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A membrane-based co-treatment strategy for the recovery of print- and beck-dyeing textile effluents

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Abstract

This paper describes the final part of a study on the recovery of print- and beck-dyeing wastewaters of the carpet manufacturing industry by membrane processes. These wastewaters had been previously treated separately where the print dyeing wastewaters were recovered by chemical precipitation followed by nanofiltration (NF) and beck-dyeing wastewaters were subjected to microfiltration (MF) and pH neutralization prior to NF. In this study, a co-treatment scheme after separate pre-treatment stages was adopted to simplify the overall process. The effect of mixing ratio on membrane fouling was also investigated. The co-treatment strategy was found advantageous since the number of NF units was minimized and the pH neutralization step in separate treatment of beck-dyeing wastewaters was eliminated, providing a reduction of chemical usage. © 2007 Elsevier B.V. All rights reserved.

Keywords: Carpet wastewater; Membrane; Wastewater mixing; Water reuse

1. Introduction

Wastewater reclamation and reuse is part of an effective environmental management program where advanced treatment methods such as filtration, UV treatment, carbon adsorption, and membrane processes are adopted. Textile is the one of the most polluting industries, where non-renewable resources are extensively used in wet processes such as dyeing, printing, degumming and finishing. Textile production is characterized by high consumption of fresh water with an average value of $160 \text{ m}^3 \text{ t}^{-1}$ of finished product and peaks above $500 \text{ m}^3 \text{ t}^{-1}$ in multi-stage processes [1]. In addition, the wastewaters generated are quite complex and variable in nature due to the diversity of manufacturing processes. In textile industry, recycling of the reclaimed water back into the most demanding processes requires that the wastewater is highly purified since the actual process water is free of any color, turbidity and hardness due to the filtration and softening processes applied on-site. To this

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end, membrane technology emerges as a unique solution and has been gaining wider acceptance, as evidenced from the fact that it is one of the suggested treatment methods for the reclamation of textile effluents in the Best Available Techniques (BAT) Reference Document published by the European Union within the framework of Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC). The technical feasibility of membrane technology has been proved; however the problem of flux decline remains, which requires the application of a suitable pretreatment method. In pre-treatment step, conventional methods like chemical precipitation, sand filtration and ozonation can be used as well as microfiltration (MF) and ultrafiltration (UF) [2,3]. After passing through one or more of these stages, the wastewater is further purified to the degree of reuse quality in other pressure-driven membrane processes, i.e., nanofiltration (NF) or reverse osmosis (RO). Hence, most approaches consist of two or more step processes. The required quality for the reclaimed process water depends on the quality of the final product, making it difficult to set some common quality criteria. Although a general guideline is provided for the desired reuse criteria for textile processes (Table 1), the water quality required for each particular type of textile process is currently not clear and needs to be established [4,5]. Regarding the existence of several sub-sectors where wastewaters of highly

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Table 1Water reuse criteria for textile processes in general

Parameter	Reuse criteria	
$\overline{\text{COD}} (\text{mg } \text{L}^{-1})$	60 [5]-80 [4]	
Color (Pt–Co)	none [5]	
Turbidity (NTU)	1 [4]	
Suspended solids $(mg L^{-1})$	5 [4]	
Dissolved solids (mg L^{-1})	500 [6]	
Total hardness (mg L^{-1} as CaCO ₃)	25 [4]–50 [5]	
Conductivity (μ S cm ⁻¹)	1000 [4]	
pH	6-8 [4]	

variable flow rates and characteristics are generated, each particular textile effluent has to be handled individually. In addition, the requirement of longer process trains points out the disadvantage of increased treatment costs. To this end, there is a need to determine the simplest and most energy efficient process combinations.

