Int. J. Nanosci. Nanotechnol., Vol. 9, No. 4, Dec. 2013, pp. 213-220

Chitosan/Polyethersulfone Composite Nanofiltration Membrane for Industrial Wastewater Treatment

A. Ghaee[1*], M. Shariaty-Niassar[2], J. Barzin[3], A. F. Ismail[4]

1- Department of Biomedical Engineering, Faculty of New Sciences and Technologies, University of Tehran, Tehran, I. R. Iran
2- Department of Chemical Engineering, College of Engineering, University of Tehran, Tehran, I. R. Iran
3- Department of Biomaterials, Iran Polymer and Petrochemical Institute, Tehran, I. R. Iran
4- Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

(*) Corresponding author: ghaee@ut.ac.ir

(Received:15 Sep. 2013 and Accepted: 08 Oct. 2013)

Abstract:

Chitosan/polyethersulfone (CS/PES) composite membrane was prepared from casting chitosan solution on polyethersulfone substrate membrane. The Substrate membrane was prepared by phase inversion technique using polyethersulfone (PES) and dimethylacetamide (DMAc) as solvent with and without the addition of polyvinylpyrrolidone (PVP) as pore-forming agent. The effects of the composition of the casting solution on membrane morphology and water permeation were investigated. The membrane prepared from 15 wt % PES with 2.25 wt % PVP demonstrated better water permeability compared to other compositions. CS/PES composite membrane flux and retention were 5.2 lit/m^{2}hr and 76.15%, respectively. The mean pore size of the composite membrane was calculated as 0.99 nm.

Keywords: *Chitosan; Composite membrane; Molecular weight cut off; Nanofiltration; Thermal analysis.*

1. INTRODUCTION

The membrane process between UF (Ultrafiltration) and RO (Reverse Osmosis) is called nanofiltration (NF) and has just developed over the past decades. Their rejection for sodium chloride floats between 20 and 80% and their molecular weight cut-offs for dissolved organic solutes from 200 up to 2000 Da [1-2].

For water treatment with chitosan, a composite nanofiltration membrane with a microporous substrate providing the mechanical strength and a selective layer coating of a different material is an appropriate solution. Chitosan, the deacetylated derivative of chitin, is the second most abundant polysaccharide found on earth next to cellulose. As a natural renewable resource, chitosan has a number of unique properties such as antimicrobial activity, non-toxicity and biodegradability [3, 4].

The amino (–NH2) and/or hydroxy (–OH) groups on chitosan chains serve as coordination sites and this is the reason why chitosan is known as a suitable sorbent for heavy metal ions. Additionally, its mentionable film forming characteristics are worthy [5]. As chitosan membranes prepared by evaporation and immersion-precipitation were dense and had low solidity respectively, they were not suitable for continuous processes [6-7]. Here, evaporation method can be useful, but low water flux is not negligible [8].

Miao *et al.* [9] has prepared a novel amphoteric composite NF membrane by casting the aqueous solution of sulfated chitosan onto a poly (acrylonitrile) (PAN) UF membrane, and then crosslinked with glutaraldehyde. Musale and Kumar [10] prepared chitosan/PAN composite NF membranes and investigated the effects of surface crosslinking of different glutaraldehyde concentrations and crosslinking times on their surface chemical composition and sieving properties. In order to introduce an effective separation layer in membranes with hollow fiber, Tsai *et al*. [11] prepared chitosan/cellulose acetate composite hollow-fiber membranes by dip-coating method. Shen and coworkers [12] also reported their work on the preparation of chitosan/polysulfone composite hollow-fiber membranes.

For dehydrating ethanol-water mixtures and isopropanol mixtures and removing ethylene glycol from aqueous systems, Chitosan /polysulfone composite membrane have been carried out [13-15]. Chitosan/polyethersulfone composite membrane was also studied for alcohol-water mixtures [16]. Wu *et. al.* prepared a hydrophilic Chitosan/Sulfonated Polyethersulfone–Polyethersulfone membrane for pervaporation [17].

To the best of our knowledge, polyethersulfone based composite membranes for the removal of metal ion in wastewater treatment were rarely studied in the open literature. Here, preparing polyethersulfone based composite membranes (due to good film-forming properties) for metal ion removal and the effects of polymer and pore-forming polymer concentration in dope on substrate membrane morphology and performance are investigated. In addition, the pure water permeability, molecular weight cut-off, rejection behavior and characteristics of CS/PES composite NF membranes are discussed.

