

# Simulated cotton dye effluents treatment and reuse by nanofiltration

S.A. Avlonitis<sup>a\*</sup>, I. Poullos<sup>b</sup>, D. Sotiriou<sup>a</sup>, M. Pappas<sup>a</sup>, K. Moutesidis<sup>a</sup>

<sup>a</sup>Laboratory of Quality Control and Operations Management, Department of Mechanical Engineering, Technological Educational Institution (T.E.I.) of Halkidas, 34400 Psaxna EVIA, Greece  
Tel. +3022280 99650; Fax +3022280 99649; email: savlon@teihal.gr

<sup>b</sup>Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece

Received 17 December 2006; accepted 3 January 2007

---

## Abstract

The textile industry uses enormous quantities of water which in many cases are disposed to the environment with inadequate treatment. The effluent contains high salts and organics concentrations and they are therefore difficult to be treated. In this work the effluents from the cotton textile industry was treated by nanofiltration membrane in order to reduce the quantity of the disposed water and at the same time to reuse the treated water. A detailed investigation of the quality of the treated wastewater was performed at various operating and feed solution conditions even at extremely high recoveries and feed concentrations.

An excellent performance for the TRISEP (4040-XN45-TSF) nanofiltration membrane was found. This type of membranes can achieve complete decolorization of the cotton dye effluents and they reduce the total salt concentration more than 72%. They practically zero the organic matter content in the permeate water. These membranes can be used even at high recoveries and reasonably low pressures, producing high quality water, which can be re-used. On the other hand the quantity of the disposed wastewater, with high salt and dye concentration is less than 10% of the initial treated quantity, leading to a better management of the wastewater.

*Keywords:* Dye effluents treatment; Nanofiltration membranes; Wastewater reuse

---

## 1. Introduction

In the recent years the removal of the pollutants from the disposed to environment water is a major

issue. The main pollutants and most difficult for physical degradation are the industrial wastes. On the other hand the reuse of industrial wastewater is very important especially for high water-consuming industries. The shortage of water worldwide makes the industrial wastewater

---

\*Corresponding author.

treatment and reuse a necessity in all cases. The increasing public pressure have forced governments to implement very strict rules and regulations for the disposal of industrial wastewater. On the other hand the water cost and shortage makes industry to pay a more serious attention in the appropriate treatment of the produced effluents and the reuse of the water. Different treatment techniques have been proposed and applied in order to address this worldwide problem taking into account the source of the pollution. The advanced oxidation methods have been used extensively as one step method [1–3] or in combination with another method [4,5] for the treatment of the industrial wastewater. Membrane based methods have been also used due to their efficiency and reliability in treating different wastewaters [6–10]. However, several other methods and techniques have been proposed for treating the industrial water wastes. Electrocoagulation has become an attractive method in recent years [11]. Jain et al. [12] have used blast furnace slag, dust and sludge from steel plants and carbon slurry from fertilizer plant as an inexpensive absorbents for the removal of phenols. Other special techniques have been also proposed [13–15].

The wastewater generated by the textile industry is the most polluting among all the industrial sector. The pollution caused by dyestuff losses during the dyeing and finishing processes has been a major environmental problem for many years. The main source of wastewater generated by the textile industry are originated from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process additives in use the conventional wastewater treatment of the textile effluent has limited application since the containing pollutants have very high complexity and diversity combined with very low biodegradability. Taking into account the new strict rules for the protection of the environment which are implemented by most countries around the

world measures have to be taken by the textile industry. New dyeing auxiliaries “environmental friendly” are produced [16,17] and new wastewater treatment methods are implemented [4,18–20]. The nature of textile wastewater can be addresses in terms of classical parameters such as BOD<sub>5</sub>, COD, TSS, TS and contents of P, N, and heavy metals [21]. The low biodegradable constituents of the textile wastewater includes dye compounds, polyacrylates, phosphonates, deflocculation agents, toxicant compounds, surfactants, AOX and heavy metals [22]. Membrane technology treatment of dye industry effluents has been always very attractive [23–28]. On the other hand the textile industry and particularly the dyeing process is using very high quantities of water. Consequently a proper and efficient treatment of the effluents, producing high quality water is not only a necessity for environmental reasons but also can reduce the cost of the dyeing process by recycling the water.

