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# Modification and characterization of prepared polysulfone ultrafiltration membranes via photografted polymerization: Effect of different additives

M. Amini[a,*], M. Homayoonfal[b], M. Arami[a], A. Akbari[b]

*[a]Textile Engineering Department, Amir Kabir University of Technology, Tehran, Iran*
*[b]NanoSciTech. Center, University of Kashan, Kashan, Iran*
*Tel. +98 361 44545219; Fax. +98 361 4451495; email: akbari@kashanu.ac.ir*

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## ABSTRACT

The modified ultrafiltration (UF) membranes were prepared by graft polymerization of acrylic acid (AA) that is a hydrophilic monomer onto the surface of ultrafiltration membranes. Primary UF membranes were formed by wet phase inversion method by using polysulfone (PSf)/ *N*-methylene-2-pyrrolidone (NMP)/ poly (ethylene glycol) (PEG) casting solution and water coagulant. PEG acts as a pore-former that in this study is used in a wide range of molecular weights (M.W.) from 600 to 20000 Da. Changing the molecular weight of PEG additive, controls the structure and permeation properties of membranes. It can be observed that an increase in the molecular weight of PEG additive leads to an increase in water permeability. By increasing the irradiation time, rejection of dye and PEG increases, although solution permeability decreases. Increasing PEG rejection by increasing irradiation time shows the developing sieving mechanism by grafting and reduction in pore size. Grafting of AA onto membrane surface is confirmed by InfraRed spectra (IR). Scanning electron microscopy (SEM) images show a significant increase in membrane pore size than the one prepared from PEG 20000 Da, but its permeability is not too high to attribute to incomplete exit of this additive. Modified membrane prepared from PEG600 ($t_{irr}$ = 30 min and [AA] = 6%) have desirable performance in separation of these dyes but other membranes prepared from higher M.W. PEG are not effective in separation of dyes. It was observed that this membrane showed acceptable performance both in terms of flux and rejection and has the characteristics of a NF-type membrane.

***Keywords:*** UV-grafting; Polysulfone; Acrylic acid; Poly (ethylene glycol); Dye

## 1. Introduction

Polysulfone (PSf) polymers have been widely used in preparation of UF membranes. Phase inversion is the most extensively used technique for preparation of asymmetric polymeric membranes with a dense top layer and the porous sub layer. Low molecular weight component or the secondary polymer is frequently used as the additive in control of membrane structure [1]. Many researchers have investigated the effect and performance of different types of additives on membrane performance and morphology. Idris et al. [2] studied the effect of PEG with different molecular weights namely as PEG200, 400 and 600 as additive for poly(ethersulfone) (PES) UF membranes. For this molecular weight of PEG, MWCO is measured to be around 26000, 36000 and 45000 Da respectively. SEM images indicate significant changes in membrane structure by adding PEG in dope solution. Purkait et al. [3] from their study on the effect of molecular weight of PEG additives (400, 6000 and 20000 Da) in the casting solution conclude that this factor has a significant influence on membrane morphology, separation and permeation performance. Preparation of nanofiltration (NF) membranes is developing quickly. Separation of salts and small organic molecules such as dyes invigorate research in this field. MWCO of NF membranes is in the range of

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*Corresponding author.

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200–1000 Da. UV-induced grafting is known to be a useful technique for modification and functionalization of polymeric membranes to attain appropriate performance for different applications such as treatment of textile dye effluents. To achieve this purpose, many researchers have worked on modification of membrane by this technique [4, 7]. By grafting of negative monomers on the membrane surface, charged sites appear on pore wall and edge that participate in separation of charged molecules from feed solution. Under suitable grafting conditions enough polymer chains are grafted on the pores wall to convert the pores of UF membrane to NF-type pores [4].

In previous works, author and coworkers [4, 5] investigated the performance of UV-grafted UF membranes for treatment of textile dye effluents. The essential goal of this research was UV-grafting modification of a set of PSf UF membranes that have the different pore size and structures. The asymmetric structure of primary UF membranes was controlled by using the PEG additive with different M.W. in dope solution. SEM images show changing the UF membrane structure via using various polymeric additives in preparation of membranes. The performance of modified membranes in separation of charged and non-charged organic materials is investigated.

