

Ultrafiltration as a pre-treatment of other membrane technologies in the reuse of textile wastewaters

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Abstract

Water consumption in textile processes is very high and moreover a large amount of polluted effluents is generated. Many textile industries perform only a biological treatment of these effluents. In countries with water scarcity, the reuse of the secondary effluents represents an interesting solution.

In this work, ultrafiltration (UF) has been studied as a pre-treatment of nanofiltration (NF) and reverse osmosis (RO) in the reuse of the secondary effluent of textile wastewaters from different processes of textile industry.

In the first experimental stage, experiments in a flat module were carried out with four UF membranes in order to select the most suitable one. The secondary effluent after a 50 micron cartridge was treated and the COD was analyzed. According to the highest COD removal, the membrane selected was the IRIS 3028 from Rhodia–Orelis with a cut-off of 10 kDa. In the second stage, experiments were performed with the membrane selected in a spiral-wound module. The aim of these experiments was to characterize the membrane performance and to optimize the cleaning procedure.

The results showed that the COD removal obtained with this membrane was not enough to directly reuse the permeate in the industry. However, the permeate quality obtained guaranteed optimal conditions for its use as a NF feed. The combined UF/NF process was more efficient than a process exclusively based on NF as the NF fouling was reduced considerably and the total water recovery was higher.

Keywords: Ultrafiltration; Wastewater; Textile; Reuse; COD removal

1. Introduction

Textile industry consumes much water and produce large amount of polluted effluents [1–4]. In this work ultrafiltration (UF) has been studied

as an alternative to treat water coming from the secondary effluent of a textile industry, either to direct reuse or as a pre-treatment of a nanofiltration stage [5–7].

The textile factory generates approximately a volume of 1.920 m³ day⁻¹ of wastewater coming mainly from processes of dyeing with indigo.

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Textile wastewater is stored in a regulation tank where its pH is modified by carbon dioxide previous to its treatment in a biological process. The aim of the UF process is to treat this whole amount with a 90% of recovery. As the concentrate stream of the process is recycled back to the bioreactor, an increase of the sludge produced is expected.

Table 1 shows the main characteristics of the effluents generated by the factory. As it can be seen, wastewater previous to acidification is very alkaline. Even after the biological treatment, the coloration of this water is still high. The temperature after the biological process is relatively high, but this improves the membrane flux. The COD values can be considered moderated, however the values of conductivity are very high.

Ultrafiltration membranes applied to this type of water present a fouling problem which can limit their applications; since fouling membrane produces a decline in flux with operating time. Membrane fouling is due to the deposition and accumulation of feed components (suspended particles, impermeable dissolved solutes, or even normally permeable solutes) on the membrane surface or within the pores of the membrane [8–10].

In the second section of this work, the secondary effluent treated, the membrane used and the methodology are described. Next, the results obtained in the experiments for membrane selection and those performed in the same factory

are shown. Finally, the main conclusions obtained with this work are indicated.

2. Materials and methods

2.1. Characterization of secondary effluent

In order to know the physico-chemical characteristics of the effluent to be treated, the secondary wastewater was monitored through daily sampling and analysis. The following parameters were measured: conductivity, pH and COD of the supernatant.

The pH of the effluent always remained between 7 and 8 in more than 95% of the measures. The conductivity oscillated between 6000 and 7500 BS cm⁻¹ depending on the factory processes. The COD values were usually in the range of 80 to 180 mgO₂ L⁻¹.

The detailed analysis of ions reported that the major ions in the wastewater were sodium (1700 mg L⁻¹), chloride (1200 mg L⁻¹), sulphate (1780 mg L⁻¹) and bicarbonate (560 mg L⁻¹).

The highest values of COD reached have been chosen in order to design the plant with a conservative criterion.

2.2. Membranes

Four flat membranes with different molecular weight cut-offs (MWCO) were studied to select the best one (see Table 2).

A spiral membrane of 10 kDa PERSEP from Rhodia–Orelis was used in the experiments with spiral-wound module. This membrane was made of PES.

2.3. Pilot plant

A small pilot plant (Fig. 1) equipped with a flat module able to operate with four sheets of 30 cm² was used in the preliminary experiments for membrane selection.

The plant has a heat exchange system in order to maintain the temperature constant at 35°C.

