Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.923202

54 (2015) 3603–3609
June

Taylor & Francis
Taylor & Francis Group

Fabrication of magnetic nanocomposite membrane for separation of organic contaminant from water

Maryam Homayoonfal[a], Mohammad Reza Mehrnia[a,*], Mojtaba Shariaty-Niassar[a], Ahmad Akbari[b], Mohammad Hossein Sarrafzadeh[a], Ahmad Fauzi Ismail[c]

[a]*School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran, Tel. +98 2161112184; Fax: +98 2166954041; emails: maryam.homayoonfal@gmail.com (M. Homayoonfal), mmehrnia@ut.ac.ir (M.R. Mehrnia), mshariat@ut.ac.ir (M. Shariaty-Niassar), sarrafzdh@ut.ac.ir (M.H. Sarrafzadeh)*

[b]*Institute of Nanoscience and Nanotechnology, University of Kashan, Kashan, Iran, Tel. +98 361 4445219; Fax: +98 361 4451495; email: akbari@kashanu.ac.ir*

[c]*Advanced Membrane Technology Research Center (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia, Tel. +607 553 5807/5625; Fax: +607 553 5925; email: fauzi.ismail@gmail.com*

Received 15 January 2014; Accepted 14 March 2014

ABSTRACT

In this work, separation of disperse dyes and polyethylene glycol (PEG) as organic contaminant by nanocomposite membrane was investigated. The main goal of this study is to achieve more efficient separation of contaminant from water at high fluxes. For this purpose, iron oxide nanoparticles (NP) were synthesized through co-precipitation, blended with polysulfone/N-methylpyrrolidone solution, and finally, dispersed in membrane structure after coagulation of casted polymeric solution. Effect of magnetic nanoparticle concentration on membrane structure and filtration performance was studied. According to filtration experiments, the increasing of nanoparticle concentration in membrane matrix cause permission flux to raise. On the other side, any increases in magnetic nanoparticle content improved disperse dyes and PEG rejection as organic contaminant. Iron oxide NP in polymeric solution act as an agent to increase viscosity and cause a delay in phase inversion, decrement in membrane pore size, and finally, solute rejection enhancement. The Fourier transform infrared spectroscopy confirmed nanoparticle existence in membrane matrix. Furthermore, the magnetic properties of nanocomposite membranes were measured by Vibrating Sample Magnetometer. Scanning electron microscopy images showed the effect of nanoparticle concentration on membrane porosity. The cross section of which confirmed the role of NP as a delay agent in membrane formation.

Keywords: Iron oxide nanoparticle; Magnetic nanocomposite membrane; Organic contaminant; Fouling mitigation

---

*Corresponding author.

Presented at the 5th IWA-ASPIRE Conference, 8–12 September 2013, Daejeon, Korea

1. Introduction

Membrane filtration is one of the wide spreading processes for separation of contaminant from water/wastewater [1]. Although membrane filtration has been developed over the existing water purification techniques because of some of its benefits such as low energy cost, easy for expanding, and low-temperature application, the key disadvantage that inevitably occurs continuously in the membrane filtration systems is membrane fouling which limits membrane application. Membrane fouling is caused by hydrophobic particles and colloidal material which are present in the feed water and are concentrated at the membrane surface. There are some techniques for the reduction and prevention of membrane fouling [2], among which the methods related to correction in membrane characteristics have been more noteworthy than others in the last years [3]. Synthesis of super-hydrophilic nanoparticles (NP) and incorporating the synthesized NP into a polymeric membrane have been developed as a novel method for fouling mitigation [4–6]. A wide range of NP has been used as hydrophilic additive in membrane structure such as Ag [7], TiO_2 [8], Al_2O_3 [9,10], ZnO [11], and Fe_3O_4 [12] for reducing the membrane fouling. The presence of NP in the membrane matrix not only changes membrane hydrophilic nature but also alters membrane structure [5] and specifications. For instance, TiO_2 [13], Ag [7], and ZnO [14] result in anti-bacterial characteristics, ZrO_2 [15] and Fe [16] create catalytic properties, SiO_2 [17] NP causes conductivity properties, and Fe_3O_4 [12] nanoparticle gives magnetic characteristics to polymeric membranes.

