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Comparison of tertiary treatment by nanofiltration and reverse osmosis for water reuse in denim textile industry

Nihel Ben Amar[a,b,*,1], Noura Kechaou[c], John Palmeri[d], André Deratani[e], Ali Sghaier[f]

[a] Laboratoire de Modélisation Mathématique et Numérique dans les Sciences de l'Ingénieur, ENIT, Campus Universitaire, B.P 37, Le Belvédère 1002, Tunis, Tunisie
[b] Institut National des Sciences Appliquées et de Technologie, B.P. 676, 1080 Tunis Cedex, Tunisie
[c] Unité d'Ecologie et Physiologie du Système Digestif, INRA Jouy en Josas, Domaine de Vilvert, 78352 Jouy en Josas cedex, France
[d] Laboratoire de Physique Théorique, IRSAMC UMR5152, CNRS-UPS Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 4, France
[e] Institut Européen des Membranes, cc 47, UMR5635 CNRS-ENSCM, Université Montpellier II, 2 Place Eugène Bataillon, 34095 Montpellier Cedex 5, France
[f] Société Industrielle des Textiles, Avenue Habib Bourguiba, 5070 Ksar Hellal, Tunisie

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ABSTRACT

The wastewaters resulting from different baths of a dyeing factory specialized in denim fabric are collected and treated by an activated sludge plant. This study investigated the coupling of activated sludge treatment with either nanofiltration (NF) or reverse osmosis (RO) to recycle water and reuse it in the process. We first conducted NF experiments with a HL membrane in different configurations: dead end and cross-flow for flat sheets and also in spiral wound form. Results on water permeation and salt rejection show that performances are configuration dependent. Then, for the study of the NF/RO textile wastewater treatment, experiments were conducted with spiral wound membranes in order to be closest to the industrial configuration. After analyzing the removal efficiencies of suspended solids and chemical oxygen demand (COD) of the treatment plant, we conducted NF experiments using an HL2514TF spiral wound membrane preceded by ultrafiltration (UF) treatment. We used as well an RO membrane (AG2514TF) to compare performances in water yield and quality for the same pumping costs. The results show that NF allows higher yield, while respecting the Tunisian standard of water reuse (COD < 90 mg L^{-1}). Above 9 bar, the TDS rejection reaches 60% and the hardness is lower than the factory constraint (100 mg L^{-1} $CaCO_3$), allowing the reuse of the water in the process.

1. Introduction

The decrease in resources in natural waters brought about by drought and population growth is inciting authorities to establish and to encourage the reuse of wastewater. Thus, in several countries (United States, Australia, South Africa, Japan, ...) the reuse of wastewater is undergoing fast expansion with the majority of the projects having an agricultural vocation, being intended for irrigation. In Tunisia, although the reuse of treated wastewater is not really advanced, it is customarily used as part of the hydraulic resources of public utilities: irrigation of golf courses, public gardens and agricultural irrigation.

Industry is not immune to this water shortage. The increase in water costs and the obligation to respect the standards of wastewater disposal in the environment, compel manufacturers to rethink their management of residual waters, like those from the textile industry. Residual water has thus become a water resource, especially for the big water consumers.

Water in the textile industry is used in large quantities in stages such as bleaching, dyeing and printing. Its consumption is estimated to be in the range of 200–400 L of water per kilogram of finished product [1]. the wastewater produced contains organic matter, products derived from fixing agents, detergents, dyes... and salts, and therefore must be treated before being discharged.

Various techniques are used for the treatment of wastewaters. The most common ones are coagulation flocculation (common in the printing industry) and biological treatment using activated sludge. As a consequence of water shortage, the treated textile wastewater, commonly discharged to the sewer in the past, is nowadays being recycled in industrial processes for use when water quality suffices. As it contains nutrients like N, P, Ca, Mg, etc., experiments are also being carried out on the reuse of treated wastewater in agriculture [2]. A beneficial savings in water with no damaging effects in agricultural, or industrial uses, may be achieved with membrane tertiary treatment.

The Tunisian dyeing, gluing and finishing company (SITEX), which specializes in the dying of denim fabric (jeans) using indigo

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* Corresponding author at: Institut National des Sciences Appliquees et de Technologie, B.P. 676, Tunis Cedex, Tunisie 1080, Tunisia. Tel.: +216 71 703 829; fax: +216 71 704 329.
E-mail address: nihel.benamar@insat.rnu.tn (N.B. Amar).
[1] Tel.: +216 71 871 022; Fax: +216 71 871 022.

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Nomenclature

BOD_5	biological oxygen demand (mg L^{-1})
$C_{i,f}$	solute concentration in feed (g L^{-1})
$C_{i,p}$	solute concentration in permeate (g L^{-1})
COD	chemical oxygen demand (mg L^{-1})
MWCO	molecular weight cut off (Da)
q_p, q_f	permeate flow, feed flow (L h^{-1})
R	rejection
SS	suspended solids (mg L^{-1})
TDS	total dissolved salts (mg L^{-1})
Y	yield (%)

and/or sulfur dyes, is equipped with an activated sludge treatment plant to treat its wastewaters and to make them comply with the Tunisian rejection standard. After this treatment, the wastewater contains a small quantity of organic matter (COD varying from 106 to 172 mg L^{-1}) and a large amount of salts [SO_4^{2-} (29.76 mM), Na^+ (102.61 mM), Cl^- (18.36 mM), Ca^{2+} (0.93 mM), Mg^{2+} (0.52 mM)]. The organic matter can be partially removed by UF and the salts and the remaining organic matter either by RO (rejection of all solutes, but expensive) or NF (removal of hardness and more generally divalent ions).

