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Municipal wastewater reclamation and reuse in the leather industry

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ABSTRACT

In the present work, an integrated pilot-scale membrane system (membrane bioreactor–nanofiltration [MBR–NF]) was applied to the treatment of municipal wastewater to produce reclaimed water. Its performance was evaluated and designed to meet the requirements of the water quality to use in the tanning process. The feasibility of using reclaimed wastewater in the different wet phases of the tanning process (beamhouse, tanning, re-tanning, dyeing, and fatliquoring) was investigated on a pilot scale for manufacturing chrome-tanned leathers. The results showed that the combination of MBR and NF processes applied to municipal wastewaters was adequate for recovering water with low hardness, very low Fe, Mn, and ammonium levels as required by tanneries. The pilot-scale tanning tests demonstrated that there were no significant differences between the wet-blue (chrome-tanned) leathers produced using treated wastewater and those produced using softened tap water in terms of physical and sensorial properties. Hence, the suitability of the treated water for use in the tanning was verified and validated.

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 [1]. Currently, about one-third of the world's population lives in areas with moderate to severe water shortage [2]. In this context, the development of effective solutions that may

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reduce the exploitation of water resources for industrial purposes assumes the aspects of urgency.

The industrial activity of leather tanning is included among those that consume large amounts of water, approximately between 20 and 30 L per kg of raw hide processed [3]. Since the leather industry is an important sector in many developing countries, the possibility of reusing reclaimed municipal wastewaters in the numerous aqueous steps of the tanning process assumes a great significance, proving a sustainable solution to the conservation of the groundwater reserves.

Different solutions have been studied and proposed to minimize the quantity of water used in the different wet stages of the process [4], and to reduce freshwater consumption by the recovery and reuse of water from the exhaust tannery effluents through the implementation of specific treatments (mainly physical/chemical and membrane processes) inside the tannery. Besides, treatments have been suggested either for effluents from specific stages of the tanning process [3,5–7] or for the global tannery wastewaters [8,9].

The combination of a membrane bioreactor (MBR) coupled to a membrane process such as reverse osmosis (RO) [10,11], nanofiltration (NF) [11,12], or ultrafiltration (UF) [13] has been successfully applied to advance the treatment of municipal wastewater to produce reclaimed water. MBR is an innovative technology that combines the traditional activated sludge (AS) process with a membrane separation process, such as microfiltration or UF, used to separate effluent from AS. In recent years, this technology has become one of the most promising and effective alternative to the conventional AS process for the treatment and reuse of industrial and municipal wastewaters due to its high-quality effluent (free of total suspended solids (TSS) and bacteria) and small foot print [14]. Furthermore, the development of MBR configurations with submerged membranes has reduced the energy consumption of such systems, and has expanded its presence in various industrial and domestic wastewater treatment applications. The coupling of membrane solid/liquid separation with AS process offers numerous advantages over conventional biological processes, including effluent suitable for reuse, elimination of settling basins, and independence of process performance from filamentous bulking or other phenomena affecting settle-ability. The separation of biomass from effluent by membranes permits to operate at higher mixed liquor-suspended solids' (MLSS) concentrations and sludge residence time in the bioreactor compared to conventional settlement separation systems, thus reducing the reactor volume to achieve the same loading rate. Recent technical improvements and significant membrane cost reduction have enabled MBRs to become an established process option to treat wastewaters, as evidenced by their constantly rising numbers and capacity [15].

The objective of the present work was to investigate the technical feasibility of an integrated pilot-scale membrane system (MBR–NF) for the municipal wastewater reclamation and reuse in leather making process. As reported in previous studies [1,3], direct NF has proved to represent an appropriate and robust technology for reclamation of wastewaters treatment plant effluents, showing good removal rates for most micro-contaminants and producing a permeate free of bacteria and viruses, with low hardness and organic matter content.

Experimental activities were performed on a pilot-scale MBR-NF plant in order to optimize the system performance mainly in terms of reduction of hardness, heavy metal (Fe and Mn), 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. The quality of the finished leathers produced with and without treated water was evaluated in terms of physical and technical properties.

