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# Investigation of lab-scale horizontal subsurface flow constructed wetlands treating industrial cork boiling wastewater

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## HIGHLIGHTS

- First application of constructed wetlands for cork boiling wastewater treatment.
- Systems planted with common reeds outperformed conventional biological treatments methods.
- Average removals reached 75% for COD, 91.7% for $BOD_5$ and 69.1% for Total Phenols.
- Decolourization was limited to 35% and not correlated with biodegradation activity.
- Effluent post-treatment is required for enhanced decolourization.

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## ABSTRACT

The feasibility and treatment efficiency of horizontal subsurface flow constructed wetlands (HSFCW) was assessed for the first time for cork boiling wastewater (CBW) through laboratory experiments. CBW is known for its high content of phenolic compounds, complex composition of biorecalcitrant and toxic nature. Two lab-scale units, one planted with *Phragmites australis* (CWP) and one unplanted (CWC), were used to evaluate the removals of COD, BOD, total phenolic compounds (TPh) and decolourization over a 2.5-years monitoring period under Mediterranean climatic conditions. Seven organic and hydraulic loading rates ranging from 2.6 to 11.5 g COD/m$^2$/d and 5.7–9.1 L/m$^2$/d were tested under average hydraulic retention time (HRT) of $5 \pm 1$ days required due to the CWB limited biodegradability (i.e., $BOD_5$/COD of 0.19). Average removals of the CWP exceeded those of the CWC and reached 74.6%, 91.7% and 69.1% for COD, $BOD_5$ and TPh, respectively, with respective mass removals rates up to 7.0, 1.7 and 0.5 (in g/m$^2$/d). Decolourization was limited to 35%, since it mainly depends on physical processes rather than biodegradation. CBW concentration of nine phenolic compounds ranged from 1.2 to 38.4 mg/L (for the syringic and ellagic acids, respectively) in the raw CBW, with respective removals in the CWP unit ranging from 41.8 to 76.3%, higher than those in the control unit. Despite CBW high concentration of TPhs (average of 116.3 mg/L), the HSFCW reached organic load removals higher than those of conventional biological treatment methods.



## 1. Introduction

Water resources protection from chemical contamination imposed from point and diffused sources is a major goal of the European Water Framework Directive (EU, 2000). Treatment of wastewaters is mandatory prior the final discharge to a water body. Several technologies are available to meet the increasingly stringent quality requirements yet biological processes are the most

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widely used (Oller et al., 2011; Ahmed et al., 2017). Constructed wetlands (CWs) have already accomplished a long record of successful applications as a proven technology for domestic and municipal wastewater treatment (Vymazal, 2011; Stefanakis et al., 2014). Today, the challenge in wetland technology lies in the effective treatment of various industrial wastewater sources (Wu et al., 2015; Tatoulis et al., 2016; Schultze-Nobre et al., 2017; Stefanakis, 2018). The success of CWs relies on complex physical, chemical and biological processes occurring simultaneously at different micro-sites and under diverse conditions, namely for oxygen availability (Faulwetter et al., 2009; Stefanakis et al., 2014; Wu et al., 2015). This multitude of conditions increases the diversity of the microbial activities, such as biological uptake, biotransformation, co-metabolism, nitrification, denitrification, etc., being advantageous in the case of wastewater with complex compositions (Faulwetter et al., 2009; Wu et al., 2015; Stefanakis et al., 2016), as it is the case of cork boiling wastewaters (CBWs).

Boiling is a low complex operation: the raw material after the extraction from the cork oak (*Quercus suber* L.) and drying in open air is immersed in boiling water for up to 1.5 h. This process intends to clean, disinfect and moisten the raw material, and is critical for the quality of the cork products, namely stoppers. To ensure close to complete removal of contaminants, the reuse of boiling water is limited to 6–30 loads of cork according to the quality requirements. Hence, the water consumption rises up to 140–1200 L per tonne of cork processed (APCOR, 2015).

Besides its large volume, CBW is a dark brown complex aqueous solution due to the high concentration of cork extracts contributing to high organic load of biorecalcitrant nature; thus, chemical oxygen demand (COD) and total phenolic compounds (TPh) concentrations are high; 1.2–11.5 g/L and 1.0–3.5 g/L, respectively. Biodegradability is restrained by the limited biological oxygen demand after 5-days ($BOD_5$) and 20-days ($BOD_{20}$) incubation period of 0.5–3.5 g/L and 0.6–1.3 g/L, respectively (Gomes et al., 2013; Benitez et al., 2003; Marques et al., 2014; Fernandes et al., 2015). The limited CBW analysis reported in literature indicate the presence of several phenolic compounds and degradation products of lignin, namely vanillic, gallic, caffeic, ferrulic, syringic and ellagic acids at concentrations ranging, e.g., from traces up to 96.5 mg/L for the vanillic and ellagic acids, respectively (Santos et al., 2013a; Marques et al., 2014). Some of these compounds have high molecular weight (MW), e.g., tannins with 500 to 3000 Da, and when polymerized can reach up to 40 kDa (Aguilera-Carbo et al., 2008). A published study on detailed and summarized information on CBW characterization (Gomes et al., 2018) indicated the high variability of CBW quality depending on the composition of the raw corkwood processed, the specific water consumption, and/or different contamination levels.