Since 1980, a lot of studies have been carried out on the NF membrane treatment of textile wastewater, and some of them have already dealt with the recycling of this water [3] and the recovery of some salts [4,5] and chemicals [6]. Researches in this area can be divided into two groups: (i) work on industrial treatment units which propose tertiary treatment processes, including NF, and (ii) more specific work on NF carried out in laboratories devoted to studying the effect of operating parameters (dye and salts concentrations, pH, applied pressure, velocity...) on NF performance [7–11].

The coupling of activated sludge treatment with NF for the denim textile wastewater treatment was approached in different studies. In [12] good COD reduction (91%) was shown, and a smaller amount of color removal (75%) can be achieved with an activated sludge reactor. Nanofiltration, conducted with a laboratory scale cross-flow module and NF270 membrane (Dow Filmtec) at 5 bar and 18 °C, permits one to respect the wastewater reuse norms, as defined by the British textile technology group [13] and specified in [12]. Only the permeate conductivity reuse norm was not achieved since the measured conductivity was higher than 1000 μS cm^{-1}. In Ref. [14], authors used the filtrate coming from the NF of wastewater as water in the dyeing process under laboratory conditions and showed that results on dyeing quality, estimated by product properties such as relative dyeing intensity, were conclusive and encouraging for the reuse of the NF treated wastewater in the dyeing process. In these experiments NF was conducted at 15 bar and 35 °C with a (81 cm^2).

As suggested by Gozalvez-Zafrilla et al. [15] in their work on biologically treated cotton thread factory wastewater subjected to NF with or without an UF step, we will also use an UF pretreatment stage (20 kDa upper limit) for NF, as it increases flux and reduces membrane fouling.

Before treating the mill effluent, and considering that a lot of work has already been conducted at the laboratory scale with small flat sheet membranes very different in scale from industrial size installations, we first study the effect of membrane configuration on permeation and rejection. Next, the denim dyeing effluent of the above mentioned mill, already treated by activated sludge on site, will be treated by NF or RO as a tertiary treatment in order to improve the wastewater quality. The NF experiments will be performed with an anisotropic HL thin film membrane (TFM) membrane, which has not yet been used in research for this specific application. Furthermore, for equivalent applied pressures, hence equivalent pumping energies, the performances of the NF treatment will be compared to that of an RO treatment with an AG membrane (TFM). These experiments were performed to compare both types of membranes using commercial spiral wound membranes in order to be closest to the actual industrial situation. The goal is to recycle the treated water and reuse it in the process.

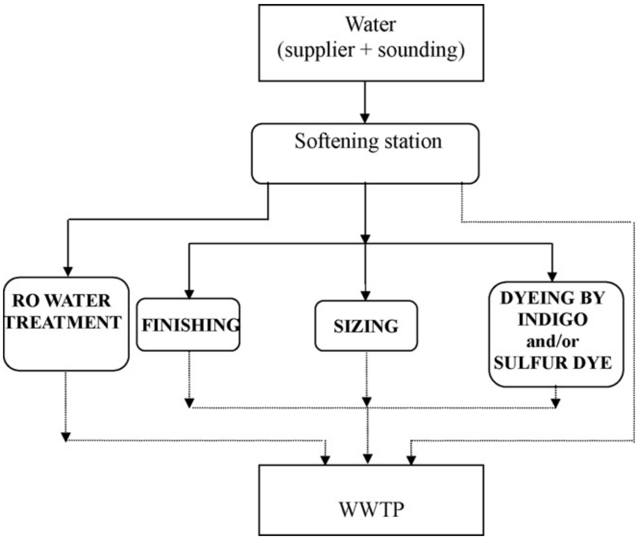

Fig. 1. Descriptive scheme of the mill water network.

2. Experimental

2.1. Mill wastewater

The bulk of the water required for the dyeing process used by SITEX Company comes from the national distribution network with smaller quantities coming from sounding wells. This water is first softened to 100 mg L^{-1} as $CaCO_3$ and then feeds the dyeing, gluing and finishing steps (Fig. 1). This water also feeds the RO treatment unit for the humidification of the workshops and the production of the steam necessary for the process.

Addition of chemical products in the process is specific to each stage. The wastewater contains indigo coming from the overflow of the dyeing and rinsing baths, sodium hydrosulfite, caustic soda, corn starch, ester of fatty acid, carboxy methyl cellulose (CMC), urea, citric acid, etc. and products such as anti-foam agents, wetting and softening agents, etc. It contains as well the retentate of the RO unit of the factory.

The purpose of the SITEX Wastewater Treatment Plant, which uses activated sludge, is to bring wastewaters into compliance with the Tunisian standard of wastewater discharge to public sewers (NT

Table 1
Mean monthly wastewater characteristics during 2006.

