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The role of tannins in conventional and membrane treatment of tannery wastewater

G. Munz[a,*], D. De Angelis[b], R. Gori[a], G. Mori[c], M. Casarci[b], C. Lubello[a]

[a] Department of Civil and Environmental Engineering, University of Florence, Via S. Marta n.3, 50139 Florence, Italy
[b] ENEA (Italian National Agency for New Technologies, Energy and the Environment), C.R. Casaccia, Via Anguillarese, 301-00060 S.Maria di Galeria, Rome, Italy
[c] Consorzio Cuoiodepur Spa, Via Arginale Ovest 8, 56020, San Romano-S.Miniato, Pisa, Italy

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ABSTRACT

The role that tannins play in tannery wastewater treatment has been evaluated employing a pilot Membrane Bioreactor (MBR) plant and a full scale Conventional Activated Sludge Process (CASP) plant conducted in parallel. The proposed methodology has established the preliminary use of respirometry to examine the biodegradability of a selection of commercial products (synthetic and natural tannins); the subsequent analysis, by means of spectrophotometric reading and RP-IPC (Reverse-Phase Ion-Pair) liquid chromatography, estimates the concentrations of natural tannins and naphthalenesulfonic tanning agents in the influent and effluent samples. The results show that a consistent percentage of the Total Organic Carbon (TOC) in the effluent of the biological phase of the plants is attributable to the presence of natural and synthetic (Sulfonated Naphthalene-Formaldehyde Condensates, SNFC) tannins (17% and 14% respectively). The titrimetric tests that were aimed at evaluating the levels of inhibition on the nitrifying biomass samples did not allow a direct inhibiting effect to be associated with the concentration levels of the tannin in the effluent. Nonetheless, the reduced specific growth rates of ammonium and nitrite oxidising bacteria imply that a strong environmental pressure is present, if not necessarily due to the concentration of tannins, due to the wastewater as a whole. The differences that have emerged by comparing the two technologies (CASP and MBR), in regards to the role that tannins play in terms of biodegradability, did not appear to be significant.

1. Introduction

Although the biodegradability and the inhibiting effect that tannins have on biological processes have each been considered in detail in the scientific literature, they must still be harmonised so that conclusions of a quantitative nature may be drawn. Furthermore, the differences between MBR and CASP in tannin (synthetic and natural) removal from the wastewater do not emerge with sufficient clarity from a bibliographic analysis. The subject on which the experiments have been conducted, on both laboratory and pilot scale, refers to two principal, yet partially distinct themes:

- the biodegradability and the inhibiting effect of tannins on the activated sludge processes;
- the treatment of tannery wastewater with conventional technologies and MBR.

The biological treatment of tannery wastewater, and more generally, the treatment of effluents containing polyphenolic compounds such as tannins, is traditionally difficult and onerous for the following reasons:

- the presence of high concentrations of non-biodegradable COD in aerobic and anaerobic conditions [1,2];
- the presence of inhibiting conditions for the biomass, especially nitrifying biomass [3–6];
- the necessity of operating at high solids retention time (SRT) to obtain stable nitrification and a complete hydrolysis of the particulate organic fraction [7,8].

According to the literature, tannins play a primary role in contributing to the difficulty of treatment and, because the effluents of each phase of the tanning process are usually mixed before the treatment commences, it is highly difficult to evaluate the impact that the tanning baths, which have elevated concentrations

* Corresponding author. Tel.: +39 055 4796317; fax: +39 055 495333.
E-mail addresses: giulio@dicea.unifi.it (G. Munz), doina.deangelis@casaccia.enea.it (D. De Angelis), riccardo.gori@dicea.unifi.it (R. Gori), gualtiero.mori@cuoiodepur.it (G. Mori), claudio@dicea.unifi.it (C. Lubello).

