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Synthesis of new composite polymer membrane from tapioca grains—polysulfone for desalination

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ABSTRACT

Nowadays, membrane technology has gained significant attention from scientific community throughout the world due to their attractive features such as low costs, low energy costs, and high efficiency in water purification. Different types of membranes and its performance study have been widely applied in the desalination processes. One of the drawbacks in membrane preparation was usage of hazardous chemicals causing serious environmental pollution. Here, we attempted to prepare partial green composite membranes using tapioca grains. The same membranes were subjected to various characterizations and the results were fairly encouraging showing salt rejection as high as 71%. This study aimed to synthesize polysulfone and tapioca membranes over nonporous support of K.C. 27.0 using diffusion-induced phase separation technique method. Newly synthesized polymer membranes were subjected to Infra-red spectral study and water uptake. Their surface morphology is visualized by SEM.

Keywords: Tapioca; Polysulfone; Porous support; Membrane preparation; Salt rejection

1. Introduction

Membrane plays a vital role in water purification. Based on the pore size, pressure driven membrane process are broadly classified into four types namely, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Among different membrane processes, RO and NF have undergone significant development in the past decade. Among the globe membranes, the type RO/NF has become an important part in desalination technology [1]. Advancement in membrane technology increased the salt removal efficiency with optimum energy savings compared to the traditional methods [2]. A large variety of membranes have been developed, and their performance in terms of percentage rejection (%) has been attributed in desalination technology.

Membrane desalination is an established technology, used commercially worldwide to reduce the salinity in potable water, wastewater reclamation and industrial applications with lesser consumption of energy [3,4]. Nanopores on the membrane surface are engineered to remove salt from water under the influence of applied pressure [5].

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This research work carried out by our team has successfully demonstrated the removal of sodium from water, utilizing tapioca grains—polysulfone membrane [6]. The present research work describes the methodology for preparation of membranes by "diffusion induced phase separation" (DIPS) method [7]. By carrying out the ATR FTIR study, the formation of the membrane has been further confirmed. To aid the research work, the distribution of pores on membrane surface was also investigated using "scanning electron microscopy" (SEM) images. The current research has thoroughly investigated the performance of the membrane on sodium removal in the drinking water [8]. The membrane performance has been interpreted in terms of important parameters like pure water permeability, solution flux, and percentage rejection of Na^+ [9]. The experimental results carried out by our team have clearly indicated that the rejection of Na^+ increased with the applied pressure.

Membranes flux/rejection studies were carried in addition, using specially made salinity-checking instrument. Membranes fabricated for these experiments have successfully shown a rejection rate between 50 and 71% for a pressure difference from 200 to 1,200 kPa.

2. Experimental

2.1. Materials and instruments

Polysulfone (PS) having molecular weight of 35,000 g mol^{-1}, crushed tapioca powder (TP), and reagent grade N-methyl pyrrolidone (NMP) was obtained from Sigma Aldrich and was used without any further purification. Tapioca grains were purchased as grocery item. K.C.27.0 a non-woven porous support (specification being 100% polypropylene along with basic weight 105 g m^{-2}, density 0.016 cm^3, tensile strength 5.40 kg/in, elongation 17.70%, and porosity 2000 at 200 Pa) was purchased from Millipore. All other analytical grade chemical reagents used in the experiment were purchased from Merck India Ltd.

ATR FT-IR spectra were recorded using a Nicolet Avatar 330 FTIR (Thermo Corporation) spectrometer. SEM images of the cross-section of the newly prepared membranes were recorded on a Jeol JSM-84 Equipment. DSC study was carried out on a Shimadzu DSC 60 instrument (Japan). The permeation experiments were performed by a self-fabricated salinity checking apparatus with membrane disk having an effective area of 6.5 cm^2. A VCA-Optima System (AST Products Inc., MA, USA) was used to measure contact angle of the membranes.

