Improvement in performance of polysulfone membranes through the incorporation of chitosan-(3-phenyl-1h-pyrazole-4-carbaldehyde)

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Improvement in performance of polysulfone membranes through the incorporation of chitosan-(3-phenyl-1h-pyrazole-4-carbaldehyde)

K. Balakrishna Prabhu1,2, M.B. Saidutta2, Arun M. Isloor3* and Raghavendra Hebbar3

Abstract: Pure polysulfone membranes are known to exhibit poor permeability, and high fouling. This study was conducted to explore the possibility of improving the permeation characteristics of polysulfone membranes by using a chitosan derivative as an additive. Polysulfone membranes blended with chitosan derivative 3-phenyl-1H-pyrazole-4-carbaldehyde (ChD) were prepared by the method of wet coagulation. The hydroxyl, amine and the imine functional groups present in the ChD evidently increased the hydrophilicity of the surface of the blended membranes which was confirmed by contact angle measurements. The contact angle of the blended membrane having 2 wt.% ChD was 62 ± 1 as compared to 70 ± 1 of neat polysulfone membrane. The SEM analysis of the blended membranes revealed a highly porous structure with a very thin surface skin layer, finger like projections in the sub-layer with a macro void structure at the base. The blended membranes also showed significant improvement in pure water flux of 351 L m⁻² h⁻¹ at 0.8 MPa trans membrane pressure (TMP) as compared to 24 L m⁻² h⁻¹ of neat polysulfone membrane at the same TMP. The anti-fouling test using bovine serum albumin exhibited improved anti-fouling characteristic of blended membranes with a maximum flux recovery ratio (FRR) of 57%. The heavy metal rejection study revealed that membrane P-1 showed maximum 36 and 29% rejection for Pb and Cu respectively.

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PUBLIC INTEREST STATEMENT

Providing clean and adequate amounts of water for human requirements is undeniably a grand challenge of the current century. On the one hand, rising population in the world is leading to ever rising need for water for purposes of drinking, sanitation, agriculture and industry and on the other, the polluted waters generated by various human activities need to be purified and safely returned to the environment. Membrane technologies have been successfully employed in desalination plants to obtain potable water; they are also widely used in purification of industrial waste waters. In the present work we have attempted to improve the permeation properties of an important class of polymeric membranes called polysulfone membranes which find wide spread use in water treatment technologies. The improvement in the performance was achieved by blending the polysulfone with a derivative of a bio-polymeric material called chitosan.
1. Introduction

In recent times membranes have played a crucial role in the field of water purification and reuse. Membranes have the ability to allow a selective chemical species in a mixture to pass through, while preventing other species from doing so (Baker, 2000). The attractiveness of membrane related processes stem from benefits such as no phase change during separation, low energy expenditure, conceptual simplicity, reduced operating outlays, easy integration and scale up. The capability of the membranes to aid selective permeation is what gives them an important place in this domain (Hebbar, Isloor, Ananda, & Ismail, 2016; Molinari, Gallo, & Argurio, 2004).

Polysulfone is an important class of polymeric material widely used in ultrafiltration, reverse osmosis and pervaporation membranes (Kumar, Isloor, Ismail, Rashid & Al Ahmed, 2013). Polysulfone possesses excellent film forming capability, has superior chemical and mechanical properties and is available at competitive prices (Padaki, Isloor, Wanichapichart, & Ismail, 2012). Further, polysulfone membranes have a wide operating temperature range (~75°C), a broad pH range (3–11) and have excellent resistance to chlorine (up to 200 ppm) (Cho, Kim, Nam, & Park, 2011). However polysulfone membranes suffer from poor permeability and inferior anti-fouling behavior. Low permeability generally, is attributed to small surface pore size and low surface hydrophilic property. Poor anti-fouling performance is attributable to low surface hydrophilicity (Kumar, Isloor, Ismail, Rashid & Al Ahmed, 2013). Earlier studies have reported that blending polysulfone with additives like polyvinylpyrrolidone (PVP), poly(ethylene glycol) (PEG) increases the hydrophilicity and improves anti-fouling characteristics (Kumar, Isloor, Ismail, & Matsuura, 2013a).