In searching for the simplest and most efficient process combinations, mixing of wastewaters for co-treatment may be one solution, which would minimize the number of units required, thus enabling cost effectiveness. It may also create a synergy in terms of improved treatment performance. In one study, a synergy was sought by Ochieng et al. [7] by mixing wastewaters from two different industries, namely petroleum and brewery, for combined biological treatment in a fluidized bed where an improved biodegradation via co-treatment was observed. Bajza and Vrcek [8] also studied the mixing of wastewaters from chrome tanning process and liming of bovine leather, where they concluded that co-treatment provided the advantage of satisfying the ecological parameters, eliminating the pre-treatment steps, and reduce the material costs for neutralization of wastewaters. On the other hand, Chmiel et al. [9] has drawn attention to possible problems in biological treatment due to the mixing of spent process waters with high and low strengths in food and beverage industry. They offered two different treatment strategies; first, separate treatment of partial streams where product recovery was achieved by treatment of the highly polluted pre-rinsing water in margarine production, and second, combined treatment of different spent process waters of a fruit juice company for water recovery through two-stage NF. The same approach can be used in water reclamation from textile industry, where the wastewaters from different dyeing and rinsing process streams may be treated in separate or combined routes depending on the performance of the treatment process applied and the reuse quality desired. In adopting membrane technology for the reclamation of textile wastewaters, both approaches have been used, i.e., membrane processes either follow the existing biological treatment plants for the wastewater mixtures [10] or they are integrated into individual wastewater streams, enabling direct



Discharge into nature

Fig. 1. Carpet manufacturing process scheme (Q represents the daily wastewater flow rate, dashed lines show wastewater streams).

Table 2	
Ingredients of print-and beck-dyeing wastewater	ſS

Aim of use	Dyestuff/auxiliary chemical	
	Print-dyeing wastewater	Beck-dyeing wastewater
Adjust pH	Citric acid	Acetic acid
Adjust viscosity	Tanaprint ST 160 Conc. (anionic ammonium salt, high electrolyte-resistant synthetic thickener)	-
Increase wetting	Tanasperse CJ (non-ionic penetrant for producing homogeneous paste)	-
Control foaming	_	Foamaster WWT
Give color	Yellow 2R, Yellow 4GN, Blue 2RA (Acid Blue 781), Blue 5G (Acid Blue 526), Black B (Acid Black 1051), Red G (Acid Red 78), Gray G, Navy R (Acid Blue 176) ^a	Yellow 2G (Acid Yellow 169), Red 2B (Acid Red 361), Red 599, Orange 4G, Blue 4R (Acid Blue 277), Blue 608 ^b

^a CIBA Lanaset (metal-complex) dyes.

^b CIBA Tectilon (acid) dyes.

recycling of water into the process itself [11]. In this regard, it is found meaningful to study the effect of mixing wastewaters from different streams on the determination of the best process train for the recovery of textile effluents. To this end, the aim of this study is to evaluate the effect of mixing of wastewaters generated from different textile dyeing processes for the optimization of the water reuse scheme towards the requirement of least number of units. For this, technical evaluation and comparison of two alternative membrane-based treatment schemes were performed for the dye-house effluents of a carpet manufacturing plant, which represent a significant sub-sector of textile industry in Turkey. In addition, the effect of mixing ratio on membrane fouling was also investigated in order to evaluate the efficiency of co-treatment.

2. Materials and methods

2.1. Treatment strategies

The major wastewater generating activities in carpet dyehouse of interest are briefly summarized in Fig. 1. Although the wastewater generation rates are highly variable with time due to changing demands, the given wastewater generation rates represent average values. The print- and beck-dyeing processes generate the highest fractions of wastewaters in the plant, where the flow rate of print-dyeing wastewater (PDW) is four times higher than that of beck-dyeing wastewater (BDW) (Fig. 1). In addition, PDW and BDW contain different dyes and auxiliary chemicals (Table 2).

The PDW and BDW had been exposed to separate process trains at the points of wastewater generation (Fig. 2(a)). Alternatively a combined process train was adopted (Fig. 2(b)). In separate process trains, PDW was first chemically precipitated with an alum dose of 250 mg L^{-1} and then treated in single NF up to the degree of reuse quality, whereas BDW was pre-filtered through a microfilter (MF) having a pore size of $1.0 \,\mu\text{m}$ and then recovered in single NF after pH neutralization. These separate process trains had been developed by evaluating several alternatives, the details of which were presented in our previous publications [12–15].