2. MATERIALS AND METHODS

2.1. Materials

Polyethersulfone (PES) (Ultrason E6020, MW= 58,000, flakes) and poly vinyl pyrrolidone (PVP) (K90) were supplied by BASF Co. and Fluka Co., respectively. Dimethylacetamide (DMAc) (Merck) was used as the solvent. Chitosan (CS) with medium molecular weight was purchased from Chitotech. All other chemicals (glutaraldehyde, acetic acid, sodium hydroxide, cupric sulfate and poly ethylene glycol) were of analytical grade used without further purification.

2.2. Membrane preparation

The substrate PES membranes were prepared by dissolving various amounts of PES (i.e. 15, 18 and 20% w/w) with and without PVP dissolved (0, 2.25%) in DMAc solvent. After aeration, the PES solution was poured onto a flat surface. A proper membrane thickness was formed by using a 200 µm slot applicator. Immediately after the solution was poured (without solvent evaporation), the process of coagulation was carried out in distilled water.

The CS/PES composite membrane was prepared as follows. The CS solution (0.5 % (w/w)) in aqueous acetic acid (10% (w/w)) was filtered. The substrate PES membrane prepared from the dope of 15% w/w PES and 2.25% w/w PVP was then immersed in the CS solution for 3 minutes, and dried at 25ºC. The cross-linking was carried out by immersing the dry membrane into a 0.25% (w/w) glutaraldehyde aqueous solution, at 25ºC for 30 min, followed by washing with distilled water to remove the unreacted glutaraldehyde residues. At the final stage the membrane was dried with filter paper.

2.3- Membrane performance

All permeation measurements for sublayers and composite membrane including pure water permeation were carried out using a flow through cell (effective membrane area 20×10^{-4} m^2) at 25°C and pressure of 506.5 kPa.

For composite membrane**,** the permeation performance was investigated by determining the fluxes and rejections for the $CuSO_4$ solution with a concentration of either 50 or 100 mg L^{-1} and at an operating pressure of 506.5 kPa. Flux (*F*) and rejection (*R*) were determined as follows. *F* was calculated by Eq. (1) [18]:

$$F = \frac{V}{A \times t} \tag{1}$$

Where, F (L m^{-2} h^{-1}) is the flux, A (m^2) is the effective area of the membrane; t (h) and V (L) are the time and the volume of permeate through the membrane, respectively. R was calculated by Eq. (2) [18]:

$$R\ (\%) = \left(1 - \frac{C_P}{C_F}\right) \times 100 \tag{2}$$

Where C_p (mg L^{-1}) and C_F (mg L^{-1}) are the concentrations of the permeate and the feed, respectively. All reported data are the mean values of three replicates.

2.4. Molecular weight cut-off (MWCO)

Molecular weight cut-off of the composite membrane was determined using the rejection data for polyethylene glycols (PEG) of different molecular weights (MW 200–1500 Da). The feed PEG concentration was 1000 mg/L. The concentrations of polyethylene glycol in feed and permeate were measured with Shimadzu 5000 Total Organic Carbon (TOC) analyzer.

2.5. Characterization

2.5.1. Scanning electron microscopy

For SEM observation, membranes were fractured in liquid nitrogen before their cross- sections covering with a thin layer of gold using a sputter coater (SCDOOS – Baltec, Switzerland). The cross-sections were then observed by a scanning electron microscope (SEM), (XL30-Philips-Netherlands).

2.5.2. Thermal analysis

Thermogravimetric analysis (TGA) is used to measure the weight of a polymeric sample as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere [19]. The CS/PES Composite membrane was analyzed with TGA/PL thermogravimetric analyzer (Polymer laboratories, United Kingdom) under a nitrogen atmosphere. The heating rate was 10 ˚C min^{-1}, from 30 to 600˚C.

DSC is a technique in which the heat flow rate difference into a substance and a reference is measured as a function of temperature, while the sample is subjected to a controlled temperature program [19]. The composite membrane was analyzed by DSC using a Netzsch DSC 200/F3 Maia with the rate of 10˚C min^{-1}, ranging from 25-350˚C under nitrogen atmosphere.

