Cork industry wastewater characterization: assessment of the biodegradability, reuse and of the relationship between BOD, COD and tannins with TOC

Ana Santos, Marisa Bernardo, Carla Vespeira, Paula Cantinho and Miguel Minhalma

ABSTRACT

Cork processing involves a boiling step to make the cork softer, which consumes a high volume of water and generates a wastewater with a high organic content, rich in tannins. An assessment of the final wastewater characteristics and of the boiling water composition along the boiling process was performed. The parameters studied were pH, color, total organic carbon (TOC), chemical and biochemical oxygen demands (COD, BOD$_5$, BOD$_{20}$), total suspended solids (TSS), total phenols and tannins (TP, TT). It was observed that the water solutes extraction power is significantly reduced for higher quantities of cork processed. Valid relationships between parameters were established not only envisaging wastewater characterization but also to provide an important tool for wastewater monitoring and for process control/optimization. Boiling water biodegradability presented decreasing values with the increase of cork processed and for the final wastewater its value is always lower than 0.5, indicating that these wastewaters are very difficult to treat by biological processes. The biodegradability was associated with the increase of tannin content that can rise up to 0.7 g/L. These compounds can be used by other industries when concentrated and the clarified wastewater can be reused, which is a potential asset in this wastewater treatment.

Key words | biodegradability, cork boiling water, tannins, wastewater reuse

INTRODUCTION

Cork oak (Quercus suber L.) is one of the most important forest types in Mediterranean countries (mainly Portugal and Spain). World cork production is about 250–450 × 10$^3$ tons per year; Portugal is the leading producer with 55% of the world’s production and 33% of the forest area (Beltran et al. 2004).

Prior to industrial uses, cork planks are subjected to several treatment processes. First, they are sorted and then stacked and exposed to open air for about 6 months. After this period, cork planks are boiled in water for approximately 1 h, this process being repeated with other planks in the same boiling water for 2 to 4 days, depending on the cork processing plant. The boiling water can only be used for a restricted number of cork loads, in order to maintain a low concentration of organic compounds as their presence in the cork used to produce stoppers can damage the organoleptic quality of wine (Mazzoleni et al. 1998). Consequently, the boiling water must be frequently replaced after 5 days of continuous process or after 2 days of rest, according to the International Code of Cork Stopper Manufacturing Practice recommendations (Confédération Européenne du Liège 1999). This process renders the planks softer and more flexible and produces a good quality cork with low concentration of corkwood extracts. However, the process consumes a large amount of water and generates a highly polluting wastewater, rich in phenolic compounds, such as phenolic acids and tannins, sugars and salts (Minhalma & de Pinho 2001; Benitez et al. 2008). Table 1 summarizes...
several parameter values mentioned in the literature for the cork processing wastewater and compares them with the EU Directive 80/68/EEC concerning the required quality of wastewater for discharge in public watercourses (Directive 80/68/EEC 1979). The values in the literature are related to discrete samples and no information is given regarding the amount of cork processed or the volume of the boiling tanks in which the boiling stage was carried out, making the comparison of different plant results very difficult. In this work a normalized characterization was carried out, with samples collected at different cork processing plants during a sampling campaign of 12 months. The aim of the study was the establishment of valid relationships between chemical and biochemical oxygen demand (COD, BOD), total phenols (TP), total tannins (TT) and total organic carbon (TOC), which we consider to be an important tool for process control/optimization in the cork industry. Waste-water monitoring and these relationships allow an easy

### Table 1 | Different values of cork processing wastewater characteristics in the literature and EU required quality for wastewater discharge to public watercourses