Parameters	Influent	Treated effluent by the activated sludge plant
Flow (m^3 day^{-1})	1547–2689	[a]
pH	10.9–12	7.6–8.1
TDS (mg L^{-1})	16,536[b]	6311–8412
SS (mg L^{-1}))	446–868	13.6–29.5
COD (mg L^{-1})	2503–3888	106–175
BOD (mg L^{-1})	984–1457	13.8–40
Color (uc)	3376–6578	127–229

[a] All the influent is treated.

[b] One sample analysis.

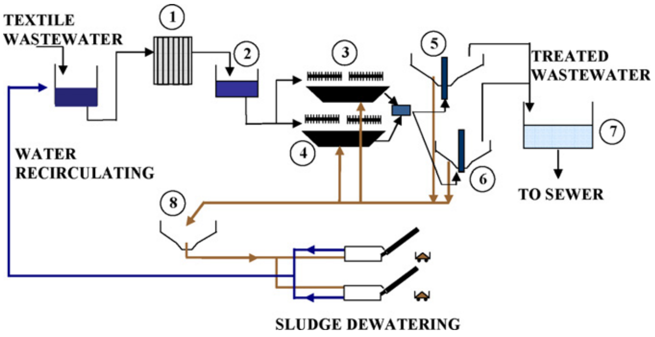

Fig. 2. The conventional biological treatment, using activated sludge, installed in the mill.

106.002). Table 1 shows the spread in the mean monthly wastewater characteristics during 2006, both at the entry of the WWTP and after treatment. Note that the influent varies both in flow and quality due to changes in production. The treatment of the wastewater (Fig. 2) begins with sulfuric and phosphoric acid neutralization and homogenization in (2) to decrease alkalinity to values appropriate for biological treatment (pH 7–9). The aerobic biological treatment is carried out in two aerated basins (3 and 4) and a polymeric coagulant agent is added if necessary at the exit of the aeration basins to help the bleaching. Then the wastewater is clarified in two parallel clarifiers (5 and 6) and stored in a tank (7) before being discharged to the municipal sewers.

2.2. Membranes

In the first part of this work, experiments were performed with the HL membrane, in cross-flow and dead end filtration (cut from the same spiral wound residential thin film membrane HL2114) and in a spiral wound shape (HL2514). Tests were made to quantify membrane performance (pure water permeability, salt rejection) in each configuration and to compare them to manufacturer performances (Table 2). In cross-flow filtration with spiral wound modules, the feed spacer used was a commercial mesh-type 30D spacer consisting of two layers of cylindrical filaments of 0.71 mm thickness and a diamond-type geometry with an angle equal to 90°. In tangential filtration tests with the Sepa CF cell, the spacer was 47D (47 mil = 1.19 mm).

In the second part of this work, the mill effluent filtration experiments were carried out with spiral wound membranes (NF and RO) equipped with the same spacer (30D) to assure the same hydrodynamics.

Table 2 lists the membrane characteristics taken from the manufacturer literature. It can be seen that salt rejection is almost the same for flat sheet and spiral wound HL membranes (95%, 98%), which seems to indicate that rejection is independent of membrane configuration. According to the manufacturer, the flat sheet membrane was characterized using the Sepa CF cell.

Table 2
Supplier membranes characteristics (GE-Osmonics).

	NF membrane: HL (flat sheet)
MWCO	150–300 Da
Salt rejection	95% ($MgSO_4$)
	NF membrane: HL2514TF
Membrane area	0.6 m^2
MWCO	150–300 Da
Salt rejection	98% (2000 mg L^{-1} $MgSO_4$ at 6.9 bar, 25 °C, pH 7.5)
Operating pH	3–9
NTU	<1
	RO membrane: AG2514TF
Membrane area	0.6 m^2
Salt rejection	99.4% (2000 mg L^{-1} NaCl at 15.5 bar, 25 °C, pH 7.5)
Operating pH	4–11
NTU	<1

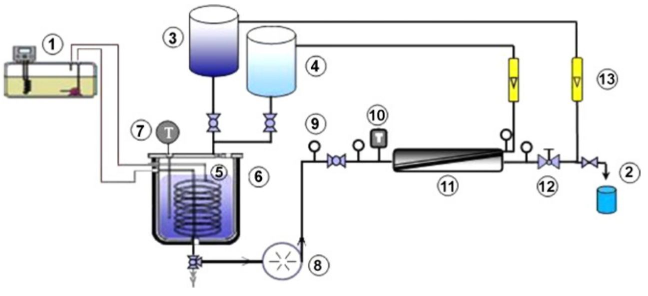

Fig. 3. Descriptive scheme of the NF/RO pilot.

NF and RO experiments were preceded by a 20 kDa hollow fiber UF step to provide a supplementary reduction in SS in order to prevent membranes fouling.

2.3. Solutes

Neutral solutes like sucrose (342 g mol^{-1}), maltose (342 g mol^{-1}), and glucose (180 g mol^{-1}) were used to determine the Molecular Weight Cut Off (MWCO) of the membranes. Experiments were conducted at 1 g L^{-1} and 25 °C. For salt rejection tests, we used $MgSO_4$ (2000 mg L^{-1} at 25 °C) to make a comparison with manufacturer data. The water used to prepare solutions was purified water delivered by a commercial system (Arium 61315, 73 μS cm^{-1} at 25 °C).

