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Reducing sulfates concentration in the tannery effluent by applying pollution prevention techniques and nanofiltration

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A B S T R A C T

The use of large quantities of sulfuric acid and other sulfur-containing chemicals causes high sulfate concentrations in the wastewater of a tannery. The aim of this work was reducing the sulfate concentration in the final wastewater from a tannery. For that, firstly a study about the main sulfate sources in a tannery was carried out and the total sulfates load in the tannery wastewater was evaluated. Two measures for sulfates reduction were studied: the recycling of unhairing wastewater to the soaking drums and the reuse of the chromium sulfate from the tanning washing wastewater after its separation by nanofiltration (NF). The first measure proposed was studied experimentally in laboratory drums of 5 L of volume. Two series of experiments with different volumes of unhairing wastewater in the soaking bath were carried out. The quality of the final leather was evaluated by means of mechanical tests. NF experiments were carried out in a laboratory pilot plant with a spiral wounded membrane element. Concerning the results, the combination of 50% unhairing wastewater and 50% of fresh water was appropriate in order to obtain leather with an acceptable quality. Besides, it drove to a diminution of approximately 10% in the addition of sulfide in the unhairing. Related to the NF experiments, 97% of the sulfates were rejected by the membrane. The separated ions could be recycled to the tanning drums. The application of the two measures (firstly the recycling of the unhairing wastewater and secondly the NF of the tanning washing wastewater) drove to a reduction of 14.82 kg SO_4^{-2} t^{-1} of raw hide.

1. Introduction

1.1. The sulfate problem

Tanneries generate sulfate-rich wastewaters because of the use of large amounts of sulfuric acid and the use of sulfide in the unhairing process, which is oxidized to sulfate before its discharge into sewer.

In Spain, some municipalities have established a limit of 1500 mg L^{-1} of sulfates for the discharge into the sewer. This is a standard very difficult to meet by the tanneries that process raw hides including beamhouse operations in addition to tanning, dyeing, greasing and finishing ones. Sulfate concentration in these types of tanneries usually ranges between 2500 and 3000 mg L^{-1}.

End of pipe treatments for sulfate elimination are very difficult to carry out. Their implementation firstly entails an exhaustive conventional treatment (physical–chemical + biological processes). After these treatments sulfate removal can be carried out basically by membrane processes (Pasilla and Tavani, 1999; Suthanthararajan et al., 2004; Scolz et al., 2005). Nevertheless, severe fouling may occur (Fababuj-Roger et al., 2007). In this type of effluents ion exchange is economically unfeasible due to the presence of other ions in high concentrations and to the high wastewater flow rate.

Another possibility for sulfate removal is treating the wastewaters with an anaerobic process. In this way, sulfate is reduced to sulfide, and then, sulfide has to be eliminated either from the gaseous phase by means of an absorption with alkaline solution or in the aqueous phase with a further oxidation to sulfur. However, in the anaerobic biological treatment there is a competence between sulfate reducing bacteria and methanogenic bacteria. Thus, sulfate and COD removal efficiencies will depend on the biodegradability of the COD and on the operating conditions. Besides, the operation of these reactors can be very complex. Operation experiences of anaerobic reactors applied to industrial wastewaters (viscose industry, yeast production, petroleum and mining industry) for sulfate elimination have been reported by several authors (Parravicini et al., 2007; Zub et al., 2008; Tang et al., 2009).

Summarizing, it can be stated that end of pipe treatments entail some drawbacks that make difficult their application for sulfate removal.

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1.2. Processes in the tanning industry

Fig. 1 illustrates the main stages performed in a tannery treating raw hides. Raw hides are firstly subjected to a series of operations, named beamhouse operations, to prepare the hide to be tanned. These operations aim to eliminate the conservation salt from the raw matter (soaking), hair and epidermis (unhairing) and the flesh side of the hide (fleshing and splitting). After that, hides are transported to the tanning operation drums, where deliming (to eliminate the residual lime added in the unhairing process), pickling (addition of acids and salts for preparing the hide to be tanned) and tanning are performed. The following operations are retanning, dyeing and greasing, which are carried out according to the requirements of the customers. They generate acidic wastewaters. The last operations are leather drying and finishing, which hardly produce liquid effluents. The dotted lines in Fig. 1 represent the effluents with high sulfate concentrations.

Table 1 shows the main auxiliary matters used in the processes that generate liquid effluents and the main characteristics of the residual floats. The most right column explains the sulfate source in the process.

1.3. Measures for sulfate reduction

Some authors have contributed to the study of measures for reducing the sulfate concentrations of particular residual floats. In this way, the sulfate reduction by replacing the sulfide by other auxiliary matters as enzymes or hydrogen peroxide and the reuse of sulfides in the unhairing process has been studied (Cassano et al., 1997; Marsal et al., 2000; Crispim and Mota, 2003; Morera et al., 2008; Valeika et al., 2009). Experiments about unhairing wastewater reuse were proposed by Nazer et al. (2006). Results indicated a considerable saving in chemicals; thereby sulfates in the wastewaters were reduced. Globally, saving in water was up to 58%, whereas chemical reduction was around 28%.