The endeavor to incorporate the property of superior fouling-resistance into membranes is of foremost importance in the preparation of new membranes. Since fouling can be reduced by increasing hydrophilicity, various methods like polymer grafting, custom-made polymers, blending, and doping with oxides have been successfully employed to increase membrane hydrophilicity. Among the aforesaid methods, polymer blending offers a facile way of improving membrane characteristics (Hebbar, Isloor & Ismail, 2014a).

An asymmetrical membrane is distinguished by a thin and compact top layer, generally identified as the skin layer, underneath which is a porous solid structure. It is well known that, the skin layer acts as the main barrier to mass transport, whereas the porous region underneath serves as a structural support. The selective permeation or exclusion of a given solute by the membrane is governed by the morphology, the pore size and the density of the skin layer. Therefore, it is essential to make asymmetric membranes with a required structure of skin layer to bring about a requisite performance (Chuang, Young, & Chiu, 2000).

Chitosan (poly-β-1→4)-2-amino-2-deoxy-D-glucose) is a nitrogenous (amino-based) polysaccharide which is produced in large quantities by N-deacetylation of its precursor chitin (Clark & Smith, 1936; Muzzarelli, 1973; Rinaudo, 2006). Chitin is the second most abundant natural polymer in nature (Baroni, Vieira, Meneghetti, da Silva, & Beppu, 2008); it occurs as a major component in the exoskeleton of crustaceans, or cartilages of mollusks, cuticles of insects and cell walls of micro-organisms. Chitosan is a non-toxic, environment friendly and an inexpensive bio-polymer (Kyzas & Bikiaris, 2015). Due to the presence of large amount of hydroxyl groups, chitosan has a hydrophilic characteristic (Bhatnagar & Sillanpää, 2009). It has been shown that, membranes having higher hydrophilicity display improved anti-fouling resistance because protein and many other foulants are hydrophobic in nature (Rana & Matsuura, 2010; Richard Bowen, Doneva, & Yin, 2001).
Modified chitosan provides better hydrophilicity whereas polysulfone would ensure structural stability of the composite blend (Padaki, Isloor, & Wanichapichart, 2011). In addition, by incorporating the chitosan derivative, an adsorbent material, into the polymer matrix, the ability of the membrane for heavy metal retention would be enhanced. Many studies related to polysulfone and chitosan or modified chitosan–polysulfone blend membranes have been reported (Kumar, Isloor, & Ismail, 2014; Kumar, Isloor, Ismail, & Matsuura, 2013a; Kumar, Isloor, Ismail, Rashid & Al Ahmed, 2013; Kumar, Isloor, Ismail, Rashid, & Matsuura, 2013; Padaki et al., 2011, 2012). In the present study a new derivative of chitosan (ChD) was prepared by grafting the ligand 3-phenyl-1H-pyrazole-4-carbaldehyde onto chitosan. Membranes were prepared by blending polysulfone with the chitosan derivative ChD and the corresponding improvement in membrane permeation properties, anti-fouling behavior and metal rejection performance were studied.

2. Methodology

2.1. Materials

The chitosan used (Degree of deacetylation = 90% and average molecular weight = 5.0 × 10^5 Da) was purchased from Seafresh Industry Public Co. Ltd. Bangkok, Thailand. Acetophenone (Merck Specialities Pvt. Ltd. Mumbai, India) and semicarbazide hydrochloride (Merck Schuchardt OHG, Germany) of AR grade were used. Polysulfone (Avg. MWt. = 35,000) was purchased from Sigma Aldrich, USA. PEG-1000 was purchased from Hi Media Laboratories (Pvt) Ltd, Mumbai, India. Bovine Serum Albumin (BSA) was purchased from Central Drug House, New Delhi, N-Methyl-2-Pyrrolidone was purchased from Merck India, Ltd. and formic acid was purchased from Merck India Ltd. The salts used Pb (NO₃)₂ and CuSO₄·5H₂O were purchased from Nice Chemicals India and Merck specialities India respectively.