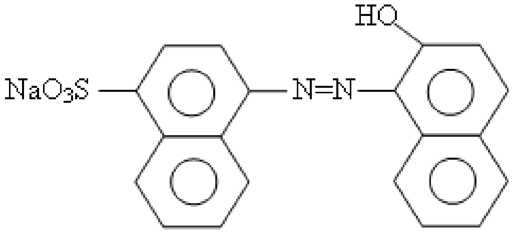
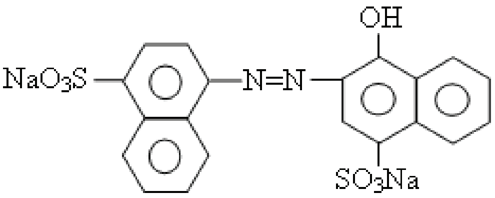
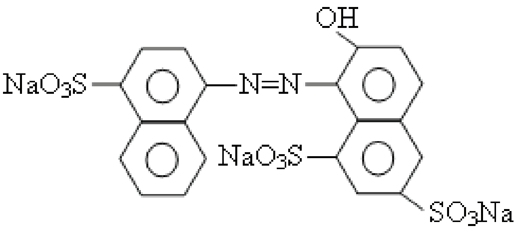
## 2. Materials and methods

PSf (MW: 75000 Da) as membrane material supplied by Acron Organics. NMP was used as solvent for PSf and PEG as additive (and tracer for MWCO determination) purchased from Merck. Dope solution prepared by dissolving PSf in NMP solvent and stirred for several hours. Then additive was subsequently added under continuous stirring and heating at 60°C until the solution became completely homogenous. The composition of the various dope solutions is shown in Table 1. To study the effect of not using PEG on permeation properties, solutions containing 18% PSf and without additive was prepared too. The dope solutions were cast onto a clean glass plate into 300 μm films by means of a gardener knife. They are then immediately immersed into a water bath at 25°C to form membranes. Phase inversion starts and after few minutes a thin polymeric film separates out from glass. AA grafting onto the PSf membranes was performed by irradiation apparatus that consists of a cylinder which the membrane place at the external wall and immersed in AA monomer solution. While cylinder rotates, UV lamp (Philips, UVC, Model TUV8W-G8TS, Netherlands) at the corner of cylinder irradiates to rotating membrane.

Table 1
Composition of casting solutions.

| psf | NMP | PEG (%/type) |
|---|---|---|
| 18 | 82 | -/- |
| 18 | 78 | 4/600 |
| 18 | 78 | 4/6000 |
| 18 | 78 | 4/10000 |
| 18 | 78 | 4/20000 |

Table 2
Characteristics of used dyes [10].

| $\lambda_{max}$ (nm) | M.W. (gr/mol) | Dye (Supplier) |
|---|---|---|
| 505 | 400 | Acid Red 88 (Sandoz)<br> |
| 515 | 502 | Acid Red 14 (BASF)<br> |
| 505 | 604 | Acid Red 18 (BASF)<br> |

For characterization of several membranes, a dead-end filtration cell was used. The filtration apparatus consisted of a 400-ml membrane filtration cell (Amicon Corp., model 8400, USA). The active membrane area was 40.7 cm$^2$. Filtration experiments were carried out at transmembrane pressures of 4 bar and room temperature. RO water was used for pure water permeability experiments. In order to reduce the concentration polarization on the membrane surface during filtration, a stirrer should be used that is contrived in the system. The water permeability (l m$^{-2}$ h$^{-1}$ bar$^{-1}$) is defined as:

$$L_p = \frac{J_W}{\Delta P} \tag{1}$$

where, $J_W$ is the permeate flux (l m$^{-2}$ h$^{-1}$) and $\Delta P$ is the applied pressure (bar). The solute rejection (R) is defined as:

$$R\% = \frac{C_b - C_p}{C_b} \times 100 \qquad (2)$$

$C_b$ and $C_p$ are the concentrations of bulk and permeate solution, respectively [8].