As commented above, other important sulfate source is the pickling process. A direct reuse of this residual bath is only partly possible, since the wastewater volume is higher than the fresh water volume due to water loss in the hide.

In order to reuse the sulfates of the excess water, nanofiltration (NF) has been proposed in the literature (Cuartas-Uribe et al., 2006).

On the other hand, the deletion of the pickling was studied by Suresh et al. (2001), who reported about a new product for cleaner chrome tanning that could be applied directly to the hides without a previous pickling. These authors reported a diminution of COD, total dissolved solids (TDS) and chlorides of 51, 81 and 99%, respectively, in the spent tan liquor. No sulfates data were mentioned but their concentration should have also been reduced substantially since the pickling process was suppressed. In the same way, sulfate reduction is one of the consequences of the process modification proposed by Kanth et al. (2009). These authors proposed an eco-friendly tanning process consisting of the suppression of the pickling and the application of enzymes to improve the exhaustion of vegetal tannins.

Other papers are referred to the reuse of the tanning process wastewater. In this case, the chromium reuse also implies the reuse of the sulfates since the tanning agent is used as basic chromium sulfate ($CrOHSO_4$). However, authors focus their discussions on the heavy metal separation and reuse, though elimination efficiencies for the sulfate are also reported (Ortega et al., 2005).

In the literature, it is discussed not only about the chromium minimization in the final wastewater by direct reuse of the exhausted tanning bath (spent liquor), but also about the treatment of the washing wastewater by membranes and the further reuse of the rejection stream. Thus, Cassano et al. (2007) applied an integrated membrane process (ultrafiltration + nanofiltration) for the chromium recovery from tanning effluents. On the other hand, Taleb Ahmed et al. (Taleb-Ahmed et al., 2004, 2006) proposed the combination of a physical–chemical treatment and nanofiltration to eliminate chromium from the tanning wastewater.

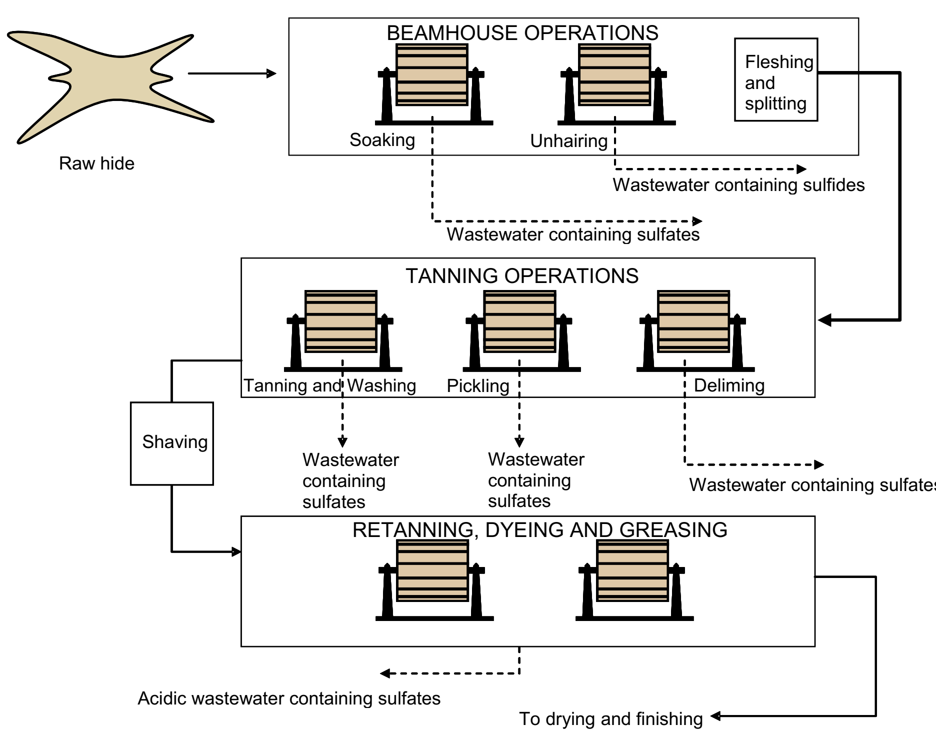

Fig. 1. Scheme of the operations carried out in a tannery processing raw hide.

Table 1
Main auxiliary matters and wastewater characteristics of the main processes in a tannery.