2.4. Experimental configurations

To test the performance dependency on device configuration, we used: (i) a dead end stirred cell (rotating speed measured by tackometer C.A. 25 of Chauvin Arnoux = 528 tr mn^{-1}), (ii) a cross-flow cell Sepa CF (already described in reference [16]), and a pilot using spiral wound commercial membranes. The spiral wound membranes used are standard modules equipped by default with the 30D spacer. In cross-flow tests with flat sheet membranes, we used the 47D spacer. The effective membrane area in each configuration is reported in Table 3.

The tangential cross-flow pilot used for NF and RO experiments (Fig. 3) is equipped with a feed tank (6), a permeate tank (3) and a retentate tank (4). The solution is pumped from the feed tank by a volumetric pump (8) which can raise the pressure up to 14 bar. The feed solution is maintained at a fixed temperature (25 or 30 °C) by a circulating thermal bath (1) and an immersed coil (5). The temperature is measured both by a bimetallic thermometer TBI (Bourdon Haenni) (7) immersed in the feed solution tank and by a temperature sensor (10) at the inlet of the spiral wound membrane (11). The pressure of the feed solution and the retentate, modified by the valve (12), are given by pressure gauges (9). The permeate and retentate flows are measured by rotameters (13).

The applied pressure varied from 5 to 13 bar. The feed flow was fixed at 400 L h^{-1} corresponding to a cross-flow rate of 1.4 m s^{-1}. As the temperature of the wastewater exiting the WWTP is around 30 °C, experiments on real effluents were performed at that temperature. The experiments with pure water and salt rejection tests were conducted at 25 °C to compare results to manufacturer data.

2.5. Analysis

Parameters used to characterize the wastewater are: COD, BOD_5, pH, color, SS and TDS. The plant influent and wastewater samples

Table 3
HL membrane pure water permeability in different configurations: dead end and cross-flow with a flat sheet membrane and spiral wound membrane.

	Spiral wound (Osmonics literature)	Cross-flow with Sepa CF	Spiral wound	Dead end
Membrane area	0.6 m^2	133 cm^2	0.6 m^2	8 cm^2
Pure water permeability (L/hm^2 bar)	[a]	12	8.2	6.9
Salt rejection	98% (2000 mg L^{-1} $MgSO_4$ at 6.9 bar, 25 °C, pH 7.5)	96% (2000 mg L^{-1} $MgSO_4$ at 7 bar, 25 °C)	86% (2000 mg L^{-1} $MgSO_4$ at 6.5 bar, 25 °C)	90% (2000 mg L^{-1} $MgSO_4$ at 8 bar, 25 °C)

Also reported the Osmonics literature and experimental rejection performances.
[a] Not mentioned.

were analyzed on site for TDS (using conductimeter HYDROCURE HI 8819), COD and color (using Direct Reading Spectrophotometer HACH/DR 2000).

The measurements of the neutral solute concentrations, used to determine the MWCO, were made using an Interferometer Refractometer (Optilab DSP, Wyatt Technology). The total salt concentrations were characterized by a conductivity/TDS measurement using a conductimeter (Jenway). Elements Ca, Na, Mg, K were analyzed with an inductively coupled plasma emission spectrometer. Anion analyses were performed using ionic chromatography.

$$R_i = 1 - \frac{C_{i,\mathrm{p}}}{C_{i,\mathrm{f}}}$$

To characterize membranes performances, rejection is calculated using the experimental data as follows:where $C_{i,\mathrm{p}}$ and $C_{i,\mathrm{f}}$ are, respectively, the ith solute concentrations (ions, neutral solutes) in the permeate and in the feed. The concentration is replaced by Total Dissolved Salts (TDS) to calculate the total salt rejection and COD to determine the COD reduction. The yield is the percentage of permeate produced,

$$Y = \frac{q_\mathrm{p}}{q_\mathrm{f}},$$

where q_p and q_f are, respectively, the permeate and the feed flow.

3. Results and discussion

3.1. Effect of device configuration on nanofiltration performances

First of all, the membranes were treated to eliminate chemical preservation products and compaction effects. They were placed in the cell or housing, and pure water permeation was performed for several hours at a pressure higher than the maximum experimental pressure to be used in experiments. Pure water permeability tests were performed until the stabilization of the permeability value, reached after 50 h for the spiral wound membranes and around 6 h for flat sheet membranes.

If we consider the supplier data, we noticed that with the HL membrane $MgSO_4$ rejection is different when considering the flat sheet membrane (95%, Table 2) or the spiral wound membrane (98%, Table 2). In the performance-literature, the supplier does not mention the feed spacers adopted in characterizing the spiral wound and flat sheet membranes. Assuming that the salt concentration (not mentioned in the flat sheet literature) is the same and that the feed spacer is also identical, the difference is relatively small and may be attributed both to a non-uniform membrane top layer and to experimental errors.

We summarize in Table 3 the $MgSO_4$ rejection obtained with the membrane HL in different configurations. We recall that experiments conducted in cross-flow filtration with flat sheet and spiral wound membranes were carried out with, respectively, the commercial spacers 47D and 30D. The effect of pressure on rejection was studied, and we found that from 5 bar the rejections remain at the plateau values. Hence, even if the operating pressures reported in Table 3 are slightly different in the two experimental configurations, it is still possible to compare results (see Table 3). Table 3 shows that the experiments conducted in the cross-flow set-up with the Sepa CF gave $MgSO_4$ rejection (96%) that is close to the literature value (98%). When considering dead end filtration, the rejection is 90%, whereas for the spiral wound membrane, the rejection is lower: 86%. The experiments conducted in cross-flow and in dead end with membranes from the same flat sheet give different rejections (respectively 96%, 90%). This variation (6.6%) may be due to differences in both the flow configuration and the structure of the thin layer membrane coupons (possible even if cut from the same sheet).

