International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2015): 6.391

Polysulfone based Ultrafiltration Membrane Preparation by Phase Inversion: Parameter Optimization

*Jayant S. Phale[1], Dr. Yogesh J. Chendake[2]

[1, 2]Department of Chemical Engineering, Bharati Vidyapeeth University, College of Engineering, Pune, India – 411043

Abstract: ***Polysulfone based ultrafiltration (UF) membranes are contemplated to be one of the most important separation material with large benefits of hydrolytic stability, chemical resistance, high strength, creep resistance etc. Due to these benefits it can be applied in diversified applications of gas separation, food and beverage processing, electro paint recovery, etc. PSF membranes are applicable in wide range of filtration spectra from microfiltration (MF) to reverse osmosis (RO). Optimization of membrane porosity and pore size are very difficult due to unstable solutions. Hence optimization of PSF membrane formation based upon effect of affecting parameters during phase inversion based membrane preparation is done. The concentration of dope solution, solvent of preparation of dope solution and other operating parameters such as humidity, temperature, pressure, etc. strongly affect membrane properties. The decreasing trend of concentration of doped solution is witnessed with the increase in the water flux. Additionally, the parabolic relation between the temperature and water flux through the membrane is noted to the extent of 60°C where is starts shrinking. A linear increase in bubble point with increase in concentration of dope solution used for preparation of membranes shows that membrane pore size and porosity reduces with increasing solution concentrations. The study shows various parameters affecting PSF based UF membrane preparation parameters, with wide range of separation applications with distinctive features.***

Keywords: Polysulfone membrane, casting parameters, solution concentration, solvent, phase inversion, water flux

1. Introduction

Over the last three decades, the use of porous polymer membranes has achieved a significant position in separation operations [1]. Phase inversion is one of the most substantial techniques for synthesizing porous polymer membrane [2]. Numerous parameters such as mechanical strength, water flux, pH resistance etc. are observed to be the influencing factors in membrane properties and applicability [4]. There is always a tradeoff between selectivity and transport rate. An increase in pore size would lead to increase in the flux but molecular weight cut off of the porous membrane would be higher [5]. This would lead to passage of undesired molecules and thus affecting desired selectivity. There is need of careful optimization of porosity and pore size for desired transport properties. Pore size and porosity are important factor in any membrane, pore size related to separation and porosity governs the flux through membrane [6]. Pore size and porosity vary according to casting condition of membrane. Casting condition, non solvent, polymer solution, solvent plays an important role in membrane preparation.

Polysulfone is the paramount material for synthesis of porous polymer membrane. Polysulfone are amorphous thermoplastics consist of aromatic units (phenylenes) subtended with Sulfone, isopropylidene or ether moieties[7], [8]. It has exemplary hydrolytic stability, chemical resistance, high strength and generous agency certifications make these polymers congruous for membranes used in stringent end-use environments [9]. Conventional application areas involve pharmaceutical production, water purification, wastewater treatment, and blood purification along with a range of industrial process separations, such as electro paint recovery, food and beverage processing, and gas separation [9],[10]. Sulfone polymers endeavor a unique combination of characteristics for membrane filtration applications. They can endure a variety of sterilization techniques, including gamma, steam, e-beam, and ethylene oxide. They can be readily transformed into UF and MF hollow fiber and flat sheet membranes with extraordinarily controllable pore size distribution. Additionally, they evince very high creep resistance, mechanical strength and stable at pH levels from 3–13, outstanding biocompatibility, good resistance to moderate concentrations of chlorine, outstanding hydrolytic stability and caustic resistance, low levels of extractable and insoluble materials, and global agency approvals [9]. Phase inversion is the mechanism by which PSF membrane can be synthesized using solvent Dimethylacetamide, methylpyrrolidone, dimethylformamide; with water as non solvent [11], [12]. The usually used solvent was dimethylformamide [13], [14], [15]. PSF has its own shortcoming such as it is hydrophobic in nature which causes the fouling. In PSF polymeric membranes, there is need of increasing rejection, transport rate, and reducing the molecular weight cut off [16].

In the presented work we plan to optimize the PSF membrane casting parameter to enhance permeation properties. Casting parameter such as humidity, temperature, concentration, pressure, polymer solution, use of non solvent would be varied to optimize membrane properties for application in waste water treatment, water purification, and purification of component.

