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Integration of membrane bioreactor and advanced oxidation processes for water recovery in leather industry

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ABSTRACT

Nowadays, the conventional tannery wastewater treatment is not established in order to obtain water in such a quality that it could be reused in the same process. This study was then carried out in order to study an integrated wastewater treatment system, membrane bioreactor–photoelectrooxidation (MBR–PEO), for the final polishing of tannery wastewater. MBR is responsible for the remaining biochemical oxygen demand removal, while the refractory matter, quantified as chemical oxygen demand, is removed by PEO. This treatment configuration has provided two wastewater streams with quality standards for reuse as process water. The wastewater treated by the MBR could be reused in beamhouse operations, while the wastewater treated by the integrated MBR–PEO processes could be recycled for the tanyard and re-tanning steps due to its appreciable quality.

Keywords: Tannery wastewater treatment; Water reuse; MBR; Photoelectrooxidation

1. Introduction

Brazil has a privileged world position related to water resources availability. Nevertheless, the use and treatment of water is not always well established and, many times, there is still an outflow of chemical compounds after the industrial effluents treatment. This situation is detectable at the hydrographical region of Atlântico Sul, located on the State of Rio Grande do Sul, which includes different hydrographical basins. One of them is the Sinos River Basin, which has 1.4 million inhabitants. The basin has 650 industries, from which 81 are tanneries [1].

The leather and footwear sector is one of the most important for this region and the largest in this sector in Brazil, accounting for nearly 60% of Brazilian's processed leather [2]. The leather industry requires a lot of water for the tanning process, around 30–35 L of water per kilogram of hides [3,4], and its survival is strongly dependent on water from the Sinos River Basin. The success of the leather industry in this region is then inwardly linked to the conservation of this water resource [5]. Thus, to improve the Sinos River Basin situation, the reuse of wastewater as

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process water on the tannery industry would be enormously important.

The production and trade of leather provide many economic and social benefits; however, it generates considerable environmental and human health costs, since the tanning processes require considerable amounts of chemicals. Besides, to ensure the complete reaction of the chemicals with the hides they are added in excess, and thus, this leftover will be present in the wastewaters [6].

Tannery wastewaters have a high variability due to the different operations associated with tanning processes and to the different procedures used for hide preparation, tanning and finishing. Therefore, tanneries are typically characterized as pollution intensive industrial complexes, which generate widely varying, high-strength wastewaters [7–9]. According to Durai and Rajasimman [7], this wastewater is among one of the most hazardous pollutants of industry, and has one of the highest toxic intensity per unit of output, since at least about 300 kg of chemicals per ton of hides are used during tanning processes. Basically, tannery wastewater is considered high strength because its components are in huge amount generating, for instance, high amount of chemical oxygen demand (COD), five-day biochemical oxygen demand (BOD_5), ammonia, suspended solids or heavy metals [10].

The high concentration of pollutants with low biodegradability in tannery wastewaters (0.3 BOD_5/COD ratio) represents a serious and current technological and environmental challenge [11], since this high-strength wastewater is difficult to be treated by the conventional processes currently employed: activated sludge and aerated lagoons [3]. Furthermore, the beneficiation process of hides employs a high amount of water and, consequently, generates a proportional amount of wastewaters.

Thus, the leather industry is being urged to search cleaner, economically and environmentally sustainable wastewater treatment technologies that can recover and recycle chemicals and water in order to avoid their discharge into environment [3,11]. Thus, technologies as photoelectrooxidation (PEO) and membrane bioreactors (MBRs) are gaining prominence for this purpose [3,12–17].

PEO process consists of a combination of electrolysis and heterogeneous photocatalysis, and, thereby, causes the generation of transitory species with high oxidative power, where the most notable is the hydroxyl radical ($HO^•$). This radical has a high oxidative power and low selectivity, being able to oxidize most of the organic pollutants in a relatively short time, and even cause their complete mineralization [18].

MBR is a combination of biological reactor with membrane separation process where the solid/liquid separation is achieved by microfiltration or ultrafiltration membranes [19]. They provide a relatively compact alternative to conventional biological treatment options, producing a high-quality effluent even at high and varying organic loading rates. However, the MBRs have a key drawback, the membrane fouling. Fundamentally, fouling gradually occurs over filtration time and can occur in different ways, such as adsorption, pores blocking, deposition of particles or gel formation on the membrane, causing, as a consequence, a large drop in the permeate flux [20]. Despite the intense researches on this subject, fouling is still the greatest problem of the MBRs, which is potentiated when it is applied to treat high-strength wastewaters like the ones from tanneries [21].

In the light of these considerations, this work investigates the feasibility of using a MBR–PEO integrated process for tertiary treatment of tannery wastewater aiming the achievement of quality water for industrial reuse. At the same time, through scanning electron microscopy (SEM) and thermogravimetric analysis (TGA), the membrane fouling is investigated.

2. Materials and methods

The general experimental flow sheet used in this work is presented in Fig. 1. The wastewater was collected at the discharge point of the conventional effluent treatment plant (CETP) of a tannery that carries out all industrial processes from raw hides to finished leather. This CETP uses physicochemical treatment followed by activated sludge.

