ELSEVIER

Journal of Hazardous Materials B135 (2006) 423–430

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Membrane based strategies for the pre-treatment of acid dye bath wastewaters

Goksen Capar [a], Ulku Yetis [a,*], Levent Yilmaz [b]

[a] *Environmental Engineering Department, Middle East Technical University, 06531 Ankara, Turkey*
[b] *Chemical Engineering Department, Middle East Technical University, 06531 Ankara, Turkey*

Received 25 October 2005; received in revised form 2 December 2005; accepted 6 December 2005
Available online 25 January 2006

Abstract

This paper, as part of a study carried out for the recovery of the acid dye bath wastewaters of a carpet manufacturing industry by membrane processes, describes the evaluation of alternative strategies for the pre-treatment of acid dye bath wastewaters. Dead-end microfiltration (MF) simulating sand filtration with MF media having pore sizes of 2.5, 1.0, 0.45 and 0.2 μm and ultrafiltration (UF) with an UF membrane having a molecular weight cut off (MWCO) of 50,000 Da were tested in single and sequential stages in order to achieve the best treatment efficiency. Four alternative process trains were tested; single MF, sequential MF, single UF, and MF followed by UF. For both MF and UF, application of sequential filtration did not provide any significant benefit over single processes. In addition, chemical oxygen demand (COD) removal performance of all the alternative processes was similar where the highest removal was only 5%. On the other hand, color removals were much better; ranging from 15 to 100%, even with single MF. Comparison of all the process alternatives revealed that, single MF (0.45 μm), as the simplest process, is the most suitable pre-treatment method for the acid dye bath wastewaters.

Keywords: Acid dye bath wastewater; Microfiltration; Ultrafiltration; Pre-treatment

1. Introduction

Acid dye bath wastewaters are the spent dye bath solutions used for polyamide carpet dyeing by the beck (piece) dyeing method. In this method, the carpet is dyed in a piece where it is placed in a dye bath solution containing acid dyes and auxiliary chemicals, which are surfactants. The dyeing process takes place at elevated temperature (90–100 °C) and acidic pH (4.5–5.0) where pH is adjusted by sulphuric or acetic acid [1]. As a result, acid dye bath wastewaters are characterized by high chemical oxygen demand (COD), dissolved solids, high temperature and acidic pH.

The acid dyes are sodium salts of organic acids and they are water soluble anionic compounds having fixation rates as high as 80–93% [2], leading to the generation of wastewaters with relatively low dye concentrations and color contents. However, some acid dyes have toxic and carcinogenic properties as they lead to the formation of aromatic amines [3], which are often bladder carcinogens. In addition, the auxiliary chemicals are not spent in the dyeing process and end up in the wastewater stream, creating toxic effects for the aquatic life. Therefore, these wastewaters must be adequately treated before being discharged into the receiving environment.

The discharge regulations are becoming more stringent, and there is a growing tendency and interest in the advanced treatment methods like ozonation, photo catalysis, and membrane filtration for a better treatment of the textile wastewaters [4,5]. Combination of several processes like chemical coagulation, Fenton's oxidation, activated carbon adsorption and activated sludge has also been suggested [6,7]. Nevertheless, all these conventional methods either applied individually or in sequence, are basically aimed to meet the discharge regulations. For textile effluents, one major concern is the high fresh water consumption, which forces the industrialists to focus on water recycling. Beck (piece) dyeing process, having water use rate of around 230 L/kg, is one of the most water demanding unit processes in textile industry [8]. Therefore, water recycling in beck dyeing streams is a key issue for saving fresh water supplies.

* Corresponding author. Tel.: +90 312 210 5868; fax: +90 312 210 1260.
E-mail addresses: goksencapar@yahoo.co.uk (G. Capar), uyetis@metu.edu.tr (U. Yetis), lyilmaz@metu.edu.tr (L. Yilmaz).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.12.008

Nomenclature

A	effective membrane area (m^2)
COD	chemical oxygen demand (mg/L)
dV/dt	permeate flow rate (L/h)
J	flux ($L/m^2/h$)
J_{cw}	clean water flux ($L/m^2/h$)
J_{ww}	wastewater flux ($L/m^2/h$)
MF	microfiltration
MWCO	molecular weight cut off
NF	nanofiltration
RO	reverse osmosis
SF	sand filtration
TMP	trans membrane pressure (kPa)
UF	ultrafiltration
UVA	ultra violet absorbance
UVA_o	ultra violet absorbance of raw wastewater

Membrane technology, with its unique separation performance holds great promise in the field of water reclamation [9,10]. The recovery of the wastewaters to the degree of reuse quality is often achieved by nanofiltration (NF) and reverse osmosis (RO). One major drawback of the membrane technology is the flux decline. The use of effective pre-treatment processes such as coagulation-flocculation, sand filtration (SF), disinfection, ozonation, flotation, or other membrane processes, i.e., microfiltration (MF) and ultrafiltration (UF), is fundamental to guarantee a good and constant performance of the NF and RO systems [11,12].