Magnetic nanocomposite membranes because of both magnetic and efficient filtration properties have been got great attention in the recent years [12,18–20]. Huang et al. [19] compared the magnetized and non-magnetized membranes (MNCMs) performance in ultrafiltration of pig blood solution. Their research showed that the MNCM has a higher blood proteins recovery, flux, and a relative flux than the corresponding non-MNCM. In another research, magnetic field was applied to fabricate magnetic nanocomposite membranes, results showed that magnetic nanocomposite membranes are fouling resistant [12]. RuiJun et al. [18] used external magnetic field during ultrafiltration of polysaccharides by magnetic composite membrane. The research showed that magnetic field decreases polysaccharide recovery. The main goal of the present study is to benefit both magnetic nanoparticle and external magnetic field for improving filtration performance.

For this purpose, iron oxide NP were synthesized by co-precipitation method then blended with polysulfone (PSf) casting solution. Structure and surface properties of synthesized nanocomposite ultrafiltration membranes were studied through scanning electron microscopy (SEM) images, Fourier transform infrared spectroscopy (FTIR), and contact angle measurement. Iron oxide NP, because of bearing some properties such as magnetization [12,21] and hydrophilicity [20,21], have manipulated membrane structure and nature. Considering the magnetic property of nanocomposite membranes, the effect of external magnetic field besides impact of NP presence on pure water flux (PWF) and organic contaminant separation of magnetic nanocomposite membranes were examined.

2. Materials and methods

2.1. Materials

PSf (MW: 7,500 Da) was purchased from Across Organics, and was used as the main polymer for the membrane (13.5 wt.%). Normal methylpyrrolidone (NMP) was purchased from Merck Company and was used as the solvent of the polymer (75 wt.%). Polyethylene glycol (PEG) (MW: 20,000 g/mol) was purchased from Merck Company, and it was used as the pore former (11.5 wt.%) or for molecular weight cut off measurement (MW: 10,000 g/mol). $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, and NH_3 supplied from Merck Company and used for iron oxide NP synthesis. Disperse dyes were bought from Rang Alvan Sabet Company.

2.2. Methods

2.2.1. Nanocomposite membrane fabrication

Fe_3O_4 entrapped PSf ultrafiltraion membranes were prepared by dispersing different concentration of nanosized particles uniformly into NMP solution and were sonicated at 70˚C for 60 min, then PSf was subsequently added under continuous sonication. After adding PEG-20000 additive and sonicating likewise for 60 min, the membrane was cast onto a clean glass plate with 350 μm casting knife and exposed under forced convection evaporation for 30 s. Then immediately immersed in a water coagulation bath at 25˚C to form membrane. Membrane fabrication conditions are listed in Table 1.

2.2.2. Filtration experiments

All experiments were done at room temperature (25 ± 2˚C) and a pressure of 3 bar using a cross-flow filtration system with 24 cm^2 effective area cell. The effect of external magnetic field on performances was examined by filtration under magnetic field (0.4 Tesla)

Table 1
Membrane preparation condition

Membrane	PSf (wt.%)	PEG (wt.%)	Solvent (wt.%)	NP/polymer (wt.%)
Neat membrane (NM)	13.5	12.5	75	0
Magnetic nanocomposite membrane ($MNCM_1$)	13.5	12.5	75	0.02
Magnetic nanocomposite membrane ($MNCM_2$)	13.5	12.5	75	0.07
Magnetic nanocomposite membrane ($MNCM_3$)	13.5	12.5	75	0.11

at the distance of 2.0 cm. By measuring permeate weight at certain times membrane PWF, was calculated by Eq. 1:

$$\mathrm{PWF} = \frac{l}{A \cdot \Delta t} \tag{1}$$

In which l is permeate volume (L), A is the membrane surface area (m^2), and Δt is the permeation time (h). After 30 min compaction, any filtration experiment (PWF or organic solute separation) has been done during 60 min cross-flow filtration. To minimize the experimental error, the filtration tests were measured and averaged three times for each sample. Following filtration, dye solutions were analyzed using a UV–visible spectrophotometer (UNICO, Model: s2100, USA) at a wavelength of 460 nm. The rejection of dye solutions was calculated through Eq. 2.