If we can conclude that $MgSO_4$ rejection is independent of device configuration to within 2–12%, we cannot say the same for the pure water membrane permeability. Table 3 shows clearly that it is dependent on the flow and the membrane type. Measured pure water permeability is higher in the case of cross-flow with a flat sheet (12 L/hm^2 bar obtained with a 47D spacer) and lower for dead end filtration (6.9 L/hm^2 bar). The difference (42.5%) is large and cannot be explained by an experimental error estimated to be 9%. We repeated the experiment with the flat sheet membrane in cross-flow filtration with a 30D spacer. The pure water permeability obtained was 8.5 L/hm^2 bar. We see from this result the importance of the feed spacer dimension on pure water permeability and permeation performance.

Although the present work is not specifically dedicated to a study of the effect of the spacer geometric characteristics (attack angle, type and dimension) on the membrane filtration, it is important to draw attention to the necessity of clearly specifying and of integrating these parameters into the operating conditions of the study in the same way as the pressure, the temperature, and the concentration, for a better transposition of the results to the industrial scale. Detailed studies of the influence of commercial spacer geometry on NF/RO processes provide numerical and experimental results on the effect of such spacers in mass transfer [17,18].

As the aim of the present work is to be as close as possible to real industrial conditions for industrial water recycling, we choose to treat the mill effluent with a spiral wound membrane.

3.2. Spiral wound membranes characterization

Pure water permeability tests achieved at 25 °C with the spiral wound membranes (HL and AG) reveal, as expected, a higher permeability for the HL membrane (8.2 L/hm^2 bar, regression coefficient $R^2 = 0.9993$) compared with the AG membrane (2.7 L/hm^2 bar, $R^2 = 0.9998$).

The HL membrane is presented by the manufacturer as one that can be used for water softening and color removing. To evaluate the MWCO, experiments were done with three neutral solutes: sucrose, maltose and glucose at 1 g L^{-1} and 25 °C. Fig. 4 shows a nearly constant solute rejection (90%) observed for sucrose and maltose, which indicates a MWCO equal to 342 Da, in concordance with manufacturer data (Table 2). We notice a decrease in glucose rejection (Fig. 4) whereas the flux is nearly linear with pressure (within 5% error) and solute independent (Fig. 5). A modeling study using the

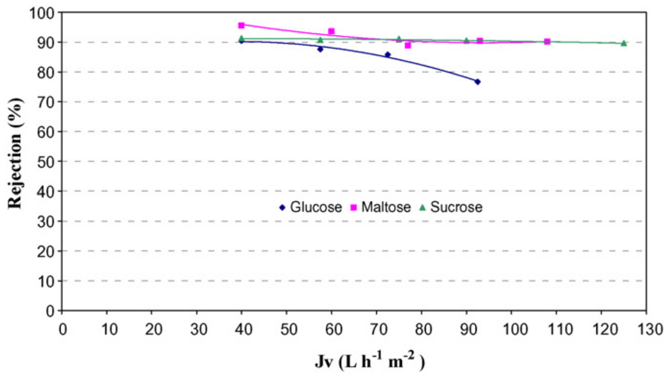

Fig. 4. Rejection vs flux for neutral solutes at 1 g L^{-1} and 25 °C with membrane HL2514.

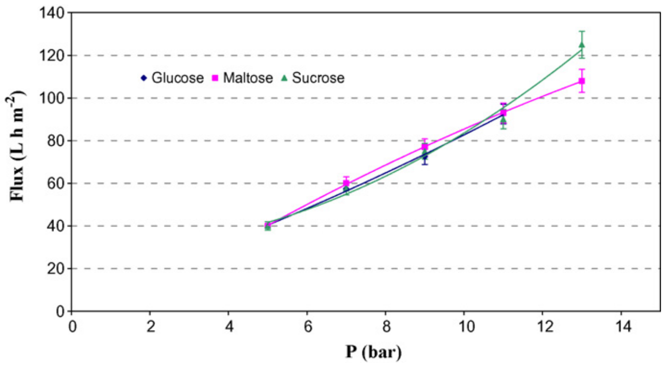

Fig. 5. Flux vs transmembrane pressure for neutral solutes at 1 g L^{-1} and 25 °C with membrane HL2514.

NanoFlux software [20] shows that the decrease in glucose rejection can be accounted for by the hindered transport theory and the presence of a concentration polarization layer of thickness 10–15 μm. This study reveals that at the same time the concentration polarization layer has only a weak influence on the rejection of the larger species, such as sucrose (at least over the volume flux density range studied experimentally).

Salt rejection experiments were performed at 25 °C with Na_2SO_4 at 1000 ppm for the HL membrane, as it is the predominant salt in the wastewater (7 mM). For the experiment with the AG membrane, NaCl was used at 1000 ppm. Fig. 6 shows that the results with this membrane are close to supplier data (Table 2). For the HL membrane, we measure a rejection of 86% for Na_2SO_4, which is lower than the supplier data for $MgSO_4$ at 2000 ppm due to the presence in the dissolved salt of both monovalent and divalent ions (Na^+, $SO_4{}^{2-}$).

