Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.794764

51 (2013) 3721–3727
May

Taylor & Francis
Taylor & Francis Group

Separation behavior of NF membrane for dye/salt mixtures

Lin Ji, Yan Zhang, Enhua Liu, Yufeng Zhang*, Changfa Xiao

State Key Laboratory of Hollow Fiber Membrane Materials and Processes (Tianjin Polytechnic University), Tianjin 300387, China
Tel. +86 22 83955078; Fax: +86 22 83955055; email: zyf9182@tjpu.edu.cn

Received 10 April 2012; Accepted 19 February 2013

ABSTRACT

The process of desalination of dye/salt mixture by nanofiltration (NF) membrane (NFT-50, Alfa Laval) was studied. Acid orange 7, Acid red 87, Mordant black 11, and NaCl were used in the experiments to prepare the dye and salt mixtures. Effects of the feed concentration and operating pressure on the permeate flux, salt, and color rejections were investigated. The results show that color rejection was realized at an average degree of 95% with Acid red 87, even higher than 99% achieved. The permeates were almost colorless. The impact of concentration and pressure on color rejection was positive but not very significant. The permeate flux was subject to osmotic pressure and was strongly influenced by the operating pressure as well. Negative salt rejection was observed with increasing salt concentration.

Keywords: Separation; Nanofiltration; Textile dye effluent; Negative salt rejection

1. Introduction

The textile industry is one that demands large quantities of water and generates huge amounts of wastewater, the characteristics of which bring about significant challenges to both the conventional and new treatment process. Dyeing process, especially active dye, acid dye, which are salted out by adding excess salt (mostly NaCl), is the main source of textile wastewater. Such water is heavily colored with high loading of inorganic salt (typically between 40 and 80 g/L) [1] and exhibit high biochemical oxygen demand (BOD)/chemical oxygen demand (COD) values. The conventional process includes neutralization, flocculation, coagulation, activated carbon adsorption, advanced oxidation using UV systems or H_2O_2 solutions, and biological treatment [2]. But none of the above methods is satisfactory in meeting environmental discharge requirements because most textile dyes have complex aromatic molecular structures that resist degradation and are stable to light, oxidizing agents, and aerobic digestion.

Membrane technology, which is known to be environmental friendly, energy saving and for its ease of process control, has drawn the attention of many researchers to treat textile effluent. The selection of membrane technologies for textile dye effluent relies on the cost balanced between flux and selectivity. Ultrafiltration has been successfully applied for recycling high molecular weight and insoluble dyes (e.g. indigo, disperse) and auxiliary chemicals (polyvinyl alcohol) [3,4]. However, ultrafiltration does not remove low molecular weight and soluble dyes (acid, direct, reactive, basic, etc.) [5], and requires further filtration by either reverse osmosis (RO) or nanofiltration

*Corresponding author.

Presented at the 2012 Qingdao International Desalination Conference June 26–29, 2012, Qingdao, China

(NF) [6]. The infeasibility of RO stems from fouling and low permeate flux is caused by high osmotic pressure. NF separations occupy an area that lies between RO and UF so that major advantages delivered when NF is incorporated into textile wastewater are low pressure/high flux operation, the maximal retention of dyestuff, and the minimal retention of monovalent salt, etc.

In the 1970s, Brandon et al. already treated textile wastewater with RO successfully to obtain purified product water and concentrated brine [7], but the problem of high energy consumption due to high osmotic pressure is economically unfavorable. NF, which can overcome this problem, has received more and more attention in purification of dye product and reuse of textile wastewater in the last decade.

Koyuncu et al. have carried out a series of experiments on textile wastewater treatment by a NF membrane. Dye rejections greater than 99% were achieved [8]. Permeate samples were colorless and remained enough for NaCl to be reused in a reactive dye bath [9]. Factors influencing the process as well as the reason of flux decline have been studied [10,11].

NF in combination with other methods is also reported. Chakraborty et al. combined adsorption and NF to treat the effluent of a garment-washing unit in Calcutta, India. The dyes remaining after NF treatment were less than 1 ppm. The percentage removal of COD was greater than 99% and the salt recovery was in the order of 90%. The permeate flux for the proposed combined method was found to be about twice that of the direct NF method [12].

