THE EFFECTS OF STRUCTURAL AND ELECTRICAL PROPERTIES OF HOLLOW FIBER NANOFILTRATION MEMBRANES ON SALT AND DYE REMOVAL UNDER DIFFERENT SOLUTION PROPERTIES

AHMAD FAUZI ISMAIL[1*] & LAU WOEI JYE[2]

Abstract. Three different characteristics of self-made hollow fiber nanofiltration (NF) membranes with different structural and electrical properties were evaluated for their suitability for removing salt and colour under different solution properties. Results showed NF achieved promising dye retention for the reactive dyes used at different concentrations and varied slightly with pH. The retention of salt was found to be dependent on solution properties and membrane electrical properties where higher retentions were achieved under alkaline condition and by using NF membrane with higher surface charge value. The greater membrane negative surface charge properties has also made the membrane less fouling-sensitive to dye absorption and improving the economic viability of the treatment process.

Keywords: Membrane separation; nanofiltration; reactive dyes; salts; sulfonated poly (ether ether ketone)

Abstrak. Tiga jenis membran gentian geronggang penurasan nano yang mempunyai perbezaan pada morfologi dan ciri elektrik digunakan untuk mengkaji kesesuaian mereka dalam pemisahan garam dan warna dalam larutan yang mempunyai sifat berlainan. Keputusan uji kaji menunjukkan bahawa semua membran penurasan nano mampu mencapai pemisahan warna yang amat baik tanpa dipengaruhi oleh kepekatan warna dan pH. Pemisahan garam yang lebih tinggi boleh dicapai dengan menggunakan membran yang mempunyai permukaan yang bercas negatif tinggi. Kewujudan cas negatif ini juga menyebabkan membran kurang sensitif terhadap penyerapan warna dan seterusnya meningkatkan daya ekonomi membran dalam proses pemisahan.

Kata kunci: Pemisahan membran; penurasan nano; warna; garam; poli (eter eter keton) disulfonasi

1.0 INTRODUCTION

Recently, the development of nanofiltration (NF) membranes for various industrial applications has drawn much attention from membrane scientists due to their unique characteristics in the separation of small neutral and charged molecules in aqueous solution. Although a number of studies has been documented in literature to investigate the separation performance of NF membrane in the treatment of textile discharge, rare work has been done to study the influence of NF specific characteristics

[1&2]Advanced Membrane Technology Research Centre, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia
* Corresponding author: Tel: +60 (7) 553-5592, Fax: +60 (7) 558-1463. Email: afauzi@utm.my

on solute separation under various feed conditions [1 - 6]. Membrane characteristics such as pore radius and effective charge density are preferentially required in the membrane selection so that one would fully explore how these properties take place in the removal of dyestuffs and dissolved salts from wastewater [7]. However, information on membrane properties specified by manufacturer is not really explicit as molecular weight cut off and solute separation efficiency of membrane may be varied depending upon the protocols used by various manufacturers [8]. Moreover, it is also lack of data about the quantification of membrane surface charge. Only NF membranes with either negatively charged or positively charged are being disclosed without taking into consideration the value of effective surface charge density, X_d. Bowen and Wahab [7] reported that a high value of X_d could maximize the Donnan effects of membrane which resulted in effective removal of dye and salt from a dye-salt-water waste stream. Besides the effect of charge density on retention characteristics, membrane surface charge is also an important parameter to minimize fouling tendency by reducing the absorption of negatively charged foulants in the feed water [9]. Due to this, NF membrane with known pore size and effective charge density is required in solute separation applications in order to obtain precise control of separation efficiency and achieve purification goal.

Over the past few years, Ismail and Hassan succeed to deduce the fine structural and electrical properties of NF membranes prepared from different preparation conditions by employing theoretical models [10 - 12]. By having these properties, it becomes possible for potential users to choose NF membrane which is best suited to particular process requirement. Despite membrane properties are always identified as the primary factors affecting the separation efficiency for the solution containing dye-salt-water components, it is also of great importance to investigate the influences of solution properties because the efficiency of NF separation is found to be greatly dependent on the feed water chemistry [13 - 16].

The objective of this study is to investigate the effects of structural and electrical properties of NF membranes on salt and dye removal under different solution properties. The differences in the properties of NF were altered by varying the sulfonated poly (ether ether ketone) (SPEEK) content in the dope solution during membrane fabrication. To evaluate membrane separation efficiency, the feed solutions were prepared by varying salt concentration, dye concentration, feed pH and etc. The study is expected to provide instructive information on the influences of membrane characteristics and feed properties on the separation performance.

