Treated municipal wastewaters as a sustainable resource of water for the leather industry

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Abstract

The leather industry employs large amounts of water in unit operations of the tanning process which occurs in an aqueous medium. Identify strategies to minimize the quantity of water used in the wet stages of the leather processing is necessary in order to increase the sustainability of this compartment.

In the present work, an integrated pilot scale membrane system (membrane bioreactor unit (MBR) coupled to nanofiltration (NF)) was developed for municipal wastewater reclamation. Its performance was evaluated and designed to meet the water quality criteria in view of its reuse in the tanning process. The feasibility of using reclaimed wastewater in the different wet phases of the tanning process (beamhouse, tanning, re-tanning, dyeing, fatliquoring) for manufacturing of calf skins was investigated on pilot scale. The results showed that the combination of MBR and NF treatments applied to municipal wastewaters is adequate for recovering water with low hardness, very low Fe, Mn and ammonium levels as required by tanneries. The pilot-scale tests demonstrated the technical feasibility of using the reclaimed water in the tanning process. The wet-blue leathers produced with treated water and with softened tap water did not show any considerable differences in terms of physical and sensorial properties and their quality fully satisfied the tannery specifications. The results indicate the use of treated municipal wastewater can be considered a promising solution to reduce the groundwater depletion.

Keywords: Wastewater reclamation, water recycling, membrane bioreactor, nanofiltration, tannery industry

1. Introduction

Wastewater reuse presents a promising solution to the growing pressure on water resources. In many Mediterranean countries water has become an insufficient public commodity because of water scarcity and quality deterioration (Angelakis et al. 1999). Currently, about one third of the world's population lives in areas with moderate to severe water shortage (Audrey and Takashi 2004). In this context, the development of effective solutions that may reduce the exploitation of water resources for industrial purposes assumes aspects of urgency.

The leather industry requires large amounts of water for the tanning process, approximately between 20 and 30 L per kg of raw hide (Bes-Piá et al. 2008). Different solutions have been studied and proposed to increase the sustainability of this compartment as far as the water resources conservation is concerned. Besides all measures and strategies to minimize the quantity of water used in the wet stages of the leather production process (Raghava Rao et al. 2003), the reduction of freshwater consumption by the recovery and reuse of water from the exhaust tannery effluents through the implementation of specific treatments inside the tannery have been proposed. These treatments (mainly physical/chemical and membrane technologies) are suggested either for specific stages of the tanning process (Bes-Pia et al. 2008; Nazer et al. 2006; Raghava Rao et al. 2003) or for the global effluent from a single tannery (Fababuj-Roger et al. 2007; Suthanthararajan et al. 2004).

In the present study, the feasibility of using reclaimed municipal wastewaters in tanning process was investigated. An integrated pilot scale membrane system, consisting in a membrane bioreactor (MBR) followed by a nanofiltration (NF) unit, was applied for the treatment of municipal wastewaters. Experimental activities were performed on the MBR-NF plant in order to optimize the system performance in terms of reduction of hardness, heavy metal and ammonium contents. In order to demonstrate the suitability of the reclaimed water for its use in tanning, upper leathers were manufactured on pilot scale using treated water in contrast with the simultaneous production using softened tap water.

2. Methods and apparatus

2.1 MBR-NF plant

The municipal wastewater effluents coming from the primary settler of the full scale Aquarno wastewater treatment plant (WWTP) (Santa Croce sull'Arno, Tuscany, Italy) were continuously fed to the MBR-NF plant at an average rate of about 400 L/h. Schematic diagrams of the pilot scale MBR and NF plants are reported in Figures 1 and 2, respectively.

The pilot-scale MBR plant reproduces a complete activated sludge biologic treatment in which the wastewaters, after the two steps of de-nitrification (anoxic) and nitrification (aerobic), are treated in a MBR unit. The MBR was provided by Kubota Corporation® (Japan) and the membrane compartment holds 30 m^2 of flat-sheet chloridated polyethylene submerged microfiltration membranes. After reaching the steady-state conditions, MBR permeate was fed to the pilot NF plant, equipped with a spiral wound membrane module. The NF membrane tested was DESAL-HL4040FF from GE-OSMOTICS®. The NF permeates were collected, analyzed and, then, used in the water reuse pilot-scale tests.

