

Preparation of novel NF membrane via interfacial cross-linking polymerization

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Abstract. The goal of present work is the preparation of a novel positively charged nanofiltration (NF) membrane and its development for the cation removal of aqueous solutions. This NF membrane was fabricated by the surface modification of polysulfone (PSf) ultrafiltration support. The active top-layer was formed by interfacial cross-linking polymerization of poly(ethyleneimine) (PEI) with p-xylylene dichloride (XDC) and then quaternized with methyl iodide to form a perpetually positively charged layer. In order to improve the efficiency of nanofiltration membrane, the concentration of PEI, XDC and methyl iodide solutions, PEI coating and cross-linking time have been optimized. As a result, a high water flux and high CaCl₂ rejection (1,000 ppm) was obtained for the composite membrane with values of 18.29 L/m².h and 93.62% at 4 bar and 25°C, respectively. The rejections of NF membrane for different salt solutions followed the order of Na₂SO₄ < MgSO₄ < NaCl < CaCl₂. Molecular weight of cut off (MWCO) was calculated via retaining of PEG solutions with different molecular weights that finally, it revealed the Stokes and hydrodynamic radius of 1.457 and 2.507 nm on the membrane selective layer, respectively. The most efficient positively charged nanofiltration membrane exhibited a Ni²⁺ rejection of 96.26% for industrial wastewater from Shamse Hadaf Co. (Kashan, Iran).

Keywords: cross-linking; nanofiltration; poly (ethyleneimine); polysulfone; positively charged membrane

1. Introduction

Nanofiltration (NF) is a kind of membrane separation technique that acts as ultrafiltration (UF)-reverse osmosis (RO) intermediate. This technique is utilized for dye removal in the textile industry (Akbari *et al.* 2007, 2006), separation of important compounds such as amoxicillin from the pharmaceutical wastewaters (Derakhsheshpoor *et al.* 2013), desalination (Rahimpour *et al.* 2010, Van der Bruggen and Vandecasteele 2003) and wastewater treatment (Li *et al.* 2008, Baker 2004) due to its own outstanding membrane properties like a high permeate flux, high rejection of multivalent salts, low operating pressure and low primary investment and operating cost (Rahimpour *et al.* 2010). Nanofiltration membranes have a composite structure with a top selective layer which controls solute transfer. The selectivity of top layer in these membranes is based on

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pore size and Donnan exclusion (Oatley *et al.* 2013, Silva *et al.* 2011, Szymczyk *et al.* 2007).

Usually, nanofiltration membranes are made by surface modification of an ultrafiltration membrane support (Lau *et al.* 2012, Van der Bruggen *et al.* 2008). Conventional methods for surface modification include interfacial polymerization (Lau *et al.* 2012, Li *et al.* 2009), UV photo grafting (Akbari *et al.* 2006, 2007, Li *et al.* 2011), low temperature plasma grafting (Kravets *et al.* 2010, Zhao *et al.* 2004) and chemical cross-linking (Huang *et al.* 2009, Wei *et al.* 2008, Huang *et al.* 2006). Most commercially available nanofiltration membranes are composite polyamide membranes prepared by interfacial polymerization of diamines (such as piperazine) and acyl chlorides (such as trimesoyl chloride, TMC). These produced nanofiltration membranes usually have a negatively charged separation layer (Zhang *et al.* 2011). To improve the separation of cations in aqueous solutions, membranes surface should have positive charge, too. A few studies have been carried out on positively charged NF membranes (Dirir *et al.* 2015, Ouyang *et al.* 2008). Therefore, it is theoretically and practically important to study the attribute of positively charged NF membranes for the separation of cations.

Chiang *et al.* 2009 synthesized a number of positively charged NF membranes via interfacial polymerization from hyper-branched poly(ethyleneimine) which was reacted with two acyl chlorides: trimesoyl chloride (TMC) and terephthaloyl chloride (TPC). These membranes had the same rejection order: $\text{MgCl}_2 > \text{MgSO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$. The PEI/TMC had a higher NaCl rejection than PEI/TPC, however it had a larger pore size. Du and Zhao 2004 fabricated polysulfone composite membrane with a thin charged layer for nanofiltration using interfacial cross-linking method. The rejection of MgSO_4 and NaCl with this membrane (1 g/L aqueous feed solution) was almost 90% and 78% at 8 bar and 30°C, respectively. Yang *et al.* 2009 hydrophilized the surface of microporous polypropylene membrane by the interfacial cross-linking of poly(ethyleneimine) and it was used for the protein filtration (bovine serum albumin and lysozyme). As a result, it suggested an excellent fouling resistant for two proteins. Also, Li *et al.* 2011 used p-xylylene dichloride (XDC) cross-linking after UV-induced grafting for the quaternization of surface membrane. Under the optimized preparing conditions, the water flux and MgCl_2 rejection (1 g/L) of composite membranes reached to 60.3 l/m².h and 93.2%, respectively.

In this study, a novel NF membrane was prepared by coating PEI on the PSf UF membrane because of its good chemical and thermal stability and followed by cross-linking with XDC. After that, the secondary and tertiary amines on the top layer were quaternized by methyl iodide. Finally, the performance of PEI/PSf nanofiltration membranes were determined and discussed using the filtration of aqueous feed solutions with CaCl_2 , NaCl, MgSO_4 and Na_2SO_4 . The optimum positively charged nanofiltration membrane will be utilized for Ni^{2+} removal from industrial wastewater in Shamse Hadaf Co. (Kashan, Iran).

2. Experimental

2.1 Materials

Polysulfone pellets were supplied by Sigma-Aldrich (PSf, $M_n = 35,000$ g/mol) and used as the polymer for the preparation of ultrafiltration membrane supports. Polyethylene glycol (PEG, $M_w = 6,000$ g/mol) and N-Methyl-2-pyrrolidone (NMP) were purchased from Merck and used as the pore former and solvent, respectively. Branched poly(ethyleneimine) (PEI, $M_w = 60,000$ g/mol) and p-Xylylene dichloride (XDC) were supplied by Across and pure Methyl iodide was supplied

by Merck as the components of positively charged thin-film. n-Heptane, Ethanol (96%), Acetone as the solvents for the membrane preparation and salts (CaCl_2 , NaCl , MgSO_4 , Na_2SO_4 and NiCl_2) for the characterization were prepared from Merck. Also, deionized water was used as the non-solvent agent in the coagulation bath.

