Journal of Engineering and Applied Sciences 12 (18): 4745-4751, 2017
ISSN: 1816-949X

Effect of Copper Oxide Nanoparticles Loading on Polysulfone Ultrafiltration Membrane

[1]N.S. Mohd Sabri, [2]M.Q.A.Z.Z. Azlan, [1]H. Hasbullah, [1]N. Said, [1]W.J. Lau, [2]N. Ibrahim, [2]R.M. Kasmani, [3]R.R. Ali and [4]S.A. Rahman
[1]Advanced Membrane Technology Research Centre (AMTEC),
[2]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia
[3]Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Wilayah Persekutuan Kuala Lumpur, Malaysia
[4]Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Kuantan, Malaysia

Abstract: Copper Oxide (CuO) is a transition metal that has been use in wide applications. The nano size of CuO demonstrates a great of improvement on mechanical, optical, biological and structural properties. Hence, in this research asymmetric Polysulfone (PSf) ultrafiltration membranes incorporated with different loadings of CuO Nanoparticles (NPs) were prepared to investigate membrane characteristic and water permeation performance. The flat sheet membranes were fabricated via phase inversion technique with polymer solution comprised of 18 wt.% PSf, 5 wt.% Polyvinylpyrrolidone (PVP) and 0.00-0.15 wt.% CuO NPs in N-Methyl-2-Pyrrolidone (NMP). The resulting membranes were characterized in terms of morphology through Scanning Electron Microscope (SEM), surface hydrophilicity by contact angle analysis and Pure Water Flux (PWF). Results showed that with increasing in loading of CuO Nps, the water contact angle decreased from 81.9° of neat Psf to 73.1° for 0.15 wt.% CuO. The high concentration of CuO NPs in PSf dope solution lead to the formation of macrovoids in the bottom region and skin layer at the top surface. Membranes with enhanced hydrophilicity and porous structure govern to improve the water flux performances. The highest PWF achieved at 103.6 $Lm^{-2}h^{-1}$ when the loading up to 0.15 wt.% CuO NPs. This study is proved the hydrophilicity and morphology of CuO/PSf membranes were enhanced as the increase of CuO loadings.

Key words: Polysulfone, ultrafiltration, copper oxide, hydrophilicity, performance, Malaysia

INTRODUCTION

Ultrafiltration (UF) membrane for separation of high molecular-weight materials such as protein has become a demanding process, considering their benefits and advantageous. The ability of UF process to operate at low pressure, favors short usage of energy and power. The surface pore sizes of UF between 1-100 nm are another characteristic that aids in filtration process (Salim and Ho, 2015). This technology is an alternative way for treatment of wastewater from the industries. Membrane technology serves as a very selective in separation, produce higher water quality product and required low space (Guo *et al*., 2012; Truttim and Sohsalam, 2016). There are several factors that control membrane performance including the membrane morphology and hydrophilicity. Hydrophilicity property is the tendency of membrane surface to become wet or can attract and absorb water better than other materials (Ahmad *et al*., 2013; Roya *et al*., 2015; Panrare *et al*., 2016). Membrane with hydrophilic surface able to allow the passage of water through the membrane and repels the hydrophobic particle such as protein. In addition, membrane having top skin layer and porous structure is the most desirable morphology which can assist in separating and purifying the wastewater (Rana and Matsuura, 2010).

Phase inversion process has been generally studied for preparation of asymmetric porous membrane. This technique involves the immersion precipitation step which the dope solution from casting support is transformed to polymer membrane in solid state. The formation of membrane occurred to the exchange of solvent and

Corresponding Author: H. Hasbullah, Advanced Membrane Technology Research Centre (AMTEC), Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

non-due solvent across the interface of dope solution and coagulation bath (Urkiaga *et al*., 2015). The precipitation and exchange rate are majorly influenced the formation of membrane. Rapid precipitation of dope results in the formation of finger-like structure with macrovoid while slow precipitation form sponge-like membrane structure (Guillen *et al*., 2011).