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EU directive 80/68/CEE</th>
<th>Values range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (mg/L)</td>
<td>–</td>
<td>1,140–1,460</td>
<td>Beltran et al. (2004)</td>
</tr>
<tr>
<td>TSSs (mg/L)</td>
<td>60</td>
<td>50–900</td>
<td>Beltran et al. (2004); Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Total mineral solids (mg/L)</td>
<td>–</td>
<td>340–400</td>
<td>Beltran et al. (2004)</td>
</tr>
<tr>
<td>Total volatile solids (mg/L)</td>
<td>–</td>
<td>850–1,010</td>
<td>Beltran et al. (2004)</td>
</tr>
<tr>
<td>Color 550 (nm)</td>
<td>Not visible at 1:20 dilution</td>
<td>Visible</td>
<td>Benitez et al. (2006); Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>–</td>
<td>1,400–1,640</td>
<td>Beltran et al. (2004)</td>
</tr>
<tr>
<td>Phenolic content (g/L C₆H₅OH)</td>
<td>0.5</td>
<td>0.2–0.6</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Phenolic content (mg/L cafeic acid)</td>
<td>–</td>
<td>480–580</td>
<td>Beltran et al. (2004)</td>
</tr>
<tr>
<td>Polyphenolic content (mg/L gallic acid)</td>
<td>0.1</td>
<td>1,000–3,500</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Polyphenolic content (mg/L tannic acid)</td>
<td>–</td>
<td>660–780</td>
<td>Machado et al. (2006)</td>
</tr>
<tr>
<td>Tannins (mg/L tannic acid)</td>
<td>0.002</td>
<td>851–1,700</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Nitrogen (mg/L)</td>
<td>15</td>
<td>60–200</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Total phosphorus (mg/L)</td>
<td>10</td>
<td>20–60</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Total sulfur (mg/L)</td>
<td>1.0</td>
<td>60–140</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Total copper (mg/L)</td>
<td>1.0</td>
<td>0.1–2.7</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Total iron (mg/L)</td>
<td>2.0</td>
<td>0.5–11</td>
<td>Teixeira et al. (2009)</td>
</tr>
<tr>
<td>pH</td>
<td>6.0–9.0</td>
<td>4.6–6.2</td>
<td>Minhalma et al. (2000); Benitez et al. (2005); Beltran et al. (2004); Mendonça et al. (2004); Machado et al. (2006); Teixeira et al. (2009)</td>
</tr>
<tr>
<td>TOC (mg C/L)</td>
<td>–</td>
<td>1,220–2,000</td>
<td>Minhalma et al. (2000); Machado et al. (2006)</td>
</tr>
<tr>
<td>Zeta potential (mV)</td>
<td>–</td>
<td>–15.0</td>
<td>Minhalma et al. (2000)</td>
</tr>
<tr>
<td>COD (mg O₂/L)</td>
<td>150</td>
<td>2,260–11,500</td>
<td>Benitez et al. (2003); Beltran et al. (2004); Mendonça et al. (2004); Machado et al. (2006); Teixeira et al. (2009)</td>
</tr>
<tr>
<td>BOD₅ (mg O₂/L)</td>
<td>40</td>
<td>500–3,500</td>
<td>Benitez et al. (2003); Beltran et al. (2004); Mendonça et al. (2004); Machado et al. (2006); Teixeira et al. (2009)</td>
</tr>
<tr>
<td>Toxicity (UT)</td>
<td>–</td>
<td>3.4–12.3</td>
<td>Mendonça et al. (2004)</td>
</tr>
</tbody>
</table>
prediction of COD and BOD values and the assessment of the content of valuable compounds (such as tannins) that can be recovered as raw material for other industries such as the tanning/leather industry. Biodegradability of cork processing wastewater was also studied in terms of the BOD/COD ratio in order to provide critical information for biological treatment in wastewater treatment plants.

METHODS

Sampling of cork boiling water and final cork processing wastewater

The samples of cork boiling water were collected at two different cork processing plants located in Montijo and Alcochete (Portugal). In the cork boiling process, two stacks of cork, 800–1,000 kg each, are boiled in tanks for approximately 1 h. This process is repeated six times per day and during a period of 2–4 days. Cork boiling water samples were collected before each stack change, allowing the monitoring of cork boiling water changes due to different amounts of cork boiled (1,600–48,000 kg). The plants’ boiling tanks capacities were 11 and 16 m³.

Cork boiling water and cork processing wastewater characterization

All the samples were analyzed in terms of pH, conductivity, color, TOC, COD, BOD₅, BOD₂₀, total suspended solids concentration (TSS), TP and TT. All the assays were performed in duplicate or triplicate according to the procedures described below.