2.2 Preparation of PSf ultrafiltration flat sheet support

Casting solution for the preparation of ultrafiltration membrane support was prepared by dissolving 16% wt. of PSf and 14 % wt. PEG in NMP at the temperature of 70°C. The solution was magnetically stirred for at least one day and sonicated (Bandelin DT 255H, Germany) for 2 min to guarantee complete dissolution of polymer. The homogenous solution stayed for 1 h where its bubbles were removed. The bubble significantly influenced the membrane porosity. After that, the prepared homogeneous solution was cast using a film applicator to 256 μm clearance gap on a glass plate substrate. Temperature and relative humidity of casting environment were $\sim 24^\circ\text{C}$ and 23%, respectively. The cast film was immediately (without a gap time) immersed in a deionized water bath to complete the phase separation, where the exchange between solvent (NMP) and non-solvent (water) was induced. After complete coagulation, the membrane was transferred into a pure water bath. The bath was refreshed frequently for at least 24 h. This was done to ensure the complete removal of the residual solvent from the membrane. The pure water permeability coefficient for this polysulfone UF membrane was 840 $\text{L}/\text{m}^2\cdot\text{h}\cdot\text{bar}$.

2.3 Interfacial cross-linking polymerization process

PEI/PSf composite NF membrane was firstly prepared by coating PEI aqueous solutions on the surface of PSf support for different durations and then drying for 2 h. PEI coated membrane was secondly immersed into 50 mL of XDC/n-heptane solutions as cross-linker with certain concentration. The interfacial cross-linking reaction between PEI and XDC was carried out at the room temperature for 5 h. After cross-linking reaction, the modified membrane was washed with ethanol to remove excess materials. At the next step, the membrane was soaked in 0.25 M NaOH solution to remove H^+ from the surface. Finally, in order to quaternize of PEI on top layer, the membrane was dipped in CH_3I /ethanol solutions in for 2 h. The interfacial cross-linking polymerization process of PEI/PSf composite nanofiltration membrane is schematically showed in Fig. 1.

2.4 Membrane characterization

Fourier transform infrared spectroscopy (FT-IR, ABB-Bomem MB100, Canada) was employed to investigate the surface chemical composition changes of PSf membrane before and after modification with the spectra of a wave number ranging from 4,000 to 400 cm^{-1} . The changes in the surface morphology and cross-section of PSf membrane was evaluated before and after modification by scanning electron microscope (SEM, KYKY-EM 3200, China) and atomic force microscopy (AFM, NanoScope E). In order to maintain constant cross-section morphology, the membrane samples were broken in liquid nitrogen and then coated with gold before SEM observation. Atomic force microscopy images were acquired in the tapping mode with silicone tip cantilevers and a constant force of 40 mN/cm. The average roughness (R_a) and root mean square

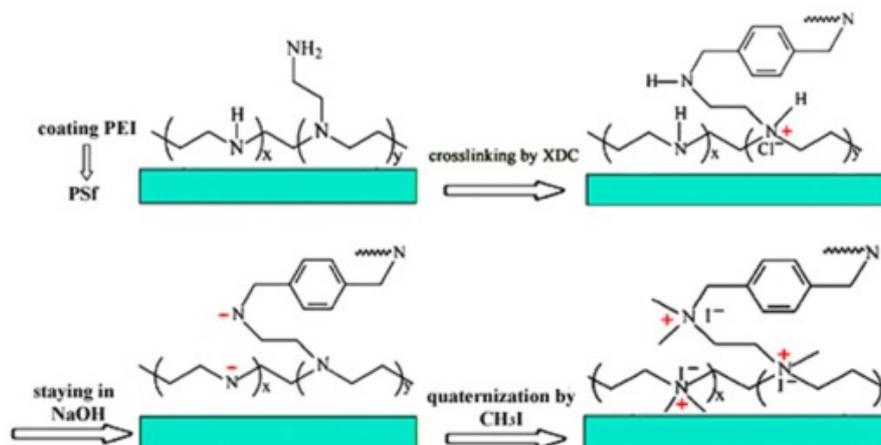


Fig. 1 Schematic representation for the stages of interfacial cross-linking polymerization process

(R_q) were used to express the membrane surface roughness, which was determined by a $5.0 \mu\text{m} \times 5.0 \mu\text{m}$ area of membrane. For each membrane, the reported R_a and R_q value were an average of three measurements taken from different regions.

2.5 Membrane permeation properties

MWCO measurement, permeability and rejection experiments were carried out by a flat sheet cross-flow nanofiltration setup (Fig. 2). It offered an effective filtration area of 32 cm^2 , a feed flow on the membrane surface of 6 L/min , a pressure of 4 bar and an operating temperature of $25 \pm 2^\circ\text{C}$. For the measurement of rejection, the concentration of salts (CaCl_2 , NaCl , MgSO_4 and Na_2SO_4) in feed was kept constant at $1,000 \text{ ppm}$. The concentration of salts was obtained through the measurement of aqueous solution conductivity by the use of a conductometer (WTW inoLab

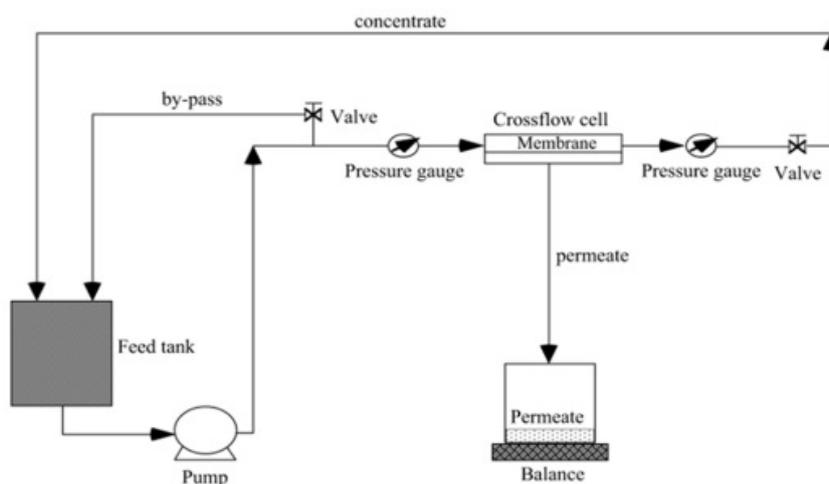


Fig. 2 NF setup using for the measurement of positively charged PEI/PSf composite membrane performance

Cond 720, Germany). For preparing of Ni²⁺ calibration curve, the concentration of this cation in aqueous solutions was measured via atomic absorption spectroscopy (AAS, Perkin-Elmer 2380, USA). The equation of calibration curve was obtained $y = 0.0236x - 0.0013$ ($R^2 = 0.998$). Molecular weight cut-off (MWCO) of cross-linked and quaternized PEI thin-film composite membranes was investigated using different molecular weights of PEG polymer (1,500, 2,000, 3,000, 4,000 and 6,000 g/mol). The analytical method for determining PEG concentration has been given by Sabde *et al.* (1997). PEG solutions were analyzed using a spectrophotometer at $\lambda = 535$ nm (GBC, model Cintra 101, Australia). The initial concentration of PEG in the feed was 500 ppm. The Stokes radius and hydrodynamic pore size of membrane surface were determined according to equations reported by Afonso *et al.* 2001 (Eq. (1)) and Causserand *et al.* 2004 (Eq. (2)), respectively.