2.2. Preparation of chitosan derivative

The synthesis of the chitosan derivative was carried out in three steps (Figure 1). In the first two steps, pyrazole aldehyde (B) was synthesized as per procedure reported in literature (Isloor, Kalluraya, & Shetty, 2009). Briefly, to 125 ml ethanol, acetophenone (15.6 mL, 0.13 mol), semicarbazide hydrochloride powder (13.38 g, 0.12 mol) and sodium acetate (16.32 g, 0.20 mol) were added and refluxed at 78°C for 4 h. to yield semicarbazone (A) (Yield: 17.4 g, 82%). To dimethyl formamide (40.38 mL, 0.525 mol), phosphorous oxychloride (20 mL, 0.21 mol) was added drop-wise under nitrogen atmosphere, to which semicarbazone (A) (17.4 g, 0.098 mol) was added portion wise over 10 min. The reaction mass was then heated to 80°C in a gradual manner and maintained there for
4 h. After the completion of the reaction, the pH was adjusted to 7 by adding sodium carbonate. It was then extracted in three stages with ethyl acetate using 75 mL each time to obtain the intermediate product, pyrazol aldehyde (B) (3-phenyl-1H-pyrazole-4-carbaldehyde, Yield: 12.1 g, 83.43%).

In the last step, 150 mL of acetic acid (1%) was used to dissolve 6 g of chitosan powder, and to the previous mixture, 600 mL of methanol was added and agitated for 16 h. To this, pyrazol aldehyde (B) (10.25 g) dissolved in chloroform was added. After this, the reaction mixture was maintained at 60°C for 18 h under agitation. The product obtained was further washed with 75 mL of chloroform and the yellow mass obtained, the final product (ChD) was filtered, and dried at 50°C (Yield: 9.3 g, 79.2%).

2.3. Preparation of membranes

2.3.1. Preparation of neat polysulfone membrane (P-0)

1.8 g of polysulfone was taken with 8 mL of NMP in a 20 mL beaker and kept under stirring for over 3 h till polysulfone completely dissolved after which 0.2 g of PEG-1000 was added and then the mixture was stirred for over 24 h until a homogeneous solution was obtained. The stirring was then stopped and the temperature was maintained at 50°C for 2 h to remove the air bubbles. This solution was then cast over a glass plate and then immersed into a coagulation bath of distilled water (27°C) acting as the non-solvent when the membrane gets formed by phase inversion (Kumar, Isloor, Ismail, & Matsuura, 2013b).

2.3.2. Preparation of PSf:ChD blend membranes P-2 and P-1

The PSf:ChD (98:2) (P-2) blend membranes were prepared by the method of wet phase inversion following the procedure given in the literature (Hebbar, Isloor, & Ismail, 2014b; Kumar et al., 2014). 1.8 g of polysulfone was taken with 8 mL of NMP in a 20 mL beaker and kept under stirring for over 3 h at 60°C until the polysulfone completely dissolved after which 0.2 g of PEG-1000 was added to the previous mixture and agitation was continued till a clear solution was obtained. Accurately weighed 0.36 g of chitosan derivative (ChD) was taken in a second 20 mL beaker with 3.0 mL of formic acid and kept under stirring for 45 min at 60°C until a clear solution was obtained. The solution is poured into the first beaker and the contents were kept under gentle stirring for over 24 h till a clear solution was obtained. The homogeneous solution was maintained at 50°C for a further period of 2 h to remove the air bubbles, if any, entrapped in the solution. This solution was then cast over a glass plate and then dipped into a coagulation bath of distilled water at 27°C, acting as the non-solvent when the membrane gets formed by phase inversion. To ensure complete phase inversion, the membrane was kept immersed under water for 24 h after which it was taken out and rinsed several times with distilled water and finally dried at 30°C. In a similar manner, the membrane with ratio of PSf:ChD (99:1) (P-1) also was prepared. A schematic representation of preparation of membrane is given in Figure 2. The prepared membranes had an average thickness of 143 μm.

Figure 2. Synthesis of Polysulfone-ChD blend membrane.
2.4. Instruments and equipment

2.4.1. Scanning electron microscopy (SEM)
To record the cross-sectional image of the membrane, the sample was prepared by first immersing in liquid nitrogen, followed by fracturing and then sputtering with gold dust. Jeol JED 2300 Analysis Station Scanning electron microscope was used to record the membrane morphology.

2.4.2. Contact angle measurement
The surface contact angle was measured by FTA-200 Dynamic contact angle analyzer based on the sessile droplet method. Contact angle was measured at three random locations and the average number was reported.

2.4.3. Powder XRD analysis
The membrane samples were characterized by Bruker D8 Advance X-ray powder diffractometer employing Cu K-radiation (operating specifications: 40 keV, 40 mA) in a scanning range of $2\theta = 5^\circ$–$80^\circ$.

