



## Research Paper

## Fabrication and Characterization of Novel Mixed Matrix Polyethersulfone Nanofiltration Membrane Modified by Iron-Nickel Oxide Nanoparticles

E. Bagheripour, A.R. Moghadassi\*, S.M. Hosseini, M. Nemati

Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak 8349-8-38156, Iran

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## GRAPHICAL ABSTRACT



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## HIGHLIGHTS

- A mixed matrix PES/iron-nickel oxide nanofiltration membrane was prepared by the solution casting technique
- SEM images showed increase of macro-voids' size with an increase of additive concentration
- The membrane water flux was increased initially by an increase of nanoparticle content and then decreased
- Salt rejection was generally improved with an increase of nanoparticle concentration

## ABSTRACT

In this study, a mixed matrix polyethersulfone/iron-nickel oxide nanoparticle nanofiltration membrane was prepared by the solution casting technique. Polyvinylpyrrolidone was also used as a membrane pore former in membrane fabrication. The effect of iron-nickel oxide nanoparticles concentration in the casting solution on the membrane structure and performance was investigated. Scanning optical microscopy (SOM) and scanning electron microscopy analysis (SEM), water contact angle, NaCl/Na<sub>2</sub>SO<sub>4</sub> salt rejection, water flux and tensile strength measurements were also carried out in membrane characterization. SOM images showed relatively uniform particle distribution and surface for the prepared membranes. Moreover, SEM images showed that the macro-voids' size was enhanced in the membrane sub-layer with an increase of additive concentration. Results showed that increasing iron-nickel oxide nanoparticles from 0 to 0.1 wt.% in the membrane matrix caused a decrease in contact angle from 63 to 43° and again increased to 56° by increasing the particles concentration to 1 wt.%. The membrane water flux was enhanced sharply with an increase of nanoparticle concentration up to 0.01 wt.% in the membrane matrix and then decreased slightly at higher additive contents. Salt rejection was generally improved with an increase of nanoparticle concentration. Membrane mechanical strength was initially declined by using iron-nickel oxide nanoparticles up to 0.1 wt.% in the membrane matrix and then increased at higher additive contents. The nanocomposite membranes showed more appropriate antifouling capacity compared to a pristine PES membrane. The effect of feed concentration on membrane salt rejection and water flux was also studied.

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## 1. Introduction

The development of nanofiltration (NF) technology in the separation processes is being greatly studied because of its advantages, such as low operating pressure, high water flux, high rejection of multivalent anion salts

and organic solutes with molecular weights (MW) above 300 g/mol. Therefore, it has got worldwide interest [1]. NF membranes are used in a wide range of drinking water, wastewater and industrial applications. Also, NF membranes have found wide applications in desalination. Desalination is defined as the process of

\* Corresponding author at: Phone: +98 86 32625422, Fax: +98 86 32625423  
E-mail address: [a.moghadassi@gmail.com](mailto:a.moghadassi@gmail.com); [a-moghadassi@araku.ac.ir](mailto:a-moghadassi@araku.ac.ir) (A.R. Moghadassi)

removing salt from seawater or brackish water. In a broader sense of the definition, desalination can also be used for removal of various inorganic ions from solution to produce soft, clean and potable water [2].

A lot of researches have already been performed to improve the NF physiochemical properties, which resulted in various modification techniques. Utilization of different polymeric matrices, polymer blending, different additives loading such as nanoparticles and surface modifications are important ways to obtain appropriate membranes [3–17]. Utilizing inorganic nanoparticles or fillers into polymeric materials have also been examined in many applications to enhance the mechanical, thermal and chemical stability of polymeric matrices in severe conditions such as high temperature and strongly oxidizing the environment and also to improve the separation properties characteristic of membranes based on synergism between the organic-inorganic component properties [18–21].

Currently, no reports have considered incorporating the iron–nickel oxide nanoparticle into the PES based NF membrane. Preparing the new type of NF membrane with appropriate physiochemical properties for application in waste water treatment was the main goal of the current research. For this aim, polyethersulfone (PES)/polyvinylpyrrolidone (PVP) NF membranes were prepared by solution casting techniques.

PES has been extremely used as membrane fabrication material because of its appropriate properties. PES is a hydrophobic polymer and is highly susceptible for fouling. These results are in severe restriction in the permeate flux with constant operation time [22]. There are many researches aiming to improve the hydrophilicity and performance of PES membranes such as modification by blending with hydrophilic polymers, surface grafting polymerization, coating and addition of inorganic fillers [23–27].

Iron-nickel oxide nanoparticles were also employed as inorganic filler additive in membrane fabrication in order to improve the NF physiochemical properties and also to obtain a new nanocomposite membrane.