Although PDW and BDW were recovered successfully in separate routes, the combined treatment of these two wastewaters was adopted in order to further optimise the water reuse scheme. In this combined treatment scheme, PDW and BDW were mixed in the NF stage after passing through separate pretreatment steps. Two mixing ratios were applied, i.e., PDW and BDW were mixed at a volumetric ratio of 4/1 and 1/1, which are expressed as "PDW/BDW = 4/1" and "PDW/BDW = 1/1". The mixing ratio scenario was based on the fact that the actual volumetric ratio of PDW to BDW in the carpet manufacturing plant is 4/1 (Fig. 1), and 1/1 is the highest possible ratio in the plant since the capacity of printing is higher than the capacity of beck dyeing, leading to the generation of PDW with higher flow rates. The effect of pH on NF separation performance was also studied since the wastewater pH had previously been observed to highly affect the NF separation performance where the organic matter rejection significantly improved for BDW at neutral pH [14]. Therefore, in this study, the rejection performances were evaluated at two pH levels; first at the original pH of the mixtures, which were 6.7-6.9 when chemically precipitated PDW having pH 7.2 was mixed with pre-filtered BDW having pH 5.3-5.9. Second, the pH of the mixtures was reduced to pH 5.7, i.e., the original pH of BDW. In this way, the possibility of having increased volumetric ratios of BDW in the mixture was tried to be simulated, because increasing the fraction of BDW in the mixture would decrease the pH of the mixture towards its acidic pH. The combined process train provided the advantage of omitting the pH neutralization step for BDW, which was required in separate treatment route, and therefore helped minimize chemical usage in the plant. Because PDW already had neutral pH, it was thought that the acidic pH of the BDW would naturally rise to neutral level if mixed with PDW. Therefore, the co-treatment of BDW and PDW in the same process train was considered to be very practical, as it would provide the recovery of these wastewaters in the simplest process train possible.

2.2. Sample

The print-dyeing wastewater stream was sampled four times and a mixture was formed for PDW, which contained wastew-

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Fresh Water

Carpet dyeing in dye-beck system

Carpet dyeing in



pH neutralization

MF (1.0 µm)

Recycle

NF



Fig. 2. Water reuse schemes for (a) separate treatment, (b) combined treatment.

aters from the washing step of four different carpets. On the other hand, two different BDW (BDW 1 and BDW 2) samples were obtained, where BDW 1 is the mixture of two wastewaters from different carpets and BDW 2 is an individual sample belonging to a single carpet. All the samples were kept at 278 K in a cold room. However the pH of the PDW and BDW 1 increased gradually with time during the time period of the study due to bacterial/fungal growth, which was observed in the samples kept for the longest period of time. The characteristics of the pre-treated samples and the characteristics of the new wastewater samples obtained by mixing PDW and BDW 1, and in 4/1 mixture, PDW was mixed with BDW 2.

 Table 3

 Characteristics of raw, pre-treated, and mixed samples after pre-treatment

Parameter	Mean value \pm	standard deviation	on (Percent remo	val) [*]						
	Quality of rav	v wastewaters		Quality of pre-tre	eated wastewaters		Quality of wa	stewaters mixed	after pre-treatm	nent
	PDW	BDW 1	BDW 2	PDW	BDW 1	BDW 2	PDW/BDW 2	=4/1	PDW/BDW 1	= 1/1
pH	7.2 ± 0.0	4.7 ± 0.0	5.3 ± 0.0	6.8 ± 0.0	5.0 ± 0.0	5.3 ± 0.0	6.9 ± 0.0	$5.7\pm0.0^{\mathrm{a}}$	6.7 ± 0.0	5.7 ± 0.0^{b}
$COD (mg L^{-1})$	852 ± 10	1407 ± 22	1928 ± 30	$423 \pm 10(50)$	$1252 \pm 5(11)$	$1832 \pm 7(5)$	782 ± 6	691 ± 32	816 ± 9	877 ± 13
Color (Pt–Co)	706 ± 0	105 ± 0	50 ± 0	$73 \pm 2(90)$	$43 \pm 1(59)$	$36 \pm 1(28)$	44 ± 6	97 ± 1	35 ± 3	34 ± 4
Turbidity (NTU)	72.0 ± 0.7	5.4 ± 0.0	3.3 ± 0.0	$7.1 \pm 0.1 \ (90)$	1.4 ± 0.1 (74)	3.2 ± 0.0 (3)	5.2 ± 0.1	9.5 ± 0.1	1.8 ± 0.4	1.8 ± 0.4
Total solids (mg L^{-1})	678 ± 9	1019 ± 4	1323 ± 23	$595 \pm 7(12)$	$968 \pm 6(5)$	$1204 \pm 88(9)$	663 ± 7	751 ± 18	765 ± 7	797 ± 35
Total hardness (mg L^{-1} as CaCO ₃)	33 ± 1.4	44 ± 0	18 ± 0	$33 \pm 0(0)$	$40 \pm 0(9)$	$18 \pm 0(0)$	40 ± 0	34 ± 0	40 ± 0	40 ± 0
Conductivity (μ S cm ⁻¹)	697	770	899	793(-)	762(1)	806(10)	883	844	755	777