2.5.3. Atomic absorption experiments

The concentrations of metal ions were measured using a flame atomic absorption spectrophotometer (Varian AA 240). All reported copper concentrations are the mean values of three replicates.

3. RESULTS AND DISCUSSION

3.1. SEM analysis

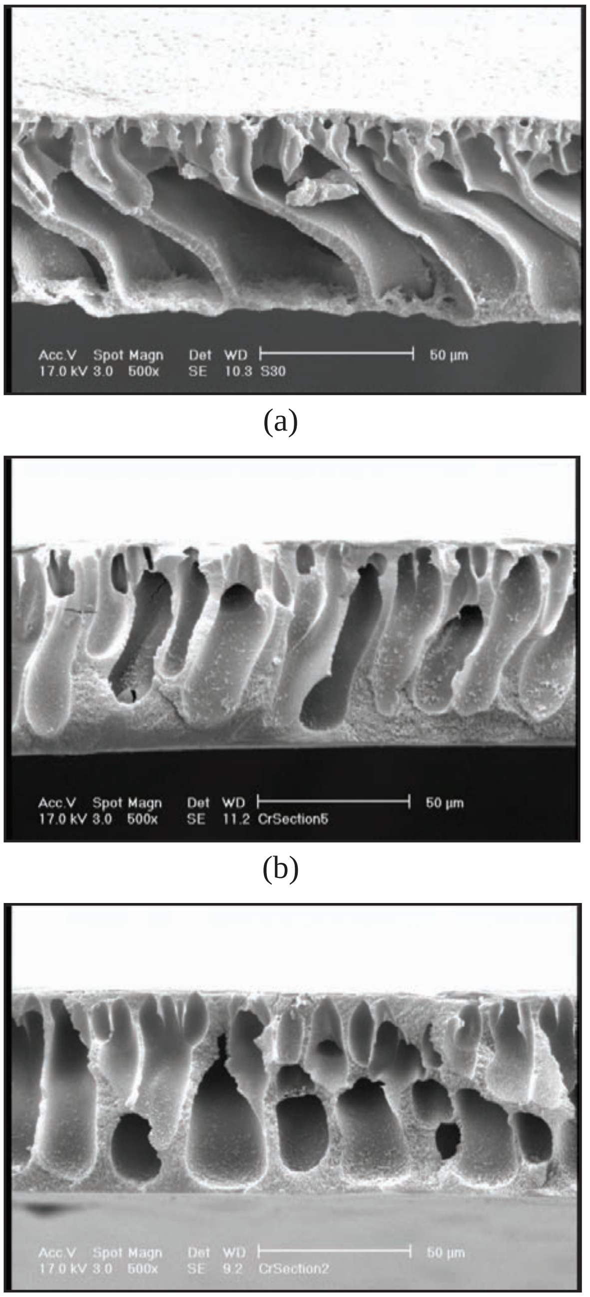
Figures 1 and 2 show SEM images of PES membranes with different PES concentrations with and without PVP. All the membranes have asymmetric morphology. In Figure 1, there was no PVP in the solutions. By increasing PES concentration, phase inversion occurred more slowly and membrane pores became smaller. The membrane with 15 wt% PES (Figure 1 (a)) had a channel-like structure with large pores. The membranes obtained from 18 and 20 wt% (Figs 1(b) and (c)), had finger-like and tear-like structures with smaller pores compared to membrane with 15 wt% PES and more sponge-like sections. Similar results were observed by Barth *et al*. [20] and Barzin *et al*. [18] for polysulfone and poly(ethersulfone) flat-sheet membranes.

The morphology of membranes with PVP is shown in Figures 2. PVP is a hydrophilic polymer used as a pore-forming agent in membrane dope and also affects the rate of solvent-nonsolvent exchange. The results indicate that by adding PVP to the casting solution, the size and number of pores increased compared to the one without PVP.

Appropriate support layer for composite membrane should have:

1. Sponge-like top layer for pressure endure with a little surface pores to graft chitosan to sublayer and prevent pore penetration.
2. Large voids to improve permeation flux.

The membrane with PES 15 wt% - PVP 2.25 wt% concentration had both properties.