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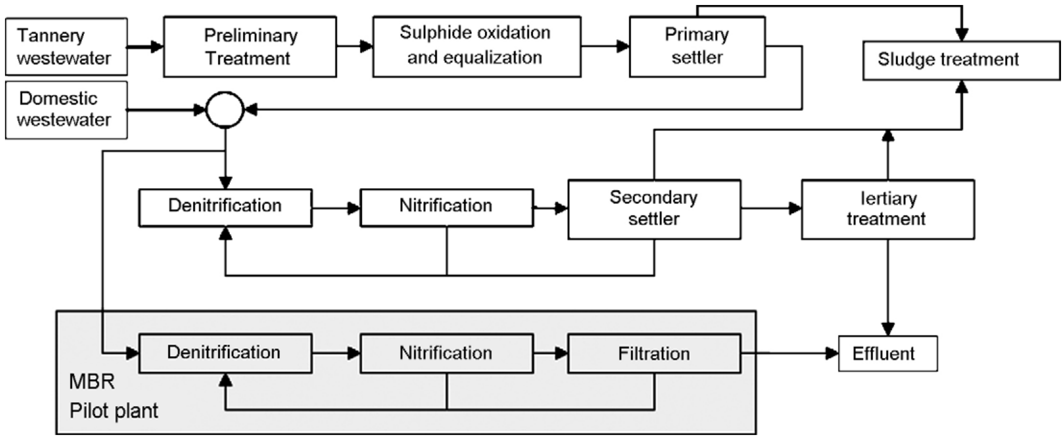

Fig. 1. A simplified block diagram of the Cuoiodepur plant and the pilot plant.

of tannins, have on the treatment process; for example, it is consequentially difficult to evaluate whether it would be opportune to treat such flows separately or not.

The tannins that are used in tanning processes are polyphenolic compounds with elevated molecular weight (from 500 to 4000 Da) and can be subdivided into natural and synthetic tannins [9,10]; natural tannins, in turn, can be subdivided into hydrolysable and condensed tannins [11].

Although strains of bacteria capable of degrading condensed tannins have been isolated and cultivated [12], the biodegradation of natural tannins in the environment is associated with fungi rather than bacteria [11]. In the typical conditions of activated sludge processes, natural tannins have been attributed with scarce biodegradability [1] even if some distinctions, such as the following, have been made: the condensed tannins, such as Wattle and Quebracho, that have a very low biodegradability, and the hydrolysable tannins, such as Chestnut and Tara that are moderately biodegradable [13].

Among the synthetic tannins, the ones based on sulfonated naphthalenes and their formaldehyde condensates (SNFC) play a primary role, for volumes and quantity used. Technical SNFC mixtures are the condensation products of 2-naphthalenesulfonic acid and formaldehyde and consist of complex combinations of mono- and disulfonated monomers and their condensed oligomers (up to $n = 11$) [14,15]. SNFC appear in tannery wastewater in significant concentrations and have been found to be persistent pollutants in surface waters [16].

On the basis of the studies conducted on naphtalenesulfonic tanning agents it is possible to highlight that:

- mono-sulfonated monomers (1-naphthalenesulfonate, 1-NSA and 2-naphthalenesulfonate, 2-NSA) prove to be biodegradable with the use of cultured bacterial strains [17] and in the active sludge processes with both the CASP and the MBR [18,19];
- di-sulfonates monomers (NDSA) have a more varied behaviour: 1,5- and 2,7-naphthalene disulfonate are not biodegradable [20] 1,6- and 2,6-naphthalene disulfonate are biodegradable and 1,7-naphthalene disulfonate seems to be minimally biodegradable [19].

Apart from several sporadic studies [21–23], it is difficult to find detailed bibliographic information on the treatment and concentrations of SNFC in wastewater. This is mostly due to the lack of a detailed knowledge of their commercial mixtures and to the absence of suitable analytical methods.