The study of this work was to study the performance of nanofiltration membrane under different operating condition in order to treat effluents of the dye industry. The membrane performance was tested at different synthetic textile dyeing wastewater, which are produced during the dying process in a textile mill industry. Operating variables such as applied pressure, recovery ratio and temperature were examined for the evaluation of the TRISEP (4040-XN45-TSF) nanofiltration membrane performances. The final aim is to produce high quality water, which can be reused.

## 2. Materials and method

### 2.1. Experimental apparatus

All the experiments were conducted in a pilot plant on laboratory scale. A SCADA system was installed in the plant and long term experiments could be performed while the performance of the plant was recorded continually. The flow

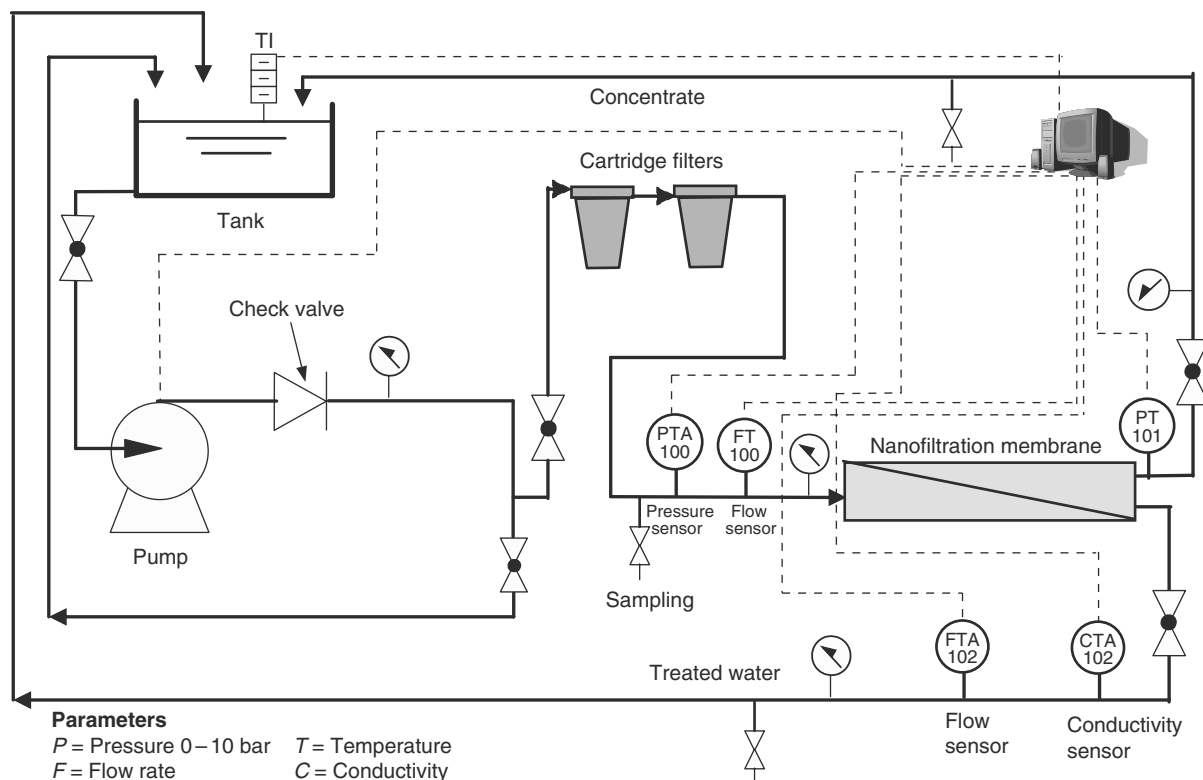


Fig. 1. Flow diagram of the nanofiltration pilot plant.

diagram of the pilot plant is illustrated in Fig. 1. The temperature of the experimental rig was controlled by a cooler and a heater at any desired value. During every experimental run samples were also taken from the sampling ports and were analyzed. The pressure pump was electronically controlled at any preset value. The by-pass valves could control the flow rates and the recovery, while the pressure was kept constant.

