PREPARATION AND CHARACTERIZATION OF ANTIFOULING NANOFILTRATION MEMBRANES FROM A RESPONSIVE PENTABLOCK COPOLYMER

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ABSTRACT

PREPARATION AND CHARACTERIZATION OF ANTIFOULING NANOFILTRATION MEMBRANES FROM A RESPONSIVE PENTABLOCK COPOLYMER

The most substantial factor restricting the extensive application of membrane processes is the fouling problem resulting from the deposition of solutes in water on the surface or within the pores of membranes. The frequently used chemical washing procedure to eliminate the fouling issue causes environmental pollution and shortens the membrane life. In order to overcome these disadvantages, the development of membranes possessing low fouling potential is needed. In recent years, the stimuli-responsive polymers have received attention for developing membranes possessing low fouling potential. The antifouling property of these membranes is controlled through the change in their conformation and hydrophilic/hydrophobic characteristics as a response to change in external stimuli such as pH, temperature and ionic strength. The aim of this study was to design antifouling nanofiltration membranes (NF) using a pentablock copolymer which consists of temperature responsive Pluronic F127 (PEO-b-PPO-b-PEO) in the middle block and pH responsive poly(N,N-(diethylamino)ethyl methacrylate) (PDEAEM) in the end blocks. Effects of pH and temperature responsiveness on the membrane fouling were investigated. Fouling tendencies of the membranes were evaluated by using Bovine Serum Albumin (BSA), Alginate (ALG) as organic foulant and *Escherichia coli (E.coli)* as biological foulant. NF membranes were characterized by scanning electron microscope (SEM), contact angle and zeta potential measurements. It was demonstrated that pentablock copolymer coated membranes displayed antifouling resistance by changing filtration pH and temperature.

ÖZET

PENTABLOK BİR KOPOLİMERDEN KİRLENMEYEN NANOFİLTRASYON MEMBRANLARININ HAZIRLANMASI VE KARAKTERİZASYONU

Membran proseslerinin yaygın olarak kullanımını kısıtlayan en önemli faktör su içinde bulunan kolloidler, çözünmüş katı maddeler, organik maddeler, mikroorganizmalar gibi kirleticilerin membran yüzeyinde ya da membran gözenekleri arasında birikmesinden kaynaklanan kirlenme problemidir. Kirliliği gidermek için sık sık uygulanan kimyasallarla yıkama işlemi hem çevreye zarar vermekte, hem de membranın ömrünü kısaltmaktadır. Bu dezavantajların ortadan kaldırılabilmesi için kirlenme potansiyeli düşük membranların geliştirilmesine ihtiyaç vardır. Son yıllarda, dış uyarıcılara tepki veren polimerler düşük kirlenme potansiyeline sahip membranlarının geliştirilmesinde önem kazanmıştır. Bu membranlarının kirlenmeme özelliği sıcaklık, pH ve iyonik güç gibi dış uyarıcılara cevap olarak konformasyonları ile hidrofilik/hidrofobik karakterlerindeki değişimden kaynaklanmaktadır. Bu çalışmanın amacı orta blok olarak sıcaklığa duyarlı Pluronic F127 (PEO-b-PPO-b-PEO) ve uç bloklar olarak pH'a cevap veren poli(N, N- (dietilamino) etil metakrilat) (PDEAEM) içeren bir pentablok kopolimerle kirlenmeyen nanofiltrasyon membranı geliştirmektir. pH ve sıcaklığın membranların kirlenmesi üzerine etkileri incelenmiştir. Membranların kirlenme yatkınlığı sığır serum albümini ve aljinik asit organik kirletici olarak ve koli basili biyolojik kirletici olarak seçilerek ölçülmüştür. NF membranları taramalı electron mikroskobu (SEM), temas açısı ve zeta potansiyeli ölçümleri ile karakterize edilmiştir. Pentablok kopolimer kaplı membranların pH ve sıcaklık değişimine bağlı olarak kirlenmeme direnci gösterdiğini belirlenmiştir.

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CHAPTER 1

INTRODUCTION

Nanofiltration membrane (NF) is an important separation process which is used in the recovery of high value cationic macromolecules in pharmaceutical industry and in the removal of dye or heavy metals in paper, textile, nuclear and automotive industries (Van der Bruggen et al., 2001). Even though NF membrane has many advantages, fouling is the major challenge of restricting the use of NF based membrane processes. During filtration molecules whose passage are blocked by the membrane deposit onto the membrane surface or into pore of the membrane and eventually cause fouling (Liu et al., 2016). Fouling of membrane leads to decrease in membrane performance through flux reduction and increase in energy consumption since high pressure should be applied to compensate flux reduction. Membrane fouling is affected by membrane surface characteristics such as charge, hydrophobicity and roughness (Hobbs et al., 2006). The hydrophobic membrane surface accelerates the adsorption of different type of foulants (Zhou et al., 2014). Therefore, hydrophobic membrane surface is changed to hydrophilic surface through various modification techniques.

In the recent years the stimuli-responsive polymers have been used to improve hydrophilic character of the membranes. Zhou et al., (2014) used temperature responsive polymer poly(N-isopropylacrylamide) (PNIPAam) as a coating and bovine serum albumin was filtrated to test antifouling tendency of the membrane. To remove BSA accumulated membrane surface was washed with pure water at 35^oC and 25^oC. It was found that flux recovery of unmodified and modified membranes with PNIPAam were 10 % and 78 %, respectively. Zhao et al., (2011) modified UF membrane with pH responsive block-like copolymer poly(butyl methacrylate)-b-poly(methacrylic acid)-b-poly(hexafluorobutyl methacrylate) (PBMA-b-PMAA-b-PHFBM). After BSA filtration and backwashing with DI water, cleaning efficiency of the unmodified support membrane was increased from 6 % to 58 % through pH responsive coating. Mondal and Wickramasinghe, (2012) used poly(NIPAM) to produce thin film composite (TFC) nanofiltration membrane by grafting. To test antifouling performance of membranes, synthetic produced water was filtrated. It was observed that grafted membrane showed almost constant permeate flux while unmodified membrane showed significant flux decline because of fouling. Zhao et al., (2013) prepared poly(N-isopropylacrylamide) zirconium oxide (PNIPAAm-g-ZrO_2) composite membranes by grafting temperature responsive polymer PNIPAam. Membrane modified with temperature responsive polymer showed higher flux recovery ratio than unmodified membrane after humic acid filtration. Cheng et al., (2011) modified PES hollow fiber membrane by blending with different ratios of pH responsive polymer poly(styrene–acrylic acid–N-vinyl pyrrolidone) (P(St–AA–NVP)). BSA solution was used as model foulant. After BSA filtration, all modified membranes with different ratio of pH responsive polymer exhibited higher flux recovery ratio than unmodified PES hollow fiber membranes. The review of literature studies indicated that there are limited numbers of studies on the use of stimuli-responsive polymers for controlling fouling on NF membranes. In these studies single responsive polymers were coated on UF support membranes and the membrane fouling is diminished. It is expected that dual responsiveness can be more effective for creating antifouling membrane surfaces.

The aim of this thesis was to develop novel nanofiltration membranes resisting to both organic and biological fouling by using a pH and temperature responsiveness pentablock copolymers. Fouling tendency of produced membranes was investigated with BSA, ALG and *E.coli*. The membranes were characterized by SEM analyses, zeta potential and contact angle measurements. It was found that temperature responsiveness was more effective than pH responsiveness. This thesis presents the first comprehensive fouling study for dual responsive NF membranes.

In addition to this Introduction chapter, the thesis consists of four more five chapters. Chapter 2 provides literature review about membrane fouling, methods to reduce fouling and stimuli-responsive polymers used for surface modification. In Chapter 3, materials and methods used for producing membranes, characterization methods and fouling tests were explained. The results on fouling tests given and discussed evaluated in Chapter 4. Finally, Chapter 5 summarizes the conclusions of the study and suggestions for the future works with stimuli-responsive membranes.

CHAPTER 2

LITERATURE REVIEW

2.1. Membrane Fouling

Membrane fouling is defined as accumulation or adsorption of dissolved substances/particles on surface or pores of the membranes (Koros et al., 1996). Membrane fouling has negative effects on membrane performance since it lowers the permeate flux beside it increases costs due to increased energy demand, chemical cleaning agents and more labour for maintenance. Finally, membrane lifetime is shortened as a result of fouling.

Membrane systems are operated under constant permeate flux by changing transmembrane pressure (TMP) or constant TMP by changing permeate flux. Membrane fouling followed by a decline in flux at constant pressure operating or an increment in TMP at constant flux. Membrane fouling is classified reversible and irreversible fouling. Reversible fouling can be easily removed by physical cleaning such as rinsing, flushing and backwashing from the membrane surface. On the contrary, irreversible fouling needs cleaning by harsh chemical cleaning agents. Proteins deposit irreversibly on the membrane as a type of foulants due to hydrophobic interactions, electrostatic interactions, hydrogen bonding, and van der Waals interactions (Guo et al., 2012).

2.2. Membrane Fouling Mechanism

In literature different membrane fouling mechanism models have been proposed to explain membrane fouling phenomena in terms of flux decline or increment in transmembrane pressure. These models are classified into 4 categories depending on the location of the dissolved particles on the membrane. These are complete pore blocking, intermediate blocking, standard blocking, and cake layer formation. Figure 2.1 illustrates schematics of different types of membrane fouling mechanism (Abbasi et al. 2012).

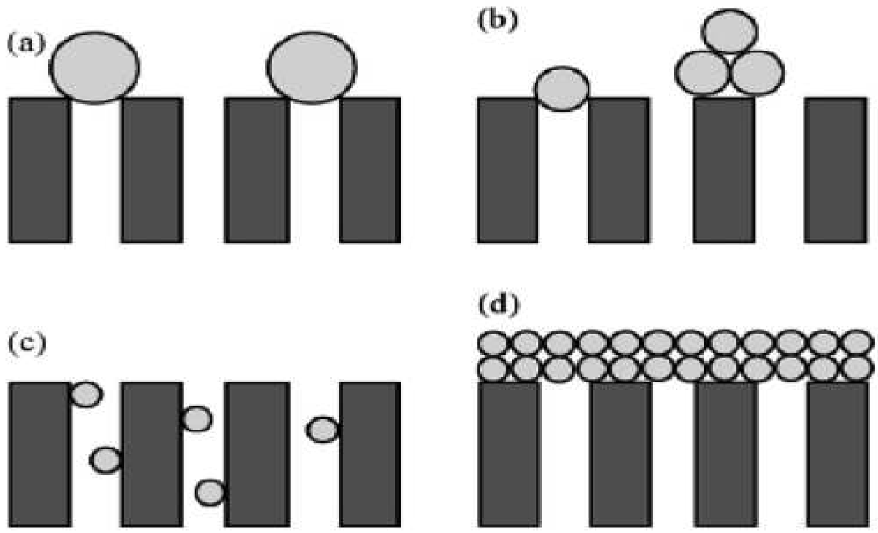

Figure 2.1. Fouling mechanism: (a)Complete pore blocking, (b)Intermediate blocking, (c) Standard blocking and (d)Cake layer formation (Source: Abbasi et al., 2012).

The standard pore blocking model is generally called adsorptive fouling or pore narrowing. This fouling mechanism model is effective when the sizes of retained particles are smaller than the pore size of the membrane. In this model, dissolved particles in the feed solution enter the membrane pores and attach to inner pores wall of the membrane but not completely block the pores. Figure 2.1.c exhibits the place of the particles in the pores wall of the membrane for this membrane fouling mechanism model. Diameter of membrane pores is decreased and membrane resistance increases as a result of this blocking.

In the case of intermediate pore blocking, each particle blocks some of the membrane pores or accumulates on other particles which already blocked the some of the other pores.

In complete pore blocking model, fouling forms when the size of particles is similar to the pore size of the membrane. In this fouling mechanism model, each particle plugs the different pores. Ultimately, complete pore blocking causes minimization of active area for filtration and increment in the membrane resistance. Thus, the membrane looses functionality and it should be replaced or cleaned.

Cake/gel fouling layer results in deposition of the particles which are larger than the size of membrane pores on the membrane surface. Over a period of time, cake/gel layer becomes thicker and creates an extra porous barrier. Therefore, permeate flux is lowered to a great extent.

2.3. Foulant Classification

Foulants are classified into 4 categories depending on fouling materials as inorganic fouling/scaling, particle/colloids fouling, microbial fouling/biofouling and organic fouling (Liu et al., 2001).

These are the common example of foulants; calcium and inorganic salts for scaling, clay, metal hydroxy, colloidal silica for colloidal fouling, macromolecules for organic fouling, bacteria and viruses for biofouling. (Schäfer et al., 2004)

2.3.1. Organic Fouling

Organic fouling forms due to the retained organic compounds and cause the irreversible flux decline. Organic particles have different effects on the membrane fouling. They change surface characteristic due to adsorption on membranes. In addition, organic particles enhance microbial fouling since they may be a food source for bacteria. Also, they prevent removal of colloids (Schäfer et al., 2004).

Natural organic matter consists of organic compounds with different molecular weight in surface or ground water. NOM has both non/humic part which includes organic molecules, proteins, polysaccharides and polyoxyaromatics are common examples of non-humic natural organic matter foulants (Abdelrasoul et al., 2013). Many studies reported that ultrafiltration (UF) membranes are affected by NOM foulants and especially, polysaccharides are defined as the dominant foulants in UF and NF membrane (Amy and Cho, 1999).

2.3.2. Inorganic Fouling

Different salts accumulate on membrane surface or pores and cause inorganic fouling. When the concentration of salts in the bulk solution is higher than their solubility limit, salts precipitate on the membrane (Ridgway et al., 2013). Generally, all kind of salts follow the same path for precipitation process. Inorganic fouling is usually formed on NF and reverse osmosis (RO) membranes operated at high pressure (Aly, 2015).