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

In Eq. 2, $R\%$ represents rejection, while C_f and C_p represent concentration of dye in the feed and concentration of dye in the membrane permeate, respectively. The analytical method for determining PEG concentration is given by Sabde et al. [22] in which PEG solutions were analyzed using a UV–visible spectrophotometer at a wavelength of 535 nm.

2.2.3. FTIR spectra

FTIR spectrum was used in order to prove the presence of Fe_3O_4 NP in the structure of PSf membrane (BRUKER, Model: TENSOR 27, Germany). Membrane samples became a little thin and transparent due to the high pressure (14 bar), and then they were analyzed.

2.2.4. VSM analysis

The magnetic measurement was carried out in a vibrating sample magnetometer (VSM, BHV 55, Riken, Japan) at room temperature.

2.2.5. SEM images

SEM image was taken by SEM microscope (Hitachi, Model: s4160, Japan) after complete sample preparation i.e. sample freezing by liquid nitrogen, breaking sample, and gold scattering.

3. Results and discussion

3.1. Effect of magnetic NP on membrane properties

The presence of NP in membrane matrix changes membrane surface properties and structure. Magnetic NP changes membrane functional groups, surface hydrophilicity, magnetization, and porosity.

Fig. 1 displays FTIR spectrum of iron oxide NP, PSf ultrafiltration membrane, and nanocomposite membrane. A peak was observed in wave number of 3,400 cm^{-1} and another one in 580 cm^{-1} in iron oxide NP spectrum that are related to –OH and Fe–O functional groups of Fe_3O_4 particles, respectively [23]. Comparison between the spectrum of neat PSf membrane and nanocomposite membrane shows a wide peak in the area of 3,000–3,600 cm^{-1}, and a sharp peak in 582–640 cm^{-1} bands, that are due to the stretching vibration mode associated to the metal–oxygen absorption band (Fe–O bonds in the crystalline lattice of Fe_3O_4) which confirms the presence of Fe_3O_4 NP in the structure of PSf membrane.

Entrapping magnetic NP in the polymer matrix endows the product with magnetic properties [18,24]. As seen from Fig. 2, an increase in NP concentration from 0.02 to 0.11 wt.% result in enhancement magnetization from 0.7 to 15 emu/g.

Blending NP with polymeric solution changes the rate of phase separation and, consequently, changes the structure and filtration performance of the synthesized nanocomposite membranes [5,9,10]. Fig. 3 displays the effect of NP entrapments in membrane matrix.

As illustrated in the SEM cross-sectional images, the addition of NP to casting solution decreases the length of finger-like pores and increases the thickness of sponge-like structure for $MNCM_1$ in comparison with NM. This behavior can be related to promoter role of NP which induces instantaneous phase

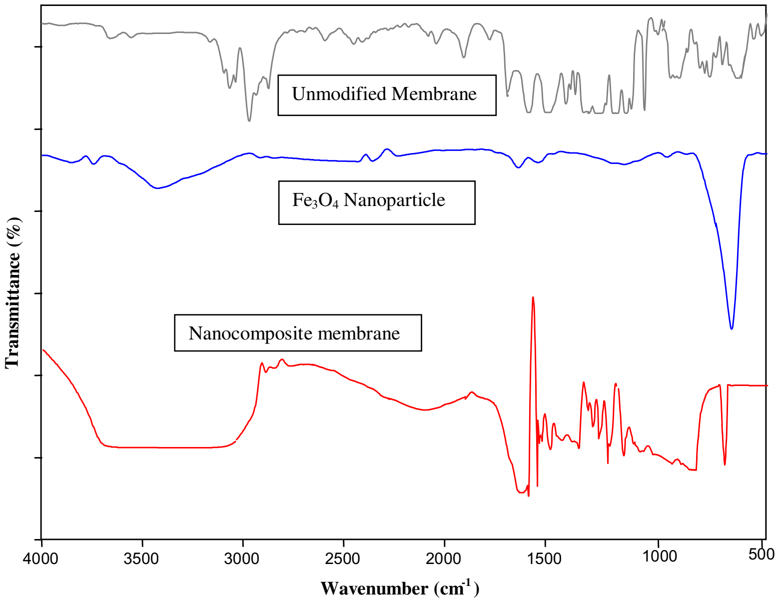

Fig. 1. FTIR spectrum of Fe_3O_4 entrapped PSf ultrafiltration membrane, PSf membrane, and Fe_3O_4 nanoparticle.