2.0 MATERIALS AND METHODS

2.1 Materials

Reactive Black 5, RB 5 (MW 991, λ_{max}: 592 nm) and Reactive Orange 16, RO 16 (MW 616, λ_{max}: 493 nm), supplied by Sigma were used as received. Charged solutes,

NaCl and Na_2SO_4 used in determination of membrane separation efficiency, were purchased from Merck. NaOH (0.1 N) and HCl (0.1 N) aqueous solution from Merck were used to modify pH value of feed solution. Other chemicals used in this study were used as purchased without further purification. All the solutions were prepared using distilled water with pH value nearly 7 unless otherwise specified.

2.2 Nanofiltration Membrane

The self-made NF membranes used in this study were prepared using a simple dry-jet wet spinning technique [17]. Dope solutions were prepared from 20 wt% PES in 70 wt% NMP which containing different concentrations of PVP K15 and SPEEK. The concentration of SPEEK was varied from zero to 4 wt% in the dope solution in order to produce different membrane properties, as shown in Table 1. These values are found in the range of twenty-nine commercial NF membranes assessed by Bowen and Mohammad [7].

Table 1 The structural and electrical properties of the self-made hollow fiber nf membranes

[a]Membrane	SPEEK Content (%)	[b]J_v ($\times 10^{-7}$ m/s)	r_p (nm)	$A_k/\Delta x$ (m^{-1})	ξ (–)
PES	–	3.75	0.77	3196	–1.17
PES/SPEEK 2	2	5.19	0.99	1986	–2.14
PES/SPEEK 4	4	7.84	0.79	5209	–2.29

[a]Membrane properties were deduced by using theoretical models as reported previously [10-12].
[b]J_v, r_p, $A_k/\Delta x$ and ξ represent the water flux, pore radius, ratio of porosity to membrane thickness and effective surface charge, respectively.

2.3 Experimental System

Filtration experiments were conducted using a laboratory-scale cross-flow permeation system. Both ends of the hollow fiber were plotted with epoxy resin (E-30CL Loctite® Corporation, USA) and then mounted into a test module. A low pressure booster pump (ROP-BP/KF, Kemflo) was used to control the desired operating pressure (5 bar) through the adjustment of the back-pressure regulator. Feed was pressurized onto the outer membrane surface into lumen side and permeate was then collected at the end of the module.

2.4 Analytical Methods

The percentage of dye retention was determined using spectrophotometer (Model DR/4000, Hach) at a wavelength as specified by manufacturer. Salt concentration in the feed and in the permeate were analyzed by conductivity using a portable

conductivity meter (EC300, YSI Inc). pH meter (HI 8424, HANNA instruments) was used to measure the pH value of aqueous solution prepared. For the determination of polyvinyl alcohol (PVA) rejection, total organic carbon (TOC) analysis was performed using TOC-V$_{CSH/CSN}$ analyzer (Shimadzu, Japan). The chemical oxygen demand (COD) analysis was carried out following the procedure handbook of DR/4000 spectrophotometer.