The naphthalenesulfonic tanning agents have been the objects of experiments with the intent of selecting strains of bacteria capable of degrading them. The cultures, however, were selected only for the monomers, 2-NSA for example, which are generally biodegradable even in the activated sludge processes [17,24]. Other tests for

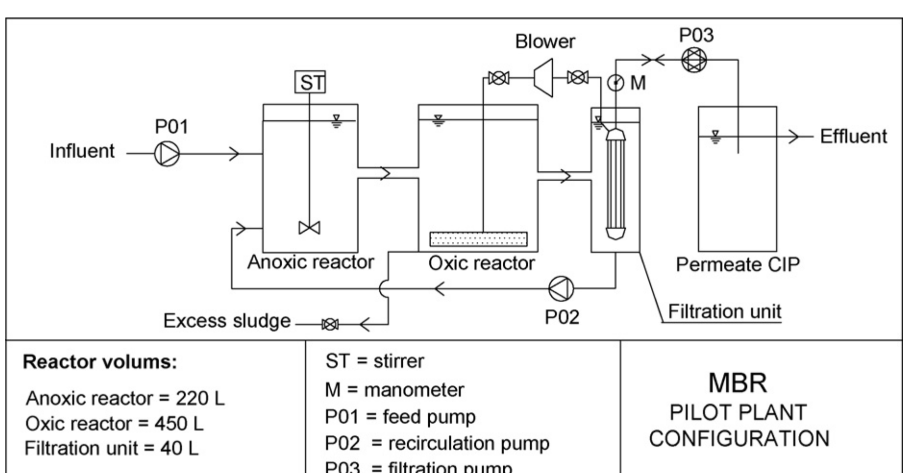

Fig. 2. P and I of the pilot plant.

Table 1
Parameters monitored throughout the experiment

Parameter	TSS	VSS	COD	TN	NH_4^+	S^{2-}	Phenols
Influent	•	•	•	•	•	•	•
Mixed liquor	•	•	•[a]				
Effluent	•	•	•	•	•		•

[a] Filtered samples (Whatman 41 filter paper 20–30 μm).

biodegradation using groups of fungi and bacteria were conducted on SNFC mixtures with the aim of exploiting the ability of the fungi to depolymerise the tannin oligomers, a passage that usually limits the biodegradation of these compounds in activated sludge treatment [25,26].

Interest in the degradation of tannins, both natural and synthetic, is further demonstrated by the numerous chemical–physical processes, especially the advanced oxidation ones [27], that have been proposed and optimised on a laboratory-scale for degradation ([20,23,28–30]) or, more generally, for the oxidation of the biorefractory fraction of the tannery wastewater ([31,32]), in substitution of and/or complementary to the biological process [33].

In regards to the inhibiting effect of tannins on micro-organisms, this effect has been known for some time in both a natural context [34–36] and in the activated sludge treatment [37]. With respect to natural tannins, these prove to be inhibiting in anaerobic processes even in moderate concentrations [38,39], while in the nitrification process intense inhibition occurs only for concentrations upwards of several g/L [40,41]. Some naphthalenesulfonic tanning agents, on the other hand, prove to inhibit nitrification even in concentrations of a few mg/L [42], although there are no studies available that have used well acclimated activated sludge samples.

With regards to the topics discussed above, the differences resulting from the use of membrane bioreactors in substitution of conventional technologies in tannin (synthetic and natural) removal are not clearly established from a bibliographic analysis. The comparison between the MBR technology and CASP pertains rather to the characteristics of tannery wastewater that might have an important role in the filtration process. The experiments in the scientific literature relative to the application of MBR technology to tannery wastewater demonstrate how it is possible to obtain COD removal that oscillates between 86% and 95% [19,43–46]. The efficiency in the removal of the organic load, however, depends on the type of industrial process that has been implemented and consequently on the quantity of non-biodegradable compounds, such as the tannins, that abound in the wastewater; thus, it would be considered useful to evaluate the CASP and MBR technologies that, other than describe the efficiency of the process in terms of macro-parameters also examine the role of tannins.

2. Materials and methods

The experimentation was conducted running and monitoring a MBR pilot plant and a full scale CASP plant which are both fed with mixed, domestic and tannery, wastewater. The wastewater used in the experiments is produced in the industrial district of S. Croce sull'Arno (Pisa, Italy) where the wastewater from chrome tanning (310 tanneries) and from vegetable tanning (120 tanneries) is separately treated in centralised plants: this separation allows to deal with a wastewater that is characterised by elevated concentrations of tannins and that has been directly and almost exclusively produced from vegetable tanning processes. The substantial number of tanneries, on the other hand, renders the wastewater and the variety of chemical products used highly representative of the industrial process. In addition, six abundantly used commercial tannins (3 synthetic and 3 natural), and thus representative of the tanning process, were chosen. Their respective levels of biodegradability and their inhibiting effect were tested through respirometric experiments and inhibition tests (pH-stat and DO-stat).