SF has been widely applied to the mixture of biologically treated textile effluents rather than being directly applied to a specific wastewater stream [12,13]. For example, two approaches including SF, i.e., SF + UF + RO and SF + MF + NF were compared for the purification of biologically treated textile effluent. In the first case, SF and UF stages provided a turbidity-free effluent, as required to minimize RO fouling. SF + UF removed COD at 30% and color at 5%. In the second case, SF + MF removed 99% of suspended solids and 80% of turbidity, whereas only 36% of COD and 13% of color were removed [12].

Another approach was the comparison of two combinations; MF + NF against clariflocculation + multimedia filtration + RO. Both treatment schemes produced acceptable permeate qualities, however the first combination required coagulant addition to assure acceptable durations of filtration cycles [14].

Alternatively, coagulation-flocculation was tested as pre-treatment to UF and NF for the reclamation of wastewaters of a printing, dyeing and finishing industry [15] where a COD reduction of 50% was achieved. A similar COD removal efficiency of 43% was achieved by ozonation preceding NF, which increased the membrane life [16]. Ozonation coupled with coagulation-flocculation has revealed that a short time preozonation enhanced the coagulation process, yielding COD and turbidity removal efficiencies of 57% and 95%, respectively, after sedimentation [17].

MF has been gaining a wider acceptance for pre-treatment since it is economically more competitive than conventional methods [18]. UF performance is highly dependent on the type of membrane material and the feed composition as well as the shape and size of the macromolecules. When UF was tested against RO for the recovery of a textile printing wastewater, UF performance was found to be inadequate, with 42% of COD and 30–37% of color removals, necessitating further treatment [19].

As clear from the existing literature, pre-treatment step is very important for developing the best process train for a given textile effluent. Requirement of more than one pre-treatment process adversely affects the economy of the overall process, and therefore achieving the highest performance in least number of units is very much appreciated. Another concern is that the pre-treatment to membrane processes have generally been applied after biological treatment, which may cause some disadvantages in terms of membrane performance and may prevent energy savings via hot water recovery. Integrating the membrane process into individual wastewater streams would allow the recycling of the treated water to the process itself [20].

To this end, this study aims to determine the most suitable process(es) among two alternatives; namely, dead-end MF simulating sand filtration and UF as a membrane process for the pre-treatment of the acid dye bath wastewaters of carpet manufacturing industry towards its recovery via further membrane processes at the point of wastewater generation. Since the selection of the whole treatment process train is influenced by the performance of the pre-treatment stage, this study specifically aimed at finding the best pre-treatment method for the acid dye bath wastewaters so that the need for the following processes could be made clear for complete purification. Other pre-treatment methods such as coagulation-flocculation and ozonation were not considered due to two reasons; first, cost of sludge treatment and disposal is a problem in the application of coagulation-flocculation and ozonation is still costly and often more successful for decolorization rather than organic removal [21,22], whereas the problem with the acid dye bath wastewaters is the high organic matter content rather than color. Furthermore, we had a previous experience with coagulation-flocculation being more suitable for another carpet dyeing wastewater, namely printing effluent, which was much more polluted than the acid dye bath wastewaters, especially in terms of color and turbidity [23]. Therefore, comparison of single and combined applications of a conventional method; sand filtration simulated by dead-end MF, and an advanced technique; UF was undertaken in this study.

2. Materials and methods

2.1. Sample

Acid dye bath wastewaters are generated in a batch process where the wastewater characteristics are subject to fluctuations from one carpet to another. In order to compensate for these fluctuations, six samples were collected from the beck dyeing stream of a carpet manufacturing plant at different times and a composite mixture was prepared by mixing them (Table 1). The

Table 1
Characteristics of the acid dye bath wastewater mixture

Parameter	Mean value ± standard deviation
COD (mg/L)	1494 ± 4
UVA at 200 nm	3.2 ± 0
Color (Pt–Co)	23 ± 1
Turbidity (NTU)	2.9 ± 0.1
Total solids (mg/L)	894 ± 20
Total hardness (mg/L as $CaCO_3$)	26 ± 3
Conductivity (μS/cm)	615 ± 7
Chloride (mg/L)	13.5 ± 0.7
pH	4.74 ± 0

Table 2
Acid dye bath wastewater contents

Dye/auxiliary chemical	Function
CIBA tectilon acid dyes: Yellow 2G (Acid Yellow 169), Red 2B (Acid Red 361), Red 599, Orange 4G, Blue 4R (Acid Blue 277), Blue 608	Give color
Acetic acid	Adjust pH
Foamaster WWT	Antifoaming agent
Solopol EPW	Levelling agent

acid dyes and the auxiliary chemicals used in beck dyeing are presented in Table 2.