There are abundant of polymers that have been use in membrane technology. Polysulfone (PSf) is one of the most widely chosen as the main polymer material in UF membrane fabrication. This is due to the ability of PSf to form a huge variation of porous asymmetric membrane structure with water as a non-solvent during phase inversion process (Guillen *et al*., 2011). It also possess a high degree of chemical, mechanical and thermal resistant properties (Sinha and Purkait, 2013). Although, PSf shows a lot of advantages but it suffers some drawbacks which are hydrophobic characteristic in nature and problem of fouling. Therefore, some research had focused on enhancing membrane hydrophilicity through membrane modification procedure (Mavukkandy *et al*., 2016). Blending of hydrophilic additive into polymeric matrix membrane is one of attractive and simple methods in membrane modification without altering the main polymer structure (Xu *et al*., 2015; Hisham *et al*., 2017). Usually, hydrophilic polymers and Nanoparticles (NPs) were used as additives to improve membrane hydrophilicity.

Emergence of nanotechnology in membranes had received more attention, recently. Incorporating the NPs into polymer matrix helps improving the membranes characteristic and performance. Various NPs have been introduced to membrane technology for wastewater treatment including Zinc Oxide (ZnO), Titanium dioxide (TiO_2), silver and iron oxide (Fe_3O_2). The addition of these NPs is offered great possibilities to enhance membrane hydrophilicity. Copper Oxide (CuO) NPs is a potential nanomaterial in membrane separation as it have excellent characteristic. A great interest of these NPs is due to their unique biological, chemical and physical property (Dizaj *et al*., 2014). It is reported that addition of Cu NPs in Polyethersulfone (PES) had reduced the hydrophobicity due to the migration of hydrophilic NPs to the membrane surface during phase inversion process (Akar *et al*., 2013). Another, investigation found that the maximum average pore size achieved when using 2.0 weight percentage (wt.%) of CuO nanoparticle in PVDF membrane (Baghbanzadeh *et al*., 2015). It was also found that incorporation of 1.0 wt.% Cu NPs in PA layer for reverse osmosis membrane allowed the pure water flux and membrane permeability to increase (Garcia *et al*., 2016).

Thus, the main focus of this work was to investigate the membrane hydrophilicity, morphology and pure water flux performance by incorporating potential CuO nanoparticle in PSf membrane at different loadings. In this study, N-Methyl-2-Pyrrolidone (NMP) and Polyvinyl Pyrrolidone (PVP) were used as a solvent and pore former agent, respectively during membrane fabrication.

MATERIALS AND METHODS

All materials and chemical products used are analytical grade, without further purification. Polysulfone (Udel-P1700) was purchased from solvay advanced polymer in pallets form as main polymer membrane material. PVP-K15 by Fluka as a pore former and NMP (99.5%, molecular weight = 99.13 g/mol) by QReC used as a good solvent for PSf. CuO size of <50 nm (Sigma Aldrich) was used as metal oxide nanoparticles in dope formulation. Glycerol (molecular weight = 92.1 g/mol) was obtained from merck for membrane post treatment.

Membrane preparation: PSf pallets were dried first in the oven at 50°C overnight to remove water content in polymer completely. The neat PSf membrane was prepared by dissolving 5 wt.% PVP in NMP solvent with stirring by a magnetic stirrer. Then, amount of 18 wt.% PSf was added slowly to the solution at 50°C after 2 h and the dope solution was left for 1 night while in stir for getting uniform solution.

As for dope solution containing CuO nanoparticle, the NPs was dispersed in NMP using sonicator for 1 h to form homogenous dispersion of CuO NPs. Followed by addition of PVP and PSf as previously described. All the dope solution prepared was degassed before preparing the membrane for removing possible air bubbles.

Table 1 shows the prepared dope composition. All flat sheet membranes were prepared by phase inversion method to form asymmetric structure UF membrane. During the casting step, ample amount of dope solution was cast on a clean glass plate and then left it for 10 sec for solvent evaporation at room temperature before immersed the glass plate into the water bath for membrane precipitation process. The formed membranes were then treated for 4 days to get rid of residual solvent and to preserve the membrane shelf-life. The post treatment began by keeping the membrane in water for 48 h before immersing it in 10% glycerol solution for another 24 h. After that, proceed with 1 day for drying the membrane at room temperature and the dried membrane was kept in a sealed bag prior to further actions.

