Research Article

Low-Pressure Membrane for Water Treatment Applications

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Three ultrafiltration membranes were prepared using phase separation techniques. The membranes were characterized by scan electron microscope, porosity, pore size distribution measurement, and mechanical properties. The membrane performance was carried out using synthetic solutions from humic acid and tap water to express the contaminated drinking water. The polyvinylidene difluoride (M2) has the highest tensile strength 33.2 MPa with elongation of 52.3%, while polyacrylonitrile (M3) has the lowest mechanical properties, tensile strength 16.4 MPa with elongation of 42.7%. Polyethersulfone membrane (M1) provides the highest removal of humic acid, which was 99.5, 98.8, and 98.2% using feed concentrations 0.1, 0.3, and 0.5 g/l, respectively, while M3 provides the highest permeate flux which was 250, 234.4, and 201.4 l/m^2 h using feed concentrations 0.1, 0.3, and 0.5 g/l, respectively. Analysis of water samples indicates that the prepared membranes can be used to treat the contaminated drinking water which produced the high quality of drinking water after treatment.

1. Introduction

Fresh water is a vital resource for human life and ecosystem. The earth is covered with 72% water, while 97% of this water is not suitable for drinking because it is salty water [1–3].

Also, the population growth causes an increasing in demand on the quantity and quality of drinking water. Although there is groundwater and rivers in many places, they are affected by different levels of pollution. The modern industries and urbanization contribute to many of such pollution [1, 2].

During the last few decades, the membrane technology is selected over other technologies for desalination and wastewater purification. This attributed to its high efficiency, saving energy, high capacity, low cost, and eases in operation for the production of clean water [4, 5].

The most common membranes used for wastewater treatment are the polymeric membranes. Flexibility, mechan-

ical properties (such as elastic strength), and chemical and thermal stability in addition to the high selectivity of perm are factors making polymeric materials the first choice in the membrane industry for water purification [6–10].

The most common membrane process for wastewater treatment is a pressure-driven processes [11, 12]. Figure 1 illustrates the classification of pressure-driven membrane processes. Polymeric membrane can be classified according to its pore size and filtration process. According to this, membranes are classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). For MF, the pore size ranges from 1 to 0.1 μm. It is applied for the separation of colloids, macromolecules, bacteria, and other particulates. UF membranes have a pore size in the range of 0.1-0.01 μm to separate out viruses/macromolecules and solutes of high molecular weights as retentate, allowing water or low molecular weight solutes to pass through the pores. Nanofiltration (NF) membranes have a
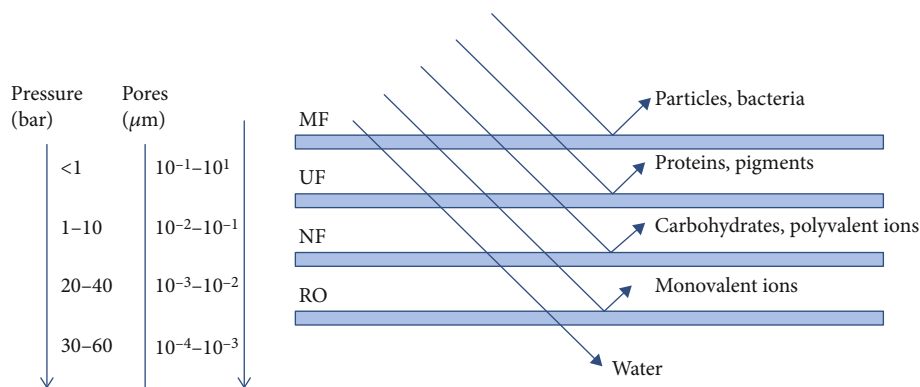
FIGURE 1: Classification of pressure-driven membrane processes.

dense surface of membrane to remove divalent ions and trivalent ions with a pore size range of 0.1-0.001 μm, while monovalent ions are separated using reverse osmosis membranes [11–15].