2. Methods and apparatus

2.1. MBR-NF plant

Schematic diagrams of the pilot-scale MBR and NF plants used for municipal wastewater treatment are reported in Figs. 1 and 2, respectively. The MBR-NF system was installed in the full-scale Aquarno AS wastewater treatment plant (WWTP) (Santa Croce sull'Arno, Tuscany, Italy) having a capacity of 20,000 equivalent inhabitants. Real raw municipal wastewater coming from the primary settler was continuously fed to the submerged-type MBR plant at an average rate of 400–420 L/h. MBR plant reproduces a complete AS biologic treatment in which the wastewaters, after the two steps of denitrification (anoxic) and nitrification (aerobic), are treated in a membrane compartment (3.65 m3) for biomass removal. The MBR was provided by Kubota Corporation® (Japan) and the membrane compartment holds 30 m^2 of flat-sheet chloridated polyethylene submerged microfiltration membranes (porous size of 0.4 μm). After reaching the steady-state conditions, MBR permeate was further treated continuously in the pilot NF plant, equipped with a spiral wound membrane module, to produce a higher quality of water. The NF membrane tested was

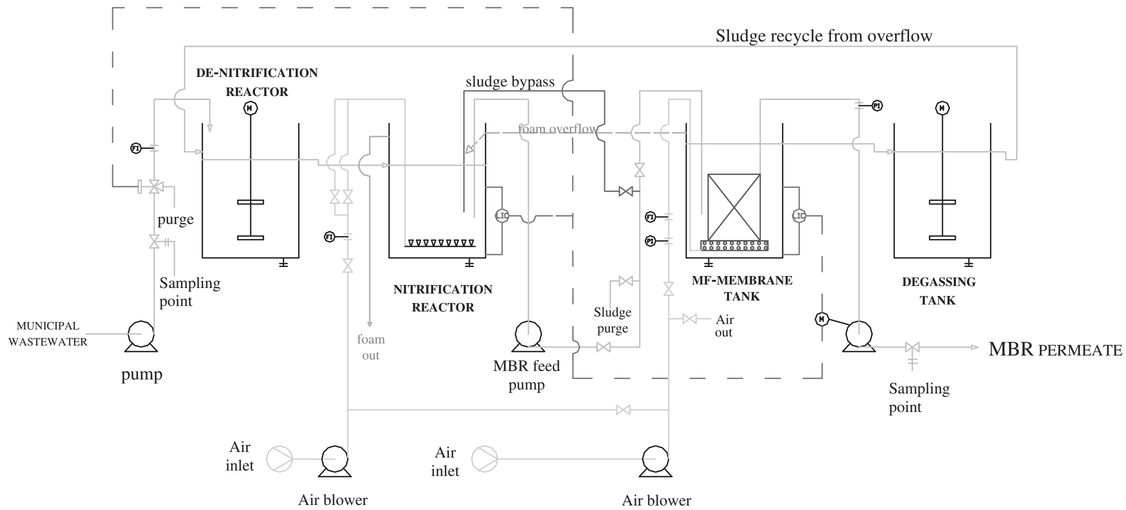

Fig. 1. Schematic diagram of the pilot-scale MBR plant.

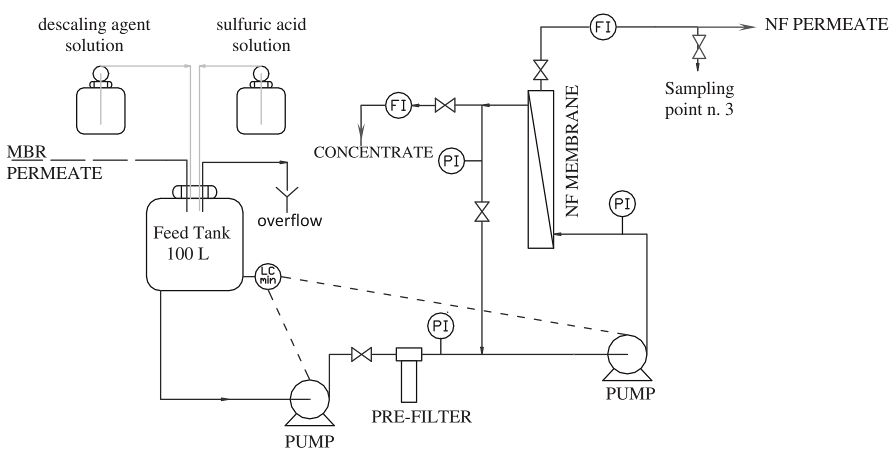

Fig. 2. Schematic diagram of the pilot-scale NF plant.

