



Performance of polyethersulfone membranes modified with low molecular weight polyacrylic acid

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Abstract: A series of poly(ethersulfone) (PES) ultrafiltration membrane blended with poly(acrylic acid) (PAA) was prepared by phase inversion method by varying the PAA composition from 0 to 10 wt% in the polymer blend compositions. Prepared membranes were analyzed for their morphology, ultrafiltration (UF) characterizations and dye rejection performance. Cross-sectional morphology study using SEM showed the increased pore size of the sublayer of the asymmetric membranes due to PAA addition. AFM studies confirmed the enhanced surface roughness of the PES/PAA blend membranes. Surface hydrophilicity was increased with increase in the PAA concentration in the composite membranes. Porosity measurements confirmed the porous nature of PES/PAA blend membranes than the unmodified PES membrane. Pure water permeability of the PES/PAA blend membranes was improved to a large extent in comparison with pure PES membrane. Dye rejection studies revealed the decrease in rejection efficiency due to the PAA addition to PES matrix owing to increased pore size. Results obtained clearly indicated the better performance of 2.5 wt% PAA blend membrane in comparison with other synthesized UF membranes.

Keywords: Ultra filtration, Polyethersulfone, Polyacrylic acid, Membrane characterization, Dye rejection.

1. Introduction

Membrane separation is one of the more promising technologies for separation operations due to high degree of advantages in comparison to other conventional methods [1,2]. Ultrafiltration (UF) is a type of membrane separation operations for separating dissolved macromolecules from fluids using asymmetric membranes [2,3]. Industrially, UF is mainly applied in the effluent and wastewater treatment processes [4]. UF membranes are usually prepared from a range of materials which includes polymers, ceramics, metal oxides, etc. Polymeric membranes are largely used now-a-days owing to their ease of fabrication and preparation [5]. These polymers include polysulfone [6,7], polyethersulfone [8-10], polyvinylidene fluoride [11,12] and cellulose acetate [13,14]. Polyethersulfone (PES) is one of the excellent polymer for UF membrane synthesis due to its desirable thermal, mechanical and chemical properties [15]. Membranes casted using PES is used in a range of applications for industrial and domestic purposes. However, PES membranes suffer from the problem of low fluxes and membrane fouling [15]. To overcome these limitations, PES membranes are often modified with various modifiers to improve the flux and fouling resistance of the resulting composite membranes [15]. These modifiers are usually of polymeric or inorganic type and these modifiers, in general, enhance the surface hydrophilicity of the blend membranes thus increasing the permeate flux [16-20]. Polymeric modifiers are largely investigated as they have several advantages over inorganic modifiers [15]. Most of the polymeric additives have uniform distribution throughout the base membrane matrix in comparison to with inorganic

additives [21]. However, the miscibility of the polymeric constituents (base and additive) is a serious limitation on the PES polymeric blend system [22]. It has been reported that low molecular weight liquid polymeric modifiers are readily miscible with the PES matrix than the high molecular weight liquid or solid polymeric modifiers [15].

Poly(acrylic acid) (PAA) is one of the most studied polymeric additive and it has been successfully employed as a modifier with polymer systems such as polysulfone [7], polyvinylidene fluoride [11] and polyethersulfone [23]. PAA is characterized by an ionizable hydrophilic property which imparts a reversible swelling–shrinking behavior to it [24]. PAA also acts a crosslinking agent to the base polymer system which increases the mechanical and thermal stability of the resulting composite membrane [24]. In most of the research studies, a high molecular weight PAA is employed as an additive to the polymer doping [7,11,23]. High molecular weight PAA enhances the permeate flux by increasing the surface pore size of the membrane which eventually results in the reduction of the rejection efficiency of the membrane [7,11]. It has been identified that low molecular weight hydrophilic polymer additives increases the flux without affecting the rejection performance of the base polymer system [25].

