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MEMBRANE TREATMENT OF SECONDARY TEXTILE EFFLUENTS FOR DIRECT REUSE

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ABSTRACT

Post-treatment of secondary textile wastewater was tested at pilot scale on membrane modules (microfiltration MF, nanofiltration NF and reverse osmosis RO) for the direct reuse of polished effluent within the dyeing processes. The main polluting parameters monitored in the post-treatment were: organic compounds (COD), colour, surfactants and salinity (as conductivity).

The first treatment scheme was made of ceramic MF followed by NF. Aluminium polychloride was added at high concentrations (of the order of 70 mg Al/L) to avoid MF membrane fouling. The quality of the final permeate, produced by NF fed on the MF permeate, was acceptable for water reuse.

Clariflocculation (CF) plus multimedia filtration (MMF) followed by low-pressure RO was also tested. This process performed quite well: the RO module ($p = 4$ bar) ran for relatively long cycles (up to 80 hours) with 5% reduction of the permeate flow rate at a 10 L m^{-2} h^{-1} fluxes.

A techno-economical analysis on the experimental data indicate that a high quality effluent (COD < 10 mg/l; conductivity < 40 μS/cm; negligible residual colour), to be recycled in the textile dyeing industry, may be produced at affordable costs (less than 0.25 ECU) from secondary textile wastewater. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Ceramic membranes; microfiltration; nanofiltration; recycle; reverse osmosis; textile industry.

INTRODUCTION

In the province of Como (Northern Italy), a large number of medium and small size textile factories, scattered throughout the countryside, consume vast quantities of fresh water, mainly drawn from an industrial aqueduct connected to Lake Como and from local wells. This process water is then discharged from the mills as polluting wastewater, mixed to the local domestic sewage and treated in four centralised treatment plants. The major part of this effluent flow (approximately 75,000 out of 120,000 m^3/d) is discharged into small ephemeral streams. The flow rate ratio between the receiving stream and the treated effluent is often closer to 1 than to 10 and in summer time may plummet to zero. As a consequence, residual refractory compounds, particularly dyestuffs and surfactants, can give rise to severe aesthetic (colour and foam) and pollution problems in the streams.

The LARIANA DEPUR agency, which runs three out of the four major waterworks in the Como area, and its subcompany CIDA decided to investigate the possibility to polish secondary effluents from treatment plants. This post-treatment would bring about several positive effects: on the one hand, the reuse of polished water by textile industry would reduce overall water consumption in the Lake Como basin, while on the other hand, it would go towards improving the quality of the local streams. Therefore LARIANA DEPUR and its main shareholders (the industrial aqueduct and the Como Association of industrialists) have funded a long term research program on wastewater treatment and recycling, which was subsequently boosted by an EC contract. The experimental results on microfiltration, nanofiltration and reverse osmosis reported in this study were obtained within the above mentioned research program.

MATERIALS AND METHODS

Influent secondary wastewater to the pilot plants

The secondary effluent was bled from the Bulgarograsso centralised biological treatment plant (pre–denitrification, organic carbon oxidation and nitrification) located in the Southern Como province (Italy). Influent dry weather flow rate is of the order of 25,000 m^3/d. The influent is prevailingly made of textile wastewater: the industrial to domestic ratio is 80:20 as organic load and 70:30 as hydraulic flow rate respectively. The industrial load is equalised over seven days per week at the textile and dyeing factories by balancing tanks.

The main characteristics of fresh water from the aqueduct, of the influent and the effluent of the treatment plant where this investigation was carried out are resumed in Table 1.

Table 1. Average characteristics of the water by the industrial aqueduct, of the influent and of the secondary effluent from the Bulgarograsso wastewater treatment plant.

Parameters	Units	Industrial aqueduct water		Treatment plant wastewater	
		from lake	from secondary effluent (*)	Influent	Effluent
pH	–	7.5	7 – 8	6.8 – 7.2	7.5 – 7.7
Hardness	$mgCaCO_3/L$	90	270	200 – 270	200 – 270
Conductivity	µS/cm	200	1,800	1,000 – 1,900	1,000 – 1,900
Colour (426 nm abs.)	–	abs.	0.01	n.a.	0.09
TSS	mg/L	0.3	10	100 – 200	40 – 60
COD_{tot}	mgO_2/L	4	30	500 – 1,000	120 – 160
Anionic surfactants	mgMBAS/L	0.01	0.025	5 – 10	0.5 – 1
Non–ionic surfactants	mgBiAS/L	< 0.05	0.5	16 – 20	1 – 2

(*) values allowed in case of reuse of the treated secondary effluent.