2.2. Dead-end microfiltration

A conventional vacuum filtration apparatus (Millipore) operating under a vacuum level of 550 mm Hg was used for testing the applicability of dead-end MF simulating sand filtration. The filter media, whose specifications are given in Table 3, were used to carry out filtration after being washed with 1 L of distilled water. The filtrates were collected and analyzed for their color, turbidity, total solids and COD contents. The initial filtration rates or initial permeate fluxes were determined based on the filtrate volumes collected during the initial period of filtration.

2.3. Ultrafiltration

The UF experiments were conducted by SEPA CF Module (product of Osmonics), which housed flat sheet membranes and provided cross-flow filtration. The UF membrane (Osmonics HZ 15) had a molecular weight cut off (MWCO) of 50,000 Da, was rectangular in shape and had the dimensions of 9.5 cm × 15 cm (Table 3). The pressures on the feed and the retentate sides were kept at 300 kPa (gauge) and 100 kPa (gauge), respectively, by the help of a nitrogen cylinder. A trans-membrane pressure (TMP) of 200 kPa (gauge) was achieved across the membrane, which was calculated by taking the arithmetic average of the pressures measured on the feed side and the retentate side. The permeate side was open to atmosphere. The samples were fed to the system at a flow rate of 0.9 L/min. The height of the feed channel was 0.86 mm (34 mil spacer was used). The retentate and permeate were continuously recirculated into the feed tank. The experimental set-up is presented in Fig. 1.

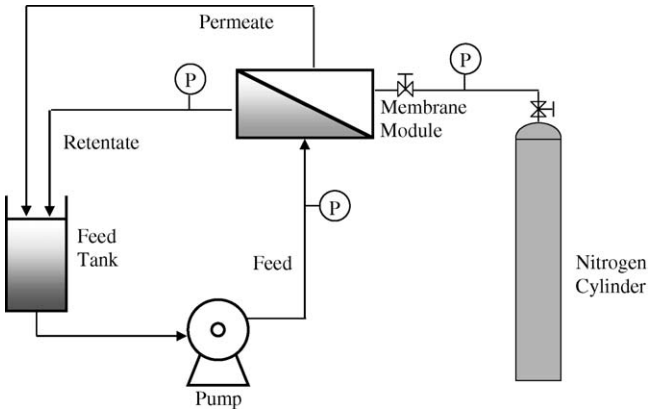

Fig. 1. Experimental set-up for UF tests.

The permeate flux was monitored throughout the UF experiments in order to determine the flux declines. Permeates were collected in a graduated cylinder and the fluxes were calculated as follows:

$$J = \frac{dV/dt}{A}$$

where J is the flux (L/m^2/h), dV/dt the permeate flow rate (L/h) and A is the effective membrane area (m^2).

2.4. Analytical techniques

COD was measured using HACH DR-2000 Model spectrophotometer at the wavelengths of 620 nm for high range and 420 nm for low range. 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. Ultra violet absorbance (UVA) measurements were performed by a Varian Cary 100 Model spectrophotometer at a wavelength of 200 nm, at which the highest absorbance values were obtained by scanning the whole range of 195–700 nm. UVA values were used as a surrogate parameter for COD in order to monitor the membrane performance during the experimental run since it can

Table 3
Membrane specifications

Process	Filter	Material	Pore size/MWCO	Effective membrane area (m^2)
MF	Whatman 42	Ashless cellulose	2.5 μm	0.0014
	Whatman GF/B	Glass microfiber	1.0 μm	
	Millipore	Cellulose mixed esters	0.45 μm	
	Sartorius	Cellulose acetate	0.2 μm	
UF	Osmonics HZ 15	Polyethersulfone	50,000 Da	0.0140