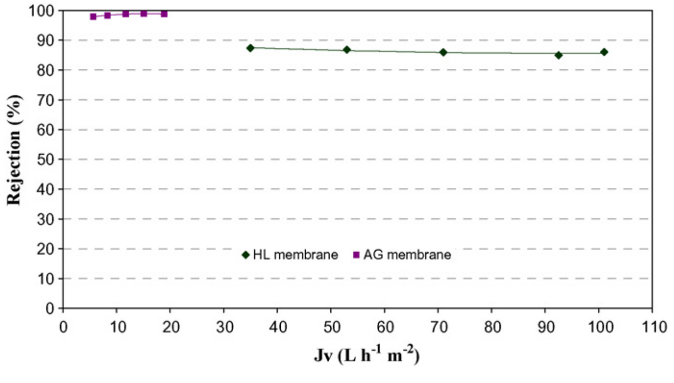

Fig. 6. Salts rejection vs flux at 25 °C with spiral wound membranes (AG: 1000 ppm NaCl and HL: 1000 ppm Na_2SO_4).

3.3. *Wastewater characterization*

Our study of the SITEX dyeing process showed that the main part of the indigo dye was recovered. Only a part of it, resulting from bath overflow and from rinsing, is found in the wastewater. The recovery of the dyeing agent is thus not of interest. Besides, dyeing with indigo does not require the addition of salts, so it will not be a question of salt recovery either. We will, therefore, focus solely on the recovery of water for reuse in the dyeing process.

The wastewater with characteristics presented in Table 1 is treated on site with the biological treatment plant. Most of the time, the values of COD exceeded the standard reused water norm, NT 106.03 (90 mg L^{-1}). The treated wastewater has high salinity (high conductivity) which is not eliminated by activated sludge treatment and is discharged to the municipal sewer (TDS = 6–8.5 g L^{-1}). Regarding the color, Table 1 shows the high reduction obtained by coupling the biological treatment with a polymer coagulant (92%). The SS and BOD parameters are consistent with the standard water reuse norm (30 mg L^{-1}).

A year-long analysis (2006) of the SITEX wastewater characteristics shows good WWTP performance. Indeed, the discharge characteristics are close to the standard for wastewater reuse, a favorable situation for attempting to develop a tertiary membrane treatment.

A preliminary analysis of the wastewater before using it in membrane experiments revealed a high level of $SO_4{}^{2-}$ (29.76 mM), Na^+ (102.61 mM), Cl^- (18.36 mM) and lower levels of Ca^{2+} (0.93 mM) and Mg^{2+} (0.52 mM).

3.4. *Membrane treatments*

3.4.1. *UF treatment*

The work began with the UF of the textile wastewater as a polishing stage before the NF and RO steps. As summarized in Table 4, the wastewater pre-treatment undertaken with a 20 kDa dead end membrane at 2 bar, allows 8% COD reduction and over 90% SS removal. This COD performance is quite different from that found in [19] obtained with a similar MWCO membrane, but in a flat sheet configuration (between 53 and 59% for COD reduction). This result suggests that the remaining organic matter is of a low molecular weight and is not rejected by UF. The SS reduction is almost total: the indigo presence is no longer noticeable, as the blue color is eliminated. The attained turbidity is in agreement with the requirements of the NF/RO membrane manufacturer (<1 NTU). We consider therefore that the UF stage is sufficient even if it has not been established to be the best compromise between cost and performance.

Thanks to the biological treatment, the BOD is reduced to a value required by the standard of wastewater reuse (30 mg L^{-1}). The BOD

Table 4
Tunisian standard of treated wastewater reuse for irrigation (NT 106.03), textile wastewater and UF filtered wastewater characteristics.

Parameters	NT 106.03 standard	Wastewater	UF wastewater	UF removal %
Color		Blue	Yellow	
pH	6.5–8.5	7.7–8.2		
Conductivity (μS cm^{-1})	7000	7600	7293	4
SS (mg L^{-1}))	30	41	3.6	91
COD (mg L^{-1})	90	184	169	8
BOD (mg L^{-1})	30	32	[a]	
Turbidity (NTU)		9.2	0.2	98

[a] Not measured.

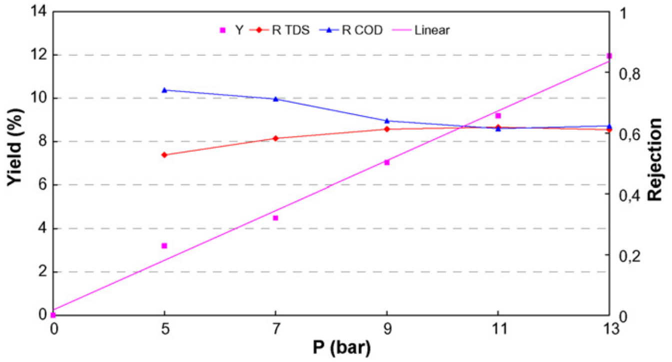

Fig. 7. Rejection and yield vs applied pressure at 30 °C; NF membrane: HL2514TF.