In order to investigate the charge repulsion in dye separation by UV grafted membranes, we used three dyes that without considering their sulfonate groups, have relatively the same structure and M.W. The characteristics of dyes used are presented in Table 2. The dye and salt rejection are calculated by Eq.(2). The concentrations were determined by UV visible spectrophotometry for the dye solution and PEG concentration is determined by an analytical method that is revealed by Misra et al. [9]. The PEG solutions were analyzed using spectrophotometry. In order to confirm the grafting of AA monomer on the surface of PSf membranes, FTIR spectra of the unmodified and modified membranes were obtained using a Nicolet NEXUS670 series II spectrometer (Nicolet Instrument Corp., Madison, WI). Cross sections and surfaces of the solidified membranes were observed by using a SEM (LEO, model 1455, England). Cross section samples were freeze-fractured under cryogenic condition using liquid nitrogen and then all samples were coated with gold before testing.

## 3. Results and discussion

### 3.1. Permeability of unmodified membranes

The unmodified membrane sheets were subjected to experiments at about 4 bar pressure. Presence of PEG with different molecular weights and absence of this additive in dope solution greatly influence the permeability of membrane as shown in Fig. 1. We observe that membrane formed from PSf/NMP solution, without any additive exhibits no flux at 4 bar. It is seen that when molecular weight of PEG increases from 600 to 20000 Da, permeability increases from 59 to 235.9 (l m$^{-2}$ h$^{-1}$ bar$^{-1}$). As it is observed from this figure, the permeability initially increases with a sharp slope (in 0–6000 Da range of molecular weight) and then the rate decreases. The obtained results are the same as the results of Purkait et al. [3]. Addition of PEG with different M.W. influences the formation of pore and pore size of UF membranes which affects the membrane permeability [12]. On the other hand, solubility and removal of additives with high molecular weight such as PEG 20000 in coagulant bath (water) decreases, so a lot of such additives remain in membrane matrix [3, 13]. It is observed that there is decline in the rate of increasing permeability by increasing the PEG M.W. attribute to incomplete exit of PEG with higher M.W.

### 3.2. Cross section SEM images

Decreasing the coagulation rate conducts the demixing mechanism from Spinodal (SD) to Nucleation and Growth (NG) [13] that leads to some changes in morphology such as reduction in the number of finger-like pores, increase in their length (skin layer) and pore size. In Fig. 2, the cross-section images of membrane prepared from PEG additive with molecular weight of 600–20000 Da are shown. From Fig. 2(a) to (d) with increasing molecular weight of PEG, we can observe decreasing number of fingers, increase in their thickness and size of finger-like pores. These phenomena are due to decreases in PEG solubility in water with molecular weight and consequently reduction in coagulation rate, that confirm the transformation from SD to NG mechanism [14]. It is clear that membranes prepared from PEG20000 has a significant increase in pore size and length of finger-like pores related to other membranes but as shown in Fig. 1, permeability of this membrane does not increase greatly that confirms incomplete exit of high M.W. PEG from membrane.

### 3.3. Effect of irradiation time

#### 3.3.1. Effect of irradiation time on permeability

Figure 3 shows the influence of irradiation time (constant AA concentration: 6%) on flux for different membranes. The results show that when UV irradiation time onto membrane surface increases, permeability develops, hence pores become narrower and permeability decreases. As expected, the lowest permeability belongs to membrane prepared from PEG 600 additive. This additive has shorter chains than other additives,

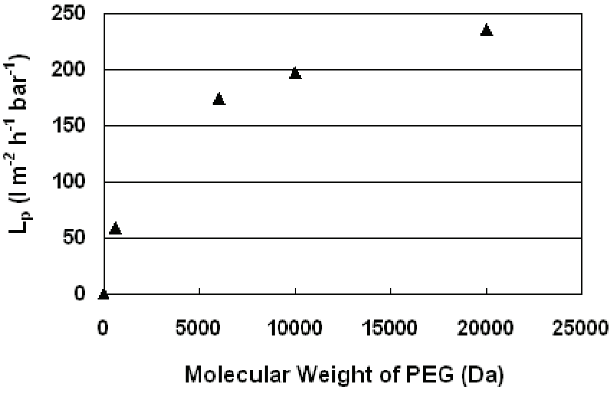


Fig. 1. Changing permeability vs. molecular weight of PEG additive.