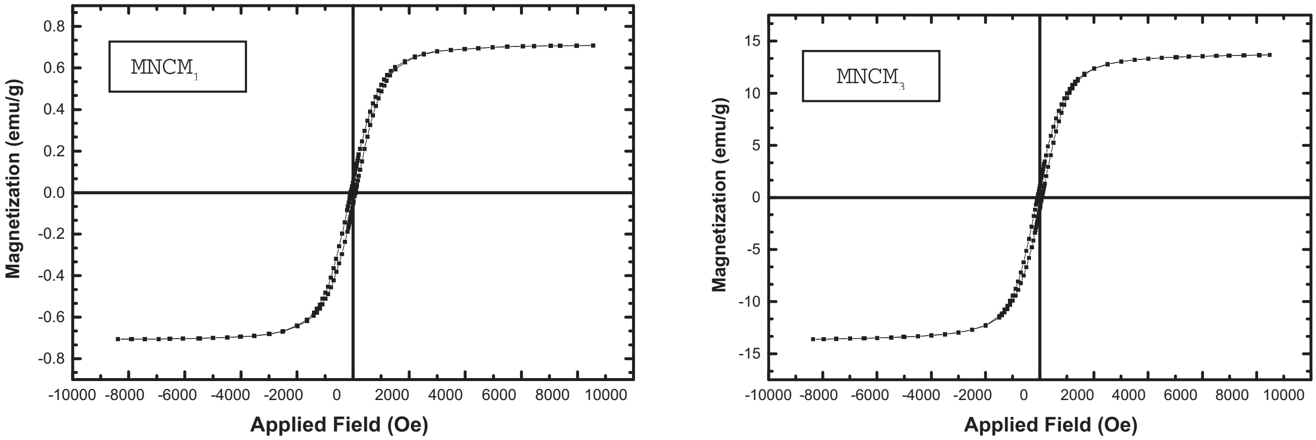

Fig. 2. Effect of Fe_3O_4 load on nanocomposite membrane magnetization.

inversion and finally porous structure [10]. The similar observation has been reported by other researchers [25]. But here, with more increment in NP loading, for $MNCM_2$ and $MNCM_3$, the increase in the length of finger pores and elimination of sponge-like structure can be seen from the Fig. 3 which produces a dense membrane with low porosity. The mentioned performance can be because of increasing in casting solution viscosity with NP loading [8]. As can be seen from Fig. 3, a structure revolution has been occurred for nanocomposite membranes at 0.07 wt.% of Fe_3O_4 NP. The mentioned concentration can be considered as an exclusive threshold concentration [5,26–30]. At concentrations lower than the threshold, any increase in nanoparticle loading, result in increasing in membrane porosity, while rheological increment is dominant at higher concentrations than the threshold which result in decreasing in membrane porosity. The threshold concentration was reported to be 0.093, 0.04, 0.05, 0.03, and 0.02 wt.% for [PSf/dimethylacetamide (DMAC)/NMP/TiO_2] [26], [Poly ether sulfones (PES)/DMAC/TiO_2] [27], [PSf/NMP/Polyvinylpyrrolidone (PVP)/C60] [28], [Polyvinylidene fluoride (PVDF)/DMAC/DMF/SiO_2] [29], and [PVDF/DMAC/Al_2O_3] [30] systems, respectively.

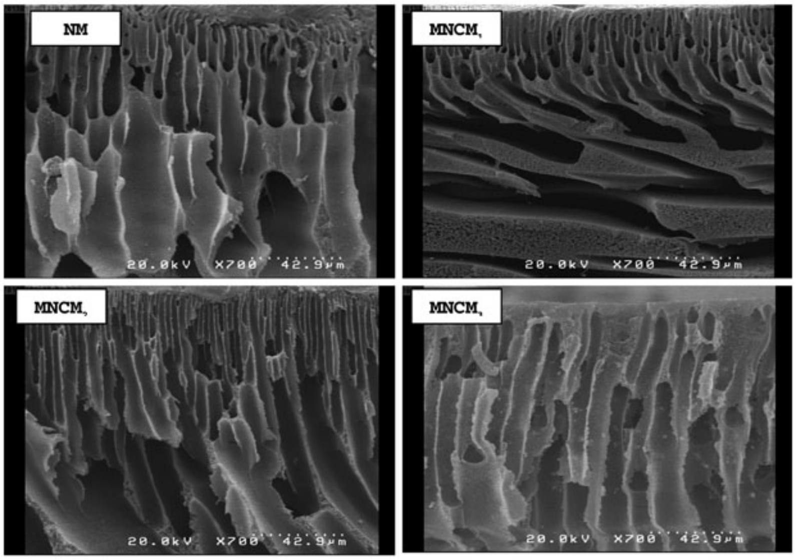

Fig. 3. Cross sectional SEM images of membrane containing different concentration of magnetic NP.