2. Experimentation

2.1 Materials

PSF polymer synthesis grade (average molecular weight 30000Da) material in pallet purchased from Otto Chemei

Pvt. Ltd. India. Dimethylacetamide (DMAc) (synthesis grade) obtained from Loba Chemei Pvt Ltd India was used as solvent for solution preparation. Water was used as non solvent.

2.2 Solution Preparation

The dope solutions for membrane casting were prepared using DMAc as solvent. Weighed quantity of vacuum dried PSF was added to the solvent containing vessel under constant stirring. The solution was stirred continuously for more than 48 hr, to insure complete dissolution of DMAc without containing any swollen particle. It was degassed using probe Sonicator and used as dope solution for membrane casting.

2.3 Membrane Casting

Flat sheet PSF membranes were prepared by automatic membrane casting machine. Prepared solution was poured on membrane casting plate. It was spread on flat glass sheet surface by doctor knife. It was air dried for predetermine time and dipped in water smoothly. The knife clearance, knife speed and air dry time was maintained carefully by using programmable casting setup. Obtained membranes were preserved under formalin at 4°C, till further use. The membranes were cut into circular coupons of 50 mm diameter and used for further analysis.

2.4 Water flux analysis

The water flux of membranes was measured at one bar pressure using distilled water in Amicon type dead end stirring cell. Schematic of UF cell is given in figure (1). The membranes were mounted on the base of cell filled with 150 ml of distilled water. Water flux was measured after passage of 50 ml water at one bar pressure. The stirring speed as 300 rpm was maintained using magnetic stirrer with rpm indicator. The variation in water flux with pressure was analyzed from 0.5 bar to 3.0 bar at an interval of 0.5 bar each show in the (figure 3)