Magnetic nanoparticles such as various types of iron oxide have attracted much attention in biomedical engineering, bio-separation technologies and membrane processes in water treatment. The iron–nickel oxide nanoparticles are a new class of advanced materials with very interesting features and capacity such as superior magnetic, electrical and selective adsorption properties, which have also been utilized in water treatment [28–31]. Like other hydrophilic metal oxide nanoparticles [27], the presence of hydrophilic iron–nickel oxide nanoparticles can directly effect phase inversion kinetics and the rate of membrane precipitation during the replacement of solvent and non-solvent leading to the growth of macro-voids in the sub-layer of the membrane matrix and result in improvement of the water flux. Additionally, due to its superior adsorptive characteristic, it may strongly affect the selective adsorption of ions and metal removal leading to enhancement of rejection capability. Thus, effects of iron–nickel oxide nanoparticle concentration in the casting solution on the physiochemical properties of prepared NF membranes were studied and evaluated. The performance of the prepared NF membranes was tested for removing sodium chloride/sodium sulfate (NaCl/Na<sub>2</sub>SO<sub>4</sub>) from water. SEM, SOM, water content, and tensile strength were also carried out in membrane characterization. The results are valuable for NF membrane processes applied in water recovery and waste water softening.

## 2. Materials and methods

### 2.1. Materials

Polyethersulfone (PES) provided by BASF, Inc., Germany (Ultrason E6020P, MW= 58,000 g/mol), polyvinylpyrrolidone (PVP) provided by Merck (MW= 25,000 g/mol), N,N dimethylacetamide (DMAc, MW= 87.12 g/mol, density= g/cm<sup>3</sup>) supplied by Merck and deionized water were used as polymer base binder, pore former, solvent and non-solvent, respectively. Iron-nickel oxide (nano powder, <50 nm particle sizes) from Sigma-Aldrich (US) was also employed as inorganic filler additives. NaCl and Na<sub>2</sub>SO<sub>4</sub> salts were supplied from Merck.

### 2.2. Fabrication of composite NF membrane

The nanocomposite membranes were prepared by the casting solution technique and phase inversion method. The fabrication was done by dissolving a certain amount of PES (20 wt.%) and PVP (1 wt.%) into the solvent (DMAc) in glassy reactors by a mechanical stirrer (model: Velp Scientifica Multi 6 stirrer) for more than 4hr. This was followed by dispersing iron-nickel oxide nanoparticles (with various concentrations) as an additive (nano-filler) in polymeric solutions. Also, for better dispersion of nanoparticles and breaking up their aggregates, the solutions were sonicated for 40min by an ultrasonic cleaner bath (Parsonic 11S model, S/N PN-88159,

Iran). The obtained homogeneous solutions were cast onto clean and dry glass plates using a casting knife with a constant thickness of 150 μm. Then, they were dipped into deionized water as non-solvent without prior evaporation time. After exchanging the solvent and non-solvent and precipitation step, membranes were formed. Then they were kept in new containers with fresh deionized water for one day to remove any soluble components in the membrane structures. The membranes were dried between two filter paper sheets at room temperature (25±2 °C) for one day before use. The composition of the used casting solutions is given in Table 1.

**Table 1**  
Composition of casting solutions used in fabrication of mixed matrix nanofiltration membrane; in constant concentration of PES and PVP (20:1 wt./wt.%).

Membrane (ID)	Nanoparticles (Iron-nickel oxide) (wt.%)	Solvent (DMAc) (wt.%)
M1	0	79
M2	0.01	78.99
M3	0.1	78.9
M4	1	78

### 2.3. Membrane characterization

#### 2.3.1. Water contact angle

To investigate the surface wettability and surface hydrophilicity of PES/iron-nickel oxide NF membranes, the water contact angle measurement was employed. Doing so, very small droplets of the deionized water were dropped on the membranes surface and the imaging of droplets were taken by use of a digital camera.

#### 2.3.2. Membrane performance

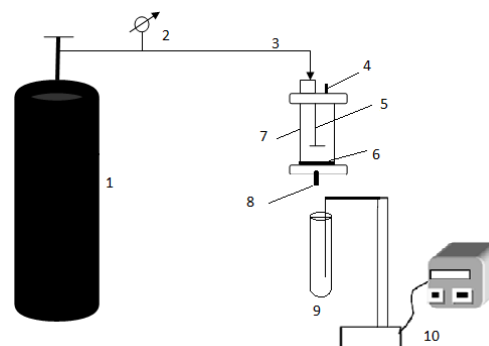
The performance of fabricated membranes was studied using the NF dead end cell (Figure 1). The feed solutions were prepared separately by dissolving 1000 mg/L salts in deionized water (Na<sub>2</sub>SO<sub>4</sub> and NaCl). The permeation flux was determined by measuring water that passed through the membranes in terms of L/m<sup>2</sup>h and calculated by the equation below [32]. The pressure was fixed at 5 bar for all.

$$J_v = Q / (A \cdot \Delta t) \quad (1)$$

where  $J_v$  (L/m<sup>2</sup>h),  $Q$  (L),  $A$  (m<sup>2</sup>), and  $\Delta t$  (h) are expressed as permeation flux, content of permeated water, membrane area and sampling time, respectively. For salt rejection percent calculations, the following equation was used [33, 34]:

$$\text{Rejection \%} = 1 - (C_p / C_f) * 100 \quad (2)$$

where  $C_p$  and  $C_f$  are ionic solution concentration in permeate and feed, respectively both of which have been measured by a conductivity meter (Ohaus Corporation, S/N B143385306, USA).