In this study, we simulated the wastewater by constructing synthetic dye/salt mixtures. The dyes used in the experiments are acid dyes, which have one or more sulfonic or other acidic groups in their molecules. For acid dyes, it is anionic groups that are responsible for the color of the specific dye and the attachment to fibers. The effects of the operating conditions on the separation process are the primary concern of this study. The effects of such significant parameters, solution concentration and operating pressure as the two fundamental characteristics of NF (flux and retention) are presented.

2. Experimental

2.1. Main chemicals and materials

Acid red 87 (AR.87) (A.R. Tianjin Oriental Sanitation Materials Plant), Acid orange 7 (AO.7) (A.R. the Third Chemical Reagent Plant in Shanghai), and Mordant black 11 (MB.11) (A.R. Tianjin Kemiou Chemical Reagent R & D Center) were used in the experiments whose chemical structure, molecular weight, and maximal absorbance wavelength are shown in Table 1. Sodium chloride (A.R. Tianjin Pharmaceutical Company) was also used in the solution of different dye/NaCl mixtures.

NFT-50 flat sheet NF membrane (kindly provided by Alfa Laval) was chosen as the test membrane, the salt rejection of which are 53% (NaCl, 1 g/L) and 98% (Na_2SO_4, 1 g/L), respectively under the operating pressure of 0.4 Mpa.

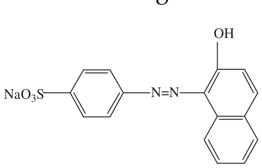
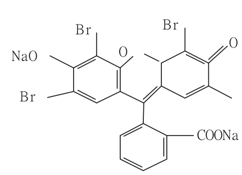
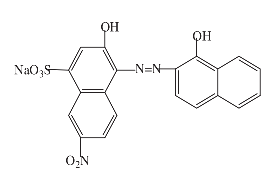
2.2. Evaluation system [13]

The NF membrane was mounted in a stainless steel round cell (5 cm diameter, 0.5 cm depth). The test cell had flow-smoothing sections at both entrance and exit. The test cell was mounted in a recycle flow loop. The pressure ranging from 0 to 1.0 MPa was provided by a diaphragm pump.

2.3. NF processes

Two models of NF processes were arranged in order to examine the effects of concentrations and pressure on the separation performance of NF membrane, respectively. The effects of feed concentration on the separation performance of the membrane were studied respectively in two series of experiments under the operating pressure of 0.4 MPa. One was

Table 1
Molecular weight and chemical structure of three acidic dyes

C.I. Acid orange 7	C.I. Acid red 87	C.I. Mordant black 11
		
MW: 350.3 λ_{max}: 480 nm	MW: 691.9 λ_{max}: 518 nm	MW: 461.4 λ_{max}: 510 nm

carried out by fixing dye concentration at 0.5 g/L while varying salt concentration from 1 to 8 g/L to examine the effects of salt concentration, the other was with fixed salt concentration of 2 g/L but at varied dye concentration from 0.1 to 0.8 g/L.

The effects of pressure varying from 0 to 1.0 MPa was performed on Mordant black 11/NaCl mixtures at a fixed Mordant black 11 concentration of 0.2 g/L with salt concentration increasing from 1 to 8 g/L.

All the experiments were carried out at a constant temperature of 20±1℃.

2.4. Measurements

The permeate flux (F) can be calculated by

$$F = \frac{J(\mathrm{L})}{A(\mathrm{m})^2 \times T(\mathrm{h})}\ (\mathrm{L/m^2/h}) \tag{1}$$

where J is the volume of the permeate flux, A is the surface area of the membrane, and T is time.

The salt concentration of solutions was fixed by MC226 METTLER TOLEDO. Salt rejection (R_s) is given by

$$R_s = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

where C_f and C_p are the concentrations of the feed and the permeate, respectively.

Since the dye concentration of solutions is linear with its absorbance (A), the color rejection (R_{dye}) is given by

$$R_s = \left(1 - \frac{A_p}{A_f}\right) \times 100\% \tag{3}$$

where A_p and A_f is the absorbance of the permeate solution and the feed solution, respectively. The absorbance is determined using a 7220 Visible Spectrophotometer (Beijing Ruili Analytical Instruments Factory).