The experiments were carried out comparing the performances of the biological section of a full scale wastewater treatment plant (WWTP) managed and operated by the Consorzio Cuoiodepur Spa (S. Miniato, Pisa) and a MBR pilot plant, both supplied with the same influent (55% of the tannery wastewater having already undergone primary treatment and 45% domestic wastewater). The Consorzio Cuoiodepur plant, where the experiments were performed, is a centralised WWTP in which the wastewater of roughly 120 tanneries, who have prevalently adopted vegetable tanning processes, is treated.

2.1. Configuration and operating conditions of the pilot plant

A diagram of the full scale plant (CASP) and the MBR pilot plant may be seen in Fig. 1. The configuration of the process in the biological section is the same for both plants (predenitrification, nitrification and separation). The pilot plant (Fig. 2) is equipped with a filtration module, manufactured by Ge-Zenon Environmental, which has a nominal pore size of 0.04 μm. The module is a hollow fibre unit with a filtration surface of 0.93 m^2 and is positioned in an external-submerged configuration. The net filtering capacity has been maintained throughout the duration of the experiment at 11 L m^2 h^{-1}, thus permitting the same Hydraulic Retention Time (HRT) to be obtained in the pilot plant as in the full scale plant (70 h). The re-circulation factor and the concentration of oxygen in the pilot plant have also been maintained equal to those in the full scale plant.

The analyses that will be referred to below, were carried out on samples taken throughout the course of a 70-day period of time during which the sludge age was maintained at 150 d. The adaptation of the biomass to the characteristics of the influent was guaranteed by the fact that the inoculum was taken from the Cuoiodepur plant and the aforementioned period was preceded by a start-up phase of 70 d.

2.2. Monitoring

In the two plants, the entire process was monitored weekly and according to the parameters summarised in Table 1. The analyses of Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), COD, Total Nitrogen (TN), NH_4^+, S^{2-} and Phenols were performed in accordance with the Standard Methods [47].

Measurements relative to the concentrations of tannins and TOC were carried out on average weekly samples drawn from the influent and effluent of the biological section of the two plants and in

Table 2
Characteristics of the influent

Parameter	COD (mg/L)	TN (mg N/L)	N–NH_4^+ (mg N/L)	Phenols (mg/L)	pH	Cl^- (mg/L)	S^{--} (mg/L)	TSS (mg/L)	VSS (mg/L)
Mean	2102	171	118	251	7.2	3260	27	576	459
Maximum	3380	312	205	520	8.1	4810	80	1240	1030
Minimum	359	34	18	45	6.6	1890	3	130	115
Standard deviation	385	59	34	58	0.3	611	131	217	188

the tertiary treatment of the full scale plant effluent. To measure TOC, a DC 190 high temperature TOC analyser by Dohrmann was used.

2.3. Analytic methodologies and sludge characteristics

The influent load demonstrates significant variability relative to the macro-parameters and to the monitored pollutants (Table 2).

RP-IPC (Reverse-Phase Ion-Pair Chromatography) technique was applied to the synthetic tannins using tetrabutylammonium bromide (TBABr) as Ion-pair reagent. The HPLC is a Beckman System Gold model that consists in a binary system with high pressure mixing, a Rheodyne 7125 model injector with a 20 μL loop and model 166 UV Detector System Gold (wavelength fixed at 280 nm). A Merck LiChrosphere 100, RP18 (5 micron) column (250 mm × 4 mm i.d. with a 5 × 4 mm i.d. precolumn), was used. The aqueous mobile phase (A) was HPLC grade water 4 mM in TBABr. A 25/75 mixture of H_2O and CH_3CN both 4 mM in TBABr was used as organic modifier (B). Chromatographic separation and quantification was performed using a binary gradient elution consisting of A and B.