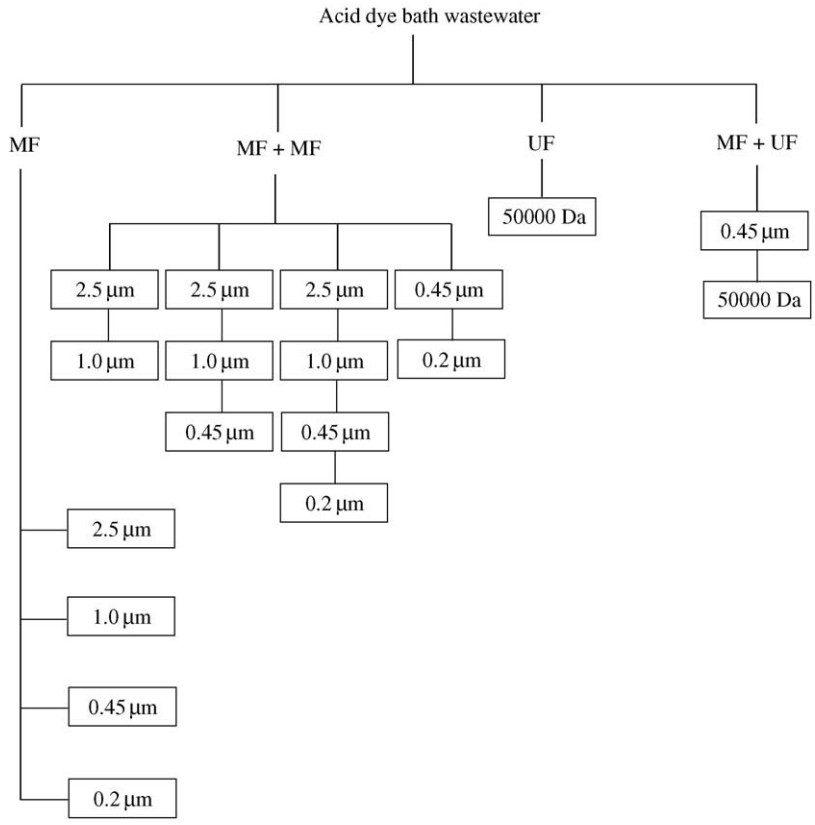

Fig. 2. Pre-treatment alternatives for acid dye bath wastewater.

be measured easily in a short time. Turbidity was measured with a HACH Model 2100A turbidimeter. Total solids content of the samples were determined by gravimetric analysis. All the analyses were performed according to the Standard Methods [24], except COD, which was measured following USEPA approved HACH Method 8000.

2.5. Alternative strategies

Four different strategies were adopted for the pre-treatment of acid dye bath wastewaters (Fig. 2). As seen, dead-end MF and UF were tested alternatively in single and sequential modes of filtration to achieve the highest removal performances.

3. Results and discussion

3.1. Single MF

The performance of dead-end MF was compared for all the media tested, and the results shown in Table 4 were obtained. As seen, the COD and total solids removal efficiencies were very low. This was quite expected since MF is able to remove particulates mostly and the COD causing organic matter is generally in dissolved form to a great extent. Acid dye bath wastewater contains acetic acid, which is a small molecule causing COD and therefore was not removed by MF.

In single MF, the best color and turbidity removal efficiencies were achieved by the MF medium having the smallest pore size of 0.2 μm (Table 4). However, the performance of the 0.45 μm MF medium was comparable to that of 0.2 μm filter with respect to color and COD removals. In terms of the initial filtration rates, 0.45 μm was found to be 12 times slower than the 1.0 μm MF media (Table 4). However, 0.45 μm pore size filter still appeared to be the best selection among the single MF media alternatives when the removal performances were taken as the basis of the comparison. It is clear that the determination of time dependent behaviour of the MF permeate fluxes would be essential at the scale-up stage to verify the suitability of dead-end MF.

Complete removal of color by MF may indicate the adsorption of dyes onto particulates which were retained on the MF surface, which would otherwise easily pass through the MF media since the color causing acid dyes have much smaller molecular size than the MF pore sizes. The low removal for total solids indicated that the solids were in dissolved form to a great extent, namely the sodium salts found in the dye structure. It was observed that the removal efficiencies improved with decreasing pore size for especially color and turbidity, further confirming the association of color with particulates.

3.2. Sequential MF

In an attempt to improve the performance of MF, sequential application of different MF media was tested. It was presumed that a fine filter preceded by a coarser one would improve the organics and solids removal efficiencies achieved in single MF alternatives. In sequential MF, the extent of

Table 4
Single MF performance

Parameter	MF filtrate quality[a]			
	2.5 μm	1.0 μm	0.45 μm	0.2 μm
COD (mg/L)	1434 (4)	1419 (5)	1419 (5)	1419 (5)
Color (Pt–Co)	20 (15)	12 (49)	0 (100)	0 (100)
Turbidity (NTU)	1.10 (62)	0.93 (68)	0.90 (79)	0.41 (86)
Total solids (mg/L)	805 (10)	805 (10)	778 (13)	787 (12)
Filtration rate[b] ($L/m^2/h$)	–	42857	3571	–

