Check for updates

Pergamon

Wat. Sci. Tech. Vol. 40, No. 4–5, pp. 443–450, 1999
© 1999 IAWQ
Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0273–1223/99 $20.00 + 0.00

PII: S0273-1223(99)00528-4

SAVING OF WATER AND CHEMICALS IN TANNING INDUSTRY BY MEMBRANE PROCESSES

A. Cassano*, R. Molinari** and E. Drioli*,**

* *Research Institute on Membranes and Modelling of Chemical Reactors, c/o Department of Chemical Engineering and Materials, University of Calabria, I-87030 Arcavacata di Rende (CS), Italy*
** *Department of Chemical Engineering and Materials, University of Calabria, I-87030 Arcavacata di Rende (CS), Italy*

ABSTRACT

Some results on pressure-driven membrane operations able to improve chromium recovery from spent chromium tanning baths and to desalinate water discharged from filterpress after Cr(III) precipitation are reported. Nanofiltration was employed to concentrate chromium(III) using a spiral-wound module. Chromium concentration and COD in permeate were respectively about zero and 2-3 g/l as compared to initial feed values of 2.8 and 5.2 g/l; the high chloride concentration in the permeate suggested to reuse this solution in the pickling step saving fresh water and salts. The concentrate solution presented a higher chromium purification with respect to initial feed. It was tested in retanning, and after further concentration by chemical precipitation-dissolution method, in tanning operations. Chemical and physical analyses on leather treated with these solutions showed similar characteristics with respect to use of traditional chromium solution. Reverse osmosis was employed to reduce the high salt content in waste water from filter pressing of chromium hydroxide panels. Good rejection of reverse osmosis membrane to chloride and sulphate ions suggested the use of this operation for obtaining water, to be used in washings, or to sent to biological treatment of final waste water. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Desalination; membrane processes; nanofiltration; recycling of water and chemicals; reverse osmosis; waste water cleaning-up.

INTRODUCTION

In tanning industry transformation of raw skin into leather is obtained by means of a series of chemical and mechanical operations. Water and chemicals are consumed in high amount in every chemical step of the process with significant pollution phenomena due to organic substances removed from the skin and to the chemicals not completely reacted with it.

Chromium salts, particularly the basic sulphate, are the most widely used tanning substances to treat skin to prevent its putrefaction. About 30% of the trivalent chromium supplied is discharged in waste water. This creates serious problems in biological waste water treatment; furthermore, it ends up into sludges giving many problems for their disposal and/or for their agricultural use.

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest

Stringent environmental regulations imply the use of appropriate strategies to meet the imposed limits for waste water discharge and to reduce their amount. In Italy various associated leather companies created a Consortium for recovering chromium(III), from spent tanning baths, by using a conventional precipitation-dissolution method (Consorzio Recupero Cromo) in order to reduce the amount of discharged chromium into the waste water treatment plant. The spent float is precipitated with sodium carbonate and filtered through a filter press. Chromium hydroxide panels are dissolved in sulphuric acid and transformed into a tanning solution with 33% basicity and standard concentration which is then used for tanning again (Gauglhofer, 1986).

A problem observed by tanners was the poor quality of this chromium due to organic lipolytic components, metals and other impurities. Membrane processes such as cross flow microfiltration, ultrafiltration, nanofiltration, reverse osmosis, etc., opportunely integrated among them, and/or with other traditional techniques, can be used in the tanning cycle for recovering and recycling water, primary raw materials and chemicals species produced in the process (Molinari, 1995).

In this paper some results on pressure-driven membrane operations able to improve chromium recovery from spent chromium tanning baths and to desalinate water discharged from filter press after Cr(III) precipitation are reported. Nanofiltration was employed to recover concentrate chromium(III) and water, in first case, and reverse osmosis was employed to desalinate water coming from filterpress, in second case.

EXPERIMENTAL

Materials

Exhaust chromium solution and wastewater were, respectively, drawn off from the equalization tank and from the filterpress of Consorzio Recupero Cromo (S. Croce S/Arno, Pisa, Italy). Sepaclean EZ-1 (enzymatic powder), Sepaclean AC-1 (acidic solution) (Separem) were of commercial grade. Other chemicals were commercial grade reagents. Nanofiltration (MOCD 4040N50, polyamide, NMWCO 150 Da, 5.5 m^2, pressure max. 28 bar, temperature max. 50°C, pH 2-11, water permeabilty 47.27 l/m^2h) and reverse osmosis (MSCB 4040, TFC/polyamide, 6.6 m^2, typical salt rejection 99.2%, pressure max. 42 bar, temperature max. 50°C, pH 4-11, axial flow rate 1.5-4 m^3h) spiral-wound 10x101 cm (4x40") membrane modules were supplied by Separem (Biella, Italy). The pilot plant was also supplied by Separem.

