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Development of nano hybrid polyphenylsulfone (PPSU) ultrafiltration membranes: preparation, characterization and antifouling studies

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Abstract: The present work focuses on fabricating nano TiO_2 incorporated mixed matrix PPSU ultrafiltration membranes. Initially, nano TiO_2 was synthesized and characterized using X-ray diffraction analysis (XRD) and transmission electron microscope (TEM).The different weight % of nano TiO_2 was incorporated into PPSU membranes, all membranes were prepared by using diffusion induced phase inversion method. The prepared membranes were characterized by using X-ray diffraction (XRD), Scanning electron Microscopy (SEM), pure water flux, water content, porosity, and mean pore size. Further, the performance of the prepared membranes was tested against bovine serum albumin (BSA) protein filtration.

Keywords: ultrafiltration, nano TiO_2 , diffusion induced phase inversion, BSA protein

Introduction

Recent years, increasing population, globalization and industrial growth arises the demand of safe and pure water resources . The increasing need for fresh water resources find the suitable water treatment technique. Now days, the emerging membrane separation process overcomes the other traditional separation techniques such as centrifugation, sedimentation, coagulation etc [1].membrane can be defined as a semi permeable solid polymeric material which can regulate and restrict the passage of solute from one side to another side.The membrane can be classified as microfiltration, ultrafiltration, nanofiltration, reverse osmosis etc.Among them, ultrafiltartion membranes have been received greater attention in industries. This is due to their major advantages such as removal of dissolved and dispersed contaminants, low energy consumption, no additive requirements, no phase change and environmental friendly [2]. Recently, various membrane forming polymers have been used such as cellulose acetate, poly(vinylidene fluoride), poly(etherimide) etc [1]. Among these potential membrane materials, the Polyphenylsulfone (PPSU) is one of the best membrane material with salient features such as amorphous nature, high thermal stability, high mechanical strength, good chemical resistance (pH at 1-13) and chlorine tolerance [3]. However, its hydrophobic nature limits its use in aqueous separation processes [4]. This is because of its strong interaction with foulants, which leads to the severe pore plugging. So, it is essential to modify the PPSU membrane surface to suppress the physical interaction with foulants. The membrane fouling can be minimized by making the surfaces to be hydrophilic. There are various modification methods to improve hydrophilicity such as coating, blending, composite, grafting, etc. Among

them, incorporation of nanoparticles is being an effective membrane modification method. Recently, the polymeric composite membranes have been reported with various nanoparticles such as Mg $(OH)_2$, ZnO, Al_2O_3, Carbon nanotube (CNT), Graphene oxide, and Cu, and Ag etc.[5]. Among them, the nano TiO_2 has better characteristics such as thermal stability, mechanical strength, hydrophilic property and photo catalytic activity etc.[6]. In this work, the incorporation of nano TiO_2 enhanced the hydrophilic characteristics of poly phenyl sulfone (PPSU) membranes. The effect of an addition of a different weight % of nanoparticles on membrane morphology was studied. The 0.3% of nano TiO_2 were identified as reliable particle concentration during membrane formation to produce effective membrane with higher flux and rejection for BSA.

Materials and method

Polyphenylsulfone (PPSU, M_w: 53,000-59,000 g/mol) was used as a base polymer for membrane preparation after drying at 80^0C for 12h, Sodium azide ($\geq$ 9.5%), all the chemicals were received from Sigma-Aldrich, India. N-Methyl-2-pyrolidone, extra pure (NMP, from Sisco Research Pvt. Ltd., India), n-Hexane (synthesis),Sodium Laryl Sulphate (pure), (Sisco Research Pvt. Ltd., India). Molecular Sieve $3A^0$ (purified), Ethyl alcohol (AR), 99% v/v min was received from Hayman Speciality products, UK. Pure distilled water was used to prepare the coagulation bath.

Synthesis of nano TiO_2 by solution based method

The nano TiO_2 was synthesized by using previous method [7].In the round bottom flask, 3M concentration of $TiCl_4$ was dissolved in distilled water and kept in the ice bath. Then, $(NH_4)_2SO_4$ was added with above aqueous solution at 70^0C. Here, the constant stirring was provided by using a magnetic stirrer. It was maintained for 1h. Then, the pH of the solution mixture was maintained at 7 by using NH_4OH. The whole reaction mixture was allowed to react for 5h. The resultant nano TiO_2 particles were collected by centrifugation and washed with water thoroughly to remove the excess of chloride.The obtained nano TiO_2 particles were dried in oven at 90°C for 12h.after that, calcined at 300°C for 6h. The resulted nano TiO_2 was characterized by using XRD and TEM.