## 2.2. Materials

The composition and characteristics of the synthetic dye effluents, which were used in the experimental work, are given in Table 1. The

preparation of the synthetic dye effluents was accomplished by the use of tap water, which is a common practice in dye industry. The tap water had a conductivity of 362  $\mu\text{S}/\text{cm}$  and hardness of 160 ppm CaO. The No 1 composition is a typical cotton dye industry effluent. However, other feed solutions at higher salt and dye (Reactive Black-5, RB5) concentrations were used in order to test the rejection properties of the nanofiltration membranes at much higher concentrations. The pH of the simulated wastewater was adjusted by a 88% HCOOH solution to 6.5–7.0. The solution has dark blue color due to RB5, see Fig. 2. The nanofiltration membranes were 4' modules, made by TRISEP (4040-XN45-TSF).

Table 1  
Composition of the simulated dyestuff

A/A	Substance	Feed solution, experimental run			
		No 1	No 2	No 3	No 4
1.	Reactive Black 5 (RB5) (mg/L)	70	130	260	230
2.	NaCl (mg/L)	300	600	1200	1500
3.	Na <sub>2</sub> CO <sub>3</sub> (mg/L)	20	40	80	100
4.	NaOH (mg/L)	10	20	40	50
5.	COD (mg/L)	100	180	360	360
6.	Conductivity (μS/cm)	1000	1500	2120	3070

These membranes have minimum rejection properties for MgSO<sub>4</sub> and sucrose 92% at solute concentration 2000 ppm and operating pressure 100 psi. The maximum recommended recovery is 15%. However, much higher recoveries were used to test the performance of the membrane at extreme conditions. As a pretreatment stage two cartridge filters were used, one of 20 μm and one of 5 μm.

### 2.3. Experimental procedure

Different experiments were carried out at given concentration and temperature. As it is shown in Table 1, four different solution concentrations were selected. At composition No 3 experiments were conducted at three constant different temperatures, at 20°C, 25°C and 30°C. For every experimental run at constant temperature and concentration the rejection properties of the nanofiltration membrane were tested at different applied pressures and recovery ratios. The system was working as a closed loop and the effect of the operating time to the performance properties

of the membrane was also examined in a long time experiment. The readings were taken when the corresponding values were stable at least for 15 min. The composition of the feed was tested periodically and it was adjusted accordingly.

### 2.4. Analytical methods

For every run the feed solution was prepared at desired concentration and pH. The pilot plant was run until the desired temperature was reached and then readings were taken automatic by the SCADA system and manually. The parameters which are under investigation and recorded for the operating parameters and permeate characteristics are:

- RB5 concentration, by spectrophotometric method at 584 nm (BAUSCH & LOMB, Spectronic 20)
- pH, by pH meter, (HOEZLE & CHELIUS KG)
- Conductivity, by conductivity meter (HANNA HI 8733)
- Hardness, by titration
- COD, by photometric method

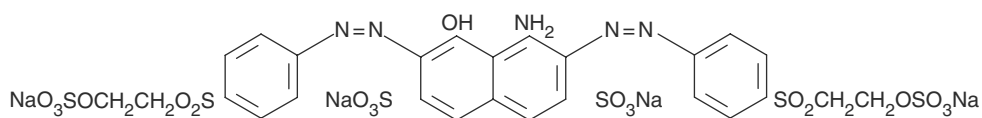


Fig. 2. Molecular structure of the Reactive Black 5 dye.

- Turbidity, by turbidity meter (HANNA HI 93703)
- Permeate and brine flow rates, by paddle wheel flow meters
- Temperature, by thermocouple
- Applied pressure, by a pressure transducer

The efficiency of the nanofiltration membrane was determined as decolorization efficiency  $E$  [3], which is calculated as,

$$E = \frac{C_{\text{RB5}(i)} - C_{\text{RB5}(p)}}{C_{\text{RB5}(i)}} \times 100 \quad (1)$$

where  $C_{\text{RB5}(i)}$  the initial RB5 concentration at the feed solution and  $C_{\text{RB5}(p)}$  the permeate dye concentration.

The recovery,  $R$ , of the membrane is defined as,

$$R = \frac{Q_p}{Q_f} \times 100 \quad (2)$$

where,  $Q_p$  is the permeate flow rate and  $Q_f$  is the feed flow rate.

The rejection properties of the membrane is estimated by the rejection,  $r$ ,

$$r = \frac{c_f - c_p}{c_f} \times 100 = \left(1 - \frac{c_p}{c_f}\right) \times 100 \quad (3)$$

where  $c_p$  the permeate concentration and  $c_f$  the feed concentration. In our calculations instead of concentration the equivalent conductivity readings were used.