DESAL-HL4040FF from GE-OSMOTICS®. Periodically, the NF membrane was cleaned by circulating chemical products' solutions in the system for 10 min without applying any pressure in order to eliminate the organic and inorganic substances that clogged the membrane.

The NF retentate was purged, and the permeate was collected in a storage tank (20 m^3) and analyzed before being used in the pilot-scale tanning tests.

Four experimental and sampling campaigns lasting 35–40 days each were performed in order to produce the water quantity necessary for the tanning tests. Water samples were taken daily for 5 days per week. The sampling points were: (1) fresh wastewater from primary settler (MBR feed); (2) MBR permeate, i.e. feed for NF modules; and (3) total NF permeate. The MBR feed, MBR permeate, and NF permeate were analyzed in terms of TSS, chemical oxygen demand (COD), ammoniacal nitrogen ($N–NH_4$), nitrate ($N–NO_3$), nitrite nitrogen ($N–NO_2$), phosphate phosphorous ($P–PO_4$), chloride and sulfate levels, permanent and temporary hardness, and iron and manganese contents.

All the analyses were carried out by technical personal of the Consorzio Aquarno using standard procedures and analysis equipments.

The average operating conditions of the MBR and NF membrane processes adopted during the experimental campaigns are summarized in the Tables 1 and 2, respectively.

2.2. Water reuse tests in pilot scale

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

Table 1
The operating conditions of the MBR unit

Feed flow rate (L/h)	420
Permeate flow rate (L/h)	400 ± 8
Retentate recycle (L/h)	1,304 ± 98
Dissolved oxygen (mg/L)	30 ± 0.5
Mixed liquor suspended solids (MLSS) (g/L)	7.3 ± 0.97
MBR Feed pH	7.8 ± 0.2
Hydraulic retention time (HRT) (h)	20.8
Transmembrane pressure (kPa)	7.8 ± 3.7
Temperature (℃)	10–15
Cleaning air flow rate (Nm^3/h)	38.9 ± 2.8
Oxidation air flow rate (Nm^3/h)	2.5

Table 2
Operating conditions of the NF unit

Permeate flow rate (L/h)	180 ± 28
Concentrate flow rate (L/h)	100 ± 8
Transmembrane pressure (kPa)	652 ± 164
Temperature (℃)	12 ± 3
pH	6.9 ± 0.3

the procedure schematized in Fig. 3. The hides were cut into two halves (left and right) by the backbone. The hides were soaked, limed, delimed, bated, pickled, and chrome-tanned in parallel applying the 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 side using groundwater and on the left side of the same hides using treated water. The labels reported in Fig. 3 indicate the type of water used in the early stages (beamhouse, tanning) of the process and in the final stages (retanning, dyeing, and fatliquoring).

The final crust wet-blue leathers obtained were characterized in terms of physical and technical properties. Physical tests were conducted according to Italian standards (UNI 10594) for upper leather. The organoleptic properties with regard to hand, softness, fullness, roundness, dye quality, and possible defects were assessed by the technical personnel of PO.TE. CO.

3. Results

3.1. MBR-NF performance

The main characteristics of the fresh groundwater, actually used in the Tuscan leather district, are reported in Table 3 along with the specifications required for use in the wet stages of the tanning process and the average characteristics of the real effluent of the full-scale Aquarno WWTP. As shown, the local groundwaters do not meet all the required specifications, particularly in terms of total hardness, iron, and