In this current study, modification of the PES membrane using low molecular weight PAA as modifier have been carried out using phase inversion technique. Morphology (cross section and surface) analysis of the pure and blend membranes was analyzed using SEM and AFM. The prepared membranes were characterized for porosity, hydrophilicity and pure water flux. Dye rejection capacity for the pristine and blended PES membranes was analyzed using various dyes solutions. Results for the characterization and performance analysis of the PES/PAA blend membranes were compared against the pure PES membrane.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES, Veradel 3200P) in powder form was supplied by Solvay specialities India Pvt. Ltd (India) and it was dried at 120 °C for 8 h before being used. Low molecular weight Polyacrylic acid (PAA, average $M_w = 2000$) in liquid form was purchased from Sigma Aldrich (India). *N, N*-dimethyl formamide (DMF) solvent was obtained from SRL Chemicals (India). Congo red and Orange II dye powders were purchased from Avra Synthesis Pvt. Ltd (India). Freshly prepared deionized water was employed for the preparation of gelation bath, dye solution preparation and membrane storage. All the reagents used in the membrane preparation process were of analytic grade and were used as such in the experimental work.

2.2. Membrane Preparation

Phase Inversion technique is the most versatile and widely used membrane preparation method for asymmetric membrane synthesis [4]. The cast solution for a given membrane was prepared by dissolving required amounts of the PES and PAA in DMF solvent, as shown in Table 1, in a round bottom flask. The solution was magnetically stirred (along with mild heating) for 12 h to ensure complete dissolution. Subsequently, the cast dope was debubbled for 4 h. The solution was then cast on smooth glass plate with the help of a doctor blade for a fixed thickness of 200 μm . The membrane film was allowed for dry phase inversion for 30 sec. Then the glass plate along with the resulting film was immersed in a water bath for wet phase inversion. After 30 min of gelation, the membrane was removed from the water bath and washed with distilled water to remove any residual solvent. The composite UF membrane sheet was subsequently stored in deionized water container.

2.3. Membrane Characterization

Scanning electron microscopy (SEM) (Supra 55-Carl Zeiss, Germany) was used to analyze the cross section morphology of the prepared membranes. The membranes were cut into pieces of various sizes and mopped with filter paper. These pieces were frozen in liquid nitrogen and fractured for the analysis.

Atomic Force Microscopy (AFM) (NTEGRA PRIMA-NTMDT, Ireland) was used to analyze surface roughness (R_a) of the synthesized membranes. Results obtained were for an effective sampling area of 25 $\mu\text{m} \times 25 \mu\text{m}$.

Hydrophilicity of the pristine and blended PES membrane surface was measured in terms of water contact angle. The water contact angle on the membrane surface was measured using a goniometer (DGX Digidrop, France). The mean water contact angle of each membrane was obtained by averaging the static water contact angle measured at four different positions on the membrane sample's surface.

Membrane porosity for all the membranes was calculated by measuring the water uptake capacity of the membrane sample. A given membrane sample was taken and soaked in

deionized water for 24 hours. The wet sample weight was then weighed after mopping the excess water on the sample surface using filter paper. Then the wet sample was placed in a vacuum oven at 80 °C for 24 h. The dry weight of the membrane sample was then weighed until the weight became constant. The membrane porosity of the sample was then calculated using Eq. (1).

$$\varepsilon = \frac{W_w - W_d}{\rho_w Al}$$

where ε is the membrane porosity, W_w and W_d (kg) are the wet and dry weight of the membrane sample, A (m²) is the membrane surface area, l (m) is the membrane thickness and ρ_w (kg m⁻³) is water density.

Pure water flux and rejection analysis for the prepared membranes were carried out in a dead-end UF stirred cell filtration system connected to a nitrogen gas cylinder. The UF stirred cell (Amicon, Model 8400) had an inner diameter of 76 mm and a volume capacity of 400 mL with teflon coated magnetic paddle. The effective filtration area was 38.5 cm². The nitrogen gas cylinder served as a pressure source for the feed stream. All membranes were compacted at a pressure for 414 kPa for about 1 h before water flux measurement. Pure water flux of every membrane sample was then measured at an operation pressure of 276 kPa using Eq. (2).

$$J_w = \frac{Q}{A \Delta T} \quad (2)$$

where, J_w – permeate flux (lit m⁻² h⁻¹), Q – quantity of permeate (lit); A – membrane area (m²), ΔT – sampling time (h)

Performance of the pure and blended PES membranes was analyzed through dye solution rejection studies. Congo red and Orange II dye solutions at a feed concentration of 0.1 g L⁻¹ were used for the dye rejection studies. The ultrafiltration of the dye solutions was carried out at a pressure of 276 kPa. Permeate was collected over defined time intervals in graduated tubes and the tube contents were analyzed for dye concentration. Solute rejection percentage (%SR) was calculated using Eq. (3).

$$\%SR = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (3)$$

where, C_p and C_f are dye concentrations in the permeate and feed streams, respectively. The dye concentration of the dyes in the permeate and feed streams was measured using a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu Corp., USA).