Contact angle measurement: The hydrophilic or hydrophobic characteristic of prepared membrane was analyzed using contact angle. Declinations in contact angle value indicate the improvement of membrane

Table 1: Formulation of membranes (wt. %)

Membrane	PSf	PVP	CuO NPs	NMP
Neat PSf	18	5	-	77.00
0.01 CuO/PSf	18	5	0.01	76.99
0.05 CuO/PSf	18	5	0.05	76.95
0.15 CuO/PSf	18	5	0.15	76.85

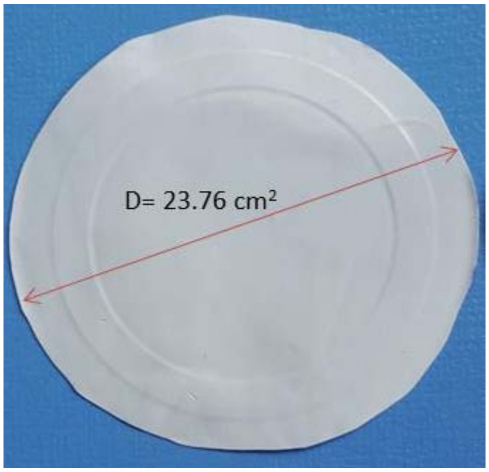

Fig. 1: Prepared membrane with specific effective surface area for water flux analysis

hydrophilicity. Contact angle measurement was carried out by using goniometer (Kruss Gambult, Germany) with 0.5 μL of water were dropped with the help of a syringe on the clean and dry for both (top and bottom) membrane surface at 25°C. The angles were verified by the software and were performed at eight different locations for each sample to minimize the experimental error. Then, the measurement was averagely reported. The angle between a water droplet and flat sheet membranes was captured for better observation.

Scanning Electron Microscopy (SEM) analysis: The morphological properties of the membrane cross-section was observed using SEM (HITACHI TableTop TM3000). The sample preparation involves by fractured all the membranes in liquid nitrogen to obtain clear and smooth cross section. The fractured membranes were stick onto a metal plate at lateral side using double-sided carbon tape and then all the prepared samples were sputter-coated with platinum/palladium before being examined. The pictures of cross-sections for all membranes were captured.

Pure water flux study: The membrane was first cut into desired shape as shown in Fig. 1 with effective surface area (23.76 cm^2) before fitted in separation system.

The Pure Water Flux (PWF) were measured by testing the membrane using a dead-end ultrafiltration system that passing through effective surface area at a trans-membrane pressure of 0.981 bar. The PWF measurement was calculated by using the following Eq. 1:

$$J = \frac{V}{A \times \Delta t} \qquad (1)$$

Where:

J = Represents the PWF ($Lm^{-2}h^{-1}$)
V = Volume of permeate (L)
A = Effective surface area (m^2) of membrane
Δt = Permeation time (h)

RESULTS AND DISCUSSION

Membrane hydrophilicity: Hydrophilicity of the membrane is the key parameters in determining water permeability to pass through the membranes. Water contact angle measurement is an indicator describing the surface hydrophilicity. Generally, a decrease in contact angle value show improvement in the membrane hydrophilic property (Phelane *et al*., 2014). Table 2 shows the contact angle of PSf membranes with different wt.% of CuO NPs. As loading of NPs increases, the contact angle value declined.

From Table 2, the contact angle measurement decreased from neat PSf of 81.9-73.1° of 0.15 Cu/PSf membrane. It can be clearly seen that, the contact angle became smaller by the increment of CuO NPs loading in PSf membrane. The introductions of CuO NPs were observed to lower down the contact angle and it could be understood from reported data depicted by Fig. 2. This trend is coherent with the research done by Koseoglu-Imer *et al*. (2013) upon addition of NPs to the polymeric membranes.

Increase of CuO Nps content in membranes known to affect the correlation of water at membranes solid surface. This could happen due to the rearrangement of interfacial water molecules to the solid-liquid interface (Al-Hobaib *et al*., 2015). The presence of NPs reduced the surface tension of PSF membrane that led to enhancement of the attraction of water on membrane surfaces (Basri *et al*., 2011).