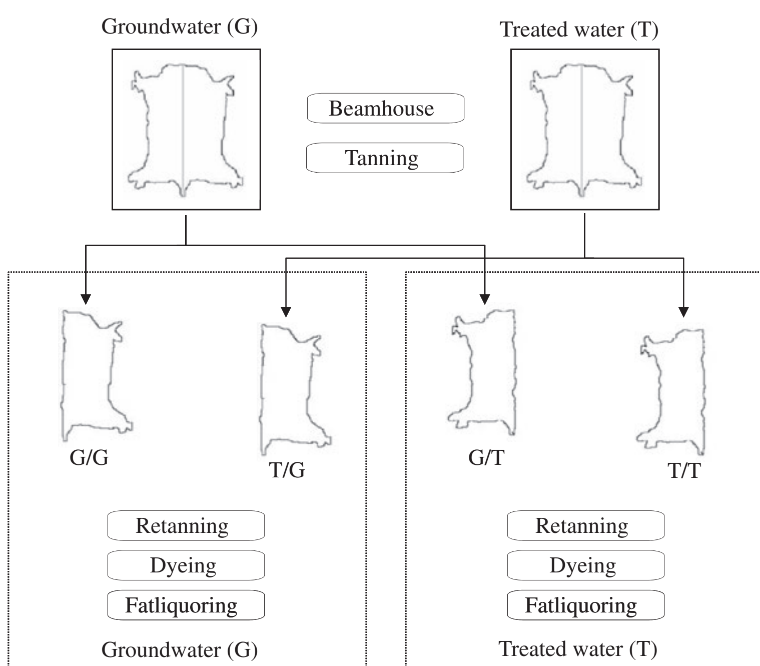

Fig. 3. Flowchart of pilot-scale tanning tests.

Table 3
Average characteristics of the fresh groundwaters, the Aquarno WWTP effluent, and specifications for tanning process

Property	Groundwater	Aquarno WWTP effluent	Water specifications
pH	7–7.5	7.5–8.5	6.5–7.5
Conductivity (μS/cm)	1,500–2,000	2,000–3,000	1,500–2,000
COD (mg/L)	5–10	80–120	<5
TSS (mg/L)	–	20–40	<5
Ammonium ($N–NH_4^+$) (mgN/L)	0.5–2.5	<5	<0.1
Total hardness (°F)	40–60	80–120	10–20
Phosphates ($P–PO_4^{3-}$) (mgP/L)	0.5–1	1.5–3.5	<0.5
Sulfates (SO_4^{2-}) (mg/L)	150–300	150–300	150–300
Chlorides (Cl^-) (mg/L)	300–400	500–700	300–400
Fe (mg/L)	1.5–2.5	0.2–0.5	<0.1
Mn (mg/L)	1.5–2.5	0.2–0.5	<0.1

manganese. Hard waters are undesirable in the tanning process: collagen softening and deliming in the preparation of hides is hindered [16]. Calcium and magnesium may form insoluble compounds with vegetable and synthetic tannings resulting in incomplete tanning. The uneven deposition of these salts on the hides causes patchiness during dyeing operation. In addition, calcium and magnesium may react with dyes and fatliquors reducing their effectiveness in the post-tanning operations. To prevent all these problems caused by hardness, the local groundwaters are usually softened by ion exchange resins prior to being used by the tanneries.

Also iron and manganese interfere in various ways. Iron and manganese can form dark-colored precipitates during tanning, which subsequently reduce tanning efficiency. In dyeing operations, they may form complexes with dyes, rendering them inactive and resulting in discoloration, color changes, and dulling of shades. The ion exchange processes used for reducing the hardness are efficient also for the removal of Fe and Mn.

As shown in Table 3, for the WWTP effluent, also COD, salt concentrations, TSS, and chlorides are higher than those required. Consequently, the WWTP