Microfiltration module and pilot plant

The main characteristics of the ceramic microfiltration KERASEP K01BW module (Tech Sep, Rhone Poulenc group, France) are reported in Table 2. The membrane is made of ZrO_2 supported on a $Al_2O_2 – TiO_2$ monolite. Tubes are 3.5 mm diameter.

Table 2. Characteristics of the pilot–scale membrane modules.

Process	Module	MWCO	S	rejection	Max. pressure	Max. temperature	pH range
		(dalton)	(m^2)	% on	(bar)	(°C)	–
MF	CF	300,000	0.245	–	5	350	0 – 14
NF	SW	150	8.36	96 $MgSO_4$	28	50	2 – 11
LpRO	SW	58	11	98 NaCl	21	1 – 40	4 – 11

LEGEND: CF: cross flow; SW: spiral wound; S: surface; MWCO: molecular weight cut off.

The 300,000 dalton cut–off has been selected after a thorough experimental investigation on molecular distribution of the organic compounds remaining in textile/domestic secondary effluent (Malpei et al., 1997). The study showed that the residual pollutants could be subdivided into two major fractions, one over 300,000 dalton and the other below 3,000 dalton, both of the order of 45 – 50% COD.

The permeate or/and the concentrate from the MF module may be recycled into the feed tank or discharged, depending on the experimental procedure. The pilot plant is equipped with all the required auxiliary equipment in order to control flow rates, pressures and temperatures. More information on the flow–sheet of this pilot plant is found in Rozzi et al. (1996) and Rozzi et al. (1997).

Nanofiltration module and pilot plant

The nanofiltration MOCD404N050 module (Separem, Biella, Italy) used on the pilot scale plant was a spiral wound composite polyamide membrane deposited on a polysulphone support. This type of membrane allows to separate low molecular weight organic compounds and divalent salts, with an appreciable softening effect. Compared to conventional RO modules, the main advantage of NF membranes is the possibility to obtain high fluxes at relatively low pressures, of the order of 5 – 10 bar, quite lower than conventional RO. The specification "conventional" refers to RO modules operating at much higher pressures than the "low pressure" module described below. The main characteristics of the NF module are reported in Table 2. The pilot plant configuration is similar to the MF one (Rozzi et al., 1997).

Low pressure RO module and pre–treatment (clariflocculation and multimedia filtration)

Conventional equipment was used in this study for the clariflocculation step. The multimedia filter is made of six layers of various media (pebbles, gravel, quartz sand and anthracite; average diameter of the upper layers is 0.6 – 0.8 mm). The filter has a section surface of 0.196 m^2, a height of 1.015 m and a volume of 0.3 m^3. The project flow rate is 2 m^3/h corresponding to a velocity of 10 m/h.

The low–pressure reverse osmosis (LpRO) module was a thin film spiral wound module 99XHUEY™ (Fluid System Corporation, San Diego, CA specifically designed for Società Membrane, Milano, I) whose characteristics are also reported in Table 2. This module was specially designed to operate at low pressure (less than 5 bar) with feed water relatively high in colloids and suspended solids. The operating conditions are therefore closer to NF modules than "conventional" RO, which runs at pressures higher than 20 bar. The pilot plant operated as a once–through system without concentrate and/or permeate recycle.

Analytical methods

Conductivity, pH, COD, total and suspended solids, total hardness and alkalinity were performed according to Italian official methodologies (IRSA, 1994) which are quite similar to those described on the Standard Methods (1995). Colour absorbance was measured on filtered samples (0.45 μm) using a Shimatzu Spectrophotometer. Silt Density Index (SDI) tests were carried out according to Dupont (1977).

RESULTS AND DISCUSSION

Membrane process control

Permeate flux through the membrane is controlled by the transmembrane pressure TMP, defined as:

$$TMP = (p_{feed} + p_{retentate})/2 - p_{permeate}$$

The permeate flux is proportional to the TMP and inversely proportional to the resistance. Permeation tests were carried out at constant permeate flow rate. In order to keep the flux constant, the TMP was adjusted either by throttling of the valves on the concentrate and on the permeate compartments or by controlling the flow rate of the permeate (by a volumetric pump) which adjusted automatically the value of the transmembrane pressure. An increase of transmembrane pressure indicated an increase of membrane resistance and therefore fouling phenomena.

First treatment scheme: MF followed by NF

The first treatment scheme was made of two filtration modules: ceramic microfiltration followed by nanofiltration. The preliminary filtration on a ceramic MF module was intended to reduce or eliminate the fractions of pollutants (suspended solids and colloids) which induce a rapid fouling in the downstream membrane at a much lower cut off.