The ultrafiltration separation technology has received increased attention for water purification and can be used in food, medical, biotechnology, papermaking, and dairy industry [11]. The most common of ultrafiltration polymeric membrane materials, including polyvinylidene fluoride (PVDF), polyethylene (PE), polysulfone (PSF), polyethersulfone (PES), and polypropylene (PP), have been commonly chosen as the backbone materials of membrane [11–14].

Major problems of membrane are fouling, which lead to decline in the permeation flux, removal percentage, and reduction in membrane life during filtration operation. According to the membrane processes, the fouling can be categorized into inorganic fouling, colloidal fouling, organic fouling, and biofouling [5, 6]. Thus, fabrication of antifouling membranes is a common strategy to overcome this problem because the fouling causes membrane pore clogging. Hence, antifouling membranes can help to reduce the demand for energy. These membranes are characterized according to the hydrophilicity, surface smoothness, and its biocidal properties which avoid the accumulation of foulants on membrane surface [7–9].

In this work, three ultrafiltration membranes were prepared by phase inversion technique. The prepared membranes were characterized using scan electron microscope, mechanical testing, porosity, and pore size determination. Membrane performance was tested using synthetic solutions of drinking water contaminated with humic acid to be as a contaminated drinking water by sewage wastewater.

2. Experimental Work

2.1. Materials. Polyethersulfone (PES) was purchased from BASF (Germany). Polyvinylidene difluoride (PVDF) and polyacrylonitrile (PAN) were purchased from the Sigma-Aldrich Company. N-Methyl pyrrolidone (NMP) was used as a solvent, polyvinylpyrrolidone K 90 (PVP K90) was used as a pore former, and they were purchased from Roth (India).

2.2. Membrane Preparation. PES/PVP blending membranes were prepared using the phase inversion technique. Figure 2 illustrates a summary for the steps of this technique.

Both of PES and PVP K90 were dissolved in N-methyl pyrrolidone (NMP). The mixture was stirred under 45°C for 10 h. The PVDF/PVP membrane was also prepared using the phase inversion process, and the mixing process (using magnetic stirrer) was carried out for 8 h. The PAN/PVP blending membrane was also prepared by phase inversion, and the mixing was carried for 6 h. The percentage of polymeric blend compositions was depicted in Table 1. The wet casted membrane thickness of 200 μm on the glass plate was immersed in water coagulation bath. After membrane formation, the prepared membranes were stored in distilled water until use.

2.3. Membrane Characterization

2.3.1. Scanning Electron Microscopy. To investigate the prepared blend membrane morphology, scanning electron microscopy (JEOL 5410) was used after coating the sample surface with gold. The examination of the sample was carried out under 20 kV and magnification of 6000x.

2.3.2. Mechanical Properties. H5KS TINIUS OLSEN mechanical system was used to investigate the tensile strength for the prepared samples. The samples were tested at room temperature (25°C) in uniaxial tension at the rate of 0.5 mm/min.

2.3.3. Porosity Measurements. Densometers represent one of the accepted standard methods for measuring the porosity and air permeability of membrane. The Gurley Standard Densometer was used to investigate our samples with an area of about 25 cm^2.

The porosity was determined by knowing the weight of the wet sample and of the same sample after drying to reach its stable value. The following equation was used to calculate porosity

