 8.B-C). Moreover, the surface structures of MPD-based membranes prepared with ionic liquid were smooth and homogenous according to PIP-based membranes.

After determination of PIP+TEA+NaOH based membrane steady state using pure water, feed solution experiments were carried out for an extended period. Four kinds of salts were chosen for the feed solution such as $MgSO_4$, NaCl, $CaCl_2$ and Na_2SO_4. The properties of salt solutions were given in Table 2 and the filtration performances of four kinds of solution were illustrated in Figure 9.

Table 2. Properties of salt that were used for feed solutions.

Type of salts	Conductivity (ms/cm)	pH	Part per million (ppm)
$MgSO_4$	2.21	5.59	2000
Na_2SO_4	5.74	6.87	2000
NaCl	3.52	6.15	2000
$CaCl_2$	3.62	5.75	2000

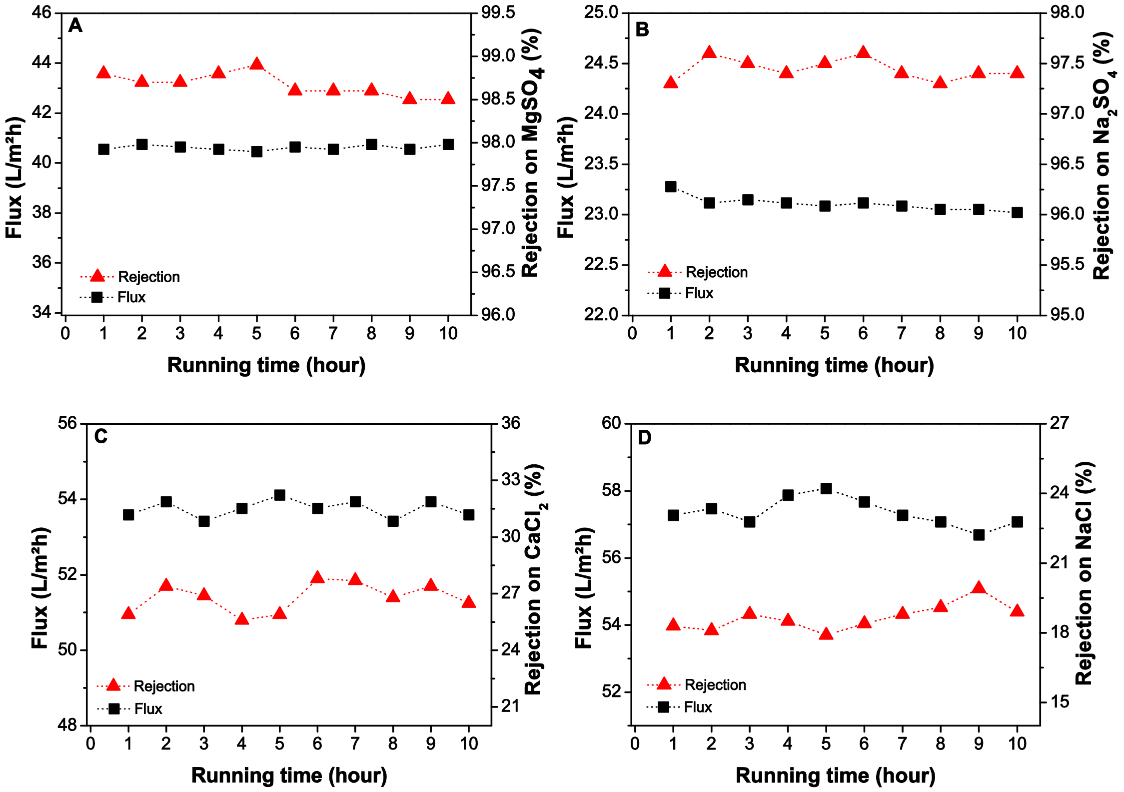

Figure 9. Extended filtration of (A) $MgSO_4$, (B) Na_2SO_4, (C) $CaCl_2$ and (D) NaCl feed solutions at 2000ppm and 4.8 bar using dead-end cell.

The stable flux and rejection performance were seen all graph in Figure 9 except graph (B), with the filtration of Na_2SO_4. The flux performance was performed decreasing trend which means that PIP+TEA+NaOH based membrane showed slightly fouling behavior during the filtration of Na_2SO_4 feed solution. Eventually, the PIP+TEA+NaOH based membrane was achieved high rejection performance against to divalent salts. Inherently, retained monovalent salt ratios were low.

Filtration experiments of different salts feed solution using MPD+TEA+Synferol AH were given in Figure 10. The rejection rates of divalent salts were higher than 98 %, and monovalent salts were around 96 - 97 %. The flux performance of the MPD+TEA+Sy-AH based membrane showed a slightly decreasing trend. This may be explained with the concentration polarization due to the usage of dead-end filtration cell.

