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Investigating the Fouling Tendency of Polyelectrolyte Complex Membranes

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ABSTRACT

Aqueous phase separation (APS) is a sustainable method for fabricating polymeric membranes without using toxic organic solvents. In this study, membranes were prepared using poly(sodium 4-styrene sulfonate) (PSS) and polyethyleneimine (PEI) via a pH-shift-induced APS. The membranes were tested for organic fouling using bovine serum albumin (BSA) as a model foulant in a dead-end filtration setup. The pure water flux, flux recovery ratio (FRR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR), and total fouling ratio (TFR) were evaluated over three filtration cycles. The initial water flux was 255 $Lm^{-2}h^{-1}$ at 1 bar. After exposure to BSA, the flux significantly decreased to approximately 19% of its original value after three cycles. The FRRs remained low (0.19–0.31), while the IFRs were high (0.69–0.81), indicating dominant irreversible fouling. UV–vis analysis showed unstable rejection behavior, including negative rejection values in later cycles, likely due to insufficient cleaning and concentration polarization. The results show that although the PSS–PEI APS membranes exhibited high initial flux, their fouling resistance toward BSA was limited under the tested conditions.

Keywords: fouling, aqueous phase separation, membrane, water treatment, polyelectrolyte complexes

1. INTRODUCTION

Aqueous phase separation (APS) has gained significant research attention in recent years as a sustainable alternative to traditional membrane fabrication methods.[1–8] Unlike nonsolvent-induced phase separation (NIPS), APS avoids the use of toxic organic solvents such as N-methyl-2-pyrrolidone (NMP). Several recent studies have demonstrated that APS can produce microfiltration, ultrafiltration, and nanofiltration membranes with controlled pore sizes and competitive performance compared with the NIPS membranes.[2,4,9]

In APS, oppositely charged water-soluble polyelectrolytes are combined to form water-insoluble polyelectrolyte complexes. This can be achieved by varying the pH or salt concentration. In pH-shift-induced APS, the polymers are first mixed under conditions where complexation is prevented (for example, at a high pH where the weak polyelectrolyte is uncharged).[3] After casting, immersion in an acidic bath causes protonation of the weak polyelectrolyte, leading to immediate complex formation and membrane precipitation. By adjusting parameters such as the polymer concentration and bath pH, the membrane structure and pore size can be tuned.[9]

One of the most widely studied pH-shift-induced APS membrane systems is the polyelectrolyte pair of poly(sodium 4-styrene sulfonate) (PSS) and polyethyleneimine (PEI), or commonly referred to as PSS–PEI. The advantage of the PSS–PEI system is that the phase inversion and polyelectrolyte complexation is achieved by a mild pH shift, i.e., from a pH of approximately 12 to a pH of approximately 4.[7,10] In this system, PEI acts as the weak polyelectrolyte (pKa ≈ 8.5), while PSS is a strong polyelectrolyte that remains charged over a wide pH range. Phase inversion typically occurs when the pH is shifted from approximately 12 to 4. Previous studies reported PSS–PEI ultrafiltration membranes prepared with different monomer mixing ratios with water permeabilities of approximately 40–200 $LMH \cdot bar^{-1}$ and bovine serum albumin (BSA) rejection ranging from 36% to 98%.[10] However, the fouling behavior of PSS–PEI membranes has not been systematically studied.

Membrane fouling is one of the main challenges in filtration processes.[11,12] Fouling reduces water flux owing to the deposition of particles, organic matter, microorganisms, or inorganic compounds on the membrane surface or inside the pores.[12] Fouling can occur through several mechanisms depending on the type of molecule, for example, pore blocking, adsorption inside the pores, or formation of a cake layer on the surface (Figure 1).

For water filtration systems, particulate fouling (Figure 1a) occurs in two ways: inside the pores, which decreases the diameter for the water flux, and other types that decrease the water flux from the top of the membrane by creating a layer, in extreme cases a cake layer, that prevents the water from entering the membrane smoothly, with particles such as slat clay that are generally >100 μm. Inorganic fouling (Figure 1b) occurs when dissolved inorganic compounds or elements, such as iron, are absorbed by the membrane surface, forming particles that are generally 10