During the preliminary tests carried out on the MF module, it was found that excessively high values of transmembrane pressure (and related flux of permeate), obtained by leaving the permeate outlet at atmospheric pressure, induce a very rapid fouling of the membrane. Tight control of the permeate flow was found to be very effective to control the fouling of the membrane and to obtain long working cycles (tens of hours). The best operating conditions were found to be 80 ÷ 120 L m^{-2} h^{-1} and TMP = 1 ÷ 1.5 bar.

Addition of high concentrations of aluminum polychloride was necessary to obtain a satisfactory performance, otherwise rapid fouling of the membrane was observed. The coagulant was added directly in the feed tank, its concentration was initially 10 mg Al/L, but it was progressively increased up to 70 mg/L to reduce MF membrane fouling and increase working cycle time length. Module permeability was restored by an alkaline + acid high cleaning procedure (T = 60 ÷ 70°C).

Firstly, discontinuous daily operation of the module was tested (about 9 hours on and 15 hours off), then continuous operation was made possible by a dosing pump to keep permeate flow constant.

In Fig. 1a the transmembrane pressure is plotted vs. time for discontinuous operation. It is interesting to note that after each stop the performance of the membrane improved appreciably, even though no anti–fouling cleaning procedures were used. Moreover the working line, obtained ignoring the first part of each cycle till TMP is lower than the final TMP of the previous cycle, as plotted in Fig. 1b, looks quite similar to the one obtainable for continuous operation. An example of continuous operation line is reported in Fig. 2, where the intermittent segments indicate the time intervals (nights) when the transmembrane pressure was not monitored and recorded.

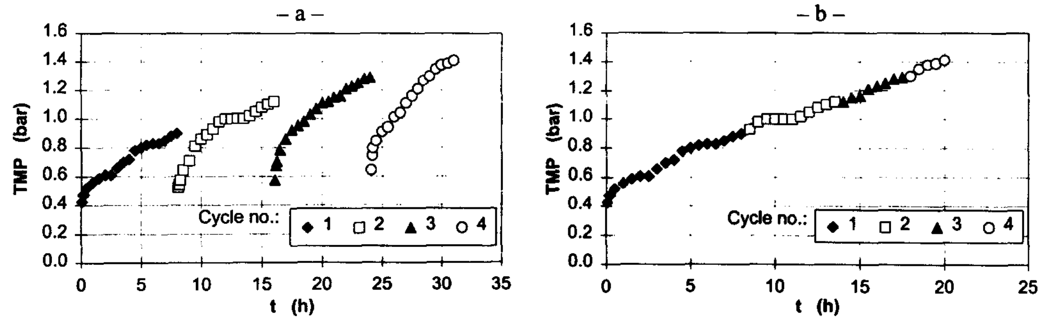

Fig. 1. Transmembrane pressure vs. time during discontinuous operation of the MF (flux:100 L m^{-2} h^{-1}).

The permeate obtained from the ceramic MF module was stored in a tank and then fed into the NF. The latter pilot plant was operated in batch mode, both with constant and increasing feed concentration, with an operating pressure of 10 bar. In the former case, the permeate was recycled back to the feed tank. In the latter case, the module was tested at a concentration factor ≤ 6, according to the results obtained during previous NF experiments (Bonomo et al., 1992).

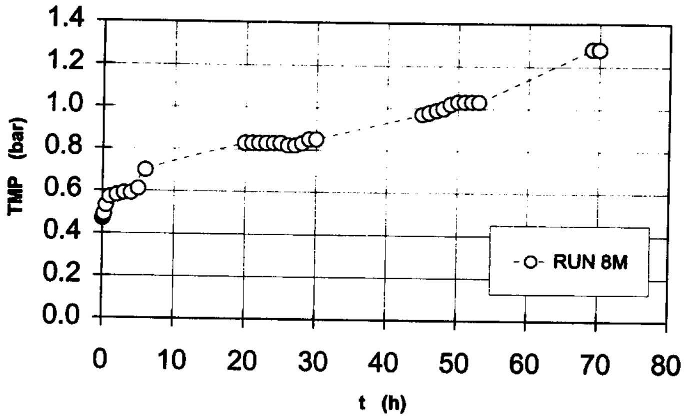

Fig. 2. Transmembrane pressure vs. time during continuous operation of the MF (flux: 80 L m^{-2} h^{-1}).