Preparation of membranes

Initially, different wt. % of (**see table 1**) nano TiO_2 was dispersed in an NMP solvent using ultrasonicator for 20 minutes at 30kHz. Then, 15.5 wt% of PPSU polymer was added into the solution and stirred for 12h. The resulted homogeneous dope solution was left for 2h to remove the air bubbles. Meanwhile, the coagulation bath was prepared using 2L of water with 2.5% of solvent (NMP) and 0.2wt.% of SLS. After deairation step, the dope solution was cast in the polished glass plate, uniformly cast by using a doctor's blade [8]. The membrane thickness was maintained at 0.22mm (±0. 02).

Table 1 Composition of the membranes

Membrane	PPSU (wt. %)	Nano TiO_2 (wt. %)	NMP (Wt. %)
M0	100	--	84.5
M1	100	0.1	84.4
M2	100	0.3	84.2
M3	100	0.5	84

Note: total polymer concentration of 15.5 wt. %

Membrane characterization

Analysis of membrane morphology

The prepared membranes were characterized using Scanning Electron Microscope (SEM, Cam Scan MV 2300). The small piece of membranes was cut and freeze dried in liquid nitrogen for 60-90 S. Before SEM analysis, the nonconducting membranes were gold sputtered to make an electrical conductivity on membrane surface, cross section and surface images were captured under high vacuum (10Kv) condition.

X-ray diffraction (XRD) analysis

The membranes were characterized using Wide angle X-ray diffraction pattern (Bruker AXS D8 Advance X-ray diffractometer). The diffraction patterns were recorded within the range 10°-70° using CuKα radiation (λ=1.54Å).

Pure water flux (PWF)

Before the experiment, all membranes were compacted at 414kPa.Then, the pure water permeation was measured for all prepared membranes for every one hour in the UF cell (Model 8400, Amicon, USA) with an internal diameter of 76 mm at a specific operating pressure (345kPa) at 25°C.The amount of pure water flux (Jw1) was calculated using **Eq.(1).** For each membrane, pure water flux experiment (Jw1) was conducted in three different areas and average values were reported for accuracy.

$$\mathbf{J}_{W_1} = \frac{Q}{A(\Delta t)} \qquad (1)$$

Analysis of porosity and mean pore size (nm) of the membranes

The gravimetric method was used to calculate the porosity (ε, %) of all prepared membranes. This can be defined as the ratio between the amount of water content presence in the pores and total membrane volume. The given **Eq.(2)** was used to determine the porosity of the membranes [9],

$$\varepsilon(\%) = \frac{W_0 - W_1}{\rho A h} \times 100 \qquad (2)$$

Where, W_0 is the wet weight of the membrane; W_1 is the dry weight of the membrane; ρ is the density of water (0.998gcm^{-3}); A is the effective membrane area (m^2); h is the membrane thickness (cm).

Guerout–Elford–Ferry **Eq.(4)** was used to calculate the mean pore size (r_m) of all prepared membranes based on the results of pure water flux (Jw1) and porosity value [10].

$$\mathbf{r}_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\eta h Q}{\varepsilon \times A \times \Delta P}} \qquad (3)$$

Where η is the water viscosity (8.9×10^{-4} Pa s), Q is the quantity of permeate of pure water flux per unit time (m^{3}S^{-1}), ΔP is the operating pressure (345kPa), h is the membrane thickness (m) and ε is the porosity of the membranes.

Analysis of fouling resistant properties of membranes

The antifouling ability of all prepared membranes was checked by using BSA protein filtration. All membranes were operated at constant pressure 345kPa for 3h using dead end ultra filter cell to filter BSA protein molecules (1g in 1000ml of PBS (pH=7)). Here, concentration polarization was minimized effectively by stirring at 450 rpm. The resulting rate of permeation was calculated using following **Eq. (4),**

$$\mathbf{J}_p = \frac{Q}{A(\Delta t)} \qquad (4)$$

Q is the volume of permeate (L), A is the area of membrane (m^2), Δt is the permeate time (h).

At the same time, collected permeate was analyzed using a UV spectrophotometer for BSA protein at a wavelength 280nm. The rejection performance was evaluated by using **Eq.(5).**

$$SR(\%) = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100 \qquad (5)$$

C_p is the concentration of permeate (g/L); C_f is the concentration of feed (g/L).
The fouling resistant properties of the membranes were calculated [11] by using following **Eqs. (6,7, &8)**.