### 3. Results and discussion

The membrane efficiency and performance was tested at different operating conditions. The applied pressure was varied from 4 to 8 bar and the recovery from 4.6 to 54%. In all the experiments, even at extremely high recoveries, the decolorization efficiency was 100%, proving an excellent performance of this type of nanofiltration membranes for the treatment of dye effluents. A data sheet of run No 1 experiments is given in Table 2. The feed concentration for run No 1 has been given in Table 1. Similar results with those in Table 1 were found at higher concentrations, see Table 3.

The membrane showed excellent rejection properties ( $r > 96.25\%$ ) of all the salts causing hardness regardless of the operating conditions and feed concentration. On the other hand the total rejection of all ions is between 72 and 93% depending on the operating conditions and feed concentration. An excellent COD reduction was noticed by the membrane. Even in the highest COD feed concentration (360 mg/L) the permeate

Table 2

Data for experimental run No 1, at 20°C, pH = 7.0, feed COD = 100 mg/L, feed conductivity = 1000  $\mu\text{S}/\text{cm}$ ,  $C_{\text{RB5}} = 70 \text{ mg/L}$

$P_{\text{feed}}$ (bar)	$Q_{\text{feed}}$ (L/h)	$Q_{\text{permeate}}$ (L/h)	pH <sub>permeate</sub>	$C_{\text{RB5}}$ (ppm)	Conductivity permeate ( $\mu\text{S}/\text{cm}$ )	COD permeate (ppm)	Hardness (ppm CaO)
4.0	670.0	97.0	5.73	0.0	129.0	<16	6.0
4.0	1041.0	96.0	5.87	0.0	120.0	<16	6.0
4.0	1946.0	90.0	5.89	0.0	108.0	<16	5.0
4.0	1935.0	90.0	5.89	0.0	108.0	<16	5.0
6.0	1690.0	145.0	5.02	0.0	75.0	<16	4.0
6.0	695.0	150.0	4.62	0.0	77.0	<16	4.0
6.0	900.0	156.0	4.71	0.0	77.0	<16	4.0
8.0	1015.0	200.0	5.07	0.0	103.0	<16	3.0
8.0	370.0	200.0	5.05	0.0	107.0	<16	3.0

Table 3  
Data for experimental run No 2 and No 3

$P_{\text{feed}}$ (bar)	$Q_{\text{feed}}$ (L/h)	$Q_{\text{permeate}}$ (L/h)	$\text{pH}_{\text{permeate}}$	$C_{\text{RB5}}$ (ppm)	Conductivity permeate ( $\mu\text{S}/\text{cm}$ )	COD permeate (ppm)	Hardness (ppm CaO)
Run No. 2, at 20°C, pH = 7.0, feed COD = 180 mg/L, feed conductivity = 1500 $\mu\text{S}/\text{cm}$ , $C_{\text{RB5}} = 130$ mg/L							
4.0	625.0	88.0	5.44	0.0	147.0	<16	5.0
4.0	1025.0	88.0	5.60	0.0	143.0	<16	5.0
4.0	1736.0	82.0	5.52	0.0	171.0	<16	5.0
6.0	1672.0	138.0	5.19	0.0	123.0	<16	5.0
6.0	1115.0	144.0	5.19	0.0	123.0	<16	5.0
8.0	945.0	193.0	4.73	0.0	106.0	<16	4.0
8.0	382.0	180.0	6.01	0.0	130.0	<16	4.0
Run No. 3, at 20°C, pH = 7.0, feed COD = 360 mg/L, feed conductivity = 2120 $\mu\text{S}/\text{cm}$ , $C_{\text{RB5}} = 260$ mg/L							
4.0	635.0	74.0	5.52	0.0	318.0	<16	4.0
4.0	1010.0	70.0	5.53	0.0	400.0	<16	4.0
4.0	1710.0	63.0	5.56	0.0	314.0	<16	4.0
6.0	1670.0	112.0	5.70	0.0	227.0	<16	4.0
6.0	1075.0	120.0	5.23	0.0	250.0	<16	3.0
8.0	955.0	171.0	5.25	0.0	206.0	<16	3.0
8.0	339	156.0	5.33	0.0	241.0	<16	3.0

COD concentration was always less than 16 mg/L, which is the lowest limit of the method used. The turbidity of the permeate water was always 0.00 NTU unit in all cases.