3. Results and Discussion

The various characterization results for the PES/PAA blend membranes were compared against the pure PES membrane. The advantages and limitations of the blend membrane system over the unmodified PES membrane is discussed in the below section.

Table 1. Composition and characterization results for the pure and blended PES membranes

Membrane ID	Membrane Composition (by weight %)			Surface roughness, R_a (in nm)	Contact angle	Porosity, ε
	PES	PAA	Solvent (DMF)			
M1	18	0	82	39.55	65.5	0.53
M2	18	2.5	79.5	42.21	61	0.57
M3	18	5	77	59.03	57	0.62
M4	18	7.5	74.5	84.27	53.5	0.69
M5	18	10	72	111.25	53	0.73

3.1. Scanning Electron Microscopy

SEM images of the cross section of the prepared membranes are shown in Fig. 1. The SEM images clearly revealed that all the membranes exhibited asymmetric nature comprising of a very thin skin layer and a porous sub layer. It could be seen that the PES/PAA blend membranes possessed a more porous sub layer than the pure PES membrane. In addition, it was observed that at low concentration of PAA (upto 2.5 wt%), the hydrophilic effect of PAA was more dominant which resulted in a regular finger like sublayer. For higher PAA concentration (above 2.5 wt%), the dominant viscous effects of PAA resulted in a spongy sublayer which was caused due to the delayed polymer demixing rate during the phase inversion.