3. Results and discussion

3.1. Effects of salt concentration

Feed concentration is one of the most important factors that has major impact on NF membrane separation [14]. The discussion about the effects of feed concentration on the separation process was based on three characteristics: permeate flux, color rejection, and salt rejection.

With the purpose of examining the influence of the variation of salt concentration, we set the dye concentration to be constant and vary only the salt concentrations. The results show that the higher the salt concentration, the higher is the osmotic pressure, and the lower is the permeate flux, which is also known as a general conclusion [15]. We can see clearly in Figs. 1–3 that the permeate flux decreases as the salt concentration increases. Take Acid red 87 (Fig. 1), for example, the permeate flux was around 10 L/m^2·h and decreased as a result of increasing salt concentration.

The color rejections of Acid red 87 were above 95%, and decreased slightly with increasing salt concentration. For a charged NF membrane, the mechanism responsible for solute transport is the

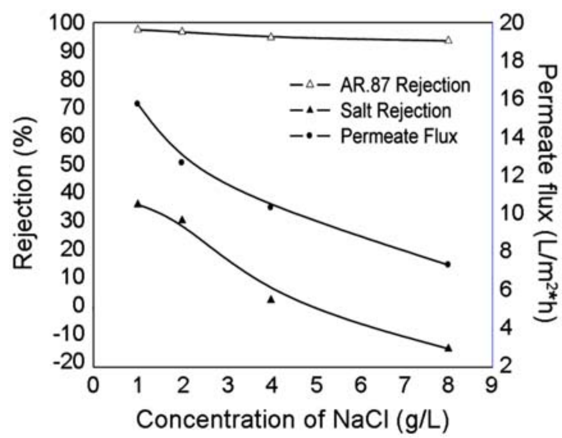


Fig. 1. Rejection and flux of Acid red 87/NaCl mixture vs. the concentration of NaCl.

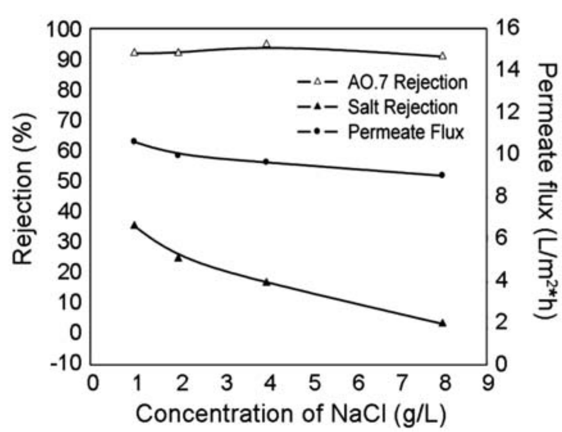


Fig. 2. Rejection and flux of Acid orange 7/NaCl mixture vs. the concentration of NaCl.

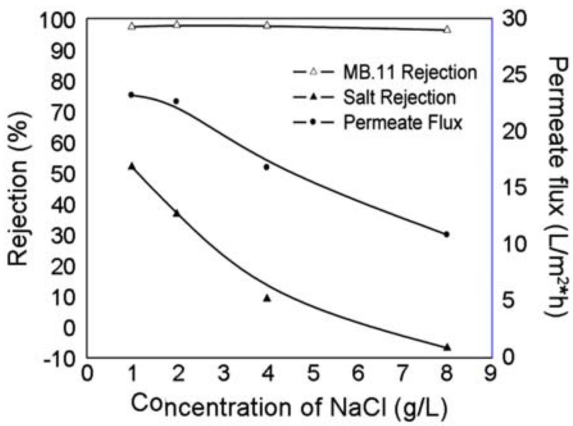


Fig. 3. Rejection and flux of Mordant Black 11/NaCl mixture vs. the concentration of NaCl.

combination of steric and Donnan effects [16]. Donnan effects are less obvious with salt concentration increasing [17] which results in the reduction of interactions between the dye and the negatively-charged membrane. So dye rejection lessened as the salt concentration increased, but the extent of decrease was slight as the salt concentrations were not very high compared with that of actual dying wastewater.