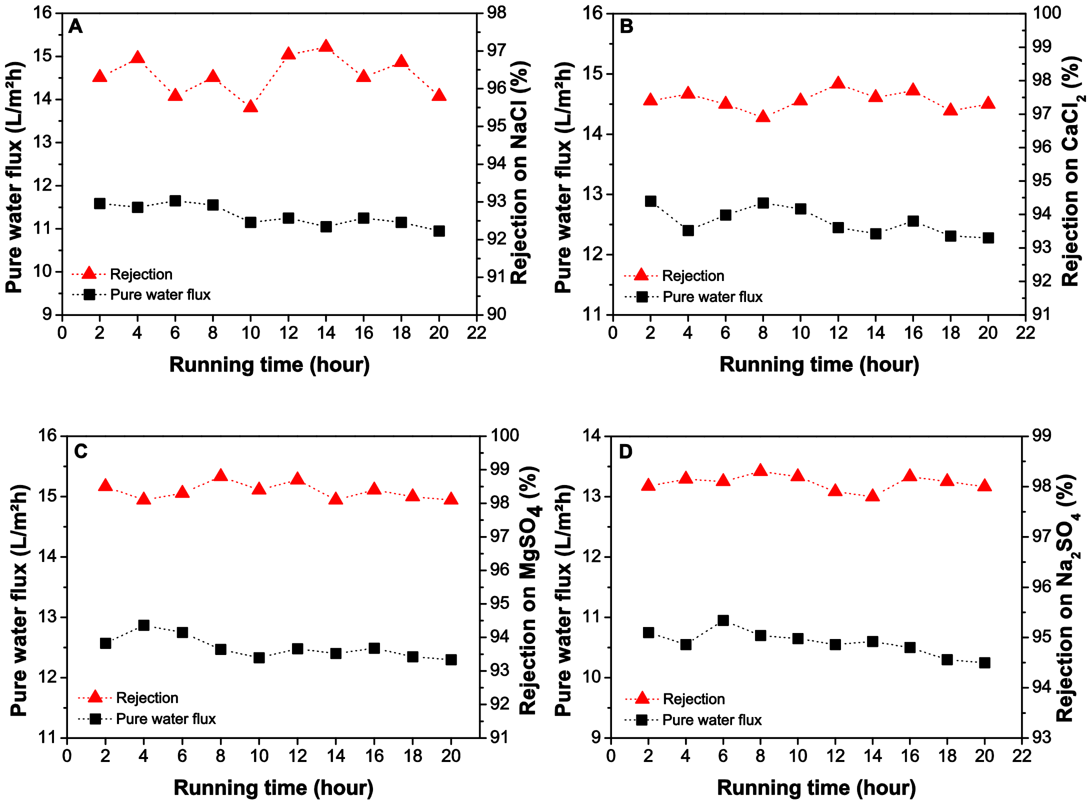

Figure 10. Extended filtration of (A) NaCl, (B) $CaCl_2$, (C) $MgSO_4$ and (D) Na_2SO_4 feed solutions at 2000ppm and 4.8 bar using dead-end cell.

The certain amount of feed water was asused in each experiment, and the circulation of feed water was impossible in the dead-end filtration system. As water molecules diffuse through the TFNC membrane, the salt ion retains and concentration of feed water increases continuously. Due to the number of salt ions increased rapidly, concentrated feed solutions accumulate on the surface of the membrane, and lead salt leakage or fouling. Moreover, the osmotic pressure of feed water increases proportionally to the concentration of feed solution. For this reason, the flux of feed water tended to decrease during filtration using MPD-based membranes.

The desalination of seawater by membrane technology is a promising technique, which is necessarily required more than one-step to produce drinkable water such as pre-filtration, microfiltration, softening, etc. The ion-exchange chromatography analysis result and conductivity measurement show that the amount of main dissolved salt ions and conductivity of seawater was extremely high for NF membrane filtration process (Table 3).

Table 3. Main dissolved ions in Mediterranean seawater sample

Cations	mg/L
Na^+	11741
Mg^{+2}	1447
Ca^{+2}	433
K^+	411
Anions	mg/L
Cl^-	21384
SO_4^{-2}	2357
NO_2^-	<100
NO_3^-	<100
Conductivity of seawater	53.2 ms/cm

The primarily filtration experiment were carried out using PIP+TEA+NaOH and MPD+TEA+Sy-AH based membranes by measuring the only conductivity of feed (seawater) and permeate water (Fig. 11).

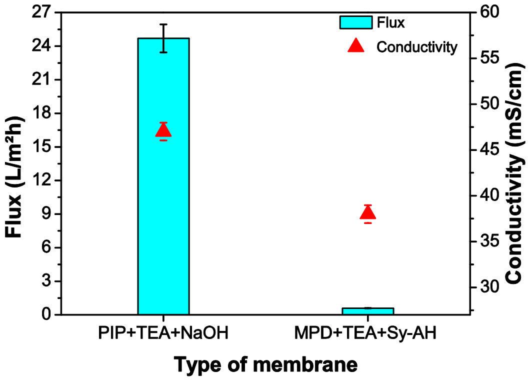

Figure 11. The filtration experiment of seawater using different membrane and dead-end cell at 4.8 bar.

The results were shown in Figure 11 that the conductivity value of permeate water dropped from 53.2 mS/cm to 47 mS/cm and 38 mS/cm, respectively while the flux performance was 24.6 L $m^{-2}h^{-1}$ and 0.65 L $m^{-2}h^{-1}$, respectively. It was obvious that the PIP and MPD based membranes were remained incapable of retaining an excessive amount of salt ions in the seawater all at once. For this reason, the same feed seawater was circulated and was used more than once while the same membrane fixed on the dead-end cell.

The filtration experiment of circulated seawater started with PIP-based membranes and repeated 6 times then the same permeate water were used as a feed water by using MPD-based membranes and repeated 2 times (Fig. 12). The flux performance of PIP+TEA+NaOH based membranes in the filtration of seawater was higher compared that of MPD+TEA+Sy-AH based membranes. Moreover, the flux performance of PIP based membranes increased after each filtration process while the conductivity of feed seawater decreased. The conductivity of feed seawater remained stable in fifth (32.5 ms/cm) and sixth (32.0 ms/cm) times of filtration (Fig. 12.A). We understand that after 6 times filtration using PIP based membranes; there were no divalent salt ions in the feed seawater.

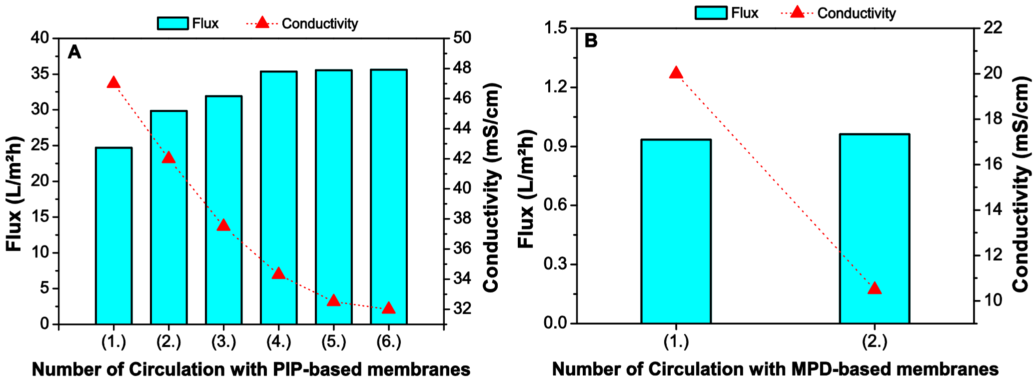

Figure 12. Circulated filtration of seawater using (A) PIP and (B) MPD based membranes

The further filtration was continued with MPD+TEA+Sy-AH based membrane using pre-filtered feed seawater, which had conductivity 32.0 mS/cm (Fig. 12.B). In the first attempt of filtration, the conductivity was dropped to 20 mS/cm while flux performance was 0.935 L $m^{-2}h^{-1}$, which was slightly higher than that of Figure 11. In the second filtration of feed seawater, the conductivity decreased to 10.5 mS/cm while the flux performance was more or less same (0.965 L $m^{-2}h^{-1}$).

At the end of the combined filtration process, the conductivity of obtained permeate water was 10.5 mS/cm which means that approximately 80 % of salt ions was retained from the seawater using TFNC membranes by dead-end filtration. The analysis ion-exchange chromatography was carried out again, and the amounts of salt ions in the filtered water were given in Table 4.

