Fouling resistance study of poly (ether sulfone) ultrafiltration membrane which in-situ polymerized with polydopamine

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Abstract. This work focuses on the fouling resistance evaluation of polydopamine-blended poly (ether sulfone) (PES) ultrafiltration membrane for water treatment application. The supporting PES membrane was prepared via a common phase inversion method. The dopamine was introduced to the membrane by blending technique and the modification occurred by in-situ polymerization of dopamine into polydopamine which triggered by peroxide. The antifouling performances were studied in terms of flux recovery, reversible fouling, irreversible fouling, and total fouling. The relevant characteristics of the membranes such as surface porosity, chemical composition, water permeation, and solute rejection were also provided to support the analysis of antifouling performances. The results revealed that the presence of polydopamine in the membrane system significantly enhanced the fouling resistance of the polydopamine-blended PES membrane. The hydrophilic component in polydopamine reduced the interaction of membrane with foulant thus lowered the total fouling of only 18.92% with 13.50% reversible fouling and 5.42% irreversible fouling for modified membrane. In addition, the polydopamine-modified membrane successfully recovered up to 95% of the flux after backwashing, much higher than that of original PES which was only 67%.

1. Introduction

With the more intense regulation of water quality and the scarcity of high-quality water sources, ultrafiltration is considered a very promising process for the production of drinking water due to its compatibility, ease of automation, and high removal rates for turbidity, organic materials (such as humic substances), even viruses. Although ultrafiltration has developed rapidly in the past twenty years, membrane fouling has always been a critical problem that hinders its wider applications for drinking water production. Briefly, membrane fouling is a phenomenon that involves adsorption, accumulation, or precipitation of organic and inorganic elements on the surface of the membrane through different mechanisms in various circumstances. The negative impact of membrane fouling on membrane technology is enormous because fouling can significantly reduce productivity, increase maintenance costs as a consequence of increased energy demand, additional pre-treatment, frequent cleaning of membranes and shorter membrane life [1-3].
The main cause of fouling is the high interaction between contaminants and the surface of the polymeric membrane which are generally made of hydrophobic materials like polyethersulfone (PES), etc. One of the few options to reduce the occurrence of fouling is hindering the interaction between the membrane and contaminants by increasing the hydrophilicity of the membrane. This can be done by adding additive materials with more hydrophilic nature such as silica [4], Brij [4,5], polydopamine [6-8], and so forth.

Polydopamine has been widely known as a super-hydrophilic compound due to its catechol component [9]. Introduction of polydopamine into membrane system has been done by many researchers through various techniques, for instances, surface coating [7], or various methods of blending [6,8,10]. In this study, the PES membrane is modified with polydopamine by blending technique through the in-situ polymerization assisted by peroxide as an oxidizer to form polydopamine particles from dopamine. This study aims to look at the effects of dopamine approval through a new technique using peroxide as an oxidizer against the antifouling performance of the membrane. This study aims to investigate the effects of dopamine which introduced to the membrane through a new technique using peroxide as an oxidizer, on the antifouling performance of the membrane. Fouling resistance of the membranes is discussed deeply to study the effect of polydopamine as an antifouling agent.

2. Materials and methods

2.1. Materials

The membrane was prepared by using polyethersulfone (PES, Ultrason E6020 P, BASF, Germany) as the main polymer, and N-Methyl-2-pyrrolidone (NMP) as a solvent. 3-Hydroxytyraminium chloride (Merck, USA) was used as a dopamine source with hydrogen peroxide (H₂O₂) as an oxidator. In addition, humic acid (HA, Sigma Aldrich, Germany) was employed as a model contaminant for filtration experiment, also, distilled water was used as a nonsolvent during immersion precipitation, solvent for HA solution preparation, feed for pure water flux experiment.

2.2. Membrane preparation

The membrane was prepared through common non-solvent induced phase separation method and the modification was conducted by means of blending. Firstly, 1 wt% of dopamine (3-Hydroxytyraminium chloride) and 0.5 wt% peroxide was mixed together in 85 wt% of NMP solvent with stirring for 84 hours at a temperature 70°C to allow the formation of polydopamine (PDA) particle from the oxidative polymerization reaction. Following that, PES was added into the PDA solution and further stirred for another 12 hours at a temperature of 70°C. Once the homogeneous PES/PDA solution was obtained, it was left overnight in a refrigerator for debubbling. The solution was then cast on a glass plate into a thin membrane film at an approximate thickness of 2mm using a casting knife. The cast plate was immersed in nonsolvent until the membrane film peeled off the glass. After that, the ready membrane was stored in a container containing distilled water for subsequent use.