3.0   RESULTS AND DISCUSSIONS

3.1   Salt Rejection

3.1.1   Effect of Salt Concentration

NaCl and Na$_2$SO$_4$ are the most common inorganic salts that have been widely used in dyeing process for the purpose of enhancing the degree of dye fixation onto fabric. The dissolved salt in waste stream must be treated properly before being discharged into environment. Figure 1 shows the salt rejection of different characteristics of NF at salt concentration in the range of 250-5000 ppm. As can be seen from the figure, PES/SPEEK 4 membrane showed the highest values while PES membrane the lowest in the separation of NaCl and Na$_2$SO$_4$ solute. With the addition of small amount of SPEEK into PES membrane, it showed that both PES/SPEEK blend membranes displayed higher salt separation than that of PES membrane. It is because of the enhancement in membrane surface charge properties resulting from SPEEK added. Increase in surface charge properties, however resulted in larger variation in NaCl separation in PES/SPEEK membrane compared to PES membrane. This observation was similar to the work carried out by Van der Bruggen *et al.* [4],
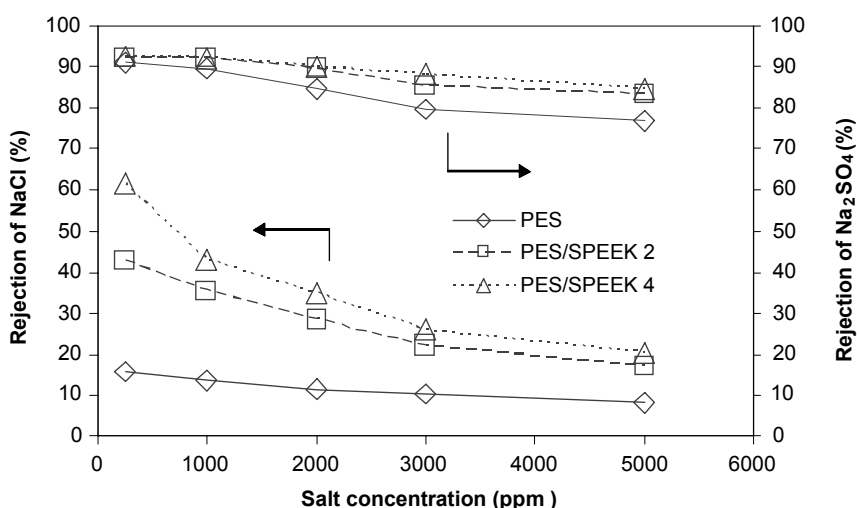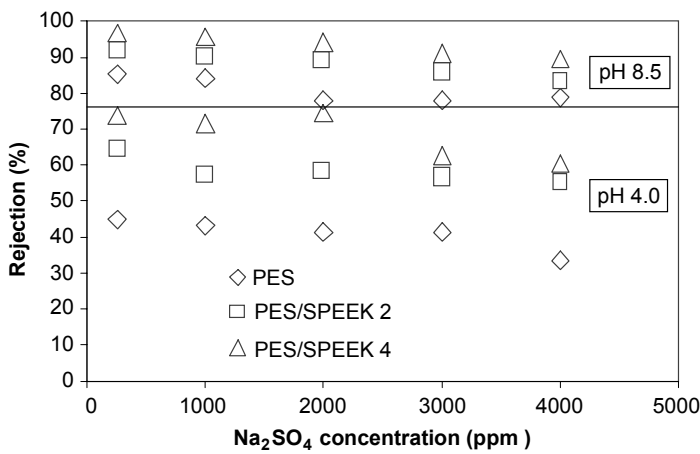

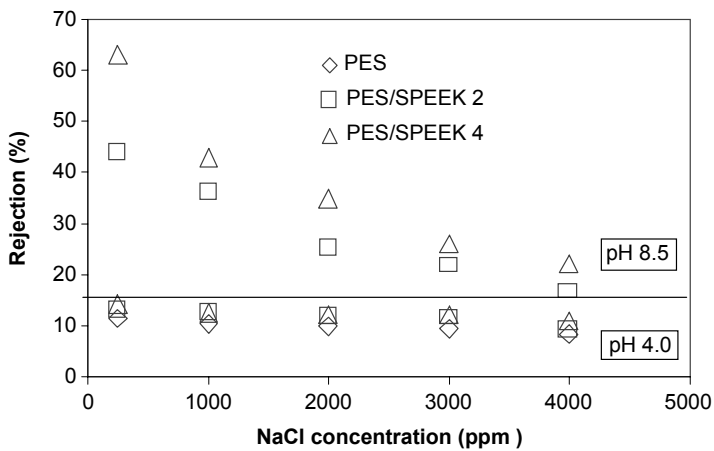**Figure 1**   Effect of salt concentration on salt removal using different NF

where salt concentration plays an important role in damping out electrostatic repulsion, causing electrolyte retention decreases significantly with concentration.