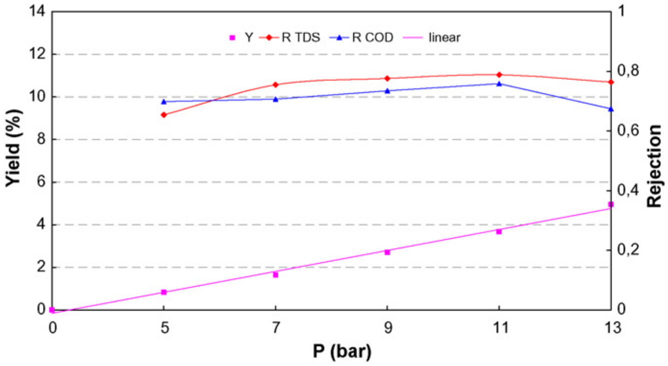

Fig. 8. Rejection and yield vs applied pressure at 30 °C; RO membrane: AG2514TF.

of the UF wastewater was not measured. The TDS remains constant in concordance with the fact that the UF step does not eliminate salts.

3.4.2. NF/RO treatment

The NF step was conducted on the pilot plant (Fig. 3) filled with 50 L of the WWTP wastewater having the characteristics summarized in Table 4.

Fig. 7 shows the COD and the TDS rejections and the yield for the NF treatment with the HL membrane at different applied pressures. We observe an increase in TDS rejection with the applied pressure until a plateau at 61% is reached at 9 bar. As for the COD reduction, it reaches a maximal value at a low pressure (74% at 5 bar) and decreases with increasing applied pressure till a constant value (62%). The COD rejection seems to be correlated with the TDS rejection: when the TDS rejection reaches a constant value, the diminution of COD rejection stops. The COD decrease was already observed in [15] with the NF200 and the NF270 membranes, but not with the NF90 membrane which is thought to be tighter. The COD rejection plateau was observed at 94% and 9 bar and COD rejection dropped by 56% at 19 bar for the NF200 and 86% for the NF270. With the NF90 membrane, the COD rejection is almost constant 98%. Based on our results, the HL membrane behaves like the NF270 and the NF200 ones in terms of COD rejection decrease. Although it would be interesting to study in greater detail this membrane-dependent COD rejection decrease and its correlation with TDS rejection, this is beyond the scope of the present article (the difficulty comes from obtaining uniform well-defined characteristics of the real textile effluent).

Nevertheless, the measured COD after NF treatment is in compliance with the Tunisian water reuse standard (<90 mg L^{-1}). As for the yield, it increases linearly with applied pressure. The COD reduction is around 64% between 9 and 13 bar, the TDS rejection increases weakly, and there is a considerable yield increase (56%) in going from 7 to 9 bar. In going from 11 to 13 bar, the TDS rejection and COD reduction increase by about 1% accompanied by an almost constant yield increase of 30%. We conclude that 11 bar is a suitable applied working pressure, allowing a yield equal to 9%. This yield value is very low due to the single pass through a short module, but can be enhanced by considering multi-stage configurations (with the added complication of changing feed concentrations). We notice that the hardness is reduced from 200 to 70 mg L^{-1} as $CaCO_3$, producing water in compliance with the Sitex water process constraint (hardness between 80 and 110 mg L^{-1} as $CaCO_3$) and hardness close to the British Textile Technology Group reuse criteria for textile wastewaters (60 mg L^{-1} as $CaCO_3$, [12]). Although our achieved performances are lower than those of reference [15] where a salt rejection >85% and a COD reduction >95% were found with the NF90 flat sheet membrane, we must bear in mind that the membrane and the configuration are not the same.

According to DyStar Dyes Supplier, the textile mill water process must meet the following criteria: hardness <90 mg L^{-1} as $CaCO_3$, SS <1 mg L^{-1}, and organic load <20 mg L^{-1}. Except for the organic load, we note that the NF treatment permits one to respect these constraints.

We carried out a lower pressure RO treatment with the AG2514 membrane (Table 2). When comparing the NF treatment with the RO one (Fig. 8), we observe with the RO membrane a higher TDS rejection (increase of 29%) and a higher COD reduction (increase of 1–23%) along with a strong reduction of 58–74% in yield. At 11 bar, although the COD level (60 mg L^{-1}) complies with the Tunisian water reuse standard, the yield for RO is only 40% of the yield for NF. If the pressure is increased to 13 bar, corresponding to a permeate flux of 31 L/hm^2, we observe a decrease in COD reduction, similar to the one found earlier for the NF treatment (Fig. 7).

The above results show that if the aim is to reuse treated wastewater in compliance with both factory requirements on water quality and Tunisian water reuse standards, NF is a suitable method of treatment and the best operating pressure is 11 bar.

4. Conclusion

This work deals with the membrane treatment of wastewater from a Tunisian textile company. The wastewater has already been treated at the factory by a biological treatment plant with activated sludge to make it conform to Tunisian rejection standards. We have studied the possibility of reusing the wastewater after a membrane treatment step. For this purpose, we treated the wastewater by NF and RO at the same pressures.

The experiments conducted with the HL membrane in different configurations (dead end and cross-flow filtration) show that water permeation and salt rejection depend on the test configuration. The tests with the Sepa CF cell allow one to achieve higher performances in terms of water permeation and salt rejection. In spite of this result, a spiral wound membrane configuration was selected for treating the wastewater in order to be closest to the actual industrial set-up.