Methods

Chloride, pH, ammoniacal nitrogen, organic nitrogen and COD values were determined according to the official method (CNR-IRSA, 1979). Chromium was determined by an atomic absorption spectrophotometer; sulphate was determined by colorimetric method; oils and fats were determined by extraction in petroleum ether at 40-60 °C; total suspended solids (TSS) were determined by filtration through a 0.45 μm cellulose acetate membrane. Other species (Ca^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}) were determined according to conventional methods. Chemical-physical analyses on leather samples were carried out at Stazione Sperimentale Pelli in Naples according to IUP and IUC official methods.

RESULTS AND DISCUSSION

Treatment of exhaust chromium baths

Exhaust chromium solution was treated with an ultrafiltration OSMO 411 TA (Osmonics) spiral-wound module by ENEA (Fabiani *et al.*, 1996) on a pilot plant at Consorzio Recupero Cromo. The permeate produced a strong reduction of total suspended solids and of fat substances (membrane rejections toward these species, with reference to initial feed, were 84% and 98%, respectively and chromium rejection was 28%) as shown in Table 1.

Permeate coming from ultrafiltration was processed in a nanofiltration spiral-wound module (Separem MOCD 4040 N50) at an applied pressure of 14 bar, a temperature of 25 °C and an axial feed flow rate of

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest

2200 l/h (Cassano *et al.*, 1996). The initial feed volume, 178 litres, was reduced to 55 litres (volume reduction factors, initial volume devided by the remaining volume, VRF = 3.24) recycling continuously the retentate and drawing off the permeate (concentration operation mode). Initial permeate flux was 36 l/m^2h, then decreased in the time to 4.5 l/m^2h, remaining constant in the last hours of operation. In Table 2 the results of samples analyses obtained during the process are reported.

Table 1. Analytical determinations on samples obtained from ultrafiltration tests (Fabiani *et al.*, 1996)

Parameter (mg/l)	Feed	Retentate	Permeate
pH	3.7	3.7	3.8
TSS	612	428	100
COD	5,960	6,413	5,241
Chloride	11,136	11,098	11,348
Sulphate	26,137	27,239	21,561
Chromium	4,343	5,269	3,121
Ammon. nitrogen	422	420	422
Organic nitrogen	250	301	148
Iron	24	29	25
Calcium	1,100	948	1,007
Manganese	2.2	2.5	2.4
Aluminium	91	97	84
Magnesium	867	822	787
Oils and fats	116	148	2.5

In Table 3 a material balance of the nanofiltration test is reported. The balance is quite equilibrate except for COD and TSS: it is probably due to organic matter adsorption on thr nanofiltration plant prefilter.

In Figure 1 the concentration ratio chromium/COD in retentate versus VRF is reported. Increasing the ratio means that organic substances (COD) are less retained with respect to chromium giving a more purified chromium solution. Very good separation of chromium without increasing solution salinity is another advantage in using a nanofiltration process. These results agree with those obtained by other authors (Aloy and Vulliermet, 1997).

Higher chloride concentration in permeate (Table 2) suggested reuse of this solution in the pickling step saving fresh water and salts.

Final retentate from nanofiltration (1.35% as Cr_2O_3) was tested as such in skin retanning and, after further concentration (9.2% as Cr_2O_3) using the chemical precipitation-dissolution method, in tanning operations. Chemical and physical tests (tensile strength, breaking load, elongation at break, shrinkage temperature, etc.) performed on experimental sheepskins revealed values very similar to those obtained on a control group treated with the conventional method (Cassano *et al.*, 1996). These results suggested reuse of the retentate in two alternative ways as proposed in the treatment process reported in Figure 2.

Tests for cleaning membrane modules were also carried out. Use of enzymatic (Sepaclean EZ-1) and acidic (Sepaclean AC-1) solutions showed an initial flux better restored with the second solution.