2.1. Treatment with MBR

The MBR has an external membrane and operating volume of 3 L. The wastewater is pumped, by a peristaltic pump, from the feeding tank to the bioreactor, which is kept in complete mixture by an aeration system to maintain the biomass in suspension while providing oxygen to the micro-organisms. A diaphragm pump sends the mixed liquor from the bioreactor to the membrane module, which separates it in two

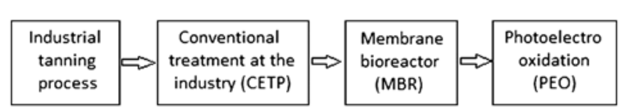

Fig. 1. Experimental scheme for the tannery wastewater treatment.

flows: retentate, which is returned to the aeration tank (bioreactor); and permeate, which is collected in the permeate tank. A flat-sheet cellulose ester membrane, supplied by Millipore, with 0.2 μm pore size, active area of 55 cm^2 and driven at tangential flow was used. The MBR experimental set-up is shown in Fig. 2.

The MBR was inoculated with activated sludge not previously acclimated obtained from a municipal sewage treatment plant (Porto Alegre, Brazil). Initial concentration of mixed liquor suspended solids (MLSS) was 10,000 mg L^{-1}. Initial hydraulic retention time was 6.25 h. Transmembrane pressure (TMP) was kept constant at 0.6 bar and the highest tangential velocity (2 m s^{-1}) was used. The MLSS, TMP and tangential velocity parameters adopted in this work are product of previous studies [22,23]. The temperature in the bioreactor remained stable over time (27–30˚C).

The MBR was ran in two campaigns (each one with a new membrane, but from the same manufacturing batch), so that the first and the second campaigns lasted for 105 and 360 h, respectively. In the first campaign, the MBR was fed with synthetic effluent. The second campaign was divided into two phases: (i) during the initial 190 h, the MBR was fed with synthetic effluent; (ii) in the second phase, lasting 170 h, the synthetic effluent was replaced, without interruption of operation, by tannery wastewater collected after the secondary treatment in a tannery located at the Rio dos Sinos Region in Southern Brazil.

2.2. Treatment by PEO process

The PEO experiments were performed in a 3 L photoelectrochemical bench-scale reactor under complete mixing. The reactor consists of a glass cylinder, jacketed with circulation of cooling solution by an ultra thermostatic bath from Nova Ética—Model 521/3D. The reactor also includes a pair of electrodes and mercury vapour lamps without bulb and inside a quartz tube. Fig. 3 schematically illustrates the photoreactor used in the experiments.

A light bulb from a 400 W high-pressure mercury-vapour lamp from Avant® was inserted in a quartz tube and used as UV source. To optimize the use of radiation, the electrodes were concentrically arranged into the photoreactor.

A pair of commercial electrodes from De Nora®—Brazil was used. The anode was coated with a mixture of ruthenium and titanium oxides in $70TiO_2/30RuO_2$ proportion, while the cathode was made of titanium oxide. The experiments were conducted using 3 L of wastewater, current density of 30 mA cm^{-2} and for a period of 1 h.

2.3. Synthetic effluent

The synthetic effluent was prepared using ethanol as carbon source to present a COD of 500 mg L^{-1}; it was complemented with micronutrients necessary to achieve adequate microbial metabolism [24]. This synthetic effluent, adapted from Provenzi [25] and Kimura et al. [26], was elaborated with these features to provide an assessment of the MBR operation. Its composition is shown in Table 1.

2.4. Tannery wastewater

A sample of 100 L of wastewater was collected at the discharge point of the CETP from a tannery, located at the Rio dos Sinos Region, where most leathers produced are chrome tanned. Immediately after collection, the wastewater was subjected to characterization.

2.5. Analytical methods

During the MBR runs, permeate flux and temperature in the bioreactor were monitored. To evaluate the

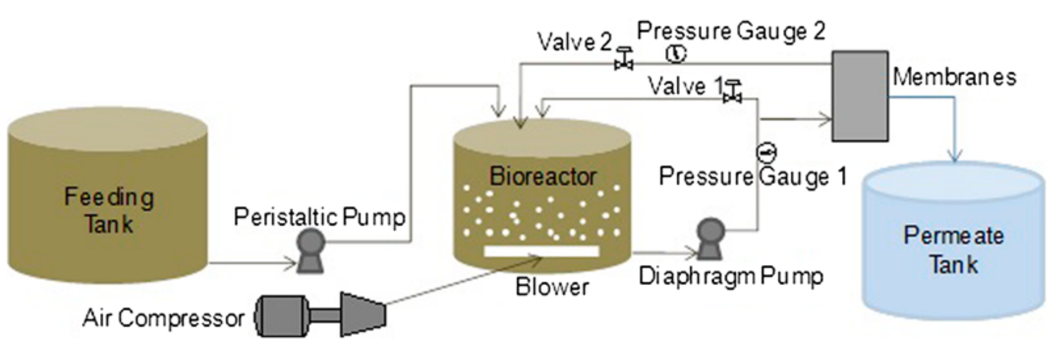

Fig. 2. MBR experimental set-up.

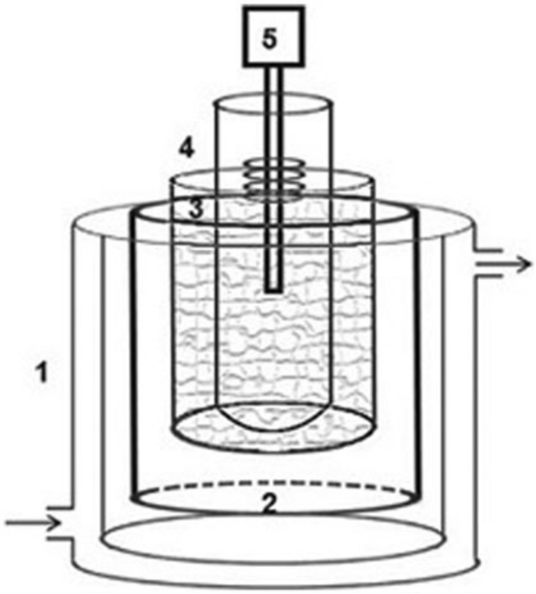

Fig. 3. Schematic representation of photoreactor: (1) glass reservoir; (2) titanium oxide cathode; (3) titanium and ruthenium oxides anode; (4) quartz tube; and (5) mercury vapour lamp.

efficiency of the treatment systems, COD, BOD_5, total Kjeldahl nitrogen (TKN), total-P, chlorides, sulphates, sodium, calcium and chrome analyses were made. All analyses were carried out in duplicate following the standard methods [27].