Table 1
Main characteristics of the textile effluents

Parameter	Wastewater	Effluent after biological treatment
pH	12–14	7.5–8.5
Colour	Blue	Yellow
COD (mgO ₂ L ⁻¹)	1500–2000	100–150
Conductivity (BS cm ⁻¹)	6000–7000	6000–7000
Temperature (°C)	35–40	30–35

Table 2
Characteristics of membranes

Membrane	Materials	MWCO (g mol ⁻¹)	Manufacturer
20 IRIS 3026	Sulfonated polysulfone (PSS)	20,000	Rhône-Poulenc
100 IRIS 3026	Sulfonated polysulfone (PSS)	100,000	Rhône-Poulenc
10 IRIS 3028	Polyethersulfone (PES)	10,000	Rhodia-Orelis
50 IRIS 3042	Acrylonitrile copolymers (AC)	50,000	Rhodia-Orelis

The feed is pre-filtered using a cartridge filter of 50 microns. It uses a volumetric pump of variable speed.

Another plant (Fig. 2) was used in order to perform the experiences with the spiral-wound module of the membrane 10 kDa PERSEP. The plant was placed in the factory next to the output of the secondary effluent. This plant has two circuits that allow to perform UF experiments and to treat the UF permeate with NF if desired. Moreover, it is equipped with a 50 micron filter and with a volumetric pump of variable speed.

2.4. Experimental methods

In the preliminary experiments, membranes were characterized by measuring the permeate

flux for pure water. Conductivity rejection was also measured in experiments with tap water.

All membranes were tested at pressures between 1.5 and 4.5 bar and at temperature of 35°C. The feed flow was of 340 L h⁻¹ what corresponded to a cross-flow velocity of 1.9 m s⁻¹ approximately.

During the experiments, volumetric flux and conductivity were measured every 30 min. The experiments were continued until stationary conditions were reached (approximately between 2.5 and 4 h). At stationary conditions, the COD was also measured using Merck photometric tests.

Long duration experiments were performed with a 4-inch spiral-wound module (PERSEP from Rhodia-Orelis) with a MWCO of 10 kDa. For all experiments, the feed was previously

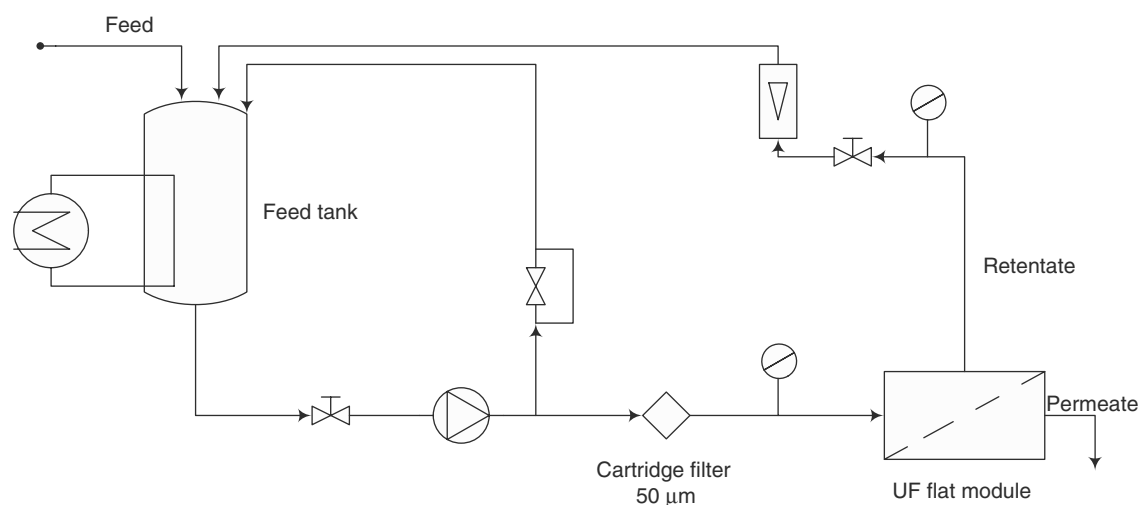


Fig. 1. Scheme of the UF pilot plant.