As expected, no fouling problems occurred during constant feed concentration tests and membrane cleaning was required only after 120 – 150 hours of filtration; moreover, the lower the concentration factor (and consequently the higher the feed and the discharged concentrate flow), the longer was the time needed before fouling was observed. During the batch tests at increasing concentration, fouling was higher, and a permeate flux reduction of 20% was observed after 4 – 5 hours of filtration. Permeate quality was always good enough to meet standards for reuse, as can be observed from Table 3 for the two operation modes. This investigation confirmed that it is possible to reuse secondary effluent for textile industry purposes after two stages (MF + NF) membrane filtration, although a pre–treatment, consisting in coagulant dosage, is necessary to assure acceptable duration of filtration cycles for the first filtration step.

Table 3. Quality of nanofiltration permeate (average values).

Parameter	Constant feed concentration			Increasing feed concentration				
	F	P	*Reduction %*	F	P	*Reduction %*	R	*CF*
COD_{tot} (mg/L)	76.5	24	*69*	71	26	*63*	350	*4.93*
COD_{sol} (mg/L)	72.0	24	*67*	68	26	*62*	326	*4.79*
TSS (mg/L)	5.5	0	*100*	2	0	*100*	8	*4.00*
Hardness ($mgCaCO_3$/L)	180	65	*63*	200	90	*55*	–	–
Conductivity (μS/cm)	1,095	880	*20*	1,160	1,030	*11*	–	–
Absorbance at 426 nm	0.081	0.003	*96*	0.077	0.004	*95*	0.514	*6.68*
Absorbance at 558 nm	0.049	0.001	*98*	0.048	0.002	*96*	0.302	*6.29*
Absorbance at 660 nm	0.017	0.000	*100*	0.015	0.001	*93*	0.105	*7.00*

LEGEND: F: feed; P: permeate, R: retentate; CF: concentration factor.

Second treatment scheme: CF + MMF + RO

Another series of tests was implemented using a clariflocculation step followed by multimedia filtration prior to a low pressure reverse osmosis module. The clariflocculation/filtration was aimed at removing the colloidal fraction which promotes fouling on RO membranes. The low pressure and high turbolence RO module was specifically designed for post–treatment of tertiary effluents.

The optimal dosing of coagulant (4 ppm on volume basis) was determined by jar tests. The SDI of the secondary effluent fed to the filter could not be measured because of excessive fouling potential. After the clariflocculation/filtration step the SDI was of the order of 8 – 9 which made the wastewater suitable for RO filtration.

The operating pressure in the module was set according to the permeate flux. The first series of tests was carried out at a low permeate flux (5 L m^{-2} h^{-1}) in order to minimise fouling risks. These preliminary tests were quite encouraging and therefore the flux was increased to 10 L m^{-2} h^{-1}. Operating conditions and module performance are reported in Table 4. During days 4 and 5 of the filtration cycle at 10 L m^{-2} h^{-1}, the module was flushed once per day to restore the permeate flux (flushing of the retentate compartment with permeate: 30 min counter–current flow + 10 min co–current flow).

Table 4. Low pressure RO performance.

	5 L m^{-2} h^{-1} Filtration Cycle				10 L m^{-2} h^{-1} Filtration Cycle			
Day	P_F	P_R	C_P	Q_P	P_F	P_R	C_P	Q_P
	bar	bar	µS/cm	L/h	bar	bar	µS/cm	L/h
1	2.5	2.0	80.5	31.0	4.9	3.9	37.4	72.5
2	2.5	2.0	76.4	29.9	4.9	3.9	36.9	72.0
3	2.5	2.0	80.0	29.3	4.9	3.9	38.9	71.2
4	2.5	2.0	83.6	29.6	4.9	3.9	39.1 *	72.3
5	–	–	–	–	4.9	3.9	36.4 *	71.2

LEGEND: P_F: feed pressure; P_R: retentate pressure; C_P: permeate conductivity; Q_P: permeate flow rate
(*) permeate flushing

The RO module ran for relatively long cycles (up to 80 hours) with a minimal reduction of the permeate flow rate (of the order of 5%) at a flux of the order of 10 L m^{-2} h^{-1}. No washing cycles were necessary for an overall working period equal to 200 hours. It is interesting to compare the permeate conductivity for the two operating conditions and to observe that when the permeate flux was doubled, the conductivity (and therefore salinity) was almost halved. This observation confirms that the salt passage through a RO membrane is practically independent of the water transport and therefore, to a certain extent, the higher the permeate flux the lower is its salinity. In Fig. 3 the absorbance reduction for the 10 L m^{-2} h^{-1} filtration cycle is reported. COD was found to be consistently lower than 10 mg/L.