$$r_s = -5 \times 10^{-8} M_{W_{PEG}}^2 + 0.0005 M_{W_{PEG}} + 0.3319 \quad (1)$$

$$r_{hyd} = \left(\frac{3[\eta]M_{W_{PEG}}}{4\pi\xi N} \right)^{\frac{1}{3}} \quad [\eta] = 4.9 \times 10^{-8} (M_{W_{PEG}})^{0.672} \quad (2)$$

where $[\eta]$ being the intrinsic viscosity of the solution ($\text{m}^3 \cdot \text{g}^{-1}$), $[\eta]M_{W_{PEG}}$ the hydrodynamic volume ($\text{m}^3 \cdot \text{mol}^{-1}$), ξ the constant proportionality between the radius of the equivalent sphere and the radius of gyration of the polymer molecule (taken as equal to 1) and N the Avogadro number (mol^{-1}).

3. Results and discussion

3.1 Physicochemical characteristics of membrane

FT-IR spectra of PSf membrane support and positively charged thin-film composite membrane prepared during the stages of interfacial cross-linking polymerization process are presented in Fig. 3. The main peaks related to polysulfone support (ν_a (C-H, aromatic ring): 3064.68 cm^{-1} , ν_a (C-H, aliphatic chain): 2967.24, 2872.61 cm^{-1} , ν_a (C=C, aromatic): 1585.22, 1492.06 cm^{-1} , ν_a (C-SO₂-C): 1322.05 cm^{-1} , ν_s (C-SO₂-C): 1152.41 cm^{-1} and ν_a (C-O-C): 1244.98 cm^{-1} , 1295.44 cm^{-1}) were truly indicated. When a layer of poly(ethyleneimine) was coated on the polysulfone ultrafiltration membrane, a strong transmittance at $\nu_a = 3278.04$ cm^{-1} was appeared due to asymmetric stretching of N-H bands on the PEI polymer chains. Of course, the peaks related to asymmetric stretching and bending of C-N bonds were overlapped with the peak of C=C benzene rings available in PSf. After cross-linking and reaction of amine functional groups by p-xylylene dichloride, the transmittance of aliphatic C-H stretching (2,800-3,000 cm^{-1}) was sharpened and the intensity of N-H bonds was slightly reduced. Also, this decrement is obvious in the spectra of quaternized membrane by methyl iodide. Therefore, it can be suggested that a successful interfacial cross-linking polymerization process occurred. Here, ν_a , ν_s and δ were the mean frequency of anti-symmetrical, symmetrical stretchings and bending, respectively.

The surface and cross-section structure of PSf membranes before and after modification were examined by SEM and AFM images as shown in Figs. 4 and 5. The main cross-section structure of these membranes has no differences and indicated a typical asymmetric structure (Fig. 4(A2), (B2), (C2) and (D2)). The all steps of surface modification process can easily be seen. When the reaction between PEI and XDC was happened, a tough layer with the thickness of 3.75 μm was formed on

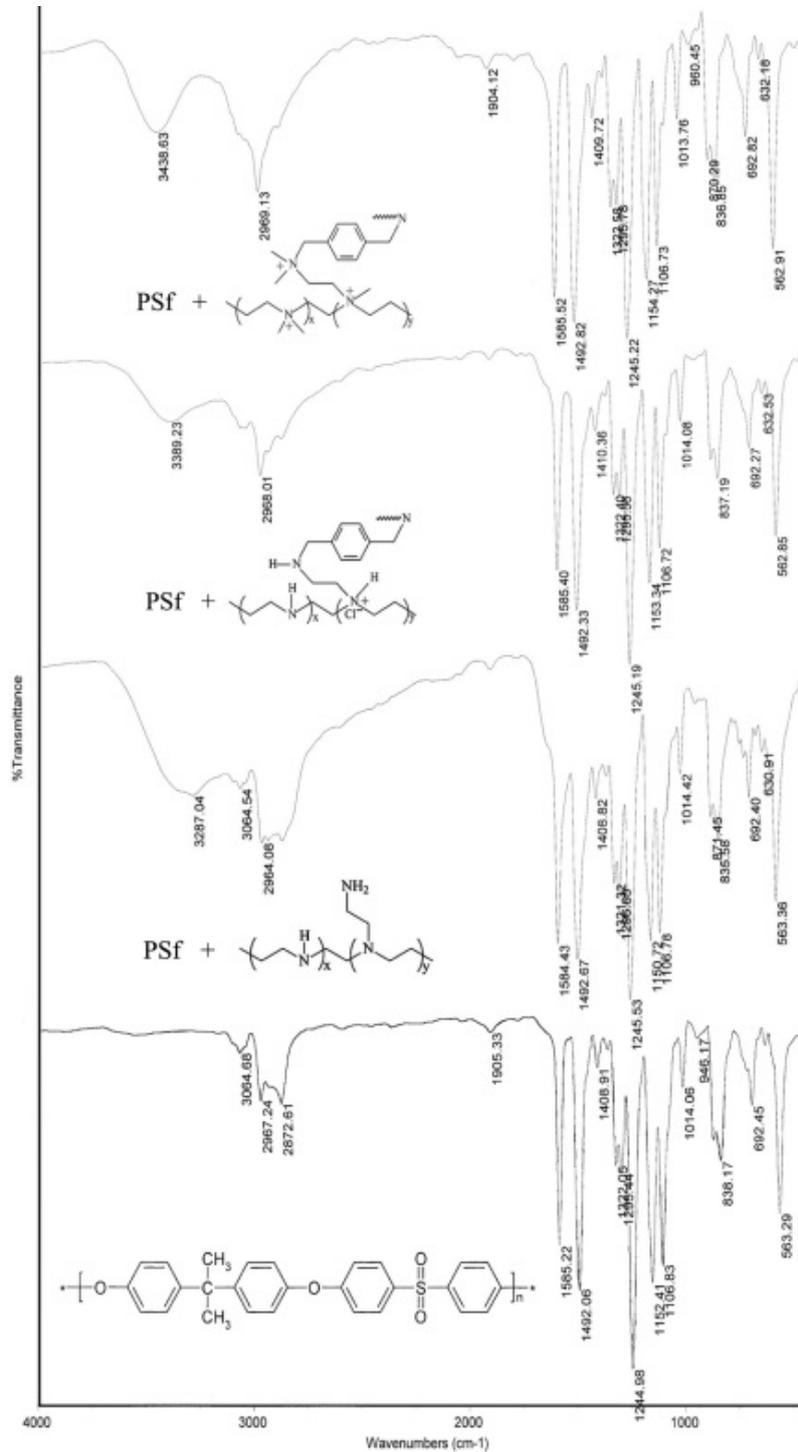


Fig. 3 FT-IR spectra of A: PSf membrane support and positively charged PEI/PSf composite nanofiltration membrane during the interfacial cross-linked polymerization process, B: PEI coated membrane, C: cross-linked PEI membrane and D: quaternized PEI membrane