With the exception of the 1 and 2-naphthalenesulfonate monomers, the determinations performed are only used to give a rough estimate. This is due to the fact that pure reference compounds are not commercially available for the oligomers and in its place the commercial synthetic tannin IMD 102 was used. With this substance, whose detailed composition is not known, it was possible to highlight the presence of Na_2SO_4 (through fractional crystallisation) as an impurity which, in turn, was quantified using ion chromatography. Moreover, the external calibration was not conducted on the basis of resolving the oligomers different peaks but rather on the total chromatographic area of all of the unresolved peaks attributed to the oligomers together; this appears to be legitimate since their degree of polymerisation has no influence on the detector response factor [21].

A rapid, selective spectrophotometric method was adopted for natural tannins. The method is an adaptation of the BSA method (bovine serum albumin) that uses both precipitation and complexation of tannins in solution [48]. The reagents used for the method include: a standard protein solution, 4.0 g/L of bovine serum albumine (BSA, Sigma, fraction V), prepared in 0.20 M sodium acetate buffer, containing 0.17 M NaCl; a dodecyl sulfate solution (SDS) and triethanolamine (TEA), 5% (v/v) in TEA and 1% (w/v) in SDS, prepared in distilled water; a solution 0.01 M ferric chloride in 0.01N HCl. All of the reagents were analytical grade (Fluka). The analytic procedure consists of two principal steps, the selective precipitation of the tannins by means of the protein and after the dissolution of the precipitate, the complexation with Fe (III) and the quantification by the spectrophotometric measurement of absorbance at a specific wavelength (522 nm). Tannic acid, generally used for hydrolysable tannins, was employed as the reference standard. However, it has to be noted that the choice of standards remains an unresolved question due to the heterogeneity of the class of compounds; it includes both the hydrolysable tannins and the condensed ones, so that, in reality, a single appropriate substance for their quantification does not exist and the results can vary greatly depending on the substance chosen.

2.4. Respirometric and titrimetric tests

Respirometry and titrimetry have been respectively used to estimate the biodegradability of the reagents used and the kinetics of the ammonium oxidising biomass in the presence of different environmental conditions. The respirometric model used is a flowing gas–static liquid respirometer produced by SPES Srl, which allows for the measurement of OUR and the parallel pH-stat and DO-stat testing in two reactors [40]. The biomass used for the measurements was maintained in endogenous (aerobic) conditions for at least 24 h before testing. During the testing period, temperature was maintained at 20 °C and pH between 7.5 and 8.

Biodegradability of the following matrices was measured: the effluent of the tanning baths, the wastewater, the standard compounds and the samples of tannins chosen because they were representative of the two classes of tannins, natural and synthetic, and because they are largely used in industrial production; three natural tannins, Cuoiotan, Quebracho and Alanbase and three synthetic tannins, IMD 102, Intertan and Adeltan were tested.

Nitrification was studied as a two-step process, subdividing the nitrifying biomass into an ammonium oxidising biomass (X_{AOB}) and a nitrite oxidising biomass (X_{NOB}). The maximum specific growth rates of X_{AOB} ($\mu_{AOB,max}$) and X_{NOB} ($\mu_{NOB,max}$) were estimated using the results of the titrimetric tests. The inhibition of the nitrifying biomass was evaluated with pH-stat testing for the non-biodegradable matrices and with measurements of the levels of nitrite and nitrate for the biodegradable matrices.

3. Results and discussion

3.1. Results of the activated sludge treatment of tannery wastewater with CASP and MBR

Monitoring the pilot MBR and the full scale CASP plant allows us to make several initial observations (Table 3). The COD is removed more efficiently (4% more) and the nitrification process appears to be more complete in comparison with the CASP. The removal of phenols, which can be associated with the presence of tannins, does not differ greatly between the two.

Examining the percentage of phenol removal and the percentage of COD removal, it is possible to observe how these, to a certain degree, are correlated: the best yields in terms of COD removal are associated with an elevated removal of the phenols.