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest

Table 2. Analytical determinations on samples from nanofiltration tests*

Parameter (mg/l)	Feed	IP	P 15	R 15	P 30	R 30	P 45	R 45	FP	FR
PH	4.1	4.1	4.1	4.1	4.2	4.2	4.2	4.0	4.0	4.0
TSS	154	17	18	112	18	192	20	2,082	28	370
COD	5,126	2,063	2,057	5,273	2,624	6,300	3,078	7,377	3,315	7,641
Chloride	10,844	11,330	11,991	10,652	12,648	9,792	13,160	8,760	13,190	7,390
Sulphate	27,996	252	410	33,547	652	38,289	1,430	58,277	4,854	83,455
Chromium	2,729	n.v.	3	3,685	4	5342	8	7,007	30	9,285
Ammon. nitrogen	367	233	260	473	261	551	266	617	320	720
Organic nitrogen	165	76	57	160	66	147	69	183	98	209
Iron	32	3.2	3.2	40	2.1	52	5.2	60	8	81
Calcium	1,086	42	38	1,061	90	1,755	180	2,999	12	1,367
Manganese	2.4	0.1	0.1	2.9	0.1	3.8	0.2	4.6	0.4	6.3
Aluminium	96	1.2	1.4	128	1.6	161	2.1	201	5	259
Magnesium	870	5	6	878	8	1,398	15	1,341	60	6,162

* Legend: IP = initial permeate; P 15 = permeate after 15'; R 15 = retentate after 15'; P 30 = permeate after 30'; R 30 = retentate after 30'; P 45 = permeate after 45'; R 45 = retentate after 45'; FP = final average permeate; FR = final retentate

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest

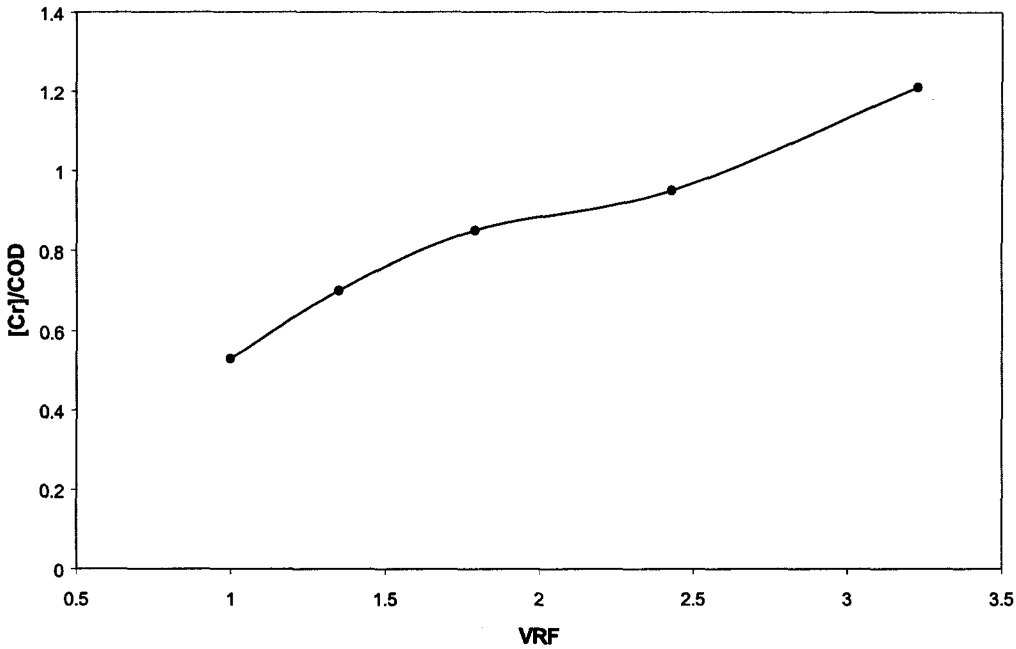

Figure 1. Concentration ratio Cr/COD vs. VRF. (Operating conditions: temperature = 25°C; applied pressure = 14 bar; axial flow rate = 2200 l/h; permeate flow rate = 20-198 l/h).

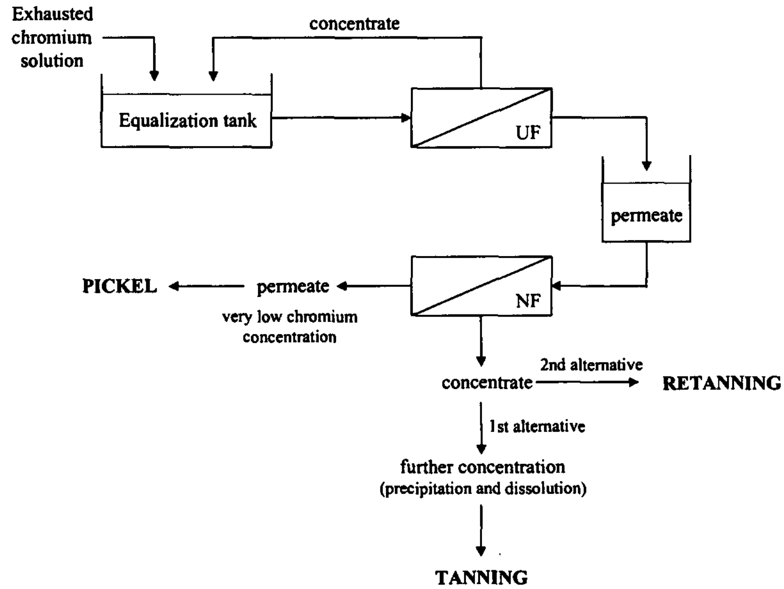

Figure 2. Proposed process scheme for reuse of exhausted chromium.