2.4.4. Metal ion concentration in permeate
Thermo-Scientific iCE 3000 series flame atomic absorption spectrometer was used to determine the concentrations of Cu(II) and Pb(II) in the permeate solutions.

2.4.5. Pure water flux study
A self-fabricated dead-end filtration kit was used for measuring the pure water flux (PWF) (Figure 3). The membrane sample used in permeation experiments was in the form of a circular disc with an effective diameter of 5 cm. The pure water flux $J_w$ (L m$^{-2}$ h$^{-1}$), was calculated using the Equation (1) (Aminudin, Basri, Harun, Yunos, & Sean, 2013):

$$J_w = \frac{Q}{A\Delta t}$$  \hspace{1cm} (1)

where $Q$ is the volume of water collected (L), $A$ is the effective membrane area available for permeation (m$^2$) and $\Delta t$ is the time interval of water collection (h).

2.4.6. Membrane hydraulic resistance
Hydraulic resistance ($R_h$) is the resistance offered by the membrane to the flow of feed (Waheed et al., 2014). It is defined by the Equation (2):
where $\Delta P$ is the TMP in MPa and $J_w$ is the pure water flux (L m$^{-2}$ h$^{-1}$) and $R_h$, the hydraulic resistance (MPa L$^{-1}$ m$^2$ h$^{-1}$).

2.4.7. Anti-fouling studies

The anti-fouling property of the membrane was studied by using BSA solution having a concentration of 0.8% by wt. Initially, the PWF, $J_{w1}$ (L m$^{-2}$ h$^{-1}$) of the membrane was determined at a TMP of 0.8 MPa with distilled water for 60 min. This was followed by the permeation study to find the flux $J_p$ (L m$^{-2}$ h$^{-1}$) using 0.8% BSA solution for 60 min at the same pressure. The membrane was then flushed with distilled water for 15 min to remove the lightly adhering molecules of protein. Subsequently, the flux through the cleaned membrane was measured for 60 min at 0.8 MPa and recorded as $J_{w2}$ (L m$^{-2}$ h$^{-1}$). The anti-fouling nature of the membrane was assessed by calculating the flux recovery ratio (FRR) using Equation (3):

$$\text{FRR(\%)} = \frac{J_{w2}}{J_{w1}} \times 100$$

(3)

To further analyze the fouling behavior, three more equations Equations (4)–(6) were used (Vatanpour, Madaeni, Moradian, Zinadini, & Astinchap, 2011).

$$R_t(\%) = \frac{J_{w1} - J_p}{J_{w1}} \times 100$$

(4)

$R_t$ is a measure of total loss of flux due to membrane fouling.

$$R_r(\%) = \frac{J_{w1} - J_{w2}}{J_{w1}} \times 100$$

(5)

$R_r$ provides a measure of flux recovery as a percentage initial flux.

$$R_{ir}(\%) = \frac{J_{w1} - J_{w2}}{J_{w1}} \times 100$$

(6)

$R_{ir}$ gives the permanent loss of flux due to fouling, as a percentage of initial flux.

3. Results and discussion

3.1. Study of membrane morphology

The cross sectional morphologies of the membrane exhibit an asymmetric structure. In case of P-1 and P-2 a porous sub layer is observed below the top surface containing numerous finger-like projections which can be very prominently seen (Figure 4(b) and (c)). However, in the case of the neat membrane (P-0), such projections are virtually missing and a dense layer is seen at the top (Figure 4(a)).

From the micrograph it is observed that, in case of both P-1 and P-2, the projections start almost from the surface, resulting in a top skin layer that is almost nonexistent. The surface images of P-1 and P-2 (Figure 5(g) and (h)) also show well-developed pores on the surface. The micrograph of the neat membrane P-0, however, showed poorly developed porous structure. It also exhibited an opaque surface (Figure 5(f)). This can be attributed to quick demixing of the polymeric solution due to the presence of formic acid when immersed in the coagulation bath in case of P-1 and P-2.
Non-solvent additives in the casting solution can significantly influence membrane morphology. According to various studies reported, addition of acetic acid to the casting solution decreased the width of the top skin layer (Chuang et al., 2000). Dicarboxylic acids such as glycolic acid and oxalic acid (Chen et al., 2008) and organic alcohols like propanol and butanol have been shown to increase the porosity and have significant bearing on the membrane morphology. A cross sectional view of the P-2 membrane showing the macrovoids and the micro porous structure on the walls of macrovoids is presented in Figure 4(d) and (e).