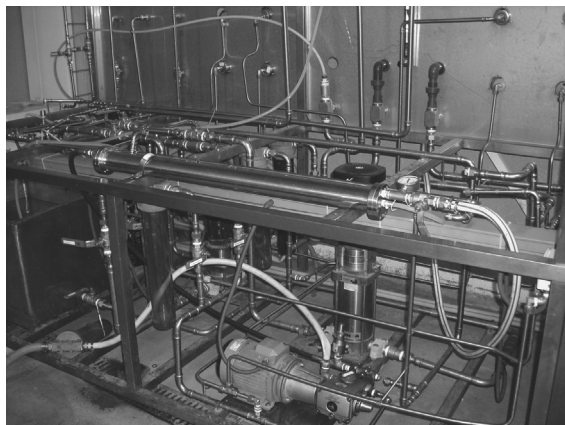


Fig. 2. Scheme of the UF/NF pilot plant.

pre-filtered using a 50-micron filter and stored in a feed tank of 1 m³. The operating pressure was established at 3.75 bar.

In order to study the efficiency of different cleaning procedures, the following types of experiments were performed with this module:

- Characterization
- Experiments at constant feed concentration
- One-step concentration experiments
- Multi-step concentration experiments

The module was characterized using tap water and solutions of polyethylene glycol (PEG) of 10 g L⁻¹ [11–13]. PEGs were of MW of 30,000 Da and were supplied by Merck. PEG rejection was obtained by means of COD analyses with test tubes supplied by Merck. The feed solution was recirculated to the tank during 24 h.

The experiments at constant feed concentration used prefiltered secondary effluent. The plant was operated in the batch recirculation mode, that is, both permeate and retentate streams were completely recirculated to the feed tank. The duration of every experiment was of 8 h approximately.

The one-step concentration experiments were performed by gradually retiring a portion of the permeate stream and had also a duration time of 8 h.

The multi-step concentration experiments were carried out by retiring the permeate stream. However, different to the one-stage experiments the retentate was stored in the feed tank and this tank was filled with additional feed up to 1 m³ for the next experiment.

Moreover, different cleaning procedures were studied in all cases (constant concentration and one-step and multi-step concentration).

3. Results

3.1. Membrane selection experiments

The experiments of membrane selection showed that membranes with a MWCO under 20 kDa were able to achieve COD removal efficiency between 53 and 59% when working at 1.5 bar and 4.5 bar. For all membranes, the observed conductivity reduction was almost zero.

3.2. Pilot plant experiments

3.2.1. Characterization of the UF module

A 4-inch spiral-wound module of the membrane selected (IRIS 3028 10 kDa) was installed on a pilot plant located at the factory. The characterisation experiments with tap water showed that the membrane had an initial permeability at 30°C of 199.7 L m⁻² h⁻¹ bar⁻¹. PEG-30000 rejection was 99.2%, therefore, these results are in agreement with manufacturer's specifications.

3.2.2. Experiments at constant feed concentration

Fig. 3 shows the obtained flux and the flux normalized to 30°C for the following experiments. Table 3 describes the different cleaning procedures employed.

In the first experiments, the flux decreased continuously. Cleaning procedures with sodium hypochlorite at 0.5% and at a cleaning time of 5 min were able to retrieve only a portion of the

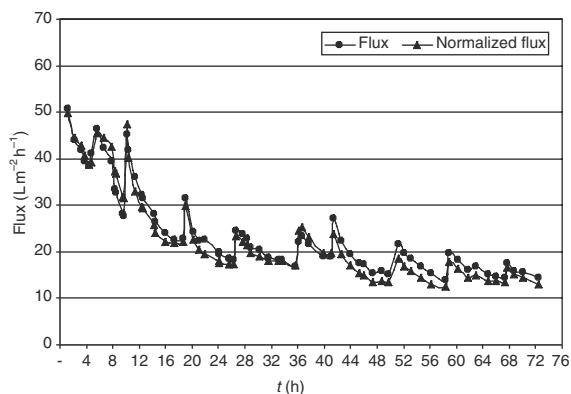


Fig. 3. Flux for experiments at constant feed concentration.

initial flux of every experiment. Tests 5–7 used increasing cleaning times that were able to reestablish the flux decline of the membrane. However, in the experiments with NaOH solutions of 1%, a smaller portion of the flux could be retrieved.

As it can be observed in Table 4, the COD rejection was similar in all experiments and remained always in the range of 35–50%. Therefore, the cleaning procedure did not affect very much the rejection performance of the membrane.