The MBR feed, MBR permeate and NF permeate were analyzed in terms of total suspended solids (TSS), chemical oxygen demand (COD), ammoniacal nitrogen ($N\text{-}NH_4$), nitrate ($N\text{-}NO_3$) and nitrite nitrogen ($N\text{-}NO_2$), phosphate phosphorous ($P\text{-}PO_4$), chloride and sulfate levels, permanent and temporary hardness, iron and manganese contents. All the analyses were carried out by technical personal of the Consorzio Aquarno using standard procedures and analysis equipments.

2.2 Water reuse tests in tanning process

The study for testing the water reuse in the tanning process was carried out in a semi-industrial scale. The technology and the chemical formulations used represent the current industrial process.

The pilot scale tests were performed in two identical stainless steel drums (1.2 m diameter, 0.8 m length), loaded with fresh salted calfskins (12-16 kg), following the flowchart shown in Figure 3. The hides were cut into two halves (left and right) by the backbone. The hides were soaked, limed, delimed, bated, pickled and tanned in parallel applying same formulas, chemical products and under the same working conditions but using groundwater (G) (preliminary softened tap water) in a drum and treated water (T) in the other one. Afterwards, chrome re-tanning, dyeing and fatliquoring were carried out on the right sides using groundwater water and on the left half-hide using treated water. This procedure is used to compare the two sides of the original hide (the twin halves) that differ only for the kind of water used in the final stage of the process and it highlights the effect of the water on the quality of the finished leather.

Table 1 shows the experimental runs performed in this study using the method described above.