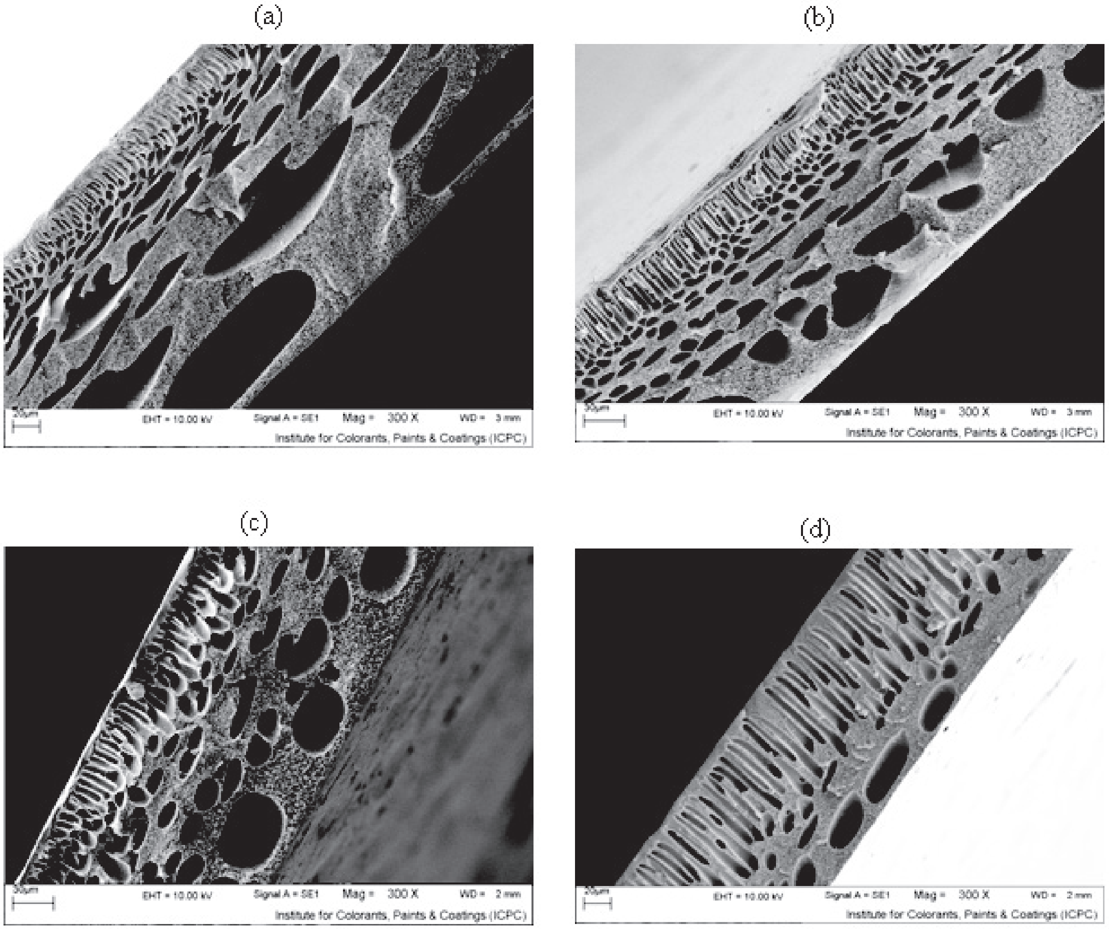


Fig. 2. SEM cross-section of membranes prepared by different molecular weight of PEG: (a) 600, (b) 6000, (c) 10000, (d) 20000 in a casting solution.

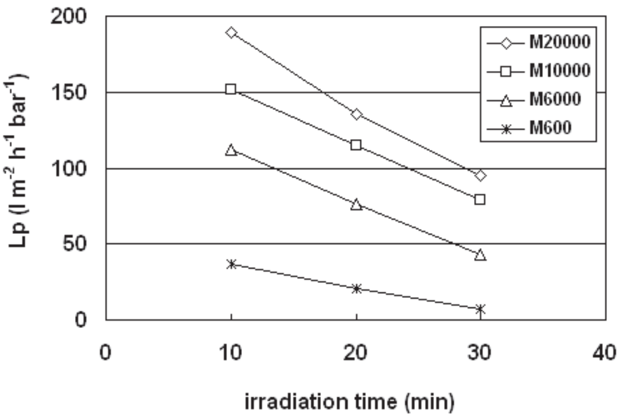


Fig. 3. Effect of irradiation time on permeability of modified membranes ([AA] = 6%).