pH and conductivity were determined using a Multi 340i/SET from WTW, following Standard Methods (APHA 1998). TSS was determined according to the gravimetric method, 5540D (Standard Methods, APHA 1998). TOC was determined according to the high-temperature combustion method, 5310B (Standard Methods, APHA 1998), using an Aurora 1030 Combustion TOC Analyzer from OI Analytical. Color was determined (in Hazen units) by a standard photometric method in a spectrophotometer DR/2000 from HACH. TP content was determined according to the following method: 200 μL 10% (vol/vol) Folin-Ciocalteau reagent and 800 μL 700 mM Na₂CO₃ were added to 100 μL of sample (2% in water), always respecting this order to avoid air-oxidation of phenols. The assay tubes were incubated at room temperature for 2 h and the absorbance was read in each tube at 765 nm (Ainsworth & Gilliespie 2007). The results were presented in g (tannic acid)/L. TT content was determined according to the following method: in 2 mL microtubes, 2 mL of sample (25% in water) was added to 100 mg of polyvinylpolypyrrolidone (PVPP). After vortexing the samples were stored at 4°C for 15 min and centrifuged at 13,400 rpm for 10 min. Finally the total phenolic content determination assay was applied to the supernatant (nontannic total phenolic content). The results were presented in g (tannic acid)/L (Makkar et al. 1995). COD was determined by the titrimetric method, 5220 B (Standard Methods, APHA 1998) and the samples were assayed in parallel with appropriate standards of potassium hydrogen phthalate for quality control. The samples were diluted in the range of 3–10% as a function of its organic matter content. Biochemical oxygen demand (BOD₅, BOD₂₀) was determined by the respirometric method, 5210 D (Standard Methods, APHA 1998) and the samples were assayed in parallel with a glucose-glutamic acid solution for quality control. The samples were diluted in the range of 3–10% as a function of its organic matter content.

RESULTS AND DISCUSSION

Parameter variation along the boiling process

The variation of the physicochemical parameters (i.e. color, TOC, COD, BOD₅, BOD₂₀, TP, TT) along the boiling process is depicted in Figures 1 and 2. Because the volume of water used in the boiling stage of the process is not the same for all industrial plants, results were normalized considering the cork processed per volume of boiling water: CPV (t/m³).

The normalized results show that for lower values of CPV, the parameter values increase linearly with the increase of the quantity of cork processed (CPV); this increase is less pronounced, reaching a plateau, towards the higher quantities of cork processed. For values higher than 3 CPV the parameters tend to stabilize, indicating a decrease in the extraction power, i.e. the organic solutes
extraction from the later cork planks processed is significantly reduced. These results indicate that, instead of the periodicity of 5 days for the replacement of the water used in the boiling tanks, recommended by the International Code of Cork Stopper Manufacturing Practice, the periodicity must be decided depending on the quantity of cork boiled in the same boiling water, and this should not be higher than 3 t/m³.

Final wastewater characterization

Since the cork processing plants have differences in the boiling stage of the process, namely the boiling tanks' capacity, stacks weight, number of loads processed per day and the periodicity of water discharge, there are large differences in the composition of the final wastewater generated by this industry. Usually, the plants change the boiling water after 2 to 5 days of the boiling stage, which corresponds to approximately 1.5-4.0 CPV, respectively. The results obtained (Figures 1 and 2) show that the cork processing final wastewater presents values of pH, COD and BOD₅ well above the VLE (limit emission value: COD = 150 mg O₂/L; BOD₅ = 40 mg O₂/L, according to EU Directive 80/68/CEE) which render its release to the environment, without appropriate treatment, unviable. The COD and BOD₅ results show that this wastewater presents a low degree of biodegradability, as the BOD₅/COD ratio is always lower than 0.5 for CPV values higher than 1.5 (Figure 3).

The characterization also envisaged the quantification of tannins in these wastewaters since these compounds have a high added value if used in other industries such as tanning, glue/resin and wastewater treatment industries. The results have shown that tannin content can rise up to 0.7 g/L after 4 days of boiling process which represents about 70% of the TP content and 10% of the TSSs.

The recovery of tannins can be carried out by, for example, membrane processes (Teixeira et al. 2009; Oliveira et al. 2009; Bernardo et al. 2011), where two streams can be generated: a tannin enriched concentrate stream that has potential application in other industries; and a permeate.
stream that can be either reused in the boiling tanks or discharged into the municipal collector, posing little treatment problems, as the organic and non-biodegradable content was significantly reduced.

Relationships between parameters

The results obtained allowed the establishment of valid relationships between color, COD, BOD, TP and TT with TOC, as the last one is measured by an easy and rapid analysis method. This was done having in mind the possibility of predicting the results of the parameters with most complex/longer experimental determinations, and therefore providing an important tool for process dimensioning and optimization and also for boiling water and final wastewater monitoring and control.