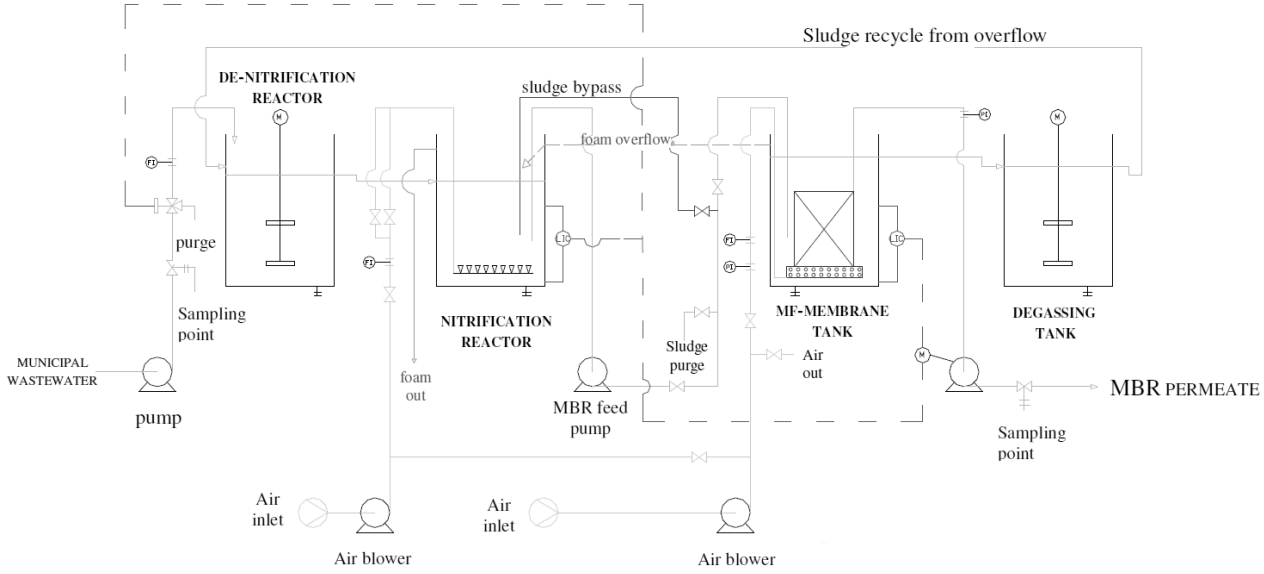

Figure 1. Schematic diagram of the pilot scale MBR plant

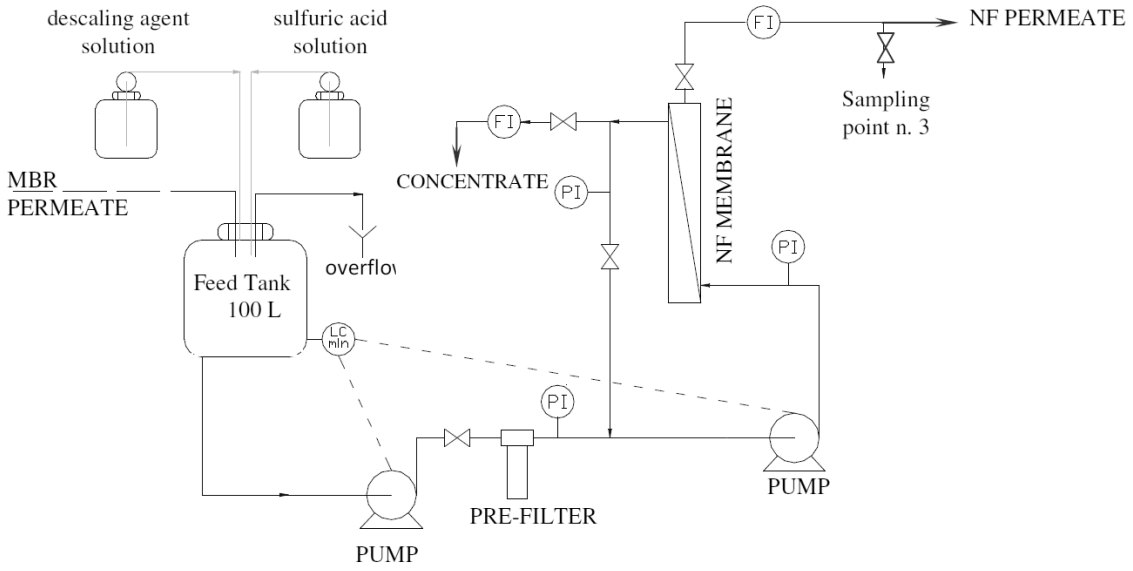

Figure 2. Pilot scale NF plant

The crust wet-blue leathers obtained were characterized in erms of physical and technical properties. Physical tests were conducted according to Italian tandards (UNI 10594) for upper leather. The elongation and load at tear was determined acco ling to the UNI EN ISO 3377:2 method using an electronic dynamometer (Pegasil, Mod. Mart . The data reported are the mean of three determinations. The extension and load at grain crack and break was determined according to the UNI 11038 method using a lastometer Pegasil Mod. EL-51E. The data reported are the mean of three determinations. Technical properties were assessed by the expertise personnel of PO.TE.CO.

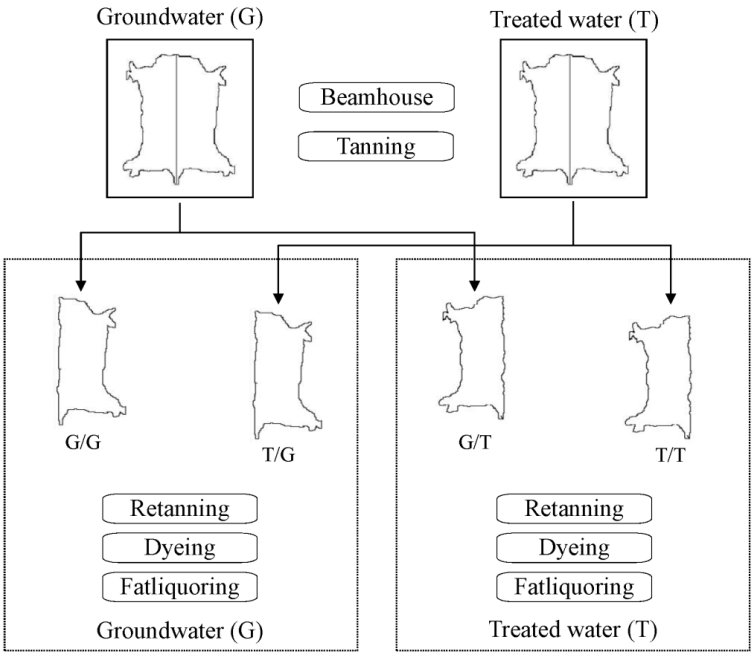

Figure 3. Flowchart of pilot scale tests

Table. 1. Experimental runs

Run	Tanning	Retanning
A	Chrome	Chrome
B	Chrome	Vegetable
C	Vegetable	Vegetable
D	Vegetable	Syntan

3. Results

3.1 MBR-NF performance

As shown in Figure 3, the only MBR process is not able to meet the required specifications in terms of COD, ammonium, total hardness and, in some cases, conductivity. But the combination of MBR-NF processes applied to municipal wastewaters is adequate for recovering water with low hardness (13.6 ± 5.3 °F), low Fe and Mn (< 0.1 mg/L) and ammonium (< 0.1 mgN/L) levels, as requested for use in the tanning process. The values reported in Figure 4 are mean values of measurements carried out daily for 5 days per week of four experimental campaigns lasted 35-40 days each.