	Process	Auxiliary matters	Wastewater characteristics	Sulfate source
Beamhouse operations	Soaking	Water Surfactant Fungicide Enzymes Sodium sulfide (low concentration) Sodium carbonate	High organic matter concentration and very high conductivity	Sodium sulfide
	Unhairing	Water Lime Sodium sulfide Surfactant	Alkaline pH, high conductivity, and hide organic matter and sulfide concentrations	Sodium sulfide
Tanning operations	Deliming	Water Ammonium salts Acids	Organic matter, ammonium, sulfides and sulfates.	Sodium sulfide remaining in the hides
	Pickling	Water Inorganic and organic acids. Salts	Low pH, organic matter and very high conductivity.	Sulfuric acid
	Tanning	Water Basic chromium sulfate	Very high chromium and sulfate concentrations. Low pH.	Basic chromium sulfate
	Washing	Water	High chromium and sulfate concentrations. Low pH.	Basic chromium sulfate
Retanning, Dying and Greasing operations	Retanning, Dyeing and Fatliquoring	Water Dyestuff. Surfactant. Oil Salts. Vegetal tanning agents	High colour. Organic matter, Surfactants. Chromium.	Sulfate from dyestuffs and other chemicals.

Other methods for chromium recovery from tannery effluents have also been reported in the literature (Guo et al., 2006; Onyancha et al., 2008; Kanagaraj et al., 2008; Kalidhassan et al., 2009).

1.4. Nanofiltration

As commented above, NF is a membrane technique that can be applied to sulfate separation from wastewater. The separation of charged compounds occurs due to both steric hindrance and electrostatic interactions. Nowadays, NF membranes are widely applied to water and wastewater treatment for the removal of divalent and multivalent ions and for partial elimination of the monovalent ones. They are also used in industrial wastewater treatments containing high salt concentrations (Wahla et al., 2008; Luo et al., 2009; Geraldes et al., 2009).

The aim of this work was minimizing the sulfate concentration in the final wastewater from a tannery. For that, firstly the different residual floats containing sulfates were analyzed. Apart from the reuse of the pickling and tanning residual baths, two additional measures were studied in order to reduce the final sulfate concentration in wastewater: the reuse of the unhairing wastewater in the soaking and the recycling of the tanning washing wastewater after its nanofiltration.

2. Materials and methods

2.1. Sulfates in the effluents from the processes

Sulfate sources were evaluated within the tannery processes. Sulfates come from the chemicals used as auxiliary matters; for example sulfuric acid added in various processes to lower the pH like in the pickling, chromium sulfate from tanning and sodium sulfide and mercaptanes used in the unhairing process that afterwards will be oxidized to sulfates.

Wastewater samples were taken from the following 7 processes: soaking, unhairing, deliming, pickling, tanning, washing after tanning (tanning washing) and retanning, dyeing and greasing (acidic wastewaters). The sampling period was one year. The whole number of samples was 30 and each one was taken every two working weeks.

2.2. Wastewater analysis

Sulfates and chromium were analyzed according to APHA (2005). Chromium measurements were performed only in the nanofiltration tests. The results of the analysis will lead to find out in which extent the NF rejection stream can be reused in the tanning drums and, consequently, the reused sulfates mass.

As the unhairing process generates primarily sulfides, the equivalent sulfates were calculated by stoichiometry. Sulfides were measured by addition of 2 mL of HCl 6 N and further titration of an excess of iodine with a $Na_2S_2O_3$ solution.

pH values were measured using a GLP 22 CRISON pH meter.

2.3. Reuse of unhairing wastewater in the soaking process

The aims of the soaking process are the gradual increase of the hide pH, the hide rehydration and the removal of the conservation salt, blood, dung and dirt from the raw matter. For the accomplishment of these objectives various chemicals are added in the soaking solutions. Thus, sodium carbonate is used to increase slightly the pH, enzymes and surfactants are used to remove blood, dung and dirt and fungicide is applied to prevent the biological degradation of the skin. Finally, low concentrations of sodium sulfide can be added since it contributes to a better hide rehydration.

By means of the unhairing process hair and epidermis are separated from the hide.

This process is performed in a drum by mixing the hides with an alkaline solution that contains mainly lime (used to swallow the hide), sulfides for the hair removal and surfactant.

Immediately after the unhairing, the residual bath is taken out of the drum and driven to a grid to separate hair before its solubilisation. At the end of the operation, a residual bath with a pH value of about 12 and with a high content of organic substances (proteins), lime and sulfide is left.

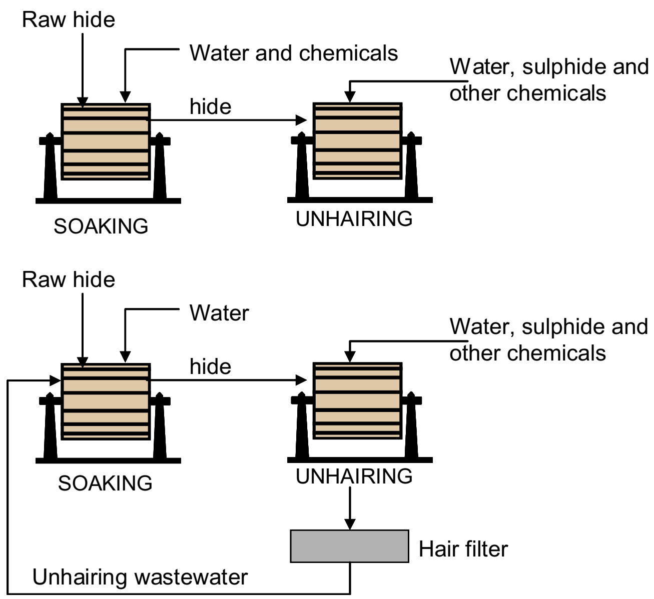

Fig. 2. Comparison of the traditional processes (top part of the figure) and the proposed scheme (bottom part of the figure).