The relationships between the different physicochemical parameters and TOC are depicted in Figure 4 and the respective regression equations are presented below (Equations (1–5)).

\[
\text{COD} = 2.204\text{TOC} + 538.11 \quad (R^2 = 0.97) \quad (1)
\]

\[
\text{BOD}_5 = 0.5704\text{TOC} + 454.85 \quad (R^2 = 0.88) \quad (2)
\]

\[
\text{BOD}_{20} = 0.9833\text{TOC} + 392.26 \quad (R^2 = 0.89) \quad (3)
\]

\[
\text{TP} = 0.3072\text{TOC} + 87.31 \quad (R^2 = 0.97) \quad (4)
\]

\[
\text{TT} = 0.2173\text{TOC} + 48.721 \quad (R^2 = 0.94) \quad (5)
\]

As can be seen, in general, there is a good correlation between all the parameters and the values obtained for TOC, indicating that TOC analysis can be used in order to estimate the other parameters and assess a more complete wastewater characterization.

The major advantages of TOC over the other techniques, such as COD or BOD, are the speed of analysis, the consequent ability to analyze replicates, the precision and accuracy of the determination (2–6% of the TOC test against 10–20% of COD and BOD tests), the low cost per test and use of the least amount of sample required. These advantages make TOC determination very useful in the analysis
of a high number of samples and provide information on the magnitude of the BOD and COD values.

The correlation between BOD5 and BOD20, presented in Figure 3 (left), is also a very important relationship, as it provides information on the biodegradation velocity of the boiling waters and allows the prediction of the ultimate BOD considering only 5 days of BOD experiments. The results show a good linear correlation between BOD20 and BOD5, considering CPV values ranging from 0.3 to 3.82. We can also see that after 5 days, only 69% of the biodegradable organic matter was degraded, which is in the same range as that observed for urban wastewater (Metcalf & Eddy 2003).

Biodegradability is a crucial aspect to take into account in the planning of the wastewater treatment, therefore the ratio BOD5/COD and the tannin content (mg tannic acid/L) were presented as a function of CPV (t/m3) in Figure 3 (right). It was noticed that, in an initial phase, the increase of the quantity of cork boiled leads to an increase of tannin content and to a reduction of the biodegradability. However, for CPV values higher than 2.0 these parameters stabilize at approximately 0.30 and 0.65 g (tannic acid)/L, respectively. These results, together with the low BOD5/BOD20 values observed, lead us to think that the polyphenolic fraction, namely the tannic fraction of the boiling water, is responsible for the low and slow biodegradability of these wastewaters and that for higher tannin concentrations there might even be an inhibition effect in the biological activity, rendering these wastewaters very difficult to treat by conventional biological treatments (for example activated sludge).

CONCLUSIONS

Cork boiling water and cork processing wastewater, collected at different cork processing plants, were characterized at different stages of the boiling process. The normalized characterization results provided extremely useful information for process dimensioning/optimization and also for boiling water and final wastewater monitoring and control.

It was observed that with increasing loads of cork planks treated in the boiling tanks (CPV), parameters such as TOC, color, COD, BOD, TPs and TTs present a linear increase up to a CPV of 5, and from then on a plateau is reached indicating a decrease in the boiling water extraction power.

The relationships established between color, COD, BOD, TP and TT with TOC, which is an easy and rapid analysis, presented a good correlation, providing a useful tool for the estimate of other parameters (based on TOC measurements) and assesses a more complete wastewater characterization.

The COD and BOD5 results shown that these wastewaters present a low degree of biodegradability, as the ratio BOD5/COD is always lower than 0.5, and that this biodegradability degree decreases for increasing loads of cork planks boiled and with the increase of the tannins concentration in the wastewater. These results indicate that for higher concentrations of tannins there is a low biodegradability and might even be an inhibition in biological activity, rendering this wastewater very difficult to treat by conventional treatments.

The quantification of tannins in these wastewaters, which are compounds that have a high added value if used in other industries such as tanning, glue/resin and wastewater treatment industries, shows that tannin content can reach values up to 0.7 g/L after 4 days of the boiling process. These compounds can be extracted from the wastewater by, for example, membrane processes, and a tannin-enriched concentrate can be obtained. At the same time, a permeate stream, with low organic matter content, can be generated and reused in the boiling process or discharged into the municipal collectors (posing little treatment problems, as the tannin content is significantly reduced).

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