The salt rejection, which was affected significantly by the salt concentration, went down sharply and even became "negative" at higher salt concentration. This phenomenon of apparent negative rejection is often observed with NF membranes in mixtures of salts and large charged organic molecules or mixed monovalent–multivalent salts, which arise from the effect of the Donnan distribution of the salt between the solution and the membrane [18]. The higher concentration of Cl^{-} ions in the feed solution contributes to an increase in the ionic or Donnan equilibrium of the Cl^{-} ions in the membrane. This results in the higher ionic fluxes through the membranes and consequently, the lower salt rejections [16]. The negative salt rejection can also quantitively explained by Donnan equilibrium equation [19]:

$$(\theta + C_L)C_L = {C_R}^2 \tag{4}$$

where θ is the equilibrium concentration of ions, C_L and C_R are the concentrations of low molecular weight electrolyte (in this case, NaCl) on the left (feed) and right side (permeate) of the membrane. It demonstrates that C_R is definitely higher than C_L, which results in the negative salt rejection. The great difference between the dye rejection and salt rejection suggested that it was possible and efficient to separate salts from the dye/salt mixtures.

The three dyes shared common profile features except for the difference in the values of color rejection. Among the three dyes, the color rejection of Acid red 87 (MW: 691.9) reached the highest of 99% while A.O.7 (MW: 350.3) remained the lowest compared with the other two dyes in the two sets of experiments. This can be explained by the steric effects of NF membrane, wherein, the larger the molecule, the higher the resistance to pass through the membrane.

3.2. Effects of dye concentration

In terms of color rejection, as shown in Figs. 4–6, a high level of 95–99% was achieved and was observed to increase slightly with increasing dye concentration. Hence, under these conditions, dye concentration would not affect dye rejection significantly, which was consistent with other findings [20]. This is due to the good mass transfer across the membrane surface (dye concentration being not very high) that does not allow for serious concentration polarization.

The expectation of permeate flux, which was for flux to decrease with increasing dye concentration due to the polarization and adsorption of the dyes on the membrane surface, was in accordance with the experimental results shown in Figs. 4–6 for each kind of dye. A gel layer probably formed by the rejected dye on the membrane surface may operate as an additional resistance to the permeation [8]. The colored membrane surface after filtration clearly indicated the adsorption of the dyes on the membrane surface.

With respect to salt rejection, when a nonpermeating large molecule of an organic Na salt is added to a NaCl solution, Donnan's theory predicts the enhancement of salt rejection [21]. The experimental results of the three dyes, which are actually nonpermeating large

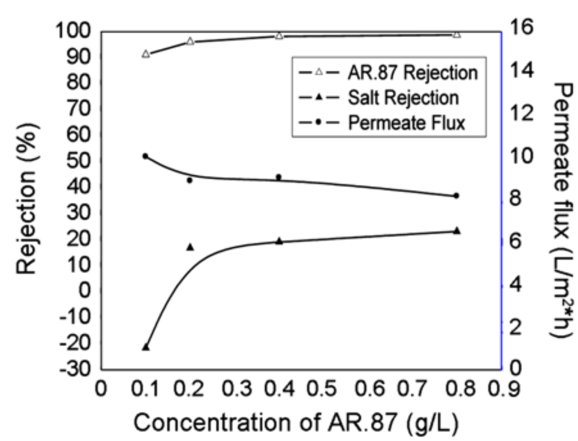


Fig. 4. Rejection and flux of Acid red 87/NaCl mixture vs. the concentration of dye.

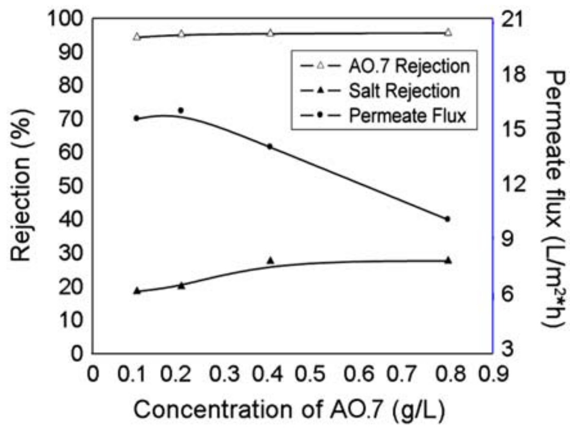


Fig. 5. Rejection and flux of Acid orange 7/NaCl mixture vs. the concentration of dye.