3.1.2 Effect of PH Value

It has been acknowledged that alkaline environment is always the best condition for enhancing the degree of dye fixation during dyeing process, though acidic condition would also be considered for certain textile operations. Figure 2 presents the effect of feed pH on the rejections of NaCl and Na_2SO_4. Higher rejection rates were found in the case of PES/SPEEK membranes which were claimed to have SO_3^- ions on the

(a)

(b)

Figure 2 Effect of pH value on the salt rejection of NF membranes at different salt concentrations, (a) Na_2SO_4 and (b) NaCl

membrane surface resulting from the addition of SPEEK. The blend membranes become more negatively charged in alkaline condition due to the presence of more OH^- ions in solutions [18-19]. This leads to an enhancement in electrostatic repulsion in the interface of membrane with aqueous salt solution and result in higher retention. However, decreasing the pH from 8.5 to 4 decreased the salt rejection of all the membranes, indicating pH had an effect on the charge of membrane due to the disassociation of functional groups. The H^+ ions dissociated from HCl can be absorbed onto membrane surface, shielding the negative charges and consequently causes significantly decrease in rejection of electrolytes. Meanwhile, with the use of HCl solution to modify the feed pH, it causes an increase of Cl^- ions in permeate which may further decrease the rejection rate. Therefore, the salt rejection varied depending on the feed properties and membrane electrical properties. In general, the use of the most negatively charged NF membrane is highly recommended under alkaline solution as higher separation efficiency can be easily achieved.

3.2   Dye Removal

3.2.1   Effect of Dye Concentration

Table 2 shows the effect of reactive dye concentration on colour removal using different characteristics of NF. Reactive dyes are selected for the investigation because they are classified as the dyestuffs which have the lowest fixation rate in dyeing operation. Results from Table 2 indicate that almost complete rejection of RB 5 and 93.7 – 99.5% rejection of RO 16 were achieved depending on type of NF and dye concentration used. The major factor affecting the excellent colour removal seems to be the sieving effect (membrane pore size). As the effective hydrodynamic radius of dye molecule is typically larger than the membrane pore radius, the retention of dye is therefore mainly controlled by sieving mechanism. It is reported that the dye molecule size for RB 5 and RO 16 are approximately 2 nm and 1.5 nm, respectively

Table 2   Effect of dye concentration on dye removal of NF membrane

| Reactive dye	Conc. (ppm)	Colour Removal (%)		
		PES	PES/SPEEK 2	PES/SPEEK 4
	50	99.69	99.62	99.54
RB 5 100	100	99.21	99.79	99.96
(991 Da)	250	99.77	99.90	99.82
	500	99.57	99.92	99.78
	50	99.47	98.14	98.34
RO 16100	100	98.60	96.99	96.96
(616 Da)	250	97.23	95.38	95.59
	500	93.71	93.77	94.10

[20]. Thus, it is less possible for dye molecules from passage through the membranes which have relatively smaller pore size (see Table 1). On the other hand, Jiraratananon *et al.* [21] reported that Donnan exclusion effect should also be taken into consideration during dye separation. The effect however was found little dependence in this study, most probably due to the large size of dye molecules relatively to the membrane pore size. Nevertheless, it is believed that Donnan exclusion mechanism may take place in separation when reactive dye used has the effective hydrodynamic radius which is relatively equal or even smaller than the membrane pore radius.

3.2.2 *Effect of PH Value*

Figure 3 details the reactive dye retention of membranes at different pH of dyeing aqueous solutions. As can be clearly seen, the variation of pH values did not affect
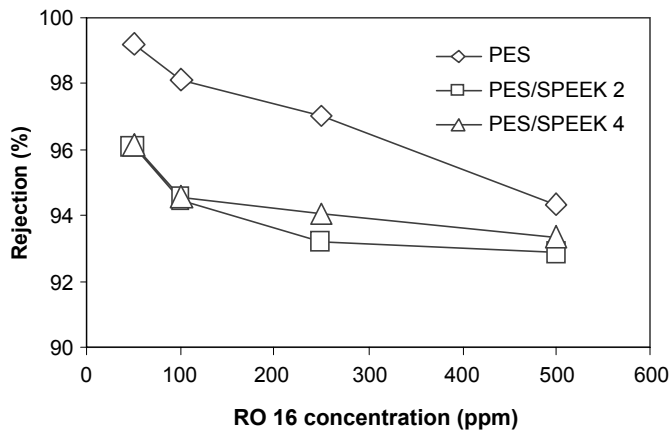
(a)
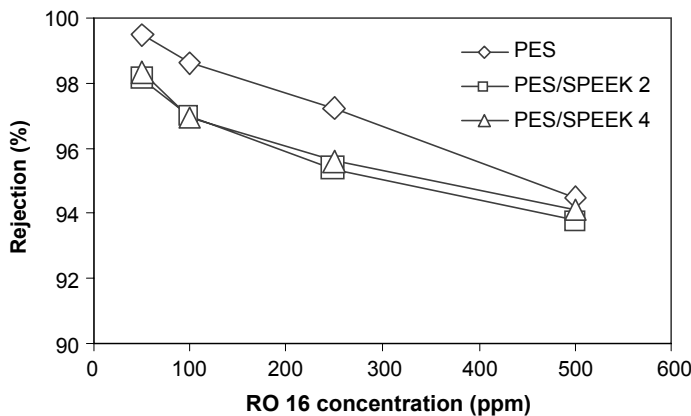
(b)