Table 4
COD rejection for experiments at constant feed concentration

Test	Feed COD (mgO ₂ L ⁻¹)	COD rejection (%)
1	76	35.5
2	139	42.5
3	124	43.6
4	167	41.9
5	126	39.7
6	91	42.5
7	162	50.6
8	104	37.5

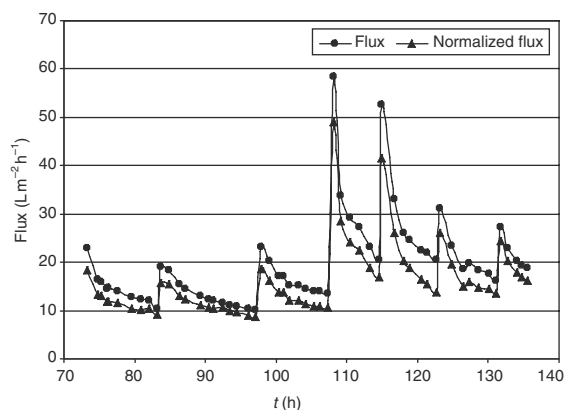


Fig. 4. Flux for one-step concentration experiments.

Table 3
Cleaning procedures for experiments at constant feed concentration

Test	Initial flushing time with water (min)	Cleaning time (min)	Water rinsing time (min)	Cleaning flow (L min ⁻¹)	Cleaning solution
1	5	5	5	25	NaClO 0.5%
2	5	5	5	30	NaClO 0.5%
3	5	5	5	30	NaClO 0.5%
4	5	5	5	30	NaClO 0.5%
5	10	10	10	25	NaClO 0.5%
6	15	15	15	30	NaClO 0.5%
7	20	20	20	35	NaClO 0.5%
8	5	5	5	30	NaOH 1%
9	10	10	10	35	NaOH 1%
10	20	20	20	35	NaOH 1%

Table 5
Cleaning procedures for one-step concentration experiments

Test	Initial flushing time with water (min)	Cleaning time (min)	Water rinsing time (min)	Cleaning flow (L min ⁻¹)	Cleaning solution
1	5	5	5	25	NaClO 1%
2	5	5	5	30	NaClO 1%
3	10	10	10	25	NaClO 1%
4	15	15	15	45	NaClO 1%
5	10	10	10	45	NaClO 1%
6	10	10	10	45	NaClO 1%
7	10	10	10	30	NaClO 1%

3.2.3. One-step concentration experiments

As it can be seen in Fig. 4, the membrane was able to work at higher feed concentrations. The most effective cleaning procedures corresponded to cleaning times greater than 10 min (Table 5).

In Table 6, it can be observed that the COD rejection was similar to that obtained in the experiments at constant feed concentration. In the COD rejection operating range, increasing feed concentration had no influence.

After these experiments, it was observed that permeate flux kept almost constant due to the daily cleaning efficiency. Results show that the membrane allows a higher COD concentration in the feed water.

Table 6
COD rejection for one-step concentration experiments

Test	Feed COD (mgO ₂ L ⁻¹)	COD rejection (%)	Final volume of concentrate (L)
1	109	29.4	260
2	151	39.8	50
3	175	38.9	200
4	170	39.4	60
5	194	37.6	20
6	218	38.5	195

3.2.4. Multi-step concentration experiments

Fig. 5 shows the flux and the normalized flux to 30°C for the experiment carried out during two weeks. Increasing concentration in feed did not affect the performance.

In this case, all cleaning procedures (Table 7) were suitable.

In Table 8, it can be observed that COD rejection increases with feed concentration.

4. Conclusions

A membrane with MWCO of 20 kDa or less is necessary in order to reduce COD and to protect a posterior treatment using NF or RO.

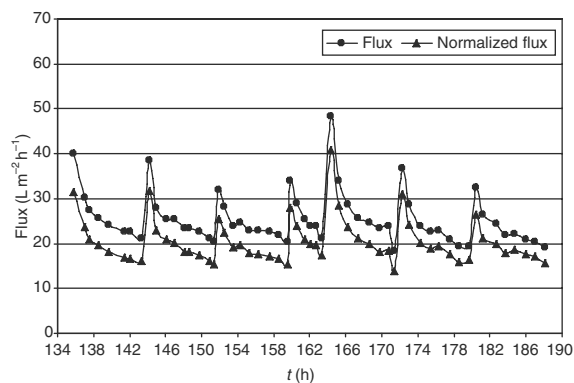


Fig. 5. Flux for multi-step concentration experiments.