**Fig. 1.** Schematic diagram of dead end cell set up: (1) nitrogen gas, (2) pressure gage, (3) nitrogen entrance, (4) feed entrance, (5) agitator, (6) membrane, (7) cell, (8) permeate output, (9) collector, (10) conductivity meter.

#### 2.3.3. Membrane mechanical strength

For characterization of the fabricated NF membranes mechanical properties, their tensile strengths were examined according to ASTM1922-03 [35]. Thus, all samples were prepared in standard sizes and the experiments were done three times to minimize the experimental errors.

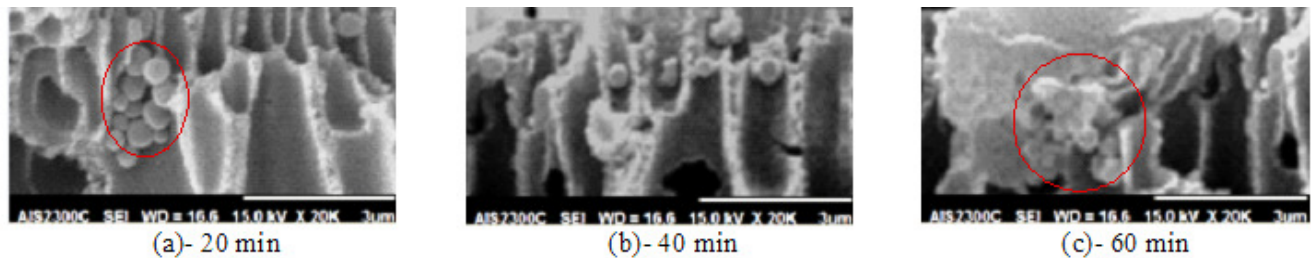


Fig. 2. The effect of sonication time on the nanoparticles dispersion (SEM analysis): (a) 20 min, (b) 40 min, and (c) 60 min.

### 2.3.4. Membrane morphology

#### 2.3.4.1. Scanning electron microscopy (SEM)

For cross sectional characterization of the fabricated membranes, scanning electron microscopy (SEM) (Seron Technology Inc. Korea) was used. Before examination of the prepared membranes by SEM, the membranes were dipped in liquid nitrogen for 5 min. After being frozen, they were broken. Then, they were sputtered with gold thin film and scanned with an electron microscope.

#### 2.3.4.2. Scanning optical microscopy (SOM)

For characterization of the surface of the fabricated membranes, scanning optical microscopy (Olympus, model IX 70, transmission mode with light going through the sample) was used. For this aim, the membranes were cut into small sizes. Then they were placed between two glassy lamellas and were observed by the optical microscope.

## 3. Results and discussion

### 3.1. Effect of sonication on nanoparticles dispersion

The effect of sonication time on the iron-nickel oxide nanoparticles dispersion in the membrane matrix was studied. As showed in Figure 2, homogeneity and nanoparticles dispersion was improved with an increase of sonication time from 20 to 40 min. As observed in the images, nanoparticles agglomeration occurred again with a further increase in sonication time up to 60 min. Thus, the optimum sonication time was selected as 40 min during membrane fabrication.

### 3.2. Effect of iron-nickel oxide nanoparticles on morphology of NF membrane

The SEM cross sectional images of prepared membranes with different concentrations of iron-nickel oxide nanoparticles are shown in Figure 3. All prepared membranes showed asymmetric structures with a dense top layer and finger like sub-layer. SEM images exhibited that an increase of additive nanoparticles in the membrane matrix led to a significant increase of the finger like channels' size in the membrane sub-layer. This may be attributed to an increase of casting solution thermodynamic instability in the coagulation bath by using iron-nickel oxide nanoparticles, which lead to a fast de-mixing process. This increases the size of macrovoids in the membrane matrix [36].

SOM analysis was also utilized to investigate the nanoparticles distribution in the membrane matrix. SOM images (Figure 4) showed relatively uniform particle distribution and surface for the prepared membrane.

### 3.3. Membrane water contact angle

To investigate the hydrophilicity and wettability of bare and mixed PES membranes, the water contact angle experiment was used. Figure 5 shows changes of water contact angle with the addition of various content of iron-nickel oxide nanoparticles. According to the results, increasing nanoparticle content from 0 to 0.1 wt.% in the casting solution has decreased water contact angle from 63 to 43° and again increased to 56° by further increasing the nanoparticles content (1 wt.%).