$$\varepsilon = \frac{M_{\mathrm{w}} - M_{\mathrm{d}}}{A\,L\,\rho}, \tag{1}$$

where A represents the effective area (cm^2), L is the thickness (cm), and ρ the density of pure water(g cm^{-3}). To
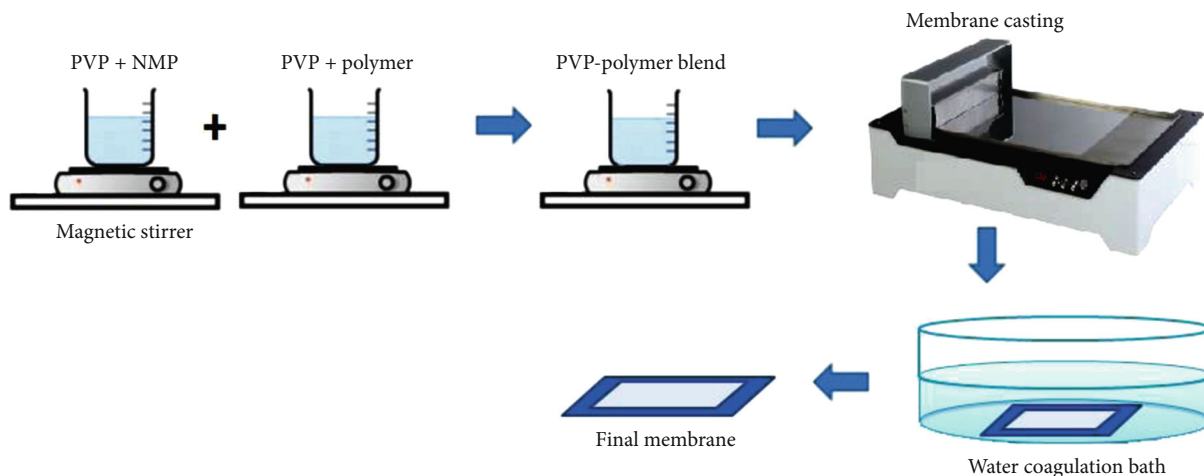
FIGURE 2: Preparation steps for PVP blend membrane.

ensure a minimum error, the calculations were repeated more than five times, and the average value was recorded.

2.3.4. Pore Size Distribution Measurement. The prepared blend membranes pore size distribution was determined using the Brunauer-Emmett-Teller (BET) method by the BET apparatus of the model (ChemBET-3000, Quanta-chrome). A long strip of samples with known weights was placed in the BET apparatus (glass column), and it was dried and degassed for 3 h at 80°C. The average area was determined by using a BET single point [13, 16].

2.3.5. Membrane Performance. A laboratory-scale dead-end cell consists of feeding tank, dead-end membrane cell, and peristaltic pump as shown in Figure 3. The effective area of the membrane under test was 13.86 cm^2.

As a simulation for the contaminated water, a synthetic solution of a humic acid with different concentrations (0.1, 0.3, and 0.5 g/l) mixed with salty water (500 ppm) was used to investigate the membrane performance.

The permeate flux and separation percentage for all membranes were calculated from equations (2) and (3) [16]:

$$J(W) = \frac{Q}{\Delta t \times A}, \tag{2}$$

where Q is the permeate volume (l), A is the effective membrane area (m^2), and Δt is the permeation time (h).

$$S = \left(1 - \frac{O_p}{O_f}\right) \times 100 \tag{3}$$

where O_p and O_f are the concentrations of the solute in permeate and feed, respectively.

3. Results and Discussion

3.1. Membranes Preparation and Characterization

3.1.1. Scanning Electron Microscopy. Three different polymer blend membranes were successfully fabricated through the

TABLE 1: Polymeric solution composition for PVP-polymer blends membranes.

Membrane symbol	Composition (weight percentage)		
	Polymer %	PVP K90%	NMP %
M1 (PES)	17	4	79
M2 (PVDF)	16	4	80
M3 (PAN)	18	4	78

wet phase inversion method. Figure 4 illustrates the surface morphology for the prepared samples. It is clear from the figure that the three samples exhibit a porous with different sizes at the membrane's top surface. The addition of PVP, as a pore former, makes a good pore distribution on the membrane surface that causes increasing in macrovoids in membranes and reduces the dense membrane at the top layer [17]. M2 represents PVDF membrane where the surface of the membrane displays the smallest pore size compared with PES and PAN, because the molecular weight of PVDF is the highest one, which was 390,000 g/mol, where PES was 62000 g/mol and PAN 53000 g/mol. M3 represents the PAN membrane which has a highly homogenous porous surface [18, 19].