2.3.3. Colloidal Fouling

Colloidal fouling is caused by the accumulation of small and charged particulate compounds on the surface due to the electrostatic interaction or as a result of adsorption with surrounding water (Boerlage, 2001). Colloidal fouling is generally reversible and may be removed by physical hydraulic cleaning such as air scrubbing, rinsing and backwash.

Rarely, colloidal compounds cause irreversible fouling when membrane pore size is larger than the size of colloidal compounds. Therefore, the membrane may trap those particles and colloids cannot be easily removed by simple hydraulic cleaning (Liu et al., 2001).

2.3.4. Microbial Fouling

Microbial fouling is induced by formation of biofilms on the membrane surface due to a living organism such as viruses, bacteria and fungi. Microbial fouling process is distinguished from other type of foulants by its dynamic nature of organisms (Schäfer et al., 2004). When bacteria hold on the membrane once, they begin to create extracellular polymetric substances (EPS) to shape a hydrated gel whose structure shields bacterial cell from biocides. Microbial fouling is influenced by the properties of the feed solution. Feed solution characteristics such as number of microbial population and nutrient availability as well as environmental conditions for microbial growth determine whether microbial fouling take places on the membrane surface or not (Liu et al., 2001).

2.4. Methods to Reduce Fouling

Methods to reduce fouling are classified into 2 categories; as minimization the effect of fouling and membrane remediation. The first group consists of adequate feed pretreatment, membrane pretreatment and membrane modification to minimize the fouling. The second group employs chemical or physical cleaning for fouled membranes.

2.4.1. Fouling Minimization

Fouling may be controlled or prevented by using feed pretreatment. The level of the pretreatment changes with quality of feed solution which includes organic and inorganic dissolved particles. Separation efficiency may be increased by using coagulant and coagulant aids as a pretreatment. After adding coagulants to feed solution, prefiltration or sedimentation is applied to eliminate potential foulants. Scale inhibitors are used to hinder scale formation. Composition of feed solution affects the degree of scaling and to get rid of the hardness ions the chemical species such as lime and soda are put in hard water (Koutsakos et al., 2010). In some cases, sonication is applied to eliminate the particles from the membrane surface or feed solution is prefiltered to remove large particles. Microfiltration (MF) and ultrafiltration are used as NF prefilters membranes since both UF and MF retain the colloids, suspended particles and bacteria.

The second strategy commonly used for minimizing fouling is to modify membrane surface. There are different surface modification techniques to make the surface less prone to fouling. Generally, fouling tendency increases with increasing surface roughness since rough membrane surfaces accelerate the accumulation of particles (Hobbs et al., 2016). Membrane surface is modified to reduce surface roughness. Hydrophobic surfaces enhance deposition of particles as a result of hydrophobic interactions and enable pertinent condition for the accumulation of organic, inorganic, colloidal and biological foulants (Zhou et al., 2014). Therefore, the aim of most of the surface modification strategies applied to reduce fouling is to change the hydrophobic character of the membrane surface to hydrophilic. For this purpose different hydrophilic polymers were used and in recent years, stimuli responsive polymers have received attention due to their hydrophilic nature and conformational change as a result of different stimuli.

2.4.2. Membrane Remediation

Once the membrane is fouled, remediation is applied by chemical or physical cleaning. Frequency and duration of cleaning steps depend on membrane process and foulant types. Either physical or chemical cleaning methods are applied. Physical cleaning methods contain backwash, air spurge and rinse. Loosely attached foulants are removed by using a physical cleaning. Although the selection of sufficient pretreatment and proper membrane type may decelerate the fouling, membrane chemical cleaning should be applied to maintain the membrane performance. The chemical cleaning should be effective for removing different types of foulants as well as delicate to the membranes to sustain separation performance. However, chemical cleaning eventually causes the degradation of the membrane structure.

2.5. Stimuli-responsive Polymers

Stimuli-responsive polymers or smart polymers are highly functional polymers that change their conformation according to their immediate environment. They can be sensitive to a number of factors, such as temperature, humidity, pH, ionic strength, intensity of light, an electrical or magnetic field and react to external stimuli to some extent by changing their conformation alongside chains, segments or end groups (Wandera et al., 2012).

Responsive polymers are used in 3 different ways to develop membranes: 1) hydrogel membrane prepared only from responsive polymer 2) blend membrane prepared by blending a responsive and nonresponsive polymers 3) TFC membrane prepared by coating a responsive polymer on a suitable membrane surface (Liangyin et al., 2011).

2.5.1. pH Responsive Polymers

Conformation of pH responsive polymers change from swollen to collapsed as a response to pH change. Types of pH responsive polymers are shown in Figure 2.2. Polybase polymers accept H^+ below the dissociation constant (pKa) value and become positively charged. These positive charges create a repulsion between the chains that causes the swelling of polymer. Above pKa value, polymer chains are in collapsed form. On the contrary, polyacid polymers release H^+ above pKa value and become swollen due to repulsion between negatively charged groups. Poly(N,N-dimethyl aminoethyl methacrylate) (PDM) hydrogels are an example of pH responsive polybase polymers and display pH responsive volume phase transition characteristic. When environmental pH is decreased below the pKa value, PDM hydrogels become swollen (Liangyin et al., 2011).

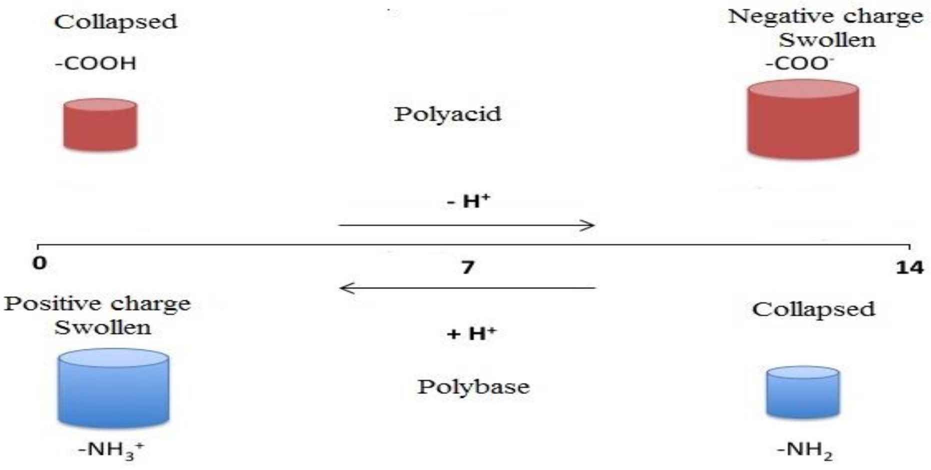

Figure 2.2. Types of pH responsive polymers.

Han et al., (2014) fabricated pH responsive UF membranes using a novel preparation strategy called as one-pot in-situ cross-linked copolymerization. In this study, commercial polyethersulfone (PES) was used as membrane matrix and poly (methyl methacrylate-co-acrylic acid) (P(MMA-AA)) with different ratios was used as pH responsive copolymer in the composite membrane. 1g/L BSA solution was filtrated through this membrane at pH:7 for 3 cycles and membrane surface was washed with deionized water for 10 minutes at the end of each cycle. Flux of phosphate-buffered saline solution (PBS) was measured before and after filtration of BSA solution to characterize the antifouling performances of unmodified and produced composite PES membranes. All modified composite membranes with different ratio of P(MMA-AA) showed better flux recovery ratio compared to commercial PES membrane and this, was attributed to hydrophilic membrane surface resulted from water layer formed between ionized carboxyl groups and water molecules above the pKa value of PAA and electrostatic repulsion between BSA and negatively charged membrane surface.

Sinha and Purkait (2014) prepared pH responsive UF membrane by blending novel cross linked pegylated functional copolymer poly(acrylic acid-co-polyethylene glycol methyl ether methacrylate) (poly-AA-co-PEGMA) and polysulfone to obtain a hydrophilic membrane. Permeate flux of 1 g/L BSA solution was measured for 2 hours to study fouling resistance behavior of membranes while pH was kept constant at 7. The modified responsive membrane experienced a slower rate of permeate flux decline than the unmodified membrane during BSA filtration. At pH:7 (above pKa), poly-AA-co-PEGMA was negatively charged due to deprotonation of COOH group to COO^- and membrane became hydrophilic. Thus, electrostatic repulsion between BSA (iep:4.7) and membrane surface and hydrophilic character of membrane surface lowered the BSA adsorption.

2.5.2. Temperature Responsive Polymers

Temperature responsive polymers display reversible conformation change at the lower critical solution temperature (LCST). At temperatures below lower critical solution temperature, chains of temperature responsive polymers display swollen conformation and hydrophilic state due to the hydrogen bonding. When temperature is higher than lower critical solution temperature, polymer chains become collapsed and hydrophobic state. As a result of conformation change of polymer chains, temperature responsive polymers show volume phase transition behavior depending on changing temperature (Liangyin et al., 2011).

Zhou et al., (2014) prepared poly(N-isopropylacrylamide) (PNIPAAm)-g-zirconium oxide (ZrO_2) tubular membranes by using the chemical grafting polymerization of PNIPAAm on zirconium oxide membrane surface to design easy-cleaning surfaces. To test this property of the membranes, 0.1g/L BSA solution (pH:6.7) was filtrated for 1 hour at 25ºC and 35ºC. After filtration of the BSA solution, the fouled membranes were washed by using deionized water at either 25ºC, 35ºC and by a combination of washing at 35ºC /25ºC for 30 minutes. BSA filtration at T:25˚C showed almost constant permeate flux performance but fouling test at T:35˚C showed high flux decline. At T: 25˚C, BSA adsorption was hindered since at a temperature below the LCST of the temperature responsive PNIPAAm polymer. PNIPAAm brushes showed swollen conformation which made membrane surface hydrophilic. The flux recovery ratio was used to compare the effect of backwash temperature. After BSA filtration at T:25˚C, the flux recovery ratios with backwashing at was 25ºC and 35ºC were found close to each other but washing at 35ºC and then at 25ºC showed the highest flux recovery ratio. This was due to change of structure and hydrophilic properties of the PNIPAAm brushes affected by temperature change. Figure 2.3 illustrates the change in conformation of the polymer chains when cleaning with alternate temperatures was applied. At first cleaning step at 35ºC, the hydrogen bond between membrane surface and the water molecules was blocked, water molecules were suspended from the PNIPAAm chains which caused damage of fouling layer as a result of collapsed conformation. When cleaning temperature was changed from 35ºC to 25ºC, chains of PNIPAAm became hydrophilic and chains conformation changed from collapsed to stretched due to the volume phase transition. As a consequence, protein fouling layer was damaged and membrane surface effectively cleaned.

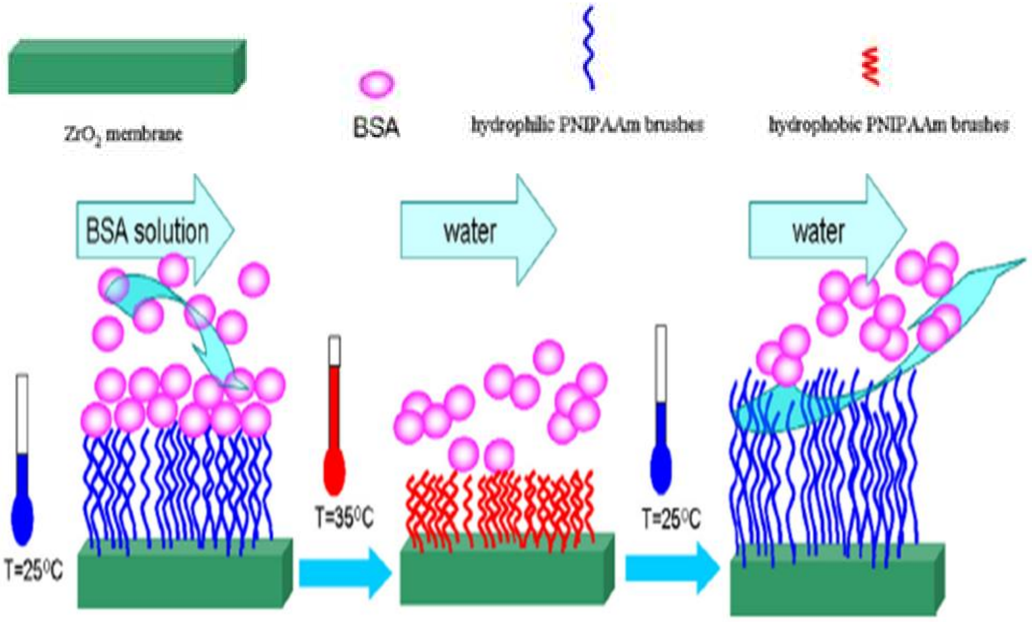

Figure 2.3. Alternate cleaning at 25 ˚C
(Source: Zhou et al., 2014).

Yu et al. (2011) modified commercial thin film composite polyamide reverse osmosis membrane by dynamically coating a thermo-responsive polymer poly(N-isopropylacrylamide-co-acrylamide) (P(NIPAM-co-Am)) to improve fouling resistance. The experiments were carried out with BSA solution containing NaCl. Fouled membranes were cleaned by alternate circulation and soaking with deionized water at different temperatures to examine the cleaning efficiency of thermo-responsive polymer coated membranes. Modified membranes showed better flux recovery rate than virgin membranes for all temperatures (30ºC -50ºC). When cleaning water temperature was changed from 40ºC (below LCST) to 45ºC (above LCST), a sharp increase in flux recovery rate was obtained due to phase transition of temperature responsive P(NIPAM-co-Am) chains which released the adsorbed BSA molecules from the membrane surface.