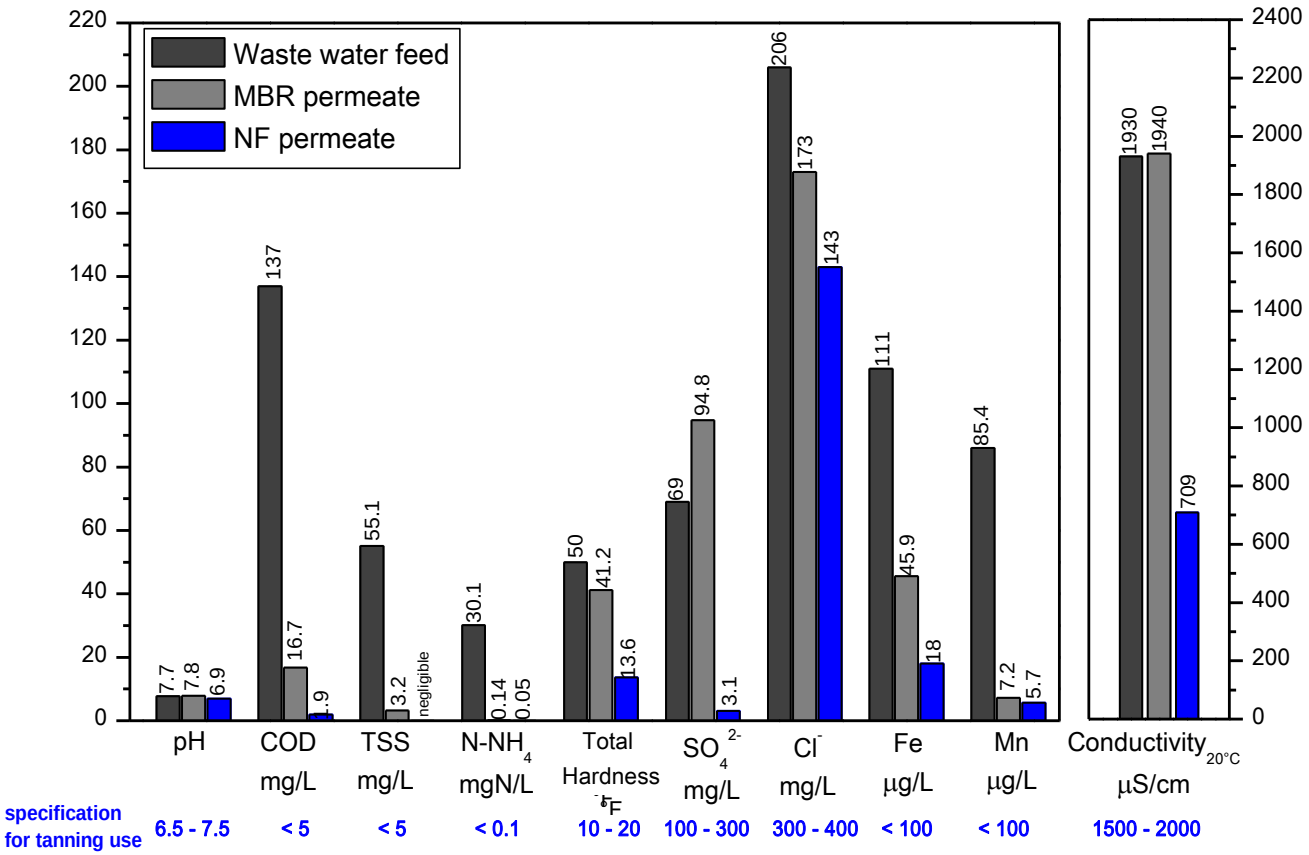

Figure 4. Change of the water properties through the MBR.NF plant

3.2. Leather production with reclaimed water

Table 2 shows the physical properties of the final crust leather samples obtained in the pilot scale tests. The wet-blue leathers produced with reclaimed water and with tap water showed similar physical properties in terms of elongation at tear and tearing load, distension and load at grain crack, extension and load at break. All the samples complied with the standards required for high quality bovine upper leather: tearing load > 80N; distension and load at grain crack ≥ 7 mm and > 200N, respectively. The results of the assessment of the technical properties of the obtained crust leathers are reported in Table 3. Also the technical properties are satisfactory and comparable with those of the crust leathers, satisfying the tannery specifications.