Figure 3 Effect of pH value on dye removal of NF (a) pH 4 and (b) pH 8.5

significantly the dye retention [22]. No large discrepancies were observed between the values obtained under different pH conditions using either PES or PES/SPEEK blend membranes. However, one can note that the values obtained by PES/SPEEK membranes with solution pH 8 were slightly higher than those obtained with solution pH 4. This could be partly due to the enhancement in electrical properties of PES/ SPEEK membranes as discussed in salt rejection. Overall, it is found that dye retention was still strongly dependent on membrane structural properties rather than electrostatic properties.

3.3 Experiments with Synthetic Dyeing Wastewater

For this experiment, a synthetic dyeing wastewater composed of 1000 ppm RB 5, 500 ppm PVA, 250 ppm NaCl and 750 ppm Na_2SO_4 was prepared and used for the evaluation of the membrane separation efficiency. The composition of the synthetic wastewater prepared was very similar to the composition of real dyeing wastewater, making the separation process more practical [6]. The permeate quality was monitored by measuring the removal efficiency of conductivity, colour, TOC and COD retention. It is observed from Table 3 that the retention of colour, TOC and COD was not affected by the types of NF used, except the salt retention. The increasing salt retention in PES/SPEEK membranes is the result of the increasing surface charge properties. As shown in Figure 4, the use of SPEEK on membrane has a great influence on decreasing flux decline, though the cake layer due to deposited dye molecules is formed on all the membrane surfaces. Figure 5 shows the FESEM images of outer surface of PES membrane with and without the addition of SPEEK after a simple chemical cleaning process. Clearly, the PES/SPEEK blend membrane was less stained with dye compared to PES membrane, indicating fouling on PES/SPEEK blend membrane was primarily cake formation (reversible) without permanent particle penetration and pore blockage of the membrane itself. Approximately 85% of water flux recovery could be retrieved using PES/SPEEK membranes compared to 78% by PES membrane. These results suggested that NF membrane was less fouling-sensitive to dye adsorption with the addition of small amounts of SPEEK into dope solution during membrane preparation.

Table 3 Performance of NF for treating synthetic dyeing wastewater

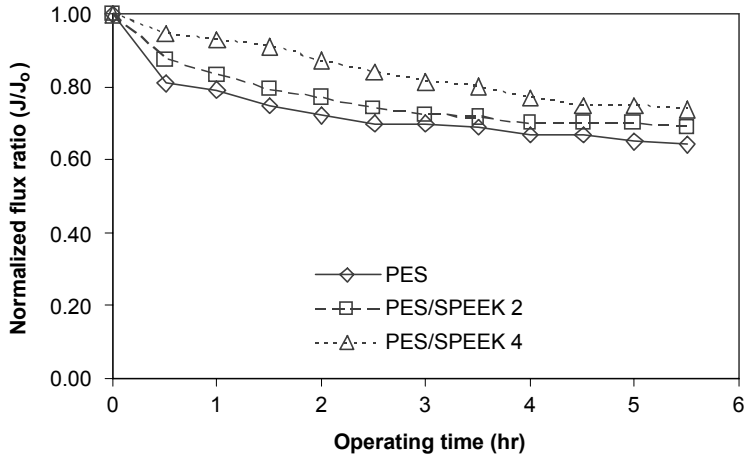| Membrane	Salt (%)	Colour (%)	TOC (%)	COD (%)
PES	60.88	99.62	97.07	98.46
PES/SPEEK 2	63.84	99.85	97.79	98.00
PES/SPEEK 4	72.80	99.89	97.70	97.29