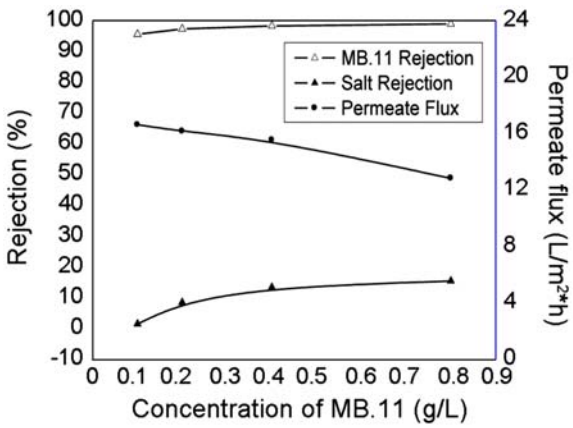


Fig. 6. Rejection and flux of Mordant Black 11/NaCl mixture vs. the concentration of dye.

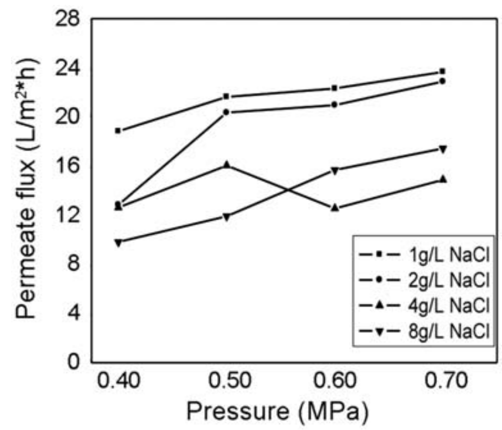


Fig. 7. Permeate flux of Mordant black 11/NaCl mixture vs. pressure.

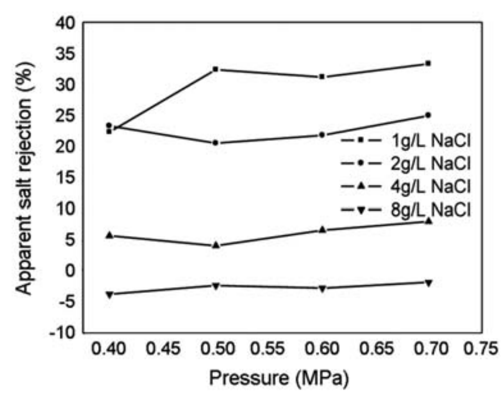


Fig. 8. Apparent salt rejection of Mordant black 11/NaCl mixture vs. pressure.

molecules of organic Na salts, were in agreement with the prediction. In addition, increase of the dye concentration, which was equal to the decrease of the proportion of NaCl to dye, was just the opposite of the situation of the first-set of experiments, thus, based on the downward trend of salt rejection in the first set of experiments, the salt rejections here were supposed to exhibit an upward trend accordingly.

So high dye concentration brings problems of low flux and high retention of salt. Dilution before treatment with membranes is a choice to obtain reasonable flux values.

3.3. Effects of operating pressure

The effects of operating pressure were performed on Mordant black 11/NaCl mixtures with fixed dye concentration of 0.2 g/L. As it could be concluded from Fig. 7 that permeate flux was most sensitive to operating pressure and increased with increasing pressure for all NaCl solutions, the increase of operating pressure enhanced the driving force for solvent to pass through the membrane. The highest flux values were obtained with the 1 g/L NaCl experiments because of the smaller effect of osmotic pressure. As for mono-component aqueous solution, according to the following Spiegler and Kedem equation, the permeate flux Jv is linearly related to applied pressure ΔP

$$Jv = Lp(\Delta P - \sigma \Delta \pi) \quad (5)$$

where Lp is solvent permeability coefficient, $\Delta\pi$ is osmotic pressure difference, σ is reflection coefficient [22]. But for dye/salt mixtures, the permeate flux was not strictly in accordance with the Spiegler and