Consequently, the use of treated water in place of the softened tap water in the whole process or in some stages did not involve a decrease in quality of the final leather.

In addition, the treated water has an average total hardness of about 14 °F and, hence, it does not need to be softened before being used in the tanning process. This implies savings since water and salt consumption for the regeneration of softener resins is avoided.

Table 2. Physical properties

		Thickness (mm)	*Elongation at tear (mm)*	*Tearing Load (N)*	*Distension at grain crack (mm)*	*Load at grain crack (N)*	*Extension at break (mm)*	*Load at break (N)*
Run A	G/G	1.43	45.3	108.9	8.1	361.3	10.2	506.8
	G/T	1.49	45.1	108.1	8.6	384.9	10.8	609.4
	T/G	1.39	47.6	107.1	8.6	385.5	11.8	572.5
	T/T	1.40	48.8	110.0	9.3	345.6	11.1	575.0
Run B	G/G	1.51	48.2	112.3	8.5	297.1	11.9	637.6
	G/T	1.49	48.8	112.9	8.7	320.0	11.8	641.9
	T/G	1.54	49.3	114.2	8.7	323.8	12.2	730.3
	T/T	1.53	49.0	123.5	9.7	390.3	13.1	705.6
Run C	G/G	1.46	42.0	139.9	7.6	497.2	9.2	775.0
	G/T	1.43	41.8	142.3	7.0	449.7	8.9	720.9
	T/G	1.68	41.9	152.3	6.9	270.2	10.4	724.0
	T/T	1.60	42.0	139.7	6.4	213.7	9.6	664.7
Run D	G/G	1.65	42.2	142.6	8.3	502.9	9.9	705.9
	G/T	1.54	39.1	135.2	8.0	337.7	9.5	675.5
	T/G	1.44	43.2	117.3	6.9	218.5	9.1	594.1
	T/T	1.62	41.2	120.9	6.8	218.5	10.5	666.5

Table 3. Technical properties (1 = Poor 2 = Fair 3 = Good 4 = Very Good 5 = Excellent)

		Hand	*Roundness*	*Fullness*	*Penetration*	*Intensity*	*Colour levelness*
Run A	G/G	3/4	2/3	2/3	2	3	3/4
	G/T	3/4	2/3	2/3	2	3	2/3
	T/G	3/4	2/3	2/3	2	3	2/3
	T/T	3/4	2/3	2/3	2	3	2/3
Run B	G/G	3	2/3	3	2	3	2/3
	G/T	3/4	3	3	2	3	2/3
	T/G	3/4	2/3	3	2	3	2/3
	T/T	4	3	3	2	3	2/3
Run C	G/G	3	4	4	4	4	2/3
	G/T	3	4	4	4	3/4	2/3
	T/G	3	4	4	4	3/4	2/3
	T/T	3	4	4	4	4	2/3
Run D	G/G	3	2/3	3/4	3	4	2/3
	G/T	3	3	3/4	3	3	2/3
	T/G	3	3	3/4	3	3/4	2/3
	T/T	3	3/4	3/4	3	2/3	2/3

4. Conclusıon

The combination MBR-NF applied to municipal wastewaters permits to obtain water that meets the quality criteria required for use in the wet stages of the tanning process. The suitability of the water obtained for its use in tanning was demonstrated in pilot scale, producing wet-blue leathers from bovine hides using reclaimed water in contrast with the simultaneous production using softened tap water. The results showed that there are no significant differences between the leathers at physical and sensorial levels, demonstrating the quality and usefulness of the reclaimed water did not involve a decrease in the quality of the leathers.

The good results obtained are of great importance, providing a real and sustainable opportunity to implement the reclaimed municipal wastewater reuse in the tanning process for a considerable reduction of large groundwater consumption by the tanning industries. In addition, the use of reclaimed water shows the great advantage that it is not subject to the variability of climatic conditions and it partly frees the groundwater resources currently consumed by the industry and makes them accessible to other uses such as domestic consumption.

5. Acknowledgements

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