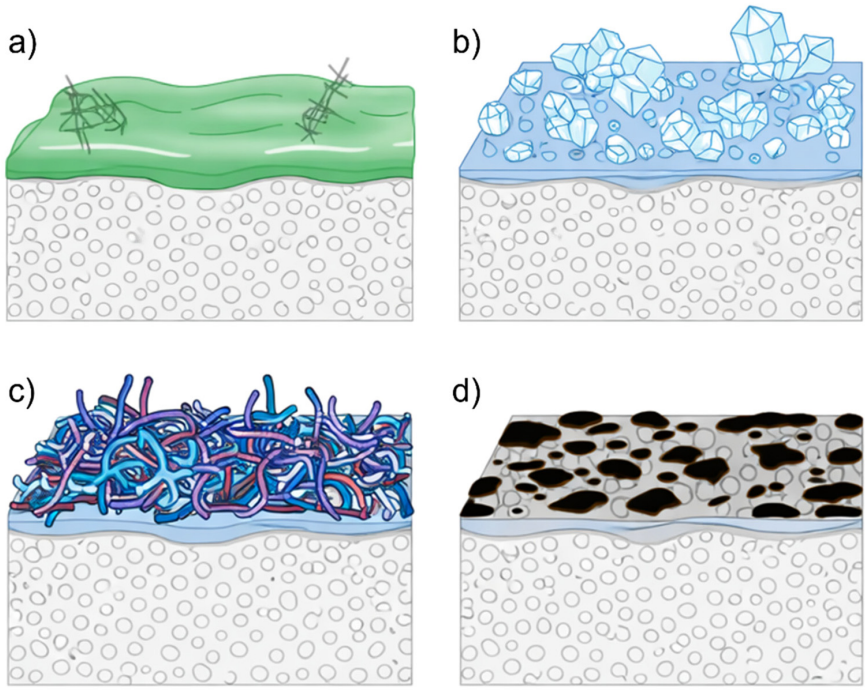

Figure 1. Schematic showing different types of fouling: a) particulate fouling, b) inorganic fouling, c) bacterial fouling (microbiological fouling), and d) organic fouling

nm–10 µm. Particulate and inorganic fouling are similar, except that they differ in size, and particulate fouling is not necessarily due to an inorganic material. Microbiological fouling (Figure 1c) occurs when a microbiological organism grows to form a viscous layer or a solid layer called a cake layer, which blocks the pores. Organic fouling (Figure 1d) occurs when the particles dissolve and collide with the membrane material, with the particles \generally 1–100 nm in size, similar to natural organic matter (NOM). Organic fouling, especially from NOM or proteins such as BSA, is common in water treatment systems.

Dissolved organic fouling refers to the formation of organic matter caused by NOM, in which the material existing in drinking water sources is absorbed and held by the membrane structure. Organic fouling can occur in the form of a decrease in the pore diameter due to the deposition of a molecular layer or slime-like layer on the membrane surface, which gradually hinders the flow of water. The water flux decreases with the level of fouling, which is a major challenge for membrane performance. Finally, a significant amount of fouling may completely inhibit the passage of water, and effective management strategies should be implemented throughout the working life of the membrane [12].

Although APS membranes have shown promising separation performance, their resistance to organic fouling remains unclear. Therefore, the objective of this study was to evaluate the fouling behavior of PSS–PEI APS membranes using BSA as a model foulant. This study focuses on the flux decline, cleaning efficiency, and rejection behavior over multiple cycles.

2. EXPERIMENTAL

2.1. Materials and Equipment. The polyelectrolyte PSS (Mw ~1000 kDa in powder form) and PEI (Mw ~750 kDa, 50 wt.% in water) were purchased from Merck. Sodium acetate and lyophilized BSA powder (>96%) were purchased from Merck. Glacial acetic acid (>99.7%) was purchased from Fisher Scientific. Deionized water was produced using a Farad Lab Equipment Factory water purification system.

2.2. Preparing and Casting the Dope Solution. Both polyelectrolytes were diluted with water to obtain 25 wt.% aqueous solutions. For example, 2.5 g of DI water was added to 2.5 g of PEI and mixed for 3 h to obtain a 25 wt.% PEI solution. Similarly, PSS in the powder form was diluted with DI water to obtain a 25 wt.% PSS solution. Subsequently, both solutions were mixed in a monomer mixing ratio of PSS:PEI (1:2) for 6 h to obtain 10 g of homogeneous dope solution. The monomer weights of PSS and PEI used to calculate the ratios were 206 Da and 43.04 Da, respectively.