3.2. *Effect of magnetic NP on filtration performance of nanocomposite membrane*

Effect of magnetic nanoparticle entrapment on filtration performance of magnetic nanocomposites investigated. The results are shown in Fig. 4.

As displayed in Fig. 4, PWF of the non-MNCM is strongly smaller than magnetized ones. This behavior can be due to the improvement of membrane surface hydrophilicity in the presence of iron oxide NP [20].This behavior has been observed for other NP by other researchers [9,15,27,30]. For MNCMs any increase in nanoparticle concentration, improves membrane PWF which can be related to Fe_3O_4 hydrophilicity [12] or membrane porosity [20]. For MNCMs with increasing in NP concentration, before threshold concentration (0.07 wt.%) separation efficiency of organic solutes declines while at higher concentrations than the threshold, separation efficiency of organic solutes improves (see Fig. 4(b)). This performance can be related to alternation in membrane porosity (see SEM images, Fig. 3) or adsorption of organic solutes by iron oxide NP [31].

3.3. *Effect of magnetic field on membrane filtration performance*

Taking into consideration, magnetic property of synthesized nanocomposite membranes, the effect of magnetic field on filtration performance of nanocomposite membranes was investigated. Application of magnetic field for recovery of polysaccharides from water has been investigated by RuiJun et al. [18]. The results of the research indicated that magnetic field increases membrane pore size and PWF while polysaccharide recovery decreases dramatically [18]. In the present work, organic solute separation has been examined in the presence of external magnetic field. Results are shown in Fig. 5.

As shown from the Fig. 5, magnetic field increases PWF of nanocomposite membrane while a negligible loss in rejection is observes. In the presence of magnetic field, blended magnetic NP can change the structure of membrane pores, increases porosity, and finally, increases membrane water flux [12,18,32]. The changes in magnetic membrane structure in the

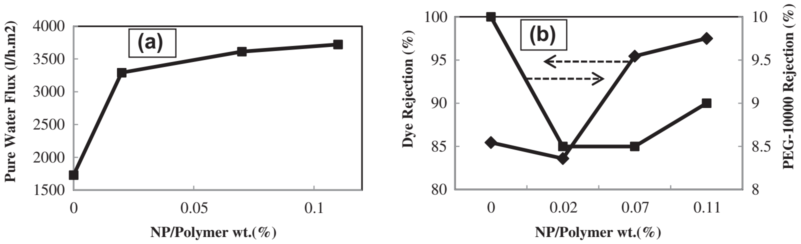

Fig. 4. Effect of NP on (a): pure water flux and (b): organic solute rejection.

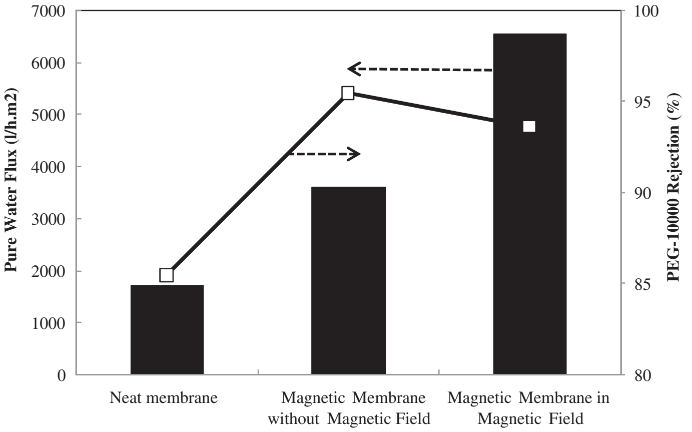

Fig. 5. Effect of magnetic field on filtration performance of neat membrane and nanocomposite membrane ($MNCM_2$).

presence of magnetic field have been reported in the other researches [32].