Table 4. Amount of ions in the filtered seawater sample [permeate (2.) in Figure 12.B]

Cations	mg/L
Na^+	2554
Mg^{+2}	5.3
Ca^{+2}	39.4
K^+	85.3
Anions	**mg/L**
Cl^-	3620
SO_4^{-2}	<100
NO_2^-	<100
NO_3^-	<100
Conductivity of seawater	10.5 mS/cm

It is obvious from Figure 12 that the rejection ratio of salt ions from seawater was depended on the number of repetition of the circulated feed seawater in dead-end filtration method. We are firmly believed that there was a chance to retain rest of the salt ions from the obtained permeates seawater by increasing the circulation time. However, the flux performance of MPD-based membranes was dropped remarkably. It was not reasonable to proceed to filtration of seawater experiment using dead-end filtration cell and then we limited the circulation times of feed seawater with 2 times using MPD-based membranes.

6. Evaluation of results and new findings

Electrospinning has been already adapted to industrial production by the new technological equipment, and production of electrospun nanofibrous layers has become easier than ever before. Unfortunately, weak mechanical properties of electrospun layers have been delaying to find a place in the final product. The most convenient way to use electrospun nanofibrous materials is to combine nanofibrous materials with another material or surface. However, its easy-deformable structure has limited the manipulation of nanofibrous material.

In this thesis, the mechanical issues of nanofibrous materials were overcome by a lamination method. It is essential to avoid any damage to the nanofibrous structure during the lamination process. Therefore, choosing of lamination technique has also a significant impact on the final structure of supporting material. The polyamide 6 nanofibrous layer, which was prepared in large scale electrospinning equipment, was transferred gently onto polypropylene/polyethylene bi-component spunbond nonwoven fabric under heat and pressure treatment using a lamination machine. The prepared nonwoven and nanofibrous scaffold were shown excellent adhesion and high mechanical strength.

It was necessary to cover NNC scaffold surface with thin active layer before use it in the liquid filtration for separation of salt ions. Therefore, polyamide active thin film was formed onto NNC scaffold via interfacial polymerization method. The first attempt of formation of PA active layer performed promising flux and rejection performance when $MgSO_4$ and NaCl used for the feed solutions. Thin film nanofibrous composite membranes, which were optimized by various IP reaction parameters, were able to compare with the commercial membranes without any complex additives or modifications. The TFNC membranes were used as a media filter in all filtration process without having any mechanical problems.

The further work was related to the improvement of filtration performance of TFNC membranes. The basic two additives (surfactants and acid acceptor) had a significant effect on filtration performance of the TFNC membranes. They had reached to highest rejection and flux values which were obtained in this thesis. Poly(piperazine amide) based membrane were able to retain divalent salt ions (more than 98%) due to the electrostatic repulsion mechanism of the active layer. Poly(*m*-phenylenediamine) based membrane was able to retain both monovalent and divalent salt ions (around 96% – 98%) due to the size exclusion mechanism.

At the first attempt of desalination of real seawater was failed to retain sufficient amount of salt ions due to the high salt content of the feed seawater and incapable filtration with the dead-end cell. These problems were overcome using the feed seawater repeatedly. TFNC membranes were shown that they were capable of retaining a high amount of salt from seawater. However, the low flux performance due to the dead-end filtration method was only the biggest obstacle against to TFNC membranes during the filtration of seawater. Against all the odds, the TFNC membranes were retained 80% of salt ions from seawater.

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8.1 Patent

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8.2 Book Chapter

1. Yalcinkaya, F., **Yalcinkaya, B**., Jirsak, O., Dependent and independent parameters of roller electrospinning system, Electrospinning, ISBN 978-953-51-4945-3, publisher Intech, 2016 (In press).

8.3 Publications in S. C. I., S. S. C. I., A. H. C. I. Indexed

1. Yener, F., **Yalcinkaya, B**., Jirsak, O., On the measured current in needle- and needleless electrospinning. *Journal of Nanoscience and Nanotechnology* 13, 4672-4679 (2013)
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3. Yalcinkaya, F., **Yalcinkaya, B**., Jirsak, O., Dependent and independent parameters of needless electrospinning, *Fibers and textiles*, ISSN:1335-0617,1, pages 75-80, 2015.
4. Yalcinkaya, F., **Yalcinkaya, B**., Maryska, J., Preparation and Characterization of Polyvinyl Butyral Nanofibers Containing Silver Nanoparticles, *Journal of materials science and chemical engineering* 04(01):8-12. DOI: 10.4236/msce.2016.41002

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1. **Yalcinkaya, B**., Cengiz-Callioglu, F., 'The Effect of Supporting Material Type on the Nano Fiber Morphology', September 21-23, pp.69-73, *NanoCon*, Brno Czech Republic, 2011.
2. **Yalcinkaya, B**., Cengiz-Callioglu, F., “The Roller Electrospinning of Poly(vinyl alcohol) Nanofibers”, *ITMC-3rd Edition of the International Conference on Intelligent Textiles&Mass Customisation*, Casablanca-Morocco, 2011.
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6. Yener, F., Jirsak, O., **Yalcinkaya, B**., “The Determination Of Anionic And Non-Ionic Surfactant Effect On Electrospun Nanofibers”, pp. 331-338, *Strutex*, Liberec-Czech Republic, 2011.
7. Sevgisunar, H.G., Yener, F., **Yalcinkaya, B**. “Comparision Of Needle And Rod Electrospinning System”, pp. 353-358, *Strutex*, Liberec-Czech Republic, 2011.
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14. Yalcinkaya, F., **Yalcinkaya, B**., Jirsak, O., 'Experimental Investigation of Salt Effect on Electrospinning Parameters and Nanofiber Morphology', *Nanocon*, Czech Republic - Brno, 2014.
15. Yalcinkaya, F., **Yalcinkaya, B.,** Jirsak, O., Dependent and Independent Parameters Of Needleless Electrospinning, *20th Strutex*, Liberec-Czech Republic, 2014.
16. Yalcinkaya, F., **Yalcinkaya, B.**, Hruza, J., Hrabak, P., Maryska, J., Nanofibrous composite membranes for microfiltration. , *Nanocon*, Czech Republic - Brno, 2016.