2.2. Membrane preparation method

The Tapioca grains were crushed into fine powder and appropriate wt.% of this powder was dissolved in 4.5 mL of NMP. The solution was stirred for 48 h at 45°C till complete dissolution. After filtering this solution through a "G3" sand filter, appropriate wt.% of polysulfone (Table 1) was added, keeping heating and stirring conditions for another 6 h. The resultant homogeneous polymer solution was sonicated for 10 min to remove air bubbles. Next, the solution was sprinkled and cast over K.C.27.0 nonporous support using self-made casting knife, and was immediately moved to a non-solvent bath for immersion without any evaporation. A thin polymeric film could be separated within a few minutes. After primary phase separation and membrane formation, the membranes were stored in fresh distilled water for 24 h to guarantee the complete phase separation [10,11].

2.3. Structural characterization

For the confirmation of the membranes formation, infrared (IR) sample were prepared by grinding a very small quantity of the sample with specially purified KBr. This powder mixture is then crushed in a mechanical die press to form a translucent pellet [12]. Scanning electron microscope (Jeol JSM-84) was used to observe the morphology of the dried membranes. The membrane was fractured by dipping in liquid nitrogen and then sputtered with gold.

2.3.1. Water uptake

The membrane was first immersed in deionized water for 6 h. Then the wet membrane was weighed quickly (w_w). The weight of the dry membrane (w_d) was determined after drying using hot air oven at 20°C for 24 h. The percentage of water uptake was calculated by using the following Eq. (1) [13].

$$\% \text{ Water uptake} = \left(\frac{w_w - w_d}{w_d}\right) \times 100 \quad (1)$$

2.4. Contact angle measurements

Contact angle has been used as an index of the wettability of the membrane active layer. This parameter was measured by the sessile drop method, using a goniometer VCA-Optima (AST Products Inc., MA, USA). Prior to the measurement, membranes were stored in a container of pure water for 24 h. After this,

Table 1
Solutions containing different wt.% of PS and TP

Membrane code	Wt.% composition (PS)	Wt.% composition (TP)
PTM1	90	10
PTM2	80	20
PTM3	70	30
PTM4	60	40

membranes were rinsed and dried in a desiccator. Membrane samples were cut into small pieces and mounted on a support. A roughly 2.0 μL droplet of pure water was placed on the membrane specimen and the contact angle was measured with the goniometer via a camera immediately after the drop placement. Reported values are the averages of the contact angles of five droplets. During the 30 s time of measurement, no change in contact angle was observed. Contact angle do not give absolute values but allow a comparison between each materials [14].

2.5. Thermal study of the membranes

Differential scanning calorimetry (DSC) can be used to measure a number of characteristic properties of a membrane sample. Using this technique, it is possible to observe fusion and crystallization events as well as glass transition temperatures (T_g). Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs.

The melting process results in an endothermic peak in the DSC curve [15]. Shimadzu DSC 60 instrument (Japan) was used to study the T_g values of the different prepared membranes.

2.6. Permeation experiment

At different pressure (kPa), flux/percentage rejection (R) of the prepared membranes were determined using self-fabricated and designed salinity checking equipment shown in Fig. 1 [16].

A sodium chloride salt (3,500 ppm concentration) is employed in this experiment to investigate membrane flux/rejection properties. Here, nitrogen gas is employed to apply the different pressure. Permeability (Flux, F (L m^{-2} h)) of pure water through membrane was calculated by Eq. (2).