The smaller contact angle indicates higher surface hydrophilicity [37]. Thus, it can be concluded that membrane hydrophilicity was improved by increasing iron-nickel oxide nanoparticles content in the range of 0-0.1 wt.% into the casting solution. This may be due to the hydrophilic characteristic of iron-nickel oxide nanoparticles and an increase of pore volume and size. Iron-nickel oxide nanoparticles like other metal nanoparticles tend to migrate to the membrane surface during the phase inversion process. The migration of NPs to the top of the membrane at a high nanoparticle loading ratio (1 wt.%) (see Figure 6, surface images of top and bottom of M1 and M4) results in

more changes in the membrane surface pores (pore blockage) [27] leading to a decrease in the water adsorption on the membrane surface. This may be the main reason for contact angle incensement at M4.

### 3.4. Separation performance of prepared membranes

#### 3.4.1. Water flux

The results (Figure 7) showed that a water flux of the prepared mixed matrix membranes was increased sharply with an increase of additive nanoparticles up to 0.01 wt.% in the casting solution. This may be due to an increase of the membrane water content which improves the water flux [38]. Moreover, as shown in SEM images, an increase of the channels' size in the membrane sub-layer with an increase of additive concentration facilitates the water transportation through the membrane and enhances the water flux [31, 35]. The membrane water flux was decreased slightly by a further increase of nanoparticle concentration from 0.01 to 1 wt.% in the prepared membranes. This may be attributed to the pore filling/blocking phenomenon [39, 40] at higher additive concentrations, which declines the water traffic. Moreover, inappropriate nanoparticle dispersion or nanoparticle agglomeration in the membrane matrix with high filler content reduces the membrane performance [31, 41].

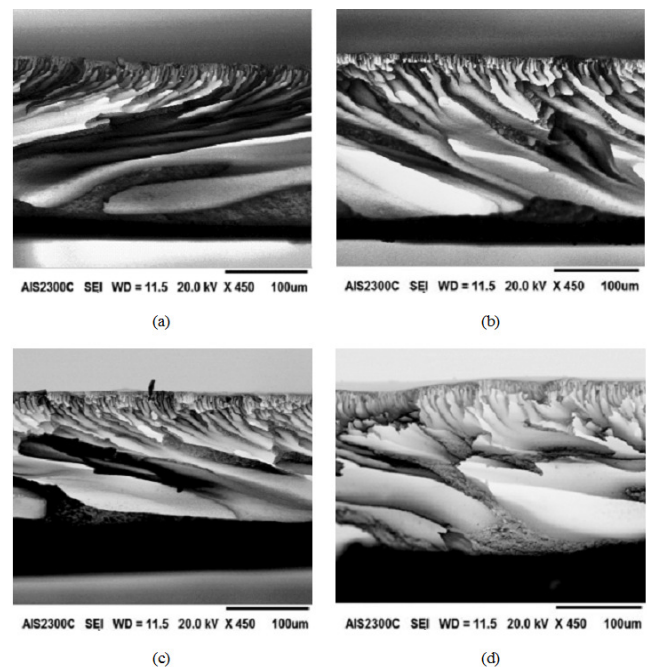


Fig. 3. The SEM cross sectional images of prepared membranes with different concentrations of iron-nickel oxide nanoparticles: (a) M1, (b) M2, (c) M3, and (d) M4.

#### 3.4.2. Salt rejection

The membranes' salt rejection was investigated by using NaCl (mono-valent) and Na<sub>2</sub>SO<sub>4</sub> (bivalent) aqueous solutions. The results (Figure 8) indicated that an increase of iron-nickel oxide nanoparticles concentration in the casting solution led to an increase of sodium chloride and sodium sulfate rejection for the prepared NF membranes. This may be due to the adsorption characteristic of additive nanoparticles, which caused superior interactions between ions and the membrane matrix. Moreover, the nanoparticles dispersion among the chain segments of the PES matrix diminishes the pore sizes on the membrane surface and consequently improves ion rejection by the sieving phenomenon.

Also, the membrane showed higher salt rejection for bivalent ions compared to the monovalent type. Among the prepared membranes, the modified membrane containing 1 wt.% nanoparticles showed the highest ionic rejection compared to others.

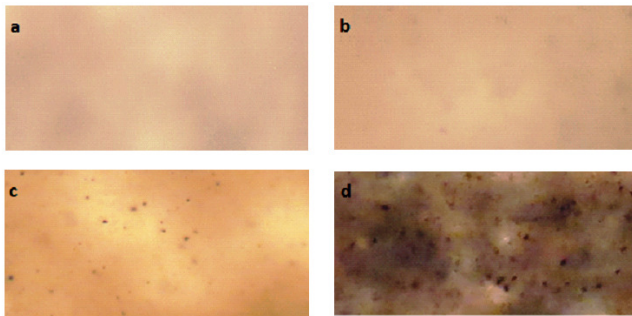


Fig. 4. The SOM images (magnification order of 10,000) of prepared membranes with different concentrations of nanoparticles: (a) M1, (b) M2, (c) M3, and (d) M4.