the polysulfone membrane (Fig. 4(C3)) that afterwards, a very thin layer was obtained via the quaternization with methyl iodide i.e., $1\ \mu\text{m}$ (Fig. 4(D3)). All layers are recognizable and it can be proved that the positively charged thin-film layer was really and successfully taken shape. Fig. 5 shows AFM images of membrane surfaces before (Fig. 5(A)) and after (Fig. 5(B)) interfacial cross-linking polymerization. As seen, the surface of PSf membrane support appeared to be rougher with the cross-linking and quaternization of poly(ethyleneimine), p-xylylene dichloride and methyl iodide and finally, the formation of positively charged selective layer (average roughness: 24.15 to 33.69 nm, root mean square: 33.80 to 45.86 nm). This increment resulted from

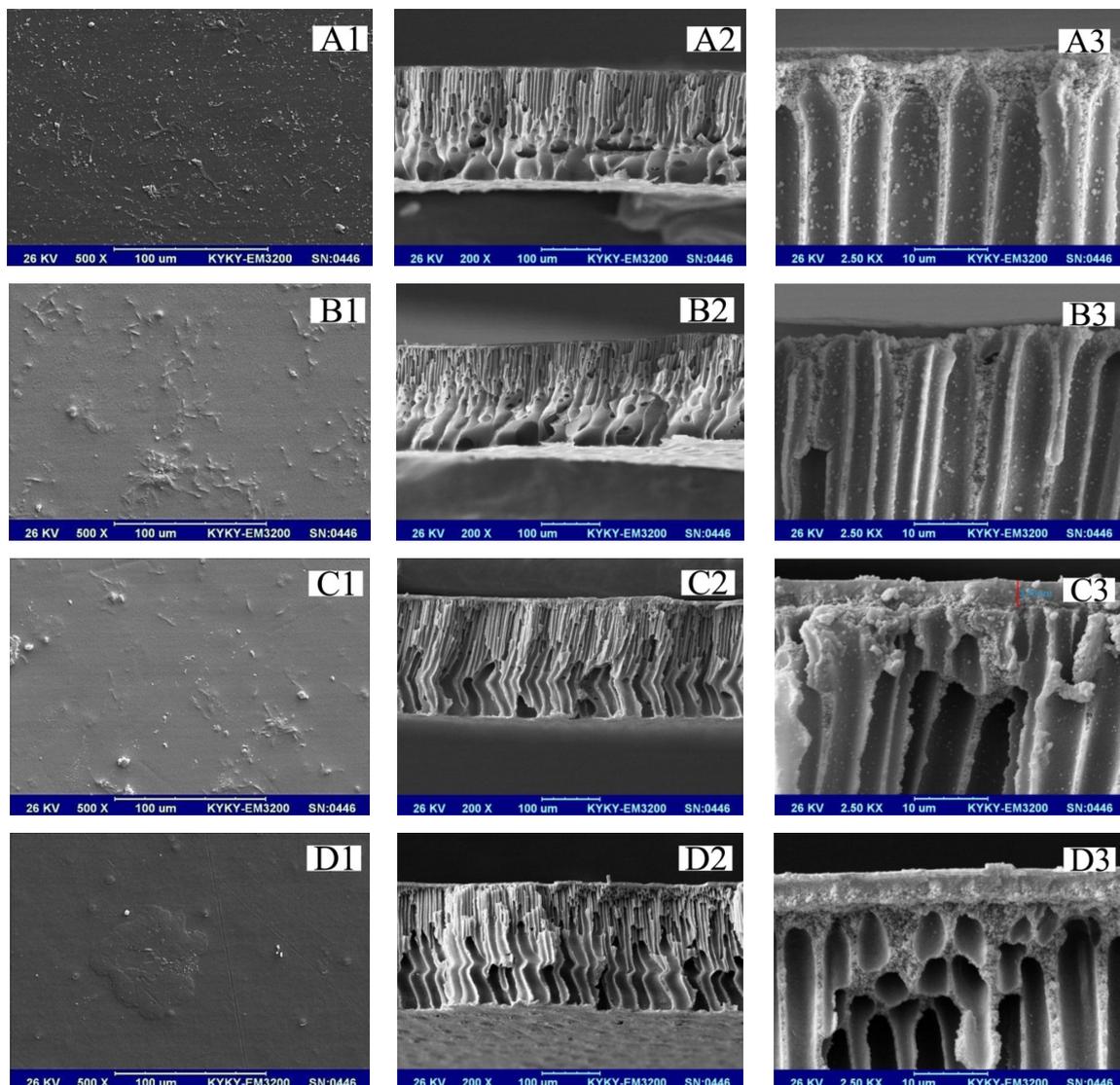


Fig. 4 Cross-section SEM images of: (A) PSf membrane support and PEI/PSf composite nanofiltration membrane during the formation process; (B) PEI coated membrane; (C) cross-linked PEI membrane and D: quaternized PEI membrane

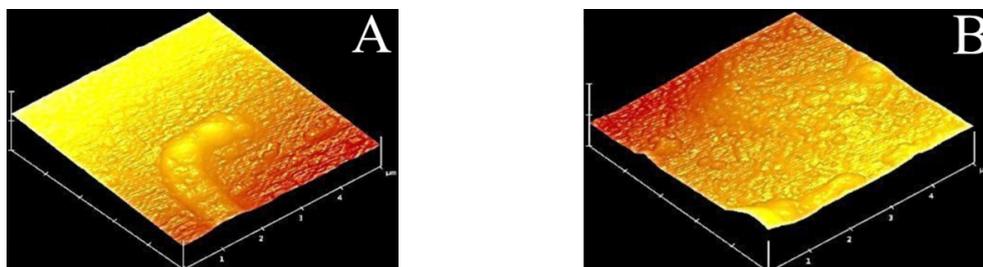


Fig. 5 AFM images of: (A) PSf membrane support surface; and (B) positively charged PEI/PSf composite nanofiltration membrane

the ability of these components to form three dimensional cross-linked structures or nets on the surface of PSf support. It should be noted that the roughness of membrane surface is apparently decreased in the SEM images.