2.6. Analysis of the membrane

After finishing the second MBR campaign, a procedure for cleaning and dismounting the system was carried out. Initially, the sludge was removed from the bioreactor. Subsequently, water was re-circulated through the system to remove the remaining material inside the pipes. This procedure was performed with fully open valves to ensure the absence of pressure in the system. Thus, the membrane was removed and subjected to analysis by SEM and TGA to evaluate its conditions after use, comparing to analysis carried out before use.

2.6.1. SEM analysis

Points in the central region of the membrane were selected for analysis by SEM (JEOL, model 6060) with image acquisition system. For sample preparation, the membranes were cryogenically fractured with liquid nitrogen and then coated with gold to make its surface conductive. Afterwards, transverse and surface micrographs of the new membrane and of the one used in the MBR were accomplished.

2.6.2. Thermogravimetric analysis

Similar samples to those analysed by SEM were forwarded to TGA (Universal V4.2E TA Instruments). Analyses on the membranes before and after the MBR operation were performed. The heating ramp was 20°C min^{-1} between room temperature and 1,000°C in a nitrogen atmosphere. This technique was used in order to identify the degradation temperature of the membrane and to determine the amount of organic and inorganic material that was deposited on or inside the membrane pores.

3. Results and discussion

3.1. Permeate flux

The first MBR campaign started with a permeate flux greater than 85 L h^{-1} m^{-2}, but has been decreasing

Table 1
Composition and concentration of the synthetic effluent fed to the MBR

Compound	Chemical formula	Concentration (mg L^{-1})
Ethanol 96 GL P. A.	CH_3CH_2OH	0.25
Ammonium sulphate P. A.	$(NH_4)_2SO_4$	97.54
Ammonium phosphate dibasic P. A.	$(NH_4)_2HPO_4$	21.29
Ferric chloride P. A.	$FeCl_3{\cdot}6H_2O$	2.42
Calcium chloride P. A.	$CaCl_2{\cdot}2H_2O$	0.37
Zinc sulphate P. A.	$ZnSO_4{\cdot}7H_2O$	0.44
Copper Sulphate P. A.	$CuSO_4{\cdot}5H_2O$	0.39
Cobalt chloride P. A.	$CoCl_2{\cdot}6H_2O$	0.42
Potassium chloride P. A.	KCl	0.42
Magnesium chloride P. A.	$MgCl_2{\cdot}6H_2O$	0.42
Manganese sulphate P. A.	$MnSO_4{\cdot}H_2O$	0.42

over time and tended to stabilize for about 60 L h^{-1} m^{-2} after 105 h of operation. Like the first MBR campaign, the second one presented a resembling permeate flux during the same operation time. However, after 360 h, the permeate flux stabilized at 43 L h^{-1} m^{-2} (Fig. 4). In equivalent conditions, i.e. 360 h and also with an external MBR, Badani et al. [28] obtained similar permeate flux, 42 L h^{-1} m^{-2}. Furthermore, it may be noted that, after the substitution of the synthetic effluent by the tannery wastewater, the permeate flux had a slight reduction and tended to stabilize, indicating that fouling was not significant. This gentle decline in the permeate flux and its stabilization at a high level, at the end of 360 h, can be attributed to the large hydrodynamic forces adopted in this work, with tangential velocity of 2 m s^{-1} that represents a regime of turbulent flow, with Reynolds number of 5,785. According to Böhm et al. [29], these outcomes were obtained because the layers that would deposit on the surface could be reduced or completely removed by the maintenance of an elevated permeate flux.

In contrast, studies with submerged MBR reported permeate fluxes of 8–13 L h^{-1} m^{-2} [30–34], while Melin et al. [35] found that the mean flux ranges from 25 to 35 L h^{-1} m^{-2}. These authors explain that, in submerged MBRs, working with smaller permeate fluxes increases the interval between membrane cleanings.

In this work, with an external MBR, permeate fluxes of 43 L h^{-1} m^{-2} were obtained after 360 h of operation. This high flux should indicate no fouling in the membranes, but considering that all the researches with MBR treating tannery wastewaters explain that the main problem associated to this technology is the membrane fouling; and that at higher operation times, there could be a more pronounced drop in permeate fluxes, the membrane after use was investigated by SEM and TGA.

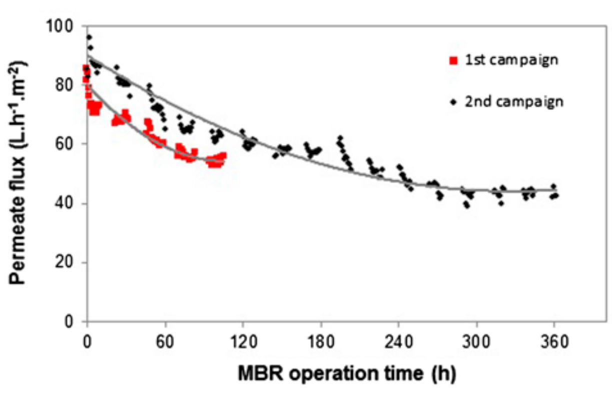

Fig. 4. Permeate flux variation vs. MBR operation time.