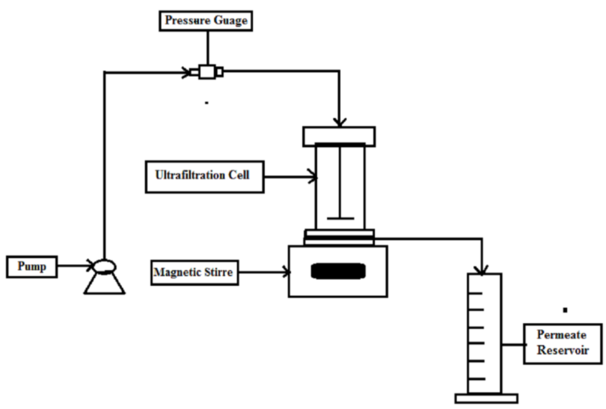

Figure 1: Schematic Diagram for Ultrafiltration Cell

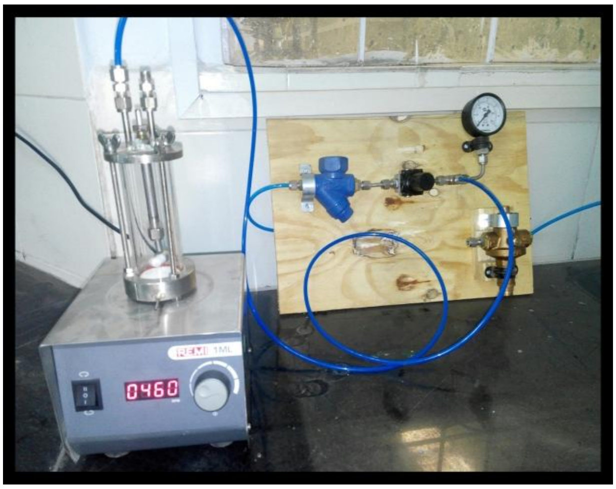

Figure 2: Actual Photograph of Ultrafiltration Cell

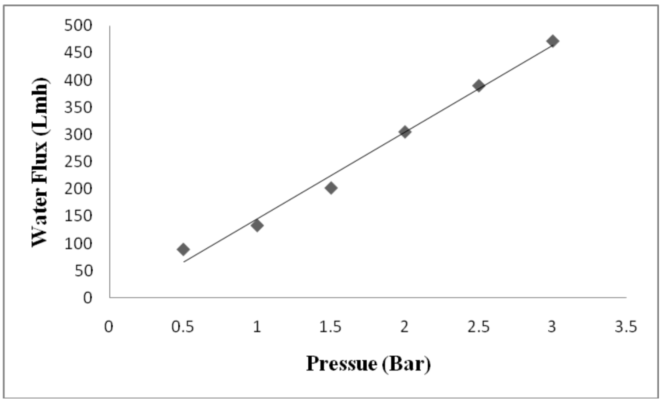

Figure 3: Effect of Pressure on Water Flux

2.4 Effect of Temperature

The effect of temperature on membrane morphology was analyzed by treating the membranes with distilled water for various temperatures from 30 – 60 °C. The membrane coupons based on 21% PSF dope solutions were kept in the distilled water at predetermined temperature for one hr and then analyzed for water permeation (Figure 4).

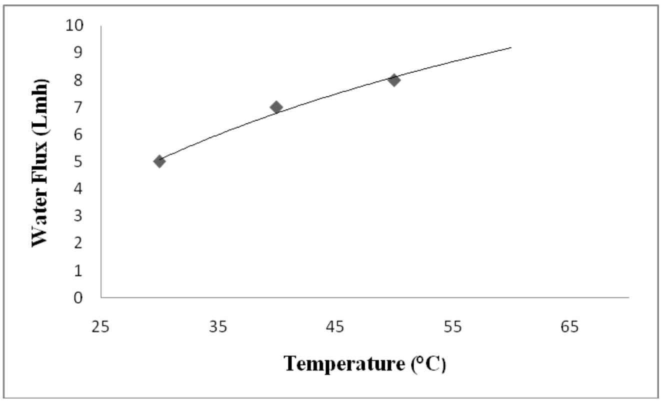

Figure 4: Effect of Temperature on Water Flux

2.5 Effect of Concentration

The effect of dope solution concentration on water flux through the membrane was analyzed by treating the different concentration dope solution (15, 17, 19 and 21%) based membrane. These membranes were analyzed for water flux at one bar pressure (Figure 5).

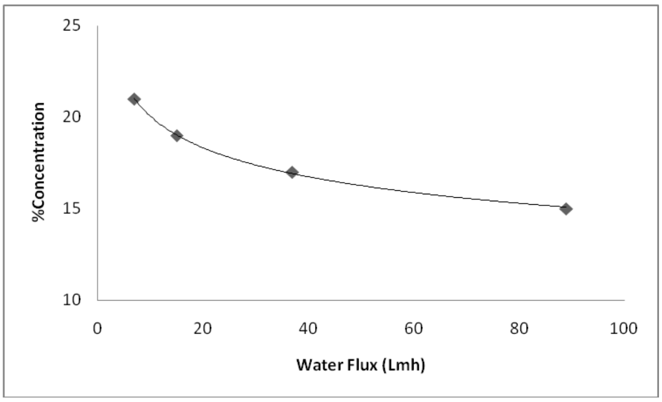

Figure 5: Effect of Dope Solution Concentration on Permeate Water Flux

2.6 Bubble point analysis

The membrane coupons mounted in Amicon cell with little water on surface. Air was used as second fluid. The air pressure was increased at the rate 0.2 bar. After each pressure increase a time of half hr was allowed to pass the air and then pressure was increased. This was done up till constant air flow rate was obtained.

3. Result and Discussion

3.1 Selection of Materials

Polysulfone are amorphous thermoplastics comprised of aromatic units (phenylenes) link with Sulfone, isopropylidene or ether moieties [9]. Polysulfone has the highest concentration of Sulfone moieties in the polymer repeating unit. The structure gives Polysulfone the highest water absorption of all commercial Sulfone polymers, making it the most hydrophilic Sulfone polymer [9].

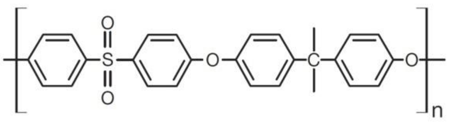

Fig. (6) : Structure of Polysulfone

Polysulfone offer a unique combination of features for membrane filtration applications. They can withstand a variety of sterilization techniques, including steam, gamma, e-beam, and ethylene oxide [15]. They can be readily formed into MF and UF hollow fiber and flat sheet membranes with highly controllable pore size distribution. They exhibit following property such as very high mechanical strength and creep resistance, Stable at pH levels from 3 – 13, outstanding hydrolytic stability and caustic resistance, good resistance to moderate concentrations of chlorine, low levels of extractable and insoluble materials, outstanding biocompatibility and global agency approvals.

