CORK BOILING WASTEWATER MANAGEMENT BY ANAEROBIC DIGESTION

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Keywords: cork, wastewater, anaerobic digestion

Abstract

Cork boiling wastewater (CBW) is an aqueous and complex effluent of the cork industry which is produced during the boiling of the cork planks, one of the key operations in cork processing for cork stoppers production. CBW contains suspended and dissolved solids and organic materials such as phenolic compounds and is characterized by a low biodegradability and an acid pH. This boiling wastewater has no utility, being a serious environmental hazard. Anaerobic digestion is a promising technology for the treatment of organic effluents and for the simultaneous recovery of its energetic potential through methane production. Its application to cork effluents has never been subject of research. An anaerobic assay was conducted in order to determine the gas potential and biodegradability of the substrate using a mesophilic anaerobic consortium. Biodegradability batch experiments were performed at CBW concentrations of 3 and 6 kg COD m^{-3}. The cork industry effluent was characterized (COD = 6.5 kg m^{-3}; pH = 5.8). The liquid phase was analysed at the end of the experiment (pH, COD, total phenols). The methane accumulated in the vessels headspace was measured by gas chromatography. The maximum methane production was achieved after 15 days of experiment, and maintained until the end (44 days). The resultant methane potentials were 0.126 - 0.142 m^3 CH_4 kg^{-1} COD. The results suggest that CBW could be an interesting substrate for the anaerobic digestion process. The highest concentration (6 kg COD m^{-3}) did not inhibit or significantly influenced the methane production. Concluding, a novel approach for the treatment and valorisation of the cork boiling effluent was revealed. The results demonstrate that the effluent from cork boiling can be treated and valorised by anaerobic digestion.

1- INTRODUCTION

Cork is the outer bark of the cork-tree (*Quercus suber* L.) of high economic and social importance in the Mediterranean region. Portugal is the world-leading producer and exporter of cork and cork products. One of the firsts and key steps in cork processing for cork stoppers production (the main cork product) is cork boiling in water. This operation allows for a cleaning/disinfection of the material, an increase of its volume and an improved workability. The boiling is usually carried out for at least one hour at a temperature near 100ºC. Sometimes, after the boiled cork stabilization a second shorter boiling operation is carried out. Cork boiling wastewater (CBW) is an aqueous and complex effluent of the cork industry which is produced during the first step of cork processing, the boiling of the cork planks. CBW contains suspended and dissolved solids and organic materials such as phenolic compounds and is characterized by a low biodegradability and an acid pH. This boiling wastewater has no utility, being a serious environmental hazard.

Anaerobic digestion is a promising technology for the treatment of the strength organic effluents and for the simultaneous recovery of its energetic potential through the methane production. Despite the inherent advantages of anaerobic process, its application to cork effluents has never been subject of research.

Fig. 1. Cork boiling water

Fig. 2. Cork boiling tank

2- MATERIALS AND METHODS

2.1. Inoculum and Substrate

The sludge was obtained from a hybrid reactor treating olive mill wastewater, as described elsewhere [1, 2]. The inoculum was pre-incubated at 37ºC in order to deplete the residual biodegradable organic material. Cork boiling effluent was obtained from cork industry in Alcácer do Sal, Portugal. The substrate was stored at 4ºC until being used. The effluent was characterized and the values obtained are summarized in table 1. Before using the substrate, pH was adjusted to 7.0-7.2 with NaOH.

Parameter	CBW*
pH	5.8 ± 0.0
Conductivity (mS cm^{-1})	1.5 ± 0.1
Total COD (kg m^{-3})	6.5 ± 0.1
Soluble COD (kg m^{-3})	6.2 ± 0.1
TS (kg m^{-3})	5.13 ± 0.08
VS (kg m^{-3})	4.05 ± 0.04
TSS (kg m^{-3})	0.58 ± 0.11
VSS (kg m^{-3})	0.15 ± 0.07
Total Phenols (kg m^{-3})	0.60 ± 0.00
Total Nitrogen (kg m^{-3})	0.04 ± 0.00

**The values are expressed as an average ± standard deviation of three replicates*

Table 1: Main characteristics of cork boiling wastewater (CBW) used in the batch experiments

2.2. Batch experiments: set up and procedure

The biodegradability experiments were performed in closed vials with a total volumes of 35 cm^3 and a working volume of 12.5 cm^3. The sludge was added to the vials at a final concentration of about 5 kg VSS m^{-3}. The basal medium was made up with demineralised water and sodium bicarbonate (3 kg m^{-3}). The batch tests were performed with cork boiling water at concentrations of 3 and 6 kg COD m^{-3}. The vials were closed with a butyl rubber stopper and sealed after transferring the inoculum, the basal medium and the substrate. The headspace of the batch vials was flushed with N2. The tests were performed in triplicate and were incubated at 37º C. The methane accumulated in the vessels headspace was measured by gas chromatography, as described in the analytical methods section, by collecting 500 uL of sample volume using a gas-tight syringe. Methane production was corrected for standard temperature and pressure (STP) conditions. The amount of methane produced was converted to its COD equivalent (mg COD-CH_4) considering the biochemical methane potential (350 L CH_4/kg COD). The methane yield was expressed as the ratio between methane produced and the COD added to the batch vials (m^3 CH_4 / kg COD added).