3.1.2. Mechanical Properties. Figure 5 demonstrates a comparison between the tensile strength and elongation % for the three polymers blends M1, M2, and M3. The curve indicates that membrane M2 has the most highest tensile strength (33.2 MPa) with an elongation of 52.3%, while M3 has the lowest mechanical properties. It has a tensile strength of about 16.4 MPa with an elongation of 42.7%, while the M1 membrane has a tensile strength of about 24.4 MPa with an elongation of 44.75%. So the tensile strength for the prepared sample can be ordered as M2>M1>M3.

Although the polyacrylonitrile (PAN) membrane (M3) has the highest level of porosity compared to other membranes, it must be wet during testing as well as upon application. This is due to the formation of microcracks on its surface when the membrane is dried, and this in turn reduces
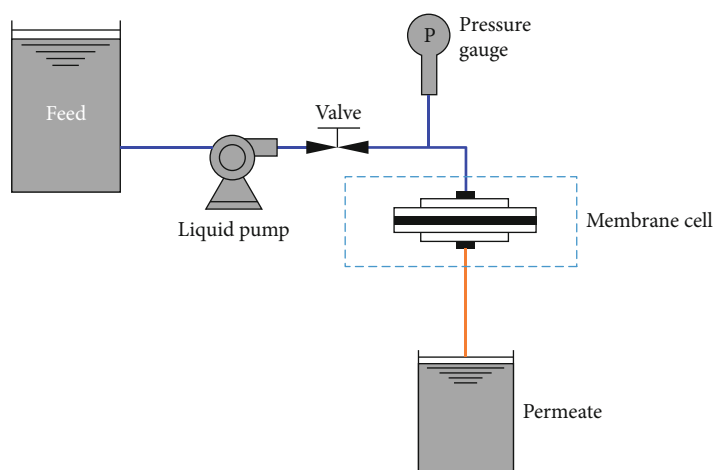
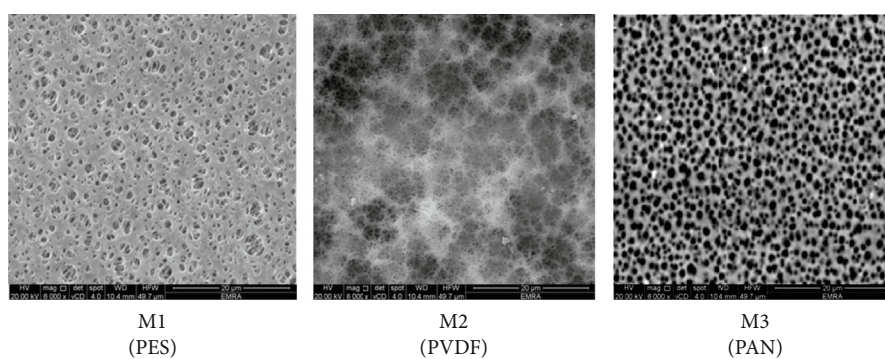FIGURE 3: Schematic of membrane testing experimental laboratory setup.