Yu et al., (2012) investigated the cleaning effect of thermo responsive polymer poly(N-isopropylacrylamide-co-acrylic acid (P(NIPAm-co-AAc) on the protein fouled thin film composite reverse osmosis membrane. At 25˚C, 0.1 g/L BSA solution was filtrated until reaching steady state condition at pH 6.8. Cleaning experiments were performed by using deionized water with and without thermo responsive polymer as shown in Figure 2.4. Firstly, fouled membranes were soaked in deionized water or deionized water containing P(NIPAm-co-AAc) at a temperature below the LCST of P(NIPAm-co-AAc). Then alternate circulation and soaking in deionized water were applied above the LCST. Finally, fouled membranes were rinsed with deionized water at T: 25˚C. Water flux of the cleaned membrane by P(NIPAm-co-AAc) was found higher than membrane cleaned by using only deionized water. The better antifouling property was explained by the phase transition of thermo responsive polymer at the cleaning stage. At the first step of cleaning process (below the LCST), P(NIPAm-co-AAc) showed extended conformation and diffused into fouling layer. At the second step of cleaning process (above the LCST), diffused P(NIPAm-co-AAc) chains became insoluble and changed conformation to collapsed form. The phase transition of P(NIPAm-co-AAc) chains damaged the structural integrity of the BSA fouling layer, which resulted in less protein adsorption on the reverse osmosis membrane surface.

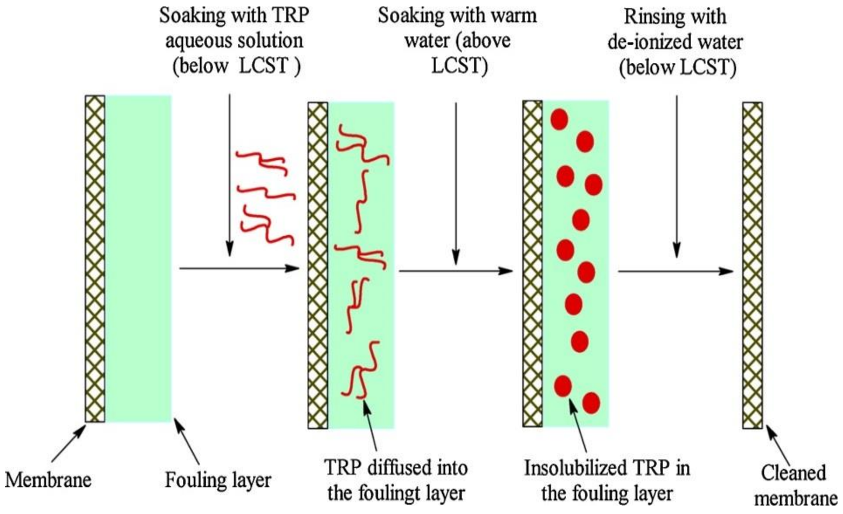

Figure 2.4. Cleaning steps of protein fouled RO membranes
(Source: Yu et al., 2012).

2.5.3. Dual Responsive Polymers

Dual responsive polymers are used in membrane preparation to get benefit from two different responsive properties. Generally, temperature and pH responsiveness are combined to make dual responsive polymers and used for advance separation (Sinha and Purkait 2014a).

Chen et al., (2014) prepared pH and temperature responsive ultrafiltration membranes by blending cross linked poly (N-isopropylacrylamide-co-acrylic acid) (PNA) microgels and polyvinylidene difluoride (PVDF). pKa value and lower critical solution temperature of produced membranes were found to be pH 4.0 and T:32˚C, respectively. To investigate antifouling property of the membrane, BSA solution with 1g/L concentration was filtrated for 1 h at different pH and temperatures. Then, membranes were washed with stirring for 2 hours. High flux recovery ratio was found when pH was increased above pKa value or temperature decreased below LCST since membrane surface became hydrophilic with stretched PAA or PNIPAM chains.

Sinha and Purkait (2014a) also studied fouling tendency of ultrafiltration membranes produced by blending pH and temperature responsive copolymer poly(N-vinylcaprolactam-co-acrylic acid) (poly (VCL-co-AA) and polysulfone. For this purpose, 1 g/L BSA solution was filtered at pH 7 and at room temperature. After 1 h BSA filtration, membranes were washed with DI water and fluxes of used membranes were measured. Flux recovery ratios of modified and unmodified membrane were found to be as 93.35 %, 33.33%, respectively since adsorption of protein on the membrane surface was diminished by poly (VCL-co-AA). When pH (7) was above the pKa value of poly (VCL-co-AA), membrane surface became hydrophilic and negatively charged. Thus, hydrophilicity and charge repulsion between membrane surface and BSA enabled the decreasing total membrane fouling.

Bera et al., (2015) produced pH and temperature responsive ultrafiltration membrane by blending responsive polymer of poly(methylmethacrylate) co- poly (dimethylaminoethylmethacrylate) (PMMA-co-PDMA) and PVDF to improve water flux and antifouling property of membrane. Pure water was filtrated by changing pH. It was found that pure water flux increased when pH was changed from 5 to 7 since DMA part swells due to protonation at lower pH. This implied that pKa value of produced membrane was between 5 and 7. To test fouling resistance ability 0.5 g/L BSA in PBS solution was filtrated at pH 5, 7 and 8.5 for 3 hours. Then membranes were washed with DI water for 10 minutes. Lowest flux recovery ratio of tested membranes was obtained for pH:5. Although membrane surface was hydrophilic below pKa values, BSA adsorbed because of electrostatic interaction, which caused the flux reduction.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Polysulfone (PSf, Mw = 35 kDa) and sulfonated polyethersulfone (SPES, Mw = 80 kDa) were used to prepare porous support membrane. PSF was purchased from Sigma Aldrich and SPES was kindly donated by Konishi Chemicals, Japan. 1-methyl-2-pyrrolidone (NMP, 99.5%) and N,N-Dimethylacetamide (DMAc, 99%) were used to dissolve PSf and SPES. NMP and DMAc were purchased from Fluka and Sigma Aldrich, respectively. As polyelectrolytes, alginic acid sodium salt from brown algae (ALG, Mw= 80-120 kDa) and polyethyleneimine (PEI, Mw=25 kDa) were purchased Sigma Aldrich Co. for fabrication of TFC membrane. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) with 37% purity were used to adjust pH of the polyelectrolytes solution and pure water and purchased from Sigma Aldrich and Merck, respectively. Polyethylene glycol (PEG, Mw = 1 kDa) was purchased from Sigma-Aldrich Co. Albumine from bovine serum (BSA, MW=66 kDa) was used for fouling test and purchased from Sigma Aldrich. *Escherichia coli* was received from Biotechnology Research Center (BIOMER) of Izmir Institute of Technology and used as a model microorganism for biofouling tests. Pentablock copolymer (PBC) was prepared at Iowa State University by the group of Prof. Dr. Surya Mallapragada and its structure is shown in Figure 3.1.

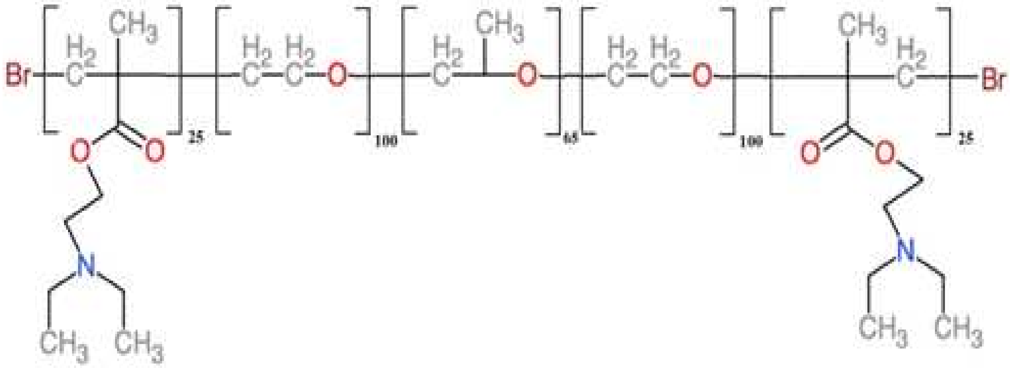

Figure 3.1. Structure of Pentablock Copolymer (PBC).

3.2. Membrane Preparation

3.2.1. Porous Support Membrane Preparation

Porous support membrane was prepared via nonsolvent induced phase inversion method (NIPS). Firstly, sulfonated polyethersulfone and polysulfone were dried for 24 hours at 80°C. Dried polymers with 25 wt% in (1:3) ratio of SPES: PSf were dissolved in 75 wt% in (1:2) ratio of NMP: DMAc solvent mixture to under 120 rpm continous stirring for 24 hours. After complete dissolution, the polymer solution was poured onto the glass which was covered with nonwoven. The poured solution was casted by a knife with 250 µm gate size at 25˚C. The polymer solution was put into a coagulation bath at 25˚C which consists of 0.5 wt% polyethyleneimine solution and kept in the bath for 12 hours. Then membranes were washed 24 hours with deionized water to remove excess polyethyleneimine and solvents and stored in deionized water at 4˚C until it is coated.

3.2.2. Thin Film Composite Membrane Fabrication via Layer by Layer Assembly

To produce thin film composite nanofiltration membranes, positively charged porous support membrane was first coated with negatively charged alginate and then with the pentablock copolymer in a dead end filtration unit (Millipore, Amicon Stirred Cell 8010) at 1 bar as shown in Figure 3.2. Alginate and pentablock copolymer were separately dissolved in pure water at 1g/L concentration and pH of solutions was adjusted to 4 by using NaOH and HCl solutions. Firstly, alginate solution was coated on the positively charged porous support membrane for almost 15 min. Then, membrane surface was rinsed for 10 times and washed with deionized water for 10 minutes to remove excess alginate. Following rinsing the membrane surface, the pure water was filtrated at 2.5 bar until a steady state condition was reached. For the second layer, positively charged pentablock copolymer was coated for 2 h. Finally, produced pentablock copolymer coated thin film composite nanofiltration membranes were washed with deionized water for 30 min.

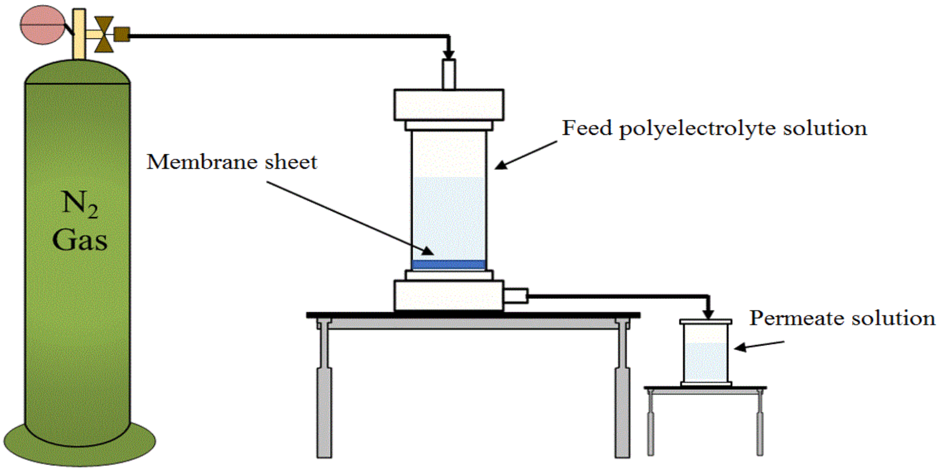

Figure 3.2. Layer by layer polyelectrolyte deposition by dynamic coating (Source: https://f1000research.com/articles/6-668/v1 Accessed in June, 2017).

3.3. Filtration Experiments

3.3.1. Water Flux Measurement

Pure water flux was measured by using dead-end filtration module (Millipore 8010) with 10 ml volume. The membranes with an area of 4.1 cm^2 were cut as circular. After placing the membrane to the bottom of filtration cell, pure water was filtrated by applying pressure through nitrogen gas. Firstly, produced membranes were compacted to obtain steady state flux at 2.5 bar. Then applied pressure was decreased to 2 bar and pure water was filtrated at pH:4.0. Amount of permeated water was recorded for 30 min during pure water filtration and used to calculate the water flux J_w (L/m^{2}h) and the pure water permeability (PWP) of the membranes by the following equations:

$$\mathrm{Jw} = \left(\frac{\Delta \mathrm{V}}{A\ x\ \Delta \mathrm{t}}\right) \tag{3.1}$$

$$\mathrm{PWP} = \left(\frac{\Delta \mathrm{V}}{A\ x\ \Delta \mathrm{t}\ \mathrm{x}\ \Delta \mathrm{P}}\right) \tag{3.2}$$

where ΔV is the volume of permeate (L), A (m^2) is the active membrane area, Δt (h) is the time for filtration and ΔP (bar) is the transmembrane pressure difference.