3.2. Analysis of the membrane

The membrane analyses (SEM and TGA) provided information about the conditions of post-use membrane.

3.2.1. SEM analysis

Fig. 5(a) and (b) present micrographs of the membrane before being used in the MBR, showing that the membrane structure is homogeneous both in the surface and in the cross-section.

According to the transversal micrograph of the post-use membrane (Fig. 5(c) and (d)), the fouling layer has approximately 12 μm of thickness. The visual appearance of the material layer deposited on the membrane seems compact, creating a physical barrier that hinders the permeability. However, there is no hint that the fouling penetrates in the membrane pores, with a deposit only on its surface, forming a micro-organisms and organic matter cake layer. The Fig. 5(e) and (f) show the surface of the fouled membrane, so that the presence of micro-organisms can be observed, which meets the reports of other studies [36–39]. The slight fouling present only on the membrane surface indicates that, when it is necessary to restore the permeate flux, a brief cleaning procedure would be sufficient.

3.2.2. Thermogravimetric analysis

Fig. 6 shows the TGA curve of the new membrane; it can be observed that the membrane consists of a single material, because in a small temperature range, around 200˚C, there was approximately 97% of mass loss. The analysis was finished at 675˚C, resulting in only 0.2% of residues. Thus, it can be stated that the sample has high purity, namely, it is virtually free from contamination and/ or mineral fillers.

The TGA of the post-use membrane shows that up to 200˚C there was a weight loss of about 10%, which can be attributed to the presence of humidity and volatile organic compounds in the sample, which are not part of the membrane constitution. Around 200˚C, namely, the characteristic temperature of the membrane degradation, there was a 46% loss. Following this temperature until 500˚C, taken by the Standard Methods [27] as the temperature adopted to volatilize any organic compound in volatile solids analysis, the loss was around 21%, which is mostly attributed to organic matter (micro-organisms and

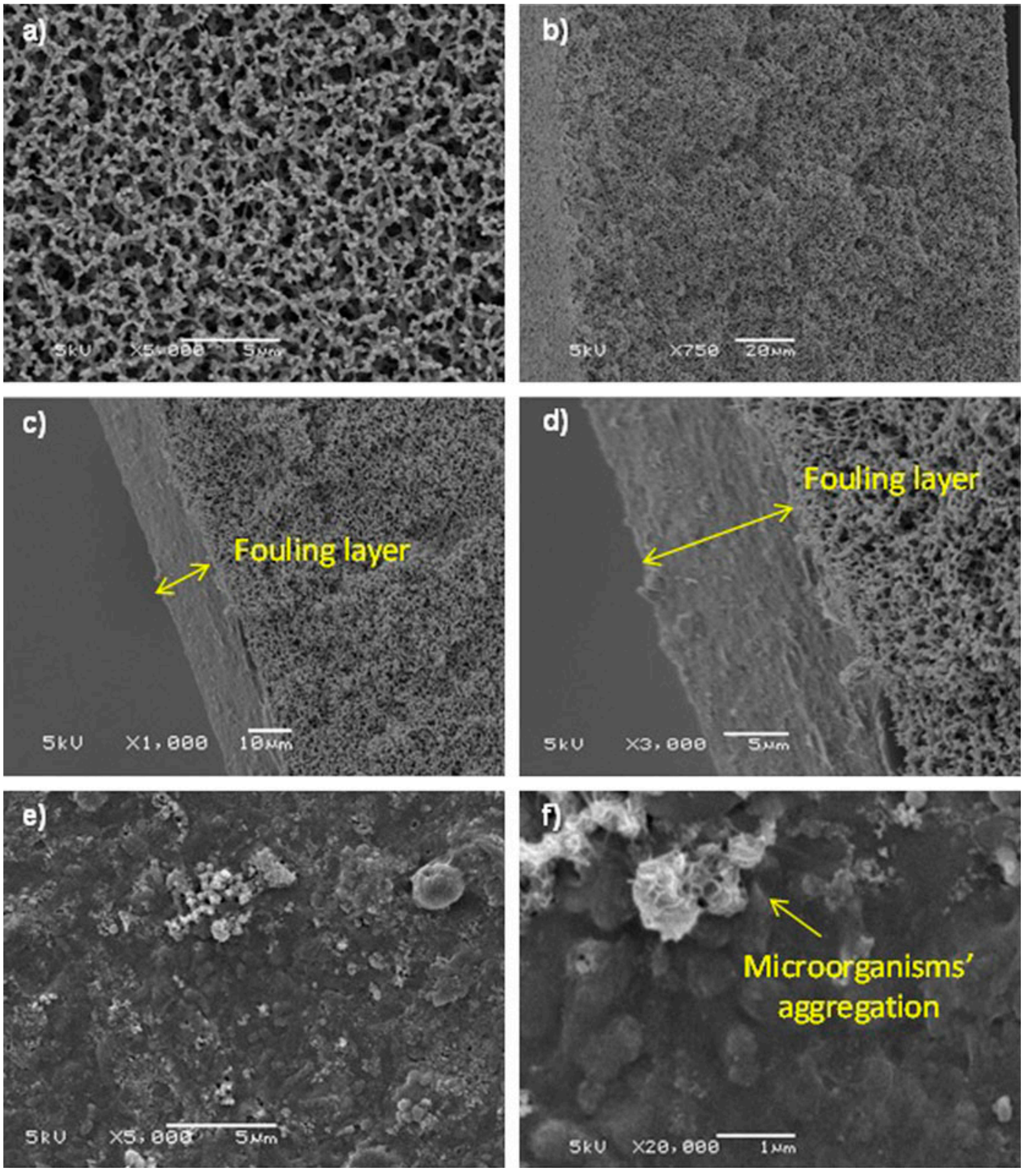

Fig. 5. SEM images of the membrane: ((a) and (b)) surface and cross-section of the new membrane; ((c) and (d)) cross-section of fouled membrane; ((e) and (f)) surface of fouled membrane.