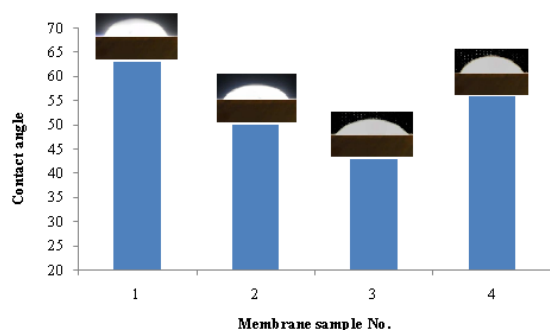


Fig. 5. The effect of iron-nickel oxide nanoparticles concentration on water contact angle.



Fig. 6. Digital photograph of top and bottom surface of M1 and M4.

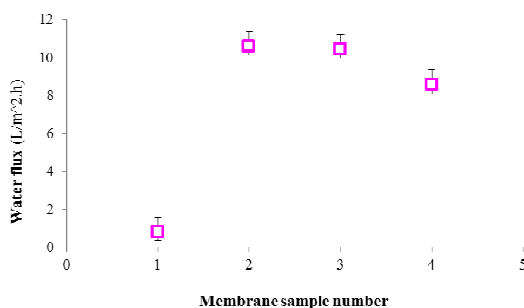


Fig. 7. The effect of iron-nickel oxide nanoparticles concentration on membrane water flux.

### 3.5. Salt rejection stability of fabricated membranes

Figure 9 described the membranes rejection stability against increasing in flux. The obtained results revealed that modified membranes containing iron-nickel oxide nanoparticles showed more stable performance/salt rejection stability characteristics compared to a pristine PES membrane. The modified membrane containing 0.1 wt.% nanoparticles showed more appropriate stable performance compared to other modified membranes and pristine ones. This may be explained by the more appropriate nanoparticles loading content and dispersion. The nanoparticles loading with the optimum content in the casting solution provides homogeneity in the membrane performance. In this condition, lower changes of performance during filtration time can be expected.

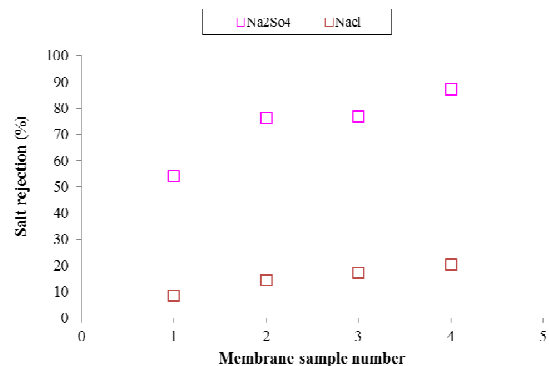


Fig. 8. The effect of nanoparticles concentration on membrane rejection (mono and bivalent).

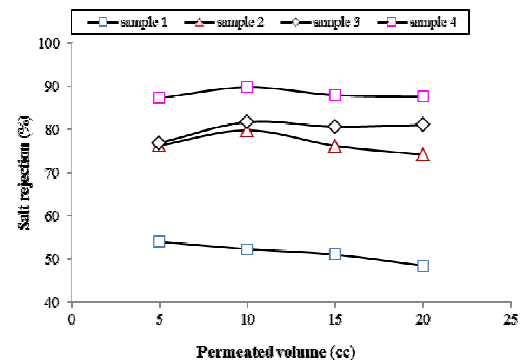


Fig. 9. Salt (Na<sub>2</sub>SO<sub>4</sub>) rejection stability of fabricated membranes.

### 3.6. The effect of feed concentration on separation performance

The effect of feed concentration on salt rejection of modified NF membranes containing 1 wt.% nanoparticles is shown in Figure 10. The results showed that membrane salt rejection was improved initially by an increase of feed concentration from 1000 to 1300 mg/l Na<sub>2</sub>SO<sub>4</sub> solutions. This may be due to more ions adsorption on the membrane surface, which reduces the membrane pore sizes and thus restricts the ions passage through the membrane. Salt rejection was decreased again with a further increase of feed concentration from 1300 to 1800 mg/l. This is attributed to the polarization phenomenon on the membrane surface at high feed concentration which makes possible the ions percolation and reduces the rejection.

Also, the effect of feed concentration on water flux is shown in Figure 10. The obtained results illustrated that membrane water flux was decreased with an increase of feed concentration. This may be due to membrane shrinkage at high electrolyte concentrations, which reduces the water flux because of pore size reduction. Similar results were reported by others [42, 43].