The MWCO value is referred to the molecular weight of PEG that was 90% rejected by the membrane. The Stokes radius and hydrodynamic pore size of membranes can without difficulty be estimated from the relationship between MWCO obtained by PEG solutions and corresponding equations reported (Afonso *et al.* 2001, Causserand *et al.* 2004). Based on the MWCO analysis, the molecular weight of PEG for the cross-linked and quaternized PEI/PSf composite nanofiltration membranes was 3623.093 and 3421.085 g/mol, respectively; also, their hydrodynamic pore size was calculated to be 2.589 and 2.507 nm, respectively (Sabde *et al.* 1997, Causserand *et al.* 2004). In addition, the Stokes radius of these membranes was 1.487 and 1.457 nm, respectively (Afonso *et al.* 2001). This pore size decrement indicated that interfacial cross-linking polymerization process, as required on the surface of PSf support, occurred and a positively charged selective layer was formed.

3.2 Performance evaluation of membrane

In order to optimize the membrane performance, the effective factors in the membrane formation process such as: PEI concentration, PEI coating time, XDC concentration and methyl iodide concentration were carefully considered. Poly(ethyleneimine) is one of the most important polymers in the cationic polymer fields (Xia *et al.* 2009, Wang *et al.* 2009) and the positively charged amine functional groups in their chains improves the surface charge and therefore, the membrane performance in the field of membrane science and technology. In this research, the concentration of this important polymer was altered in the range of 5-30 g/L and physically deposited on the PSf UF membrane. At low concentrations of PEI aqueous solution, the coating was not truly accomplished on the support surface and it just went down to the pores of sub-layers that caused by inadequate entanglements of polymer chains in the solutions. Low concentrations had not any appropriate effect on the coefficient of permeability and CaCl_2 rejection as shown in Fig. 6. By increasing poly(ethyleneimine) concentration up to 25 g/L, a good coating is formed on a top layer of ultrafiltration support which had the best active layer with the best permeability coefficient and CaCl_2 rejection, i.e., 4.60 $\text{L/m}^2\cdot\text{h}\cdot\text{bar}$ and 87.0%, respectively. By further increase in the PEI concentration, the thickness of top layer enhances and this leads to decrease the coefficient of permeability. Finally, 25 g/L was selected as an optimum poly(ethyleneimine) concentration for the interfacial cross-linking polymerization process.

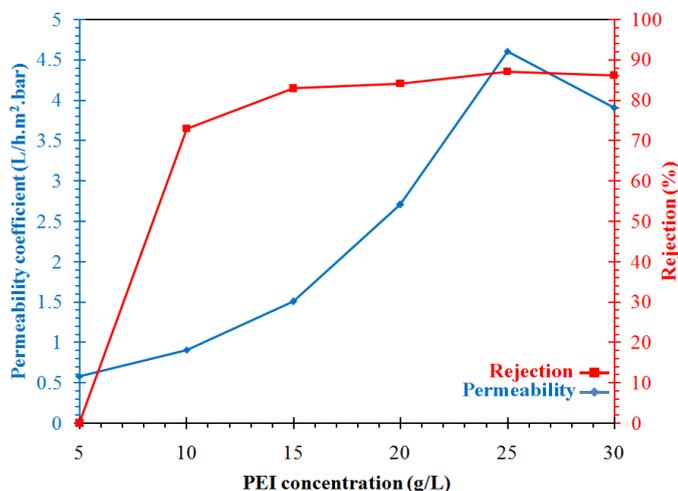


Fig. 6 Influence of PEI concentration on the performance of positively charged composite nanofiltration membrane (PEI coating time = 2 h, XDC concentration = 5 g/L, CaCl₂ concentration in feed = 1,000 ppm)

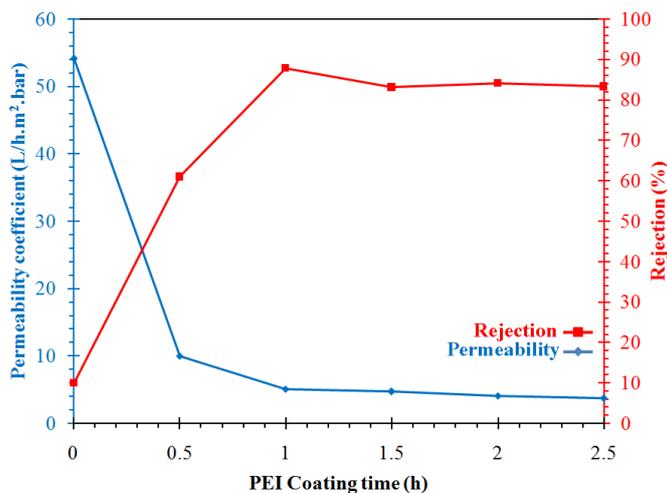


Fig. 7 Influence of PEI coating time on the performance of positively charged composite nanofiltration membrane (PEI concentration = 25 g/L, XDC concentration = 5 g/L, CaCl₂ concentration in feed = 1,000 ppm)

Due to the formation of hydrogen bonds between the amine groups of poly(ethyleneimine) chains and the oxygen atom of SO₂ groups in the polysulfone chains, the duration of staying in the PEI solution is an important factor. Fig. 7 illustrates that with increasing of staying time, the permeability coefficient was decreased and the rejection was increased e.g., 9.95 L/m².h.bar and 60.96% at 0.5 h to 5.08 L/m².h.bar and 87.82% at 1 h. Of course, the conditions were remained almost constant after 1 h because of forming of all hydrogen bonds between two above functional groups. So, the best time for coating PEI on the PSf UF membrane was selected 1 h.

