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Dyes and Pigments 64 (2005) 147–152
DYES and PIGMENTS
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Wastewater treatment after reactive printing

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Received 13 February 2004; received in revised form 29 March 2004; accepted 7 April 2004
Available online 8 July 2004

Abstract

Membrane filtration of wastewater after textile printing with reactive dyes is described. The wastewater from a Slovenian factory, whose output is approx. 80% reactive dyes printed and dyed on cotton, was studied. In particular, the presence of urea, sodium alginate, oxidation agent and reactive dyes, used for the printing paste preparation, in the wastewater was studied. Chemical analyses of actual, non-purified, wastewater showed that many Slovenian regulations were exceeded.

The study of membrane filtration is based on a pilot wastewater treatment plant: ultrafiltration (UF) and reverse osmosis (RO) units. The quality of the wastewater was improved by ultrafiltration, but its effluent still does not conform to the specification of concentration limits for emission into water. Permeate coming from RO meets the required specification and, therefore, could be re-used in the washing process of printed textiles.

Keywords: Textile wastewater; Reactive printing; Membrane filtrations; Pilot plant

1. Introduction

The textile industry is one of the most complicated in manufacturing industry because of its fragmented and heterogeneous character. The main environmental impacts of the textile chain come from the so called "wet processes", of the textile finishing industry. The effluent from textile processing is often discharged into a municipal sewage treatment plant or directly into waterways [1]. Textile wastewater may include many types of dyes, detergents, insecticides, pesticides, grease and oils, sulphide compounds, solvents, heavy metals, inorganic salts and fibres, in amounts depending on the processing regime [2]. Colour removal of effluent from the textile dyeing and finishing operation is becoming important because of aesthetic as well as environmental concerns [3].

The problem of coloured effluent has become particularly identified with the use of reactive dyestuffs, as 10 and 40% of total dyes applied can be discharged into the effluent [4]. Reactive dyes are soluble anionic dyes that contain one or more reactive groups capable of forming a covalent bond with the hydroxyl groups in the fibre and are unsuitable for recycling.

The treatment of wastewater from cotton textile processing industry has been widely explored in the literature, especially for the wastewater from dyeing operations [5–7]. Relatively less attention has been paid to the problem of the wastewater from printing factories [8]. The wastewater produced during cotton printing comes from washing the printing equipment (the printing screens, the tanks for paste preparation, pipework etc.) and from the washing of printing fabric after fixation. The composition closely resembles that of the

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doi:10.1016/j.dyepig.2004.04.001

wastewater from the textile dyeing industry, with the difference that solid pollutants from the paste thickening agents and sometimes solvent are present. Printing pastes contain 800–900 g of water per kg wet paste, 10–40 g of dry thickener agent (alginate, guar, etc.) per kg, urea, dyes and various chemicals (surfactants, solvents, chelating agents) [9]. Sodium alginate thickener could be removed from wastewater after reactive printing by ultrafiltration, and almost all quantitatively recycled. Printing results with such alginate are comparable with those of original alginate [10].

Processes such as coagulation, carbon adsorption and biological treatment, used currently for the purification of textile dyeing wastewater can be employed for the treatment of printing wastewater [8]. The physical–chemical processes alone were not, however, considered appropriate for the treatment of wastewater, because of their high costs and due to the fact that they are not effective to meet the required levels.

Membrane processes are very promising advanced treatment methods for colour removal as well as for reducing the volume of wastewater generated and recovering and recycling valuable components from the waste stream [11]. Several approaches have been proposed to implement membrane processes in the treatment of textile wastewater from different production streams.

Ultrafiltration (UF) is effective for the removal of particles and macromolecules and does not decolourise the waste stream. Nanofiltration (NF) allows the separation of low molecular weight organic compounds and divalent salts, with an appreciable softening effect. Reverse osmosis (RO) is suitable for removing ions and larger species from dye bath effluents [12]. The reverse osmosis membrane also removes the colour and desalinates the waste stream considerably (NaCl retention of 93%), however, the retention for the reactive dyes is somewhat lower in the nanofiltration process [13]. It is proposed as a pre-treatment to UF in this work.