Table 3
Efficiency of the removal processes of COD with CASP e MBR

Sample	Mixed liquor TSS (mg/L)	SRT (d)	COD removal (%)	$N–NH_4^+$ out (mg N/L)	Phenol removal (%)
CD	8780	50	75	5.9	73.6
MBR	13440	150	79	4.1	74.5

Table 4
Biodegradability of several synthetic and natural tannins (commercial products) measured with the MBR sludge

Parameter	Cuoiotan	Quebracho	Alanbase	IMD 102	Intertan	Adeltan
COD (mg/g)	1159	1425	1114	618	741	507
SCOD (mg/g)	958	1000	955	600	701	347
BCOD/COD (%)	22	16	25	17	<5	<5
SBCOD/COD (%)	34	14	26	13	<5	<5

Table 5
Biodegradability of the tannic acid and 2-NSA from the incoming sludge and from a tanning bath measured with the MBR sludge

Parameter	2-NSA (1 g/L)	Tanning bath	Influent wastewater
COD (mg/L)	1610	55400	1890
SCOD (mg/L)	1580	43400	1115
BCOD/COD (%)	>98	27	73
SBCOD/COD (%)	>98	34	22

3.2. Analysis of the biorefractory COD

The biodegradability of the selected commercial products was measured with respirometry using the biomass which was chosen with the membrane bioreactor. The results, as indicated below in Table 4, allow several conclusions to be made. As was to be expected, filtration at 0.04 μm did not allow for a consistent reduction of the COD; the biodegradability of the analysed samples proves to be generally reduced, especially in the case of the synthetic tannins. This is in alignment with the extremely low levels of biodegradability of the tanning bath which is inferior to that of the influent. The tannic acid and 2-NSA monomers (Table 5) do not appear to be representative of the biodegradability of the classes of tannins to which they belong to. The results of these first analyses represent an indication of the consistent presence of tannins, both natural and synthetic, in the effluents of the biological section of the pilot plant and of the full scale plant.

The concentration of natural tannins in the analysed samples is expressed in terms of concentration of tannic acid equivalent. Table 6 shows the measured concentrations of TOC in the samples and TOC values which were calculated with the empirical formula of tannic acid ($C_{76}H_{52}O_{46}$). Based on the TOC obtained results, compared to the values of the organic load of the wastewater, it is possible not only to confirm the presence of natural tannins in the wastewater but also conclude that a significant percentage of the non-biodegradable fraction is attributable to them. This fraction is expressed as the presence of TOC in the effluent from the biological section of the plant and a large percentage of it is removed in the tertiary treatment of the full scale plant.

The analyses relative to the synthetic tannins required a slightly more complex re-elaboration. Table 7 shows the results of the rough estimate that was conducted using solutions of IMD 102 as standard and the theoretical values of TOC relative only to the synthetic tannins. These values were calculated using the SNFC chemical formula shown here ($[C_{10}H_5O_3S{\cdot}CH_2]_x^{-}$-$x$Na) considering the contribution of the monomer $[C_{11}H_7SO_3]^{-}$ which, independently from the degree of polymerisation of the tannin oligomers, is present in the solution.

Based on the obtained results, which were opportunely compared to the values of the wastewater organic load, it is possible to confirm the presence of synthetic tannins and to conclude that, similarly to the natural tannins, a good percentage of the outgoing non-biodegradable fraction in the biological section of the plant is attributable to them and is expressed as TOC; this fraction, as well, proves to be largely removed (over 70%) only in the tertiary effluent.

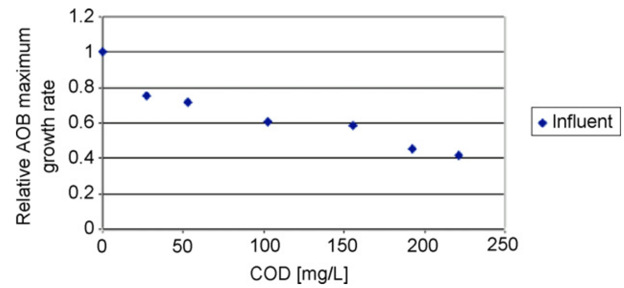

Fig. 3. Effect of the dosage of the influent on specific growth rate of nitrifiers.