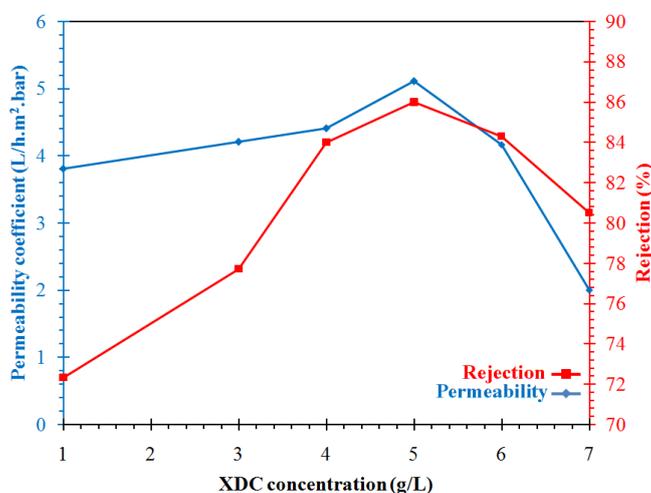


Fig. 8 Influence of XDC concentration on the performance of positively charged composite nanofiltration membrane (PEI concentration = 25 g/L, PEI coating time = 1 h, CaCl₂ concentration in feed = 1,000 ppm)

Fig. 8 shows the effect of XDC cross-linker concentration on the membrane filtration performance. The permeability coefficient and CaCl₂ rejection of coated membranes were increased with the increment of XDC concentration from 1 to 5 g/L and after that, they were decreased. This observation was probably attributed to the fact that when XDC concentration exceeds the cross-linking reaction stoichiometry of 1:2 between XDC molecules and amino functional groups of PEI chains, the excess XDC cannot play as a cross-linking agent (Yang *et al.* 2009). Namely, one of the chloro groups in the XDC reacts with one of the amino groups in the PEI chain and unreacted chloro groups hang freely and swing loosely (as dangling groups). In the aqueous solutions, these chloro groups react with water and hydroxyl functional groups are formed. Because of the decrement of positive charges in the final membrane, these functional groups reduce rejection of cations from feed solution (Yang *et al.* 2009). Also, the probability of reaction of all amine functional groups (primary and secondary) in the poly(ethyleneimine) with XDC cross-linker can be increased. In other words, it can be due to the improvement in the degree of chemical quaternization cross-linking reaction between PEI and XDC by increasing the XDC concentration. Thus, 5 g/L was suggested as an optimum concentration.

As shown in Fig. 1, R⁺ functional groups can covalently be applied to the amine groups on the cross-linked PEI chains that lead to quaternize them. In this study, it was taken an advantage of methyl iodide to form quaternary ammonium groups because of short substituent compound and good reactivity. The CH₃⁺ groups compete in the quaternization reaction with protons (H⁺), hence the membranes stayed in NaOH aqueous solution (0.25 M) after cross-linking for a few minutes. In order to obtain the best concentration of methyl iodide/ethanol solution, the membranes were firstly modified in the optimum condition of other factors i.e. coating with 25 g/L of PEI aqueous solution for 1 hour and cross-linking by 5 g/L XDC solution to 5 hours. In the second stage, the quaternization was performed with four concentrations i.e., 2, 4, 8 and 16% vol. Fig. 9 shows the effect of methyl iodide concentration on the filtration performance of membranes. By increasing of the value of methyl iodide concentration from 2 to 16% vol., the CaCl₂ rejection of membrane

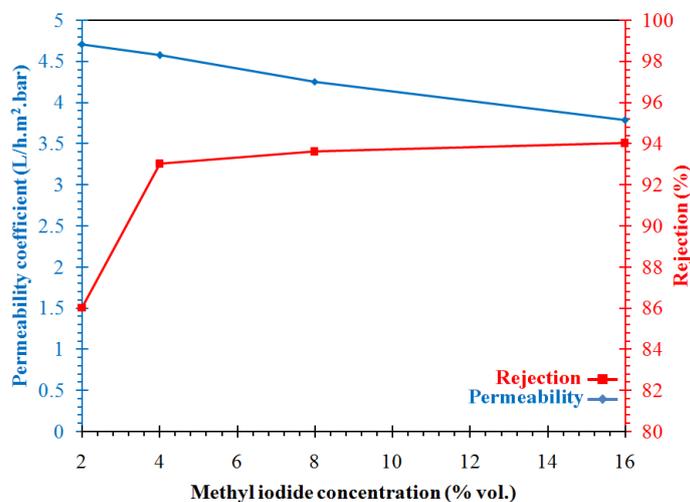


Fig. 9 Influence of methyl iodide concentration on the performance of positively charged composite nanofiltration membrane (PEI concentration = 25 g/L, PEI coating time = 1 h, XDC concentration = 5 g/L, CaCl₂ concentration in feed = 1,000 ppm)

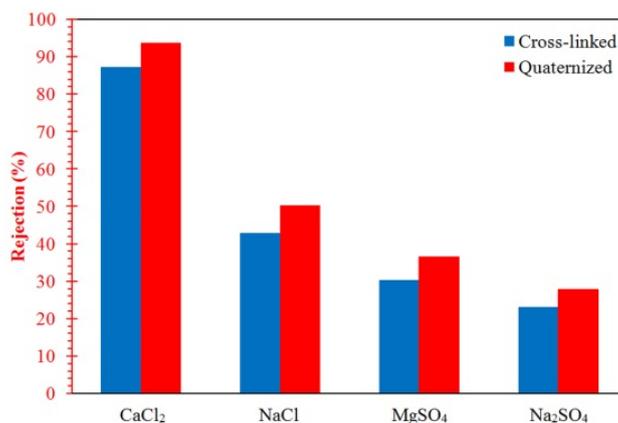


Fig. 10 Salt rejection of positively charged composite nanofiltration membrane in the cross-linking and quaternization stages

increased but there was a slight decline in the permeability coefficient. According to the results, the best concentration of methyl iodide for the quaternization stage was 4% vol., because of salt rejection increased up to 93.62% without the significant decreasing of permeability.

The salt rejection of optimum membrane was examined for different inorganic salt solutions (Na₂SO₄, MgSO₄, NaCl, and CaCl₂) with a concentration of 1,000 ppm at 25°C and 4 bar (Fig. 10). The order of rejection for different salt solutions is as follow: Na₂SO₄ < MgSO₄ < NaCl < CaCl₂. This order confirms the positive charges on the thin-film selective surface of NF membrane (Afonso *et al.* 2001). Generally, the PEI coated PSf NF membranes have higher rejection for high valence cations and low valence anions rather than low valence cations and high valence anions. According to the Donnan exclusion theory (Afonso *et al.* 2001), this is due to the stronger

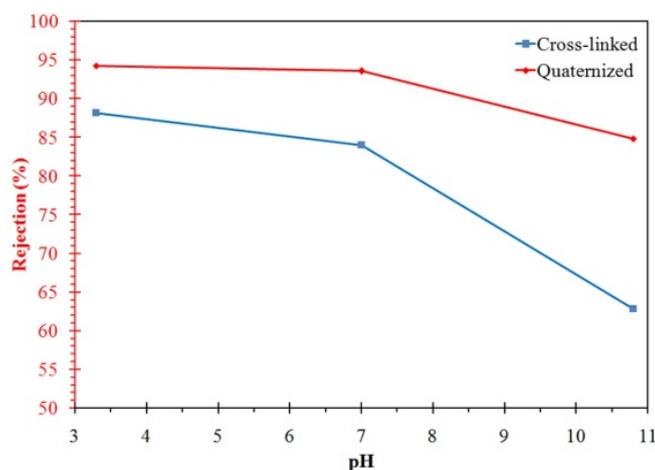


Fig. 11 Influence of pH on the CaCl_2 rejection of positively charged composite nanofiltration membrane in the cross-linking and quaternization stages (CaCl_2 concentration in feed = 1,000 ppm)

electrostatic repulsive interaction between high valence cations and quaternary ammonium of PEI coating on the PSf ultrafiltration membrane surface. Of course, it was noted that the sulphate or chloride anions can counteract with the positive charge on the nanofiltration membrane and the rejection of cations was reduced. The effect of sulphate is more than chloride that causes MgSO_4 rejection is lower than CaCl_2 rejection. Also, these results indicate that quaternizing with methyl iodide after cross-linking processes improves the rejection for every inorganic salt solution and proves that the salt rejection of a charged NF membrane is related not only to the membrane pore size, but mostly depends on the electrostatic repellent interaction between the membrane and cations in the solution.