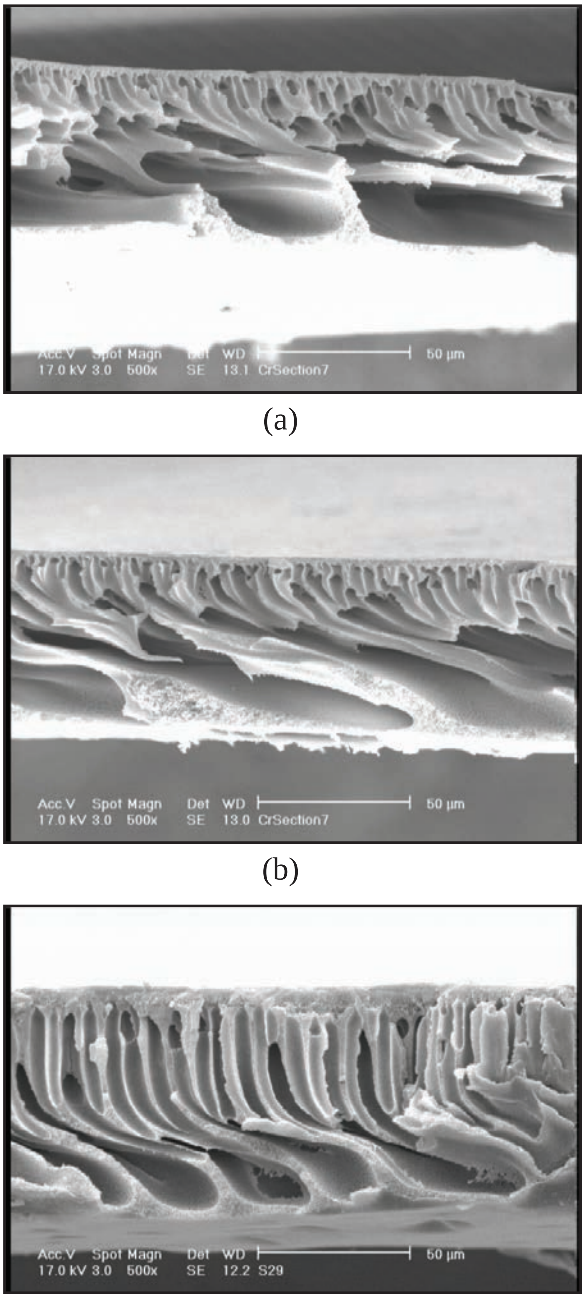


(a)

(b)

(c)

Figure 1: *PES sublayer with (a) 15 % (b) 18% (c) 20% PES and 0% PVP*



(a)

(b)

(c)

Figure 2: *PES sublayer with (a) 15 % (b) 18% (c) 20% PES and 2.25% PVP*

3.2. Membrane performance

3.2.1. Substrate membrane

The membrane performances for different PES concentrations are reported in Table1. Table 1 shows that the water flux is lower for higher PES concentrations. It could be anticipated by observing SEM images that membrane with PES 15 wt% has channel-like structure with more and larger pores but the size and number of tear-like voids in membranes of 20 wt % PES decreases and sponge-like structure spreads (compare Figs. 1(b) and (c)).

Table 1: *Substrate membrane water permeability*

PES concentration (wt %)	PVP concentration (wt %)	Water Flux (Lm^2h^{-1})
15	0	435.8
18	0	375.0
20	0	293.4
15	2.25	843.2
18	2.25	719.1
20	2.25	654.7

By increasing the PVP concentration to 2.25 wt%, the water flux tremendously increased. This would be a result of larger pores in these membranes. The SEM images confirm these observations.

3.2.2. CS/PES composite membrane

The Substrate membrane with 15% PES and 2.25% PVP was chosen as the support layer of the composite membrane. The reason is that this membrane has a sponge-like layer at the top and so sufficient mechanical stability and also its large pores result in higher water flux.

The membrane performance is reported in table 2. The substrate layer retention is about 12.4% and for composite membrane with 100 ppm initial concentration this value is 76.59%. The water flux in composite layer decreased sharply due to the chitosan layer at the top.