$$F = W/A \times t \quad (2)$$

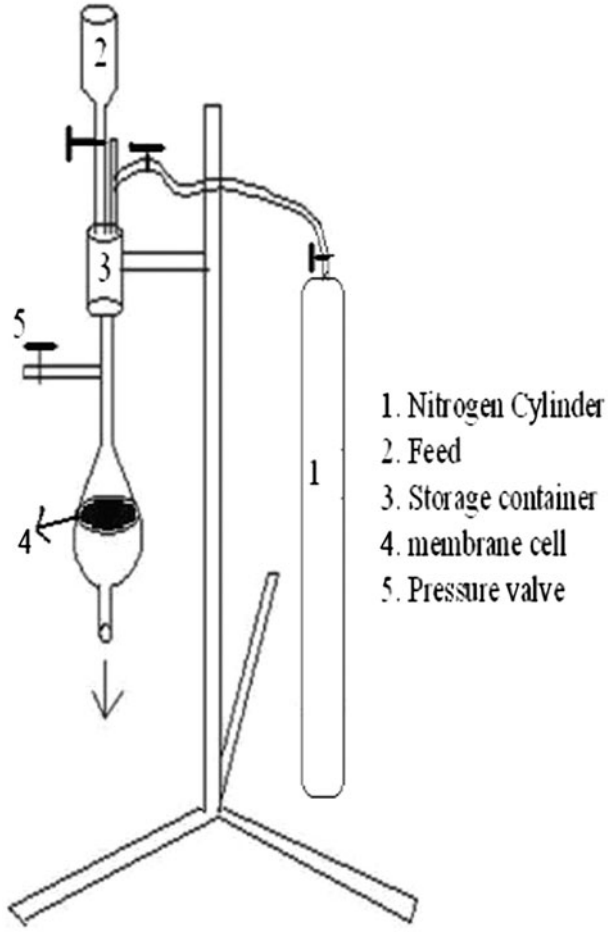

Fig. 1. Schematic representation of desalination equipment.

where "W" (L) is the total volume of the water or solution permeated during the experiment, A (m^2) is the membrane area, and "t" (h) is the operation time. Rejection percentage of the membrane is calculated using following Eq. (3),

$$R = (1 - \text{Concentrate permeates/Concentrate feed}) \quad (3)$$

3. Results and discussion

3.1. Infra-red spectral studies

ATR FT-IR spectrum (Fig. 2) of the membrane shows the common peaks such as 3,299 cm^{-1} for –OH stretching vibrations, 2,921 cm^{-1} for asymmetric and symmetric C–H stretching vibrations involving entire methyl group, 2,107 cm^{-1} for CH stretching, 1,643 cm^{-1} for amide C=O stretching, 1,147 cm^{-1} for asymmetric O=S=O stretching of sulfonate, were observed in, it is interesting to observe that, above mentioned some peaks commonly seen in individual FTIR spectra of PS (Fig. 3) and TP (Fig. 4). Hence, this collectively confirms formation of composite membrane of PS and TP.

3.2. Water uptake

The water uptake plays an important role in membrane filtration performance. From Table 2, it can be observed that, water uptake of the membranes increased with increase in TP concentration. This is

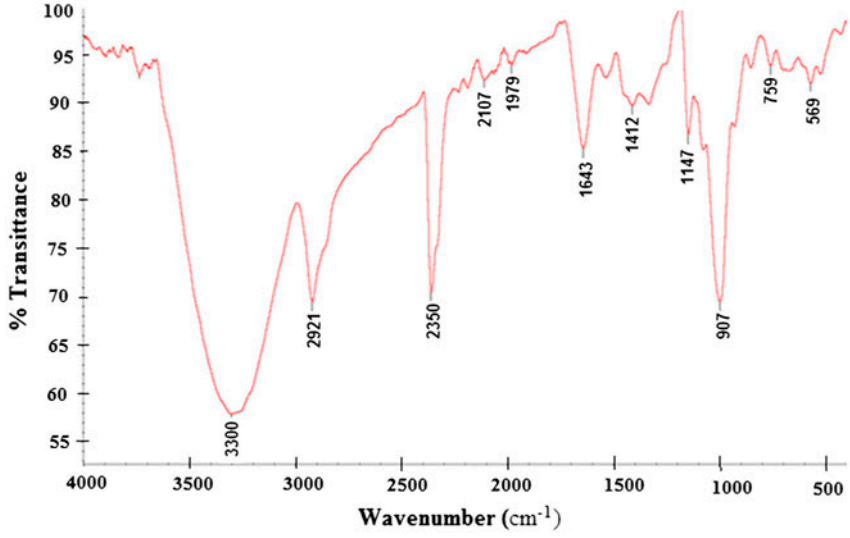

Fig. 2. ATR FT-IR spectrum of the PTM1.