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2. Yener, F., **Yalcinkaya, B**., Jirsak, O., “Effect of Jet Electric Current on Jet Regimes in Electrospinning of Polyvinyl Butyral Solutions”, *Fiber Society 2012,* Empa/Switzerland.
3. **Yalcinkaya, B**., and Chaloupek, J., `Synthesis of Nanofiber Based Thin Film Membrane via Interfacial Polymerization. *1st International Conference on Desalination Using Membrane Technology*. Sitges, 2013.
4. **Yalcinkaya, B**., and Chaloupek, J., Usage of composite membranes based on nanolayers in the liquid filtration; Separation of salt. *International Textile Summit and Project Market*, Kahramanmaraş, 22-24 October, 2014.
5. **Yalcinkaya, B**., and Chaloupek, J., Effects of support material structure on interfacial composite membranes, *2nd International Conference on Desalination Using Membrane Technology*. Singapore, 2015.

8.7 National conference posters presentations in abstract

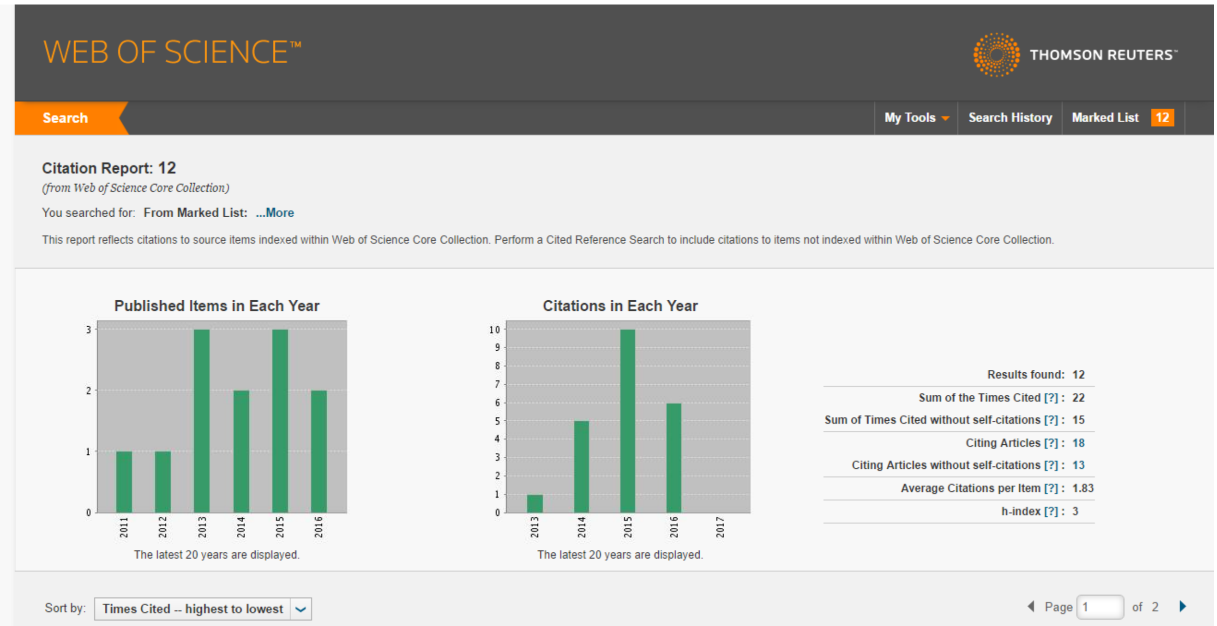
1. **Yalcinkaya, B**., Cengiz-Callioglu, F., Yener, F., Jirsak, O., Relationships Between Solutions Conductivity and Current of jet in Electrospinning, *8th Nanoscience and Nanotechnology Conference,* Abstract: pp.401 Ankara, Turkey, 2012.

2. Yener, F., **Yalcinkaya, B.**, Jirsak, O., Kumalo, M., Increasing Fabric Performance of Electrospun Nano Mat', *8th Nanoscience and Nanotechnology Conference*, Abstract: 0162, pp.393, Ankara, Turkey, 2012.

8.8 Honors and Awards

1. 2nd Place Project Award, International Textile Summit and Project Market, Kahramanmaraş, 22-24 October, 2014.
2. 2nd Best Poster Award, International Nanocon, Czech Republic - Brno, 2014.

8.9 Quotation



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Curriculum Vitae

BATURALP YALÇINKAYA

TEL :	+90 541 813 54 52 (TR) +420 777 119 880 (CZK)
ADDRESS :	Technická univerzita v Liberci Studentská 1402/2 461 17 Liberec 1
E-Mail:	baturalpyalcinkaya@hotmail.com baturalp.yalcinkaya@tul.cz
DATE OF BIRTH:	11.01.1988
DATE OF PLACE:	Osmaniye/Turkey

Education

PhD:
2012 - 2016 Technical University of Liberec, Faculty of Textile

Master
2010-2012 Suleyman Demirel University Textile Eng. Department
Degree: 84/100

Undergraduate
2006-2010 Suleyman Demirel University Textile Eng. Department
Degree: 3.0/4.0

Subspeciality
2008-2010 Suleyman Demirel University (Dept. Of Business Administration)

2009-2010
(5 months) Obuda University (Hungary- Erasmus Programme) Textile Eng. Department

2002-2006 Alanya -Ayşe Melahat Erkin Anatolian High School
DEGREE: 4.11/5

OTHER LANGUAGES: **ENGLISH** (Good at reading, writing and speaking)

BACHELOR THESIS:

TUBITAK (The Scientific and Technological Research Council of Turkey): I had a scholarship from Tubitak under the program of Research Projects in Domestic/ Foreign Universities. I worked about semi conductor fibers. The name of Project is **"Obtain of Prototype Textile Surface for Objective of Sensor Application"** with Project number 2209. Suleyman Demirel University, 2010.

MASTER THESIS:

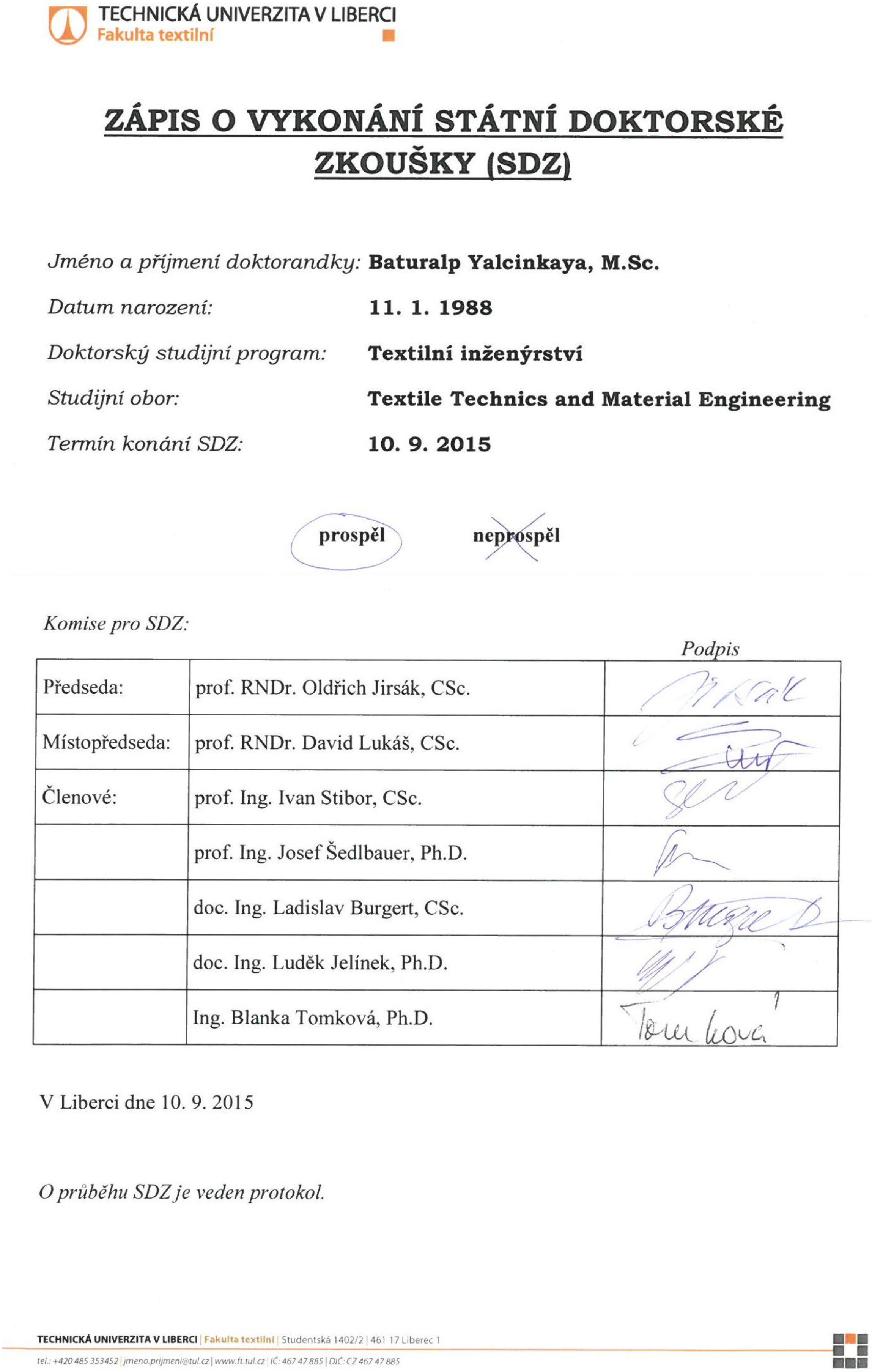
Analysis Of Taylor Cone Structure And Jet Life On The Nanofiber Production With Needle And Needle-Less Electrospinning Methods'', Suleyman Demirel University, 2012.

A brief description of the current expertise, research and scientific activities.

Doctoral studies

Studies	Textile Engineering
	Textile Technics and Materials Engineering
	Full time
Exams	Differential Equations, 03.12.2012
	Chemical Thermal Technologies of nonwovens, 16.01.2013
	Nanofibers and Nanotechnologies, 28.06.2013
	Macromolecular Chemistry, 20.03.2014
	Experimental Technique of the Textile, 18.11.2014
	Compressive Doctoral Exam, 10.09.2015
Research Projects	Nanofiber materials for tissue engineering (VaVpl, Ministry of Education Youth and Sports of the Czech Republic), researcher, 2014-2015.
	Manufacture of polymeric membranes based on nanofibrous layers (Student Grant Competition), investigator, 2014.

Record of the state doctoral exam



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ZÁPIS O VYKONÁNÍ STÁTNÍ DOKTORSKÉ ZKOUŠKY (SDZ)

Jméno a příjmení doktorandky: **Baturalp Yalcinkaya, M.Sc.**

Datum narození: **11. 1. 1988**

Doktorský studijní program: **Textilní inženýrství**

Studijní obor: **Textile Technics and Material Engineering**

Termín konání SDZ: **10. 9. 2015**

[✓ prospěl] **~~neprospěl~~**

Komise pro SDZ:

		Podpis
Předseda:	prof. RNDr. Oldřich Jirsák, CSc.	
Místopředseda:	prof. RNDr. David Lukáš, CSc.	
Členové:	prof. Ing. Ivan Stibor, CSc.	
	prof. Ing. Josef Šedlbauer, Ph.D.	
	doc. Ing. Ladislav Burgert, CSc.	
	doc. Ing. Luděk Jelínek, Ph.D.	
	Ing. Blanka Tomková, Ph.D.	Tomková