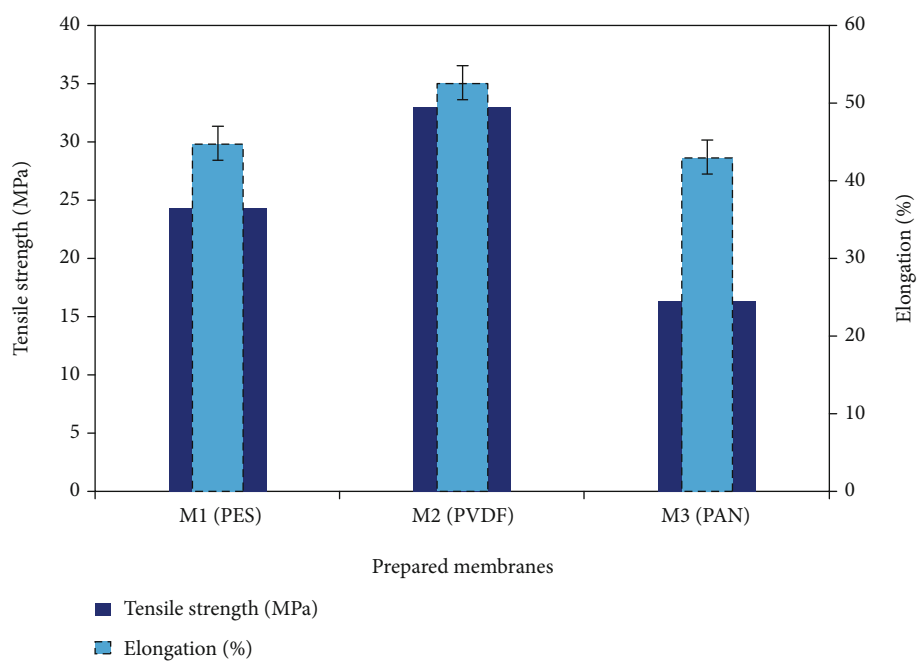FIGURE 4: SEM photos for prepared membranes.

FIGURE 5: Mechanical properties of prepared membranes.

its mechanical properties especially its tensile strength. This can interpret the reason of its low tensile strength. Polyvinylidene difluoride (PVDF) membrane (M2) represents one of the common membranes which has a high mechanical strength and thermal and chemical stability with high hydrophobic nature. The polymer chains in PVDF are in the polar zigzag confirmation that has a high dipolar moment and can exhibit interesting electroactive that leads to high mechanic properties of prepared membrane [16]. Polyethersulfone (PES) membrane has high hydrolytic strength over a large range of pH (from 2 to 12) and also has high thermal and chemical stability. Its mechanical properties represent the intermediate between PVDF and wet PAN membranes as shown in Figure 5.

3.1.3. Porosity Measurements and Pore Size Distribution.
Table 2 illustrates the overall porosity percentage and average pore size of the prepared membranes. The results indicated that polyacrylonitrile (PAN) membrane (M3) has the highest porosity of 75.3%, while polyethersulfone (PES) membrane (M1) has a porosity of 66.8% and polyvinylidene difluoride (PVDF) membrane (M2) has a porosity of 65.1% [19, 20]. The mean pore size indicates that the prepared membranes are in the range of ultrafiltration membranes, where the pore size of prepared membranes (18.2 to 33.6 nm) matched with the range of the ultrafiltration membranes pore size from 2 nm to 100 nm [13, 16].

3.2. Membrane Performance Test.
Humic acid solutions of 0.1, 0.3, and 0.5 g/l were mixed with tap water that was used for the membrane performance test. Figures 6 and 7 show the performance of prepared membranes in terms of humic acid removal percentage and permeate flux, respectively. Figure 6 indicates that PES membrane (M1) provides the highest removal of humic acid, which are 99.5, 98.8, and 98.2% for feed concentrations 0.1, 0.3, and 0.5 g/l, respectively. The lowest removal percentage was 97.6, 95.7, and 93.4% for PAN membrane (M3) for feed concentrations 0.1, 0.3, and 0.5 g/l, respectively. However, the PAN membrane (M3) provides the highest permeate fluxes which are 250, 234.4, and 201.4 l/m^2 h for feed concentrations 0.1, 0.3, and 0.5 g/l, respectively, as shown in Figure 7, while M1 and M2 permeate fluxes are comparable to each other. Polyethersulfone polymer has two groups, the ether group and sulfone chain, so the membrane surface has a hydrophobic/hydrophilic nature. Accordingly, using PVP improves the hydrophilic nature of PES membrane surface, and this will lead to the improvement of the permeate flux and removal percentage for the membrane. The PVDF membrane has a high hydrophobic nature, so using PVP provides a slight improvement in the hydrophilic nature of the surface; therefore, PES (M1) will provide less fouling as compared with PVDF (M2) due to the polymorphs of PVDF which can cause various interaction between PVDF surface and the feeding solution leading to surface fouling. PAN (M3) provides the lowest removal and high permeate flux due to high porosity of the membrane as shown in Table 2. Also, PAN is a high-hydrophilic membrane, but the membrane is brittle and the aggregation of it can occur after drying which can oppose