Figure 4 The normalized flux ratio against operating time of NF membranes for treating synthetic wastewater
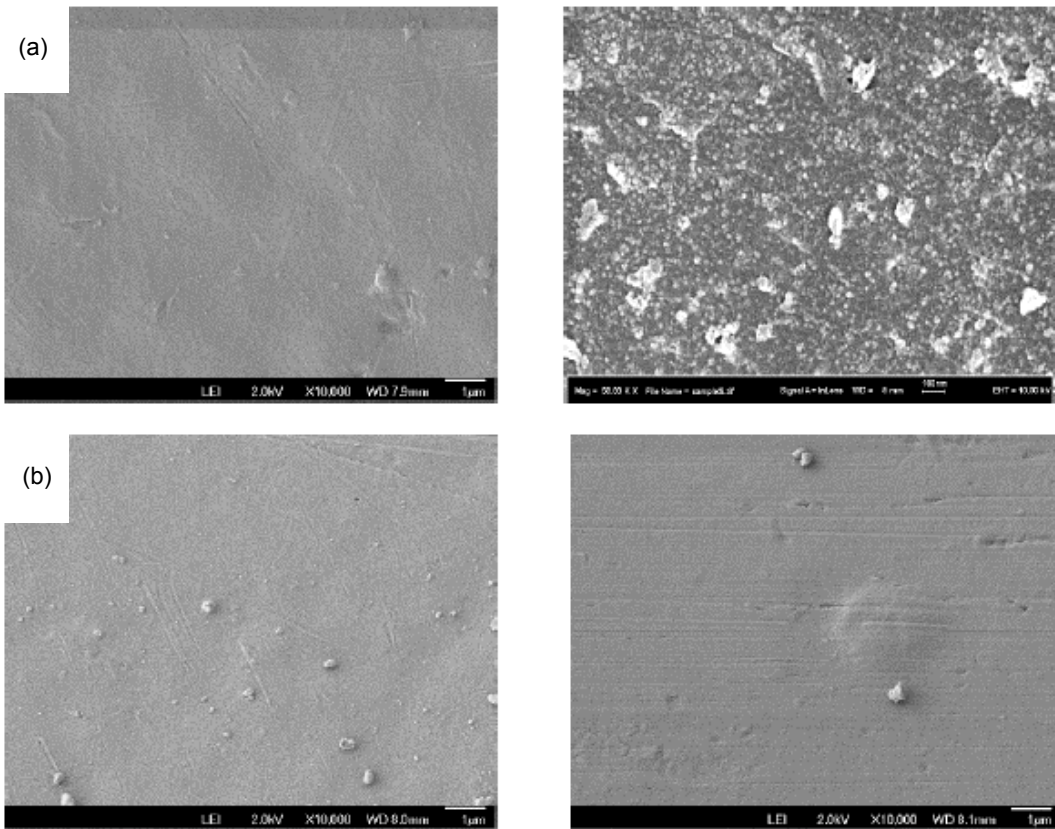

Figure 5 FESEM of clean membrane surface (left) and used membrane surface after chemical cleaning (right) process (a) PES and (b) PES/SPEEK 4 membrane

4.0   CONCLUSIONS

This study demonstrates the importance of NF characteristics and the feed properties on the NF separation performance. The salt retention was found to be decreased with salt concentration but increased with pH. The surface charge introduced by SPEEK on PES/SPEEK membranes fully explained the better separation performances compared to PES membrane. Since membrane pore size was relatively smaller than the effective hydrodynamic radius of reactive dye used, notably high retention could be easily achieved and the dye retention seemed to be not affected by dye concentration and pH. Membrane fouling is inevitable for dyeing treatment process, however it is reversible with the addition of small amount of SPEEK into membrane. This is in fact helpful in extending membrane lifespan and improving the economics of the process.