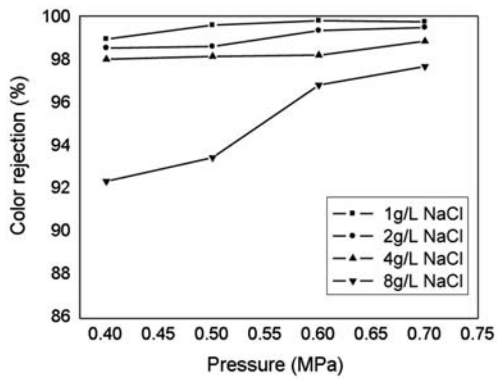


Fig. 9. Color removal of Mordant black 11/NaCl mixture vs. pressure.

Kedem model which was probably caused by interactions between the two solutes and polarization concentration [23]. It is considerable to increase operating pressure to promote permeate flux, but this will no doubt increase the energy consumption.

Salt rejection (Fig. 8) is seen to increase with increasing operating pressure due to the increased solvent flux [20], color rejection (Fig. 9) increased with the operating pressure slightly too, both in agreement with other studies [10].

4. Conclusion

Effects of the operating conditions on the separation process of three synthetic acidic dye/salt mixtures by NF membrane were studied. For most experiments conducted, permeate samples were colorless and dyestuff rejections of greater than 95% were achieved indicating that the acidic dyestuffs were effectively rejected. Apparent salt rejection decreased with the increase of salt concentration and even dropped down under zero depending on the salt concentration, which suggested that NF membranes could be applied not only to wastewater treatment but also to dye production due to the amazingly effective purification effect by negative salt rejection. The permeate flux was dominated by osmotic pressure and the operating pressure had a strong influence on it as well. Increase of both dye concentration and salt concentration gave rise to notable flux decline, in this sense, high feed concentration of actual textile dye effluent will cause the problem of the unacceptable low flux, dilution before treatment with membranes is necessary to obtain reasonable flux values under such occasions. It is always considerable to increase operating pressure to promote permeate flux, but energy consumption must be taken into consideration.

Like all the other membrane processes, operating conditions have great influence on the separation process, the optimum operating conditions should be based on optimization between rejection and permeate flux. It is suggested from the experimental results that membrane-based separation processes are technically feasible processes to treat dye-containing effluent, which will be more important in the near future for textile factories.

Acknowledgments

The study was supported by China High-Tech R & D Program (863 Program, 2012 AA03A602), the National Basic Research Development Program of China (973 Program, 2012CB722706), and the Science and Technology Plans of Tianjin (10SYSYJC27900). The tested membrane was kindly supplied by Alfa Laval Company.

Nomenclature

F	—	permeate flux, L/m^2·h
J	—	volume of the permeate, L
A	—	surface area of the membrane, m^2
T	—	time, h
R_s	—	salt rejection, %
C_f	—	the concentrations of the feed solution, g/L
C_p	—	the concentrations of the permeate solution, g/L
R_{dye}	—	color rejection, %
A_p	—	the absorbance of the permeate solution
A_f	—	the absorbance of the feed solution
θ	—	the equilibrium concentration of ions, mol/L
C_{L}	—	the concentrations of low molecular weight electrolyte (in this case, NaCl) on the left side (feed) of the membrane, mol/L
C_{R}	—	the concentrations of low molecular weight electrolyte (in this case, NaCl) on the right side (permeate) of the membrane, mol/L
Jv	—	permeate flux, m/s
Lp	—	solvent permeability coefficient, m/(s Pa)
ΔP	—	applied pressure, Pa
σ	—	reflection coefficient
$\Delta\pi$	—	osmotic pressure difference, Pa

References

[1] A.I. Schafer, A.G. Fane, T.D. Waite, Nanofiltration—Principles and Applications, Elsevier, Oxford, UK, pp. 380–393 (2005).

[2] A. Akbari, J.C. Remigy, P. Aptel, Treatment of textile dye effluent using a polyamide-based nanofiltration membrane, Chem. Eng. Prog. 41 (2002) 601–609.