In Fig. 3 the permeate flow rate and rejection is illustrated as a function of the applied pressure at different feed concentrations. All the data are at about the same feed flow rates. It can be seen that as the pressure increases the quality of the permeate water and the flow rate increase, as it was expected. On the other hand the higher the feed concentration (run No 3) the lower the permeate flow rate and the rejection. With this type of membranes the quality of the permeate is very high so that the produced water can be reused with no other treatment.

In Fig. 4 the effect of the temperature on the membrane performance is presented. All the experiments were run at the same recovery. Even at 30°C the membrane has a very good performance. One degree Celsius increase on temperature increases the permeate flow rate by an average

3% and decreases the permeate quality by an average 6%.

The performance of the membrane was tested in a 10 days experiment at even higher feed concentration, see Fig. 5. The membrane after an initial improve showed a very stable performance

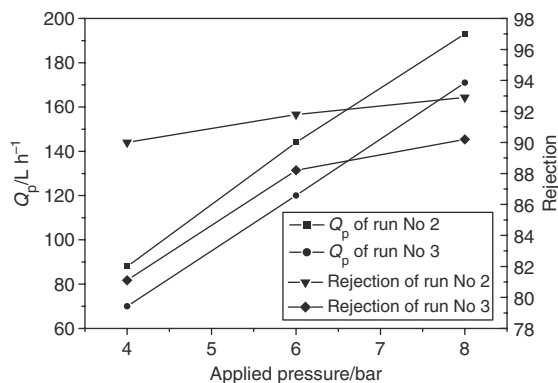


Fig. 3. Membrane performance at 20°C at different applied pressures and feed concentrations (run No 2 and run No 3).

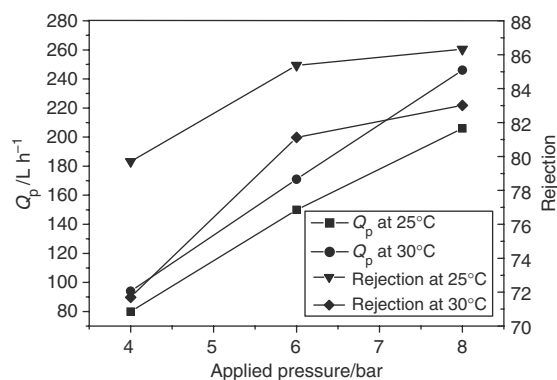


Fig. 4. Membrane performance at different temperatures for run No 3 (feed COD = 360 mg/L, feed conductivity = 2120  $\mu$ S/cm,  $C_{RB5}$  = 260 mg/L).

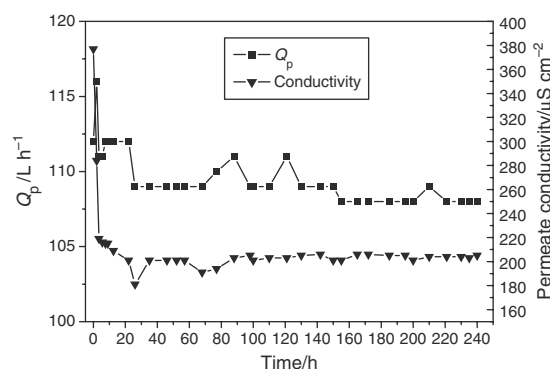


Fig. 5. Membrane performance at 20°C for run No 4 (feed COD = 360 mg/L, feed conductivity = 3070  $\mu$ S/cm,  $C_{RB5}$  = 230 mg/L).

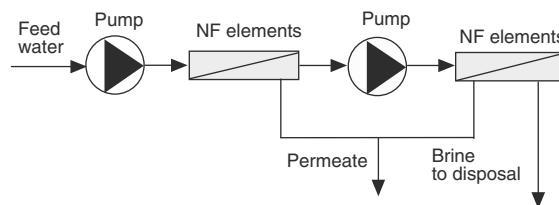


Fig. 6. Two passes configuration of nanofiltration system.

for the time it was tested. For this test high concentration feed solution was used. The feed conductivity was 3070  $\mu$ S/cm and the RB5 concentration was 230 mg/L.

In this pilot plant a single membrane was used in one pass. In industrial applications the pressure vessel can contain more than one membranes and recoveries about 60% can be achieved. If two passes are used in series, see Fig. 6, then the recovery can be increased up to 90% [22]. As it has been proved experimentally the membranes can operate perfectly even at high salt and RB5 concentration, so that no operational problems can be faced in the use of a second pass. The life time of this type of membranes can not be estimated at this work. In similar work it was suggested to be more than one (1) year [22].