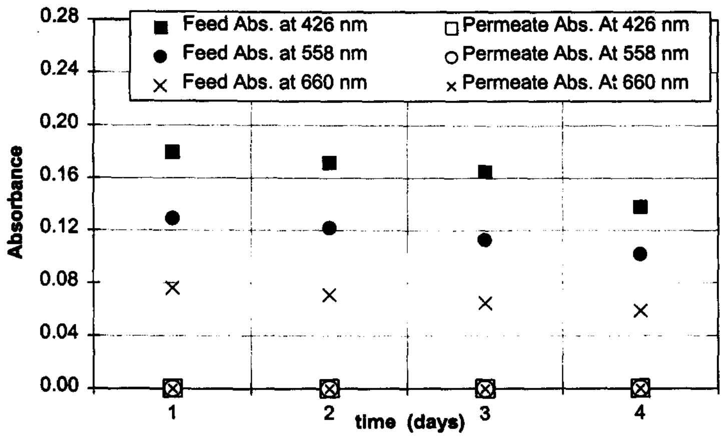

Fig.3. Feed and permeate absorbance during 10 L m^{-2} h^{-1} filtration cycle.

Experimental tests carried out on the treatment scheme CF + MMF + RO indicate that it is possible to obtain a polished effluent of high quality (COD < 10 mg/L; conductivity < 40 μS; negligible residual colour) which may be reused in the textile mills. Previous experiments on conventional RO (Bonomo et al., 1992) gave similar results at much higher pressures (about 30 bar).

Techno–economical analysis

The quality of the permeate produced by the NF module fed on the MF permeate was quite satisfactory and totally acceptable for water reuse in textile printing mills. Approximated preliminary calculations on this coupled membrane process indicated that at present this process cannot be transferred in a full scale plant, on account of the high price of the ceramic MF membranes and the need of high dosing of coagulants.

A more detailed techno–economical analysis was carried out on the flow–sheet based on clariflocculation/filtration followed by low pressure RO for a demonstration plant producing 150 m^3/h of permeate. The clariflocculation/filtration section is composed by 3 in–parallel filtration units with an on–line coagulant dosage. For the RO section, staging = 26:13 and recovery factor = 70% were assumed. The main parameters considered for the calculations are reported in Table 5.

The electric power consumption (recovery factor = 70%, staging = 26:13) to produce 3600 m^3/d of permeate is very low, about 38 kW corresponding to a 0.25 kWh per m^3 of product, because of the low operating pressure.

Table 5. Main parameters considered for the RO demonstration plant

		Feed	Permeate	Retentate
Pressure	bar	4.8	0.3	3.8
Flow rate	m^3/h	214	150	64
pH	–	7.10	6.22	7.58
TDS	mg/L	1,063	80	3,360
Hardness	$mgCaCO_3/L$	200	3.3	660

The capital cost related to pre–treatment is only 10% of the plant total cost (about 880,000 EURO). The specific cost of product water related to investment is 0.071 EURO/m^3, assuming a useful life period of 15 years and a 8% interest rate. The specific operating and maintenance, equal to 0.13 EURO/m^3, was computed taking into account energy, consumption of chemicals (coagulant and antiscaling agents), labour and membrane replacement (a yearly substitution of 33% of membranes has been assumed as a conservative estimate). The total specific cost per m^3 of permeate is 0.202 EURO, which is quite low considering the high quality of the produced water.

COD and salinity in the RO retentate do increase appreciably and make the overall process design more complex: either the retentate is directly discharged into the surface streams or it is recycled into the biological wastewater treatment process, in both cases accurate mass balances must be carried out in order to keep the characteristics of the final effluents within the required standards (Rozzi et al., 1999).

CONCLUSIONS

Experimental results obtained from pilot plant tests indicate that membrane post–treatment of effluents, to be recycled as water supply for the textile dyeing industry, is feasible.

Fouling in the MF ceramic module was controlled by addition of a suitable coagulant and by adequate choice of the operating parameters (crossflow velocity and transmembrane pressure). Chemical cleaning was required only once per week. The upstream MF module fully protected the NF module which could operate without any fouling problem even without any addition of chemicals.

Clariflocculation and multimedia filtration coupled to RO allows to obtain satisfactory effluents too using less expensive equipment than in the above solution. NF and low pressure RO are preferable to conventional RO because comparable fluxes might be obtained at quite lower pressure and therefore at lower energy costs.

RO and NF membrane processes desalt the purified effluent and increase the concentrate salinity which must be taken into account in the overall process treatment.

Costs related to the complete polishing by low pressure RO are comparable to the cost of a conventional secondary wastewater treatment and quite affordable (of the order of 0.20 – 0.25 EURO) even for the Italian situation, where water price is much lower than in most industrialised countries.

ACKNOWLEDGMENTS

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