3.3.2 Rejection Measurement

For rejection experiments PEG solution (Mw: 1000 Da) with 1g/L concentration was used at pH:4.0. Filtrations of PEG solution was carried out in the same dead-end filtration cell system at 2 bar. Before PEG filtration, pure water was filtrated at pH:4.0 and T: 25˚C. 10 ml of PEG solutions were poured into the filtration cell and filtration continued until half of the solution was collected. Concentration of PEG in permeate (C_p), retentate (C_r) and feed solutions (C_f) were measured by using Rudolph J357 Automatic Refractometer. The rejection of the membranes was calculated by using the following equation;

$$R\,(\%) = \left(1 - \frac{C_p}{C_{avg}}\right) x100 \qquad (3.3)$$

$$C_{avg} = \frac{C_f + C_r}{2} \qquad (3.4)$$

3.3.3. Fouling Measurement

3.3.3.1. Organic Fouling

To investigate pH responsiveness of the membranes, fouling tests were performed at pH 4.0 (< pKa), 7.6 (= pKa) and 8.5 (> pKa). To evaluate the effect of temperature on fouling, the foulants were filtered at 4˚C (< LCST) and 25˚C (> LCST). While investigating the pH effect, filtration temperature was kept at 25˚C. During testing the effect of temperature, pH of foulant solution was adjusted to 7.6. BSA and ALG were chosen as model organic foulants and tested individually. During typical fouling test, firstly, pure water flux (J_{w1}) of the clean membranes was measured. Foulant solution at a concentration of 1 g/L was filtrated for 4 h and the permeate flux of foulant solution (Jp) was measured during the test.

After filtration, membranes were backwashed with water adjusted to pH:8.5 first at 25˚C for 30 min and then at 4˚C for another 30 min. Then water flux (J_{w2}) of the washed membranes was remeasured. The flux reduction (FR) was calculated as follow:

$$\mathrm{FR} = \frac{J_{w1} - J_{w2}}{J_{w1}} * 100 \qquad (3.5)$$

Reversible and irreversible fouling resistances were calculated by using following these equations:

$$J_{w1} = \frac{\Delta P}{\eta_w * R_m} \qquad (3.6)$$

$$J_{w2} = \frac{\Delta P}{\eta_w * (R_m + R_{ir})} \qquad (3.7)$$

$$J_P = \frac{\Delta P}{\eta_w * (R_m + R_{ir} + R_r)} \qquad (3.8)$$

where η_w : the viscosity of the permeate (Pa.s), $R_{m:}$ clean membrane hydraulic resistance (1/m), R_{ir}: reversible fouling resistance (1/m) and $R_{r:}$ irreversible fouling resistance (1/m).

3.3.3.2. Biological Fouling

E.coli was used to determine the biofouling tendency of the membranes. The *E. coli* was cultured until obtaining midlog phase on Mueller-Hinton agar at 37°C. After incubation, bacteria colonies were picked off with a swap from Mueller-Hinton agar plate and mixed with 0.1% (w) peptone water to adjust *E. coli* concentration to the value of 0.5 as McFarland value and $2.5 .10^7$ CFU/mL as CFU value. Then, of *E. coli* solution was serially diluted with Mueller-Hinton broth to obtain the final concentration of $2.5 .10^6$ CFU/mL.

Before *E.coli* filtration, pure water flux was measured. (J_{w1}) *E.coli* with $2.5.10^6$ CFU/mL concentration was filtrated and test conditions are shown in Table 3.1. The flux of *E.coli* solution permeating through the membrane was recorded for 1 hour (Je). Following filtration, membrane surface was rinsed with deionized water for 15 minutes at test condition. After the rinse, pure water flux of used membrane was measured (J_{w2}). Flux reduction was calculated by using same formula with organic fouling tests.

Table 3.1. Biological fouling test conditions.

pH Conditions (at 25°C)			Temperature Conditions (at pH:7.6)		
pH: 4.0	pH: 7.6	pH: 8.5	T: 4°C	T: 8°C	T: 37°C

3.4. Surface Characterization

3.4.1. Contact Angle

The hydrophilic character of the produced PBC coated nanofiltration membranes was obtained by water drop contact angle measurement using Attension Optical tensiometer. Before contact angle measurement, membranes were dried to remove the moisture for 24 h. Then membranes were cut in a square shape and taped on a thin glass. The measurements were carried out at different pH (4.0 7.6 and 8.5) and temperature (4^{o}C, 25^{o}C and 37^{o}C) values with 5 µl volume of the liquid droplet.

3.4.2. Zeta Potential

The zeta potential of the PBC coated nanofiltration membranes was measured by Zeta Sizer (DLS Particle Size and Zeta Potential) in tangential flow mode. The measurements were taken at different pH values 4.0, 7.6 and 8.5 and repeated 3 times.

3.4.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy, FEI Quanta 250 FEG, was used to visualize of the morphology of dried membrane surfaces. Before SEM measurement, dried membranes were coated with gold via Magnetron Sputter Coating Instrument.

CHAPTER 4

RESULTS AND DISCUSSION

pKa value and lower critical solution temperature of pentablock copolymer coated NF membranes were found to be as pH 7.6 and T:8^{o}C, respectively (Determan et al., 2005). In this section, fouling tendency of the membranes was discussed with organic and biological foulants.

4.1. The Effect of pH on Alginate and Bovine Serum Albumin Fouling on Pentablock Copolymer Coated Membranes

The thin film composite nanofiltration membranes used in fouling studies were developed by coating alginate modified support membrane with a pentablock copolymer. The pentablock copolymer consists of pH responsive poly (2-diethylaminoethyl methacrylate (PDEAEM) blocks in the end blocks and Pluronic F127 (PEO-PPO-PEO blocks) in the middle block. The pKa of the pentablock copolymer was reported as pH:7.6 (Determan et al., 2005). End blocks are weak polybase and below pKa value of pH responsive polymer part these groups become protonated. To investigate the influence of pH on the fouling tendency of the membranes, the pH of the feed solution was adjusted to pH 4.0 (below pKa), pH 7.6 (pH=pKa) and pH 8.5 (above pKa) value. The fouling behavior of produced thin film composite nanofiltration membranes was examined by using bovine serum albumin and alginite as representatives of the two groups of macromolecule foulants: proteins and polysaccharides, respectively.

Figure 4.1 and Figure 4.2 show the change in normalized flux with respect to time during filtration of alginate and bovine serum albumin, respectively. Reduction in flux or at constant transmembrane pressure (TMP) is a signal of fouling during the filtration. Figure 4 shows normalized flux results for pH 4.0, 7.6 and 8.5. At pH 4.0, the rate of decrease in alginate flux was found significantly higher than at pH 7.6 and 8.5 while in the case of BSA filtration the effect of pH on the flux decline was found moderate.

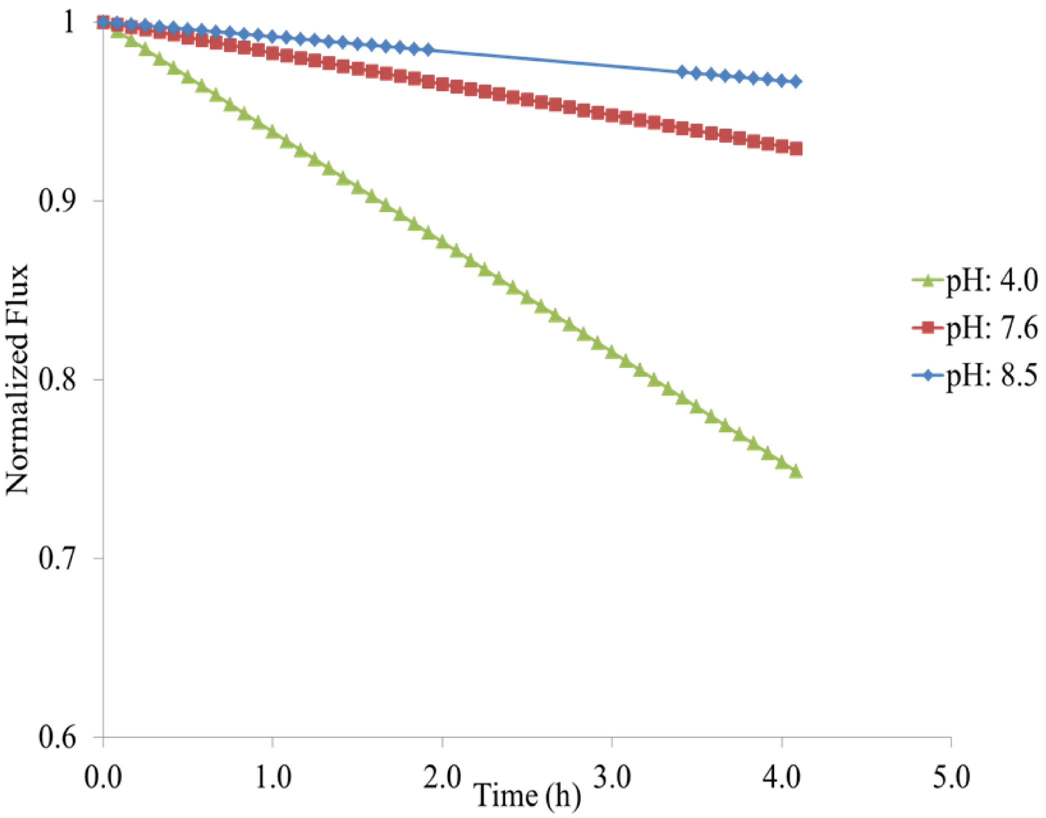

Figure 4.1. Normalized flux during ALG filtration at T: 25˚C.

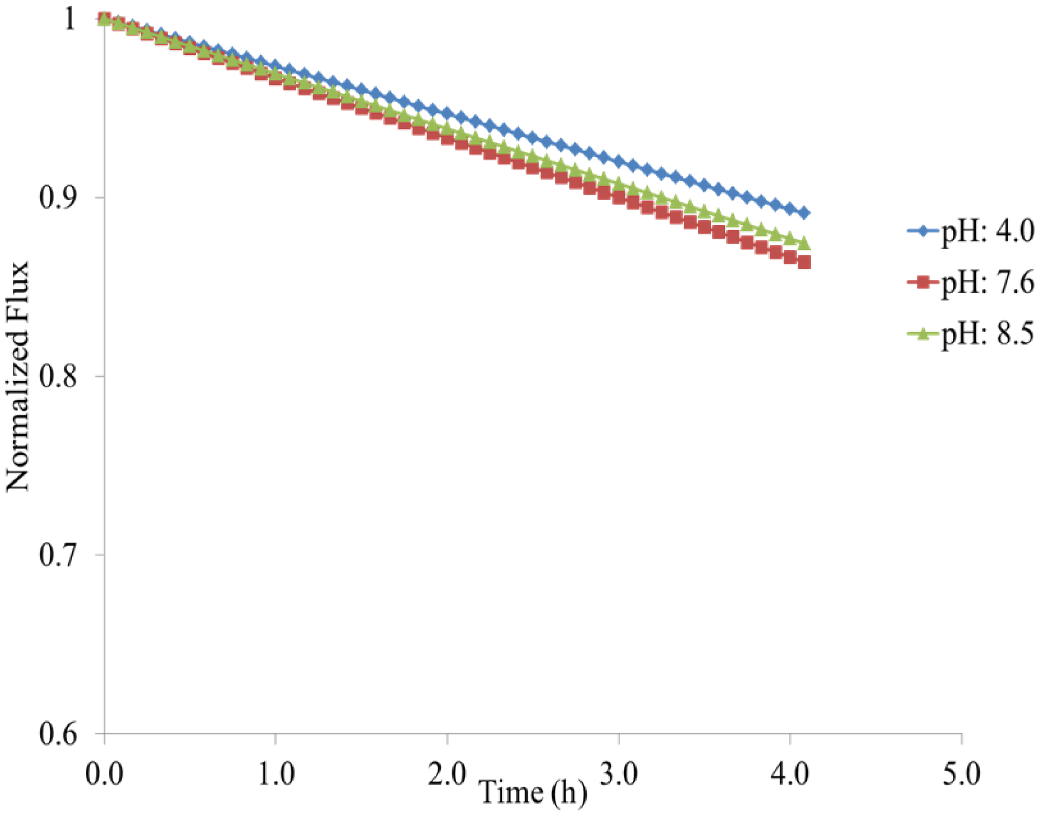

Figure 4.2. Normalized flux during BSA filtration at T: 25˚C.

At the end of 4 h of filtration, membranes were backwashed and pure water permeabilities were remeasured. Flux reduction values due to ALG and BSA filtration are shown in Figure 4.3, respectively.

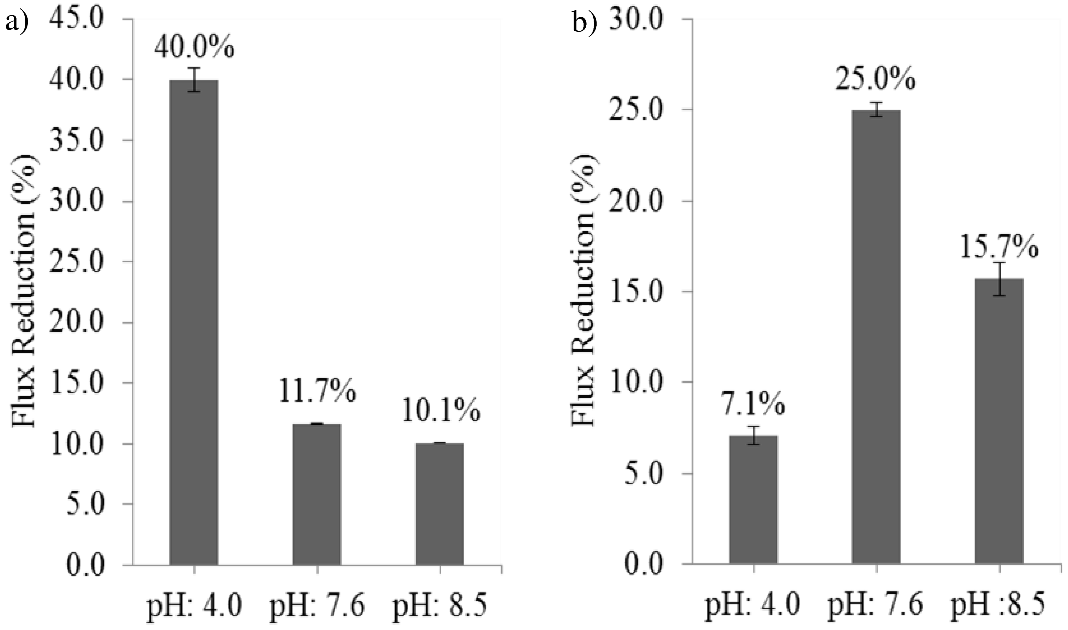

Figure 4.3. Flux reduction after ALG (a) and (b) BSA filtration at T:25 ˚C.