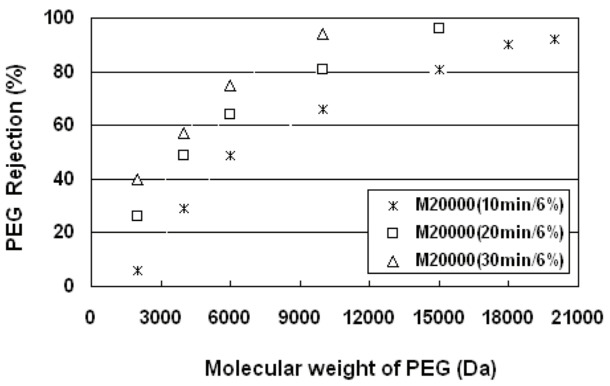


Fig. 4. Effect of irradiation time on rejection of PEG (membrane prepared from PEG 20000).

hence migrates by lower rate and produces smaller and narrower pores. Therefore after grafting smaller pores are produced. It is observed due to narrower pores in membrane prepared from lower M.W. PEG, they are less exposed to UV irradiation, therefore their permeability decreases, with lower rate decreases. The results also indicate that permeability linearly drops with irradiation time. Generally when irradiation time

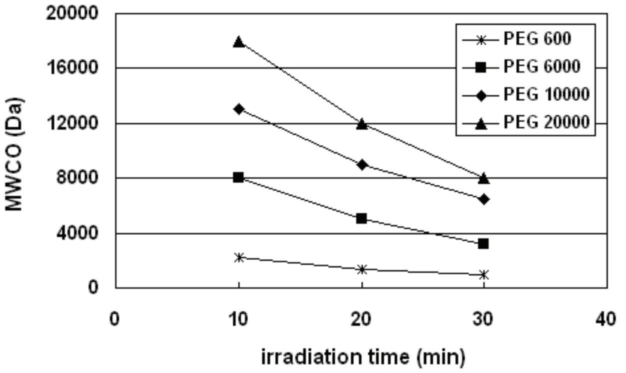


Fig. 5. Effect of irradiation time on MWCO of modified membranes.

increases, grafting and polymerization on pore walls and edges increase.

### 3.3.2. *Effect of irradiation time on MWCO*

Effect of three irradiation time on PEG rejection of membrane prepared from PEG 20000 is illustrated in Fig. 4. By increasing the irradiation time, intensity of polymerization on the membrane surface increases, and therefore PEG rejection by this membrane increases. It is observed that increasing the irradiation time from 10 to 30 min (constant monomer concentration: 6%), MWCO of this membrane obtained 18000, 12000 and 8000 respectively.

Figure 5 illustrates the changes of MWCO by irradiation time. It is clear from this figure that only membranes prepared from PEG 600 as additive can have the MWCO in the range of NF type membranes. The MWCO of membrane prepared from PEG 600 that irradiated in 6% AA concentration for 10, 20 and 30 min is 2200, 1400 and 950 Da, respectively.

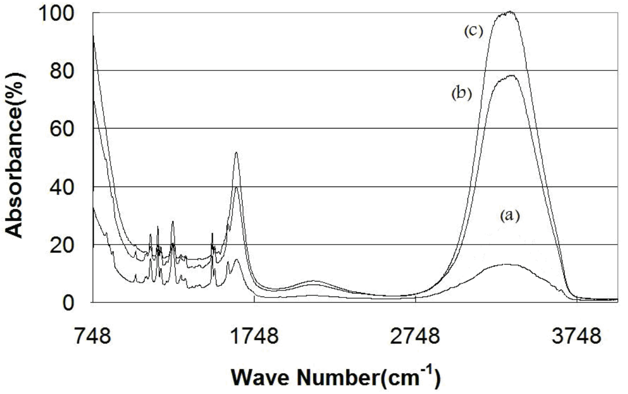


Fig. 7. FTIR spectra of PSf membrane modified with grafted AA for different irradiation time: (a) 0 min; (b) 20 min; (c) 30 min; in [AA] = 6%.