Reversible Fouling

Irreversible Fouling

$$R_r = \frac{J_{w_2} - J_{w_p}}{J_{w_1}} \times 100 \qquad (6)$$

$$R_{ir} = \frac{J_{w_1} - J_{w_2}}{J_{w_1}} \times 100$$

Flux Recovery Ratio $\qquad (7)$

$$FRR(\%) = \frac{J_{w_2}}{J_{w_1}} \times 100 \qquad (8)$$

J_{w_1} is the pure water flux (lm^2h^{-1}): J_{w_2} is the pure water flux after cleaning the membranes (lm^2h^{-1}); J_{w_p} is protein flux (lm^2h^{-1}).
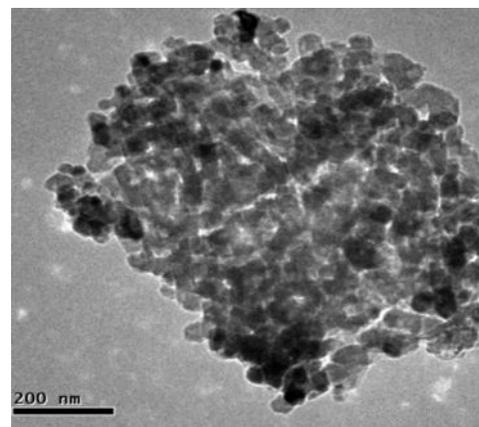
Results and Discussion

Synthesis of nano TiO_2

The XRD pattern of nano TiO_2 is shown in **Fig.1**.All the peaks were indexed by using JCPDS (21-1272). The peaks at 25.3, 37.8, 48.1 and 54.6 represents the corresponding planes such as (101),(004),(200) and (211) [12].So, the formation of pure anatase phase of nano TiO_2 is confirmed.Further, the TEM image of aggregated nano TiO_2 particles is shown in **Fig.2**.
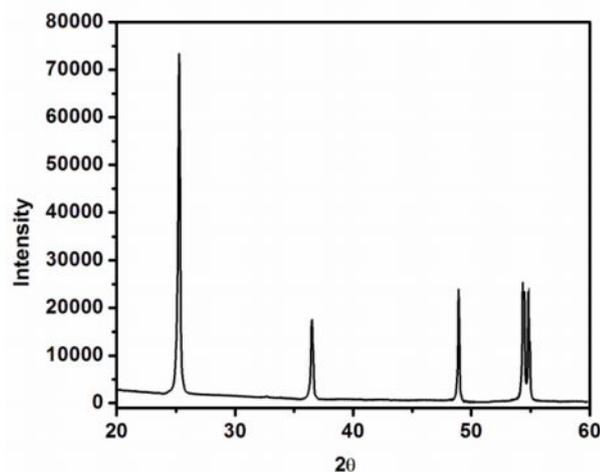
**Fig.1 XRD pattern of nano TiO_2**   **Fig.2 TEM image of nano TiO_2**

Morphological analysis

Fig.3 shows the cross sectional SEM images of pure and modified PPSU membranes. The effect of incorporating different concentration of nano TiO_2 was observed in modified PPSU nanocomposite membranes. The incorporation nanoparticles concentration, such as 0.1% and 0.3wt% produced good improvement in the membrane pore growth. This was seen in the SEM images such as M1 and M2, respectively. But, 0,5wt.% of nano TiO_2 produced a negative impact on the membrane structure (shown in SEM image M3). This can be explained due to the following facts that the hydrophilic nature of the TiO_2 nanoparticles interacts strongly with water molecules. So, the nonsolvent (water)-solvent exchanges take place longer time during phase inversion technique. The longer nonsolvent (water)-solvent exchange results the more finger like pore growth in the sub layer structure of the membrane. Meanwhile, the skin layer thickness of the membranes decreases by incorporating nano TiO_2.However increases higher concentration of nano TiO_2 makes a negative impact on the