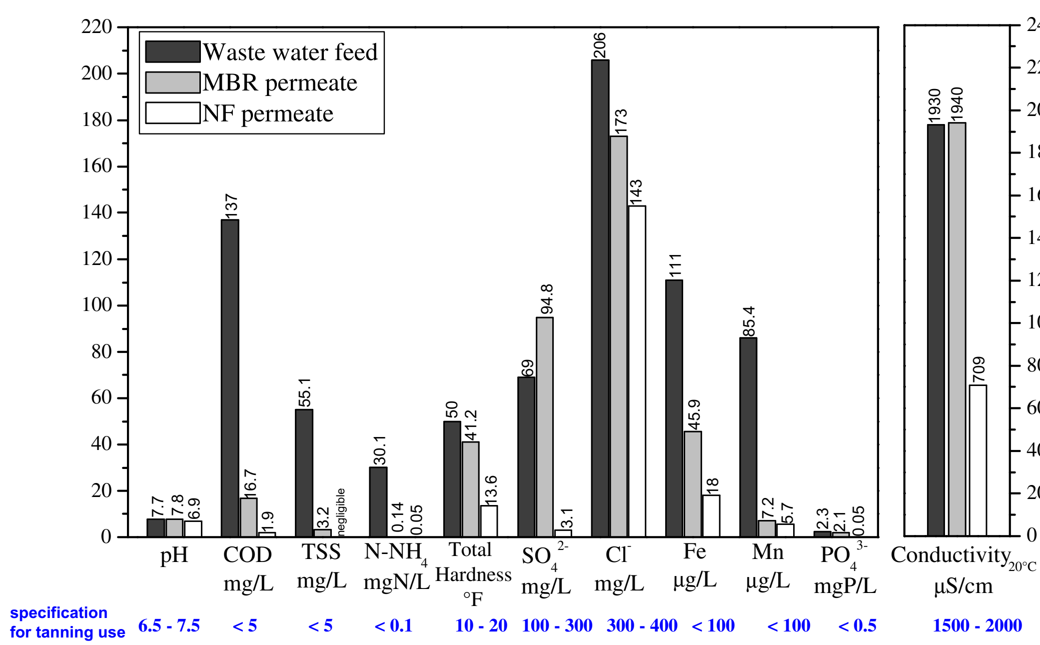

Fig. 4. Changes of the water properties through the MBR-NF plant.

Table 4
Physical and technical properties of the produced leathers

Tanning/retanning	Chrome/Chrome				UNI 10,594
Type of water[a]	G/G	G/T	T/G	T/T	guidelines
Physical properties					
Thickness (mm)	1.43	1.49	1.39	1.40	
Elongation at tear (mm)	45.3	45.1	47.6	48.8	–
Tearing load (N)	108.9	108.1	107.1	110.0	30–80[b]
Distension at grain crack (mm)	8.1	8.6	8.6	9.3	⩾7
Load at grain crack (N)	361.3	384.9	385.5	345.6	150–200
Extension at break (mm)	10.2	10.8	11.8	11.1	–
Load at break (N)	506.8	609.4	572.5	575.0	–
Technical properties[c]					
Hand	3/4	3/4	3/4	3/4	
Roundness	2/3	2/3	2/3	2/3	
Fullness	2/3	2/3	2/3	2/3	
Penetration	2	2	2	2	
Dyeability	3	3	3	3	
Color brightness	3/4	2/3	2/3	2/3	

[a]G: groundwater and T: treated water.
[b]Depending on the end use.
[c]1 = Poor, 2 = fair, 3 = good, 4 = very good, 5 = excellent.

effluent cannot be directly used in the tanning process but it must be properly treated before being used.

Fig. 4 shows the average performance of the only MBR system and the combined MBR-NF processes. The values reported are mean values of measurements carried out daily for 5 days per week of the four experimental campaigns. As it can be seen, the only MBR process was not able to meet the required specifications in terms of COD, ammonium, total hardness, and, in some cases, conductivity. But the combination of MBR coupled to NF process was adequate for recovering water with low hardness (13.6 ± 5.3˚F), Fe and Mn (<0.1 mg/L) and ammonium (<0.1 mgN/L) levels, and COD (<5 mg/L), as requested for its use in the tanning process.

3.2. Leather production with reclaimed water

Table 4 shows the physical and technical properties of the final crust leather samples obtained in the pilot-scale tests. The data reported are mean values of at least three determinations (three samples obtained using the same combinations of water). The wet-blue (chrome-tanned) leathers produced with reclaimed water and with tap water showed similar physical properties in terms of thickness, elongation at tear, tearing load (>80 N), distension (⩾7 mm), and load (>200 N) at grain crack, extension, and load break. All the samples complied with the standards required for high-quality bovine upper leather. Also the technical properties are comparable with those of the crust leathers, satisfying the tannery specifications. Consequently, the use of the treated water in place of the softened tap water in the whole process or in some stages did not involve a decrease in the quality of the final leather. In addition, the treated water does not need to be softened before being used in the tanning process having an average total hardness of about 14˚F. This implies further savings since water and salt consumption for the regeneration of softener resins would be avoided.

4. Conclusion

The combination of MBR-NF treatment applied to municipal wastewaters permitted to obtain water that met the quality criteria required for use in the wet stages of the tanning process in terms of low hardness (about 14˚F), very low levels of Fe and Mn (<0.1 mg/L), and ammonium (<0.1 mgN/L). The suitability of the water obtained for its use in tanning was demonstrated on 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 were no significant differences between the produced leathers at physical and sensorial levels, demonstrating that the quality and usefulness of the reclaimed water did not involve a decrease in the quality of the finished 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 on industrial scale for a considerable reduction of large groundwater consumption by the tannery industry. 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.

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