The use of unhairing wastewater as a part of the soaking solution entails savings of water and chemicals, since no additional chemicals have to be added to the soaking. Thus, sodium carbonate is not necessary since the pH of the soaking solution increases when fresh water is mixed with the unhairing wastewater. Surfactant will be equally provided by unhairing wastewater and sulfides will begin to react with the hide in the soaking, what implies a saving in sulfide in the subsequent unhairing. However, this sulfide concentration will not be high enough to begin the hair elimination from the hide.

Fig. 2 compares the traditional process with the proposed scheme.

Two series of experiments were carried out in laboratory drums of 5 L of volume. In the first series the soaking was performed using a 50% of fresh water and a 50% of unhairing wastewater (PW50, U50). In the other experiment series, the percentage of unhairing wastewater was raised up to 75 (PW25, U75). 10 hide samples of different thickness ranging between 0.9 and 2.6 mm were inserted in the drums in each series of experiments. The width of the hide samples was 200 mm and their length was equally of 200 mm. The experiments were repeated three times to check the reproducibility of the results. Thickness was measured according the international standard (ISO 2589, 2002).

2.4. *Test for measuring the mechanical properties of the final leather*

The soaked hides with the unhairing wastewater were subjected to the whole process of the tannery in the laboratory drums to check whether the final leather met the required quality standards in terms of tear load in N, grain stretch in mm and tensile strength in N mm^{-2}. The procedures were performed according to the guidelines of the International Organization for Standardization (ISO 3377:2, 2002; ISO 3372, 2002; ISO 3379, 2005).

In the tear load test, a regular leather sample with a hole of a specified shape was placed over the turned up ends of a pair of holders attached to the jaws of a testing machine. The highest force exerted during tearing of the test piece was recorded.

The test for measuring the tensile strength determines the load required to rupture a leather test specimen. The load to rupture

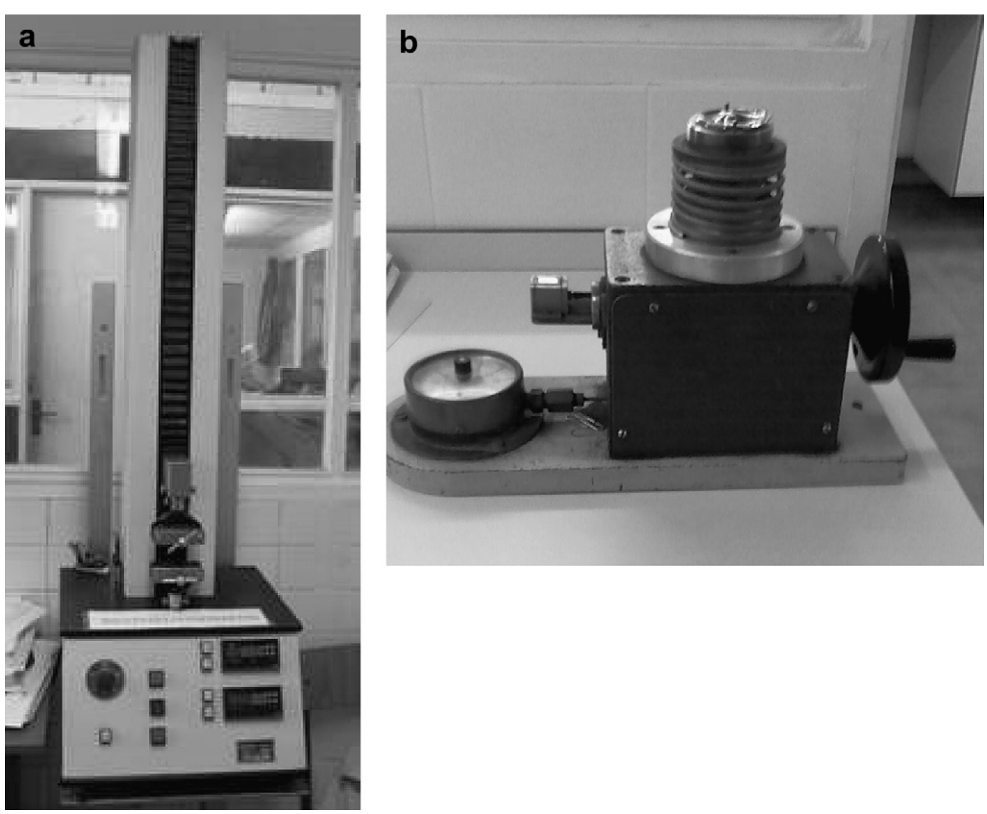

Fig. 3. (a) Dynamometer for tear load and tensile strength determination. (b) Apparatus for the measurement of the grain stretch.