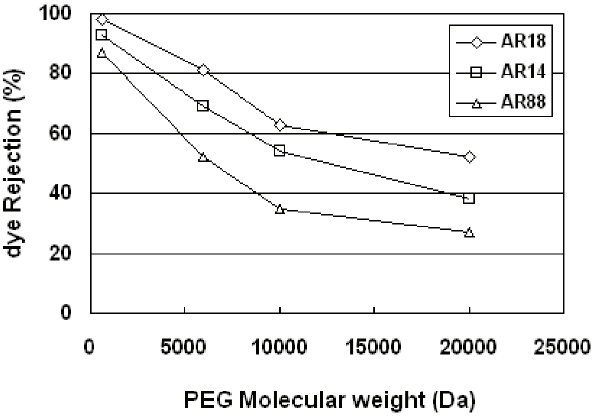


Fig. 6. Separation of dyes by different modified PSf membranes ($t_{irr}$ = 30min, [AA] = 6%).

### 3.4. *Performance of UV-grafted membranes in dye separation*

Separation mechanism in UV grafted membranes is comprised of both sieving (steric-hindrance) and Donnan effect. To study the impress of negatively charged sites in Donnan repulsion of dyes by different pore-size membranes, three dyes were selected with relatively the same structure and various valences. Without considering the sulfonate groups all of the selected dyes have proportionately the same structure. As shown in Fig. 6, Donnan effect in all the grafted membranes causes higher rejection of three valent dyes than one and two valent dyes. Because of smaller pore size in membrane prepared from PEG600 related to other membranes, obviously it is seen that this membrane has good efficiency in separation of selected dyes. Due to stronger sieving mechanism in these membranes, higher dye rejection is obtained. The rejection of AR18, AR14 and AR88 by this membrane is 98.1, 92.6 and 86.8%, respectively. It seems that by amplifying the grafting conditions, we can attain suitable performance in membrane prepared from PEG6000. But other modified membranes are not effective for dye separation and their dye rejection is less than 75% that is not suitable for treatment of colored effluents.

### 3.5. *FTIR-ATR study*

In order to obtain detailed information about the structural changes of PSf membrane resulting from UV graft modification, FTIR spectra of the surface region of virgin membrane and modified ones were recorded (Fig. 7). After photografting with AA, a new peak at 1710 and 3300 cm$^{-1}$ appeared. These peaks are assigned to the characteristic stretching vibrations of the carboxyl (C=O) and hydroxyl (O=H) group in AA and its appearance demonstrated that the grafting AA on PSf membrane was effective under the mentioned experiment conditions. With the increasing in graft reaction time, IR spectra of the membranes grafted with AA exhibited increased absorbance signals at 1720 and 3300 cm$^{-1}$. These observations indicate that grafting AA on PSf membrane performed successfully and will proceed with time.

## 4. Conclusion

Flat sheet PSf ultrafiltration membranes prepared via phase inversion process were modified by using UV photografting polymerization in presence of acrylic acid as vinyl monomer. It is observed that membrane prepared without additive have zero permeability. SEM images of membrane cross section show an asymmetric structure. From these images however it is clear that membrane from PEG 20000 has significantly large pores but permeability experiments are not compatible with SEM images that attribute to incomplete exit of PEG20000 from membrane. In grafting process, with increase of irradiation time, at constant AA concentration of 6%, permeability decreases. This decrease can be attributed to formation of chain polymers in surface and wall of pores. FTIR spectra confirm the grafting of AA monomers onto the membrane surface. Dye separation experiments show that rejection of multivalent dyes are more than monovalent dyes. This behavior mentions that charge repulsion in dye separation has an important role in modified membranes. Modified membrane prepared from PEG600 ($t_{irr}$= 30min and [AA] = 6%) have desirable performance in separation of these dyes (more than 85%) but other membranes prepared from higher M.W. PEG are not effective in separation of dyes. It was observed that this membrane showed acceptable performance both in terms of flux and rejection and has the characteristics of a NF type membrane.

## Nomenclature

| | |
|---|---|
| $\Delta P$ | applied pressure (bar) |
| $\lambda_{max}$ | maximum absorbance wavelength (nm) |
| $C_b$ | bulk concentration (l mol$^{-1}$) |
| $C_p$ | permeate concentration (l mol$^{-1}$) |
| $J_W$ | water permeate flux (l m$^{-2}$ h$^{-1}$) |
| $L_p$ | water permeability (l m$^{-2}$ h$^{-1}$ bar$^{-1}$) |
| MW | molecular weight (Da) |
| $R$ | retention (%) |
| $t_{irr}$ | irradiation time (min) |

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