* Values in parenthesis represent the percent removals in the pre-treatment stage.

^a pH of feed was reduced from 6.9 to 5.7 and kept constant at 5.7 by adding HNO₃.

^b pH of feed was initially reduced from 6.7 to 5.7 by adding HNO₃.

Table 4

2.3. Nanofiltration

NF experiments were carried out by a lab-scale plate and frame module, LabStak M20 (product of DSS Company) in cross-flow operation where NFT-50 membranes were used. The experiments were carried out in total recycle mode of filtration where permeate and retentate were both returned to the feed tank. The NFT-50 is a thin film composite membrane consisting of three layers: an ultra-thin polyamide barrier layer, a microporous polysulfone interlayer and a high strength polyester support. It is a hydrophilic membrane with a contact angle of 40° (Wilhemy Method). The molecular weight cut off (MWCO) of the NFT-50 membrane is not reported by the manufacturer however its MgSO₄ rejection is \geq 99%. Four NF membranes, each having 0.018 m² of effective area, were used in two pairs, making a total effective membrane area of 0.072 m². The NF test was carried out at a trans-membrane pressure (TMP) of 590 kPa at an operation temperature of 291 K. The samples were fed to the system at a flow rate of $360 \text{ L} \text{ h}^{-1}$. Permeates were collected when the flux declines reached steady state and analysed for their constituents.

2.4. Flux decline analysis

The flux measurements were performed initially with the clean membrane (J_{cwi}), then with wastewater (J_{ww}) at steady state conditions, followed by the clean water flux of the fouled membrane (J_{cwf}). Finally the clean water flux of the membrane was measured after chemical cleaning (J_{cwc}). The details of flux analysis are described elsewhere [14].

2.5. Membrane chemical cleaning

The NFT-50 membranes were cleaned by clean-in-place method before the first use and after the experiments. Two solutions, namely HNO₃ solution at pH 3 and NaOH solution at pH 9–10 were circulated in the system consecutively under a low TMP of 180 kPa (gauge). Each cleaning solution was circulated for 30 min in order to remove the organic and inorganic precipitates from the surface of the membranes. Flushing with clean water between the two cycles was also carried out. The retentate and permeate were continuously discarded. The cleaned membranes were always kept wet in 0.25% sodium bisulfite solution at 277 K in order to avoid bacterial growth on the membranes.

2.6. Analytical techniques

All the analyses were performed according to the Standard Methods [16], except COD, which was measured following USEPA approved HACH Method 8000. COD analysis was performed by using HACH DR-2000 Model spectrophotometer at wavelengths of 620 (high range) and 420 nm (low range), respectively. Color measurements were performed by the same instrument, which was already calibrated for color measurement in terms of Pt–Co at a wavelength of 455 nm. Turbidity was measured with a HACH Model 2100A turbidimeter. Total solids content of the samples were determined by gravimetric analy-