During alginate filtration, the highest flux reduction was observed at pH 4.0. This can be explained by two factors: First, at pH 4.0 pentablock copolymer coated NF membrane has highest positive charge (8.35 mV) as demonstrated by zeta potential measurements in Figure 4.4 and this causes strong electrostatic interaction between negatively charged carboxyl groups of alginate and positively charged membrane surface. Second, the surface hydrophilicity of membranes depends on pH values and the membrane displayed the most hydrophobic character at pH 4.0 as shown by contact angle measurements (Table 4.2). On the other hand, the contact angle values measured at pH 4.0 and 7.6 were found similar, thus, it can be concluded that for alginate filtration the surface charge rather than surface hydrophilicity is responsible for the highest flux reduction at pH 4.0 . Although surface charge of the membrane at pH 8.5 is lower than at pH 7.6, similar flux reduction values measured at these two pH values can be explained by higher hydrophilic nature of the surface at pH 8.5. It is well known that enhancing hydrophilic nature of surfaces can significantly decrease the fouling tendency of the membranes. At the first glance it seemed to be contradictory to observe that the most hydrophilic state of the membrane is at pH 8.5 since the PBC chains are in collapsed conformation at this pH (Determan et al., 2005). On the other hand, OH^- ions in NaOH solution used for adjusting pH to 8.5 form a layer on the membrane surface and make the surface hydrophilic.

Table 4.2. Contact angle of NF membranes

pH Effect (T: 25˚C)			Temperature Effect (pH:7.6)		
pH: 4.0	pH: 7.6	pH: 8.5	T: 4°C	T: 25°C	T: 37°C
71.4±1.6	69.8±0.5	61.7±1.1	51.2±1.6	69.8±0.5	69.6±0.4

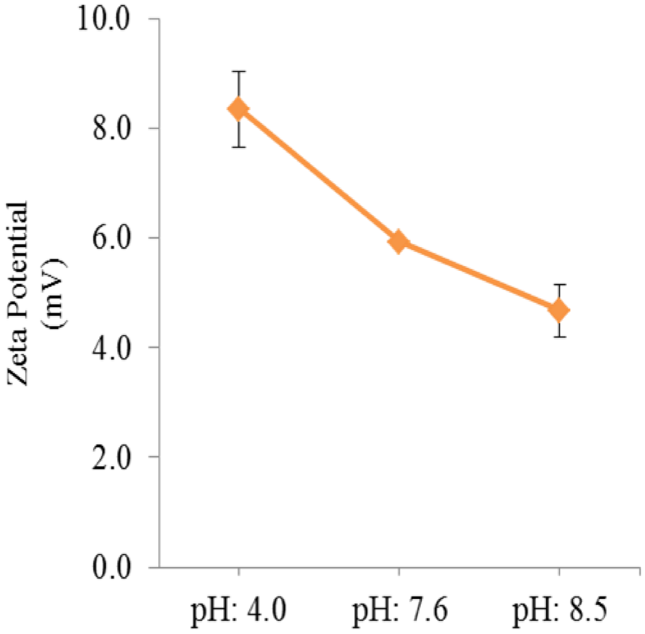

Figure 4.4. Zeta potential of PBC coated membranes.

Figure 4.3.b shows that opposite to the alginate fouling case, the lowest flux reduction during filtration of BSA was observed at pH 4.0 because of charge repulsion between positively charged PBC and positively charged BSA. The isoelectric point of BSA is 4.7-4.9 thus significant increase in BSA fouling at pH 7.6 and 8.5 both above the isoelectric point of BSA is due to electrostatic attraction between negatively charged BSA and positively charged surface. Even though BSA was negatively charged at both pH 7.6 and 8.5, lower flux reduction was observed at pH 8.5 since membrane surface was more hydrophilic at this pH. Kumar et al., (2013) modified polysulfone/poly

(isobutylene-alt-maleic anhydride) (PIAM) nanofiltration membranes with different concentration of glutaraldehyde cross-linked chitosan solutions in the coagulation bath. 0.8 g/L BSA solution was filtrated for 80 minutes and 20 minutes rinse was applied at pH:7.0. Even though BSA with low concentration was filtrated for a short period of time, 26 % reduction in pure water flux was found. Compared to this result, our membranes demonstrated lower fouling tendency.

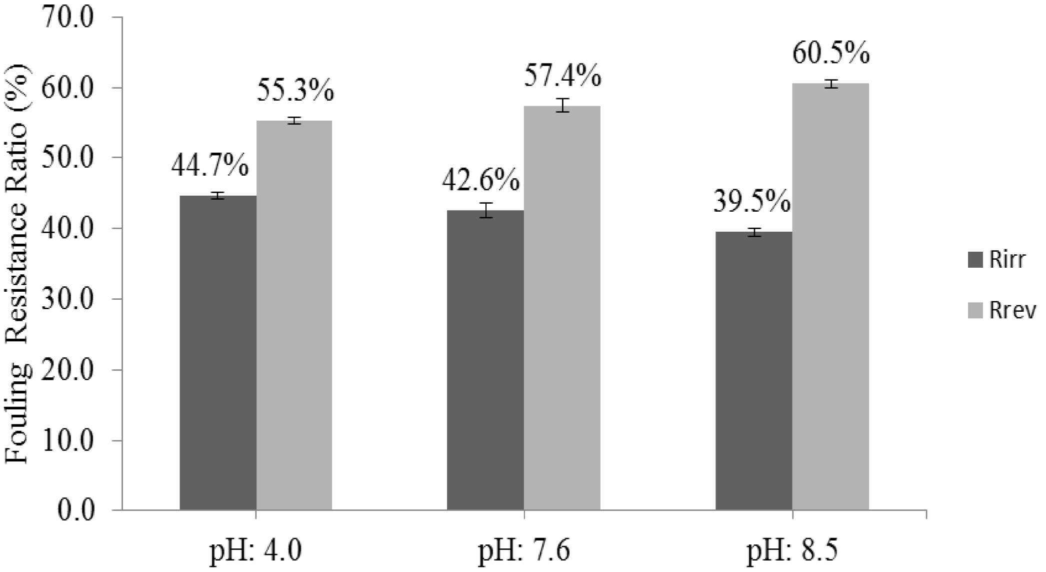

Figure 4.5. Reversible (Rrev) and irreversible (Rirr) fouling resistance after ALG filtration at T: 25˚C.

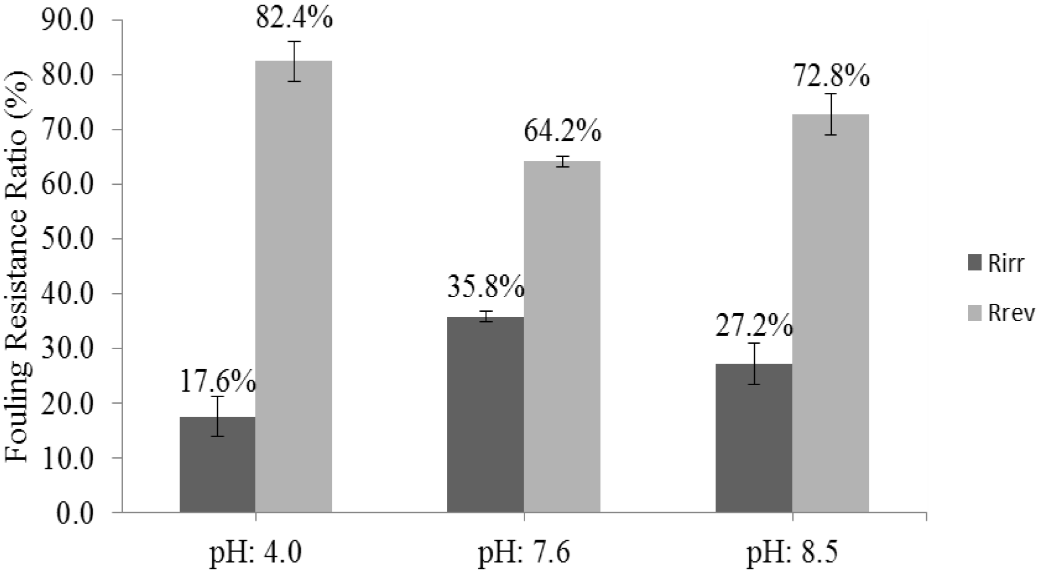

Figure 4.6. Reversible (Rrev) and irreversible (Rirr) fouling resistance after BSA filtration at T: 25˚C.

Figure 4.5 and 4.6 illustrate the reversible and irreversible fouling resistances calculated for ALG and BSA fouling, respectively. For both BSA and ALG foulant filtration, reversible fouling resistance is higher than irreversible fouling resistance at all tested pH values. On the other hand, results have shown that compared to ALG fouling, BSA fouling can be more easily removed from the surface since the irreversible BSA fouling is significantly lower than reversible fouling. Consistent with the results in Figure 4.3, the highest reversible fouling resistances were observed at pH 8.5 and pH 4.0 for ALG and BSA fouling, respectively. This simply suggests that both feed solution filtration pH and applied backwash water pH can be adjusted to control the extend of membrane fouling and remove fouling simply by physical cleaning.

4.2. The Effect of Temperature on Alginate and Bovine Serum Albumin Fouling on Pentablock Copolymer Coated Membranes

The temperature responsiveness of the pentablock copolymer comes from the Pluronic F127 group (PEO-b-PPO-b-PEO) in the middle of the structure. Lower critical solution temperature of this middle block (PPO) was reported as 8 ˚ C (Determan et al., 2005). Fouling studies with ALG and BSA were performed at below (4 ˚C) and above (25˚C) the lower critical solution temperature of the pentablock copolymer using the same protocol followed for investigating pH responsiveness of the produced TFC NF membranes.

Figure 4.7 and 4.8 illustrate the effect of feed solution temperature on the normalized flux decline during the filtration of ALG and BSA at pH 7.6. ALG filtration at T: 4˚C showed almost constant flux performance while a small flux decline was observed at T: 25˚C. On the other hand, feed solution temperature was found to have a more significant effect on the BSA fouling. The results in Figure 4.7 and 4.8 indicate that the antifouling property of the produced membrane is facilitated by the hydrophilic character at 4 ^{o}C below the lower critical solution temperature of middle block (Pluronic F127 group) of the pentablock copolymer. Mondal and Wickramasinghe, (2012) found that temperature responsive grafted thin film composite nanofiltration membranes showed lower foulant permeate flux decline during filtration than ungrafted nanofiltration membranes by changing feed solution temperature below and above the lower critical solution temperature of grafted temperature responsive polymer.

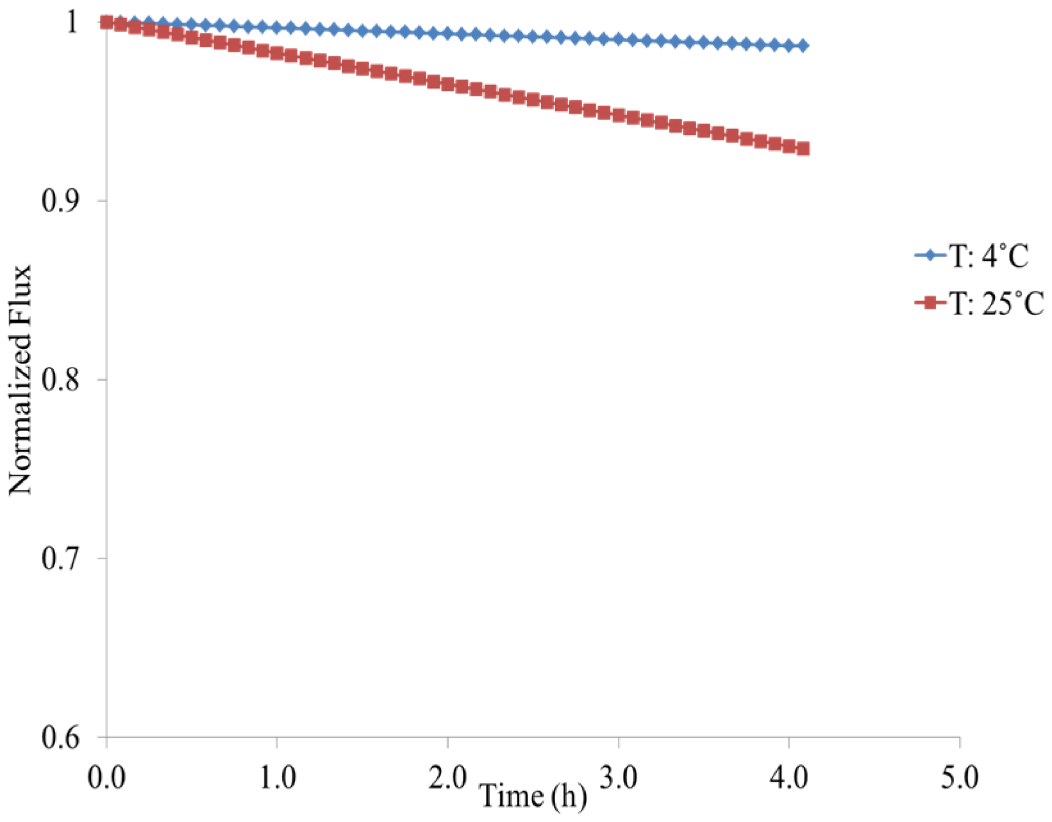

Figure 4.7. Normalized flux during ALG filtration at pH: 7.6.