### 3.7. Membrane mechanical strength

The effect of iron-nickel oxide nanoparticles concentration on membrane mechanical properties was examined by the membranes tensile strength measurement. The results (Figure 11) revealed that an increase of nanoparticle concentration in the casting solution up to 0.1 wt.% led to a

slight decrease of membrane tensile strength. This is due to an increase of the channels' size in the membrane matrix with an increase of nanoparticles content ratio, which leads to a loose structure for the membranes and declines the membranes tensile strength. For minimizing the experimental errors, all measurements were carried out three times and then their average was reported. Also, channels filling by nanoparticles at high additive concentration increase the membrane mechanical strength. Moreover, more interactions of polymer and inorganic nanoparticles at high additive content are another reason for tensile strength improvement for the membrane.

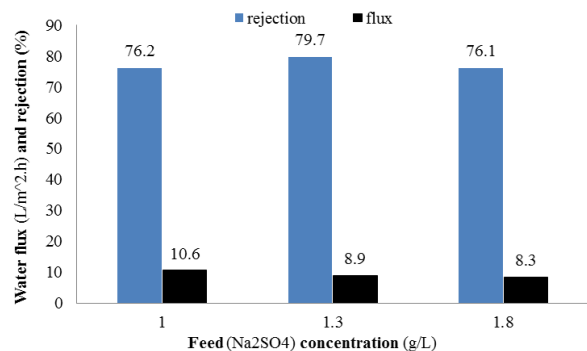


Fig. 10. The effect of feed concentration on membrane flux and rejection for modified membrane containing 1 wt.% nanoparticles.

#### 4. Conclusions

The mixed matrix polyether sulfone-co-iron-nickel oxide nanoparticles NF membrane was prepared by the solution casting technique. The effect of iron-nickel oxide nanoparticles concentration in the casting solution on the membrane structure and performance was investigated. SOM images showed relatively uniform particle distribution and surface for the prepared membranes. Moreover, SEM images showed that the macro-voids' size was enhanced in the membrane sub-layer by an increase of additive concentration. Contact angle measurements showed improvement of the membrane hydrophilicity, generally by the addition of iron-nickel oxide nanoparticles into the casting solution. The membrane water flux was enhanced sharply

#### References

[1] R.J. Peterson, Composite reverse osmosis and NF membranes, *J. Membr. Sci.* 83 (1993) 81–150.

[2] M. Al-Sofi, A. Hassan, G. Mustafa, A. Dalvi, M. Kither, NF as a means of achieving higher TBT of 120 °C in MSF, *Desalination* 118 (1998) 123–129.

[3] V.K. Shahi, S.K. Thampy, R. Rangarajan, Studies on transport properties of surfactant immobilized anion-exchange membrane, *J. Membr. Sci.* 158 (1999) 77–83.

[4] P.V. Vyas, P. Ray, S.K. Adhikary, B.G. Shah, R. Rangarajan, Studies of the effect of variation of blend ratio on permselectivity and heterogeneity of ion-exchange membranes, *J. Colloid. Interface Sci.* 257 (2003) 127–134.

[5] A. Elattar, A. Elmidaoui, N. Pismenskaia, C. Gavach, G. Pourcelly, Comparison of transport properties of monovalent anions through anion-exchange membranes, *J. Membr. Sci.* 143 (1998) 249–261.

[6] S.M. Hosseini, S.S. Madaeni, A.R. Khodabakhshi, Preparation and surface modification of PVC/SBR heterogeneous cation exchange membrane with silver nanoparticles by plasma treatment, *J. Membr. Sci.* 365 (2010) 438–446.

[7] A.R. Khodabakhshi, S.S. Madaeni, S.M. Hosseini, Preparation and characterization of monovalent ion-selective poly(vinyl chloride)-blend-poly(styrene-co-butadiene) heterogeneous anion-exchange membranes, *Polym. Int.* 60 (2011) 466–476.

[8] J. Balster, O. Krupenko, I. Punt, D.F. Stamatiadis, M. Wessling, Preparation and characterization of monovalent ion selective cation exchange membranes based on sulfonated poly(ether etherketon), *J. Membr. Sci.* 263 (2005) 137–145.

[9] R.K. Nagarale, G.S. Gohil, V.K. Shahi, R. Rangarajan, Preparation and electrochemical characterization of cation-exchange membranes with different functional groups, *Colloid. Surf. A Physicochem. Eng. Asp.* 251 (2004) 133–140.

[10] T. Sata, W. Yang, Studies on cation-exchange membranes having permselectivity between cations in electro dialysis, *J. Membr. Sci.* 206 (2002) 31–60.

[11] T. Sata, Ion exchange membranes: Preparation, characterization, modification and application, RSC Publishing, Cambridge, United Kingdom, 2004.

[12] A. Bottino, G. Capannelli, V.D. Asti, P. Piaggio, Preparation and properties of novel organic-inorganic porous membranes, *Sep. Purif. Technol.* 22–23 (2001) 269–275.