extracellular polymeric substances). At temperatures higher than 500˚C, the analysis showed a reduction of more than 8% in mass, which can be associated to the degradation of inorganic material, such as nitrates and carbonates. After the analysis, 1,000˚C, there was an occurrence of about 15% of residues, characterizing the presence of inorganic compounds such as salts, inert material or even metals, namely, inorganic scaling.

3.3. Treatment efficiency

3.3.1. Synthetic effluent

Working with the synthetic effluent in both campaigns, the MBR had a high efficiency, achieving reduction of 97 ± 2.0% for COD (Fig. 7). These results are in agreement to those obtained by Provenzi [25], who also used ethanol as carbon source in the synthetic effluent.

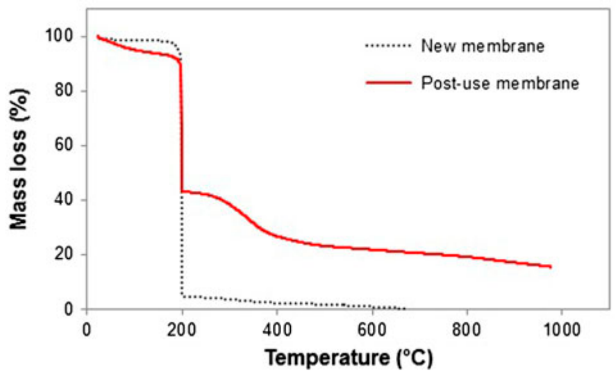

Fig. 6. Thermograms of the membrane.

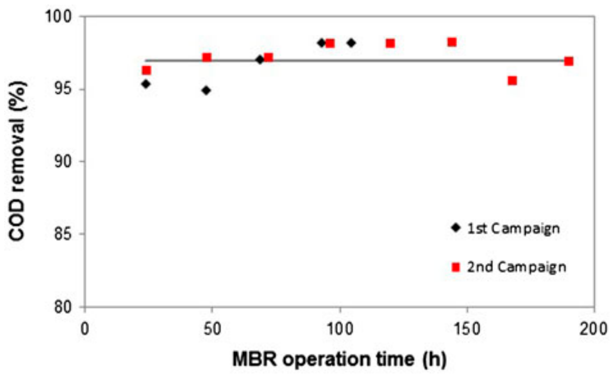

Fig. 7. MBR efficiency treating the synthetic effluent.

3.3.2. Tannery wastewater treatment and a reuse proposal

Throughout the MBR run with tannery wastewater, the efficiency treatment remained constant over time (Fig. 8) and obtained an average reduction in BOD_5 of 87.8%, which is considerably significant, since the tannery wastewater is more complex than the synthetic effluent. Achieving this efficiency, under the adverse conditions mentioned, highlights the robustness of the MBR. The COD removal was lower than BOD_5 removal, indicating that the remaining COD is refractory material, that is, non-biodegradable. These results are in agreement with the scientific literature [21,40]. Considering the remaining COD, advanced oxidation processes could be an alternative to the degradation.

Although the tannery wastewater treated by the MBR did not reach all allowed values to discharge according to Brazilian regulations [41] (Table 2), it already presents quality for reuse as process water, since there are steps in the leather industry where water with a lower quality can be required [42].

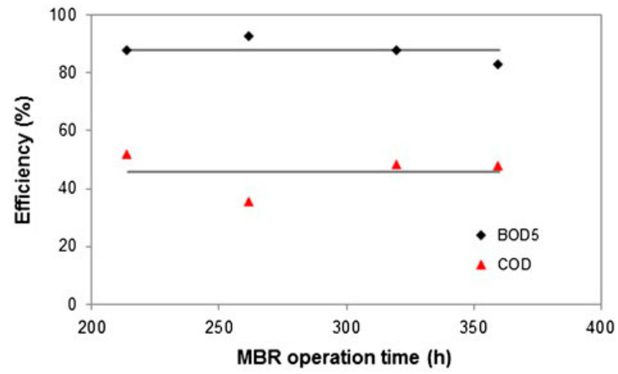

Fig. 8. MBR efficiency treating the tannery wastewater.

According to these authors, with a proper adjustment in salts concentration, wastewater with these characteristics can be recycled to several steps of the industrial process, such as the beamhouse operations including soaking and unhairing–liming, as well as tanyard operations like deliming and pickling. Furthermore, Bes-Piá et al. [43], with the adequate salts adjustment, applied wastewater similar to the one obtained from the MBR in pickling operation and achieved high-quality leather. On the other hand, Mendoza-Roca et al. [44] obtained high-quality leather, using, in unhairing operation, process water with inferior conditions than the one from the MBR. Employing process water with an elevated COD and TN concentrations in deliming operation, Gallego-Molina et al. [45] also achieved good quality leather. These findings show that the MBR permeate attained in the present work have sufficient quality to be recycled as process water (see Table 2).