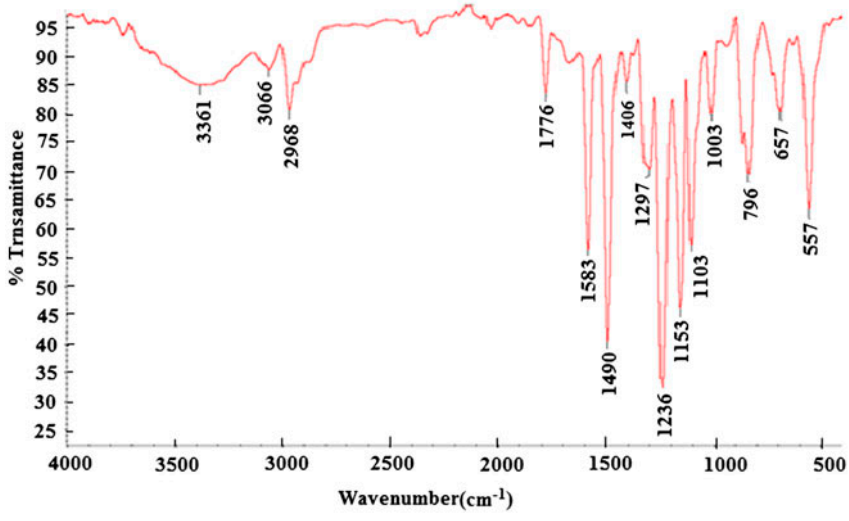

Fig. 3. ATR FT-IR spectrum of the PS.

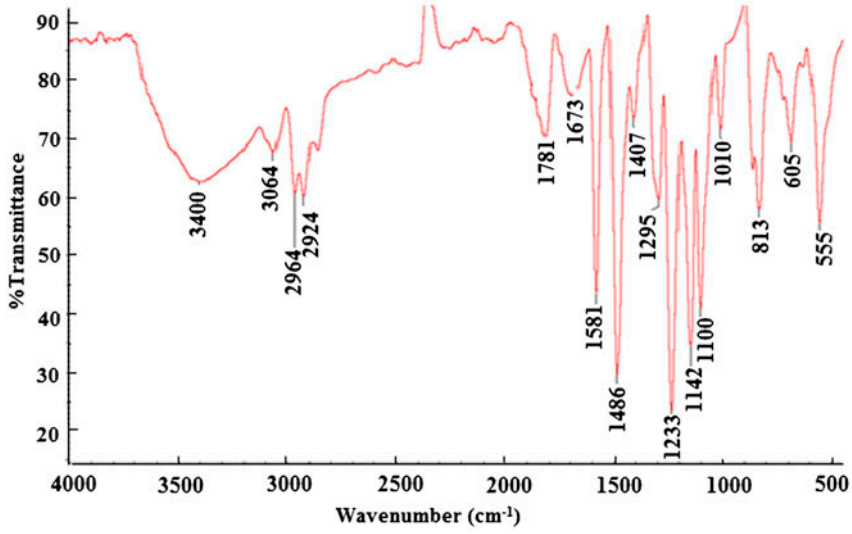

Fig. 4. ATR FT-IR spectrum of the TP.

Table 2
Water uptake and contact angle of the different membranes

Membrane code	Water uptake (%)	Contact angle (in degree)
PTM1	15	70 ± 2
PTM2	24	68 ± 2
PTM3	34	56 ± 2
PTM4	45	43 ± 2

due to the fact that TP is hydrophilic and hence the membranes with higher % TP could absorb more water. TP groups lead to increase in the hydrogen bonding on the membrane surface [17].

3.3. Contact angle measurements

It is well known fact that, membrane showing contact angle higher possess more hydrophobicity than hydrophilicity [18]. From the obtained results, it was observed that PTM1 and PTM2 membranes exhibited hydrophobic nature than hydrophilic [19]. In general, these membranes' wettability character was very little. Table 2 illustrates variation of contact angle with TP concentration. Contact angle increases as polysulfone concentration increases, hence, it implies that TP gives hydrophilicity to the membranes.