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest

Table 3. Material balance on the nanofiltration process

	Initial float	Average filtrate		Final retentate		Balance
Volume	178 liters	123 liters	69%	55 liters	31%	100%
Chromium	486 g	3.7 g	1%	511 g	105%	106%
TSS	27 g	3.4 g	12.6%	20 g	74.1%	86.7%
COD	912 g	408 g	45%	420 g	46%	91%
Chloride	1930 g	1622 g	84%	406 g	21%	105%
Sulphate	4983 g	597 g	12%	4590 g	92%	104%

Desalination of waste water from chromium(III) recovery plant

Wastewater coming from filter press for separating chromium(III) hydroxide as panels has a high salt content, above legal limits (Tab. A – Merli law) for discharging it in public sewerage. In order to reduce salt content, this liquor was processed in a spiral-wound reverse osmosis module (Separem MSCB 4040) at 30°C temperature, an applied pressure of 38 bar and an axial feed flow rate of 2500 l/h (Cassano *et al.*, 1997).

In Table 4 analytical values obtained on samples from reverse osmosis process are reported. Analytical values obtained on permeate showed a salt concentration below the limits of the law (Cl^- = 120-1000 mg/l; SO_4^{2-} = 60-240 mg/l); moreover, in all permeate samples chromium concentration and TSS were not experimentally detectable. These results suggested reuse of this solution inside the plant, e.g. in filter-press washing, with saving of fresh water.

Table 4. Analytical determinations on samples from reverse osmosis tests

Parameter (mg/l)	Feed	Initial Permeate	Half-run Retentate	Half-run permeate	Final retentate	Final Permeate
PH	7.2	9.5	7.4	6.9	7.5	8.3
TSS	130	n.v.	114	n.v.	178	6
COD	3,817	128	4,847	102	6,553	470
Chloride	8,563	178	9,136	133	14,674	1,078
Sulphate	17,655	75	21,673	41	30,982	167
Chromium	19	n.v.	22	n.v.	24	0.4
Ammon. Nitrogen	302	n.v.	281	25	418	34
Organic nitrogen	91	8	141	18	245	24
Iron	1.8	1.9	2.5	3.5	2.7	3.1
Calcium	35	2.3	45	2.3	66	6.8
Manganese	0.32	0.05	0.36	0.06	0.54	0.16
Aluminium	0.67	0.64	1.01	0.79	1	0.81
Magnesium	24	0.8	26	0.8	38	3.2
Oils and fats	23	1	12	2	14	3

Final retentate of reverse osmosis was used to carry out pickling tests on sheepskins. In this operation the last residual lime in the skin is removed using acidic solutions (sulphuric, chloridic, formic, lactic) in presence of adequate salts concentration (sodium chloride, sodium sulphate and salts of the acid used). Retentate presented a density of 8 °Bè (corresponding to a NaCl solution with a concentration of 87.9 g/l): this value was high enough to allow its reuse in pickling without sodium chloride addition in the bath. Chemical and physical analyses, carried out on treated skins (experimental group), showed that the obtained values were very similar to those measured on a control group pickled with the conventional method.

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest

Further experiments for trying to improve the performance of RO membrane were also carried out. Tests performed at different temperatures (range 15-35°C) showed that reduction percentages of salt species in permeate were slightly higher at temperatures between 20 and 30°C. At various axial flowrates (range 2000-2500 l/h) with constant pressure and temperature, rejection was not dependent on this parameter.

A good restoration of initial flux (Figure 3) using an enzymatic solution (Sepaclean EZ-1) was obtained in cleaning of membrane module.