It is important to highlight that the concentration of critical parameters like COD, BOD_5 and TKN after MBR–PEO treatment comply with the current Southern Brazilian legislation for effluent discard, as shown in Table 2. The wide TKN removal can be emphasized, considering that nitrogen removal from tannery wastewater is difficult to achieve and more complex than the one from municipal wastewaters [45]. Furthermore, the discharge of these compounds into the environment can cause serious damage like eutrophication of water bodies.

On the other hand, it would be a waste to discharge process water with quality like the one produced by the combined MBR–PEO treatment, since other authors demonstrate that similar process water can be recycled through several steps into the leather industry, including tanyard and re-tanning operations and resulted in a final product of outstanding quality

Table 2
Characterization of wastewater treated by CETP, MBR and PEO, and maximal allowed values for industrial wastewater discharge according to Brazilian regulations [41]

Parameter	Wastewater post-CETP (mg L^{-1})	Post-MBR (mg L^{-1})	MBR removal (%)	Post-PEO (mg L^{-1})	PEO removal (%)	Global removal (%)	Maximal allowed values for industrial wastewater discharge (mg L^{-1})
COD	776	420	45.8	29	93.1	96.3	150–400
BOD_5	205	25	87.8	10	60.0	95.1	40–180
TKN	149	124	16.8	2.6	97.9	98.3	10–20
Total-P	0.39	0.13	66.7	0.08	38.5	79.5	1–4
Chlorides	1,325	1,324	0	1,704	0	0	–
Sulphates	1,428	1,531	0	n.a.	0	0	–
Sodium	943	945	0	n.a.	0	0	–
Calcium	120	191	0	152	0	0	–
Chrome	0.08	0.04	50.0	0.02	50.0	75.0	0.5

Note: n.a.: not analysed.

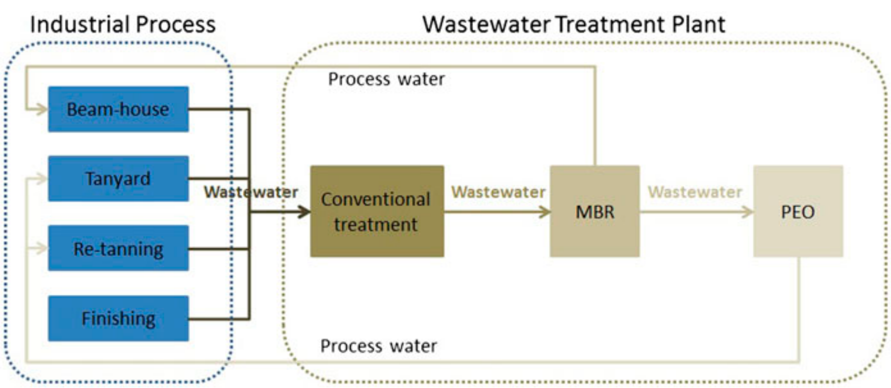

Fig. 9. Proposal of wastewater treatment and water reuse in a tannery.

that can be compared to the ones achieved applying fresh water [3,46].

In order to address the water reuse in a tannery that already mix all the wastewaters coming from different leather tanning phases and treat them together, an attempt has been presented in Fig. 9. The adoption of these technologies would be of great help to reduce the fresh water consumption that is used in huge amounts in these industries. Moreover, wastewaters represent a source of contamination but also a cheap source of reusable water. On the other hand, in tanneries where it is possible to segregate wastewaters in different streams and to treat them separately, other configurations of wastewater treatment system are possible [42]. For example, it would be possible to reuse some waters without any treatment in tannery beamhouse process [47] or to use advanced oxidation processes directly in wastewaters coming from re-tanning operations [48].

4. Conclusions

The tannery wastewater treatment plant is not supporting the effluent load and it is being discharged in disagreement with the environmental regulations, indicating that the wastewater treatment plant is undersized and needs to be re-designed or complemented with a new stage of treatment.

Regarding the MBR runs, in both campaigns, they showed a high permeate flux of around 43 L h^{-1} m^{-2} after 360 h of work, even without performing any membranes cleaning procedure. Furthermore, fouling does not penetrate in the membrane pores and has been minimal.

Working with synthetic effluent, the MBR reached a COD reduction of 97 ± 2.0%. On the other hand, operating with tannery wastewater post-CETP a reduction of 87.8, 45.8, and 16.8% for BOD_5, COD and TKN, respectively, was achieved, but some parameters were still above the Southern Brazilian regulations limits for effluents discharge. When an integrated MBR–PEO process was used, it proved to be effective as a tertiary tannery wastewater treatment, obtaining removal rates of 95.1, 96.3 and 98.3% for these parameters; such that the permissible discharge standards were reached.

The integration of the MBR to the PEO process provided two process water streams, with different characteristics. One of them could be reused for less noble steps in the tannery industry like the ones for beamhouse operations. The other one can be reused for steps that require higher quality water like the ones for tanyard and re-tanning, making possible the use of water in a practically closed circuit. The zero-discharge concept on these technologies can bring economic and environmental benefits to the companies, since it significantly reduces waste disposal, saving water and chemicals.

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References

[1] Comitesinos, Comitê de Gerenciamento da Bacia Hidrográfica do Rio dos Sinos, 2009. Available from: http:// www.comitesinos.com.br (Accessed 15 February 2014).

[2] B.F. Giannetti, S.H. Bonilla, C.M. Almeida, Developing eco-technologies: A possibility to minimize environmental impact in Southern Brazil, J. Clean. Prod. 12 (2004) 361–368.

[3] M.A.S. Rodrigues, F.D.R. Amado, J.L.N. Xavier, K.F. Streit, A.M. Bernardes, J.Z. Ferreira, Application of photoelectrochemical–electrodialysis treatment for the recovery and reuse of water from tannery effluents, J. Clean. Prod. 16 (2008) 605–611.