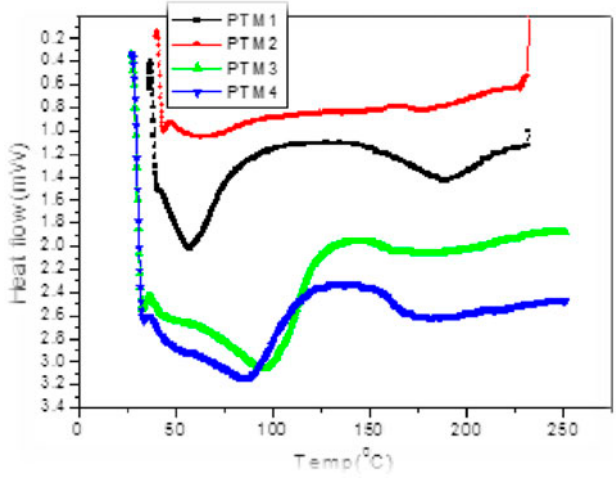

Fig. 5. T_g values of the different membranes.

3.4. DSC study

DSC was used to evaluate the T_g of the prepared membranes and results were summarized in Fig. 5. These results confirmed the formation of composite membranes, as a result of many Van der Waals interactions between two polymers which lose their individual identity and show different T_g, which is

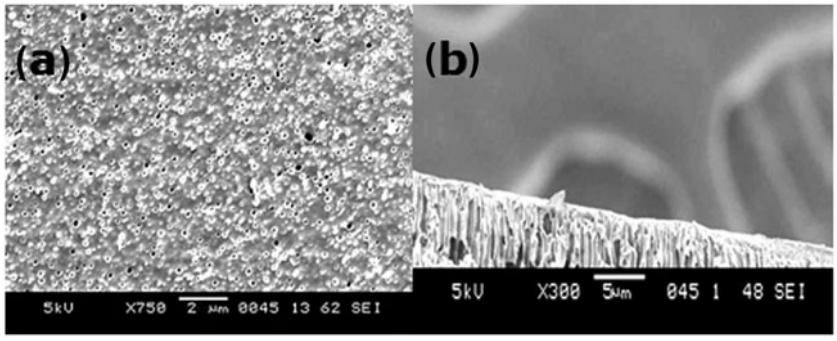

Fig. 6. (a) SEM image of the surface of the membrane PTM1 and (b) cross-section image of the membrane PTM1.

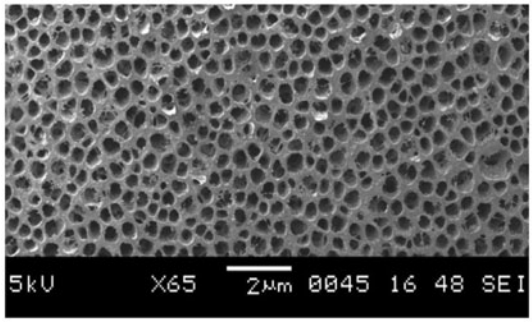

Fig. 7. SEM image of the surface of the membrane PTM4.

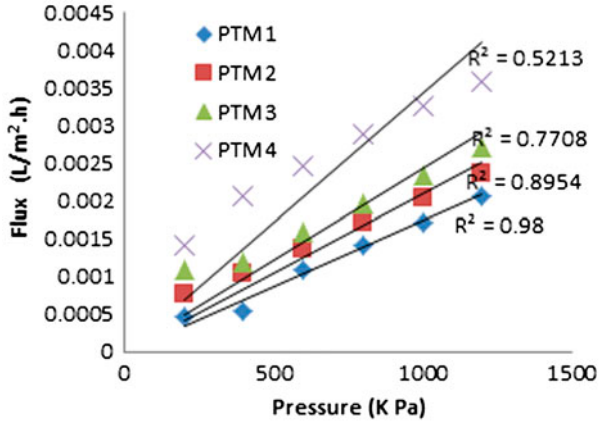

Fig. 8. Pure water flux of the membranes at different pressure.

different from both [20]. T_g of PTM3 and PTM4 is in between 110 and 120°C, whereas, PTM1 and PTM2 shows in the range of 175–180°C. Thus, our prepared membranes clearly indicated that, higher the polysulfone content, higher is the T_g.