The NF experiments conducted with the HL 2514 membrane showed that 11 bar is a suitable operating pressure. It allows a yield of 9% and a COD reduction and TDS rejection of 62%, values in conformity with the Tunisian water reuse standards. For low pressure RO experiments with the AG 2514 membrane, results showed that the yields obtained at the same pressure of 11 bar are much lower than those obtained with NF (4% vs 9%), although there is a 30% increase in rejection performance. As the NF membrane treatment achieves a suitable hardness value (lower than the factory requirement) and permits an increased water production for nearly equivalent water quality, it seems to be the appropriate tertiary treatment. In a subsequent study, we will focus on the modeling and scaling-up of such a NF plant using the NanoFlux software.

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References

[1] M. Marcucci, G. Nosenzo, G. Capanelli, I. Ciabatti, D. Corrieri, G. Ciardelli, Treatement and reuse of textile wastewaters based on new ultrafiltration and other membrane technologies, Desalination 138 (2001) 75–82.

[2] M.D. Saravanamoorthy, B.D. Ranjitha Kumari, Effect of textile wastewater on morphophysiology and yield on two varieties of peanut (Arachis hypogaea L.), Journal of Algriculture 3 (2) (2007) 335–343.

[3] Jian-Jun Qin, Maung Htun Oo, Kiran A. Kekre, Nanofiltration for recovering wastewater from a specific dyeing facility, Separation and Purification Technology 56 (2007) 199–203.

[4] A.E. Simpton, C.A. Buckley, Recovery of caustic soda from caustic wastewaters, CHEMSA 14 (3) (1988) 80, 76-78.

[5] Carine Allègre, Philippe Moulin, Michel Maisseu, Françoise Charbit, Savings and reuse of salts and water present in dye house effluents, Desalination 162 (2004) 13–22.

[6] S.N. Gaeta, U. Fedele, Recovery of water and auxiliary chemicals from wastewaters of textile dye houses, Desalination 83 (1–3) (1991) 183–194.

[7] S. Chakraborty, M.K. Purkait, S. DasGupta, S. De, J.K. Basu, Nanofiltration of textile plant effluent for color removal and reduction in COD, Separation and Purification Technology 31 (2003) 141–151.

[8] Cristiane N. Lopes, J. Carlos, C. Petrus, H.G. Riella, Colour and COD retention by nanofiltration membranes, Desalination 172 (1) (2005) 77–83.

[9] B. Van der Bruggen, I. De Vreese, C. Vandecasteele, Water reclamation in the textile industry: nanofiltration of dye baths for wool dyeing, Ind. Eng. Chem. Res. 40 (2001) 3973–3978.

[10] 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 pre-treatment, Desalination 178 (2005) 343–349.

[11] I. Koyuncu, E. Kural, D. Topacik, Pilot scale nanofiltration membrane separation for waste management in textile industry, Water Science and Technology 43 (10) (2001) 233–240.

[12] E. Sahinkaya, N. Uzal, U. Yetis, F. Dilek, Biological treatment and nanofiltration of denim textile wastewater for reuse, Journal of Hazardous Materials 153 (2008) 1142–1148.

[13] BTTG, Report 5: Waste Minimization and Best Practice, British Textile Technology Group. http://www.e4s.org.uk/textilesonline/content/6library/fr_library.htm (1999).

[14] R. Zylla, J. Sojka-Ledakowicz, E. Stelmach, S. Ledakowicz, Coupling of membrane filtration with biological methods for textile wastewater treatment, Desalination 198 (2006) 316–325.

[15] J.M. Gozalvez-Zafrilla, D. Sanz-Escribano, J. Lora-Garcia, M.C. Leon Hidalgo, Nanofiltration of secondary effluent for wastewater reuse in the textile industry, Desalination 222 (2008) 272–279.

[16] N. Ben Amar, H. Saidani, J. Palmeri, A. Deratani, Effect of temperature on the transport of water and neutral solutes accross nanofiltration membranes, Langmuir 23 (2007) 2937–2952.

[17] M. Shakaib, S.M.F. Hasani, M. Mahmood, CFD modeling for flow and mass transfer in spacer-obstructed membrane feed channels, Journal of Membrane Science 326 (2009) 270–284.

[18] C.P. Koutsou, S.G. Yiantsios, A.J. Karabelas, A numerical and experimental study of mass transfer in spacer-filled channels: effects of spacer geometrical characteristics and Schmidt number, Journal of Membrane Science 326 (2009) 234–251.

[19] J.M. Arnal, M.C. Leon, J. Lora, J.M. Gozalvez, A. Santafé, D. Sanz, J. Tena, Ultrafiltration as a pre-treatment of other membrane technologies in the reuse of textile wastewaters, Desalination 221 (2008) 405–412.

[20] J. Palmeri, J. Sandeaux, R. Sandeaux, X. Lefebvre, P. David, C. Guizard, P. Amblard, J.F. Diaz, B. Lamaze, Modeling of multi-electrolyte transport in charged ceramic and organic nanofilters using the computer simulation program nanoflux, Desalination 147 (2002) 231–236.

Glossary

NF: nanofiltration
RO: reverse osmosis
TFM: thin-film membrane
UF: ultrafiltration
WWTP: wastewater treatment plant