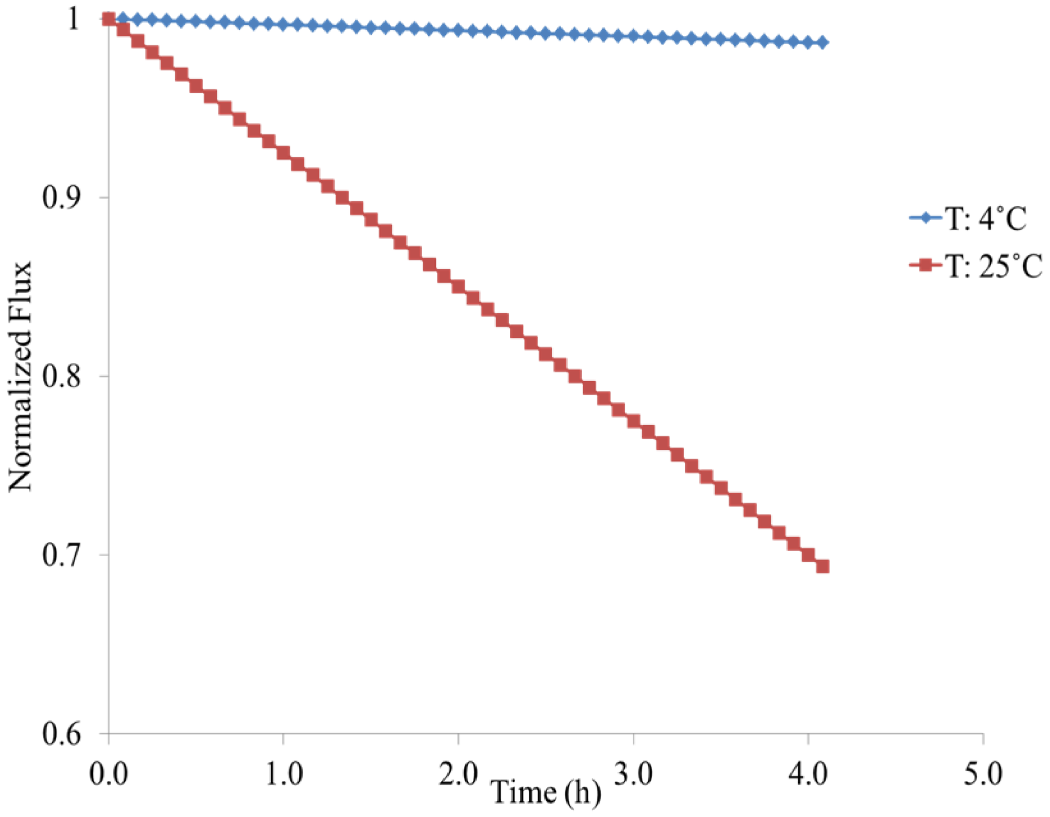

Figure 4.8. Normalized flux during BSA filtration at pH: 7.6.

Flux reduction values at the end of 4 h ALG and BSA filtration followed by backwashing are demonstrated in Figure 4.9. It was seen that flux reduction at 4°C is lower than at 25°C due to more hydrophilic nature of the membrane surface as demonstrated by lower contact angle values at 4°C (Table 4.2). When the water molecules contact with hydrophilic membrane surface, hydrogen bonding between membrane surface and water molecules forms. This results in the layer of tightly bound water molecules on the membrane surface that blocks the direct interaction between membrane surface and foulants (Almeida et al., 2012). At 25°C above LCST of the temperature responsive polymer part (LCST: 8°C), the interactions between the PBC and water molecules are limited, the copolymer dehydrates and becomes hydrophobic, hence, swollen. For filtration tests either at 4°C or 25°C, the charge of membrane surface is the same since pH of the solution was kept constant at 7.6. Thus, the fouling tendency of the membranes is controlled by the hydrophilic nature of the surface rather than its surface charge (Mondal., 2016).

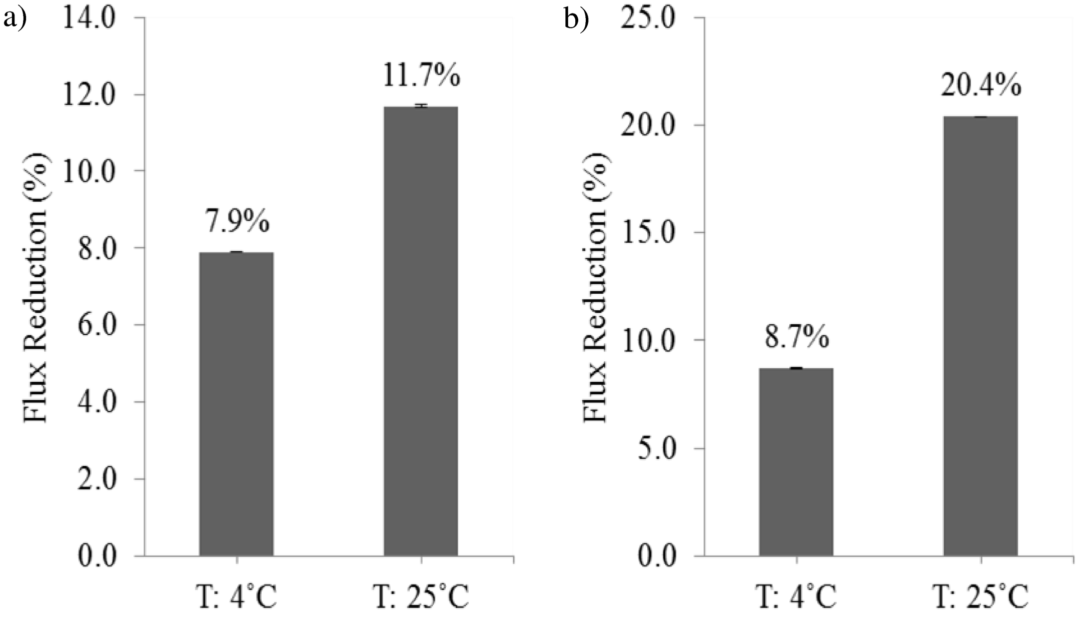

Figure 4.9. Flux reduction after ALG (a) and (b) BSA filtration at pH: 7.6

The effect of temperature responsiveness of pentablock copolymer on the irreversible and reversible fouling resistances for ALG and BSA filtration is shown in Figure 4.10 and 4.11, respectively. It was noted that most of the ALG and BSA fouling is reversible and can be removed by backwashing and the physical cleaning is more effective at 4°C than at 25°C. The extent of irreversible fouling is higher at 25°C due to hydrophobic interactions between the foulants and more hydrophobic membrane surface at this temperature.

The results in Section 4.1 for flux reduction demonstrated that the temperature responsiveness of pentablock copolymer is more effective than the pH responsiveness on both ALG and BSA fouling levels.

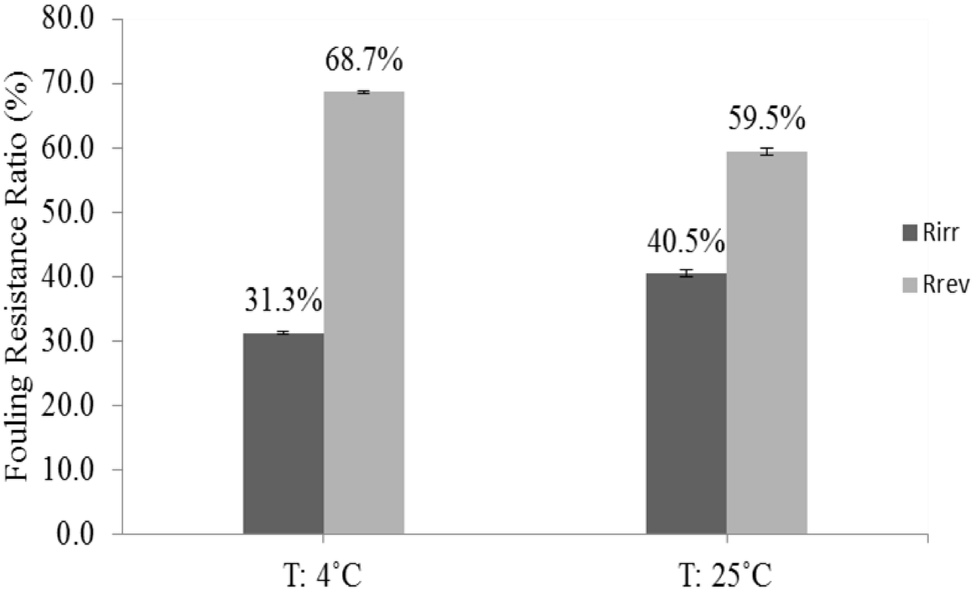

Figure 4.10. Reversible (Rrev) and irreversible (Rirr) fouling resistance after ALG filtration at pH: 7.6.

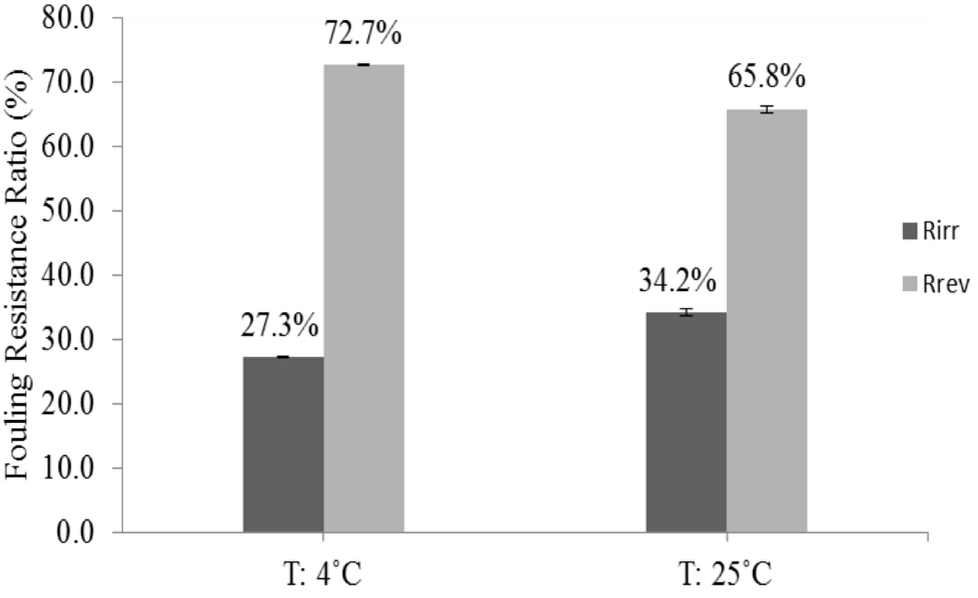

Figure 4.11. Reversible (Rrev) and irreversible (Rirr) fouling resistance after BSA filtration at pH: 7.6.

4.3. The Effects of pH and Temperature on Antibiofouling Property of Pentablock Copolymer Coated Membranes

The antibiofouling property of the pentablock copolymer coated TFC nanofiltration membranes was tested by filtering model bacteria, *Escherichia coli (E. coli),* solution through the membranes. Figure 4.12 and 4.13 show the normalized flux decline during E coli filtration at different pH values and the flux reduction values, respectively.

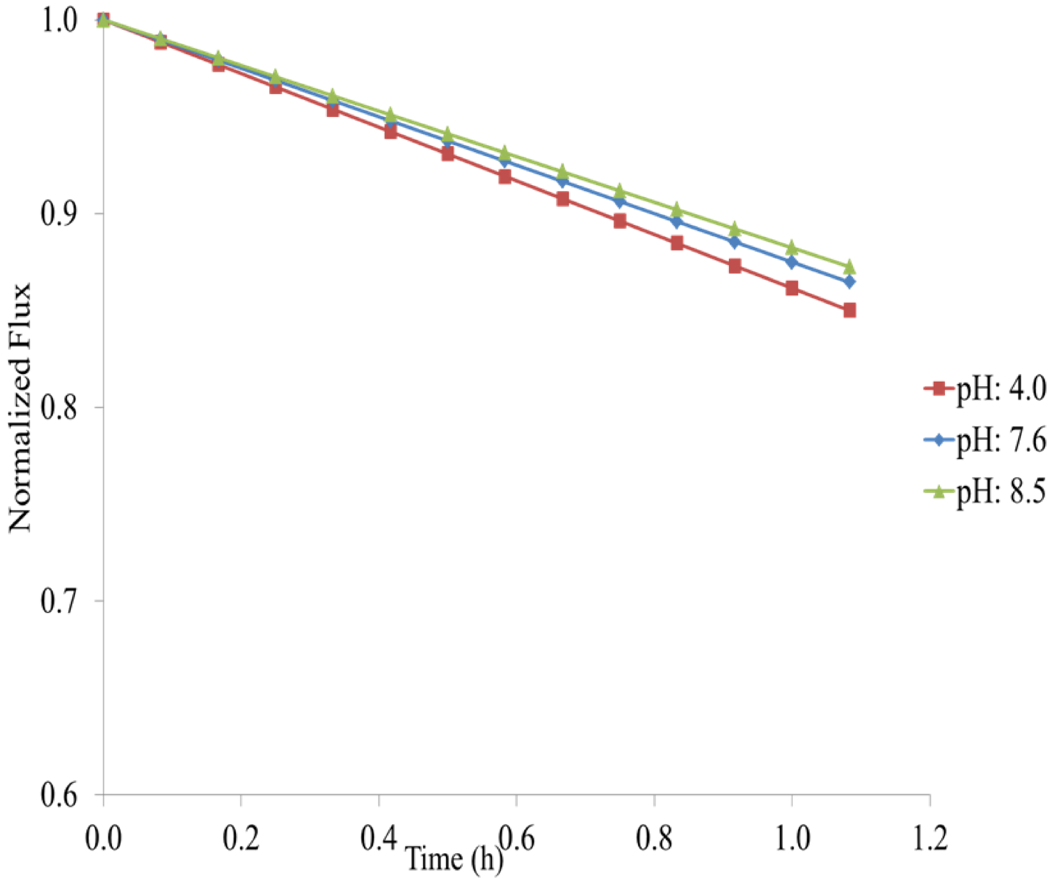

Figure 4.12. Normalized flux during *E.coli* filtration at T: 25°C.