Table 2
Sulfate concentrations measured in effluents from seven processes in a tannery.

Process	Average sulfate concentration (mg L^{-1})	Relative standard deviation (%)
Soaking	450	6.7
Unhairing	2350	7.6
Deliming	1755	8.2
Pickling	5315	5.7
Tanning	6021	3.8
Tanning washing	5724	3.9
Retanning, dyeing and greasing	2360	27.9

divided by the original unstretched cross-sectional area gives the tensile strength.

In the grain stretch determination, a disc-shaped piece was tested. A steel ball pressed against the centre of the flesh side of leather, firmly attached at its periphery. The elongation of the test specimen was recorded once the grain was cracked.

Fig. 3 illustrates the equipment used for the mechanical tests.

2.5. NF experiments

The objective of the NF experiments was the study of the separation of chromium and sulfate by the membranes, evaluating the possibility of obtaining a chromium concentrated solution that could be recycled to the tanning drum. Together with the chromium, sulfates could also be recycled to the tanning drum avoiding their discharge. The membrane permeate could be used in the tannery for washing processes.

NF experiments were performed in a laboratory pilot plant with a pressure vessel prepared to test spiral wounded membrane elements of 2.5 inches of diameter.

The membrane used in the tests was Desal5 DL from GE Osmosnics, whose operating pH ranged between 2 and 11.

Three tests at total recirculation mode (reject and permeate streams recirculation) were carried out. The samples used as NF feeds were collected from the tanning washing effluents from the processing of three different hides.

Temperature was maintained constant at 26 °C and the permeate flow rate was adjusted in order to work with a constant recovery (permeate flow rate divided by the feed flow rate) of 0.12, i.e. 12%.

The initial membrane water permeability was measured. At the end of each test (24 h), a membrane rinsing with distilled water was realized and the membrane water permeability was again checked.

The membrane permeate flux ($L\,m^{-2}\,h^{-1}$) was measured and the chromium and sulfate ions retention were determined with the aim of studying the viability of their reuse with the consequent reduction of the amount of sulfate discharged. From the ions retention results the volume of concentrate that can be reused in the tanning drums can be calculated.

2.6. Economical benefit

The economical balance was carried out to find out the savings achieved by the two proposed measures to reduce the sulfate discharge. Savings both in water and in chemicals have to be considered. Concerning the expenses, the operating costs of the proposed NF plant have to be estimated.

3. Results

3.1. Sulfate balance in the tannery. Environmental impact

Table 2 shows the average sulfate concentration of various process wastewaters in the tannery studied. Relative standard deviation of the data series can also be observed. It can be seen that pickling wastewater and the spent liquor (tanning) and the draining stream (tanning washing) from the tanning operation have an average sulfate concentration of more than 5000 mg L^{-1}. Unhairing residual stream and acidic wastewaters have lower concentrations (between 2300 and 2400 mg L^{-1}). It has to be commented that the indicated sulfate concentration from the unhairing wastewater has been calculated from the analysis of reduction chemicals as sulfide, as commented in Section 2.

Finally, the least sulfate-charged wastewaters among the studied streams corresponded with those coming from the soaking.

Concerning the relative standard deviations, it has to be highlighted that all calculated values for this parameter were lower than 10%, i.e. the sulfates values measured were similar independently from the sampling day. The only exception was the acidic wastewater, whose relative standard deviation is 27.9%. This was basically due to the variation in the retanning and the dyeing processes, which are always carried out according to the requirements of the customer.

Table 3 shows the amount of sulfates discharged by a tannery per year and per ton of raw hide. They have been calculated considering the daily wastewater volume generated in the studied operations (second column in Table 3), 222 working days and the processing of 5000 t of raw hide in a year.

However, in a tannery it is usual the reuse of both the pickling and the tanning exhausted baths. Considering that only the excess wastewaters from these operations are discharged, the ratio kg of sulfate/t raw hide is reduced to values of 0.15 for the pickling and 0.12 for the tanning. This difference can be observed comparing in Table 3 the values in the column 4 (without taking into account the sulfates reused in the tanning and in the pickling) with those in the column 5 (considering the reuse of these exhausted baths). In this way, after taking into account the reuse, the sulfates discharged to the municipal sewer were 34.87 kg $SO_4^{-2}\,t^{-1}$ of raw hide.

Table 3
Sulfates discharged by a tannery per year and per ton of raw hide (annual hide processing: 5000 t $year^{-1}$).