membrane structure. This is due to the strong interaction of nanoparticles-solvent interaction that leads to the dense polymeric chains at the interface. The more dense skin layer forms with lower porous structure.
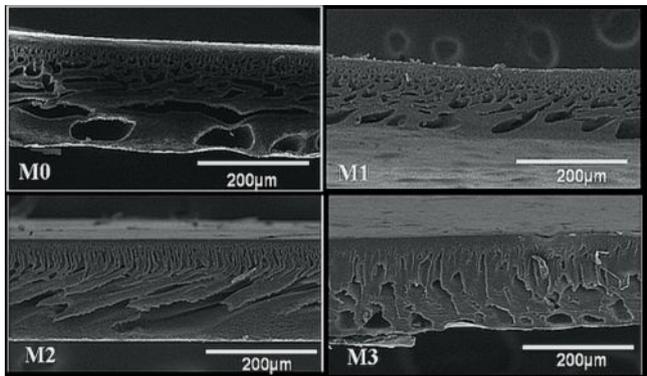
Fig.3 cross sectional morphological images of membranes

XRD analysis

      Fig.3 displays the XRD pattern of the pure and nanomodified PPSU membranes. The pure PPSU membrane (a) shows the highest diffraction peak at 19.7°. The modified PPSU membrane (b) shows the corresponding peak of nano TiO_2 small peak at 25.3°. This result confirms the distribution of nano TiO_2 in PPSU membrane matrix.
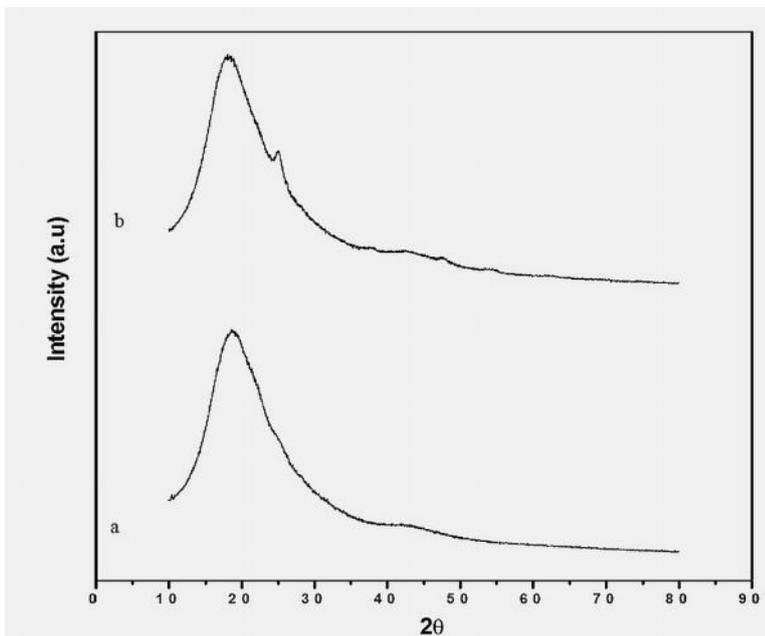
Fig.3 XRD pattern of membranes a-pure PPSU and b- 0.3% of TiO$_2$

Water content, pore size and porosity (%) analysis

      Table 2 represents the results of the water content, porosity, mean pore of the pure and modified membranes. The pure PPSU membrane shows the lower water content of 56%. Incorporation of nano TiO_2 increases the water content up to 76 % for membrane M3.This can be due to the presence of hydrophilic TiO_2 nanoparticles into the membrane matrix.The porosity and pore size values increased by incorporating nano TiO_2 up to 0.3%. The 0.5% of nano TiO_2 decrease the porosity and pore size value significantly. This is due to the higher nanoparticles concentration that blocks the pore during membrane formation. Further, increasing the membrane dope solution viscosity also reduces the number of pore growth significantly and results the lower porosity value (**see table 2**).

Table 2 water content, Porosity, water content, mean pore size, of the membranes

Membrane	Porosity (%)	Water content (%)	Mean pore Size (µm)
M0	40.06	56	0.029
M1	46.3	72	0.025
M2	51.92	74	0.024
M3	49.46	76	0.021