Table 2: *Composite and substrate membrane performance*

	Initial copper concentration (mg L^{-1})	50	100
Substrate layer	Water permeability (Lm^2h^{-1})	-	843.2
	Retention (%)	-	12.40
Composite membrane	Water permeability (Lm^2h^{-1})	5.2	5.2
	Retention (%)	76.15	76.58

3.3. Thermal analysis

The DSC curves for chitosan, PES membrane and CS/PES composite membrane are shown in figure 3. A broad endothermic peak between ambient temperature and 100ºC is seen in all curves due to water evaporation from membrane structures. Sharp exothermic peak at 268ºC is observed in chitosan membrane DSC thermogram, due to decomposition of chitosan. The endothermic peak at 100ºC indicates water existence in the

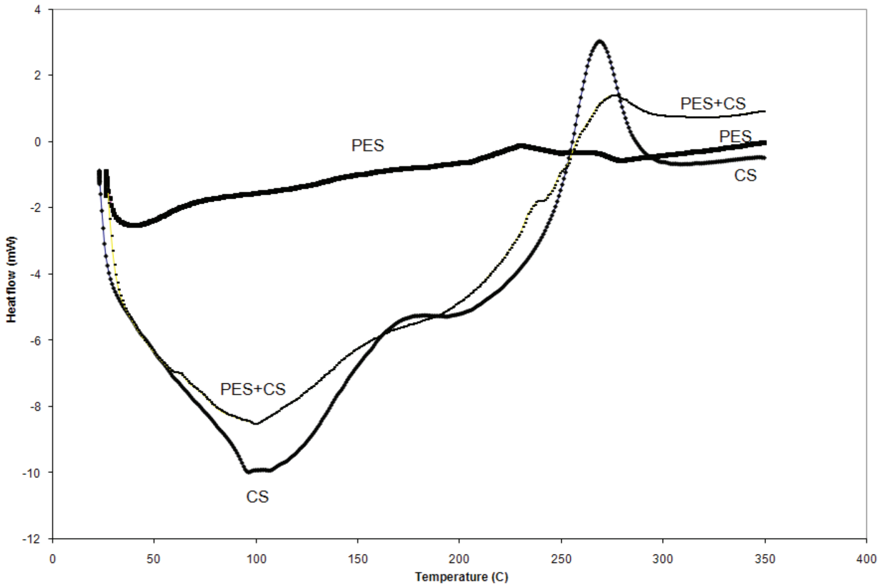


Figure 3: *DSC curves of PES, CS and CS/PES membranes*

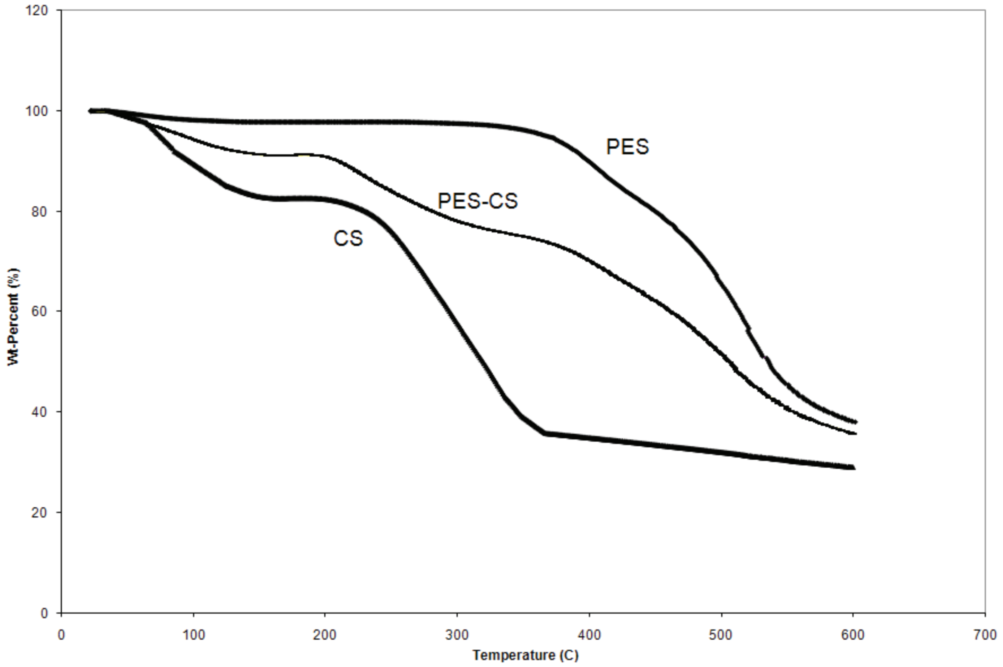


Figure 4: *Thermogravimetric analysis of PES, CS and CS/PES membranes*

film [21-22]. Polyethersulfone DSC thermogram showed characteristic glass transition (Tg) at nearly 228.96ºC [23-24]. The DSC thermogram of composite membrane is also shown in figure 3. Peak at 234.1ºC is due to PES glass transition. Peak at 272.28ºC is due to chitosan degradation. So, DSC analysis confirms the existence of chitosan layer on PES sublayer.