Fig. 11 shows the changes of membrane salt rejection in the different pHs (3.3, 7 and 10.8) of feed solution. The pH was adjusted by addition of NaOH and HCl to the feed solution. The salt rejections were decreased at pH = 10.8, but for the quaternized membrane, the rejection loss is less than cross-linked one. In this case, the variations of salt rejection were apparently due to Donnan exclusion change, rather than structural change in the surface layer. In the chains of cross-linked poly(ethyleneimine) exist some N-H bonds that with increasing of feed solution pH (i.e., OH^- ions), these bonds eliminate from the chains and the negative charge on the selective layer are achieved ($=\text{N}-\text{H} \rightarrow =\text{N}^-$). But, OH^- base groups are weaker than CH_3 groups that can remove them from the quaternized membrane surfaces and therefore, the positive charge of these membranes almost keeps constant. They cause that the CaCl_2 rejection of these two membranes is different. This result shows that the quaternized membranes have a more stable surface charge, too.

In comparison with other membranes, these new positively charged NF membranes have the best performance (Table 1). The cross-flow configuration of nanofiltration setup has an excellent effect on the separation of different salts. In relation to Huang *et al.*, our new membrane had better permeability coefficient and salt rejection (Huang *et al.* 2006). This novel nanofiltration membrane with the optimum preparation condition was finally utilized for nickel ion removal from wastewater of Shamse Hadaf Company in Kashan. The initial concentration of this ion in the

Table 1 Comparison of membrane performance formed in this study with other membranes

Membrane support	Components	Setup type	Active area (cm ²)	Pressure (bar)	Flow rate (L/h)	Pure water permeability coefficient (L/h.m ² . bar)	Solute concentration (ppm)	Rejection (%)	Ref.
PSf	PEI XDC as cross-linker Methyl iodide as quaternizer		32	4	360	18.29	CaCl ₂ 1000	93.62	here
PSf	DMAEMA XDC as cross-linker & quaternizer	Cross-flow	23.75	6	30.5	6.03	MgCl ₂ 1000	93.2	Li <i>et al.</i> 2011
PAN	Chitosan TDI as cross-linker TAC as quaternizer		19.6	4	30	1.41	MgCl ₂ 1000	94	Huang <i>et al.</i> 2006
PES-TA	-		20.4	5	-	3.72	MgCl ₂ 1000	64.6	Zhang <i>et al.</i> 2011
PAN	EDA, TMC DETA, TMC PEI, TPC PEI, TMC	Dead-end	11.95	4	-	1.7 4.5 3.1 9.5	MgCl ₂ 1000	55.01 44.98 93.94 78.97	Chiang <i>et al.</i> 2009
sPPSf	[2-(Methacryloyloxy)ethyl] trimethyl ammonium chloride Diallyldimethylammonium chloride		38.46	5	-	14 9	MgCl ₂ 200	92.76 95.20	Zhong <i>et al.</i> 2012

wastewater was 189.41 ppm that it was decreased to 7.08 ppm after nanofiltration process. Therefore, the rejection of Ni²⁺ was obtained 96.26%.

4. Conclusions

A novel positively charged NF membrane was successfully prepared via interfacial cross-linking polymerization and the important factors in this method were truly optimized. This procedure showed at least two advantages: (1) the formed hindrance layer was more compact and had a high selectivity, and (2) the surface of polysulfone ultrafiltration membrane support had been positively charged after coating by poly(ethyleneimine), cross-linking with p-xylylene dichloride and quaternization of methyl iodide. The optimum condition for the membrane formation was coating with 25 g/L of PEI aqueous solution for 1 hour, cross-linking by 5 g/L XDC/n-hexane solution to 5 hours and finally, quaternizing with 4% vol. methyl iodide/ethanol

solution. The MWCO determination revealed that hydrodynamic pore size and Stokes radius of optimum membrane were 2.507 and 1.457 nm, respectively with 18.29 L/m².h permeability and 93.62% CaCl₂ rejection. The cross-section SEM image confirmed the formation of a quaternized thin layer with thickness of around 1 μm. The order of salt rejections for inorganic salts was as follow: CaCl₂ > NaCl > MgSO₄ > Na₂SO₄. The optimum nanofiltration membrane exhibited a Ni²⁺ rejection of 96.26% for industrial wastewater from Shamse Hadaf Co. (Kashan, Iran).

