Anaerobic treatment of natural tannin extracts in UASB reactors

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Abstract Tannin extracts are substances commonly used in leather production processes. Since most of the steps of tannery manufacturing processes are carried out in aqueous environments, the presence of these compounds in the wastewaters is important. The aim of this work is to study the feasibility of the anaerobic degradation of three natural tannin extracts in three Upflow Anaerobic Sludge Blanket (UASB) reactors, which were fed with increasing concentrations of two condensed (quebracho and wattle) and one hydrolysable tannin extract (chestnut). Concentrations of applied extracts were 100, 200, 400, 800 and 1,000 mg/l, and 5 g/l of glucose was used as cosubstrate. Reactors were operated during 210 days and their performance was evaluated from the values of total and soluble COD, total and intermediate alkalinity, volatile fatty acids, pH and UV absorption at 280 nm. COD removal efficiencies higher than 85% were achieved in all cases. However, tannin extract removal efficiencies (based on UV-280 nm absorption measurements) were significantly lower, around 20% for condensed extracts and 60% for the hydrolysable one, when the reactors operated with the highest tannin extract concentration. The operation of the reactors was stable, commonly with alkalinity ratios below 0.30. Mass balances carried out indicate that most of the COD removal efficiencies are due to the removal of the readily biodegradable organic matter (glucose), whereas the tannin extracts are hardly anaerobically biodegradable, especially condensed extracts (wattle and quebracho).

Keywords Anaerobic; chestnut; quebracho; UASB reactors; vegetable tannin extracts; wattle

Introduction

Tanneries use an important quantity of chemicals in their industrial processes, as well as large amounts of water, which results in the generation of large flows of heavily polluted wastewaters. Physico-chemical units based on chemical precipitation have been commonly used to treat these effluents, but during the last decade processes based on biological treatments have been increasingly studied and applied. In a first step, aerobic processes were used to treat the remaining pollution present in the effluent of the physico-chemical step. However, the most common trend nowadays consists in the direct treatment of these effluents by high-rate biological units, such as modern anaerobic reactors, because of their suitability for the treatment of highly loaded complex wastewaters (Macarie, 2000). Tannery effluents are characterised by their high organic load and the significant presence of different toxic, recalcitrant or slowly biodegradable substances, some of them have been successfully biodegraded anaerobically (Omil et al., 1999; Field and Lettinga, 1987). Moreover, the current European directives about the development and application of cleaner technologies to this sector implies, among other strategies, a step by step implementation of a better process water management, which commonly results in the discharge of lower flows of wastewaters but more highly loaded, these characteristics being more suitable for anaerobic processes.

Natural tannin extracts were the main compounds used in old tanning processes, nowadays being almost completely replaced by chromium. However, these substances are still used in modern industries both in the fabrication of shoe soles and as a complement to chromium in the retanning process. Their presence in the wastewaters discharged by these
factories has been reported (Reemtsma and Jekel, 1994). Anaerobic biological treatment has been successfully applied both for simple tannin compounds (Field and Lettinga, 1987) as well as more complex wastewaters such as those generated by the forest industry (Field et al., 1991).

The aim of this work is to study the anaerobic treatment of wastewaters containing natural tannin extracts. Three Upflow Anaerobic Sludge Blanket (UASB) reactors were fed with increasing concentrations of tannin extracts, and their performance was evaluated in terms of COD and UV removal efficiencies, as well as process stability. Quebracho, wattle and chestnut were the extracts used in this work, which were provided by a local tannery (PICUSA, Spain). These compounds are typical substances utilised in the retanning step.

Materials and methods
Experiments were carried out using three lab-scale UASB reactors (R1, R2 and R3), each one with a useful volume of 0.18 l. These reactors were operated at mesophilic temperature (37°C) for 210 days and with an average hydraulic retention time (HRT) of 2 days. Upward velocity was fixed at 0.25 m/h. 15 g VSS/l of granular sludges were used as inoculum, with a specific methanogenic activity of 0.40 g COD/g VSS d. Glucose (5 g/l) was used as cosubstrate and NaHCO₃ (5 g/l) was added in order to maintain a proper buffering capacity in the medium. Macronutrients and micronutrients were supplied as Field et al. (1988) reported previously. Quebracho and wattle, both condensed tannin extracts, were fed to reactor R1 and R2, respectively; whereas chestnut, a hydrolysable tannin extract, was fed to reactor R3.