In TGA curve of chitosan (Figure 4), the first weight loss of 11.7%, due to water vaporization, occurred above 100 ºC. The second loss corresponding to chitosan decomposition began at 181.8ºC [25]. Polyethersulfone TGA curve shows about 6% water loss and Polyethersulfone decomposition started at 371.4ºC. In composite membrane water loss was about 8.5% and membrane degradation started at 192.62 ºC due to chitosan presence. Also, membrane degradation continued more sharply at 358.8 ºC due to PES existence. These graphs confirm chitosan layer existence in the composite membrane.

3.4. MWCO of the CS/PES composite NF membrane

To determine MWCO, a set of reference solutes in the molecular weight range of 200–1500 Da (PEGs 200, 400, 600, 1000 and 1500 Da) were chosen and the separation experiments were conducted at a concentration of 1000 mg/L. The MWCO is defined as the molecular weight of organic solute with retention of 90%. The curve about the rejection versus molecular-weight is shown in Figure 5. The MWCO of this membrane was determined by interpolation to be approximately 1045.5 Da, which is in NF range.

3.5- Mean pore size and pore size distribution

Solute diameter was obtained by equation (3) from the molecular weight of PEG.

$$a = 16.73 \times 10^{-10} \times M^{0557} \qquad (3)$$

Where a (cm) is solute diameter and M is the PEG molecular weight (Da). When the solute separation is plotted versus the solute diameter on a log-normal probability paper, a straight line is yielded as reported by [26]. From this log-normal plot (Figure 6), mean solute size can be calculated as solute diameter corresponding to retention of 50%. Mean pore size of composite membrane is 0.99 nm in the range of nanofiltration membranes.