### 3.2. Contact angle

Contact angle is a measure of surface hydrophilicity. Higher the hydrophilicity, lower is the surface contact angle (Hebbar et al., 2015). As shown in Figure 6, the contact angle of the neat polysulfone membrane was $70 \pm 1$ as compared to $62 \pm 1$ for blended membrane (P-2) having 2 wt.% ChD. Hence the blending of the polysulfone membrane with ChD reduced the contact angle significantly.

### 3.3. XRD analysis

The XRD patterns of the chitosan derivative (ChD), PSf-ChD (P-2) membrane (with 2 wt.% ChD) and neat PSf (P-0) membrane (with 0% ChD) is presented in Figure 7. The XRD pattern for ChD exhibits peaks at 19° and 21° which are characteristic of chitosan. The XRD plot of P-0 exhibits a wide peak placed around 18° which is consistent with that given in literature (Ganesh, Isloor, & Ismail, 2013).

The general increase in peak intensity of P-2 vis-à-vis P-0 at all $2\theta$ values and the XRD pattern of P-2 manifesting in between those of P-0 and ChD clearly confirms the uniform incorporation of ChD into the polysulfone (PSf) polymer matrix.
3.4. Permeation studies

The permeation studies were carried out in the dead-end filtration cell given in Figure 3 at a temperature of 27°C under pH = 7 ± 0.2 with TMP values in the range of 0.2–0.8 MPa. During the permeation experiments, significant increase in flux was observed in case of ChD doped membranes when compared to the neat membranes (Figures 8 and 9). Steady state pure water flux values obtained for P-2, P-1 and P-0 were 188, 101 and 18 L m⁻² h⁻¹ respectively at a TMP of 0.4 MPa. A much smaller skin layer thickness, higher porosity and the increased hydrophilicity due to the presence of ChD on the membrane surface were responsible for the increase in the flux of the blended membranes P-1 and P-2.

3.5. Membrane hydraulic resistance

The hydraulic resistance is the reciprocal of the slope of the graph obtained by plotting the transmembrane pressure against the pure water flux. The hydraulic resistance offered by the P-0, P-1 and...
P-2 membranes were 0.02721, 0.0039 and 0.0023 MPa/L m$^{-2}$ h$^{-1}$ respectively. The decreases observed in hydraulic resistances for P-1 and P-2 membranes when compared to P-0 membrane is attributed to the increased porous structure and the increase in hydrophilicity of the P-1 and P-2 membrane surfaces due to the presence of ChD. Our results are consistent with those of Kumar, Isloor, Ismail, Rashid & Matsura (2013) who reported that appropriate additive added to PSf membrane may act as pore former during the phase inversion process and result in decreased hydraulic resistance.

3.6. Anti-fouling studies

With an increase in membrane surface hydrophobicity, hydrophobic organic molecules gravitate more toward the surface, leading to an increase in surface contamination. In general, membrane fouling refers to an extreme decrease in post-filtration flux that occurs when organic foulants like proteins are present in the permeate solution. Fouling is attributed either to the clogging of the pores by the proteins, or build-up of the proteins on the membrane surface. When the clogging of pores and protein build up is just due to a loose deposition, it is termed as reversible fouling, as it can be cleaned by a facile hydraulic wash. In comparison, when the protein build up is due to strong adsorptive forces, leading to a permanent loss of flux, it is called irreversible fouling (Vatanpour et al., 2011). It is always desirable to develop membranes that have a high degree of resistance to fouling and display self-cleaning behavior.

It has been reported that membranes which show a higher hydrophilic characteristic have a higher resistance to fouling (Richard Bowen et al., 2001). The hydroxyl, amine and the imine groups of the ChD augmented hydrophilicity of the membranes P-1 and P-2. These groups present on the membrane surface aided the adsorption of water molecules whereby a hydrated layer was formed on the functioning surface. This layer formed on the top of the membrane surface resulted in the decrease in protein-membrane interaction.
The catastrophic drop in flux within the initial few seconds of commencement of BSA filtration (Figure 10) indicated the extremely rapid deposition of the protein molecules on the membrane surface (Shenvi, Ismail, & Isloor, 2014). However, the presence of a hydrated layer on the hydrophilic surface prevented strong bonding between the protein molecules and the membrane surface, thereby making the membrane amenable to simple hydraulic cleaning and recovery in PWF. The preceding discussion confirmed that the ChD blended membranes had superior anti-fouling behavior. The results of the anti-fouling studies are tabulated in Table 1.