Parameter	Permeate quality	(mean value \pm stand	ard deviation (Per	cent removal)*)					
	Separate treatmen	t				Combined treatme	ent		
	PDW	BDW 1		BDW 2		PDW/BDW 2 = 4/	1	PDW/BDW 1=1	/1
	Feed pH 7.2 ^a	Feed pH 5.9 ^a	Feed pH 7.2 ^b	Feed pH 5.3	Feed pH 7.1 ^c	Feed pH 6.9	Feed pH 5.7 ^d	Feed pH 6.7	Feed pH 5.7 ^e
pH (permeate)	8.7	6.4	6.9	5.4	6.7	6.6	5.8	6.4	6.0
$COD (mg L^{-1})$	$19 \pm 2(96)$	272 ± 23 (78)	$36 \pm 4 (97)$	$415 \pm 8(77)$	$55 \pm 2(97)$	$25 \pm 4(97)$	$68 \pm 1 (90)$	$17 \pm 5(98)$	$235 \pm 16(73)$
Color (Pt-Co)	$0 \pm 0(100)$	$0 \pm 0(100)$	$0 \pm 0 (100)$	$0 \pm 0(100)$	$0 \pm 0(100)$	$3 \pm 1(93)$	$0 \pm 0 (100)$	$0 \pm 0 (100)$	$0 \pm 0(100)$
Turbidity (NTU)	$0.2 \pm 0.0 \ (97)$	$0.1 \pm 0.0 \ (93)$	0.2 ± 0 (86)	0.2 ± 0.0 (94)	$0.2 \pm 0 \ (94)$	0.3 ± 0.0 (96)	0.2 ± 0.0 (98)	$0.1 \pm 0.0 \ (94)$	$0.1 \pm 0.0(94)$
Total solids ^f (mg L^{-1})	$75 \pm 18(87)$	$247 \pm 7(74)$	$60 \pm 31(94)$	$535 \pm 10(56)$	$106 \pm 17 (91)$	$136 \pm 3(79)$	$197 \pm 16(74)$	$36 \pm 11 (95)$	$146 \pm 14(82)$
Total hardness (mg L ⁻¹ as CaCO ₃)	$0 \pm 0(100)$	$0 \pm 0(100)$	$(001) 0 \pm 0$	$2\pm0(89)$	$0 \pm 0(100)$	$0 \pm 0(100)$	$(001) 0 \pm 0$	$(001)0 \pm 0$	$0 \pm 0(100)$
Conductivity $(\mu S \text{ cm}^{-1})$	106(87)	226 (70)	72(91)	530(34)	100(88)	188(79)	405(52)	71 (91)	205 (74)

Feed pH was increased from 5.9 to 7.2 by adding NaOH.

Feed pH was increased from 5.3 to 7.1 by adding NaOH.

¹ Feed pH was decreased from 6.9 to 5.7 and kept constant at 5.7 by constant addition of HNO₃.

 $^{\circ}$ Feed pH was initially decreased from 6.7 to 5.7 by HNO₃ and was not kept constant during filtration.

Since there are no suspended solids in NF permeate samples, total solids measurements also represent dissolved solids.

Treatment scheme	Feed	pH	Ranking with respect to permeate quality				
			COD	Total solids	Conductivity		
Separate	PDW	7.2	2	3	4		
	BDW 1	5.9	8	8	7		
	BDW 1	7.2	4	2	2		
	BDW 2	5.3	9	9	9		
	BDW 2	7.1	5	4	3		
Combined	PDW/BDW = 4/1	6.9	3	5	5		
	PDW/BDW = 4/1	5.7	6	7	8		
	PDW/BDW = 1/1	6.7	1	1	1		
	PDW/BDW = 1/1	5.7	7	6	6		

Table 5
Ranking of all the permeate qualities for COD, total solids and conductivity

sis. The pH of the NF feed samples was monitored by a WTW pH 330 Model portable pH meter.

3. Results and discussion

3.1. Effect of wastewater mixing on the co-treatment efficiency

In order to evaluate the performance of co-treatment, the separate and combined treatment of PDW and BDW were compared in Table 4. In separate treatment of these wastewaters, it was observed that the permeate of print dyeing wastewaters had quite good quality and satisfied the reuse criteria (Table 1). Similarly, pH neutralization provided significant improvement in the rejection performance for COD and total solids for the beckdyeing wastewaters to reach the specified reuse criteria (Table 1). The effect of pH on membrane performance has been studied [17–19]. Zeta potential, which is used to quantify the membrane surface charge, has been observed to become increasingly more negative for most membranes as pH is increased [20]. Accordingly, increasing the surface charge of the membrane would result in increased electrostatic repulsion between a negatively charged solute and membrane. Hence, the improved membrane rejection via pH neutralization for BDW was attributed to a possible change of the membrane surface charge. At acidic pH values, NF membranes are expected to lose their surface charge and become almost neutral. Thus, low COD rejection at acidic pH can be speculated as the passage of acetate ions, which were present due to the addition of acetic acid at the dyeing stage, to the permeate site possibly by sieving mechanism. When the pH was neutralized, the membrane surface became negatively charged causing higher rejection of acetic acid probably due to the repulsive forces.