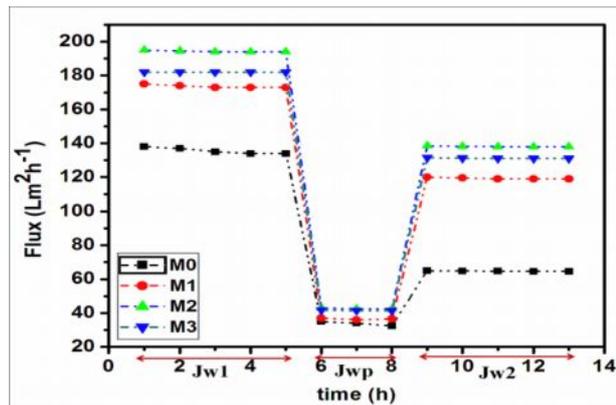**Permeation and rejection analysis**

Fig.4 permeation of pure and modified PPSU membranes

Fig.4 and Table 3 represents the permeation profile of profiles of all membranes against pure water and BSA protein. In the case of pure water permeation, all the membranes show higher water flux initially, then decreases to attain stable flux with increases of time. The modified PPSU membranes (M2-M3) show the higher permeation rate than pure PPSU membrane (M0).The same type of permeation profile was obtained against BSA protein. Among them the membrane M2 showed higher BSA protein permeation. But, protein flux was lower than pure water flux. This is due to the high viscosity macromolecular protein solution. Further, the BSA rejection analysis shows that modified membrane M2 shows reliable rejection of 93.7% than pure membrane. The same type of observation was noticed in the previous literature [13].

Table 3 Permeation properties, BSA rejection and fouling analysis

Membrane	Flux (Lm^{-2}h^{-1})			R_r (%)	R_{ir} (%)	FRR (%)	Rejection (%) BSA
	Jw1	Jp	Jw2				
M0	134	32.4	64.6	24.1	51.7	48.2	88.6
M1	173	36.5	119	47.6	31.2	68.7	93.5
M2	194	42.3	138	49.3	28.8	71.1	93.7
M3	182	41.5	131	49.1	28.2	71.9	94.8

Jw1-pure water flux; Jwp- protein flux; Jw2-pure water flux (after cleaning); R_r-reversible fouling; R_{ir}-irreversible fouling; FRR-flux recovery ratio.

Fouling resistance analysis of membranes

After the protein permeation experiment, the membranes were cleaned with water. Once again, the membranes were subjected to pure water flux (**see Table 3**). The modified membranes M2 showed a better permeation profile than other modified membranes due to reliable membrane formulation. The membrane was further analyzed their reusability in terms of flux recover ration (FRR) and pore plugging effect in terms of reversible fouling (R_r) and irreversible fouling (R_{ir}). The modified membrane M2 shows higher flux recovery ratio of 71.1% and reversible fouling (R_r) of 49.3% and irreversible fouling (R_{ir}) of 28.8%.These results indicated that lower pore plugging (or) weak interaction with BSA protein [14]. Finally, the membrane M2 was identified as better fouling resistance membrane than among the modified membranes. Further, from the comparison of the results with other nanocomposite membranes, It can be concluded that our PPSU/TiO$_2$

ultrafiltration membrane had comparable protein rejection performance along with higher FRR(%) than that of previously reported nanocomposite membranes [15-20]: PSf/CaCO$_3$, PES/ZrO$_2$, PES/AgZ, PES/SiO$_2$,PVDF/Al$_2$O$_3$ and PES/Ag.This is because of the formation of more hydroxyl content (-OH) on the membrane surface due to hydrolysis of TiO$_2$ particles. Moreover, this causes the stable hydration film to avoid the severe fouant interactions with membrane surfaces [21].

Conclusion

The nano TiO$_2$ incorporated PPSU composite membranes were successfully prepared by using the phase inversion technique. The effect of a different weight % of nano TiO$_2$ was studied. The nano composite membranes showed better performance than pure PPSU membranes. The 0.3wt.% of nano TiO$_2$ incorporated PPSU nanocomposite membrane showed better fouling resistance properties and reusability than other modified and pure PPSU membranes. So, these membranes can be used effectively in water treatment application. In future, these photocatalytic composite membranes will be studied in the removal of oil/emulsion.