TABLE 2: Porosity and average pore size distribution for prepared membranes.

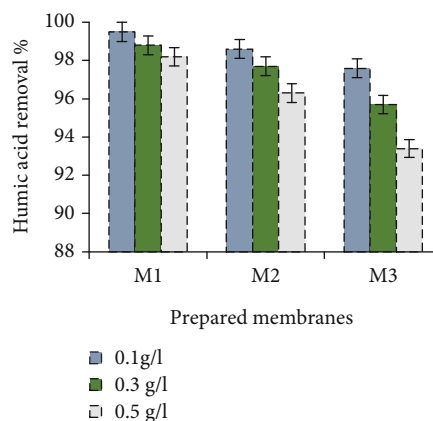| Membrane type	BET area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)	Porosity (%)
M1	8.23	12.5×10^{-3}	22.3	66.8
M2	2.22	5.1×10^{-3}	18.2	65.1
M3	9.42	15.2×10^{-3}	33.6	75.3

FIGURE 6: Removal percentage of humic acid using prepared membranes.
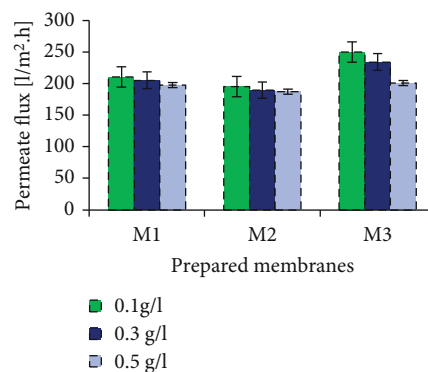

FIGURE 7: Permeate flux using prepared membranes.

its application [17, 20–22]. Dang et al. studied the performance of ultrafiltration polyethersulfone membranes after the addition of hydrophilic modifier during membrane preparation; the experiments were carried out for long term using polyethylene glycol 600 and ethylene oxide as a feeding solution. The results indicated a high hydraulic resistance for PES, which is inversely proportional to the flux, so after 50 h, the flux declined. Applying continuous stages from feeding and washing indicated that the flux reduced at the first 6 h and reached to the steady state after 80 h; the decline in flux is related to the mean pore diameter and the pore structure. Dang et al. also studied the PES-LSMM membrane flux using real river water feeding where the results indicated that flux has not been

TABLE 3: Analysis of produced water after treatment by membrane.

Parameter	Unit	Tap water with humic acid	M1 (PES)	M2 (PVDF)	M3 (PAN)	Limits of WHO [22]
Chloride	mg/L	45	45	45	45	200
Sulphate	mg/L	39	35	35	38	200
Total hardness	mg/L	148	140	140	144	200-500
Potassium	mg/L	6.5	6.5	6.5	6.5	10
Sodium	mg/L	51	51	51	51	200
Magnesium	mg/L	8.5	8.5	8.5	8.5	30
Calcium	mg/L	45	45	38	45	75
Turbidity	NTU	33	<1	<1	<1	<1
pH		7.5	7.5	7.5	7.5	7.5-8.5
EC	μs/cm	500	500	489	500	1500
TDS	mg/L	278	278	244	278	1000
COD	mg O_2/L	36	3.5	2.5	3.6	10
BOD	mg/L	16	1.2	1.01	1.41	<3

declined significantly; it was held rather steady during the Ottawa River water filtration test [23].