[a] Values in parenthesis correspond to the percentage removals.
[b] Average value for the first 5 min.

improvement of the removal performances with respect to single MF was almost none or little (Table 5). For example, the color and turbidity removal efficiencies of single MF (0.45 μm) were 100 and 97% (Table 4), and those of the sequential MF (2.5 + 1.0 + 0.45 μm) were 100 and 82%, respectively. Similarly, for single MF (0.2 μm) and sequential MF (2.5 + 1.0 + 0.45 + 0.2 μm); the color and turbidity removal efficiencies were the same, i.e., 100 and 84–86%, resulting in similar permeate qualities. Only total solids removal was improved by sequential filtration, i.e., 12% in MF (0.2 μm) increased to 25% in MF (2.5 + 1.0 + 0.45 + 0.2 μm). The insignificant improvement due to sequential microfiltration indicated that acid dye bath wastewater is composed of small sized compounds such as acetic acid and sodium salts, which contribute greatly to COD and total solids contents of the wastewater. As a result, sequential MF did not provide any benefits over single MF and therefore it was eliminated. In order to improve the COD and total solids removal efficiencies, single UF was considered as the third alternative, where the UF membrane had smaller pore size than that of MF media tested.

3.3. Single UF

Single UF was applied with a UF membrane having a MWCO of 50,000 Da. The UVA and permeate flux were recorded during the experiment. As seen from Fig. 3, the normalized UVA (UVA/UVA_o) is around 1.0, indicating no reduction of UV absorbing organic matter at all. This was in agreement with the COD removal efficiency, which was only 2%. Similarly, total solids removal efficiency was very low, i.e., 5% (Table 6). On the other hand, color was removed completely as in the case of single MF, which can be explained by adsorption rather than sieving since the molecular sizes of the acid dyes are much smaller than the MWCO of the UF membrane, and hence not expected to be rejected completely.

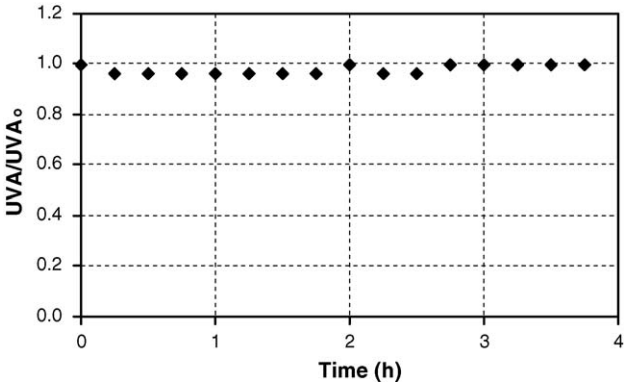

Fig. 3. UVA removal in single UF (50,000 Da).

The turbidity removal efficiency of the UF (50,000 Da) membrane was 67% (Table 6), which was observed to be same with that of MF (1.0 μm), and lower than those of MF (0.45 μm) and MF (0.2 μm) (Table 4). The UF was expected to perform better than MF and the lower performance of UF membrane for turbidity removal was due to the fact that the turbidity content of the acid dye bath wastewater, which was originally 2.9 NTU while performing the MF tests, decreased to 1.9 NTU when performing the UF test, which might have occurred due to insufficient mixing of the raw wastewater before collecting the required volume for the UF test. Therefore, this reduction in the UF feed turbidity content caused a reduction in the removal efficiency calculated for turbidity. Indeed, both the UF permeate and the MF (0.45 μm) filtrate had a turbidity of 0.62 NTU.

The clean water and wastewater fluxes were also monitored during UF experiment in order to find the flux decline levels. The initial permeate flux was 151 $L/m^2/h$ and reduced to 93 $L/m^2/h$ in 15 min, resulting in a flux decline of 35% with respect to clean water flux (Fig. 4). These values are quite low as com-

Table 5
Sequential MF performance

Parameter	MF filtrate quality[a]		
	A	B	C
COD (mg/L)	1419 (5)	1449 (3)	1419 (5)
Color (Pt–Co)	12 (50)	0 (100)	0 (100)
Turbidity (NTU)	0.93 (68)	0.52 (82)	0.46 (84)
Total solids (mg/L)	751 (16)	760 (15)	671 (25)

[a] Values in parenthesis correspond to the percentage removals. A: 2.5 + 1.0 μm, B: 2.5 + 1.0 + 0.45 μm, C: 2.5 + 1.0 + 0.45 + 0.2 μm.