Process	Daily wastewater volume (m^3)	Annual sulfates load (t $year^{-1}$)	Sulfates per ton of raw hide (kg $SO_4^{-2}\,t^{-1}$)	Discharged sulfates per ton of raw hide[a] (kg $SO_4^{-2}\,t^{-1}$)
Soaking	130	12.99	2.6	2.60
Unhairing	70	36.52	7.3	7.30
Deliming	30	7.66	1.5	1.50
Pickling	70	82.59	16.5	0.15
Tanning	50	66.83	13.3	0.12
Tanning washing	50	63.53	12.7	12.70
Acidic wastewaters	100	52.39	10.5	10.50
Total	500	322.51	64.4	34.87

[a] Values considering the usual reuse of the pickling and tanning exhausted baths.

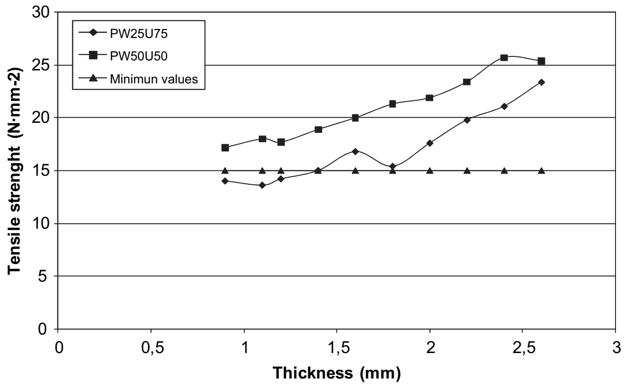

Fig. 4. Tensile strength of the leather made from hide samples soaked partially with unhairing wastewater.

3.2. *Measures for the environmental impact reduction by sulfates in the tannery*

After studying the possibilities for minimizing the sulfate concentration in the wastewaters, two of them were carried out at laboratory scale: the reuse of the unhairing wastewater in the soaking process and the nanofiltration of the tanning washing wastewater.

3.2.1. *Results of the reuse of unhairing wastewater in the soaking process*

3.2.1.1. Reuse process and sulfate reduction. Soaking of the hide samples using a mixture of unhairing wastewater and fresh water was carried out in the laboratory drums described in the materials and methods Section 2.3. The minimum unhairing wastewater percentage in the soaking was estimated in 50, since lower values drove to a H_2S formation due to the pH decrease. Percentages higher than 75% were not considered since the wastewater volume generated in the unhairing is not enough to cover the water demand for the soaking and because unhairing would begin in the soaking drums what could damage the hides.

The reuse of the unhairing wastewater in the soaking process implied a diminution of approximately 10% in the addition of sulfide in the unhairing. This was due to the beginning of the reaction sulfide-hide proteins in the soaking. Thus, the discharge of 2.5 kg of sulfate per ton of raw hide it was avoided.

3.2.1.2. Leather quality. After the soaking with the mixtures fresh water-unhairing wastewater, the hides were subjected to the whole process of the tannery, evaluating their final characteristics. This is of paramount importance since it has to be checked that the final leather quality is not affected.

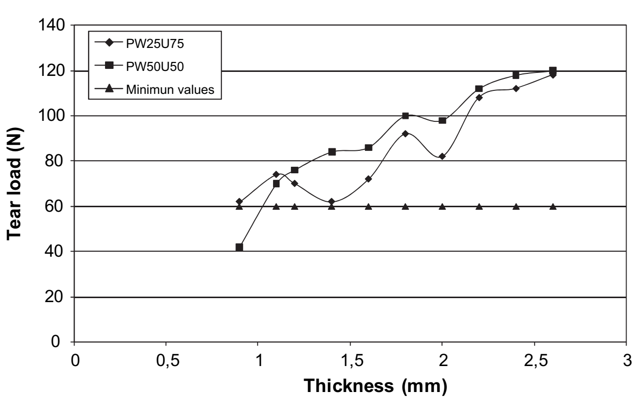

Fig. 5. Tear load of the leather made from hide samples soaked partially with unhairing wastewater.

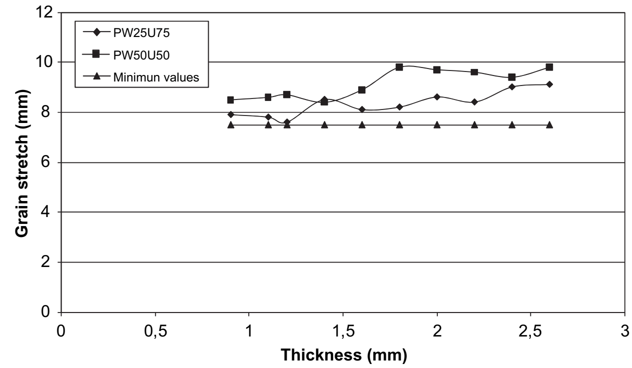

Fig. 6. Grain stretch of the leather made from hide samples soaked partially with unhairing wastewater.