References

1. Liu Y., Yue X., Zhang S., Ren J., Yang L., Wang Q., et al., Synthesis of sulfonated polyphenylsulfone as candidates for antifouling ultrafiltration membrane, Separation and purification technology, 2012, 98, 298–307.
2. Yong L., Wahab A., Peng C., Hilal N., Polymeric membranes incorporated with metal / metal oxide nanoparticles : A comprehensive review, Desalination, 2013, 308, 15–33.
3. Hwang L.L, Tseng H.H., Chen J.C., Fabrication of polyphenylsulfone/polyetherimide blend membranes for ultrafiltration applications: The effects of blending ratio on membrane properties and humic acid removal performance, Journal of Membrane Science, 2011, 384, 72–81.
4. Peeva P.D., Pieper T., Ulbricht M., Tuning the ultrafiltration properties of anti-fouling thin-layer hydrogel polyethersulfone composite membranes by suited crosslinker monomers and photo-grafting conditions, Journal of Membrane Science, 2010, 362, 560–568.
5. Gohari R.J., Halakoo E., Nazri N.A.M., Lau W.J., Matsuura T., Ismail A.F., Improving performance and antifouling capability of PES UF membranes via blending with highly hydrophilic hydrous manganese dioxide nanoparticles, Desalination, 2014, 335, 87–95.
6. Moghimifar V., Raisi A., Aroujalian A., Surface modification of polyethersulfone ultra filtration membranes by corona plasma-assisted coating TiO$_2$ nanoparticles, Journal of Membrane Science, 2014, 461, 69–80.
7. Rajesh S., Ismail F., Mohan D.R., Structure-property interplay of poly (amide-imide) and TiO$_2$ nanoparticles, RSC Advances, 2012, 6854–6870.
8. Rajesh S., Maheswari P., Senthilkumar S., Jayalakshmi A., Mohan D., Preparation and characterisation of poly (amide-imide) incorporated cellulose acetate membranes for polymer enhanced ultrafiltration of metal ions, Chemical Engineering Journal, 2011, 171, 33–44.
9. Kumar R., Ismail A.F., Kassim M.A., Isloor A.M., Modi fi cation of PSf / PIAM membrane for improved desalination applications using Chitosan coagulation media, Desalination, 2013, 317, 108–115.
10. Yu L.-Y., Xu Z.-L., Shen H.-M., Yang H., Preparation and characterization of PVDF–SiO$_2$ composite hollow fiber UF membrane by sol–gel method, Journal Membrane Science, 2009, 337, 257–265.
11. Fan X., Su Y., Zhao X., Li Y., Zhang R., Zhao J., et al., Fabrication of polyvinyl chloride ultrafiltration membranes with stable antifouling property by exploring the pore formation and surface modification capabilities of polyvinyl formal, Journal Membrane Science, 2014, 464, 100–109.
12. Dai S., Wu Y., Sakai T., Du Z., Sakai H., Abe M., Preparation of Highly Crystalline TiO 2 Nanostructures by Acid-assisted Hydrothermal Treatment of Hexagonal- structured Nanocrystalline Titania / Cetyltrimethyammonium Bromide Nanoskeleton,Nanoscale Research Letter, 2010, 1829–1835.
13. Saleh T.A., Gupta V.K., Synthesis and characterization of alumina nano-particles polyamide membrane with enhanced flux rejection performance, separation and purification technology, 2012, 89, 245–251.
14. Fan X., Su Y., Zhao X., Li Y., Zhang R., Fabrication of polyvinyl chloride ultra fi ltration membranes with stable antifouling property by exploring the pore formation and surface modi fi cation capabilities of polyvinyl formal, Journal Membrane Science, 464, 100–109.

15. Nair A.K., Isloor A.M., Kumar R., Ismail A. F., Antifouling and performance enhancement of polysulfone ultrafiltration membranes using CaCO3 nanoparticles, Deasalination, 2013, 322, 69–75.
16. Pang R., Li X., Li J., Lu Z., Sun X., Wang L., Preparation and characterization of ZrO2/PES hybrid ultrafiltration membrane with uniform ZrO2 nanoparticles, Deasalination, 2014, 332.
17. Huang J., Arthanareeswaran G., Zhang K., Effect of silver loaded sodium zirconium phosphate (nanoAgZ) nanoparticles incorporation on PES membrane performance, Deasalination, 2012, 285, 100–107.
18. Huang J., Zhang K., Wang K., Xie Z., Ladewig B., Wang H., Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties, Journal Membrane Science, 2012, 423-424, 362–370.
19. Liu F., Abed M.R.M., Li K., Preparation and characterization of poly(vinylidene fluoride) (PVDF) based ultrafiltration membranes using nano γ-Al2O3, Journal Membrane Science, 2011, 366, 97–103.
20. Zhang X., Shi B., Liu X., Preparation of polysulfone ultrafiltration membranes modified by silver particles, Desalination and Water Treatment, 2013, 51, 3762–3767.
21. Vatanpour V., Madaeni S.S., Khataee A.R., Salehi E., Zinadini S., Monfared H.A., TiO_2 embedded mixed matrix PES nanocomposite membranes: Influence of different sizes and types of nanoparticles on antifouling and performance, Desalination, 2012, 292, 19–29.

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