The polymer solution was cast on a clean glass plate using a casting knife with a 400 µm gap height. The film was immediately immersed in an acidic coagulation bath (pH ~4) and maintained for 24 h to allow membrane formation. After detachment, the membranes were stored in DI water before testing. The acetate buffer bath was prepared using sodium acetate and acetic acid in water.

2.3. Filtration Experiment. The membrane was cut into circular disks with diameters of 5 cm. The membrane was then pressurized with deionized water for 1 h at 1 bar for compaction. The membrane was ready for filtration immediately after compaction. First, the flux was measured using equation (1).

$$J = \frac{V}{A \times t} \tag{1}$$

where (J) represents the flux ($Lm^{-2}h^{-1}$), Arepresents the effective membrane area in m^2, and t represents the time (h).

The filtration cell was then fed with a 1 gL^{-1} aqueous solution of BSA, which was filtered through the membrane for 20 min at 1 bar of pressure. After filtration, the membrane was backwashed with DI water at 1 bar. The volume of the filtrate was measured, and the permeance was calculated using equation 1. Subsequently, the membrane was backwashed with DI water at 1 bar of pressure by flipping the membrane. The membrane was then returned to its original position to measure the flux for 5 min, thus completing the first cycle. The experiment was conducted for three cycles. The rejection (R) of BSA was calculated using equation (2).

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100, \tag{2}$$

where C_p and C_f are the BSA concentrations in the permeate and feed, respectively. The BSA concentration was measured using a UV–vis spectrophotometer (Agilent Cary 60, Agilent Technologies). The maximum absorption peak for BSA was observed at 275–280 nm. A straight-line calibration curve was constructed by measuring the UV absorbance of BSA at known concentrations.

2.4. Fouling and the Flux Recovery Ratio (FRR). The FRR was determined using equation (3).

$$FRR = \frac{J_2}{J_0} \tag{3}$$

where J_0 is the initial water flux of the membrane before fouling (measured after compaction and before introduction of the foulant). J_2 is the water flux measured after fouling occurred (after running the feed solution). Flux ratios were obtained to determine the amount of fouling that occurred on the membrane. This indicates the amount of the original flux recovered after cleaning. A value close to one indicates excellent recovery. The reversible fouling ratio (RFR) was determined using equation (4).

$$RFR = \frac{J_2 - J_1}{J_0}, \tag{4}$$

where J_1 is the flux after 5 min of BSA filtration. This represents fouling that can be removed by cleaning, and a value close to one indicates excellent recovery from the backwash.

The irreversible fouling ratio (IFR), which indicates the fouling that remained even after cleaning (irreversible fouling), was calculated using equation (5).

$$FR = \frac{J_0 - J_2}{J_0} \tag{5}$$

Therefore, the total fouling (TF) was calculated as the sum of the RFR and IFR.

Table 1. *Fouling behavior of the PSS–PEI membrane*

Fouling	1st cycle	2nd cycle	3rd cycle
FRR	0.31	0.2	0.19
RFR	0.15	0.07	0.06
IRF	0.69	0.8	0.81
TF	0.84	0.87	0.87

3. RESULTS AND DISCUSSION

This experiment was designed to investigate the impact of organic fouling on PSS–PEI APS membranes. Table 1 summarizes the FRR, RFR, IRF, and TF of the complex membranes.

The initial pure water flux (J_0) was 255 $L \cdot m^{-2} \cdot h^{-1}$. As shown in Table 1, the membrane experienced a significant reduction in flux after the first fouling cycle. The flux decreased by 69% compared with the initial value. In the second cycle, the flux was approximately 20% of the original water flux. In the third cycle, the flux was approximately 19.4% of the original water flux. The difference between the second and third cycles was very small, indicating that the fouling behavior became nearly stable after the second cycle.

The RFR represents the portion of fouling that can be removed by cleaning, in this case, by backwashing. A value close to one indicates effective cleaning. In the first cycle, the RFR was approximately 0.15, indicating that only a small amount of fouling was removed. In the second cycle, the RFR was approximately 0.07, and in the third cycle, the RFR was approximately 0.06, indicating very limited cleaning efficiency in both cycles.

The IFRs were approximately 0.69, 0.80, and 0.81 for the first, second, and third cycles, respectively. Values close to one indicate severe irreversible fouling. These results indicate that most of the fouling was irreversible, particularly during the second and third cycles.