Table 6
Single UF performance

Parameter	Removal (%)	UF (50,000 Da) permeate quality
COD (mg/L)	2	1403
Color (Pt–Co)	100	0
Turbidity (NTU)	67	0.62
Total solids (mg/L)	5	765

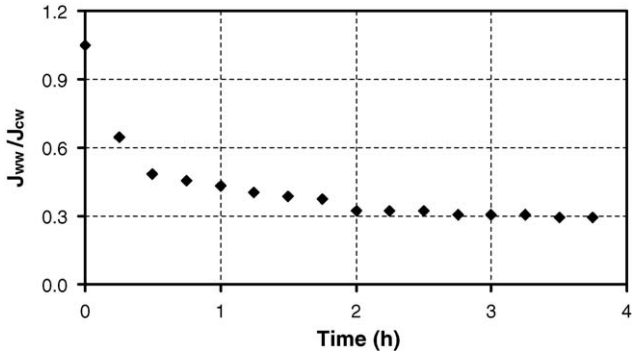

Fig. 4. Change of relative flux in single UF (50,000 Da) (J_{cw} = 144 L/m^2/h).

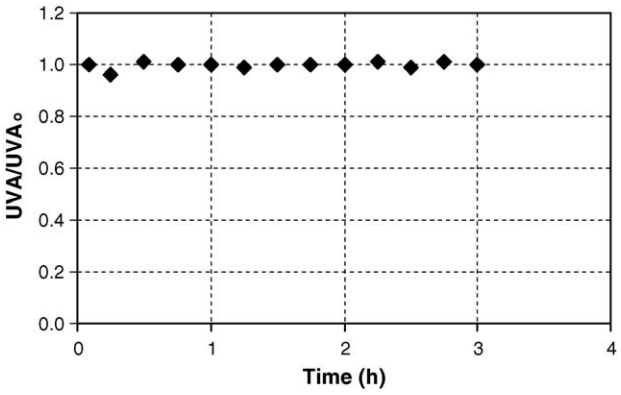

Fig. 5. UVA removal in MF (0.45 μm) + UF (50,000 Da).

pared to the initial fluxes observed for 0.45 and 1.0 μm MF (Table 4).

As seen in Fig. 4, the UF permeate flux stabilized within 2 h. However, the permeate flux continued to decrease severely, and a flux of 42 L/m^2/h was recorded at the end of a filtration period of almost 4 h, corresponding to a decrease of 72% in flux from the start to the end of the experiment and a flux decline of 71% with respect to clean water flux. The flux decline in membrane separation processes is caused by concentration polarization and fouling, which occur due to the accumulation of compounds near or on the membrane surface as well as within the pores (pore plugging). Although concentration polarization is totally reversible by the release of applied pressure, fouling can be reversible or irreversible due to adsorption, precipitation, pore blocking, and cake formation [25,26]. Two types of fouling are reported to be general for microfiltration and ultrafiltration: (i) macrosolute or particle adsorption and (ii) filtration-induced macrosolute or particulate deposition [27]. Van der Bruggen et al. [20] observed 65–85% flux decline in ultrafiltration of actual rinsing waters from the production of polyamide carpet where the wastewater contained surfactants and hence the flux decline was attributed to adsorption. The high levels of immediate flux decline (50–80%) with respect to clean water fluxes were reported to be due to pore blocking. Similarly, the flux decline of 71% observed during ultrafiltration of the acid dye bath wastewater is probably due to adsorption and pore plugging due to the presence of surfactants and acid dyes.

These results revealed that single UF was not feasible as a pretreatment process for the acid dye bath wastewater since it did not provide better performance than MF, and the flux decline of 71% was very severe. In order to reduce the flux decline, MF + UF was considered as the last alternative.

3.4. MF followed by UF

The sequential filtration of MF and UF was performed with MF (0.45 μm) and UF (50,000 Da) membranes. As mentioned before, the reason for choosing the 0.45 μm pore size in the MF stage was that the performance of this MF membrane was almost equivalent to that of the tightest filter (0.20 μm), which eliminated the need to use the smallest pore size (Table 4). Table 7 compares the removal performance of MF and UF applied in sequence. As seen, MF did not improve the removal performance of the following UF membrane at all. The color and turbidity removal efficiencies, which were 96 and 60% in the MF stage slightly increased to 100 and 78%, respectively, in the proceeding UF stage. Similarly, no UVA rejection was achieved (Fig. 5), meaning that all the UVA causing compounds had passed through both membranes.