3.5. Morphology of the membranes

Surface SEM picture of synthesized membrane were made to characterize the membrane morphology, the membrane overall thickness, and defects on the membrane. Surface image (Fig. 6(a)) of one of the sample, concretely PTM1, exhibits a pores size of approximately 2 µm. Cross-section image (Fig. 6(b)) of the membranes exhibit distinct finger like projections which eases the flux of the water. Larger voids in the Fig. 7, indicates increase in %TP produces a more open membrane structure.

3.6. Pure water flux

At pressure difference (kPa), flux for pure water with respect to different prepared membranes is shown in Fig. 8. The plot depicts a linear relationship between the pure water flux and transmembrane pressure. A slow and steady increase of pure water flux with respect to an increase in TP wt.% was observed.

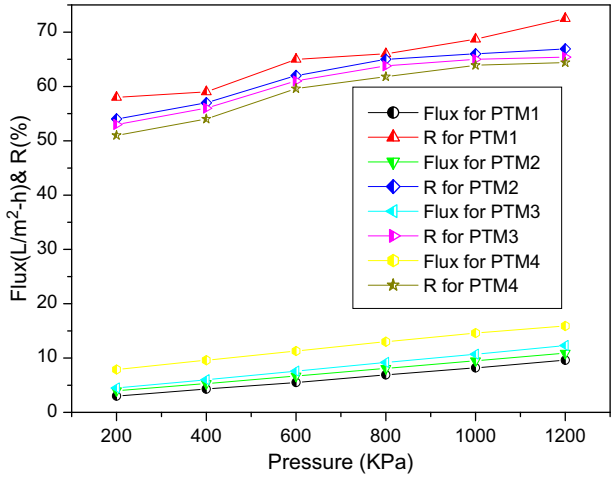

Fig. 9. Flux and % R performance of the 3,500 ppm NaCl by the different membranes.

Table 3
The mechanical properties for membranes and polymer

Membrane/polymer code	Wt.% composition (PS)	Wt.% composition (TP)	Modulus (MPa)	Tensile strength (MPa)
PS	100	0	3,047.90	25.3
TP	0	100	87.90	1.3
PTM1	90	10	3,021.90	24.8
PTM2	80	20	2,761.90	22.9
PTM3	70	30	2,156.60	17.2
PTM4	60	40	1,798.32	14.6

This result may be due to the fact that TP seems to lead predominantly to swelling (as observed in Table 2, PTM4 have 45% water uptake) of the membrane rather than leaching out water from the membrane-forming system. Consequently, the flow path in the membrane was reduced, and hence, the increase in the flux was not steep. By considering the slope of the curves we can conclude that, prepared membranes are of the type of in between NF and UF membranes.

3.7. Salt rejection (R)/flux by different membranes

The rejections to NaCl (3,500 ppm) salts solutions by four different membranes were studied using self-designed equipment and the results are presented in Fig. 9.

All the four studied membranes show approximately linear increase in the flux with increase in pressure. But PTM1 gives higher salt rejection (nearly 71%) than other membranes. Higher rejection in PTM1 may be due to the fact that PS induces negative charge to membrane surface which in turn increases more repulsion of sodium giving higher rejection percentage. From Table 3, it is observed that more, the PS concentration gives better mechanical strength to the membrane and at higher TP percentage may lead to leaching of the membrane surface.

4. Conclusions

The results of this study have been very encouraging and DIPS method was successfully employed for the preparation of partial green composite membranes. As we know, one of the starting material (Tapioca) is cheaper and widely available which makes membrane preparation part much economical. The purification technique is simple; hence with suitable funding and commercial transfer of technology, these composite polymer membranes can provide easy, economical, and safe drinking water to the common man, especially to the ones who live in rural areas. The aim of this work is to study the preparation and influence of salt removal of membranes which have naturally available tapioca grains as one of the ingredients. The results of this work allow selecting an optimal membrane for a specific application. Moreover, this work will provide useful information in the field of membrane development, with regard to particular membrane characteristics to control for an optimal membrane performance.