### 3.7. Heavy metal rejection study

The performance of the membranes for Pb(II) and Cu(II) rejection was studied with aqueous solutions of Pb (NO₃)₂ and CuSO₄·5H₂O respectively, containing the respective metal ion concentration of 100 mg/L, at pH = 6 ± 0.2, at a temperature of 27°C and TMP of 0.2 MPa. A pH close to neutral value was chosen because at lower values of pH < 4 the amino groups of the chitosan derivative get protonated which results in repulsion of the cationic metal ions from the membrane. The findings of the study are presented in Figure 11. The maximum value rejection of 36% of Pb(II) was obtained in the case of P-1 membrane. The rejection was ~70% higher than the values obtained with neat membrane (21%). In the case of P-2 membrane a rejection of 29% was observed which was lower than that obtained for P-1. In case of studies with Cu(II), a maximum rejection of 29% was observed for P-1 (Figure 11) compared to ~20% rejection of the neat membrane. For the P-2 membrane, Cu(II) rejection of 21% was obtained which was lower than value obtained for the P-1 membrane. All the rejection experiments were duplicated and the experimental data and results were within 5% error.

As observed during the permeation studies, the observed order of flux at the same TMP was: P-2 > P-1 > P-0. As the flux increases, the drag force on the solvent through the pores also increases. The surface forces (i.e. frictional forces, adsorptive forces) on the pore walls, however, are constant and unchanging with flux. The surface forces are responsible for the retention of the solute by adsorptive forces (e.g. chelation, electrostatic binding). Comparatively, surface forces are greater than the drag force at lower flux than at higher flux (Pontalier, Ismail, & Ghoul, 1997). Hence, the maximum rejection observed in case of P-1 membranes was probably due to the favorable combined effect of drag and the surface forces. It is inferred that the blending of PSf with ChD aided in increasing the retention of metal ions by surface adsorption. The hydroxyl, amine and the imine groups present in the ChD are the potential sites for the metal adsorption by chelation and complexation.

### Table 1. Filtration and antifouling performances of the membranes (TMP = 0.8 MPa)

| Membrane | $J_w$ | $J_p$ | $J_{w2}$ | FRR | $R_t$ | $R_r$ | $R_{ir}$ |
|----------|-------|-------|----------|-----|------|------|--------|
| P-0      | 23.6  | 0.3   | 7.6      | 32.4| 98.3 | 30.8 | 67.5   |
| P-1      | 148.6 | 21.6  | 76.8     | 51.6| 85.4 | 37.1 | 48.3   |
| P-2      | 350.7 | 27.0  | 199.5    | 56.8| 92.2 | 49.1 | 43.1   |

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4. Conclusion
Polysulfone membranes blended with chitosan derivative (PSf-ChD) showed increased porosity and lower hydraulic resistance compared to the neat membranes. Lower values of contact angle were also recorded for blended membranes, indicating an increase in surface hydrophilicity. The PSf-ChD membranes exhibited increased pure water flux with a maximum flux of 351 L m⁻² h⁻¹ and improved resistance to fouling with a maximum flux recovery ratio of 56%. The increase in flux was attributed to the combined effect of increased hydrophilicity (as evidenced by lower contact angle), smaller skin thickness and macropores. The scanning electron micrograph showed finger-like projections and macrovoids in case of blended membranes. The skin thickness was observed to be significantly lower for the PSf-ChD membranes. The metal rejection studies revealed a maximum rejection of 36 and 29% for Pb(II) and Cu(II) respectively. Hence addition of ChD can be effectively used for improving the performance of the PSf ultrafiltration membranes.

Abbreviations

| Abbreviation | Description                  |
|--------------|------------------------------|
| BSA          | Bovine serum albumin         |
| ChD          | Chitosan derivative          |
| FRR          | Flux recovery ratio          |
| NMP          | N-Methyl-2-Pyrrolidone       |
| PEG          | Polyethylene glycol          |
| PSf          | Polysulfone                  |
| PWF          | Pure water flux              |
| TMP          | Trans membrane pressure      |

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