The main objective of this study was to purify the actual reactive printing wastewater taken from a Slovenian factory, whose output is approx. 80% printed and dyed cotton using reactive dyes, by using a laboratory pilot plant equipped with UF and RO units. The characteristics of the effluent (Table 2) were used to demonstrate the performance of membrane filtrations.

2. Materials and methods

2.1. Materials

In this research, cotton was printed with reactive dyes using the recipe in Table 1.

Alginate (CHT Alginate EHV) and oxidation agent (Rapidoprint XRG) were produced by CHT Beitlich, Germany. All three reactive dyes were produced by Ciba, Switzerland.

Table 1
Printing paste recipe

Alginate	40 g
Na_2CO_3	15 g
Urea	100 g
Oxidation agent	10 g
Cibacron Rot P-B	40 g
Cibacron Brown PGR(P6R)	10 g
Cibacron Black PGR(PSG)	50 g
H_2O	X g
	1000 g

A Stork Rotary Screen Printing Machine Model RD IV, working width 1820 mm, was used to print the cotton textiles. Maximum printing speed was 80 m/min. Dye fixation is carried out by steaming followed by washing to remove dye and thickener. The washing process consisted of three washing cycles. The washing machine (Arioli, Italy) has five washing baths with double fabric lengths, capacity 25 m per bath. The system was closed after filling each bath with upto 1200 L of water. The goods to liquor ratio in the washing process was 1:40. In the second and third cycles, the washing agent Tanaterge LFN (Sybron/Tanatex, USA) at 80–95 °C and at γ (0.5 g/L) was added. After the rinsing process was repeated three times, a wastewater sample was taken.

2.2. Analytical methods

The parameters for the wastewater after reactive printing were set according to the Slovenian regulation [14]. The concentration limit of emission into the water, the standard procedure and the used methods for chemical analyses from the above regulation are given in Table 2.

2.3. Pilot plant

The studies of UF and RO were performed using a pilot plant (MDS, Germany) equipped with a tubular ceramic membrane module for UF and a polyether sulfone membrane of spiral wound type for RO (Fig. 1). At the beginning of the test, the wastewater was poured into storage tank 1 from where it was pumped (pump 1) into the UF module where the cross flow filtration started. About 80% of feed volume was separated as permeate, which was collected in storage tank 2. Twenty percent of the feed volume circled back into the storage tank under pressure 4–5 bar as the retentate. The pressure of the permeate was regulated by the valve and the permeate flow velocity was 15–20 L/h.

An RO feed was pumped through a pre-filtration unit under pressure 1–2 bar, then it was pumped under high-pressure (20–30 bar) into the spiral wound module from

Table 2
Concentration limits of emission into water, standard procedures and methods used

Parameter	Concentration limit of emission into water	Standard	Method/apparatus
pH-value	6.5–9.0	SIST ISO 10523	Electrochemical/pH-meter Iskra MA 5740
Suspended substances (mg/L)	80	ISO/DIN 11923	Gravimetrical/weighing machine Mettler AE 100
Sediment substances (mL/L)	0.5	DIN 38409-H9	Sedimentation
Colour at:			
436 nm (m^{-1})	7.0		
525 nm (m^{-1})	5.0	SIST EN ISO 7887/3	Spectrophotometer/Perkin–Elmer Cary 1E
620 nm (m^{-1})	3.0		
Daphnia magna (Sd)	4	SISTEN ISO 6341	Toxicity test/48 h-EC50
Al (mg/L)	3.0	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Cu (mg/L)	1.0	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Zn (mg/L)	3.0	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Cd (mg/L)	0.1	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Co (mg/L)	0.5	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Sn (mg/L)	1.0	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Cr total (mg/L)	2.0	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Cr^{6+} (mg/L)	0.1	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Pb (mg/L)	0.1	DIN 38406-29	ICP-MS/Perkin–Elmer Elan 6000
Free Cl_2 (mg/L)	1.0	ISO 7393/1	Reagent DPD—colourimetric
Total Cl_2 (mg/L)	0.5	ISO 7393/2	Reagent DPD—colourimetric
Nitrogen ammonia (mg/L)	5	SIST ISO 6778	Spectrophotometer/Perkin–Elmer Cary 1E
Total phosphorus (mg/L)	–	SIST ISO 6878-1	Spectrophotometer/Perkin–Elmer Cary 1E
Sulphate	400	SIST ISO 9280	Titrimetric
Sulphide (mg/L)	1.0	SIST ISO 7875-1	Spectrophotometer/Perkin–Elmer Cary 1E
TOC (mg/L)	60	SIST ISO 7875-1	Spectrophotometer/Perkin–Elmer Cary 1E
COD (mg O_2/L)	200	SIST ISO 6060	Titrimetric
BOD_5 (mg O_2/L)	30	SIST ISO 5815	Electrochemical/oximeter WTW
Mineral oil (mg/L)	20	DIN 38409-18	Gravimetrical/weighing machine Mettler AE 100
AOX (mg/L)	0.5	SIST ISO 9562	Colourimetric/DX-200 Dorhmann
VCOC (mg/L)	0.1	ISO 10301 Section 3	GC–MS/Hewlett Packard
Phenols (μg/L)	10	SIST ISO 7875-1	Spectrophotometer/Perkin–Elmer Cary 1E
Anionic surfactant (mg/L)	1.0	ISO 8245	TOC analyser/Dohrmann DC-190