4. Conclusion

In this work, flat sheet PSf/Fe_3O_4 nanocomposite membrane was synthesized through phase inversion method. The FTIR analyses indicated that magnetic nanocomposite films have O–H and F–O functional group which confirms the presence of magnetic particles in membrane matrix. Moreover, VSM measurements showed that by increasing NP composition the membrane magnetization was also improved. The SEM cross-section images showed that at concentrations lower than 0.07 wt.% of nanoparticle/polymer the hydrophilicity of NP promotes instantaneous phase inversion, increases porosity and permeability, and decrease organic solute rejection of the nanocomposite membrane. When the concentration of NP becomes higher than 0.07 wt.%, the viscosity of the casting solution increases and slows down the phase inversion process, and causes the porosity and permeability to increase. Also organic solute rejection of the nanocomposite membrane is increased. Finally, results showed that it is possible to continuously separate organic contaminate with a high-permeability nanocomposite membrane by adjusting the external magnetic field.

References

[1] M. Amini, M. Homayoonfal, M. Arami, A. Akbari, Modification and characterization of prepared polysulfone ultrafiltration membranes via photografted polymerization: Effect of different additives, Desalin. Water Treat. 9 (2009) 43–48.

[2] P. Le-Clech, V. Chen, T.A.G. Fane, Fouling in membrane bioreactors used in wastewater treatment, J. Membr. Sci. 284 (2006) 17–53.

[3] D.S. Kim, J.S. Kang, Y.M. Lee, The influence of membrane surface properties on fouling in a membrane bioreactor for wastewater treatment, Sep. Sci. Technol. 39(4) (2004) 833–854.

[4] J. Kim, B. Van der Bruggen, The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment, Environ. Pollut. 158 (2010) 2335–2349.

[5] M. Homayoonfal, M.R. Mehrnia, Y.M. Mojtahedi, A.F. Ismail, Effect of metal and metal oxide nanoparticle impregnation route on structure and liquid filtration performance of polymeric nanocomposite membranes: A comprehensive review, Desalin. Water Treat. 51 (2013) 3295–3316.

[6] L.Y. Ng, A.W. Mohammad, C.P. Leo, N. Hilal, Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review, Desalination 308 (2013) 15–33.

[7] K. Zodrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, Water Res. 43 (2009) 715–723.

[8] S.J. Oh, N. Kim, Y.T. Lee, Preparation and characterization of PVDF/TiO_2 organic–inorganic composite membranes for fouling resistance improvement, J. Membr. Sci. 345 (2009) 13–20.

[9] Y.M. Mojtahedi, M.R. Mehrnia, M. Homayoonfal, Fabrication of Al_2O_3/PSf nanocomposite membranes: Efficiency comparison of coating and blending methods in modification of filtration performance, Desalin. Water Treat. 51 (2013) 6736–6742.

[10] N. Maximous, G. Nakhla, W. Wan, K. Wong, Preparation, characterization and performance of Al_2O_3/PES membrane for wastewater filtration, J. Membr. Sci. 341 (2009) 67–75.

[11] S. Balta, A. Sotto, P. Luis, L. Benea, B. Van der Bruggen, J. Kim, A new outlook on membrane enhancement with nanoparticles: The alternative of ZnO, J. Membr. Sci. 389 (2012) 155–161.

[12] P. Daraei, S.S. Madaeni, N. Ghaemi, M.A. Khadivi, B. Astinchap, R. Moradian, Fouling resistant mixed matrix polyethersulfone membranes blended with magnetic nanoparticles: Study of magnetic field induced casting, Sep. Purif. Technol. 109 (2013) 111–121.

[13] H.L. Yang, J.C.T. Lin, C. Huang, Application of nanosilver surface modification to RO membrane and spacer for mitigating biofouling in seawater desalination, Water Res. 43 (2009) 3777–3786.

[14] L.H. Li, J.C. Deng, H.R. Deng, Z.L. Liu, L. Xin, Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes, Carbohydr. Res. 345 (2010) 994–998.

[15] N. Maximous, G. Nakhla, W. Wan, K. Wong, Performance of a novel ZrO_2/PES membrane for wastewater filtration, J. Membr. Sci. 352 (2010) 222–230.