References

- Afonso, M.D., Hagmeyer, G. and Gimbel, R. (2001), "Streaming potential measurements to assess the variation of nanofiltration membranes surface charge with the concentration of salt solutions", *Sep. Purif. Technol.*, **22-23**, 529-541.
- Akbari, A., Desclaux, S., Rouch, J.C., Aptel, P. and Remigy, J.C. (2006), "New UV-photografted nanofiltration membranes for the treatment of colored textile dye effluents", *J. Membr. Sci.*, **286**(1-2), 342-350.
- Akbari, A., Desclaux, S., Rouch, J.C. and Remigy, J.C. (2007), "Application of nanofiltration hollow fibre membranes, developed by photografting, to treatment of anionic dye solutions", *J. Membr. Sci.*, **297**(1-2), 243-252.
- Baker, R.W. (2004), *Membrane Technology and Applications*, John Wiley & Sons, Chichester, England.
- Causserand, C., Rouaix, S., Akbari, A. and Aimar, P. (2004), "Improvement of a method for the characterization of ultrafiltration membranes by measurements of tracers retention", *J. Membr. Sci.*, **238**(1-2), 177-190.
- Chiang, Y.C., Hsub, Y.Z., Ruaan, R.C., Chuang, C.J. and Tung, K.L. (2009), "Nanofiltration membranes synthesized from hyperbranched polyethyleneimine", *J. Membr. Sci.*, **326**(1), 19-26.
- Derakhsheshpoor, R., Homayoonfal, M., Akbari, A. and Mehrnia, M.R. (2013), "Amoxicillin separation from pharmaceutical wastewater by high permeability polysulfone nanofiltration membrane", *J. Environ. Health Sci. Eng.*, **11**(9), 10 p.
- Dirir, Y.I., Hanafi, Y., Ghoufi, A. and Szymczyk, A. (2015), "Theoretical Investigation of the Ionic Selectivity of Polyelectrolyte Multilayer Membranes in Nanofiltration", *Langmuir*, **31**(1), 451-457. DOI: 10.1021/la5044188
- Du, R. and Zhao, J. (2004), "Properties of poly (N,N-dimethylaminoethyl methacrylate)/polysulfone positively charged composite nanofiltration membrane", *J. Membr. Sci.*, **239**(2), 183-188.
- Huang, R., Chen, G., Sun, M., Hu, Y. and Gao, C. (2006), "Studies on nanofiltration membrane formed by diisocyanate cross-linking of quaternized chitosan on poly(acrylonitrile) (PAN) support", *J. Membr. Sci.*, **286**(1-3), 237-244.
- Huang, R., Chen, G., Sun, M. and Gao, C. (2009), "Preparation and characterization of composite NF membrane from a graft copolymer of trimethylallyl ammonium chloride onto chitosan by toluene diisocyanate cross-linking", *Desalination*, **239**(1-3), 38-45.
- Kravets, L., Dmitriev, S., Lizunov, N., Satulu, V., Mitu, B. and Dinescu, G. (2010), "Properties of poly(ethylene terephthalate) track membranes with a polymer layer obtained by plasma polymerization of pyrrole vapors", *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **268**(5), 485-492.
- Lau, W.J., Ismail, A.F., Misdan, N. and Kassim, M.A. (2012), "A recent progress in thin film composite membrane: A review", *Desalination*, **287**, 190-199.
- Li, N.N., Fane, A.G., Winston Ho, W.S. and Matsuura, T. (2008), *Advanced Membrane Technology and Applications*, John Wiley & Sons, Hoboken, NJ, USA.
- Li, L., Zhang, S. and Zhang, X. (2009), "Preparation and characterization of poly(piperazineamide) composite nanofiltration membrane by interfacial polymerization of 3,3',5,5'-biphenyl tetraacyl chloride and piperazine", *J. Membr. Sci.*, **335**(1-2), 133-139.

- Li, X.L., Zhu, L.P., Xu, Y.Y., Yi, Z. and Zhu, B.K. (2011), "A novel positively charged nanofiltration membrane prepared from N,N-dimethylaminoethyl methacrylate by quaternization cross-linking", *J. Membr. Sci.*, **374**(1-2), 33-42.
- Oatley, D.L., Llenas, L., Aljohani, N.H.M., Williams, P.M., Martínez-Lladó, X., Rovira, M. and de Pablo, J. (2013), "Investigation of the dielectric properties of nanofiltration membranes", *Desalination*, **315**, 100-106.
- Ouyang, L., Malaisamy, R. and Bruening, M.L. (2008), "Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations", *J. Membr. Sci.*, **310**(1-2), 76-84.
- Rahimpour, A., Jahanshahi, M., Mortazavian, N., Madaeni, S.S. and Mansourpanah, Y. (2010), "Preparation and characterization of asymmetric polyethersulfone and thin-film composite polyamide nanofiltration membranes for water softening", *Appl. Surf. Sci.*, **256**(6), 1657-1663.
- Sabde, A.D., Trivedi, M.K., Ramachandhran, V., Hanra, M.S. and Misra, B. (1997), "Casting and characterization of cellulose acetate butyrate based UF membranes", *Desalination*, **114**(3), 223-232.
- Silva, V., Martín, Á., Martínez, F., Malfeito, J., Prádanos, P., Palacio, L. and Hernández, A. (2011), "Electrical characterization of NF membranes. A modified model with charge variation along the pores", *Chem. Eng. Sci.*, **66**(13), 2898-2911.
- Szymczyk, A., Fatin-Rouge, N. and Fievet, P. (2007), "Tangential streaming potential as a tool in modeling of ion transport through nanoporous membranes", *J. Colloid Interface Sci.*, **309**(2), 245-252.
- Van der Bruggen, B. and Vandecasteele, C. (2003), "Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry", *Environ. Pollut.*, **122**(3), 435-445.
- Van der Bruggen, B., Mänttari, M. and Nyström, M. (2008), "Drawbacks of applying nanofiltration and how to avoid them: A review", *Sep. Purif. Technol.*, **63**(2), 251-263.
- Wang, X., Zhou, L., Ma, Y., Li, X. and Gu, H. (2009), "Control of aggregate size of polyethyleneimine-coated magnetic nanoparticles for magnetofection", *Nano Res.*, **2**(5), 365-372.
- Wei, X.Z., Zhu, L.P., Deng, H.Y., Xu, Y.Y., Zhu, B.K. and Huang, Z.M. (2008), "New type of nanofiltration membrane based on crosslinked hyperbranched polymers", *J. Membr. Sci.*, **323**(2), 278-287.
- Xia, T., Kovochich, M., Liong, M., Meng, H., Kabehie, S., George, S., Zink, J.I. and Nel, A.E. (2009), "Polyethyleneimine coating enhances the cellular uptake of mesoporous silica nanoparticles and allows safe delivery of siRNA and DNA constructs", *ACS Nano*, **3**(10), 3273-3286.
- Yang, Y.F., Wan, L.S. and Xu, Z.K. (2009), "Surface hydrophilization of microporous polypropylene membrane by the interfacial crosslinking of polyethylenimine", *J. Membr. Sci.*, **337**(1-2), 70-80.
- Zhang, Q., Wang, H., Zhang, S. and Dai, L. (2011), "Positively charged nanofiltration membrane based on cardo poly(arylene ether sulfone) with pendant tertiary amine groups", *J. Membr. Sci.*, **375**(1-2), 191-197.
- Zhao, Z.P., Li, J., Zhang, D.X. and Chen, C.X. (2004), "Nanofiltration membrane prepared from polyacrylonitrile ultrafiltration membrane by low-temperature plasma: I. Graft of acrylic acid in gas", *J. Membr. Sci.*, **232**(1-2), 1-8.
- Zhong, P.S., Widjojo, N., Chung, T.-S., Weber, M. and Maletzko, C. (2012), "Positively charged nanofiltration (NF) membranes via UV grafting on sulfonated polyphenylenesulfone (sPPSU) for effective removal of textile dyes from wastewater", *J. Membr. Sci.*, **417-418**, 52-60.