It should be noted that, the hydrophilic nature by the NPs influenced the water contact with the membrane surface (Homayoonfal *et al*., 2014). The interaction of water was also influenced by the availability of polar functional group such as hydroxyl group and oxygen element from the surface of the metal oxide (Sotto *et al*., 2014).

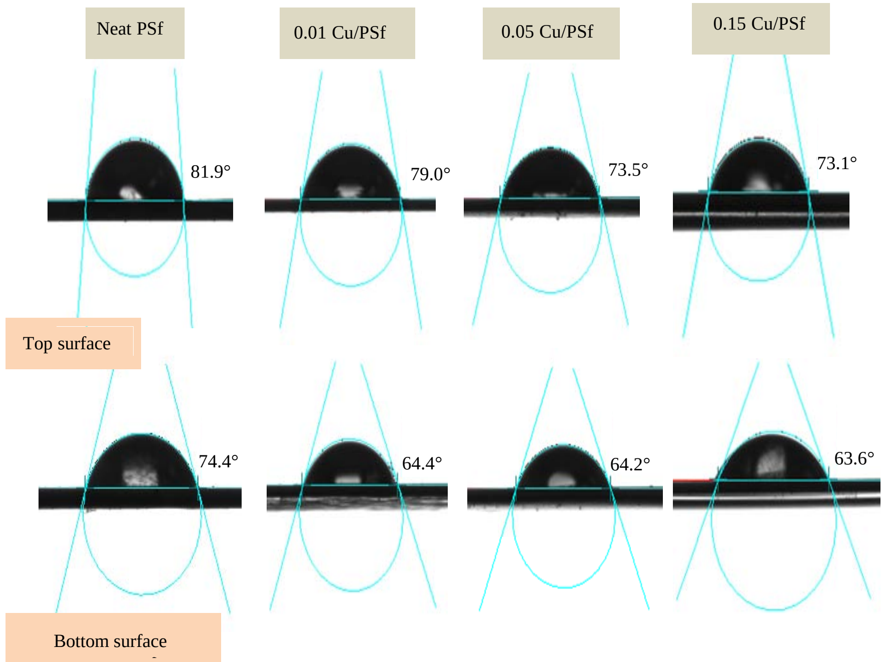

Fig. 2: Contact angle between water droplet with flat sheets membrane at top and bottom surface

Table 2: Contact angle value for top and bottom membrane surface

Membranes	Contact angle-top (degrees)	Contact angle-bottom (degrees)
Neat PSf	81.9	74.4
0.01 CuO/PSf	79.0	64.4
0.05 CuO/PSf	73.5	64.2
0.15 CuO/PSf	73.1	63.6

The data reported in Table 2 and Fig. 2 describes the membrane hydrophilicity at top and bottom surface. The contact angles of modified PSf membranes by CuO NPs at bottom surface show more significant declination compared to the top surface and the lowest contact angle value is 63.6°. This happen might be due to the agglomeration phenomenon that caused CuO NPs to sink and located at the bottom region of the membranes (Ng *et al*., 2013).

Scanning Electron Microscopy (SEM) analysis: The cross-sectional membrane morphology was confirmed by visual analyses of SEM images (Fig. 3). A typical asymmetric porous structure was presented in all membranes. At the top region, the thin skin layer was distinctly seen while bottom part of the membranes consists of finger-like structure and also macrovoids. The development of this structure is generally referred to the interaction of dope solution and non-solvent (water) during phase inversion (Lalia *et al*., 2013). The appearances of bigger macrovoids were depicted in Fig. 3 as the loading of CuO NPs increased. This could be attributed to the instantaneous precipitation during phase inversion (Abdelrasoul *et al*., 2015). The red arrow lines indicated the presence of NPs in the prepared membranes.