At the end of 1 hour E.coli filtration, the highest flux reduction was obtained at pH: 4.0. This could be first of all attributed to the highest positive surface charge at pH 4.0 which favors significant electrostatic attraction between negatively charged *E.coli* and positively charged membrane surface. In addition, the highest hydrophobicity observed at pH 4.0 also enhances adsorption of E.coli on the membrane surface causing highest flux decline at this pH.

Malaisamy et al., (2010) modified commercial polyethersulfone microfiltration membrane with positively charged and hydrophilic [2-(acryloyloxy)ethyl] trimethyl ammonium chloride (AETMA) polymer. After 1 h *E.coli* bacteria filtration, flux recovery ratio of the modified membrane was found higher than the unmodified membrane. They proposed that negatively charged *E.coli* bacteria attacked the positively charged membrane surface, which caused damage to the integrity of the *E.coli* cells and extra-cellular polymetric substance was adversely affected by this damage. It was found that dead and damaged *E.coli* cells were easy to remove from the membrane surface. They claimed that biofilm formation and microbial fouling were prevented by decreasing or stopping extra-cellular polymetric substance of *E.coli* bacteria production.

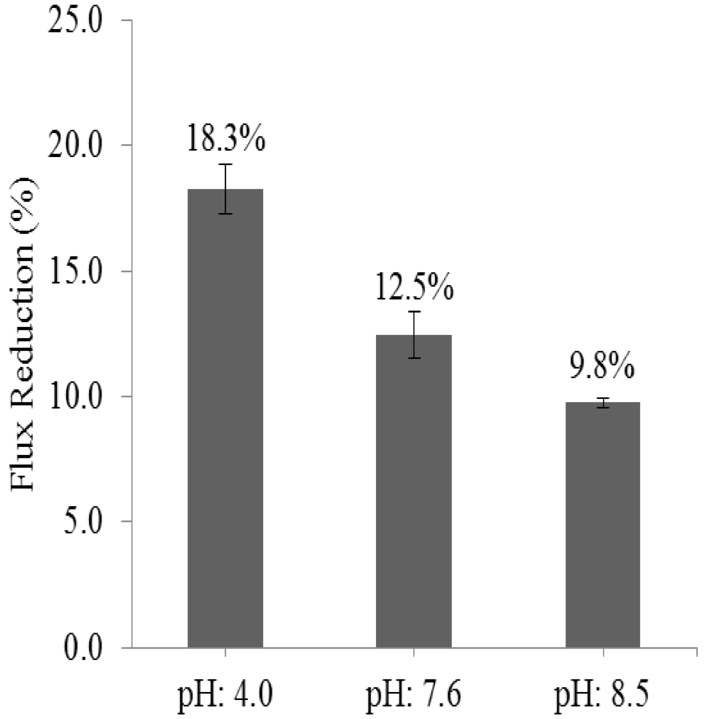

Figure 4.13. Flux reduction after *E.coli* filtration at T: 25^{o}C.

SEM pictures in Figure 4.14 through Figure 4.16 were used to visualize the effect of pH on the *E.coli* bacteria deposition on the membrane surfaces. It was seen that *E.coli* filtration at pH 4.0 caused more dead/alive bacteria deposition on the membrane surface due to both more positively charged and hydrophobic membrane surface at this pH compared to other *E.coli* filtration pH values of pH 7.6 and 8.5 (Figure 4.16).

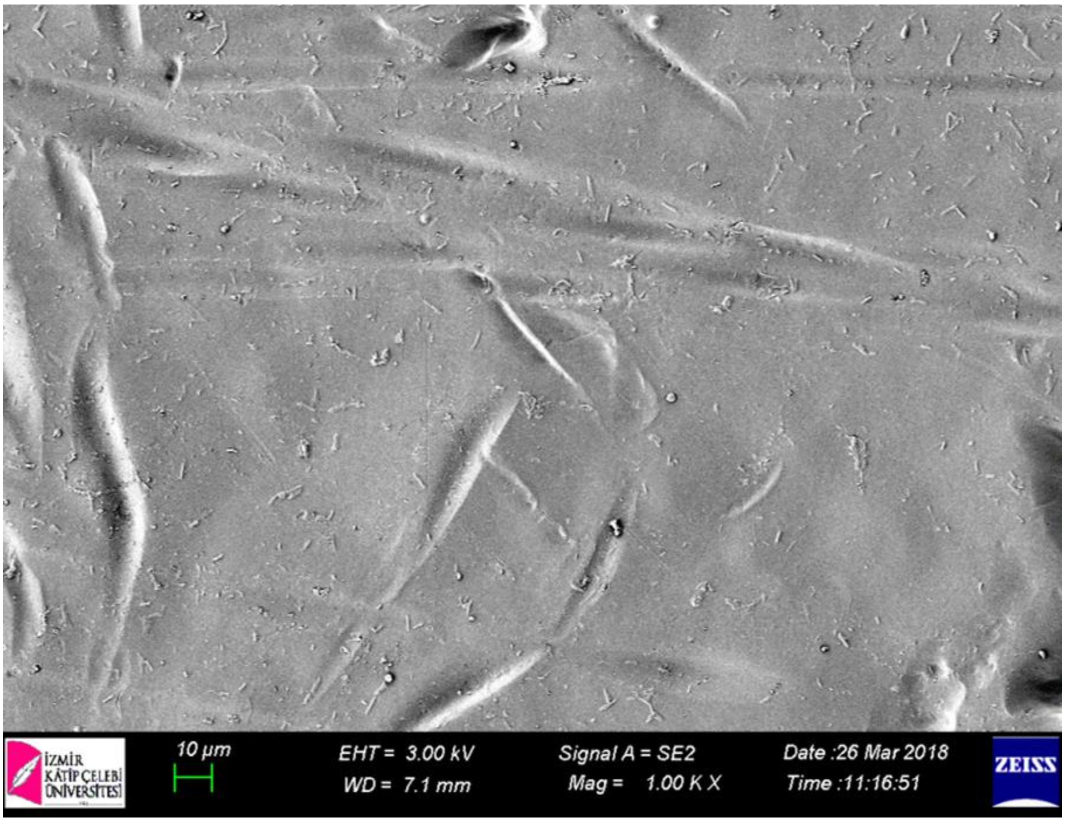

Figure 4.14. SEM image after *E.coli* filtration at T: 25 ˚C and pH: 4.0.

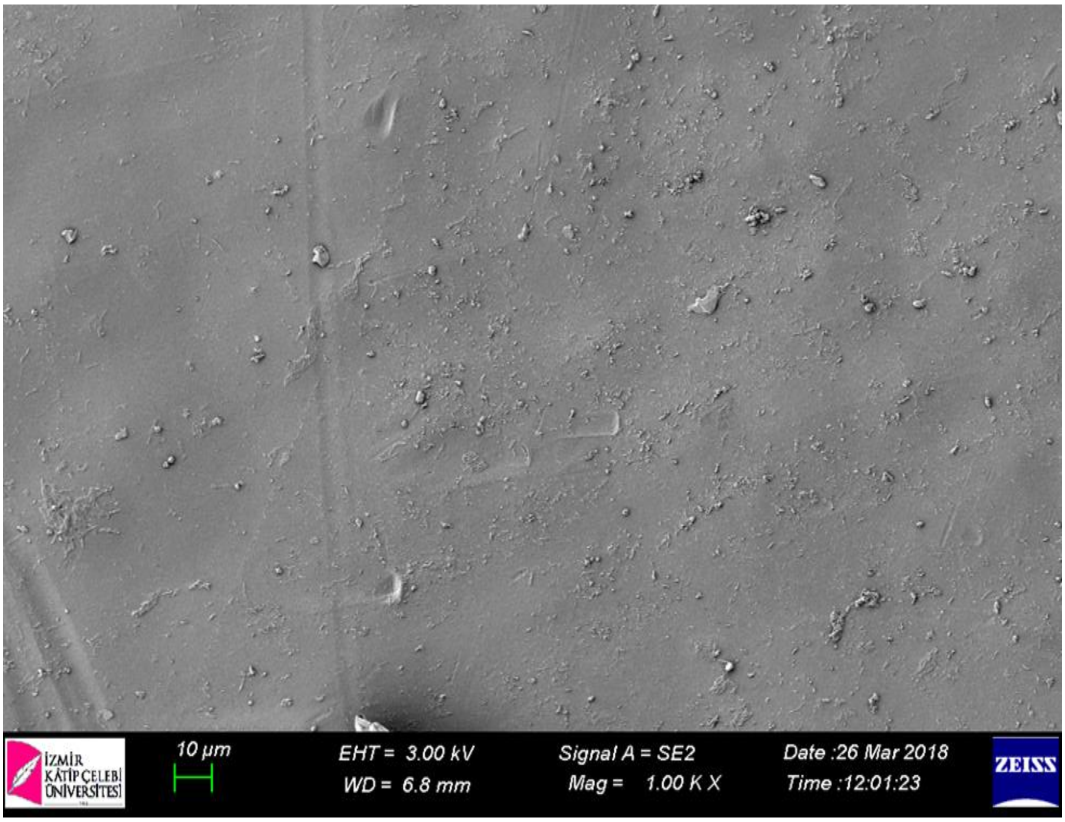

Figure 4.15. SEM image after *E.coli* filtration at T: 25˚C and pH: 7.6.

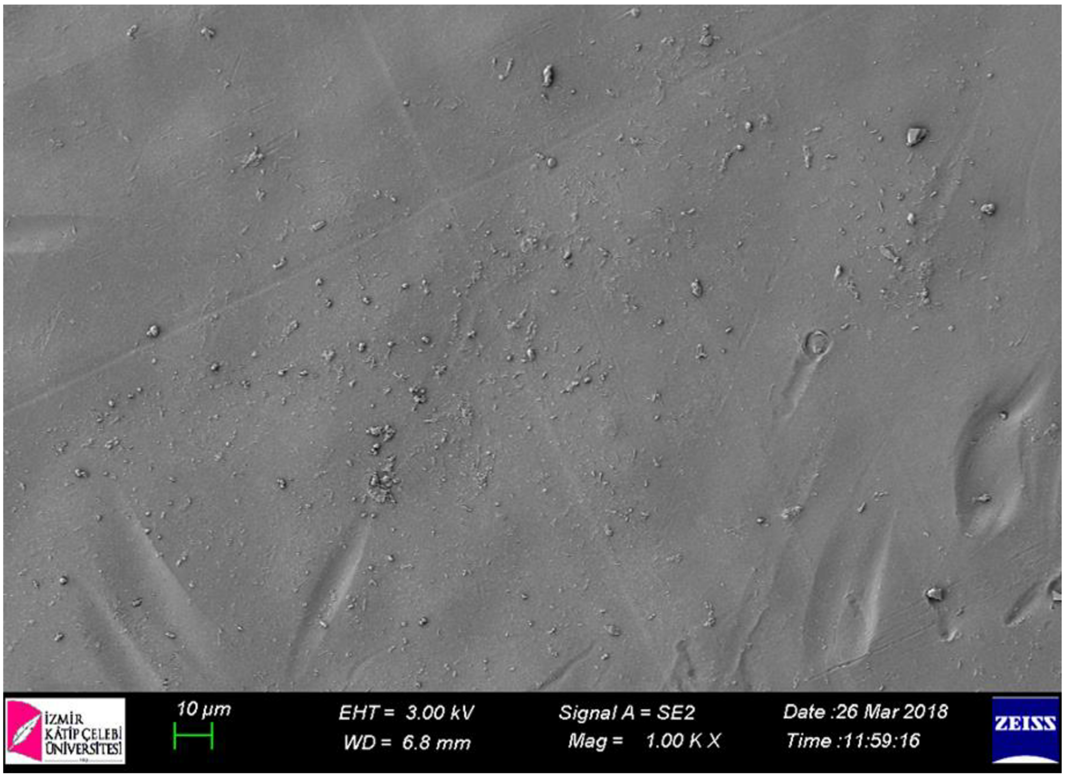

Figure 4.16. SEM image after *E.coli* filtration at T: 25˚C and pH: 8.5.

Fouling resistance after rinsing the *E.coli* filtrated membranes was investigated to evaluate the antibiofouling property for different pHs. As shown in Figure 4.17 reversible fouling resistance is significantly higher than irreversible fouling resistance at all pH values.