The little improvement in color and turbidity removal efficiencies by the implementation of MF + UF was considered to be insignificant, with very similar permeate qualities obtained in single UF and MF + UF (Tables 6 and 7) and hence this alternative was found useless in terms of removal performances. Furthermore, the wastewater flux of 211 L/m^2/h was reduced to 143 L/m^2/h at the end of a filtration period of 3 h, yielding a decrease of 32% of wastewater flux and a flux decline of 70% with respect to clean water flux (Fig. 6). An average UF flux of 211 L/m^2/h obtained in the first 5 min of filtration after MF stage was found to be higher than the average flux of 151 L/m^2/h obtained in single UF. This indicated achievement of 70% increase of the UF flux due to the preceding MF stage. On the other hand, the decrease of wastewater flux of UF following MF with respect to clean water flux was at the same level as that observed in single UF (Fig. 4). Hence, there was no

Table 7
MF + UF performance

Parameter	Removal (%)			Overall permeate quality
	MF (0.45 μm) (1st stage)	UF (50,000 Da) (2nd stage)	MF + UF (overall)	
COD (mg/L)	1	2	3	1450
Color (Pt–Co)	96	100	100	0
Turbidity (NTU)	60	45	78	0.64
Total solids (mg/L)	8	0	8	823

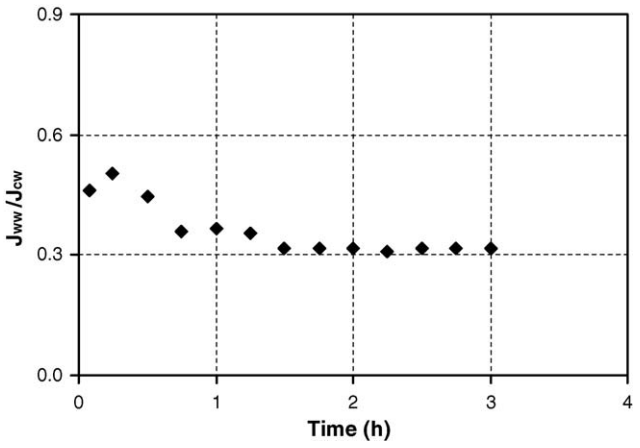

Fig. 6. Relative flux decline in MF (0.45 μm) + UF (50,000 Da) (J_{cw} = 455 L/m^2/h).

improvement in the UF flux decline by implementing the MF stage beforehand. Since the removal efficiency of MF (0.45 μm) was very poor for COD and total solids, the dissolved organics and salts reached the UF membrane, resulting in similarly poor performance of the single UF. Therefore, it was concluded that the sequential filtration of MF and UF had no benefit over single UF, and hence eliminated from the alternatives.

4. Conclusion

The most suitable pre-treatment process was determined for acid dye bath wastewaters of carpet manufacturing industry at the point of wastewater generation from dye beck process. Single stage processes were as effective as the sequential ones; hence there was no advantage in implementing sequential filtration. Therefore, selection of the simplest one was found to be feasible; single MF, which achieved 15–100% color and 62–86% turbidity removal efficiencies. The color and turbidity removal performances of MF improved as the pore size decreased from 2.5 to 0.2 μm. However, there were no improvements in COD and total solids removal with a decrease in pore size of MF. The highest removal efficiencies were achieved by MF (0.2 μm) media, however the performance of MF (0.45 μm) was very close to that of MF (0.2 μm). Therefore, there was no need to choose the tightest MF media, and the most suitable pore size was determined as 0.45 μm. Since COD and total solids reduction was very low (5 and 13%, respectively) in the pre-treatment stage, the MF filtrate contained high amounts of COD and total solids that need to be removed, which necessitated the implementation of a post membrane process, i.e., NF or RO to achieve complete purification of acid dye bath wastewater.

Acknowledgment

This research was funded by the Scientific and Technical Research Council of Turkey (TUBITAK) via Grant No. MISAG 214.