Pure water flux analysis: Membrane capability and performances were tested by using PWF study. The water flux property is strongly depending on the membrane characteristic and structure (Ahmad *et al*., 2013). From the graph presented in Fig. 4, the PWF for CuO NPs incorporated in PSf membranes reported to have higher water transport as compared to the neat PSf. The chart shows clear trend of increasing PWF when higher amount of NPs added to the PSf membrane. The PWF had elevated up to 103.6 $Lm^{-2}h^{-1}$ by 0.15 CuO/PSf membranes as compared to 49.9 $Lm^{-2}h^{-1}$ for neat PSf.

The findings were in coherent with the results of SEM and membrane hydrophilicity. Improvement of membrane hydrophilicity has direct effect on the PWF. The presence of hydrophilic CuO NPs prompted the membrane surface to have better water permeation crossing through the membrane. Similar results were obtained by previous studies (Alam *et al*., 2013; Homayoonfal *et al*., 2015; Kumar *et al*., 2013) showed that high loadings of NPs improved the water transport properties.

Referring to the SEM result, the enhancement of PWF was also influenced by the membrane structure. The

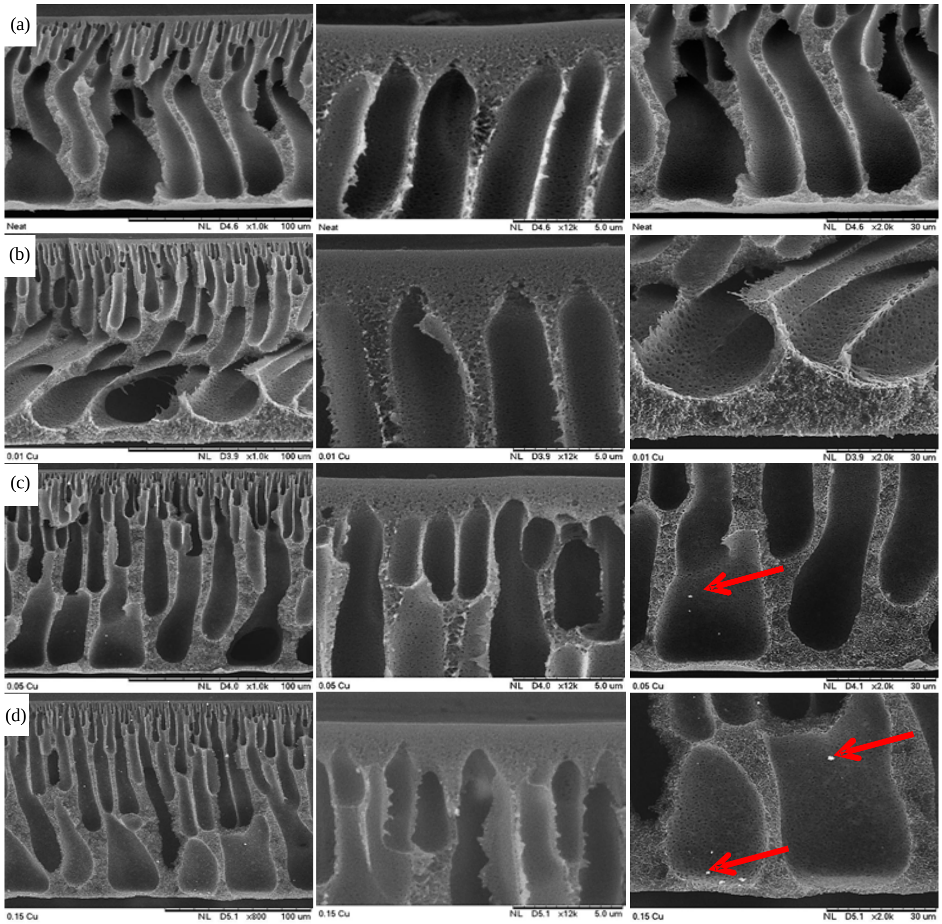

Fig. 3: Cross-sectional view of SEM image: a) neat PSf; b) 0.01CuO/PSf; c) 0.05CuO/PSf and d) 0.15 CuO/PSf (left to right: whole cross-section, top region, bottom region)