2.3. Analytical methods

Total and soluble chemical oxygen demands (CODt and CODs) and Total Nitrogen (Nt) were evaluated using Spectroquant® test kits (Merck). Total and volatile solids (TS and VS) and suspended total and volatile solids were determined according to Standard Methods [3]. Total phenols (TP) were assessed by a modified Folin-Ciocalteau method [4]. Gases were separated in a 1/8" x 3 m Porapak® column (80-100 mesh) and determined with a thermal conductivity detector in a Varian 3800 chromatograph with column, injector and detector temperatures at 50 ºC, 60 ºC and 100 ºC, respectively.

3- RESULTS AND DISCUSSION

The biodegradability tests were performed with 3 and 6 kg COD m^{-3} of CBW. The methane production was assessed along 44 days (Figure 1). No lag phases were observed in the presence of CBW. In the batch experiments performed with 3 kg COD m^{-3} the maximum methane production (15 mg COD-CH_4/batch) was attained after 15 days and it was stable until the end of the experimental time. In the batch experiment performed with 6 kg COD m^{-3}, most of the methane was produced in the first 15 days of the experiment and a production of 27 mg COD-CH_4/batch was achieved at the end.

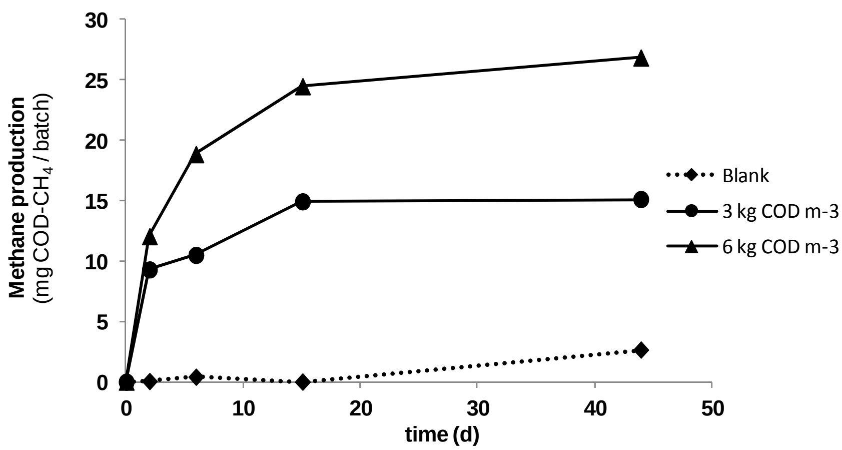

Figure 1 – Methane production throughout the biodegradability batch experiments performed with 3 and 6 kg COD m^{-3} of Cork Boiling Wastewater and performed in the absence of the effluent (blank).

Considering these results, the methane potential of CBW (without any pretreatments, pH correction, only) was determined as 0.126-0.142 m^3 CH_4 kg^{-1} COD_{added} (Table 2).

CBW (kg m-3)	pH	CH_4 Yield (m^3 CH_4 kg^{-1} COD_{added})
3	7.67 ± 0.02	0.142 ± 0.014
6	7.52 ± 0.12	0.126 ± 0.016

Table 2: Methane yield and pH at the end of the experiments performed with 3 and 6 kg COD m^{-3} of cork boiling wastewater (CBW).

Up to about 40% of the COD of CBW was converted into methane. The remaining fraction was not degraded by anaerobiosis and it might be due to the inhibition of the microbial consortium or to the presence of non/difficult biodegradable substances, wherein the latter is more likely to have occurred. Microbial population is sensitive to changes in pH and also to the presence of inhibitory substances [5]. Nevertheless, the pH was neutral at the end of the experiment which is favourable to the anaerobic process. These wastewaters contain a significant concentration of phenolic compounds (TP= 0.6 Kg m^{-3}). At the end of the experiment, the effluent was dark which suggests that the phenolic compounds were still present. Field and Lettinga (1989) studied the effect of oxidative colouration on the methanogenic toxicity and biodegradability of a synthetic phenolic solution. They found that coloured compounds were not biodegradable and their presence did not affect the biodegradability of colourless compounds [6].

The effluent after anaerobic digestion can be degraded with a post-treatment. Gonçalves et al. (2012b) showed recently the feasibility of a two-step process combining anaerobic digestion and electrochemical oxidation for the treatment and valorisation of olive mill wastewater wherein the dark colour, phenolic fraction and remaining COD of the effluent after anaerobic digestion was removed by the electrochemical process [7].

The present work suggests that CBW could be an interesting substrate for the anaerobic digestion process. The highest concentration (6 kg COD m^{-3}) did not inhibit or significantly influenced the methane production.

4- CONCLUSIONS

A novel approach for the treatment and valorisation of the cork boiling effluent was revealed. The results demonstrate that the effluent from cork boiling can be treated and valorised by anaerobic digestion. Without any pre-treatments (pH correction, only), a CBW methane potential of 0.126-0.142 m^3 CH_4 kg^{-1} COD_{added} was obtained.

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