Table 7
Cleaning procedures for multi-step concentration experiments

Test	Initial flushing time with water (min)	Cleaning time (min)	Water rinsing time (min)	Cleaning flow (L min ⁻¹)	Cleaning solution
1	15	15	15	30	NaClO 1%
2	10	10	10	45	NaClO 1%
3	10	10	10	45	NaClO 1%
4	5	10	10	45	NaClO 1%
5	5	10	10	45	NaClO 1%
6	5	10	10	45	NaClO 1%
7	5	10	10	45	NaClO 1%

All UF membranes were severely fouled, mainly due to the biological matter.

The selected UF membrane (IRIS 3028) was able to reject more than 50% of COD.

In our case, the most effective cleaning procedure was the use of a solution of sodium hypochlorite of 10 g L⁻¹ during more than 10 min.

The use of UF previous a NF stage contributes to largely diminish the fouling of the NF membranes. However, fouling mechanisms originated for this type of water are an important drawback for the application of UF. The convenience of an UF stage previous to a NF one will depend on the balance between the UF cleaning costs compared to the energetic and investment cost reductions obtained in the NF stage.

Table 8
COD rejection for multi-step concentration experiments

Week	Test	Feed COD (mgO ₂ L ⁻¹)	COD rejection (%)
1	1	175	25.7
	2	289	56.1
	3	309	60.2
	4	491	80.0
2	5	211	20.7
	6	342	73.6
	7	529	81.5

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References

- [1] M. Mignani, G. Nosenzo and A. Gualdi, Innovative ultrafiltration for wastewater reuse, *Desalination*, 124 (1999) 287–292.
- [2] P. Schoeberl, M. Brik, R. Braun and W. Fuchs, Treatment and recycling of textile wastewater — case study and development of a recycling concept, *Desalination*, 171 (2005) 173–183.
- [3] M. Marcucci, G. Ciardelli, A. Matteucci, L. Ranieri and M. Russo, Experimental campaigns on textile wastewater for reuse by means of different membrane processes, *Desalination*, 149 (2002) 137–143.
- [4] A.M. Brites Alves and M. Norberta de Pinho, Ultrafiltration for colour removal of tannery dyeing wastewaters, *Desalination*, 130 (2000) 147–154.
- [5] A. Bes-Pia, M.I. Iborra-Clar, A. Iborra-Clar, J.A. Mendoza-Roca, B. Cuartas-Urbe and M.I. Alcaina-Miranda, Nanofiltration of textile industry wastewater using a physicochemical process as a pre-treatment, *Desalination*, 178 (2005) 343–349.
- [6] G. Ciardelli, L. Corsi and M. Marcucci, Membrane separation for wastewater reuse in the textile industry, *Resour. Conservat. Recycl.*, 31 (2001) 189–197.
- [7] C. Fersi, L. Gzara and M. Dhahbi, Treatment of textile effluents by membrane technologies, *Desalination*, 185 (2005) 399–409.

- [8] K.N. Bourgeois, J.L. Darby and G. Tchobanoglous, Ultrafiltration of wastewater: effects of particles, mode of operation, and backwash effectiveness, *Water Res.*, 35 (2001) 77–90.
- [9] J. Kim and F.A. DiGiano, A two-fiber, bench-scale test of ultrafiltration (UF) for investigation of fouling rate and characteristics, *J. Membr. Sci.*, 271 (2006) 196–204.
- [10] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho and H.H. Ngo, Fouling of ultrafiltration membrane by effluent organic matter: a detailed characterization using different organic fractions in wastewater, *J. Membr. Sci.*, 278 (2006) 232–238.
- [11] B.K. Chaturvedi, A.K. Ghosh, V. Ramachandhran, M.K. Trivedi, M.S. Hanra and B.M. Misra, Preparation, characterization and performance of polyethersulfone ultrafiltration membranes, *Desalination*, 133 (2001) 31–40.
- [12] M. Sulaiman, N.M. Sulaiman and B. Abdellah, Prediction of dynamic permeate flux during cross-flow ultrafiltration of polyethylene glycol using concentration polarization-gel layer model, *J. Membr. Sci.*, 189 (2001) 151–165.
- [13] M.C.V. Vela, S.A. Blanco and J.L. Garcia, Crossflow ultrafiltration of cake forming solutes: a non-steady state model, *Desalination*, 184 (2005) 347–356.