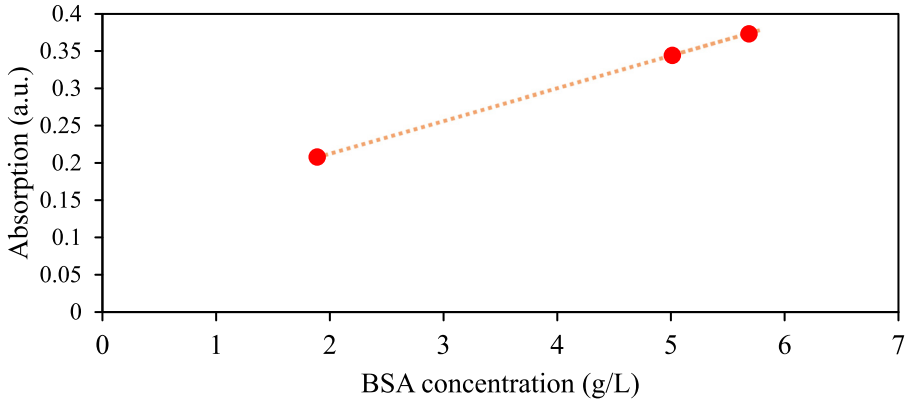

Figure 2. Calibration curve of known concentrations of BSA solution and their absorbance

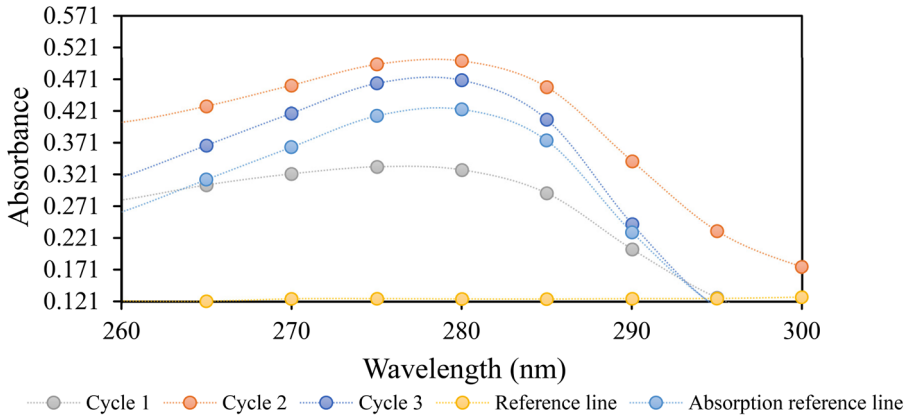

Figure 3. UV–vis spectra of the filtrates after three cycles

The total fouling ratio (TFR), which represents the overall fouling (both reversible and irreversible), was approximately 0.84 in the first cycle and 0.87 in the second and third cycles. These high values confirmed that significant fouling occurred on the membrane surface and inside the pores during all the cycles. These results can be explained by the charged nature of the PSS–PEI membranes. These membranes exhibit a net positive surface charge.[7] Consequently, the fouling tendency of the membranes is significantly enhanced, resulting in the lower FRRs obtained here.

3.1. Filtration Analysis. The filtrates from the fouling experiments were analyzed using a UV–vis spectrophotometer to measure the BSA concentration. Figure 3 shows the UV spectra of the filtrates before and after three filtration cycles. The feed solution containing 1 gL^{-1} BSA showed maximum absorption in the range of 275–280 (nm) for all trials. The concentration of BSA in the filtrate was significantly lower after the first cycle, and the membrane exhibited a rejection rate of approximately 25% rejection. However, the absorption in the second and third cycles was higher than the feed absorption because of the backwashing step. The elevation is most likely from the first cycle, and the backwash was not sufficient to remove all possible BSA; in more depth, the BSA from first cycle was released in the second cycle, and the BSA from second cycle was released in third cycle, resulting in a higher concentration of BSA in the permeate. Another explanation, assuming that physical cleaning and backwashing were sufficient, is that water cannot remove BSA, and other solvents may be able to dissolve BSA from the membrane into the bulk.