Acknowledgments

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References

[1] M. Mulder, Basic Principle of Membrane Technology, second ed., Kluwer Academic Publisher, Boston, MA, 2003.
[2] H. Zhou, D.W. Smith, Advanced technologies in water and waste water treatment, J. Environ. Eng. Sci. 1 (2002) 247–264.
[3] S. Chellam, C.A. Serra, M.R. Wiesner, Estimating costs for integrated membrane systems, J. Am. Water Works Assoc. 90 (1998) 96–104.
[4] M. Elimelech, W.A. Philip, The future of seawater desalination: Energy, technology, and the environment, Science 333 (2011) 712–717.
[5] V. Romero, M.I. Vazquez, J. Benavente, Study of ionic and diffusive transport through a regenerated cellulose nanoporous membrane, J. Membr. Sci. 433 (2013) 152–159.
[6] Y. Medina-Gonalez, P. Aimar, J.F. Lahitte, J.C. Remigy, Towards green membranes: Preparation of cellulose acetate ultrafiltration membranes using methyl lactate as a biosolvent, J. Sustain. Eng. 4 (2011) 75–83.
[7] C. Hegde, A.M. Isloor, M. Padaki, P. Wanichapichart, Y. Liangdeng, Synthesis and desalination performance of Ar^{+}-N^{+} irradiated polysulfone based new NF membranes, Desalination 265 (2011) 153–158.

[8] W.R. Bowen, B. Cassey, P. Jones, D.L. Oatley, Modeling the performance of membrane nanofiltration-application to an industrially relevant separation, J. Membr. Sci. 242 (2004) 211–220.
[9] F.P. Cuperus, C.A. Smolders, Characterization of UF membrane: Membrane characteristics and characterization technique, Adv. Colloid Interface Sci. 34 (1991) 135–173.
[10] X. Lu, X. Bian, L. Shi, Preparation and characterization of NF composite membrane, J. Membr. Sci. 210 (2002) 3–11.
[11] C. Hegde, A.M. Isloor, M. Padaki, A.F. Ismail, W.J. Lau, New PS-PPEES blend membranes for $CaCl_2$ and NaCl rejection, J. Membr. Water Treat. 3 (2012) 25–34.
[12] M. Helen, B. Viswanathan, S.S. Murthy, Synthesis and characterization of composite membranes based on α-zirconium phosphate and silicotungstic acid, J. Membr. Sci. 292 (2007) 98–105.
[13] K. Boussu, C. Vandecasteele, B. Van der Bruggen, Study of the characteristics and the performance of self-made nanoporous polyethersulfone membranes, Polymer 47 (2006) 3464–3476.
[14] Y. Baek, J. Kang, P. Theato, J. Yoon, Measuring hydrophilicity of RO membranes by contact angles via sessile drop and captive bubble method: A comparative study, Desalination 303 (2012) 23–28.
[15] J.M. Sturtevant, Calorimetric studies of biopolymers, Protein Sci. 5 (1996) 391–394.
[16] T. Tsuru, K. Ogawa, M. Kanezashi, T. Yashioka, Permeation characteristics of electrolytes and neutral solutes through titania nanofiltration membranes at high temperatures, Langmuir 26 (2010) 10897–10905.
[17] M. Manttari, A. Pihlajamaki, M. Nystrom, Effect of pH on hydrophilicity and charge and their effect on the filtration efficiency of NF membranes at different pH, J. Membr. Sci. 280 (2006) 311–320.
[18] M. Padaki, A.M. Isloor, G. Elavadi K.N. Prabhu, Preparation, characterization and performance study of poly (isobutylene-alt-maleic anhydride) [PIAM] and polysulfone [PSf] composite membranes before and after alkali treatment, Ind. Eng. Chem. Res. 50 (2011) 6528–6534.
[19] M. Siddiq, R. Ravi, J.B. Harte K.D. Dolan, Physical and functional characteristics of selected dry bean (*Phaseolus vulgaris* L.) flours, LWT, Food Sci. Technol. 43 (2010) 232–237.
[20] L. Zhang, G. Yang, L. Xiao, Blend membranes of cellulose cuoxam/casein, J. Membr. Sci. 103 (1995) 65–71.