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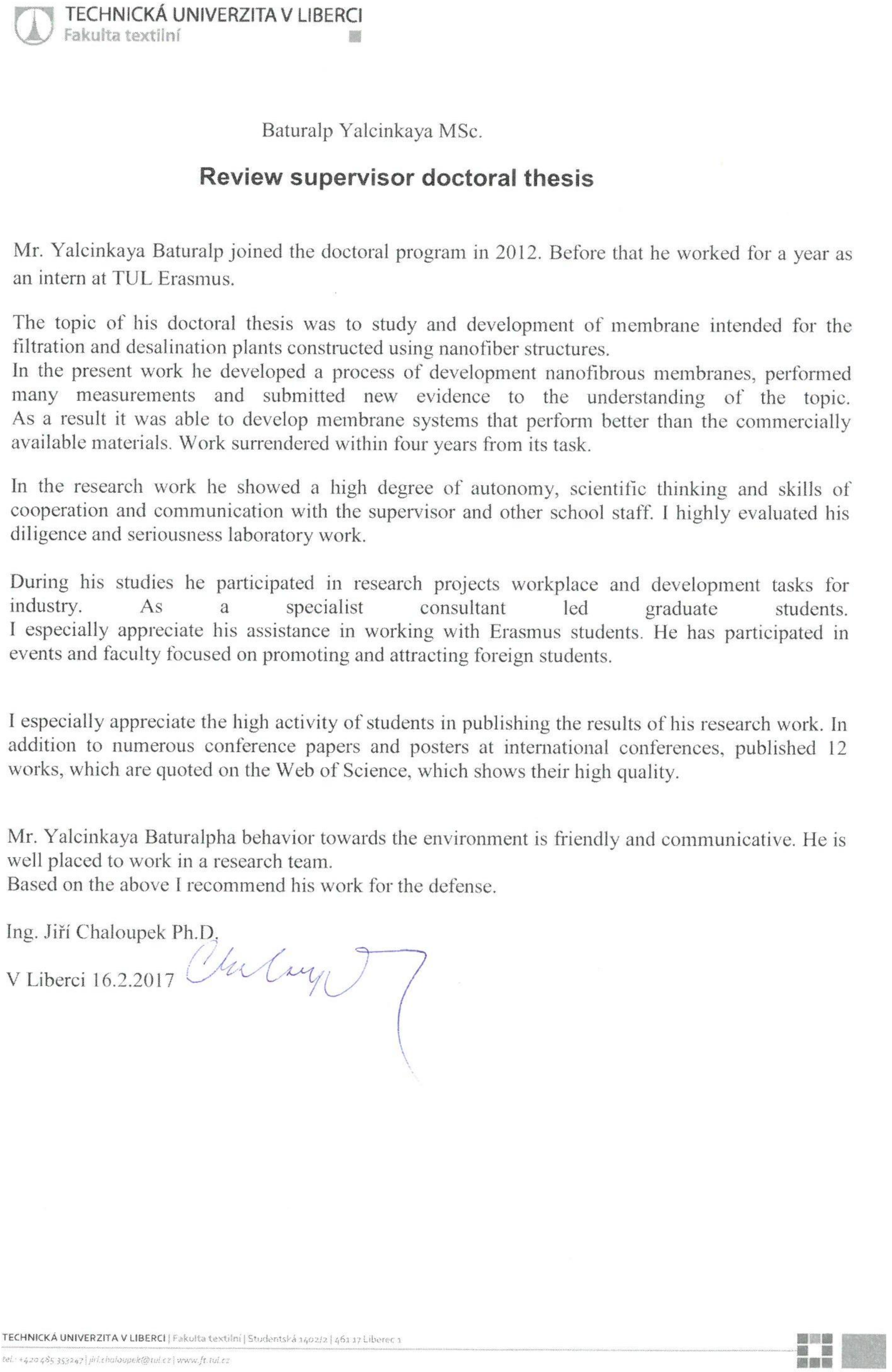
Reccomedation of the supervisor



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Baturalp Yalcinkaya MSc.

Review supervisor doctoral thesis

Mr. Yalcinkaya Baturalp joined the doctoral program in 2012. Before that he worked for a year as an intern at TUL Erasmus.

The topic of his doctoral thesis was to study and development of membrane intended for the filtration and desalination plants constructed using nanofiber structures.
In the present work he developed a process of development nanofibrous membranes, performed many measurements and submitted new evidence to the understanding of the topic. As a result it was able to develop membrane systems that perform better than the commercially available materials. Work surrendered within four years from its task.

In the research work he showed a high degree of autonomy, scientific thinking and skills of cooperation and communication with the supervisor and other school staff. I highly evaluated his diligence and seriousness laboratory work.

During his studies he participated in research projects workplace and development tasks for industry. As a specialist consultant led graduate students.
I especially appreciate his assistance in working with Erasmus students. He has participated in events and faculty focused on promoting and attracting foreign students.

I especially appreciate the high activity of students in publishing the results of his research work. In addition to numerous conference papers and posters at international conferences, published 12 works, which are quoted on the Web of Science, which shows their high quality.

Mr. Yalcinkaya Baturalpha behavior towards the environment is friendly and communicative. He is well placed to work in a research team.
Based on the above I recommend his work for the defense.

Ing. Jiří Chaloupek Ph.D.
V Liberci 16.2.2017

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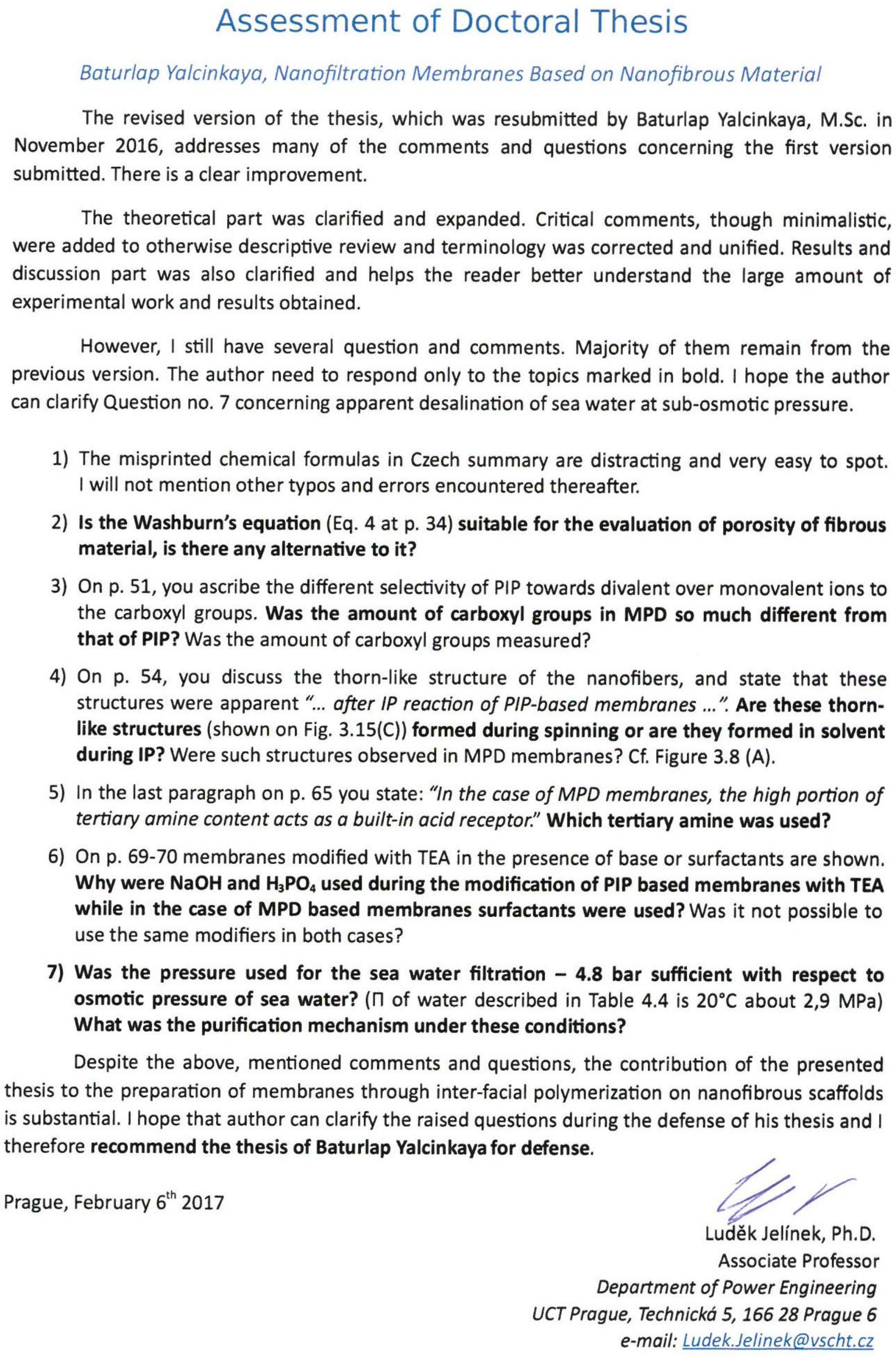