Another observation regards one of the constituent unit of the naphthalenesulfonic tannins. From the HPLC determinations it was observed how the 2-naphthalenesulfonate is subject to removal during both traditional biological treatment and in the membrane bioreactors while the tannin oligomers appear to be substantially bio-refractory. Respirometric analyses that were carried out on the monomer confirmed this result, demonstrating that the biomass in the two plants is able to completely degrade this compound.

3.3. The nitrification process

Taking into consideration the age at which the sludge was maintained, the nitrification process during the period of time considered appeared to be relatively unstable and incomplete; this observation, however, is not new in the context of tannery wastewater treatment. Measuring the maximum growth rates of ammonium and nitrite oxidising bacteria with titrimetric testing is the first step in the analysis of these observations. The results ($\mu_{max,AOB} = 0.35\,d^{-1}$ and $\mu_{max,NOB}\,d^{-1} = 0.47$ for MBR at 20 °C; $\mu_{max,AOB} = 0.28\,d^{-1}$ and $\mu_{max,NOB} = 0.53\,d^{-1}$ for CAS at 20 °C), refer to the sludge that has been preventively maintained in endogenous conditions, in other words, in the absence (or almost) of biodegradable compounds; from these results it is possible to infer how the kinetics of nitrification are effectively reduced and how there are not large differences between the kinetics of the biomass selected with either the CASP and the MBR. In particular, it can be observed how the ammonium oxidising bacteria shown to have greatly reduced growth kinetics in comparison to traditional reference values. However, given the sludge age at which the process was conducted, such kinetics would be enough to guarantee complete and stable nitrification. Thus, it is probable that the reason for the observed phenomenology, on both pilot and full scales, depends on the presence of biodegradable inhibitors whose effect is not detectable through testing on the sludge in endogenous conditions. To verify the presence of these biodegradable inhibitors, inhibition tests on the raw wastewater and the concentrated (to factor 10) supernatant of the sludge in endogenous conditions were conducted.

In all of the tests taken, the dose of supernatants in incrementing volume in the mixed liquor did not reveal significant phenomena of nitrification inhibition. The commercial tannins (synthetic and natural) did not produce percentages of inhibition above 5% for

Table 6
Average values of the results of the analysis of the natural tannins in the MBR and CASP samples expressed in terms of tannic acid equivalent—(1 g tannic acid 507 mg TOC)

Sample	Tannic acid (mg/L)	Tannic acid TOC (mg/L)	Sample TOC (mg/L)	Fraction of tannic acid TOC on sample TOC (%)
Influent	72	365	643	5.7
MBR effluent	44	223	125	17.8
CD effluent	48	243	143	17.0
Tertiary effluent	N.R.	–	64	–

Table 7
Average values of the results of the analyses of the synthetic tannins in the MBR and CASP samples expressed in terms of IMD 102—(1 g SNFC 600 mg TOC)

Sample	IMD 102 (mg/L)	IMD 102 TOC (mg/L)	Sample TOC (mg/L)	Fraction of IMD 102 TOC on sample TOC (%)
Influent	120	216	643	3.3
MBR effluent	102	184	125	14.7
CD effluent	110	198	143	13.8
Tertiary effluent	30	54	64	8.4

dosages up to 200 mg/L of COD equivalent. Conversely, the dosage of the influent caused significant inhibition (measured in the first 20 min of the reaction) of the nitrification process even for low concentrations of dosed COD, as can be seen in Fig. 3.

4. Conclusions

The experiments carried out allowed for several significant conclusions to be made relative to the role of tannins in the treatment of vegetable tanning wastewater with MBR and CASP; in particular, it was possible to conclude that:

- natural and synthetic tannins constitute a relevant fraction of the organic biorefractory fraction of tannery wastewater;
- the removal of natural and synthetic naphthalenesulfonic tannins does not greatly differ between the two treatments with MBR and CASP;
- independently of the technology adopted (MBR or CASP), the nitrification process, and especially the nitrosation process, presents extremely reduced kinetics;
- the non-biodegradable fraction of the wastewater does not present an inhibiting effect on nitrosation which instead appears to be slowed by the influent and so inclusive of the biodegradable fraction.

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