3.2. Comparison with EVOH, PES, PVDF Membranes. For comparison, commercial membranes fabricated via NIPS were also tested for their fouling propensity. The membrane was pressurized with an aqueous solution of BSA at 0.5 bar following the same steps, that is, three cycles, 20 min of running the foulant, then 1 min of backwash. The first membrane, ethylene vinyl alcohol (EVOH), had a $J_0 = 140$ $Lm^{-2}h^{-1}$ and showed a FRR of 0.65 with 10% rejection of BSA. The polyethersulfone (PES) ultrafiltration-type membrane had a $J_0 = 180$ $Lm^{-2}h^{-1}$ and showed a FRR of 0.6 with 50% to 30% rejection. The polyvinylidene fluoride (PVDF) membrane had a $J_0 = 200$ $Lm^{-2}h^{-1}$ and showed a FRR of 0.4 with 65% to 50% rejection.[13]

4. CONCLUSION

In this study, PSS–PEI membranes were fabricated by aqueous phase separation and tested for organic fouling using BSA. The membranes exhibited a high initial water flux (255 $Lm^{-2}h^{-1}$ at 1 bar). However, after three fouling cycles, the flux decreased to approximately 19% of its original value. FRRs remained low, while IFRs were high (0.69–0.81), indicating dominant irreversible fouling. UV–vis analysis showed unstable rejection behavior, including negative rejection values, in later cycles. This was likely caused by insufficient cleaning and the release of previously adsorbed BSA. Although the fabrication of APS membranes is environmentally friendly, their fouling resistance to protein solutions needs improvement. This study was limited to dead-end filtration and deionized water cleaning. Future work should investigate cross-flow filtration, alternative cleaning methods, and membrane surface modifications to enhance the fouling resistance.

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REFERENCES

(1) Sadman, K. *et al.* Versatile and High-Throughput Polyelectrolyte Complex Membranes via Phase Inversion. *ACS Appl. Mater. Interfaces* **11**, 16018–16026 (2019).

(2) Kamp, J., Emonds, S., Borowec, J., Restrepo Toro, M. A. & Wessling, M. On the organic solvent free preparation of ultrafiltration and nanofiltration membranes using polyelectrolyte complexation in an all aqueous phase inversion process. *J. Membr. Sci.* **618**, 118632 (2021).

(3) Baig, M. I., Durmaz, E. N., Willott, J. D. & de Vos, W. M. Sustainable Membrane Production through Polyelectrolyte Complexation Induced Aqueous Phase Separation. *Adv. Funct. Mater.* **30**, 1907344 (2020).

(4) Nielen, W. M., Willott, J. D. & de Vos, W. M. Aqueous Phase Separation of Responsive Copolymers for Sustainable and Mechanically Stable Membranes. *ACS Appl. Polym. Mater.* **2**, 1702–1710 (2020).

(5) Willott, J. D., Nielen, W. M. & de Vos, W. M. Stimuli-Responsive Membranes through Sustainable Aqueous Phase Separation. *ACS Appl. Polym. Mater.* **2**, 659–667 (2020).

(6) Durmaz, E. N., Baig, M. I., Willott, J. D. & de Vos, W. M. Polyelectrolyte Complex Membranes via Salinity Change Induced Aqueous Phase Separation. *ACS Appl. Polym. Mater.* **2**, 2612–2621 (2020).

(7) Baig, M. I., Sari, P. P. I., Li, J., Willott, J. D. & de Vos, W. M. Sustainable Aqueous Phase Separation membranes prepared through mild pH shift induced polyelectrolyte complexation of PSS and PEI. *J. Membr. Sci.* **625**, 119114 (2021).

(8) Durmaz, E. N. *et al.* Polyelectrolytes as Building Blocks for Next-Generation Membranes with Advanced Functionalities. *ACS Appl. Polym. Mater.* **3**, 4347–4374 (2021).

(9) Baig, M. I., Willott, J. D. & de Vos, W. M. Tuning the structure and performance of polyelectrolyte complexation based aqueous phase separation membranes. *J. Membr. Sci.* **615**, 118502 (2020).

(10) Haque Mizan, M. M. *et al.* Organic solvent-free polyelectrolyte complex membrane preparation: Effect of monomer mixing ratio and casting solution temperature. *J. Membr. Sci.* **668**, 121197 (2023).

(11) Wang, L. *et al.* Prediction of membrane purification by membrane fouling based on mathematic and machine learning models combined with image processing technology. *J. Environ. Chem. Eng.* **11**, 111154 (2023).

(12) Ma, Y. & Chew, J. W. Investigation of membrane fouling phenomenon using molecular dynamics simulations: A review. *J. Membr. Sci.* **661**, 120874 (2022).

(13) Hashino, M. *et al.* Effect of kinds of membrane materials on membrane fouling with BSA. *J. Membr. Sci.* **384**, 157–165 (2011).