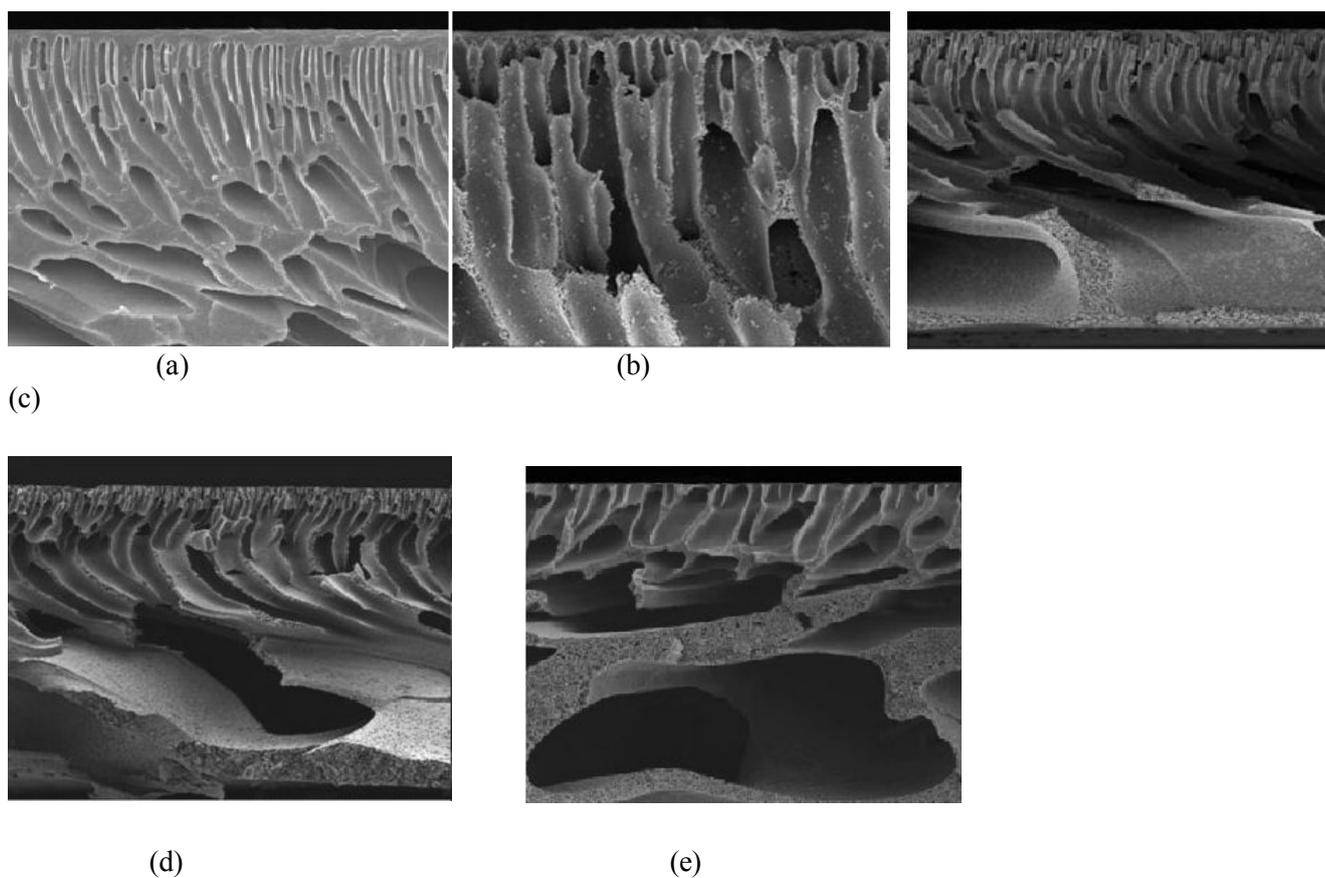


Fig. 1. SEM images for the cross section of pure and blended PES membranes – a) M1 b) M2 c) M3 d) M4 e) M5

3.2. Atomic Force Microscopy

In the AFM analysis, as shown in figure 2, the lighter or the brighter regions shows the nodular structures and the darker regions shows the depressions or pores of the membrane. In general, increase in surface roughness cause more membrane fouling which will in turn results in flux decline [26]. As shown in Table 1, it was observed that the addition of PAA to PES matrix increased the surface roughness. The rate of increase in surface roughness had a rapid growth after a cut-off concentration of 2.5 wt% for PAA in the casting dope.