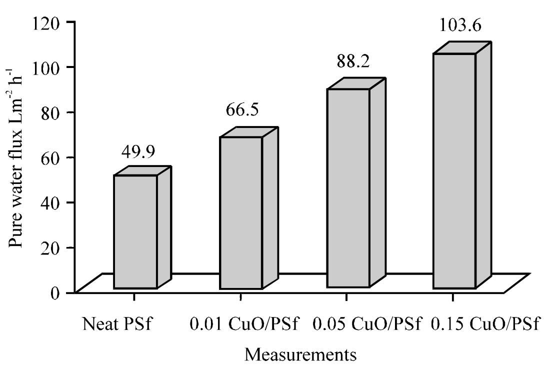

Fig. 4: Pure water flux measurement

addition of NPs and PVP in this study produced the membrane with porous substructure. The development of this void space in the prepared membrane aids the water to pass through the membrane (Richards *et al*., 2012).

CONCLUSION

In this research, flat sheet CuO/PSf membranes were successfully fabricated through phase inversion method. The effect of CuO NPs loading on the membrane structural properties and performance were investigated. The experimental results discovered that these NPs have a great influence on the hydrophilicity PSf membrane and the performances. It was found in this study that membranes contact angle decreased as the CuO NPs loading was increased. It is also revealed the formation of asymmetric structure with thin skin layer from the prepared membranes and the PWF improved significantly at high NPs loading. As a conclusion, the loadings of CuO Nps were proven to enhance the membrane hydrophilicity, morphology structure and water transport across the membranes.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support from Universiti Teknologi Malaysia and Ministry of Higher Education Malaysia (Grant No.: 13H64 and 4J206).

REFERENCES

Abdelrasoul, A., H. Doan, A. Lohi and C.H. Cheng, 2015. Morphology control of polysulfone membranes in filtration processes: A critical review. Chem. Bio. Eng. Rev., 2: 22-43.

Ahmad, A.L., A.A. Abdulkarim, B.S. Ooi, S. Ismail, 2013. Recent development in additives modifications of polyethersulfone membrane for flux enhancement. Chem. Eng. J., 223: 246-267.

Akar, N., B. Asar, N. Dizge and I. Koyuncu, 2013. Investigation of characterization and biofouling properties of PES membrane containing selenium and copper nanoparticles. J. Membrane Sci., 437: 216-226.

Al-Hobaib, A.S., K.M. Al-sheetan, M.R. Shaik, N.M. Al-Andis and M.S. Al-Suhybani, 2015. Characterization and evaluation of reverse osmosis membranes modified with Ag2O nanoparticles to improve performance. Nanoscale Res. Lett., 10: 379-379.

Alam, J., L.A. Dass, M. Ghasemi and M. Alhoshan, 2013. Synthesis and optimization of PES-Fe3O4 mixed matrix nanocomposite membrane: Application studies in water purification. Polym. Compos., 34: 1870-1877.

Baghbanzadeh, M., D. Rana, T. Matsuura and C.Q. Lan, 2015. Effects of hydrophilic CuO nanoparticles on properties and performance of PVDF VMD membranes. Desalin., 369: 75-84.

Basri, H., A.F. Ismail and M. Aziz, 2011. Polyethersulfone (PES)-silver composite UF membrane: Effect of silver loading and PVP molecular weight on membrane morphology and antibacterial activity. Desalination, 273: 72-80.

Dizaj, S.M., F. Lotfipour, M. Barzegar-Jalali, M.H. Zarrintan and K. Adibkia, 2014. Antimicrobial activity of the metals and metal oxide nanoparticles. Mater. Sci. Eng. C., 44: 278-284.

Garcia, A., B. Rodriguez, D. Ozturk, M. Rosales and C. Paredes et al., 2016. Desalination performance of antibiofouling reverse osmosis membranes. Mod. Environ. Sci. Eng., 2: 481-489.

Guillen, G.R., Y. Pan, M. Li and E.M. Hoek, 2011. Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review. Ind. Eng. Chem. Res., 50: 3798-3817.

Guo, W., H.H. Ngo and J. Li, 2012. A mini-review on membrane fouling. Bioresour. Technol., 122: 27-34.

Hisham, M.H.H., A.A. Rahman and I.S. Mustafa, 2017. UV-visible spectrophotometer analysis on polymerization of 2-hydroxyethyl methacrylate. Intl. J. Appl. Phys. Sci., 3: 42-45.