Assessment of Doctoral Thesis

Baturlap Yalcinkaya, Nanofiltration Membranes Based on Nanofibrous Material

The revised version of the thesis, which was resubmitted by Baturlap Yalcinkaya, M.Sc. in November 2016, addresses many of the comments and questions concerning the first version submitted. There is a clear improvement.

The theoretical part was clarified and expanded. Critical comments, though minimalistic, were added to otherwise descriptive review and terminology was corrected and unified. Results and discussion part was also clarified and helps the reader better understand the large amount of experimental work and results obtained.

However, I still have several question and comments. Majority of them remain from the previous version. The author need to respond only to the topics marked in bold. I hope the author can clarify Question no. 7 concerning apparent desalination of sea water at sub-osmotic pressure.

1) The misprinted chemical formulas in Czech summary are distracting and very easy to spot. I will not mention other typos and errors encountered thereafter.
2) **Is the Washburn's equation** (Eq. 4 at p. 34) **suitable for the evaluation of porosity of fibrous material, is there any alternative to it?**
3) On p. 51, you ascribe the different selectivity of PIP towards divalent over monovalent ions to the carboxyl groups. **Was the amount of carboxyl groups in MPD so much different from that of PIP?** Was the amount of carboxyl groups measured?
4) On p. 54, you discuss the thorn-like structure of the nanofibers, and state that these structures were apparent *"... after IP reaction of PIP-based membranes ..."*. **Are these thorn-like structures** (shown on Fig. 3.15(C)) **formed during spinning or are they formed in solvent during IP?** Were such structures observed in MPD membranes? Cf. Figure 3.8 (A).
5) In the last paragraph on p. 65 you state: *"In the case of MPD membranes, the high portion of tertiary amine content acts as a built-in acid receptor."* **Which tertiary amine was used?**
6) On p. 69-70 membranes modified with TEA in the presence of base or surfactants are shown. **Why were NaOH and H_3PO_4 used during the modification of PIP based membranes with TEA while in the case of MPD based membranes surfactants were used?** Was it not possible to use the same modifiers in both cases?
7) **Was the pressure used for the sea water filtration – 4.8 bar sufficient with respect to osmotic pressure of sea water?** (Π of water described in Table 4.4 is 20°C about 2,9 MPa) **What was the purification mechanism under these conditions?**

Despite the above, mentioned comments and questions, the contribution of the presented thesis to the preparation of membranes through inter-facial polymerization on nanofibrous scaffolds is substantial. I hope that author can clarify the raised questions during the defense of his thesis and I therefore **recommend the thesis of Baturlap Yalcinkaya for defense**.

Prague, February 6th 2017

Luděk Jelínek, Ph.D.
Associate Professor
Department of Power Engineering
UCT Prague, Technická 5, 166 28 Prague 6
e-mail: Ludek.Jelinek@vscht.cz

Baturalp YALCINKAYA :
Dissertation: Nanofiltration Membranes based on Nanofibrous Material

REVIEW

The **subject itself** is very important and full of activity. It is witnessed by many books, reports, patents and application notes that have been and still being published. Consequently, it is not easy task to find the „untouched" original subject, suitable for PhD dissertation. Accordingly, it should examine important general problem with the point of view of basic science. On the other hand, it should be closely related to application, too. Unfortunately, research presented in this dissertation cannot be regarded as original as well as related to basic science. I am not specialist in membrane technology, but looking to commercial literature, I have soon realized that nanofiltration membranes based on almost any materials are routinely produced by many companies and massively used. Moreover, membrane with almost any separation characteristics can be developed on demand strictly on commercial basis. It means that basic knowledge acquired by several producers is broad and deep enough. Most of membranes studied are polyamide – based membranes and it is exactly the subject of this dissertation. Having this in mind I dare to sayfollowing: The dissertation submitted is doing research on subject that is already and repeatedly done and its application potential is well documented. To illustrate it, I would add following. Results, obtained in this dissertation have been compared with those of commercial membranes (namely, NF 90 and NF 270). Looking in the commercial literature (author did not bother with it) I have found that each of both acronyms denote the whole family of membranes and that there are dozens of other families, all with detailed separation profile and property specification. It is not surprising, that unfortunately, no "sensitive" information on structure, porosity e.t.c. are disclosed by producers. I am sorry but I see no sense in doing comparison with membrane of unknown structure and other characteristics. Based on such comparison, we can only say, that commercial membrane is better, worse or equal, but we do not know why as we know nothing about its structure, composition and method of fabrication.

To sum it up, I have found the subject of the dissertation submitted as almost fully overlapping already well developed and commercially utilized "nanofiltration membranes business".

Literature review.

Literature citation is problematic in itself for such subject. Nevertheless, there are problems also with more simple things as accessibility and validity of literature cited. One can see it on page 21 where in electrospinning paragraph almost only domestic, sometimes inaccessible, works are cited. I would like to express my strong criticism to practice, that only domestic papers and no important works of others are cited.

Fabrication and optimization of composite membranes for the removal of salts.