where the permeate was collected into a storage vessel, while the retentate was recycled into the feed tank (storage tank 2).

The ceramic membrane used was α-Al_2O_3 membrane with a pore diameter of 0.1 μm. The membrane is 25.4 mm in diameter and 900 mm in length. It has a filtrating surface area of 0.13 m^2. Ceramic membranes are ideal for in-place cleaning. This membrane was back-pulsed, which is a permeate flow reversal technique to reduce fouling [15]. It was achieved by applying pressure to the filtrate side, so that permeate was forced back through the membrane every 3 min. The pressure of the back-pulsing air was 6–8 bar.

Chemical cleaning of the membrane was conducted with 1% Ultrasil (Ecolab, Slovenia) solution. Ultrasil is composed of 25–50% NaOH, 2.5–10% non-ionic surfactant, 2.5–10% Na_2CO_3 and 25–50% Na_4EDTA [16].

3. Results and discussion

Samplings of effluent were performed in order to test the performance of the pilot plant for UF and RO, and to determine whether UF and RO are adequate processes for wastewater purification. Table 3 presents the results of analysing the wastewater sample, the concentration limits of emission into water and the next two treatment stages, permeate from UF and RO. All other measurements were done in the laboratory at room temperature, 25 °C.

Several wastewater parameters were too high under Slovenian regulations, namely: SAC at three wavelengths, total phosphorus, ammonium nitrogen, sulphide, TOC, COD, BOD_5, total hydrocarbons, and phenols. The tests showed the wastewater sample to be very toxic: the value for *Daphnia magna* was 5 times too high. The heavy metals and volatile chlorinated organic compounds (VCOCs) were unproblematic due to the already very low concentrations in the wastewater sample.

Several of the measured parameters were lowered after ultrafiltration, namely: TOC was reduced by 37%, COD by 42%, phenols by 71%, total phosphorus by 59%, and the SAC values dropped to a range of 63–70% at all three wavelengths. The SAC values were approximately 4 times (525 nm) to 6 times (436 nm and 620 nm) too high. These measurements confirm the