It is soluble in polar solvents such as dimethylformamide (DMF), Dimethylacetamide (DMAC) and N-methyl-2-pyrrolidone (NMP) and water is non-solvent for the same [17]. This makes PSF as material of choice for preparation of membranes.

Dimethylacetamide was used as solvent for membrane preparation because it is easily available in major quantity, possibility of using water as non-solvent. Though PSF membranes were prepared with DMF as solvent [14], these solutions were unstable nature at high concentration [17]. This inability of high solution concentration generated need for alternative solvent which would allow high concentration solution. Presence high concentration would lead to dense surface layer and membranes with lower pore size. This would lead to membranes with desired rejection analysis but result in decrease of permeation flux, transport resistance and increase in concentration of solution.

Effect of dope solution Concentration on permeates Water Flux Selection of solvent plays an important consideration in solution preparation. It is important to select a solvent with high purity and minimal water content. When using a solvent recovery system, monitor solvent purity regularly and ensure that the recycling system is working properly. To optimize solution viscosity, select the most appropriate molecular weight polymer in order to tightly control the process parameters. High molecular weight polymers lead to high viscosity solutions and take longer to dissolve however; a higher molecular weight may be required to ensure adequate strength of the nascent membrane during processing as well as the finished membrane during use.

During preparation of polymer solution, slowly add the polymer to the solvent while agitating. Adding it too quickly can lead to the formation of aggregates that will take longer to dissolve. The geometry of the stirrer, the agitation rate, and the temperature all affect the time needed to dissolve the polymer.

It can be seen from the (Figure 5); the water flux was decreased exponential with increase in dope solution. This would be due to decrease in pore size and lower porosity of membrane due to increase in solution concentration. This lower pore size and porosity increases the resistance for water transport through membrane [10] .This increase in resistance would result in lower permeate flux through the membranes. Similar reduction in flux with increase in dope solution concentration has been reported in literature [20]. The water flux reduced exponentially from 88 LMH to 7 LMH for 15 and 21 % dope solution concentration, respectively. The reduction in flux can be said to be a sign of reduction in pore size and porosity depending upon dope solution concentration. This lower pore size would reduce MWCO. This interrelation between pore size and dope solution concentration would be highly important while designing a membrane for specific separation operation, where specific pore size would help for better balance in membrane rejection properties and permeate flux.

3.2 Effect of driving pressure on water transport rate

The real life application would require use of membranes for treatment of process streams at different pressures. Use of membranes at high pressures might damage the pores of membranes. This is known as compaction of membranes [17]. Hence the stability and effect of pressure on transport rate for various membranes is used [18]. The membranes prepared with 15 % PSF dope solution were analyzed for effect of pressure on permeate flux. The trans-membrane pressure was increased from 0.5 bar to 3.0 bar. The permeate flux was increased linearly from 89 LMH to 472 LMH. This linear increase is according to Fick's law, which states linear variation in transport rate with driving force [20], [22]. This variation shows that membranes are stable without any damage to pores. Thus membranes have excellent mechanical stability and no compaction even at lower solution concentration. With increase in dope solution concentration the amount of polymer in solution would increase mechanical support for the pores of membranes and thus the stability would increase [23]. This shows prepared membranes have excellent mechanical stability.

3.2 Effect of Temperature on Water flux

The real life application would require use of membranes at varying temperature. Exposure to such temperatures might affect membrane properties. Hence the membranes prepared with 21 % dope solution were analyzed for variation in properties after exposure to temperature of 30, 40, 50 and 60 °C, respectively; for one hour. The temperatures were chosen are room temperature in Indian conditions and above those.
These membranes showed linear increase in permeate flux with increase in treatment temperature from 30 to 50 °C. This might realign the polymer chains and change the pore size of membranes. Such realign and increase in pore size would increase the transport rate of membrane [13]. Though this realignment have positive effect on transport rate, but the increase in pore size would increase the MWCO which is unwanted while rejection properties are concerned. Continuous exposure of the membranes to high temperature would damage the membranes and have undesired effect on their transport properties.