Color, turbidity and total hardness were all removed very efficiently for all the feed types in both treatment schemes. All the permeate samples were very soft, free of any color and had negligible turbidity. In order to evaluate these nine possible treatment schemes, all the permeate qualities were ranked from 1 to 9 with respect to COD, total solids and conductivity removal efficiencies for separate and combined treatment schemes (Table 5). In other words, the treatment scheme, which provided the best permeate quality, was ranked as 1st with respect to each specific parameter of interest. Color, turbidity and total hardness were not included in the comparison since they were highly removed in all cases. Although the ranking changed among the pollutant parameters and the feed types, a general trend was observed such that the permeate quality for all parameters was the best for the mixture of PDW and BDW at a volumetric ratio of 1/1 and pH of 6.7 in the combined treatment scheme. On the other hand, the lowest ranking belonged to BDW, which was not exposed to pH neutralization, and hence treated at its original acidic pH in the separate treatment scheme. In the second best place, there was PDW and BDW exposed to pH neutralization in separate treatment schemes. The combined treatment scheme at lowered pH resulted in the second worst permeate quality. These ranking results obviously reveal that combined treatment at neutral pH produces the highest permeate qualities. The choice of the water reuse scheme might be done taking into account the purpose of reuse at the factory of interest, such as rinsing, dyeing of dark colors, or the very light colors, since each process requires different water qualities. However, the optimized scheme offered for the combined treatment of PDW and BDW at neutral pH, provides the production of the highest quality water, thus ensures the satisfaction of all quality requirements. Furthermore, the combined treatment scheme suggested elimination of the pH neutralization step for separate treatment of BDW, which in turn helped minimize the number of units in the process train (Fig. 2). This result needed to be verified in terms of flux declines. Therefore, the effect of combining the treatment schemes on the flux declines was also investigated (Table 6).

3.2. Effect of co-treatment on the membrane flux declines

The relative fluxes (J_{ww}/J_{cwi}) for separate and combined treatment schemes are depicted in Figs. 3 and 4, respectively. In separate treatment, the flux declines at the original pH levels of the wastewaters were 19%, 20.4% and 15.4% for PDW, BDW 1 and BDW 2, respectively (Fig. 3). Although the pH neutralization did not affect the flux decline of BDW 1, which remained at 20%, it caused an increased flux decline, i.e., 24.5% for BDW 2. All the flux declines were reversible in separate treatment, where 100–108% flux recovery was achieved via chemical cleaning (Table 6). The recovery ratio being greater than 100% for the neutralized BDW samples may indicate opening of the mem-

Effect of combin	ing the tre	atment schei	mes on flux c	lecline							
Sample	Hq	Flux (Lm ⁻²	(q			Flux recovery (%)	Flux decline (%)				
		Clean water			Wastewater	(J_{cwc}/J_{cwi})	Total	Concentration polarization	Fouling		
		Initial	Final	Cleaned	(Jww)		$(J_{\rm cwi} - J_{\rm ww})/J_{\rm cwi}$	$(J_{\rm cwf} - J_{\rm ww})/J_{\rm cwf}$	Reversible	Irreversible	Total
PDW	7.2	(Jewi) 18.9	16.5	(Jewe) 18.9	15.3	100	19.0	6.1	12.7	ucwi – Jewe Jucwi 0	Ucwi - Jcwf)/Jcwi 12.7
BDW 1	5.9	23.0	18.9	23.0	18.3	100	20.4	3.2	17.8	0	17.8
	7.2	22.0	21.0	23.8	17.6	108	20.0	16.2	ಷ	ಷ	4.5
BDW 2	5.3	19.5	17.1	18.9	16.5	97	15.4	3.5	9.5	3.1	12.3
	7.1	18.8	17.6	20.1	14.2	107	24.5	19.3	ಡ	ಡ	6.4
PDW/BDW2=4/1	6.9	21.8	18.3	20.7	16.5	95	24.3	9.8	11.6	5.0	16.1
	5.7	18.9	15.9	18.9	15.3	100	19.0	3.8	15.9	0	15.9
PDW/BDW1 = 1/1	6.7	21.8	19.5	23.6	16.5	108	24.3	15.4	ಷ	53 5	10.6
	5.7	23.6	20.1	21.2	18.3	90	22.5	9.0	5.2	10.2	14.8
a These data could i	not be calculs	ated since the cle	an water fluxes o	obtained after clean	ing were greater than th	e initial values (due to openi	ig of the pores).				