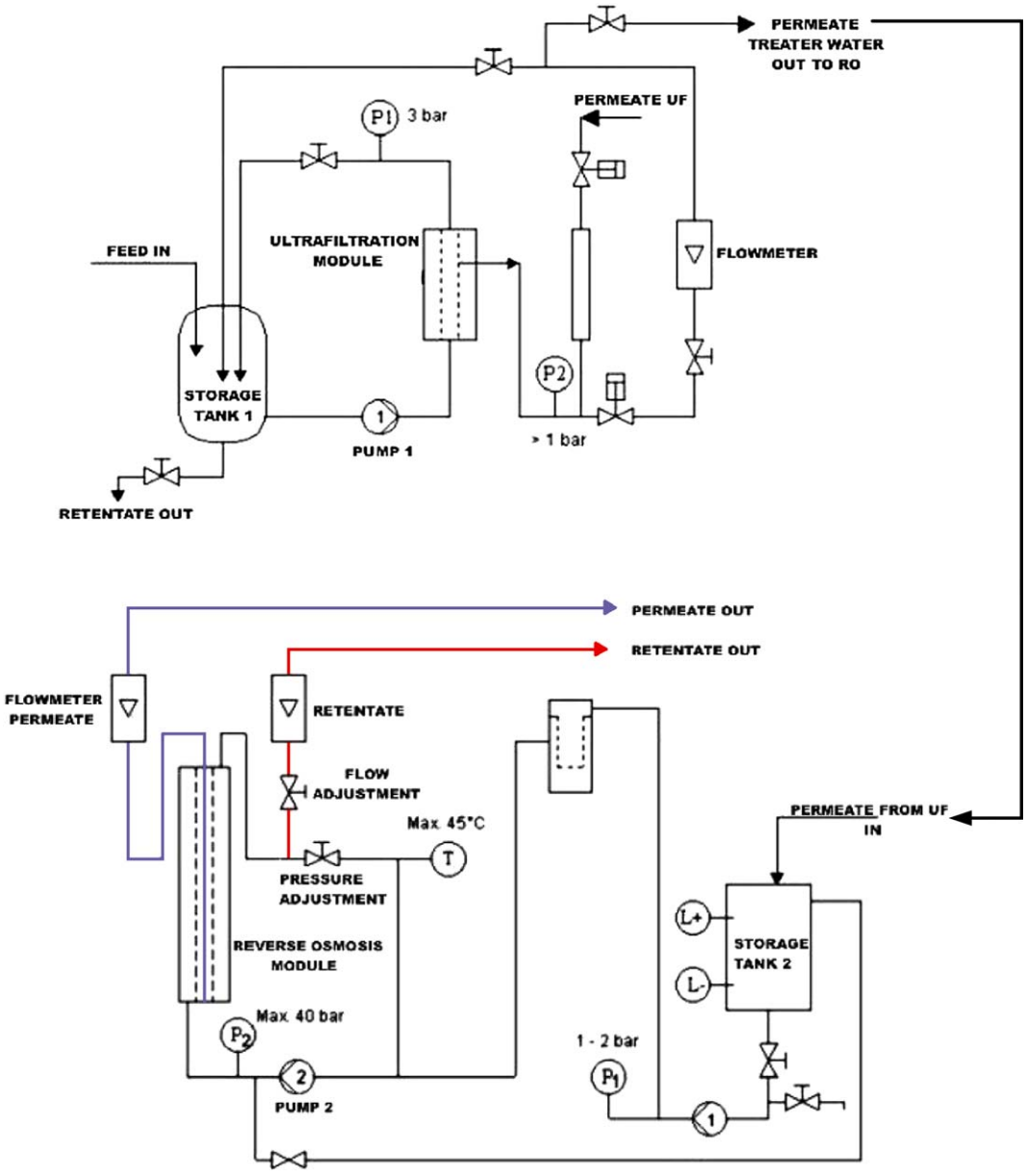

Fig. 1. UF and RO units.

literature data [17] that UF does not remove colour from wastewater samples and that further treatment is required. All the encountered measurements still did not meet the required concentration for emission into water [14]. The concentration of ammonium nitrogen dropped by 66% to 4.6 mg/L and was the only one among the excessive parameters where the concentration dropped below the allowed limit. UF permeate was not toxic due to the high number of surviving *D. magna* species.

The reverse osmosis permeate had good analytical characteristics: the COD value was reduced by up to 94%, BOD_5 up to 95%, phenols up to 98%, TOC up to 85%, total phosphorus was reduced from 13 mg/L to 0.3 mg/L, which means 97%. Following RO, the water samples were no longer toxic because almost all the *D. magna* species survived. These results agreed with the calculated biodegradability in the water samples. The values for COD and BOD_5 were 430 mg/L and 140 mg/L in the wastewater, this means that the biodegradability was only 32% and after reverse osmosis these values were 25 mg/L (COD) and 13 mg/L (BOD_5), which gives a biodegradability of 52%. The SAC values at all three wavelengths were reduced to below 0.2 m^{-1}, which means a 99% reduction for all the above three values. The colour intensity was good as seen in Fig. 2.