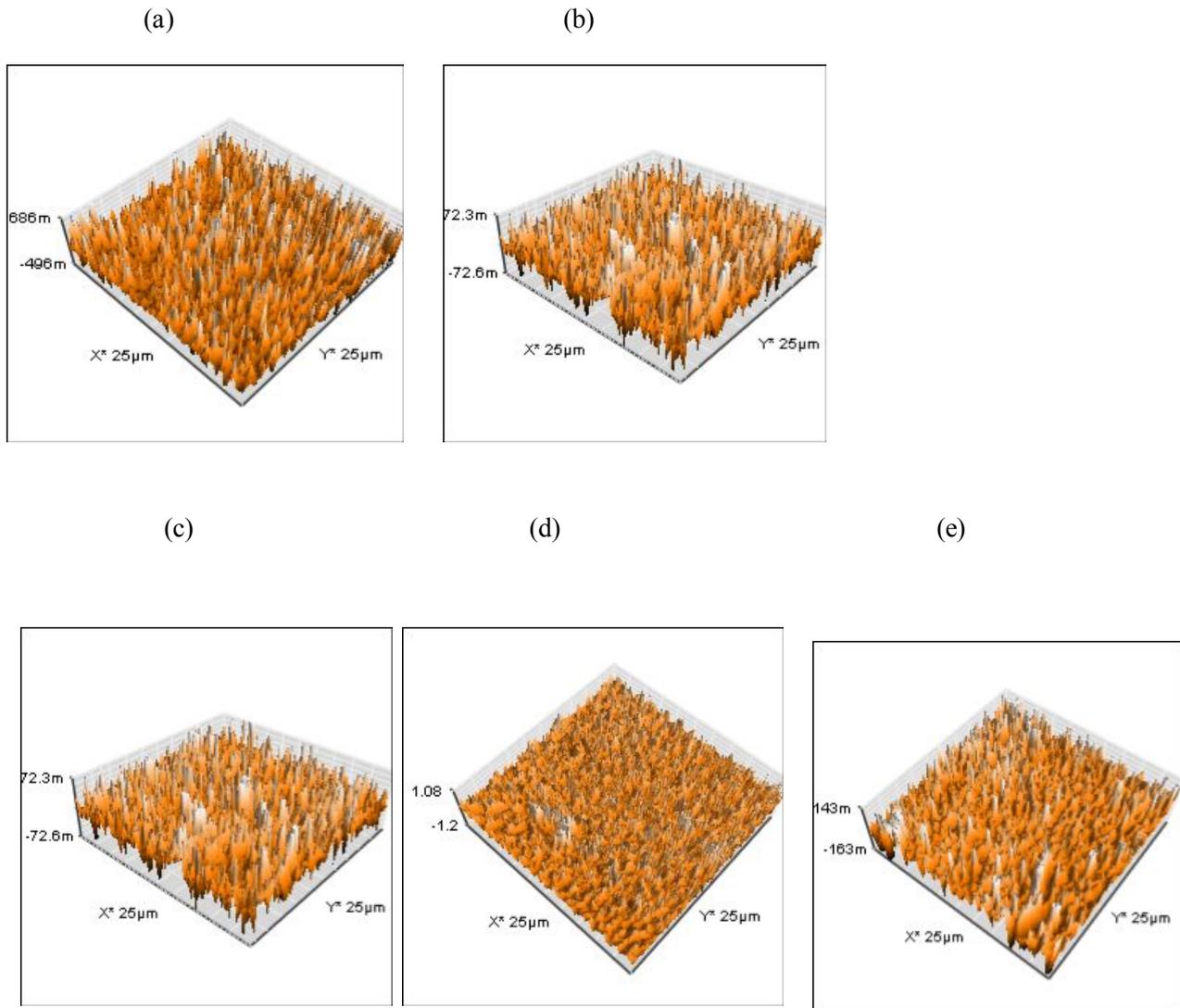


Fig. 2. AFM images of pure and blended PES membranes – a) M1 b) M2 c) M3 d) M4 e) M5

Results of SEM and AFM analysis clearly showed that the addition of PAA to the PES polymer has influenced the morphology of the blend membranes. Also, the morphology of blend membranes showed a drastic change at a cutoff concentration of 2.5 wt% PAA.

3.3. Surface hydrophilicity, Porosity and Pure Water Flux

Water contact angle measurement is one of the most suitable methods for evaluating the surface hydrophilicity of UF membranes [15]. By theory, contact angle of hydrophilic surface should be less than that of hydrophobic surface [27]. As shown in Table 1, it could be seen that the contact angle of the PES/PAA blend membranes was decreased due to the addition of PAA. This confirmed the enhanced hydrophilicity of the blend

membranes. Also, it was also observed that the surface hydrophilicity improvement almost flattened when the PAA concentration was increased from 7.5 wt% to 10 wt%.

Results of the membrane porosity studies, as shown in Table 1, clearly indicated that the porosity values of the blend membranes was increased with the addition of PAA. As the PAA concentration was increased, the support layer consisted of larger size macrovoids (as observed from the SEM images) resulting in more porous membrane.

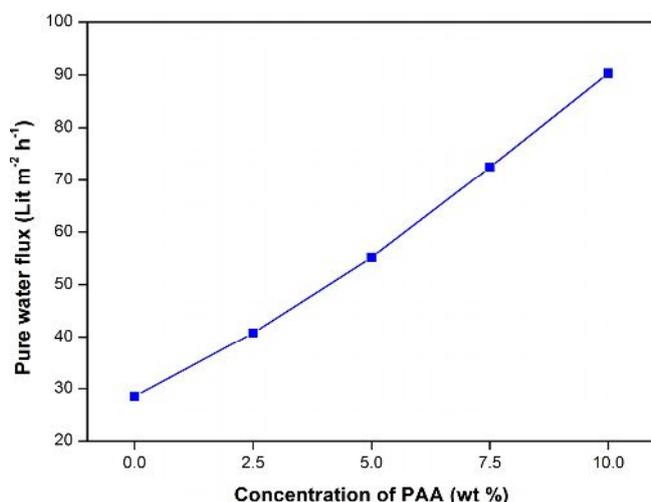


Fig. 3. Pure water flux measurement for the pure and blended membranes

Pure water flux values for the pure PES and blended PES/PAA membranes are presented in Fig. 3. From the figure, it could be seen that the addition of PAA to the PES matrix boosted the pure water flux upto a maximum of three times as compared with the pure PES membrane. This is due to the enhanced hydrophilicity and the enlarged sublayer of the blend membranes which was caused due to the addition of low molecular weight PAA.