The electronically controlled pressure pump has the capacity to show the consumed power at specific operating conditions. Some of these data are presented in Table 4. If the specific energy consumption, SEC, is defined as the energy consumed for every  $m^3$  of produced water, then the SEC can be calculated at every operating condition.

Table 4  
Pressure pump operating characteristics

$P_{\text{feed}}$ (bar)	Frequency ( $s^{-1}$ )	$Q_{\text{feed}}$ (L/h)	$Q_{\text{permeate}}$ (L/h)	Recovery (%)	Power (W)	Specific energy consumption ( $\text{kW h/m}^3$ )
4.0	2000.0	670.0	97.0	14.47	400	4.12
6.0	2450.0	1690.0	145.0	8.57	600	4.13
8.0	2850.0	1015.0	200.0	19.70	700	3.50
8.0	2900.0	370.0	200.0	54.05	750	3.75

The average SEC in this work, at normal and high recoveries, was found to be 4 kW h/m<sup>3</sup>. Similar SEC values have been found for micro-filtration treatment of wastes [7]. However, in real industrial nanofiltration plants the specific energy consumption should be less than 2 kW h/m<sup>3</sup>. If small energy consumption is achieved then the ability to reuse the produced water make the proposed nanofiltration method very attractive to industrial applications.

#### 4. Conclusions

Nanofiltration has been proved an efficient process to remove and separate dyes and salts from wastewaters of dye industry. It was shown in this work that TRISEP (4040-XN45-TSF) nanofiltration membranes have excellent decolorization efficiency combined with adequate salt rejection properties at reasonable energy consumption. These membranes can be used not only to treat the dye industry effluents but also to recycle and reuse the wastewater. It must be pointed out that the treatment of dye effluents by nanofiltration is a separation process and even at high recoveries splits the feed wastewater to permeate and brine. The permeate water can be reused with no other treatment. The much smaller quantities of wastewater at higher pollutants concentration than the initial feed solution should be treated before disposed to the environment. Consequently the nanofiltration technology for the treatment of dye industry effluents should always be combined with another industrial wastewater method for the integrated management of the industrial wastes.

#### Acknowledgement

This work is a part of the project “*Arximidis I-Environment, TEI-X*” financed 25% by the Greek Government and 75% by the E.U. under the framework of “*Operational Programme for Education and Initial Vocational Training*”.

#### References

- [1] I. Arslan, I.A. Batcioglu and Bahnemann, Heterogeneous photocatalytic treatment of simulated dyehouse effluents using novel TiO<sub>2</sub> photocatalysts, *Appl. Catal. B: Environ.*, 26 (2000) 193–206.
- [2] J. Arana, E.T. Rendon, J.M.D. Rodriguez, J.A. Melian, O. Diaz and J. Pena, Highly concentrate phenolic wastewater treatment by the Photo-Fenton reaction mechanism study by FTIR-ATR, *Chemosphere*, 44 (2001) 1017–1023.
- [3] V. Augugliano, C. Baiocchi, A. Prevot, E. López, V. Loddo, M. Malato, G. Marci, L. Palmisano and E. Pramauro, Azo-dyes photocatalytic degradation in aqueous suspension of TiO<sub>2</sub> under solar irradiation, *Chemosphere*, 49 (2002) 1223–1230.
- [4] Nadar M. Al-Bastaki, Treatment of synthetic industrial wastewater with UV/TiO<sub>2</sub> and RO using benzene as a model hydrocarbon, *Desalination*, 156 (2003) 193–197.
- [5] M. Kositzi, A. Antoniadis, I. Poulis, I. Kiridis and S. Malato, Solar photocatalytic treatment of simulated dyestuff effluents, *Solar Energy*, 77 (5) (2004) 591–600.
- [6] A. Casano, R. Molinari and E. Drioli, Saving of water and chemicals in tanning industry by membrane process, *Water Sci. Technol.*, 40 (4–5) (1999) 443–450.
- [7] W. Scholz and M. Lucas, Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals, *Water Res.*, 37 (2003) 1859–1867.
- [8] P. Janknecht, A.D. Lopez and Adelio M. Mendes, Removal of industrial cutting oil from oil emulsions by polymeric ultra and microfiltration membranes, *Environ. Sci. Technol.*, 38 (2004) 4878–4883.
- [9] L.D. Nchiem, A.I. Schäfer and M. Elimelech, Removal of natural hormones by nanofiltration membranes: measurement, modeling and mechanisms, *Environ. Sci. Technol.*, 38 (2004) 1888–1896.
- [10] A. Bódalo-Santoyo, J.L. Gómez-Carrasco, E. Gómez-Gómez, M.F. Máximo-Martin and A.M. Hidalgo-Montesinos, Spiral-wound membrane reverse osmosis and the treatment of industrial effluents, *Desalination*, 160 (2004) 151–158.
- [11] O.T. Can, M. Bayramoglu and M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, *Ind. Eng. Chem. Res.*, 42 (2003) 3391–3396.