Homayoonfal, M., M.R. Mehrnia, M. Shariaty-Niassar, A. Akbari and A.F. Ismail et al., 2014. A comparison between blending and surface deposition methods for the preparation of iron oxide/polysulfone nanocomposite membranes. Desalination, 354: 125-142.

Homayoonfal, M., M.R. Mehrnia, M. Shariaty-Niassar, A. Akbari and M.H. Sarrafzadeh et al., 2015. Fabrication of magnetic nanocomposite membrane for separation of organic contaminant from water. Desalination Water Treat., 54: 3603-3609.

Koseoglu-Imer, D.Y., B. Kose, M. Altinbas and I. Koyuncu, 2013. The production of polysulfone (PS) membrane with silver nanoparticles (AgNP): Physical properties, filtration performances, and biofouling resistances of membranes. J. Membr. Sci., 428: 620-628.

Kumar, R., A.M. Isloor, A.F. Ismail, S.A. Rashid and T. Matsuura, 2013. Polysulfone chitosan blend ultrafiltration membranes: Preparation, characterization, permeation and antifouling properties. RSC. Adv., 3: 7855-7861.

Lalia, B.S., V. Kochkodan, R. Hashaikeh and N. Hilal, 2013. A review on membrane fabrication: Structure, properties and performance relationship. Desalination, 326: 77-95.

Mavukkandy, M.O., M.R. Bilad, A. Giwa, S.W. Hasan and H.A. Arafat, 2016. Leaching of PVP from PVDF/PVP blend membranes: Impacts on membrane structure and fouling in membrane bioreactors. J. Mater. Sci., 51: 4328-4341.

Ng, L.Y., A.W. Mohammad, C.P. Leo and N. Hilal, 2013. Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review. Desalination, 308: 15-33.

Panrare, A., T. Tondee and P. Sohsalam, 2016. Effect of plant density in constructed wetland on domestic wastewater treating efficiency. Intl. J. Appl. Phys. Sci., 2: 7-12.

Phelane, L., F.N. Muya, H.L. Richards, P.G. Baker and E.I. Iwuoha, 2014. Polysulfone nanocomposite membranes with improved hydrophilicity. Electrochim. Acta, 128: 326-335.

Rana, D. and T. Matsuura, 2010. Surface modifications for antifouling membranes. Chem. Rev., 110: 2448-2471.

Richards, H.L., P.G. Baker and E. Iwuoha, 2012. Metal nanoparticle modified polysulfone membranes for use in wastewater treatment: A critical review. J. Surf. Eng. Mater. Adv. Technol., 2: 183-193.

Roya, P., R. Hadi, A. Hossein and M. Vahedian, 2015. Survey of wastewater stabilization pond potential in meeting environmental standards. Intl. J. Appl. Phys. Sci., 1: 19-21.

Salim, W. and W.W. Ho, 2015. Recent developments on nanostructured polymer-based membranes. Curr. Opin. Chem. Eng., 8: 76-82.

Sinha, M.K. and M.K. Purkait, 2013. Increase in hydrophilicity of polysulfone membrane using polyethylene glycol methyl ether. J. Membr. Sci., 437: 7-16.

Sotto, A., J. Kim, J.M. Arsuaga, G.D. Rosario and A. Martinez, 2014. Binary metal oxides for composite ultrafiltration membranes. J. Mater. Chem. A., 2: 7054-7064.

Truttim, P. and P. Sohsalam, 2016. Comparison of electrocoagulation using iron and aluminium electrodes for biogas production wastewater treatment. J. Adv. Technol. Eng. Res., 2: 35-40.

Urkiaga, A., D. Iturbe and J. Etxebarria, 2015. Effect of different additives on the fabrication of hydrophilic polysulfone ultrafiltration membranes. Desalin. Water Treat., 56: 3415-3426.

Xu, Z., S. Ye, Z. Fan, F. Ren and C. Gao et al., 2015. Preparation of Cu2O nanowire-blended polysulfone ultrafiltration membrane with improved stability and antimicrobial activity. J. Nanoparticle Res., 17: 401-409.