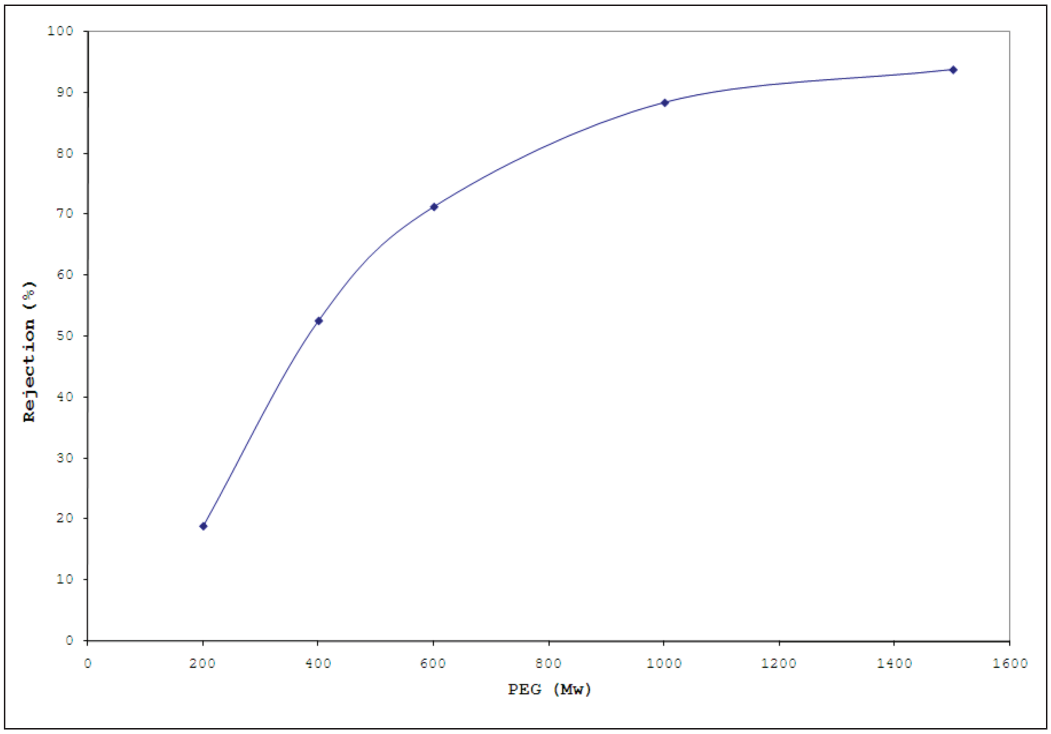


Figure 5: *Rejection vs PEG molecular weight for composite membrane*

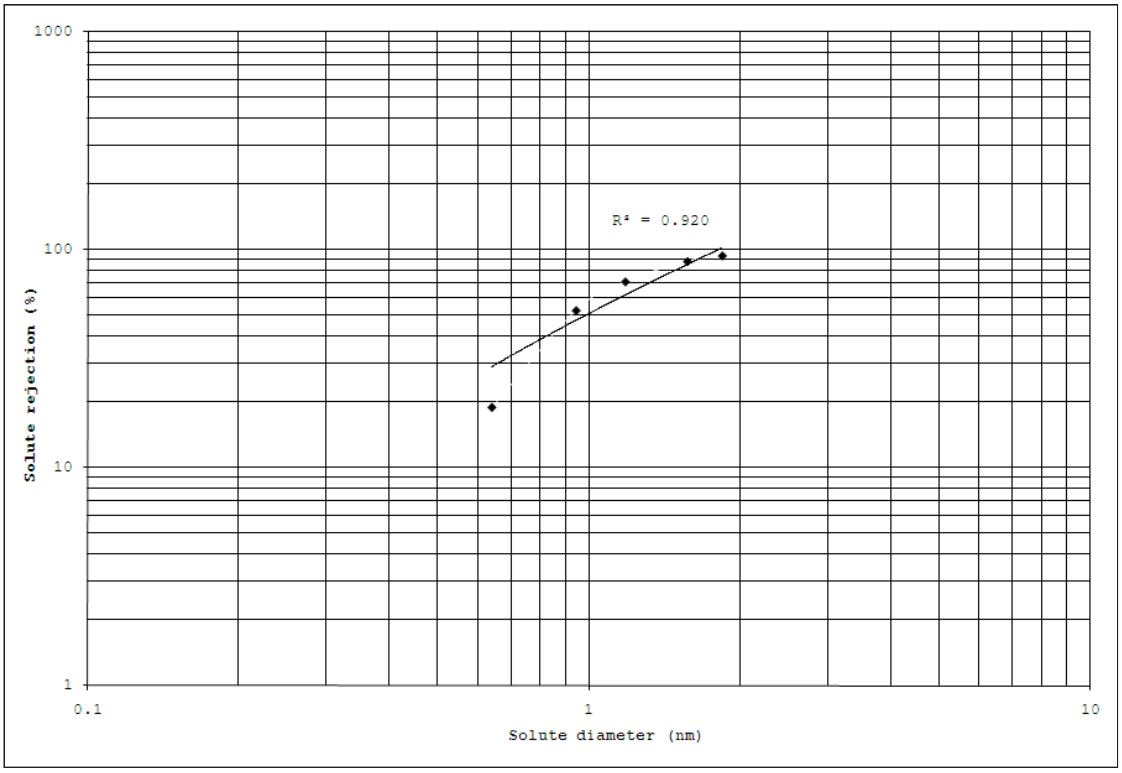


Figure 6: *Rejection vs PEG solute diameter plotted on log-normal basis for composite membrane*

4. CONCLUSIONS

By increasing PES concentration, the size and number of pores decreased and the sponge-like area spread which affect the water permeation through the membrane. By adding 2.25 wt% PVP to dope, pores became larger and water flux increased. Substrate membrane with 15% PES and 2.25% PVP had appropriate morphology and water flux and was chosen for composite membrane. CS/PES composite membrane had 76.58% retention of copper ions. The MWCO of the resultant membrane was 1048.5 Da (in the NF range) and mean pore size was about 0.99. These results indicated that the Chitosan/polyethersulfone (CS/PES) composite membrane is a very promising membrane materials used for the removal of metal ion from industrial wastewater.