2.3. Membrane characterization

To study the effects of modification on the membrane, several characterizations were carried out such as analysis of chemical composition using Fourier-transform infrared spectroscopy (FTIR). Moreover, the porosity of the membrane was also evaluated by adapting the gravimetric calculation using Eq. (1) as follows.

\[ \varepsilon = \frac{(\omega_w - \omega_d)}{\rho \times A \times l} \times 100\% \]  

(1)

Here, \( \omega_w \) and \( \omega_d \) denote the membrane weights without drying (wt) and after overnight drying (kg). \( \rho \) is the density of water (998 kg/m³), \( A \) is the membrane area (m²), and \( l \) represents the thickness (m) of the membrane.
2.4. Filtration and antifouling experiments
The filtration process was carried out using an ultrafiltration module with a cross-flow cell type at an operating pressure of 1 bar. Experiments were carried out using distilled water and HA as model feeds. The experiment was carried out in three stages. The first stage was done using distilled water as a feed to obtain initial pure water flux ($J_1$) data by means of accommodating the generated permeate at a time interval of 10 minutes, and Eq. (2) was used to determine the pure water flux. Subsequently, the experiment was proceeded by changing the feed (from distilled water) to artificial HA solution with a concentration of 50 ppm. Similar to earlier, the filtered permeate was collected and weighed every 10 minutes, and HA flux ($J_{HA}$) was also calculated by using Eq. (2). In addition, the concentration of HA and generated permeate was measured using UV-VIS, and the rejection of HA was calculated using the Eq. (3).

\[
J = \frac{Q}{A \Delta t} \quad (2)
\]

\[
R = \left(1 - \frac{c_p}{c_f}\right) \times 100 \quad (3)
\]

After that, membrane cleaning was carried out by means of backwash at a pressure of 0.1 bar for 20 minutes. Subsequently, filtration experiment was continued using distilled water as a feed to obtain the after-cleaning pure water flux ($J_2$). From this one-set experiment, the data of fouling resistance properties such flux recovery ratio (FRR), total fouling (Rt), reversible fouling (Rr), and irreversible fouling (Rir) were obtained through calculation using Eq. (4-7):

\[
FRR = \left(\frac{J_2}{J_1}\right) \quad (4)
\]

\[
R_t = \left(\frac{J_2 - J_{HA}}{J_1}\right) \quad (5)
\]

\[
R_r = \left(\frac{J_2 - J_{HA}}{J_1}\right) \quad (6)
\]

\[
R_{ir} = \left(\frac{J_1 - J_2}{J_1}\right) \quad (7)
\]

3. Results and discussion

3.1. Effects PDA addition on membrane chemical composition
Changes in the chemical composition of the PES membrane after modification with polydopamine can be seen from the results of the analysis using FTIR as shown in Figure 1.

![Figure 1. Spectra analysis of pure and PDA-blended PES membranes.](image-url)
From Figure 1, significant differences between modified PES membrane and PES membranes without modification can be observed by the emergence of new peaks at a wavenumber of 1640 1/cm and in the wavenumber range of 3000-3600 1/cm. These peaks indicate the presence of NH and OH groups from polydopamine which is a compound composed of a long and repeated catechol chain (NHOH) [9,11]. Both of these functional groups have a high affinity for water which causes polydopamine to be highly hydrophilic. From the IR results in Fig. 1, it can be concluded that polydopamine has been successfully blended in the membrane system.