Fig. 3. Relative flux decline for PDW and BDW at the original pH values.

brane pores due to chemical exposure when NaOH was added for pH adjustment.

In combined treatment, the same flux decline of 24.3% was observed for mixing ratios of 4/1 and 1/1 at the original pH of the mixtures, which were 6.9 and 6.7, respectively. Decreased flux declines were observed at lowered pH, i.e., 19% for 4/1 mixture and 22.5% for 1/1 mixture at pH 5.7 (Fig. 4). Although not complete, the flux declines observed in combined treatment were recovered to a great extent, i.e., 90–97% (Table 6). Complete restoration of fluxes may be achieved by increasing the duration of cleaning. Indeed, the flux declines slightly varied, i.e., from 15.4% to 24.5% in all cases, which implies that co-treatment of these wastewaters did not cause significant deterioration of the flux declines.

The flux declines caused by concentration polarization and fouling were also compared for all cases (Table 6). In separate treatment, fouling was dominant for the flux declines of PDW and BDW at acidic pH, however it was reversible to a great extent. On the other hand, the effect of concentration polarization on the flux decline was dominant for BDW at neutralized pH. In combined treatment, fouling was dominant for mixing ratio of 4/1 at both pH levels as in the case of separate treatment of PDW. This result is expected since the volumetric ratio of PDW in the mixture is four times higher than that of BDW, and there-



Fig. 4. Effect of pH on flux decline for mixtures of PDW and BDW.

Table 6

fore PDW characteristics is more pronounced. The reversible fraction of fouling was higher than its irreversible fraction, and furthermore, all the fouling became reversible at pH 5.7, which was also confirmed with the effectiveness of cleaning. In the case of 1/1 mixing ratio, concentration polarization was higher at pH 6.7 than at pH 5.7, which means fouling became dominant at acidic pH. These results resembled those obtained for BDW alone, i.e., the effect of concentration polarization became much higher at neutral pH. This is also expected since the BDW characteristics became more pronounced when it was mixed with PDW at equal volumes.

4. Conclusions

The co-treatment strategy was applied for the dye-house effluents of the carpet manufacturing industry. The separate water reuse schemes offered for print-dyeing and beck-dyeing wastewaters were combined into a single route by mixing these wastewaters after separate pre-treatment stages. The comparison of permeate qualities and the flux declines revealed that printdyeing wastewaters and beck-dyeing wastewaters can be treated together to the degree of reuse quality in a single NF unit even when mixed at equal volumes. This conclusion is considered to be significant in terms of the management of these wastewaters, since the co-treatment is expected to be less costly than the separate treatment due to the requirement of less NF units and elimination of the pH neutralization step, which is required in the separate treatment of beck-dyeing wastewaters.

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Glossary

- BDW: Beck dyeing wastewater
- *COD:* Chemical oxygen demand (mg L^{-1})
- J_{cwc} : Clean water flux of cleaned membrane (L m⁻² h)
- J_{cwf} : Clean water flux of fouled membrane (L m⁻² h)
- J_{cwi} : Clean water flux of clean membrane (L m⁻² h)
- J_{ww} : Wastewater flux (L m⁻² h)
- MF: Microfiltration
- MWCO: The molecular weight cut off
- NF: Nanofiltration
- PDW: Print dyeing wastewater
- RO: Reverse osmosis
- TMP: Trans membrane pressure (kPa)
- UF: Ultrafiltration