REFERENCES

1. X. L. Wang, C. Zhang and P. Ouyang: J. Membr. Sci. Vol. 204, (2002), pp. 271–281.
2. R. Huang, G. Chen, M. Sun and C. Gao: Desalination. Vol. 239, (2009), pp. 38-45.
3. Y. C. Chang and D.H. Chen: J. Colloid Interface Sci. Vol. 283, (2005), pp. 446-451.
4. N. Prakash, P.N. Sudha and N.G. Renganathan: Environ Sci Pollut Res. Vol. 19, (2012), pp. 2930–2941.
5. A. Ghaee, M. Shariaty-Niassar, J. Barzin, T. Matsuura: Chem. Eng. J. Vol. 165, (2010), pp. 46-55.
6. S. S. Shenvi, S.A. Rashid, A.F. Ismail, M.A. Kassim and A.M. Isloor: Desalination. Vol. 315, (2013), pp. 135-141.
7. D. Kolodynska: Chem. Eng. J. Vol. 179, (2012), pp. 33-43.
8. A. Ghaee, M. Shariaty-Niassar and J. Barzin: Sustainable Membrane Technology for Energy, Water, and Environment, Chapter 12, New York, John Wiley & Sons, 2012.
9. J. Miao, G. Chen and C.Gao: Desalination, Vol. 181 (2005), pp. 173-183.
10. D. A. Musale and A. Kumar: Sep. Purif. Technol. Vol. 21, (2000), pp. 27–38.
11. H. A. Tsai, H.C. Chen, W.L. Chou, K.R. Lee, M.C. Yang and J.Y. Lai: J. Appl. Polym. Sci. Vol. 94, (2004), pp. 1562-1568.
12. J. N. Shen, L.G. Wu, J.H. Qiu and C.J. Gao: J. Appl. Polym. Sci. Vol. 103, (2007), pp. 1959-1969.
13. J.J. Shieh and R.Y.M. Huang: J. Membr. Sci. Vol. 127, (1997), pp. 185-202.
14. M. Nawawi, M. Ghazali and R.Y.M. Huang: J.Membr. Sci. Vol. 124, (1997), pp. 53-62.
15. X. Feng and R.Y.M. Huang:J. Membr. Sci. Vol. 116, (1996), pp. 67-76.
16. Y. M. Lee, S.Y. Nam and D.J. Woo: J. Membr. Sci. Vol. 133, (1997), pp. 103-110.
17. H. Wu , X. Li , C. Zhao , X. Shen , Z. Jiang and X. Wang: Ind. Eng. Chem. Res. Vol. 52, No.16, (2013), pp. 5772–5780**.**
18. J. Barzin, C. Feng, K.C. Khulbe, T. Matsuura, S.S. Madaeni and H. Mirzadeh: J. Membr. Sci. Vol. 237, (2004), pp. 77–85.
19. J. D. Menczel and R.B. Prime, Thermal analysis of polymers: Fundamentals and applications, John Wiley & Sons., Vol. 7, (2009), p. 314.
20. C. Barth, M. C. Gonçalves, A. T. N. Pires, J. Roeder and B. A. Wolf**:** J. Membr. Sci. Vol. 169, (2000), pp. 287-299.
21. S. Tripathi, G.K. Mehrotra and P.K. Dutta: Int. J. Biol. Macromol. Vol. 45, (2009), pp. 372–376.
22. C. E. Orrego and S. J. Valencia: Bioprocess Biosyst. Eng. Vol**.** 32, (2009), pp. 197-206.
23. Z. Yi, L.P. Zhu, Y.Y. Xu, Y.F. Zhao, X.T. Ma and B.K. Zhu**:** J. Membr. Sci. Vol. 365, (2010), pp. 25–33.
24. N. Bolong, A.F. Ismail, M.R. Salim and D. Rana, T. Matsuura: J. Membr. Sci. Vol. 331, (2009), pp. 40–49.
25. H. H. Oo, K. Naing, K. M. Naing, T. T. Aye and N. Wymr: J. Myan. Acad. Arts & Sc.Vol. 3, (2005), pp. 62-72.
26. S. Singh, K. C. Khulbe, T. Matsuura and P. Ramamurthy: J. Membr. Sci. Vol. 142, (1998), pp. 111-127.