3.2. Effects of PDA addition on membrane porosity and filtration performance

The pore property of the membrane is closely related to the filtration performance in terms of pure water flux (PWP), solute water flux, and solute rejection. In Fig. 2 (a), it can be seen that the performance of pure water flux of the membrane with PDA modification is 1.5 times higher than pure water flux from the experiment using the original PES membrane. The increase in pure water flux value is influenced by the pore properties of the PDA/PES membrane which represented by the surface porosity data of 11.27%, much higher compared to the unmodified PES membrane porosity which is only 2.69%. The PDA-blended membrane has more pores because PDA particles played a role as pore formers during the fabrication process. Hydrophilic PDA particles have a high affinity for water thus in the precipitation immersion process the PDA particles which located in the membrane tend to be attracted to the surface or top layer of the membrane or even leached out into the nonsolvent (water). The particles released from this membrane system leave marks on the surface of the membrane film in the form of pores [6,12].

Figure 2. Porosity and pure water flux performance (a) and humic acid water flux and rejection performances (b) of the pure and PDA-blended PES membranes.

The increase in pore property also has an impact on HA filtration performance as shown in Fig. 2(b). From Fig. 2(b), it can be seen that, similar to pure water flux, the flux of HA is also seen to increase in the PDA/PES membrane. This is due to an increase in pore property as mentioned earlier. On the contrary, the increase in porosity causes a 2% decrease to HA rejection of the PDA/PES membrane because some HA particles escaped into the permeate through the pores.

3.3. Effects of PDA addition on membrane antifouling performance

Membrane fouling is a complex phenomenon that involves physical and chemical interactions between foulant and membrane surfaces. The overall effect of fouling is reducing the active membrane area or increasing resistance across the membrane leading to a decline in operating flux [13]. For applications
in membrane technology, fouling must be avoided at all cost in order to maintain the efficiency of the separation process. In general, membrane fouling can occur in the form of adsorption, pore blockage, particle deposition, or gel formation [13,14]. Membrane fouling can be reversible or irreversible. Reversible fouling (Rr) refers to fouling that can be cleaned by a simple physical method, such as water-flush or backflush. Meanwhile, that which cannot be recovered by physical cleaning is called irreversible fouling (Rir) [15]. Commonly, the performance of membrane antifouling can be evaluated from the flux recovery ratio (FRR) which is the ability of the membrane to recover water flux after cleaning. Moreover, FRR can also be used to observe the effectivity of membrane cleaning on the membrane. In this work, HA was used as an artificial NOM to study the fouling resistance of the membrane in one-set three-stage filtration experiment and results are presented in Fig. 3.

![Antifouling profiles of the pure and PDA-blended PES membranes.](image)

**Figure 3.** Antifouling profiles of the pure and PDA-blended PES membranes.

As seen in Fig. 3, it is clear that modification with PDA particles can increase overall fouling resistance performance of the PES membrane. Without modification, it appears that PES pure membrane is only able to restore about 67% of the initial pure water flux due to severe fouling which can be seen from total fouling data of reaching 41%. This is attributed to the hydrophobic nature of PES polymer which causes the HA particles which also hydrophobic to attach easily and strongly on the membrane surface due to the high hydrophobic-hydrophobic interactions [16]. This phenomenon causes the accumulated HA particle difficult to detach from the surface of the membrane even after backwash. This is confirmed by irreversible fouling (Rir) and reversible fouling (Rr) data of 33% and <8%, respectively.

As for the PDA-bended membrane, the total fouling occurred was only about 19% with 13.5% reversible fouling and only 5.4% irreversible fouling. The high reversible fouling and low irreversible fouling indicate that the membrane cleaning is effective and can recover flux up to 94.58%. This finding is consistent with the hypothesis that increased hydrophilicity due to the presence of NH and OH functional groups from the addition of PDA reduces hydrophobic interaction between HA particles and membrane surface, weakening their ability to attach to the surface, and resulting in fairly stable operating flux. These results are in agreement with those reported in previous studies using dopamine or PDA in other polymeric membranes with different modification techniques [6-8].
4. Conclusion
Hydrophilic modification has been done to PES membrane using polydopamine particle which made through in-situ oxidative polymerization of dopamine assisted by peroxide by blending method. It is confirmed that the addition of PDA particle increased membrane hydrophilicity with the appearance of catechol functional groups affirmed by IR spectra analysis. The improved hydrophilicity brought about the enhancement in overall fouling resistance performance of the PDA/PES membrane which proven by FRR value up to 95% and total fouling occurred of only 19%. In addition, PDA particle acts as a pore-former which enhances water permeation performance due to increased porosity. This modification method is promising to fabricate membrane with high flux and antifouling performance.

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