[3] N.K. Majewska, T. Winnicki, J. Wisniewski, Effects of flow conditions on ultrafiltration efficiency of dye solutions and textile effluents, Desalination 71 (1989) 127–135.
[4] T.H. Liu, K.M. Simms, S.A. Zaidi, Selection of ultrafiltration and nanofiltration membrane for treatment of textile dyeing wastewater, Water Treat. 9 (1994) 189–198.
[5] K.M. Nowak, Synthesis and properties of polysulfone membranes, Desalination 71 (1989) 83–95.
[6] J.C. Watters, E. Biagtan, O. Senler, Ultrafiltration of a textile plant effluent, Sep. Sci. Technol. 26(10–11) (1991) 1295–1313.
[7] Craig A. Brandon, Ali M. El-Nashar, John J. Porter, Potential for reuse of textile dyeing and finishing wastewater by hyperfiltration, NWSIA J. (National Water Supply Improvement Association) 4 (1977) 45–58.
[8] Ismail Koyuncu, Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: Effects of feed concentration and cross flow velocity, Desalination 143 (2002) 243–253.
[9] Ismail Koyuncu, Dincer Topacik, Ebubekir Yuksel, Reuse of reactive dyehouse wastewater by nanofiltration: Process water quality and economical implications, Sep. Purif. Technol. 36 (2004) 77–85.
[10] Ismail Koyuncu, Dincer Topacik, Effects of operating conditions on the salt rejection of nanofiltration membranes in reactive dye/salt mixtures, Sep. Purif. Technol. 33 (2003) 283–294.
[11] Ismail Koyuncua, Dincer Topacika, Mark R. Wiesner, Factors influencing flux decline during nanofiltration of solutions containing dyes and salts, Water Res. 38 (2004) 432–440.
[12] S. Chakraborty, S. De, J.K. Basu, S. DasGupta, Treatment of a textile effluent: Application of a combination method involving adsorption and nanofiltration, Desalination 174 (2005) 73–85.
[13] Yufeng Zhang, Changfa Xiao, Enhua Liu, Du. Qiyun, Xiang Wang, Yu. Hongliang, Investigations on the structures and performances of a polypiperazine amide/polysulfone composite membrane, Desalination 191 (2006) 291–295.
[14] Kausick Auddy, Sirshendu De, Sunando DasGupta, Flux enhancement in nanofiltration of dye solution using turbulent promoters, Sep. Purif. Technol. 40 (2004) 31–39.
[15] Y. Xu, R. Lebrun, P. Gallo, P. Blond, Treatment of dyehouse water by nanofiltration membrane, Sep. Sci. Technol. 34 (1999) 2501–2519.
[16] W. Richard Bowen, A. Wahab Mohammad, Nidal Hilal, Characterisation of nanofiltration membranes for predictive purposes: Use of salts, uncharged solutes and atomic force microscopy, J. Membr. Sci. 126 (1997) 91–105.
[17] R. Jiraratananon, A. Sungpet, P. Luangsowan, Performance evaluation of nanofiltration membranes for treatment of effluents containing reactive dye and salt, Desalination 130 (2000) 177–183.
[18] M. Perry, C. Linder, Intermediate reverse osmosis ultrafiltration (RO/UF) membranes for concentration and desalting of low molecular weight organic solutes, Desalination 71 (1989) 233.
[19] A.K. Akred, A.J. Fane, J.P. Field, Negative rejections of cations in the ultrafiltration of gelatin and salt solutions, Polym. Sci. Technol. 13 (1980) 353.
[20] B. Van der Bruggen, B. Daems, D. Wilms, C. Vandecasteele, Mechanisms of retention and flux decline for the nanofiltration of dye baths from the textile industry, Sep. Purif. Technol. 22–23(1–3) (2001) 519–528.
[21] R. Levenstein, D. Hasson, R. Semiat, Utilization of the Donnan effect for improving electrolyte separation with nanofiltration membranes, J. Membr. Sci. 116 (1996) 77–92.
[22] K.S. Spiegler, O. Kedem, Thermodynamics of hyperfiltration (RO): Criteria for efficient membranes, Desalination 1 (1966) 311.
[23] Ku Young, Pei-Lin Lee, Wen-Yu Wang, Removal of acidic dyestuffs in aqueous solution by nanofiltration, J. Membr. Sci. 250 (2005) 159–165.