Narbaitz et al. studied the modification of cellulose acetate membrane by incorporating charged surface to increase their surface charge. The results indicated that increasing the operating pressure led to increase in permeate flux. However, commercial thin film composite composed of polysulfone or polyether sulfone support provided higher fluxes than the modified CA membrane [24].

Total tap water analysis was performed to indicate the effect of membranes in the drinking water treatment or purification. Table 3 indicates all prepared membranes provide good separation of turbidity, COD, and BOD, while there was no separation for di- or trivalent ions, because ultrafiltration membranes separate only organics, high molecular weight substances, bacteria, and viruses, but divalent and trivalent ions need nanofiltration membrane. The high turbidity, COD, and BOD in tap water are related to the addition of humic acid in the water samples to simulate the contaminated water by sewage water. Prepared membranes exhibit good separation especially PVDF membrane for COD and BOD. This can be attributed to the fact that it has the lowest porosity and pore size compared with other membranes [22].

4. Conclusions

Ultrafiltration membranes were prepared using phase separation techniques. The polyvinylidene difluoride (M2) has the highest tensile strength of 33.2 MPa with elongation of 52.3%, while polyacrylonitrile (M3) has the lowest mechanical properties, tensile strength of 16.4 MPa with elongation of 42.7%.

The membranes mean pore size indicates that the prepared membranes are in the range of ultrafiltration membranes, where the pore size of prepared membranes (18.2 to 33.6 nm) matched with the range of the ultrafiltration membranes pore size from 2 nm to 100 nm.

Polyethersulfone membrane (M1) provides the highest removal of humic acid, which was 99.5, 98.8, and 98.2% using

feed concentrations 0.1, 0.3, and 0.5 g/l, respectively, while M3 provides the highest permeate flux which was 250, 234.4, and 201.4 l/m^{2}h using feed concentrations 0.1, 0.3 and 0.5 g/l, respectively.

Analysis of water samples indicates that the prepared membranes can be used to treat the contaminated drinking water which produced the high quality of drinking water after treatment, where the turbidity, COD, and BOD after treatment by membranes reached the World Health Organization standard for drinking water.

Data Availability

Data are available with the corresponding author under request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

References

[1] B. Nicolaisen, "Developments in membrane technology for water treatment," Desalination, vol. 153, no. 1-3, pp. 355–360, 2003.

[2] M. M. Pendergast and E. M. Hoek, "A review of water treatment membrane nanotechnologies," Energy & Environmental Science, vol. 4, no. 6, pp. 1946–1971, 2011.

[3] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Marinas, and A. M. Mayes, "Science and technology for water purification in the coming decades," in Nanoscience and Technology, pp. 337–346, 2010.

[4] V. Kochkodan, D. J. Johnson, and N. Hilal, "Polymeric membranes: surface modification for minimizing (bio) colloidal fouling," *Advances in Colloid and Interface Science*, vol. 206, pp. 116–140, 2014.

[5] V. Kochkodan and N. Hilal, "A comprehensive review on surface modified polymer membranes for biofouling mitigation," *Desalination*, vol. 356, pp. 187–207, 2015.

[6] M. Rezakazemi, A. Dashti, H. Riasat Harami, N. Hajilari, and Inamuddin, "Fouling-resistant membranes for water reuse," *Environmental Chemistry Letters*, vol. 16, no. 3, pp. 715–763, 2018.

[7] C. A. C. van de Lisdonk, J. A. M. van Paassen, and J. Schippers, "Monitoring scaling in nanofiltration and reverse osmosis membrane systems," *Desalination*, vol. 132, no. 1-3, pp. 101–108, 2000.