Table 1 summarises the different concentrations of each extract fed to the reactors during each period of operation. Feeding solutions were maintained at pH 6.5 in an oxygen-free environment in order to minimise potential tannin polymerisation/oxidation. Volatile Fatty Acids (VFA) were determined as Omil et al. (1999). COD was evaluated through a semi-micro method (Soto et al., 1989). UV absorption at 280 nm was measured as reported previously (López-Fiuza et al., 2001). Total and intermediate alkalinity (TA and IA, respectively) and ratio of alkalinity (IA/TA) were measured according Ripley et al. (1986).

Results and discussion
The start-up period was carried out during the first 50 days. There was no tannin extract content in the influent fed during this period. Once stable anaerobic conditions were achieved and maintained in the reactors, the selected tannin extract was added to each influent at the desired concentration. Organic loading rates corresponding to the influent were maintained around 2.5–3 kg COD/m³·d throughout all periods of operation, since most of the influent COD was due to the presence of the cosubstrate. The COD contribution of the tannin extracts varied from 2.5% to 20%, approximately.

<table>
<thead>
<tr>
<th>Operation time (d)</th>
<th>Quebracho in R1 (mg/l)</th>
<th>Wattle in R2 (mg/l)</th>
<th>Chestnut in R3 (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–50</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>50–70</td>
<td>100</td>
<td>100</td>
<td>100</td>
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<tr>
<td>70–95</td>
<td>200</td>
<td>200</td>
<td>200</td>
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<tr>
<td>95–122</td>
<td>400</td>
<td>400</td>
<td>400</td>
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<tr>
<td>122–157</td>
<td>800</td>
<td>800</td>
<td>800</td>
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<tr>
<td>157–178</td>
<td>1,000</td>
<td>1,000</td>
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</tr>
<tr>
<td>178–203</td>
<td>1,000</td>
<td>0</td>
<td>1,000</td>
</tr>
<tr>
<td>203–210</td>
<td>1,000</td>
<td>400</td>
<td>1,000</td>
</tr>
</tbody>
</table>
Operation with quebracho extract

Figure 1 shows the evolution of the main parameters used to determine the stability of reactor R1: alkalinity ratio and VFA concentration. The concentration of the tannin extract was increased stepwise during each period of operation, up to 1,000 mg/l. However, the anaerobic process was very stable even when the highest concentration of quebracho was used, with average alkalinity ratios below 0.30 and no VFA accumulation (Figure 1). Only a few sporadic increases of alkalinity ratios were detected, which corresponded to the appearance of acetic and propionic acids, but these compounds were quickly removed from the system.

Mean values for total COD and quebracho (also in terms of COD) present in the influent, as well as total and soluble outlet COD are shown in Figure 2A. Standard deviations are also represented for total and soluble outlet COD. Figure 2B represents the total COD removal efficiencies for R1 as a function of the fraction of quebracho present in the feeding. COD removal efficiencies were always above 85%, with some punctual decreases that were quickly corrected. Furthermore, Figure 2B shows also the mean values obtained for the removal efficiencies of the tannin extract, calculated from the UV 280 nm absorption measured in the influent and effluent.

Influent without any tannin extract had no absorption at 280 nm whereas a value around 0.5 was obtained for the effluent. This factor was taken into account when UV-based removals were calculated (Figure 2B). The evolution of the tannin extract removal efficiency shows a continuous decrease when higher quebracho concentrations were treated (Figure 2B). Only when quebracho concentration was below 200 mg/l were the UV removal efficiencies higher than 75%. With higher concentrations the removal efficiencies were lower, around 50% and 20% when 400 and 1,000 mg/l was fed, respectively.

![Figure 1 A: Alkalinity ratio for R1 (●). B: Evolution of acetic (○) and propionic (□) acid concentrations during the operation of the reactor fed with quebracho extract (R1)](image)

![Figure 2 A: Total influent COD (■), quebracho extract influent COD (□□), total effluent COD (■■) and soluble effluent COD (□). B: Total COD removal (●), soluble COD removal (○) and UV-280 removal (△). All series belongs to the reactor fed with quebracho extract (R1)](image)
Operation with wattle extract

The evolution of the alkalinity ratio and VFA content corresponding to the reactor fed with wattle extract (R2) is shown in Figure 3. A relatively stable operation, with alkalinity ratio values below 0.30, was maintained in this reactor except when the maximum concentration of the wattle extract was used (1,000 mg/l).