3.4. Dye rejection

Performance of all the prepared membranes was analyzed through dye rejection studies. Congo red and Orange II dyes were used as probe agents for the rejection study. Results of the dye rejection study are presented in Fig.4.

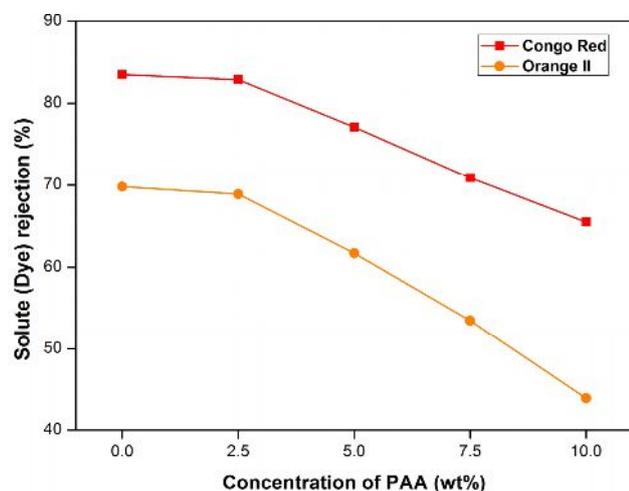


Fig. 4. Dye rejection performance of the pure and blended PES membranes

It could be seen that the dye rejection of the 2.5 wt% PAA blend membrane was almost as same as that of the pristine PES membrane. Further increase of PAA concentration in the membrane composition led to the decrease of the rejection percentage. This could be due to the enlarged surface pore size of the PES/PAA blend membranes. However, the high flux and better rejection efficiency of the 2.5 wt% PAA blend membrane makes it to be suitable and promising UF membrane candidate instead of pure PES membrane for dye polluted waste water treatment.

Analyzing the characterization and performance results, it was clear that the 2.5 wt% PAA composite UF membrane was possessing better separation characteristics in comparison with the other synthesized membranes.

4. Conclusions

A series of ultrafiltration composite membranes was prepared by blending low molecular weight polyacrylic acid (PAA) as modifier with polyethersulfone (PES). Prepared membranes were characterized by studying the membrane morphology, hydrophilicity, porosity and pure water flux. The addition of PAA to the base PES membrane influenced the membrane properties and morphology remarkably. Characterization studies showed that the PES/PAA blend membranes had enlarged sublayer, enhanced surface hydrophilicity and increased porosity. Pure water flux of the composite membranes was increased to a maximum of three times as that of pure PES membrane. Dye rejection studies using Congo red and Orange II dye solutions clearly indicated that the rejection efficiency of the PAA blend membrane was decreased considerably when the PAA concentration was more than 2.5 wt%. A very close analysis on the obtained results revealed the better separation characteristics of 2.5 wt% PAA blend membrane among the synthesized series. Thus the 2.5 wt% PAA blended PES membrane seems to be a promising candidate for treatment of dye polluted waste water, ensuring high fluxes and effective rejection.

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Nomenclature and Abbreviations

List of symbols used:

R_a	-	Surface roughness average
ε	-	Membrane porosity
W_d	-	Weight of dry membrane
W_w	-	Weight of wet membrane
ρ_w	-	Density of water
A	-	Membrane surface area
l	-	Membrane thickness
J_w	-	Pure water flux
Q	-	Permeate quantity
ΔT	-	Sampling time
% SR	-	Percentage solute rejection
C_p	-	Solute (Dye) concentration in the permeate
C_f	-	Solute (Dye) concentration in the feed

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