[4] K. Joseph, N. Nithya, Material flows in the life cycle of leather, J. Clean. Prod. 17 (2009) 676–682.

[5] J.A.S. Figueiredo, E. Drumm, M.A.S. Rodrigues, F.R. Spilki, The Rio dos Sinos watershed: An economic and social space and its interface with environmental status, Braz. J. Biol. 70 (2010) 1131–1136.

[6] W. Scholz, M. Lucas, Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals, Water Res. 37 (2003) 1859–1867.

[7] G. Durai, M. Rajasimman, Biological treatment of tannery wastewater—A review, J. Environ. Sci. Technol. 4 (2011) 1–17.

[8] G Devikavathi, C. Muralidharan, An approach towards redefining water quality parameters for leather industry Part 1. Effect of hardness and chlorides in water, Desalin. Water Treat. 21 (2010), 53–59.

[9] S. Kanagasabi, Y.L. Kang, M. Manickam, S. Ibrahim, S. Pichiah, Intimate coupling of electro and biooxidation of tannery wastewater, Desalin. Water Treat. 51 (2013) 34–36.

[10] N.S.A. Mutamim, Z.Z. Noor, M.A.A. Hassan, G. Olsson, Application of membrane bioreactor technology in treating high strength industrial wastewater: A performance review, Desalination 305 (2012) 1–11.

[11] G. Lofrano, S. Meriç, G.E. Zengin, D. Orhon, Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review, Sci. Total Environ. 461–462 (2013) 265–281.

[12] A. Goltara, J. Martinez, R. Mendez, Carbon and nitrogen removal from tannery wastewater with a membrane bioreactor, Water Sci. Technol. 48 (2003) 207–214.

[13] W.G. Scholz, P. Rougé, A. Bódalo, U. Leitz, Desalination of mixed tannery effluent with membrane bioreactor and reverse osmosis treatment, Environ. Sci. Technol. 39 (2005) 8505–8511.

[14] G. Munz, M. Gualtiero, L. Salvadori, B. Claudia, L. Claudio, Process efficiency and microbial monitoring in MBR (membrane bioreactor) and CASP (conventional activated sludge process) treatment of tannery wastewater, Bioresour. Technol. 99 (2008) 8559–8564.

[15] F.M. Paschoal, M.A. Anderson, M.V. Zanoni, Simultaneous removal of chromium and leather dye from simulated tannery effluent by photoelectrochemistry, J. Hazard. Mater. 166 (2009) 531–537.

[16] I.R. Siqueira, C. Vanzella, P. Bianchetti, M.A.S. Rodrigues, S. Stülp, Anxiety-like behaviour in mice exposed to tannery wastewater: The effect of photoelectrooxidation treatment, Neurotoxicol. Technol. 33 (2011) 481–484.

[17] N.S.A. Mutamim, Z.Z. Noor, M.A.A. Hassan, A. Yuniarto, G. Olsson, Membrane bioreactor: Applications and limitations in treating high strength industrial wastewater, Chem. Eng. J. 225 (2013) 109–119.

[18] G.C. Molina, C.H. Cayo, M.A.S. Rodrigues, A.M. Bernardes, Sodium isopropyl xanthate degradation by advanced oxidation processes, Miner. Eng. 45 (2013) 88–93.

[19] W.T. Zhao, X. Huang, D.J. Lee, X.H. Wang, Y.X. Shen, Use of submerged anaerobic–anoxic–oxic membrane bioreactor to treat highly toxic coke wastewater with complete sludge retention, J. Membr. Sci. 330 (2009) 57–64.

[20] Y. Marselina, Lifia, P. Le-Clech, R.M. Stuetz, V. Chen, Characterisation of membrane fouling deposition and removal by direct observation technique, J. Membr. Sci. 341 (2009) 163–171.

[21] Keerthi, V. Suganthi, M. Mahalakshmi, N. Balasubramanian, Development of hybrid membrane bioreactor for tannery effluent treatment, Desalination 309 (2013) 231–236.

[22] A. Giacobbo, M.A.S. Rodrigues, A.M. Bernardes, A. Meneguzzi, Comportamento do fluxo de permeado durante microfiltração de lodos ativados (Behavior of permeate flux during activated sludge microfiltration), in: Proceedings of the Seventh Ibero-American Conference on Membrane Science and Technology CITEM, 2010, Sintra, Portugal (in Portuguese).

[23] A. Giacobbo, G.L. Feron, M.A.S. Rodrigues, A.M. Bernardes, A. Meneguzzi, Utilização de biorreator à

membrana para tratamento de efluentes (Membrane bioreactor for effluents treatment), Holos 1 (2011) 13–29 (in Portuguese).

[24] Metcalf and Eddy, Wastewater Engineering—Treatment and Reuse (Submerged membrane bioreactor for biological wastewater treatment: Hydrodynamic and physico-chemical studies on fouling control), fourth ed., McGraw-Hill, Boston, MA, 2003.

[25] G. Provenzi, Biorreator à membrana submersa para tratamento biológico de efluentes: estudos hidrodinâmicos e físico-químicos no controle da colmatação (Submerged membrane bioreactor for biological wastewater treatment: Hydrodynamic and physico-chemical studies on fouling control), PhD Thesis, Federal University of Santa Catarina, Florianópolis, Brazil, p. 154, 2005 (in Portuguese).

[26] K. Kimura, T. Naruse, Y. Watanabe, Changes in characteristics of soluble microbial products in membrane bioreactors associated with different solid retention times: Relation to membrane fouling, Water Res. 43 (2009) 107–113.