[8] S. Lee, J. Kim, and C.-H. Lee, "Analysis of CaSO4 scale formation mechanism in various nanofiltration modules," *Journal of Membrane Science*, vol. 163, no. 1, pp. 63–74, 1999.

[9] C.-J. Lin, S. Shirazi, and P. S. Shakya, "Closure to "Mechanistic model for CaSO$_4$ fouling on nanofiltration membrane" by Che-Jen Lin, Saqib Shirazi, and Pritesh Rao," *Journal of Environmental Engineering*, vol. 133, no. 9, pp. 942-943, 2007.

[10] L. Song and G. Singh, "Influence of various monovalent cations and calcium ion on the colloidal fouling potential," *Journal of Colloid and Interface Science*, vol. 289, no. 2, pp. 479–487, 2005.

[11] M. Ulbricht, "Advanced functional polymer membranes," *Polymer*, vol. 47, no. 7, pp. 2217–2262, 2006.

[12] Y. Yampolskii, "Polymeric gas separation membranes," *Macromolecules*, vol. 45, no. 8, pp. 3298–3311, 2012.

[13] E. S. Mansor, H. Abdallah, and A. Shaban, "Fabrication of high selectivity blend membranes based on poly vinyl alcohol for crystal violet dye removal," *Journal of Environmental Chemical Engineering*, vol. 8, no. 3, article 103706, 2020.

[14] M.-Y. Zhou, P. Zhang, L.-F. Fang et al., "A positively charged tight UF membrane and its properties for removing trace metal cations via electrostatic repulsion mechanism," *Journal of Hazardous Materials*, vol. 373, pp. 168–175, 2019.

[15] C.-C. Sun, M.-Y. Zhou, J.-J. Yuan et al., "Regulating the aggregation of anionic nanoparticles for size-tunable nanochannels," *Journal of Membrane Science*, vol. 604, article 118076, 2020.

[16] H. Abdallah, R. Taman, D. Elgayar, and H. Farag, "Antibacterial blend polyvinylidene fluoride/polyethyleneimine membranes for salty oil emulsion separation," *European Polymer Journal*, vol. 108, pp. 542–553, 2018.

[17] Y. Huang, D. Wu, X. Wang, W. Huang, D. Lawless, and X. Feng, "Removal of heavy metals from water using polyvinylamine by polymer-enhanced ultrafiltration and flocculation," *Separation and Purification Technology*, vol. 158, pp. 124–136, 2016.

[18] M. Sarbolouki, "A general diagram for estimating pore size of ultrafiltration and reverse osmosis membranes," *Separation Science and Technology*, vol. 17, no. 2, pp. 381–386, 2006.

[19] B. Chakrabarty, A. K. Ghoshal, and M. K. Purkait, "Effect of molecular weight of PEG on membrane morphology and transport properties," *Journal of Membrane Science*, vol. 309, no. 1-2, pp. 209–221, 2008.

[20] M. Barakat and E. Schmidt, "Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater," *Desalination*, vol. 256, no. 1-3, pp. 90–93, 2010.

[21] H. Abdallah, T. S. Jamil, A. Shaban, E. S. Mansor, and E. R. Souaya, "Influence of the polyacrylonitrile proportion on the fabricated UF blend membranes' performance for humic acid removal," *Journal of Polymer Engineering*, vol. 38, no. 2, pp. 129–136, 2018.

[22] WE Federation, APH Association, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association (APHA), Washington, DC, USA, 2005.

[23] H. T. Dang, R. M. Narbaitz, T. Matsuura, and K. C. Khulbe, "A comparison of commercial and experimental ultrafiltration membranes via surface property analysis and fouling tests," *Water Quality Research Journal*, vol. 41, pp. 84–93, 2006.

[24] R. M. Narbaitz, D. Rana, H. T. Dang et al., "Pharmaceutical and personal care products removal from drinking water by modified cellulose acetate membrane: field testing," *Chemical Engineering Journal*, vol. 225, pp. 848–856, 2013.