Instability periods were characterised by the detection in the reactor of higher concentrations of VFA, mainly acetic acid, which indicates that the removal of this compound is the main affected step due to the presence of tanning agents, as Bajwa and Forster (1988) reported previously. Figure 4B shows that this reactor operated with high COD removal efficiencies, near to 100%, when wattle concentrations were below 400 mg/l (around 9% of COD as wattle extract). At 800 mg/l of extract this parameter decreased slightly, and a sharp decrease occurred when the wattle concentration was increased up to 1,000 mg/l (COD removals around 75%), with acetic acid concentrations around 900 mg/l (Figure 3B). In order to recover previous conditions, wattle extract was not added to the influent on day 178, which resulted in an immediate recuperation of the process, with COD removal efficiencies close to 100% again, even when 400 mg/l of wattle extract were again supplied to the feeding.

Figure 4B shows the obtained results for tannin extract removal efficiencies in R2, calculated from the UV 280 nm absorption measurements. Only when the wattle extract concentration was below 400 mg/l were these efficiencies higher than 80%. For higher tannin extract concentrations UV absorption removal efficiencies decreased significantly, with values of 60 and 20% corresponding to 800 and 1,000 mg/l, respectively (Figure 4B). Compared with reactor R1, this unit showed higher UV removal efficiencies (Figure 2B and 4B), especially at 400 and 800 mg/l of extract.
**Operation with chestnut extract**

After the initial stage, reactor R3 showed a high stability throughout all periods of operation. Only around day 180 of operation were some signs of instability detected, which were quickly corrected (Figure 5).

Mean values of each operational period for the COD applied concentrations, as well as COD and UV-based removal efficiencies can be seen in Figure 6. COD removal efficiencies ranged 90–100%, the lower values being observed when operating at the highest chestnut concentrations (Figure 6B). This reactor showed higher tannin extract removal efficiencies than those obtained with the other compounds, with chestnut removal efficiencies higher than 60% even at 1,000 mg/l of this extract.

**Recalcitrant nature of tannin extracts**

Figure 7 shows the comparison of UV-280 nm based removal efficiencies for the three reactors as a function of the tannin extract ratio (g tannin extract/100 g glucose). When reactors worked at low tannin extract ratios (lower than 4) all systems yielded similar and high UV removals (around 80%). However, for higher tannin extract ratios (7–17), UV-based removal efficiencies decreased quickly in R1 and still maintained high values in R2 and R3 (around 60–70%). Finally, for the highest tannin extract ratio R1 and R2 gave the same low values, whereas the removal efficiency achieved in reactor R3 was still higher than 60%.

Although in all reactors COD removal efficiencies were always above 85%, tannin extract removal efficiencies were much lower, especially for reactors R1 and R2 when these units were operated at tannin extract concentrations higher than 800 mg/l (tannin extract ratios higher than 16, Figure 7). Under these conditions UV-based removal efficiencies decreased even down to 20%. The same trend was observed by Vijayaraghavan and
Ramanujam (1999) when they operated an anaerobic filter with increasing concentrations of condensed tanning wastewaters, especially when low hydraulic retention times and high tannin concentrations were applied. Field et al. (1991) worked with debarking wastewaters (with an important tannin content) and reported higher COD removal efficiencies when the tannin fraction was eliminated (extracted with polyvinylpyrrolidone) from reactor influent. All this evidence confirms the typical behaviour of recalcitrant and slowly biodegradable substances of these tannin compounds, since they affect slightly the degradation of other substrates (glucose, in our case) and they have a significant persistence in the medium.

Only when the reactors were operated at the highest tannin extract concentration (1,000 mg/l), could a clear difference in UV-based removal efficiencies between systems working with condensed (R1 and R2) and hydrolysable tannin extracts (R3) be observed (Figure 7). Under these conditions, hydrolysable tannin extracts are more easily biodegradable by anaerobic bacteria than condensed tannins, very likely because of the lower toxic effect exerted on the anaerobic consortia (Sierra-Alvarez et al., 1994; López-Fiuza et al., 2001).

**Conclusions**

The main conclusions of this study can be summarized as follow.

- The anaerobic treatment of wastewaters containing 100–1,000 mg/l of natural tannin extracts (quebracho, wattle and chestnut) and 5 g/l of glucose can be successfully carried out in UASB reactors. Only when the concentration of the wattle was 1,000 mg/l did instability occur.
- COD removal efficiencies were always higher than UV-based removal efficiencies, which indicates that tannin extracts are less degraded, in accordance with their recalcitrant nature.
- The hydrolysable tannin extract used in reactor R3 (chestnut), was degraded more effectively (60–90%) than the condensed tannin extracts used in reactors R1 and R2 (quebracho and wattle, respectively).

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**References**


![Figure 7](https://iwaponline.com/wst/article-pdf/48/6/157/423524/157.pdf)