At temperature of 60°C, the membranes showed shrinking. This makes them useless for application at this temperature. This showed PSF based membranes should be used at temperatures of 50°C or lesser. Damage to polymer structures at high temperatures is well reported [20], [24], [25].

3.4 Bubble Point Test

The bubble point is analyzed to determine pore size or presence of unusually large pores in membranes. The analysis was carried out using air-water system. The wetted membranes were mounted on cell and air flow rate was measured. A linear increase in bubble point with increase in dope solution concentration used for preparation of membranes was observed. This variation shows formation of proper membranes without any defect. The linear increase in bubble point shows that the membranes are becoming tighter or the maximum pore size of the membranes in decreasing linearly with increase in dope solution concentration. This resulted in higher bubble point. Such lower pore size would result in lower MWCO, which is required for higher rejection properties. This is supported by reduction in permeate flux.

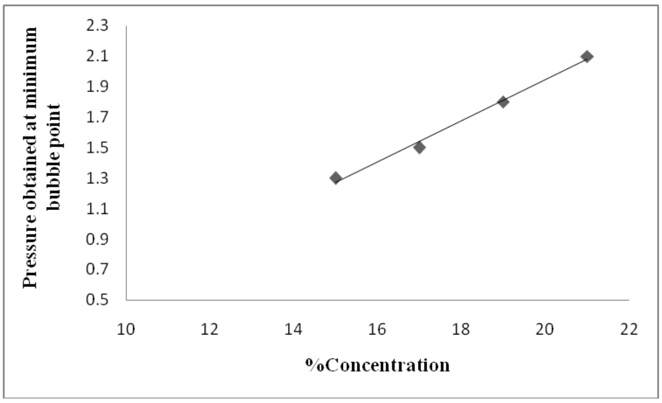

Figure (7): Effect of Bubble Point Analysis on Concentration

4. Conclusions

Various parameters affect formation of PSF membranes. Major effect is solvent used for solution preparation. A variation in solvent from DMF to DMAc makes the dope solution stable at higher concentration. This also changes gelation mechanism and varying its surface properties. In this research, formation of PSF based UF membrane is made possible with the phase inversion technique by casting mechanism. The characterization of these membranes for assorted parameters such as temperature, concentration, water flux, bubble point and pressure stability, etc. has been analyzed. Furthermore, the optimization of these process parameters are observed for numerous treads among them. It, therefore proposed that the PSF based UF membrane will have an extensive scope for further research in future, by varying the solvent for dope solution.

Acknowledgements

Authors are thankful to management of Bharti Vidyapeeth University, College of Engineering, Pune (India) for their support towards setting of membrane laboratory. Also we would like to thank TEQIP-II for financing of Institute Funded Research Project Scheme, under which we could generate research facilities used for current project.

References

[1] Baker, R.W., "Membrane Technology and Applications", 2nd ed., John Wiley & Sons Ltd. (2004).
[2] Genn I., Kuypers S., Leysen R., "Effect of the addition of ZrO2 to polysulfone based UF membranes", J Membr. Sci.113 (1996) 247-258.
[3] Vandezande, P., Li, X., Gevers, E.M.L. and Vankelecom, F.J.I. "High throughput study of phase inversion parameters for polyimide based SRNF membranes", J. Membr. Sci.330 (2009) 307 – 318.
[4] Ghosh A. K. and Hoek E.M.V., "Impacts of support membrane structure and chemistry on polyamide-polysulfone interfacial composite membranes", J. Membr. Sci. 336 (2009)140-8.
[5] Ma Y., Shi F., Ma J., Wu W., Zang J., Gao C., "Effect of PEG additive on morphology and performance of

Polysulfone ultrafiltration membrane", Desalination. 272 (2011) 51-58.