[27] APHA, AWWA and WEF, Standard Methods for the Examination of Water and Wastewater, twenty-first ed., Apha, Washington, DC, 2005.

[28] Z. Badani, H. Ait-Amar, A. Si-Salah, M. Brik, W. Fuchs, Treatment of textile waste water by membrane bioreactor and reuse, Desalination 185 (2005), 411–417.

[29] L. Böhm, A. Drews, H. Prieske, P.R. Bérubé, M. Kraume, The importance of fluid dynamics for MBR fouling mitigation, Bioresour. Technol. 122 (2012) 50–61.

[30] A. Pollice, G. Laera, M. Blonda, Biomass growth and activity in a membrane bioreactor with complete sludge retention, Water Res. 38 (2004) 1799–1808.

[31] T.Y. Jeong, G.C. Cha, I.K. Yoo, D.J. Kim, Characteristics of bio-fouling in a submerged MBR, Desalination 207 (2007) 107–113.

[32] C. Merz, R. Scheumann, B. El Hamouri, M. Kraume, Membrane bioreactor technology for the treatment of greywater from a sports and leisure club, Desalination 215 (2007) 37–43.

[33] S. Arabi, G. Nakhla, Impact of protein/carbohydrate ratio in the feed wastewater on the membrane fouling in membrane bioreactors, J. Membr. Sci. 324 (2008) 142–150.

[34] A. Huelgas, N. Funamizu, Flat-plate submerged membrane bioreactor for the treatment of higher-load graywater, Desalination 250 (2010) 162–166.

[35] T. Melin, B. Jefferson, D. Bixio, C. Thoeye, W. De Wilde, J. De Koning, J. van der Graaf, T. Wintgens, Membrane bioreactor technology for wastewater treatment and reuse, Desalination 187 (2006), 271–282.

[36] H. Ivnitsky, I. Katz, D. Minz, E. Shimoni, Y. Chen, J. Tarchitzky, R. Semiat, C.G. Dosoretz, Characterization of membrane biofouling in nanofiltration processes of wastewater treatment, Desalination 185 (2005) 255–268.

[37] Y. Miura, Y. Watanabe, S. Okabe, Membrane biofouling in pilot-scale membrane bioreactors (MBRs) treating municipal wastewater: Impact of biofilm formation, Environ. Sci. Technol. 41 (2007) 632–638.

[38] X. Yan, M.R. Bilad, R. Gerards, L. Vriens, A. Piasecka, I.F. Vankelecom, Comparison of MBR performance and membrane cleaning in a single-stage activated sludge system and a two-stage anaerobic/aerobic (A/A) system for treating synthetic molasses wastewater, J. Membr. Sci. 394–395 (2012) 49–56.

[39] W. Chen, M. Zhu, X. Zheng, M. Xu, Y. He, The characteristics of membrane fouling in the process of A/(O-MBR) treating municipal wastewater, J. Food Agric. Environ. 10 (2012) 925–928.

[40] G. Munz, D. De Angelis, R. Gori, G. Mori, M. Casarci, C. Lubello, The role of tannins in conventional and membrane treatment of tannery wastewater, J. Hazard. Mater. 164 (2009) 733–739.

[41] Rio Grande do Sul, Conselho Estadual do Meio Ambiente—CONSEMA, 2006, Resolução n. 128/2006, Dispõe sobre a fixação de Padrões de Emissão de Efluentes Líquidos para fontes de emissão que lancem seus efluentes em águas superficiais no Estado do Rio Grande do Sul (Provides about the establishment of Wastewater Emission Standards for emission sources that discard their effluents into surface waters in the State of Rio Grande do Sul), Porto Alegre, 24 November 2006 (in Portuguese).

[42] A. Cassano, R. Molinari, M. Romano, E. Drioli, Treatment of aqueous effluents of the leather industry by membrane processes, J. Membr. Sci. 181 (2001) 111–126.

[43] A. Bes-Piá, B. Cuartas-Uribe, J.A. Mendoza-Roca, M.V. Galiana-Aleixandre, M.I. Iborra-Clar, M.I. Alcaina-Miranda, Pickling wastewater reclamation by means of nanofiltration, Desalination 221 (2008) 225–233.

[44] J.A. Mendoza-Roca, M.V. Galiana-Aleixandre, J. Lora-García, A. Bes-Piá, Purification of tannery effluents by ultrafiltration in view of permeate reuse, Sep. Purif. Technol. 70 (2010) 296–301.

[45] A. Gallego-Molina, J.A. Mendoza-Roca, D. Aguado, M.V. Galiana-Aleixandre, Reducing pollution from the deliming–bating operation in a tannery. Wastewater reuse by microfiltration membranes, Chem. Eng. Res. Des. 91 (2013) 369–376.

[46] P. Bhattacharya, A. Roy, S. Sarkar, S. Ghosh, S. Majumdar, S. Chakraborty, S. Mandal, A. Mukhopadhyay, S. Bandyopadhyay, Combination technology of ceramic microfiltration and reverse osmosis for tannery wastewater recovery, Water Resour. Ind. 3 (2013) 48–62.

[47] M. Gutterres, P.M. Aquim, J.B. Passos, J.O. Trierweiler, Water reuse in tannery beamhouse process, J. Clean. Prod. 18 (2010) 1545–1552.

[48] G. Lofrano, S. Meriç, V. Belgiorno, R.M.A. Napoli, Fenton's oxidation of various-based tanning materials, Desalination 211 (2007) 10–21.