[13] S.J. Oh, N. Kim, Y.T. Lee, Preparation and characterization of PVDF/TiO<sub>2</sub> organic-inorganic composite membranes for fouling resistance improvement, *J. Membr. Sci.* 345 (2009) 13–20.

[14] T.-S. Chung, M.L. Chng, K.P. Pramoda, PAMAM dendrimer-induced cross-linking modification of polyimide membranes, *Langmuir* 20 (2004) 2966–2969.

[15] D.A. Tomalia, Starburst dendrimers-nanoscope super molecules according to dendritic rules and principles, *Macromol. Symp.* 101 (1996) 243–255.

with an increase of nanoparticle concentration up to 0.01 wt.% in the membrane matrix and then showed a decreasing trend by more additive content. Salt rejection was improved continuously with an increase of nanoparticle concentration. The membrane mechanical strength was also initially declined by using iron-nickel oxide nanoparticles up to 0.1 wt.% in the membrane matrix and then increased at higher additive contents up to 1 wt.% in the prepared membranes. The nanocomposite membranes showed more appropriate antifouling characteristics compared to the pristine PES membrane. The results showed that membrane salt rejection was initially improved with an increase of feed concentration from 1000 to 1300 mg/l Na<sub>2</sub>SO<sub>4</sub> solutions. Salt rejection was decreased again with a further increase of feed concentration from 1300 to 1800 mg/l. The obtained results also illustrated that the membrane water flux was decreased by an increase of feed concentration.

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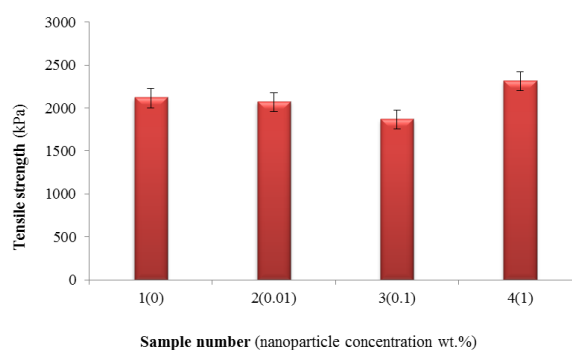


Fig. 11. The effect of iron-nickel oxide nanoparticle concentration on membrane tensile strength.

[16] M.S. Diallo, L. Balogh, A. Shafagati, Poly(amidoamine) dendrimers: a new class of high capacity chelating agents for Cu(II) ions, *Environ. Sci. Technol.* 33 (1999) 822–824.

[17] C.M. Wu, T.W. Xu, W.H. Yang, A new inorganic-organic negatively charged membrane: membrane preparation and characterizations, *J. Membr. Sci.* 224 (2003) 117–125.

[18] M.G. Nik, X.Y. Chen, S. Kaliaguine, Functionalized metal organic frame work polyimide mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation, *J. Membr. Sci.* 413 (2012) 48–61.

[19] C.C. Yang, Y.J.J. Li, T.H. Liou, Preparation of novel poly(vinyl alcohol)/SiO<sub>2</sub> nanocomposite membranes by a sol-gel process and their application on alkaline DMFC, *Desalination* 276 (2011) 366–372.

[20] M.A. Zulfikar, A.W. Mohammad, N. Hilal, Preparation and characterization of novel porous PMMA-SiO<sub>2</sub> hybrid membranes, *Desalination* 192 (2006) 262–270.

[21] T.V. Gestel, C. Vandecasteele, A. Buekenhoudt, Alumina and titania multilayer membranes for NF: preparation, characterization and chemical stability, *J. Membr. Sci.* 207 (2002) 73–89.

[22] M.L. Luo, J.Q. Zhao, W. Tang, C.S. Pu, Hydrophilic modification of poly(ether sulfone) ultrafiltration membrane surface by self-assembly of TiO<sub>2</sub> nanoparticles, *Appl. Surf. Sci.* 249 (2005) 76–84.

[23] I. Genne, S. Kuypers, R. Leysen, Effect of the addition of ZrO<sub>2</sub> to polysulfone based UF membrane, *J. Membr. Sci.* 113 (1996) 343–350.

[24] Y.N. Yang, P. Wang, Q.Z. Zheng, Preparation and properties of polysulfone/TiO<sub>2</sub> composite ultrafiltration membranes, *J. Polym. Sci.: Part B Polym. Phys.* 44 (2006) 879–887.

[25] X.C. Cao, J. Ma, X.H. Shi, Z.J. Ren, Effect of TiO<sub>2</sub> nanoparticles size on the performance of PVDF membrane, *Appl. Surf. Sci.* 253 (2006) 2003–2010.

[26] H.S. Lee, S.J. Im, J.H. Kim, Polyamide thin-film NF membranes containing TiO<sub>2</sub> nanoparticles, *Desalination* 219 (2008) 48–56.