References

[1] J. Clipson, Handout for the IAP Summer School Course on Dyes and Dye Identification, 1990.
[2] USEPA, Profile of the Textile Industry, Office of Compliance Sector Notebook Project, EPA/310-R-97-009, 1997.
[3] GCGO (German Consumer Goods Ordinance), Fünfte Verordnung zur Anderung der Bedarfsgegenstandeverordnung, Bundesgesetzblatt, 1997, Teil, 24, pp. 796–800.
[4] C. Tang, V. Chen, Nanofiltration of textile wastewater for water reuse, Desalination 143 (2002) 11–20.
[5] I. Arslan, I.A. Balcioglu, D.W. Bahnemann, Advanced chemical oxidation of reactive dyes in simulated dyehouse effluents by ferrioxalate–Fenton/UV-A and TiO_2/UV-A processes, Dyes Pigments 47 (2000) 207–218.
[6] S. Kim, C. Park, T. Kim, J. Lee, S.W. Kim, COD reduction and decolorization of textile effluent using a combined process, J. Biosci. Bioeng. 95 (1) (2003) 102–105.
[7] D.H. Ahn, W.S. Chang, T.I. Yoon, Dyestuff wastewater treatment using chemical oxidation, physical adsorption, and fixed bed biofilm processes, Process Biochem. 34 (1999) 429–439.
[8] S. Wagner, Improvements in products and processing to diminish environmental impact, in: COTTECH Conference, Raleigh, NC, November, 1993, pp. 11–12.
[9] 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.
[10] M. Marcucci, G. Nosenzo, G. Capannelli, I. Ciabatti, D. Corrieri, G. Ciardelli, Treatment and reuse of textile effluents based on new ultrafiltration and other membrane technologies, Desalination 138 (2001) 75–82.
[11] C. Coste, J.C. Jacquart, O. Marmagne, Effluents decoloration, L'Ind. Textile 1278 (1996) 46–51.
[12] M. Marcucci, I. Ciabatti, A. Matteucci, G. Vernaglione, Membrane technologies applied to textile wastewater treatment, Ann. N. Y. Acad. Sci. 984 (2003) 53–64.
[13] G. Ciardelli, L. Corsi, M. Marcucci, Membrane separation for wastewater reuse in the textile industry, Resour. Conserv. Recycl. 31 (2001) 189–197.
[14] A. Rozzi, F. Malpei, L. Bonomo, R. Bianchi, Textile wastewater reuse in Northern Italy (Como), Water Sci. Technol. 39 (5) (1999) 121–128.
[15] A. Bes-Pia, J.A. Mendoza-Roca, M.I. Alcaina-Miranda, A. Iborra-Clar, M.I. Iborra-Clar, Reuse of wastewater of the textile industry after its treatment with a combination of physico-chemical treatment and membrane technologies, Desalination 149 (2002) 169–174.
[16] A. Bes-Pia, A. Iborra-Clar, J.A. Mendoza-Roca, M.I. Iborra-Clar, M.I. Alcaina-Miranda, Nanofiltration of biologically treated textile effluents using ozone as a pre-treatment, Desalination 167 (2004) 387–392.
[17] S. Barredo-Damas, M.I. Iborra-Clar, A. Bes-Pia, M.I. Alcaina-Miranda, J.A. Mendoza-Roca, A. Iborra-Clar, Study of preozonation influence on the physical–chemical treatment of textile wastewater, Desalination 182 (2005) 267–274.
[18] C.V. Vedavyasan, Combating water shortages with innovative uses of membranes, Desalination 132 (2000) 345–347.
[19] S. Sostar-Turk, M. Simonic, I. Petrinic, Wastewater treatment after reactive printing, Dyes Pigments 64 (2005) 147–152.
[20] B. Van der Bruggen, G. Cornells, C. Vandecasteele, I. Devreese, Fouling of nanofiltration and ultrafiltration membranes applied for wastewater regeneration in the textile industry, Desalination 175 (2005) 111–119.
[21] C.D. Adams, W. Fusco, T. Kanzelmeyer, Ozone, hydrogen peroxide/ozone and UV/ozone treatment of chromium and copper complex dyes: decolorization and metal release, Ozone Sci. Eng. 17 (1995) 149–161.
[22] A. Bes-Pia, M.I. Iborra-Clar, A. Iborra-Clar, J.A. Mendoza-Roca, B. Cuartas-Uribe, M.I. Alcaina-Miranda, Nanofiltration of textile industry

wastewater using a physicochemical process as a pretreatment, Desalination 178 (2005) 343–349.
[23] G. Capar, Development of a membrane based treatment scheme for water recovery from textile effluents, Ph.D. Thesis, Middle East Technical University, Ankara, Turkey, 2005.
[24] APHA/AWWA/WEF, in: A.D. Eaton, L.S. Clesceri, A.E. Greenberg (Eds.), Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, USA, 1995.
[25] M. Manttari, M. Nystrom, Critical flux in NF of high molar mass polysaccharides and effluents from the paper industry, J. Membr. Sci. 170 (2000) 257–273.
[26] K.L. Jones, C.R. O'Melia, Protein and humic acid adsorption onto hydrophilic membrane surfaces: effects of pH and ionic strength, J. Membr. Sci. 165 (2000) 31–46.
[27] H. Ma, L.F. Hakim, C.N. Bowman, R.H. Davis, Factors affecting membrane fouling reduction by surface modification and backpulsing, J. Membr. Sci. 189 (2001) 255–270.