In this way, tensile strength of the final leather should be higher than 15 $N\,mm^{-2}$ as quality criterion for the final leather. It is expected that the tensile strength increases linearly with the hide thickness for the tested thickness range.

In Fig. 4, the tensile strength of the final leather samples can be observed. It is clear that the tensile strength is higher for the hide samples soaked with only a 50% of unhairing wastewater than for the hide samples soaked with a 75% of unhairing wastewater. Besides, an uncharacteristic behavior was detected when a 75% of unhairing wastewater was used, since the sample with 1.8 mm of thickness has lower tensile strength than the sample of 1.6 mm. This behavior is anomalous since increasing values of the tensile strength are expected for increasing values of the thickness, as explained above.

Concerning the tear load (Fig. 5), the variation of the values measured versus the thickness is more irregular for the case of using a 75% of unhairing wastewater. This could imply a rip in the finished product (for example a shoe) when it is sewed.

It has to be commented that tear loads can be very close to the limit for very thin hides ($<$1 mm), even if the conventional process with fresh water is applied. A slight irregularity in the hide or problem in the rest of the operations could imply the decrease of the tear load down to the limit, as occurred in the experience with 50% of unhairing wastewater.

Finally, from the point of view of the grain stretch, both types of soaking were valid to reach the required grain stretch in the final leather. The measured grain stretch was higher than 7.5, independently of the sample thickness (Fig. 6).

Summarizing, it can be stated that the hide samples soaked with a mixture of 50% of fresh water and 50% of unhairing effluent met the required quality standards in the realized mechanical tests. Higher proportions of unhairing wastewater in the soaking drums entailed unacceptable values for the tensile strength when thin hide samples were processed.

3.2.2. *Results of the NF experiments*

3.2.2.1. Nanofiltration performance. The initial water permeability of the membrane was 8.3 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ what indicated that the

Table 4
Characterization of the tanning washing wastewater (before NF).

	pH	Chromium ($mg\,L^{-1}$)	Sulfate ($mg\,L^{-1}$)
Sample 1	4.1	231	5642
Sample 2	4.1	204	5223
Sample 3	4.1	258	5950

Table 5
Sulfates discharged by a tannery per year and per ton of raw hide considering the measures proposed after the experimental results.

Process	Daily wastewater volume (m^3)	Annual sulfates load before the application of the measures proposed ($t\ year^{-1}$)	Annual sulfates load after the application of the measures ($t\ year^{-1}$)	Sulfates per ton of raw hide after the application of the measures proposed ($kg\ SO_4^{-2}\ t^{-1}$)
Soaking	130	12.99	37.01	7.40
Unhairing	70	36.52	0.00	0.00
Deliming	30	7.66	7.66	1.53
Pickling	70	0.76	0.76	0.15
Tanning	50	0.63	0.63	0.12
Tanning washing	50	63.53	1.91	0.38
Acidic wastewaters	100	52.39	52.39	10.50
Total	500	174.48	100.36	20.08

membrane was not fouled and could be used for the NF of the tanning washing wastewater. The samples characterization before its nanofiltration in terms of pH, chromium and sulfate concentrations can be observed in Table 4.

Related to NF retentions in membrane experiments, it can be commented that chromium and sulfate rejections were almost constant (around 99 and 97%, respectively). Similar removal efficiencies were obtained with the membrane DS_5 by Ortega et al. (2005). The high rejections are based on the size exclusion mechanism separation since at the working pH there are not charge interactions. This is due to the isoelectric point of membrane Desal 5DL. Its value is around 4 (Mänttäri et al., 2006; Boussu et al., 2006) practically equal to the NF feed pH.

The transmembrane pressure for adjusting to 12% of permeate recovery was around 5 bar. It was checked that no chemical cleaning was necessary to recover the membrane permeability at the end of each experiment.

3.2.2.2. Sulfates reuse. The rejection stream of the NF can be reused in the tanning since it includes the chemicals needed for the process. In this way, most of sulfates can be recycled to the tanning drums instead of discharging them into the sewer. Thus, considering a sulfate retention of 97% and estimating a permeate recovery of 80% at an industrial scale (from 50 $m^3\ d^{-1}$ of tanning washing, 10 m^3 of a sulfate-rich concentrate and 40 m^3 of permeate are obtained daily), 61.63 t of sulfate could be recovered per year in the NF and could be reused in the tanning as $CrOHSO_4$.

3.3. Total sulfate reduction

Table 3 could be revised considering the reuse of the spent liquors from pickling and tanning, what is already implemented in some tanneries, and the results of applying the measures studied in this work. These measures are the reuse of the unhairing wastewater (65 $m^3\ d^{-1}$ in the soaking and 5 $m^3\ d^{-1}$ in the unhairing itself) and the reuse of the sulfate after its separation by means of NF membranes from the tanning washing wastewater (80% of permeate recovery is supposed). The revised values calculated from the results detailed in Section 3.2 are shown in Table 5.