Several of these are toxic due to their ability to inhibit the activity of many microorganisms present in wastewater treatment plants (WWTPs) (Martins et al., 2010; Santos et al., 2013a; Stefanakis and Thullner, 2016). Therefore, COD removals (13–40%) reported for conventional biological treatment methods (e.g., activated sludge treatment (Benitez et al., 2003) and anaerobic digestion (Marques et al., 2014) do not fulfil the legal requirements. Advanced oxidation processes achieve COD removals of up to 94%, but they are not always economically feasible (Oller et al., 2011; Gomes et al., 2013; Fernandes et al., 2015). In general, combination of conventional mechanical/biological treatment technologies (e.g., activated sludge and extended aeration) with advanced technologies (e.g., membranes and oxidation processes) are usually required to achieved good removal rates and decolourization. However, such a solution is characterized by high investment and, especially, operational costs, high complexity, high maintenance and energy needs and high environmental footprint, which often render this option technically and financially infeasible.

Overall, partial or improper treatment of CBW is an important environmental problem, especially in some regions of Portugal, where the cork industry represents 61% of the world cork production estimated to surpass 200,000 ton per year (APCOR, 2015).

Therefore, there is a major need and opportunity to adopt an eco-friendly approach to CBW treatment based on CWs technology. CWs provide several advantages over conventional biological methods, such as simple operation/maintenance, significantly lower operational costs, low to zero energy requirements, no use of chemicals and an environmentally friendly character (Vymazal, 2011; Stefanakis et al., 2014; Wu et al., 2015; Stefanakis, 2018). Hence, the use of wetland technology as the biological treatment stage of CBW could significantly limit the operational costs and enhance the simplicity and the ecological character of the selected solution, among other benifits. Among the various CW types, horizontal subsurface flow (HSF) CWs are widely used worldwide (Akratos and Tsihrintzis, 2007; Albuquerque et al., 2009a; Schultze-Nobre et al., 2017; Tatoulis et al., 2017). The main limitation is the higher land requirement compared to conventional/mechanical treatment methods (Stefanakis et al., 2014; Wu et al., 2015). However, this is not critical in the case of CBW since most of the cork processing units are in rural, remote regions of the Iberian Peninsula under the warm Mediterranean climatic conditions, where large land areas are available.

The aim of this research was to investigate the feasibility and efficiency of wetland technology for CBW treatment over an extended operational period of 2.5 years. Specific goals were to evaluate the contribution of plants to the overall performance through the comparison of two lab-scale units, i.e., one planted and one unplanted, as well as the effect of different organic loading rates (OLRs). This research study is, to the best of authors knowledge, the first application of CW system to this type of industrial effluent and intends to overcome the challenges and drawbacks of conventional biological methods to fulfil the quality standards required for the discharge or reuse of treated CBW.

## 2. Materials and methods

### 2.1. Lab-scale constructed wetlands setup

Two laboratory-scale HSFCWs units made of PVC were used for the study; each unit had a surface area of 0.053 $m^2$ with dimensions $0.35 \times 0.15 \times 0.25$ (length × width × height, in m) and was filled with LECA (light weight aggregate; the commercial name of Filtralite NR) as substrate media (38% porosity) up to a height of 0.143 m from the bottom. The water level was maintained at 0.098 m from the bottom. One lab-unit was planted with *Phragmites australis* (CWP) and the other was kept unplanted and served as control unit (CWC). The CWP was provided with two sampling points (SP1 and SP2) along the unit length to collect samples at the middle of the unit and close to the outflow (at 4/5 of unit length). The CWC had only the SP1 sampling point.

The inlet structure was composed of a "T" tube with several orifices to enhance the uniform distribution of the influent along the upstream width side. The lab-units were placed indoors at the Chemistry Department of the University of Beira Interior in Covilhã, Portugal (N40°16′41.2″, W7°30′34.2″) to avoid high temperature variations but ensuring plenty of natural light at the same time. During the cold season, a thermostatic device was used to maintain the temperature inside the CW units close to 20 ± 2 °C. The influent solution (i.e., raw CBW) was kept in the refrigerator at 4 °C (to avoid any degradation) before its application to the CWs. It was fed to the CWs under intermittent flow mode using two peristaltic pumps (Ismatec BVP) operating for 15 min every hour. During all