In Fig. 2 there are 5 samples: starting 1st from the left is the wastewater sample, the 2nd is the permeate after UF and the 4th is the permeate after RO, the other two are retentates after UF and RO. The last two samples are the most highly coloured but the wastewater

Table 3
The determination of parameters of wastewater before and after treatment with membrane technology (p, permeate)

Parameters (mg/L)	Concentration limit of emission into water	Wastewater	UFp	ROp
pH (25 °C)	6.5–9.0	8.95	8.5	8.2
Suspended substances	80	57	21	2
Sediment substances	0.5	<0.5	<0.5	<0.5
SAC (m^{-1}) at:				
436 nm	7.0	**43.75**[a]	**16.19**	0.11
525 nm	5.0	**20.97**	**6.70**	0.00
620 nm	3.0	**18.2**	**5.43**	0.13
Daphnia magna (Sd)	4	**20**	2	<2
Al	3.0	0.2	<0.05	<0.05
Cu	1.0	<0.05	<0.05	<0.05
Zn	3.0	<0.05	<0.05	<0.05
Cd	0.1	<0.005	<0.005	<0.005
Co	0.5	<0.01	<0.01	<0.01
Sn	1.0	<0.1	<0.1	<0.1
Total Cr	2.0	<0.05	<0.05	<0.05
Cr^{6+}	0.1	<0.01	<0.01	<0.01
Pb	0.5	<0.05	<0.05	<0.05
Chlorine free (Cl_2)	0.2	<0.1	<0.1	<0.1
Chlorine total (Cl_2)	0.5	<0.1	<0.1	<0.1
Amonium nitrogen (N)	5.0	**13.5**	4.6	4.9
Phosphorus total (P)	2.0	**13**	**5.4**	0.3
Sulphate	400	4.5	0.4	1.2
Sulphide	0.1	2.8	1.55	1.2
TOC	30.0	**116.2**	**73.4**	17.7
COD	120.0	**430**	**250**	25
BOD_5	30.0	**140**	**110**	13
Hydrocarbons total	10.0	**35.2**	26.8	10.8
AOX	0.5	0.15	0.15	0.12
Phenols	0.1	**1.39**	**0.40**	0.017
VCOC	0.1	<0.01	<0.01	<0.01
Anionic surfactants	1.0	0.25	<0.1	<0.1

[a] Bold values—exceeded concentrations.

sample has a little less intensity. It is obvious from Fig. 2 that permeate after RO is colourless. This agrees with the measurements of SAC after RO, which all have values around 0.1 m^{-1} (Table 3). The permeate achieved such a quality after reverse osmosis that it could be recycled.

4. Conclusions

The use of membrane technology consisting of ultrafiltration followed by reverse osmosis has been very effective in wastewater treatment after reactive printing. Because of the large wastage of water in the process of reactive printing, a study of the possibility for its re-use is inevitable.

The main ecological parameters of the actual wastewater were also very high: TOC, COD, phenols, total phosphorus and colour. The wastewater sample was poisonous after reactive printing, because it has

Fig. 2. Samples of untreated and treated wastewater. This figure is published in colour online.

to be diluted 20 times to achieve poison-free water, as shown by the toxicity tests with *D. magna*. The findings of the study conclude that the ultrafiltration step was not sufficient for treatment of such textile wastewater. The quality of the wastewater was improved, but its effluent still does not conform to the specification of concentration limits for emission into water. Nevertheless, the ultrafiltration step guaranteed a good performance and prolonged the lifetime of the reverse osmosis membrane.

The quality of the reverse osmosis permeates meets the standards for re-use and thus this water can be recycled in the printing process.

Acknowledgement

We are thankful to the European Commission for its financial support in preparing this paper, through a grant from EU project EKV1-CT-2000-00049.

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