It can be checked that there is a difference of 14.79 kg $SO_4^{2-}\ t^{-1}$ between the total values of Tables 3 and 5 considering the two measures tested at laboratory scale.

In this way, it is estimated that the reuse of unhairing wastewater in the soaking drum would avoid the discharge of 2.5 kg $SO_4^{2-}\ t^{-1}$, since there will have a diminution of approximately 10% in the addition of sulfide in the unhairing.

Nevertheless, the most effective way of reducing the final sulfate concentration in the wastewater is the reuse of the sulfates in the tanning after the treatment with NF membranes of the tanning washing effluent. In fact, 12.29 kg $SO_4^{2-}\ t^{-1}$ could be reused.

Since the final tannery wastewater is discharged into sewer, the proposed sulfate reduction will entail a positive effect in the municipal wastewater treatment plant. Sulfate diminution will generate a reduction in the H_2S concentration in the biogas coming from the anaerobic sludge stabilization. It has to be commented that H_2S can damage the gas engines used to produce energy from the biogas due to its corrosion effect.

3.4. Economical benefit

From the results, it can be stated that the application of the two measures for sulfate reduction in the tannery would drive to a saving of approximately 10 € per ton of raw hide. Table 6 details these savings achieved by the reuse of both water and chemicals.

The reuse of 65 m^3 of unhairing wastewater in the soaking implies the saving of 65 m^3 of fresh water and the saving of all the chemicals that are usually applied to the soaking. This was possible since the chemicals in the unhairing effluent replaced the chemicals added for the soaking successfully. Besides, sulfides consumption in the unhairing was reduced 10%.

On the other hand, the basic chromium sulfate for the tanning is recovered in such a way that the product to be added in the tanning drum can be reduced almost totally if chromium and sulfate separated by the membranes are recycled to the tanning drums. Besides, the quality of the NF permeate lets its reuse in cleaning operations; thereby the savings of 40 m^3 of water have been considered for the balance.

A cost of 1.3 €/m^3 was considered for the water used in the process. Water comes from a reverse osmosis plant treating well water.

Concerning the expenses, no additional ones have been considered in the reuse of the unhairing wastewater in the soaking. For the NF of tanning washing wastewater, it has to be commented that considering data from industrial NF plants treating residual

Table 6
Resulting saving after implementation of the proposed measures (partial recycling of the unhairing wastewater and recycling of the tanning washing wastewater after nanofiltration).

Process	Water saving			Products saving		Products and water saving
	($m^3\ d^{-1}$)	($m^3\ t^{-1}$)	(€ t^{-1})	(€ $year^{-1}$)	(€ t^{-1})	(€ t^{-1})
Soaking	65	2.8	3.64	6000	1.20	4.86
Tanning washing	40	1.8	2.34	15651	3.13	5.38
Total			5.98		4.33	10.24

floats in the industry (DWA, 2005), the plant amortization will be carried out in less than 2 years.

Operating costs of the NF plant are difficult to predict exactly, since they will depend on the membrane cleaning cycles. Although experiments at larger scale are needed, it can be estimated an operating cost of 2 €/m^3, i.e. 3.5 €/t in our case, thereby the global benefit will be approximately of 6.5 €/t.

4. Conclusions

Sulfates are very difficult to remove from tannery wastewater by means of end of pipe treatments. The implementation of a tertiary treatment to separate them is often unfeasible economically, above all for small and medium size tanneries.

The main sulfate sources in the tannery were identified. Pickling and tanning spent liquors and the tanning washing effluent were the processes that generated the most important sulfate amounts. As recycling of the spent liquors is a usual practice in tanneries, two other innovative measures were studied in this work.

The recycling of unhairing wastewater to the soaking drums implied a sulfate reduction in the wastewaters since the use of sulfides in the unhairing was reduced. Besides, other auxiliary matters were saved in the soaking. A mixture of 50% of process water and 50% of unhairing wastewater was used successfully for the hide soaking. The further hide processing demonstrated that the finished leather met the quality standards.

On the other hand, sulfate retentions of 97% were achieved in the nanofiltration of the tanning washing wastewaters. This reject stream could be reused in the tanning drums.

A difference of 14.79 kg SO_4^{2-} ton^{-1} is obtained considering the two measures tested at laboratory scale. Integrating the experimented measures and the reuse of the pickling and tanning spent liquors, around 60% of the sulfate in wastewaters can be reduced at an industrial scale. In this way, sulfate concentrations lower than 1000 mg L^{-1} can be achieved in the final wastewater. It will drive to a better operation of the municipal wastewater treatment plant that receives the final tannery wastewater, since problems with H_2S will be avoided.

The savings in chemicals and water were very important (more than 10 €/t of raw hide). Concerning the operating costs of the NF plant, it is estimated a cost of about 2 €/m^3 of water produced, equivalent to 3.5 €/t.

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