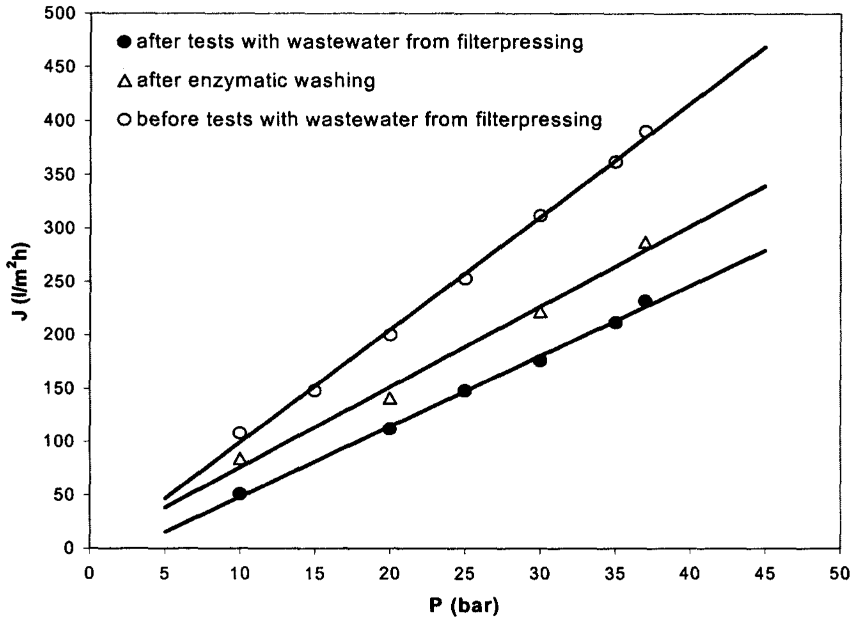

Figure 3. Effect of membrane cleaning at various applied pressures on water permeate flux (Operating conditions: temperature = 30°C; axial flow rate = 2500 l/h).

Good rejection of reverse osmosis membrane to chloride and sulphate ions suggests to employ this technology also in treatment of final waste water from tanneries for concentration reduction of these species before biological treatment.

CONCLUSIONS

The integrated ultrafiltration/nanofiltration process studied in this work, permitted the separation and concentration of chromium(III) salts from tanning exhausted baths. Higher ratio Cr/COD in the concentrate showed a better quality of recovered chromium with respect to conventional recovery processes.

Retentate chromium solutions from nanofiltration (1.35% as Cr_2O_3) were used as such and after further concentration (9.2% as Cr_2O_3) in retanning and tanning operations, respectively. Finished leather showed improved characteristics with respect to control skins. Permeate from nanofiltration with a high chloride concentration, can be used in the pickling step realizing a closed-cycle system.

Reverse osmosis treatment of wastewater coming from the filter-press, after chromium hydroxide separation, permitted us to obtain a permeate to reuse in filter-press washing (saving fresh water) and a concentrate to reuse in the pickling step (saving fresh sodium chloride).

Reduction of environmental impact, simplification of cleaning-up wastewater processes, low sludges production, saving of chemicals and water are some general advantages of these membrane operations.

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest

ACKNOWLEDGMENT

Authors would like to thank Conciaricerca Italia S.r.l. which supported this work within the MURST National Project "Piano Nazionale per la Chimica" – Tema 6; and also Dr. Bertolutti (Consorzio Recupero Cromo, S. Croce S/A, Pisa, Italy) for his help and assistance in carrying out this work.

REFERENCES

Aloy, M. and Vulliermet, B. (1997). Membrane technologies for the treatment of tannery residuals floats. In: *Proceedings of Centenary Congress of IULTCS*, London, 11-14 September 1997, 659-666.

Cassano, A., Drioli, E., Molinari, R. and Bertolutti, C. (1996). Quality improvement of recycled chromium in the tanning operation by membrane processes. *Desalination*, **108**, 193-203.

Cassano, A., Drioli, E. and Molinari, R. (1997). Recovery and reuse of chemicals in unhairing, degreasing and chromium tanning processes by membrane. *Desalination*, **113**, 251-261.

CNR-IRSA (1979). *Metodi analitici per le acque*, CNR-IRSA, vol. 1, Rome.

Consorzio Recupero Cromo. *Impianto centralizzato per il recupero del solfato basico di cromo da reflui di conceria*, Technical Brochure (1992). Consorzio Recupero Cromo, S. Croce S/Arno, Italy.

Fabiani, C., Ruscio, F., Spadoni, M. and Pizzichini, M. (1996). Chromium (III) salts recovery process from tannery wastewaters. *Desalination*, **108**, 183-191.

Gauglhofer, J. (1986). Environmental aspects of tanning with chromium. *J. Soc. Leather Technol. Chem.*, **70**(1), 11-13.

Molinari, R. (1995). Applications of membrane separation techniques to the treatment of tanneries wastewaters. In: *Membrane Technology: Applications to Industrial Wastewater treatment*, A. Caetano et al. (eds.), Kluwer Academic Publishers, The Netherlands, 101-122.

Downloaded from http://iwaponline.com/wst/article-pdf/40/4-5/443/39205/443.pdf
by guest