[16] J. Xu, D. Bhattacharyya, Fe/Pd nanoparticle immobilization in microfiltration membrane pores: Synthesis, characterization, and application in the dechlorination of polychlorinated biphenyls, Ind. Eng. Chem. Res. 46 (2007) 2348–2359.

[17] S. Yu, X. Zuo, R. Bao, X. Xu, J. Wang, J. Xu, Effect of SiO_2 nanoparticle addition on the characteristics of a new organic–inorganic hybrid membrane, Polymer 50 (2009) 553–559.

[18] W. RuiJun, C. Yan, X.H. Ming, K.G. Qing, W.Z. Yao, P. Jian, Polysaccharide separation mechanism in polysulfone-Fe3O4 magnetic composite membranes, Chin. Sci. Bull. 56(18) (2011) 1951–1956.

[19] Z.Q. Huang, X.P. Guo, C.L. Guo, Z. Zhang, Magnetization influence on the performance of ferrosoferric oxide: Polyacrylonitrile membranes in ultrafiltration of pig blood solution, Bioprocess Biosyst. Eng. 28 (2006) 415–421.

[20] J. Alam, L.A. Dass, M. Ghasemi, M. Alhoshan, Synthesis and optimization of PES-Fe_3O_4 mixed matrix nanocomposite membrane: Application studies in water purification, Polym. Compos. 34(11) (2013) 1870–1877.

[21] A.H. Lu, E.L. Salabas, F. Schuth, Magnetic nanoparticles: Synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed. 46 (2007) 222–1244.

[22] A.D. Sabde, M.K. Trivedi, V. Ramachandhran, M.S. Hanra, B.M. Misra, Casting and characterization of cellulose acetate butyrate based UF membranes, Desalination 114 (1997) 223–232.

[23] P. Granitzer, K. Rumpf, M. Venkatesan, A.G. Roca, L. Cabrera, M.P. Morales, P. Poelt, M. Albu, Magnetic Study of Fe_3O_4 Nanoparticles Incorporated within Mesoporous Silicon, J. Electrochem. Soc. 157(7) (2010) K145–151.

[24] M.Z. Kassaee, E. Motamedi, M. Majdi, Magnetic Fe_3O_4-graphene oxide/polystyrene: Fabrication and characterization of a promising nanocomposite, Chem. Eng. J. 172 (2011) 540–549.

[25] A. Razmjou, J. Mansouri, V. Chen, The effects of mechanical and chemical modification of TiO_2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes, J. Membr. Sci. 378 (2011) 73–84.

[26] Y. Yang, W. Jun, Z. Qing-zhu, C. Xue-si, Z. Hui-xuan, The research of rheology and thermodynamics of organic–inorganic hybrid membrane during the membrane formation, J. Membr. Sci. 311 (2008) 200–207.

[27] J.F. Li, Z.L. Xu, H. Yang, L.Y. Yu, M. Liu, Effect of TiO_2 nanoparticles on the surface morphology and performance of microporous PES membrane, Appl. Surf. Sci. 255 (2009) 4725–4732.

[28] J.S. Taurozzi, C.A. Crock, V.V. Tarabara, C60-polysulfone nanocomposite membranes: entropic and enthalpic determinants of C60 aggregation and its effects on membrane properties, Desalination 269(1–3) (2011) 111–119.

[29] L.Y. Yu, Z.L. Xu, H.M. Shen, H. Yang, Preparation and characterization of PVDF–SiO_2 composite hollow fiber UF membrane by sol–gel method, J. Membr. Sci. 337 (2009) 257–265.

[30] L. Yan, Y.S. Li, C.B. Xiang, S. Xianda, Effect of nanosized Al_2O_3-particle addition on PVDF ultrafiltration membrane performance, J. Membr. Sci. 276 (2006) 162–167.

[31] G.U. Semblante, S.D.R. Tampubolon, S.J. You, Y.F. Lin, T.C. Chang, F.C. Yen, Fouling reduction in membrane reactor through magnetic particles, J. Membr. Sci. 435 (2013) 62–70.

[32] P. Jian, H. Yahui, W. Yang, L. Linlin, Preparation of polysulfone–Fe_3O_4 composite ultrafiltration membrane and its behavior in magnetic field, J. Membr. Sci. 284 (2006) 9–16.