REFERENCES

[1]   Lopes, C. N., J. C. C. Petrus and H. G. Riella. 2005. Color and COD Retention by Nanofiltration Membranes. *Desalination*. 172: 77-83.
[2]   Tang, C. and V. Chen. 2002. Nanofiltration of Textile Wastewater for Water Reuse. *Desalination*. 143: 11-20.
[3]   Lau, W. J. and A. F. Ismail. Polymeric Nanofiltration Membrane for Textile Dyeing Wastewater Treatment: Preparation, Performance Evaluation, Transport Modelling, and Fouling Control – A Review. *Desalination*. Accepted for publication.
[4]   Van der Bruggen, B., B. Daems, D. Wilms and C. Vandecasteele. 2001. Mechanisms of Retention and Flux Decline for the Nanofiltration of Dye Baths from the Textile Industry. *Sep. Purif. Tech.* 22-23: 519-528.
[5]   Boussu, K., C. Vandecasteele and B. Van der Bruggen. 2006. Study of the Characteristics and the Performance of Self-made Nanoporous Polyethersulfone Membranes. *Polym.* 47: 3464–3476.
[6]   Mo, J. H., Y. H. Lee, J. Kim, J. Y. Jeong and J. Jegal. 2008. Treatment of Dye Aqueous Solutions using Nanofiltration Polyamide Composite Membranes for the Dye Wastewater Reuse. *Dyes Pigm.* 76: 429-434.
[7]   Bowen, W. R. and A. W. Mohammad. 1998. A Theoretical Basis for Specifying Nanofiltration Membranes – Dye/salt/water Streams. *Desalination*. 117: 257-264.
[8]   Bellona, C., J. E. Drewes, P. Xu and G. Amy. 2004. Factors Affecting the Rejection of Organic Solutes during NF/RO Treatment – a Literature Review. *Water Res.* 38: 2795-2809.
[9]   Bowen, W. R., T. A. Dovena and H. B. Yin. 2002. Separation of Humic Acid from a Model Surface Water with PSU/SPEEK Blend UF/NF Membranes. *J. Membr. Sci.* 206: 417-429.
[10] Ismail, A. F. and A. R. Hassan. 2004. The Deduction of Fine Structural Details of Asymmetric NF Membranes using Theoretical Models. *J. Membr. Sci.* 231: 25-36.
[11] Ismail, A. F. and A. R. Hassan. 2006. Formation and Characterization of Asymmetric Nanofiltration Membrane: Effect of Shear Rate and Polymer Concentration. *J. Membr. Sci.* 270: 57-72.
[12] Ismail, A. F. and A. R. Hassan. 2007. Effect of Additive Contents on the Performances and Structural Properties of Asymmetric Polyethersulfone (PES) Nanofiltration Membranes. *Sep. Purif. Tech.* 55: 98–109.
[13] Akbari, A., J. C. Remigy and P. Aptel. 2002. Treatment of Textile Dye Effluent using a Polyamide-based Nanofiltration Membrane. *Chem. Eng. Process.* 41: 601-609.
[14] Sungpet, A., R. Jiraratananon and P. Luangsowan. 2004. Treatment of Effluents from Textile-rinsing Operations by Thermally Stable Nanofiltration Membranes. *Desalination*. 160: 75-81.
[15] Koyuncu, I. 2002. Reactive Dye Removal in Dye/salt Mixtures by Nanofiltration Membranes Containing Vinylsulphone Dyes: Effects of Feed Concentration and Cross Flow Velocity. *Desalination*. 143: 243-253.
[16] Shu, L., T. D. Waite, P. J. Bliss, A. Fane and V. Jegatheesan. 2005. Nanofiltration for the Possible Reuse of Water and Recovery of Sodium Chloride Salt from Textile Effluent. *Desalination*. 172: 235-243.

[17] Mimi Sakinah, A. M., A. F. Ismail, R. M. Illias and O. Hassan. 2007. Fouling Characteristics and Autopsy of a PES Ultrafiltration Membrane in Cyclodextrins. *Desalination*. 207: 227-242.

[18] Wang, Z., G. Liu, Z. Fan, X. Yang, J. Wang and S. Wang. 2007. Experimental Study on Treatment of Electroplating Wastewater by NF. *J. Membr. Sci.* 305: 185-195.

[19] Boussu, K., Y. Zhang, J. Cocquyt, P. Van der Meeren, A. Volodin, C. Van Haesendonck, J. A. Martens and Van der Bruggen, B. 2006. Characterization of Polymeric Nanofiltration Membranes for Systematic Analysis of Membrane Performance. *J. Membr. Sci.* 278: 418-427.

[20] Osmonics Inc. 1996. The Filtration Spectrum, Osmonic Inc, Minnetonka, Minnesota, USA.

[21] Jiraratananon, R., A. Sungpet and P. Luangsowan. 2000. Performance Evaluation of Nanofiltration Membranes for Treatment of Effluents Containing Reactive Dye and Salt. *Desalination*. 130: 177-183.

[22] Akbari, A., S. Desclaux, J. C. Remigy and P. Aptel. 2002.Treatment of Textile Dye Effluents using a New Photografted Nanofiltration Membrane. *Desalination*. 149: 101-107.