[6] Xie-Quing X., "Additive for the preparation of Polysulfone-based ultrafiltration membranes, especially for hemodialysis and hemoosmometer", Desalination. 48 (1983) 79-84

[7] Ghosh R., Wan Y.H. and Cui Z.F., "Parameter scanning ultrafiltration: rapid optimization of protein separation", Biotechnol. Bioeng. 81 (2003) 673-682

[8] MoÈckel D., Staude E., Michael D. Guiver, "Static protein adsorption, ultrafltration behavior and cleanability of hydrophilized polysulfone membranes", J. Membr. Sci. 158 (1999) 63-75

[9] Kajekar A. J.,. Dodamani B.M , Isloor A. M, Karim A. Z, Cheer N.B,. Ismail A.F, Shilton S. J., "Preparation and characterization of novel PSf/PVP/PANI-nanofiber nanocomposite hollowfiber ultrafiltrationmembranes and their possible applications for hazardous dye rejection", Desalination 365 (2015) 117–125

[10] Liu Z., Bai Y., Sun D, C., Xiao A., Zhang Y.,"Preparation and Performance of Sulfonated Polysulfone Flat Ultrafiltration Membranes", Polym. Eng. Sci. 55 (2014) 1003-1011.

[11] Witte P.V , Dijkstra P.J., van den Berg J.W.A., Feijen J, "Phase separation processes in polymer solutions in relation to membrane formation", J. Membr. Sci. 117 (1996) 1-31

[12] Blanco, J. F., Sublet, J., Nguyen, Q T., Schaetzel, P. "Formation and morphology studies of different polysulfones-based membranes made by wet phase inversion process", J. Membr. Sci. 283(2006) 27–37.

[13] Chakrabarty B., Ghoshal A. K., Purkait M. K., "Preparation, characterization and performance studies of Polysulfone membranes using PVP as an additive", J. Membr. Sci. 315 (2008) 36-47

[14] Idris A., Zain N. M., Noordin M.Y., "Synthesis, characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives", Desalination 207 (2007) 324–339

[15] Blanco, J. F., Sublet, J., Nguyen, Q T., Schaetzel, P. "Formation and morphology studies of different polysulfones-based membranes made by wet phase inversion process", J. Membr. Sci. 283 (2006) 27–37

[16] Aryanti P.T.P., Subagjo S., Ariono D., Wenten I.G. ,"Fouling and Rejection Characteristic of Humic Substances in Polysulfone Ultrafiltration Membrane", J. Membr. Sci. 01 (2015) 41-45

[17] K. W. Lee, B. K. Seo, S. T. Nam and M. J. Han, "Trade-off between thermodynamic enhancements and kinetic hindrance during phase inversion in the preparation of polysulfone membranes", Desalination 207 (2007) 324–339

[18] Eisen M.S., Semiat R, Vainrot N, "Polysulfone polymer and membrane for reverse osmosis, nanofiltration and ultrafiltration", U.S.Patent, US 8,944,257 B2 feb (2015).

[19] H. Ohyal J.J. Kim, A. Chinch, M. Alihara, S.I. Semonova, Y. Negishi, O. Moil and M. Yasuda, "Effect of pore size on separation of microfiltration of oily water using porous glass tubular membrane", J. Membr. Sci. 145 (1998) 1-14.

[20] Toraj Moha.madi, Ashkan Esmaeelifar, "Wastewater treatment using Ultrafiltration at a vegetable oil factory", Desalination.166 (2004) 329-337

[21] Sofiah Hamzah, Nora'aini Ali, Marinah Mohd Ariffin, Asmadi Ali and Abdul Wahab Mohammad, "High performance of Polysulfone Ultrafiltration membrane:Effect of polymer concentration", ARPN Journal of Engineering and Applied Sciences, 9 (2014) 2543-2550.

[22] P.Abaticchio, A.Bottino, G.Camera Roda, G.Capannellp and S.Munari, "Characterization of Ultrafiltration Polymeric Membranes", Desalination, 78 (1990) 235-255.

[23] Panda S.R., S. De, "Preparation, characterization and performance of ZnCl2 incorporated polysulfone (PSF)/polyethylene glycol (PEG) blend low pressure nanofiltration membranes", Desalination 347 (2014) 52–65.

[24] Kumar R., Isloor A.M., Ismail A.F., Matsuura T., "Synthesis and characterization of novel water soluble derivative of chitosan as an additive for polysulfone ultrafiltration membrane", J. Membr. Sci. 440 (2013) 140–147

[25] Ong C, Lau W., P. Goh P., B. Ng B., Ismail A, "Preparation and characterization of PVDF– PVP–TiO2 composite hollow fiber membranes for oily wastewater treatment using submerged membrane system", Desalin. Water Treat. (2013) 1–11.