In this chapter, the fabrication of composite membrane should be described in detail. Unfortunately, such process is influenced by several variables. Contrary to representative literature cited (PETERSEN, 1993) author of the present Dissertation has divided the variables to two categories (page 25, Table 2.1) independent a dependent parameters. Interestingly, each so-called independent parameter is optimized separately, probably with the hope, that all others will stay unchanged, but it is definitely not true. These variables cannot be considered as independent and better methods should be found. And again, the better methods is available, published and cited. (FREGER, 2003). I have made the copy of it below in order to ask author to try to interpret them.

$$\delta \sim \left[\frac{LD}{k(C_a f_a + C_b f_b)}\right]^{1/3}$$

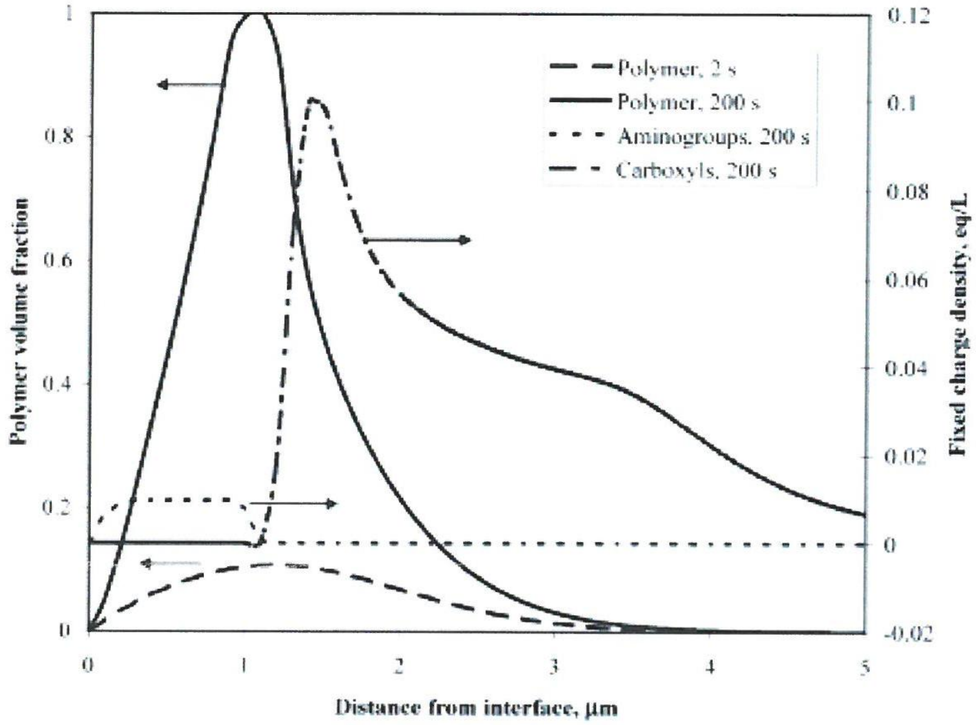

Figure 6. Calculated concentration profiles of polymer (at 2 and 200 s elapsed time) and of amine and acyl chloride groups after 200 s. The parameters used are the same as those in Figure 5.

I do not understand why this by far more sophisticated approach has not been applied? It would help to explain almost all questions related to the structure and composition of active barrier layer. Moreover, this approach would offer the rare opportunity to apply the basic science approach. Instead the attempt-error approach has been used throughout Parts 3 and 4.

I would have many questions to these parts, only several of them will be asked bellow.

First point: Figure 3.5. page 46. Both MPD as well as PIP membranes do contain –OH groups (the most probably formed by hydrolysis). What can we expect to take place in aqueous solution of amines? It is related to extraordinary low contact angle given for PIP membrane in Table 3.3. page 47 without any explanation.

Second point: the chemical equations 3.6 and 3.7. on page 48 and 49 (please correct!) are describing the ongoing reactions only incompletely. Based on any book of general chemistry one can conclude, that acid-base reactions proceed extremely quickly. During both reactions depicted, two equivalents of HCl are produced (why exactly two and not one or three?). What is the fate of this strong acid?

Third point: Page 60 – IR spectra. It seems to me that spectra in Figures 4.4 and 4.5. are almost identical. Explain your interpretation.

Fourth point: Explain the term „phase transfer catalysis", and suggest its application to understanding of interfacial polymerization mechanism.

Fifth point: Comment on data of Fig. 3.16. page 60. What is the point in changing two variables?

Conclusions.

- The dissertation is reporting about tremendous amount of work.
- Unfortunately, the methods used are not new – in fact routine methods have been applied to only slightly different compounds, than those already reported in literature.
- There is critical lack of novelty.
- What are missing completely: at least modest attempts to draw any general conclusions from the data measured. Something, what could be used in future when designing new membranes.

To sum everything up, I think that the dissertation of Baturalp Yalcinkaya **cannot be accepted** in the present form as valid basis of dissertation process that should follow.

I. Stibor

Liberec, January 1st 2017

Prof. Ing. Ivan Stibor, CSc.

Report on Baturalp Yalcinkaya's PhD Thesis
"Nanofiltration Membranes Based on Nanofibrous Material"

06/02/2017

I have read the PhD thesis written by Mr. Baturalp Yalcinkaya under the supervision of Ing. Jiří Chaloupek Ph.D attentively and evaluated the importance of the thesis for the field of science.

Nanofiber layers are still suffering due to their low mechanical properties. Therefore, the researchers keep on searching for a permanent solution. Using a supporting material is one of the logical solutions to enhance mechanical properties of nanofibers. However, the low adhesion between nanofiber layers and supporting material surface occurs another limitation to obtain end-product.

Baturalp's work offers an essential and versatile solution to use nanofibers layer in the filtration process. His contributions relate to nanofibers production, lamination of supporting substrate, formation and characterization of the responsible layer for salt ions in water.

The technique that Baturalp followed is reasonable to reach final filtration product. He carries out an extensive characterization of Polyamide active layer formation after solving the limitation of mechanical properties of nanofiber layer by the lamination method. He selects two different membrane samples which were performed high rejection rate against monovalent and divalent salts in chapter 3. His primary results in this section were able to compete for the membranes that already commercialized in filtration market. The work proceeds with enhancement performance of membranes by adding ionic liquid and acid acceptors. The membranes which were prepared within this thesis provide not only high salt ions rejection performance but also high permeate water flux.

The greatest challenge of his work relates to desalination of sea water using thin film nanofibrous membranes and dead-end filtration device. He discovered that the prepared thin film nanofibrous membranes capable of retaining sufficient amount of salt particles from sea water. However, the high osmotic pressure of sea water leads to low flux performance of permeate water. It is my opinion that the final prepared product is convenient to end-use with some further improvement.

The symbols, list of tables and figures are given clearly within the thesis. The tables and figures represent the results of the experimental work. The results and conclusions are explained clearly and carefully within the text contributing to easily understanding the aim of the scientific work.

Mr. Baturalp Yalcınkaya has made many publications in serious indexed journals and many oral and poster presentations in mostly international and national conferences concerning the valuable scientific work included in his PhD thesis and thus contributed to the field of membran technology of filtration.

Depending on the upper evaluation, I consider the PhD thesis on "Nanofiltration Membranes Based on Nanofibrous Material" is a valuable scientific work and I highly recommend it for defence.

Assoc. Prof. Dr. Funda CENGİZ CALLIOGLU
SÜLEYMAN DEMİREL UNIVERSITY
Engineering Faculty
Textile Engineering Department
e-mail: fundacengiz@sdu.edu.tr