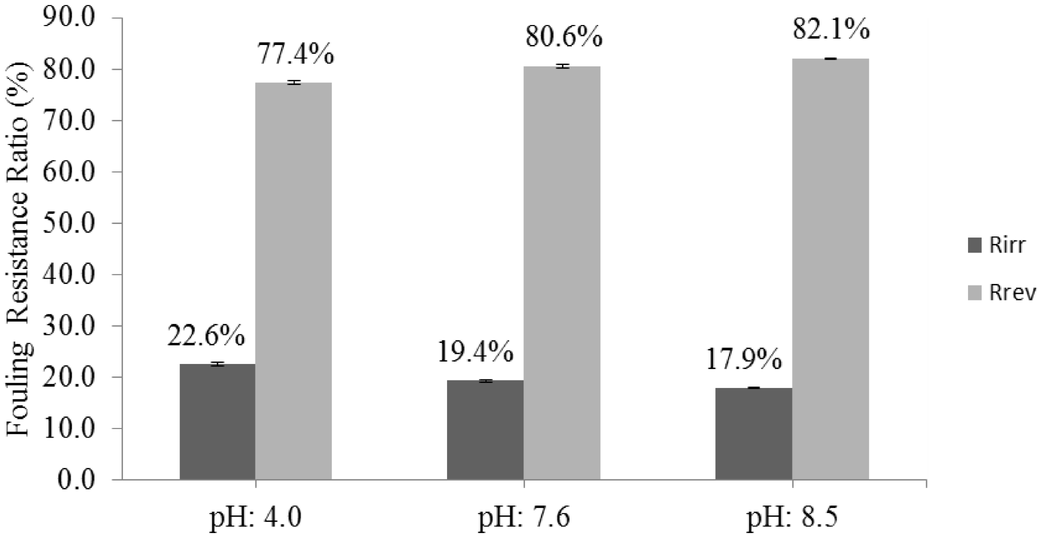

Figure 4.17. Reversible (Rrev) and irreversible (Rirr) fouling resistance after *E.coli* filtration at T: 25˚C.

The highest irreversible fouling was determined at pH 4.0 which is in accordance with relatively more bacteria observed on the surface of the membrane after *E.coli* filtration at pH 4.0. Figure 4.18 and Figure 4.19 show different temperatures flux reduction values and the normalized flux during *E.coli* filtration at, respectively.

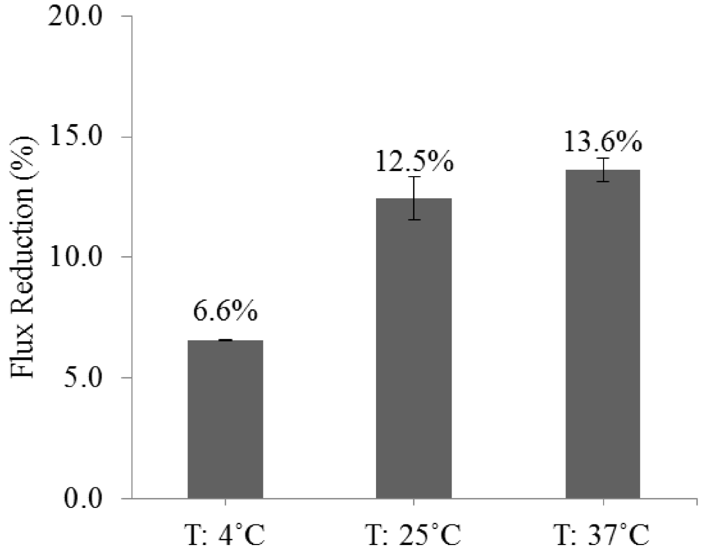

Figure 4.18. Flux reduction after *E.coli* filtration at pH: 7.6.

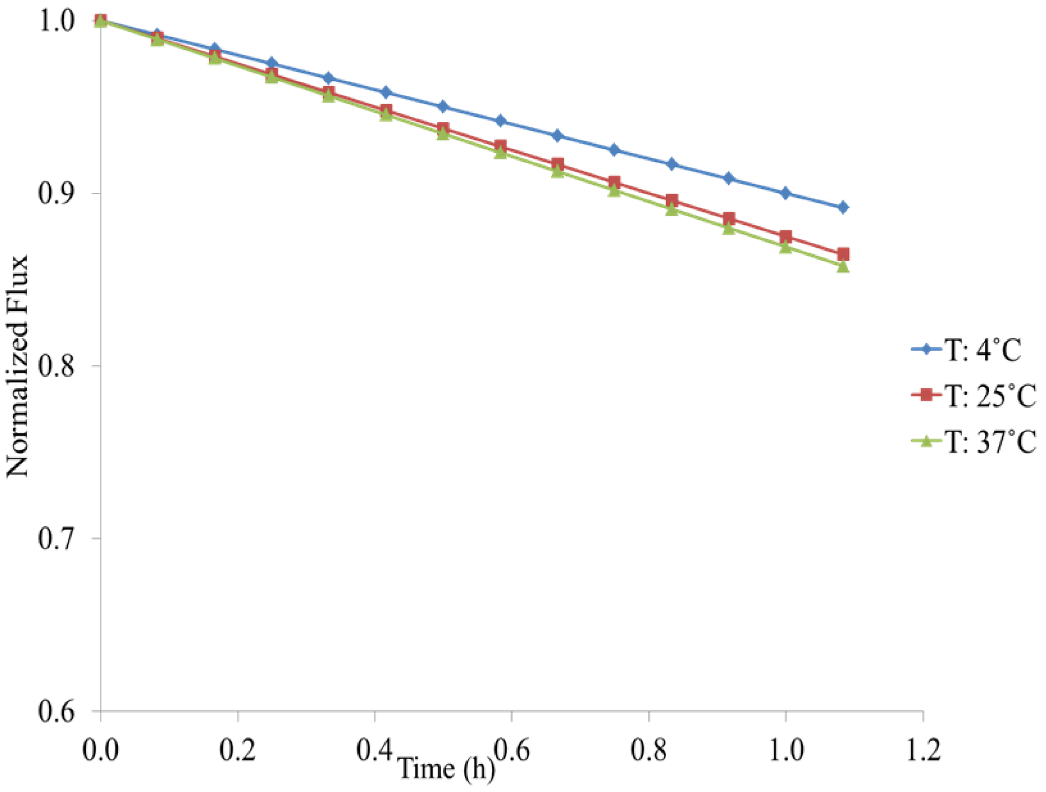

Figure 4.19. Normalized flux during *E.coli* filtration at pH: 7.6.

The lowest flux reduction was obtained at 4^{o}C since the middle block of PBC is hydrophilic below the LCST (8^{o}C). In addition, among three temperatures investigated, the growth of biofilm on the surface is expected to be lowest at 4^{o}C. The flux reduction values at temperatures above the LCST were found similar.

An obvious difference in membrane surface after *E.coli* filtration was obtained between 4˚C and 37˚C as illustrated by SEM pictures in Figure 4.20 and Figure 4.21. SEM image for the membrane exposed to *E coli* filtration at 4 ˚C exhibited almost free of *E.coli* bacteria (Figure 4.20). When size of the bacteria in the SEM pictures Figure 4.15 and Figure 4.21 taken into account it can be said that the most of the bacteria on the surface is dead. This is further proved by the comparison of the fouling resistances shown in Figure 4.22 which indicates that reversible fouling resistance at all filtration temperatures is higher than the irreversible fouling resistance. It has been known that irreversible biofouling is caused by the alive bacteria deposited on the surface.

Figure 4.20. SEM image after *E.coli* filtration at T: 4˚C and pH: 7.6.

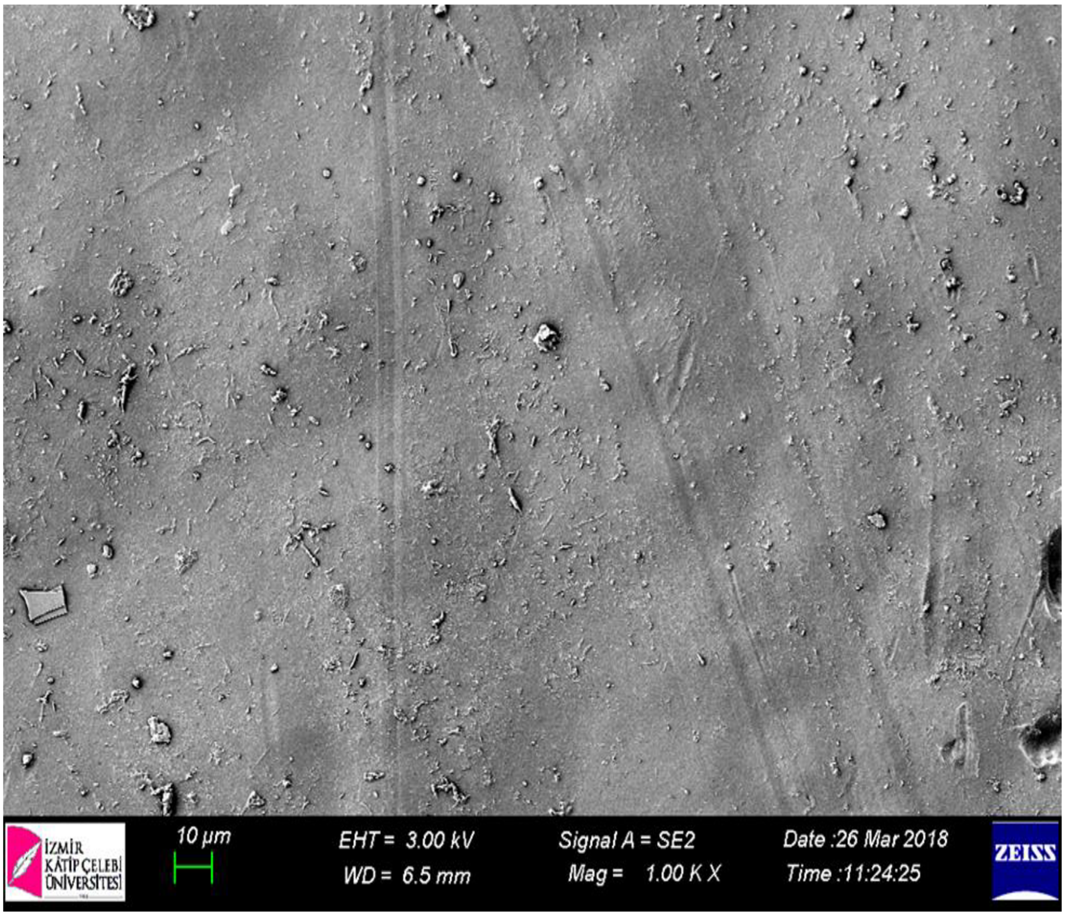

Figure 4.21. SEM image after *E.coli* filtration at T: 37˚C and pH: 8.5.

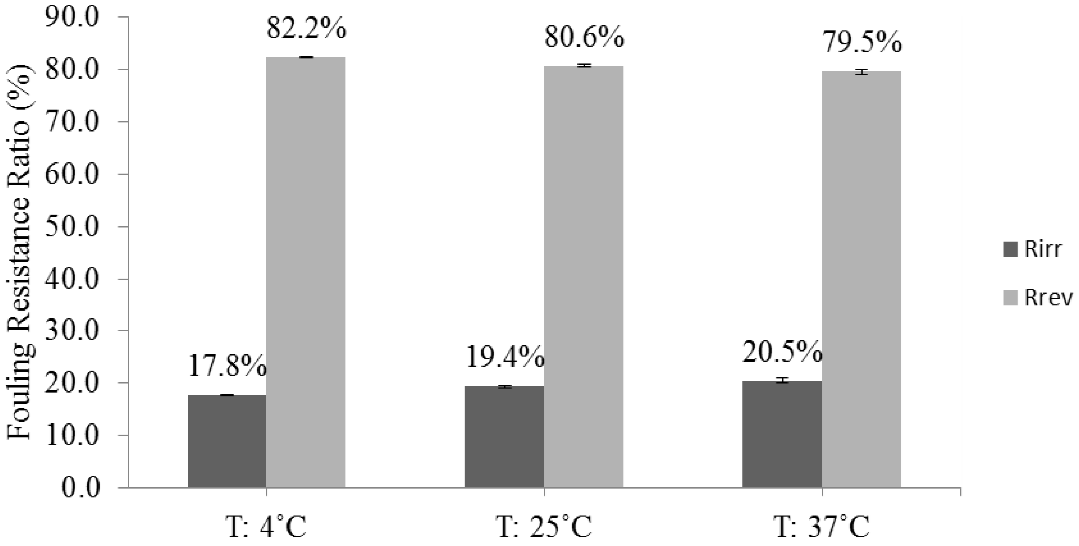

Figure 4.22. Reversible (Rrev) and irreversible (Rirr) fouling resistance after *E.coli* filtration at pH: 7.6.

CHAPTER 5

CONCLUSION

In this thesis, the fouling tendency of the produced pentablock copolymer coated NF membranes was investigated with ALG and BSA as modal organic and *E.coli* as modal biological foulant. The membranes were characterized with respect to surface characteristics, PWPs, PEG1000 rejection and, pH and temperature responsiveness by alternating the filtration and backwash conditions.

Contact angle and zeta potential measurement showed that surface properties change with filtration pH and temperature. In terms of hydrophilic character of the surface, pH responsiveness of produced NF membranes didn't show expected trend with pH due to presence of other pH responsive groups in the TFC structure. Permeate flux during foulant filtration was significantly affected by pH and temperature responsiveness of PBC coated NF membranes. The membranes exhibited better antifouling property for both organic foulants below LCST of PBC. The benefit of pH responsiveness of the membranes on their antifouling resistances depended on charge of feed solution. The lowest flux reduction during ALG and BSA filtration was obtained when pH of the solution was above (pH:8.5) and below (pH:4.0) the pKa value of the PBC. SEM pictures demonstrated that *E.coli* did not deposit on the membrane surface when filtrated at a temperature below the LCST of PBC. Lowest flux reduction values after *E.coli* filtration were obtained below the LCST and above the pKa value of PBC. For all foulants investigated, reversible fouling resistance was found significantly higher than the irreversible fouling which indicated that fouling on the developed NF membranes can be easily removed by simple physical cleaning. Temperature responsiveness of the membranes on the antifouling and antibiofouling properties was found more effective than the pH responsiveness. It can be concluded that NF membranes developed in this study can be potential candidates for applications in biotechnology and food industry due to their low fouling potentials.

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