[27] P. Daraei, S.S. Madaeni, N. Ghaemi, E. Salehi, M.A. Khadivi, R. Moradian, B. Astinchap, Novel polyethersulfone nanocomposite membrane prepared by PANI/Fe<sub>3</sub>O<sub>4</sub> nanoparticles with enhanced performance for Cu(II) removal from water, *J. Membr. Sci.* 415–416 (2012) 250–259.

[28] N. Boujelben, J. Bouzid, Z. Elougar, Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: study in single and binary systems, *J. Hazard. Mater.* 163 (2009) 376–382.

- [29] L. Wei, G. Yang, R. Wang, W. Ma, Selective adsorption and separation of chromium (VI) on the magnetic iron–nickel oxide from waste nickel liquid, *J. Hazard. Mater.* 164 (2009) 1159–1163.
- [30] S.M. Hosseini, S.S. Madaeni, A.R. Heidari, A. Amirimehr, Preparation and characterization of ion-selective polyvinyl chloride based heterogeneous cation exchange membrane modified by magnetic iron–nickel oxide nanoparticles, *Desalination* 284 (2012) 191–199.
- [31] S. Ansari, A.R. Moghadassi, S.M. Hosseini, Fabrication of novel poly (phenylene ether ether sulfone) based nanocomposite membrane modified by  $\text{Fe}_2\text{NiO}_4$  nanoparticles and ethanol as organic modifier, *Desalination* 357 (2015) 189–196.
- [32] R. Han, S. Zhang, C. Liu, Y. Wang, X. Jian, Effect of NaA zeolite particle addition on poly(phthalazinone ether sulfone ketone) composite ultrafiltration (UF) membrane performance, *J. Membr. Sci.* 345 (2009) 5–12.
- [33] H.S. Lee, S.J. Im, J.H. Kim, H.J. Kim, J.P. Kim, B.R. Min, Polyamide thin-film NF membranes containing  $\text{TiO}_2$  nanoparticles, *Desalination* 219 (2008) 48–56.
- [34] C. Hegde, A.M. Isloor, M. Padaki, H.-K. Fun, Synthesis and performance characterization of PS-PPEES nanoporous membranes with nonwoven porous support, *Arabian J. Chem.* 6 (2013) 319–326.
- [35] A. Gholami, A.R. Moghadassi, S.M. Hosseini, S. Shabani, F. Gholami, Preparation and characterization of polyvinyl chloride based nanocomposite NF membrane modified by iron oxide nanoparticles for lead removal from water, *J. Ind. Eng. Chem.* 20 (2014) 1517–1522.
- [36] N. Ghaemi, S.S. Madaeni, A. Alizadeh, P. Daraei, A.A. Zinatizadeh, F. Rahimpour, Separation of nitrophenols using cellulose acetate NF membrane: Influence of surfactant additives, *Sep. Purif. Technol.* 85 (2012) 147–156.
- [37] X. Chang, Z. Wang, S. Quan, Y. Xu, Z. Jiang, L. Shao, Exploring the synergetic effects of graphene oxide (GO) and polyvinylpyrrolidone (PVP) on poly(vinylidene fluoride) (PVDF) ultrafiltration membrane performance, *Appl. Surf. Sci.* 316 (2014) 537–548.
- [38] J.-N. Shen, H.-M. Ruan, L.-G. Wu, C.-J. Gao, Preparation and characterization of PES– $\text{SiO}_2$  organic–inorganic composite ultrafiltration membrane for raw water pretreatment, *Chem. Eng. J.* 168 (2011) 1272–1278.
- [39] C.A. Smolders, A.J. Reuvers, R.M. Boom, I.M. Wienk, Microstructures in phase-inversion membranes. Part I. Formation of macrovoids, *J. Membr. Sci.* 73 (1992) 259–275.
- [40] C.F. Xiao, Microvoid formation of acrylic copolymer (PAC)/cellulose acetate (CA) blend fibers, *J. Appl. Polym. Sci.* 41 (1990) 439–444.
- [41] P. Daraei, S.S. Madaeni, N. Ghaemi, H. Ahmadi Monfared, M.A. Khadivi, Fabrication of PES NF membrane by simultaneous use of multi-walled carbon nanotube and surface graft polymerization method: Comparison of MWCNT and PAA modified MWCNT, *Sep. Purif. Technol.* 104 (2013) 32–44.
- [42] L. Jin, W. Shi, S. Yu, X. Yi, N. Sun, C. Ma, Y. Liu, Preparation and characterization of a novel PA– $\text{SiO}_2$  NF membrane for raw water treatment, *Desalination* 298 (2012) 34–41.
- [43] L.M. Jin, S.L. Yu, W.X. Shi, X.S. Yi, N. Sun, Y.L. Ge, C. Ma, Synthesis of a novel composite NF membrane incorporated  $\text{SiO}_2$  nanoparticles for oily wastewater desalination, *Polymer* 53 (2012) 5295–5303.