- [12] A.K. Jain, V.R. Gupta, S. Jain and Suhas, Removal of chlorophenols using industrial wastes, *Environ. Sci. Technol.*, 38 (2004) 1195–1200.
- [13] A. Adachi, C. Ikeda, S. Takagi, N. Fukao, E. Yoshie and T. Okano, Efficiency of rice bran for removal of organochlorine compounds and benzene from industrial wastewater, *J. Agric. Food Chem.*, 49 (2001) 1309–1314.
- [14] S.E. Kentish and G.W. Stevens, Innovations in separations technology for the recycling and re-use of liquid waste streams, *Chem. Engin. J.*, 84 (2001) 140–159.
- [15] K. Janardhanan Sreeram, S. Saravanabhavan, J. Raghava Rao and B. Unni Nair, Use of chromium-collagen wastes for the removal of tannins from wastewaters, *Ind. Eng. Chem. Res.*, 43 (2004) 5310–5317.
- [16] F. Gähr, F. Hermanutz and W. Oppermann, Ozonation-an important technique to comply with new German laws for textile wastewater treatment, *Water Sci. Technol.*, 30 (1994) 255–263.
- [17] R. Steiner, Evaluation of peracetic acid as an environmentally safe alternative for hypochlorite, *Text. Chem. Col.*, 27 (8) (1995) 29–31.
- [18] S. Liakou, S. Pavlou and G. Lyberatos, Ozonation of azo dyes, *Water Sci. Technol.*, 35 (1997) 279–286.
- [19] I. Arslan and I. Akmeahmet Balcioglu, Degradation of commercial reactive dyestuffs by heterogeneous and homogenous advanced oxidation processes: a comparative study, *Dyes Pigm.*, 43 (1999) 95–108.
- [20] C. Hachem, F. Bocquillon, O. Zahraa and M. Bouchy, Decolourization of textile industry wastewater by the photocatalytic degradation process, *Dyes Pigm.*, 49 (2001) 117–125.
- [21] V.M. Correla, T. Stephenson and S.A. Judd, Characterization of textile wastewaters-a review, *Environ. Technol.*, 15 (1994) 917–929.
- [22] Phillippe C. Vandevivere, Bianchi Roberto and Vertraete Willy, Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, *J. Chem. Technol. Biotechnol.*, 72 (1998) 289–302.
- [23] Ratana Jiratananon, Anawat Sungpet and Piyanoot Luangsowan, Performance evaluation of nanofiltration membranes for treatment of effluents containing reactive dye and salt, *Desalination*, 130 (2) (2000) 177–183.
- [24] A. Akbari, J.C. Remigy and P. Aptel, Treatment of textile dye effluent using a polyamide-based nanofiltration membrane, *Desalination*, 41 (7) (2002) 601–609.
- [25] C. Allégre, P. Moulin, Maisseu Michel and Charbit Francise, Savings and re-use of salts and water presents in dye haouse effluents, *Desalination*, 162 (2004) 13–22.
- [26] Anawat Subgpet, Ratana Jiratananon and Piyanoot Luangsowan, Treatment of effluents from textile-rinsing operations by thermally stable nanofiltration membranes, *Desalination*, 160 (1) (2004) 75–81.
- [27] S. Chakraborty, S. De, J.K. Basu and S. Das-Gupta, Treatment of a textile effluent application of a combination method involving absorption and nanofiltration, *Desalination*, 174 (1) (2005) 73–85.
- [28] C. Allégre, P. Moulin, M. Maissen and F. Charbit, Treatment and reuse of reactive dyeing effluents, *J. Membr. Sci.*, 269 (1–2) (2006) 15–34.