Part V

Wood and Leather Processing Industry

14

Cork Boiling Wastewater Treatment in Pilot Constructed Wetlands

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14.1 Introduction

14.1.1 Cork Production and Manufacture

Cork is the natural and renewable material extracted from the out bark of the producer tree (*Quercus suber* L.) by traditional procedures after growth cycles of nine years, from trees older than 20 years. This activity is strictly regulated and intends to ensure a lifespan production over 200 years and ultimately contribute to the preservation of these natural forest ecosystems, typical of the Mediterranean region. Apart from cork production, these forests are also characterized by their high level of biodiversity, their contribution to hydrology regulation, prevention of desertification and carbon dioxide fixing (18 kg per kg of cork extracted) [1]. Thus, cork production is a model of sustainability between human activity and natural resources preservation [2–4]. Moreover, since 1993 the ecological importance of cork oak forests was also taken into account by the European Union and they were classified as protected habitats under the framework of the Natura 2000 Network [2].

Besides the environmental importance for the Iberian countries, where 51% of this natural ecosystem on earth is located (i.e., about 1,289,000 ha), the economic and social aspects have also been taken into consideration, given that Portugal and Spain produce more than 80% of the world cork annual production, estimated to surpass 200 thousand tons per year. Portugal alone has a market share of 70% for cork product exports, mostly wine stoppers and agglomerates for thermal and acoustic insulation [1]. The economic and social outlook of production and manufacture activities are critically dependent on wine consumers' preference for one-piece stoppers made with cork in compared with those produced with synthetic materials, because this application uses only 15% of the cork produced, but accounts for approximately 75% of the industry revenues [5]. Thus, if the market share of cork stoppers declines, the profit from cork extraction activity is also reduced and the maintenance of these ecosystems of high ecological value would probably decline.

The industrial processing of the cork slabs after extraction from trees starts with maturing and drying stages followed by the boiling process, a low technology operation intended to improve the cork texture and properties, making this material more homogeneous, flat, elastic and mostly free

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of biological and chemical contamination. The traditional procedure continues to be used in most industries and includes the immersion of the corkwood in boiling water for 1.0–1.5 h. Due to the critical importance of organic contamination removal, especially if the raw material is intent to produce stoppers, the reuse of hot water has to be limited and ranges from 6 up to 30 loads of raw cork according to factory procedures and quality standards [6–8]. The high-quality requirements for the water used in the boiling stage contribute to increment the fresh water consumption and consequently the volume of effluent produced, which ranges from 140 to 1,200 L/ton of corkwood processed [7, 9, 10]. Thus, this stage of the industrial cork processing raises some environmental concerns due to the high specific water consumption and the organic load of bio-recalcitrant nature of the effluent.

Hitherto, most studies published on the topic of cork boiling wastewater (CBW) treatment or valorization used physico-chemical treatment options rather than biological processes. However, the related costs are high and above those of the biological treatment alternative for wastewaters with similar organic loads but from different sources [11, 12]. Thus, constructed wetland systems (CWs) can be an alternative to conventional biological treatment systems, namely to activated sludge systems, with the prominent virtues of low construction and operation costs [13–15]. CWs are engineered to take advantage of several mechanisms to remove pollutants, namely physical processes (precipitation, filtration, sedimentation and volatilization) and biochemical processes induced by wetland plants and microorganisms [13, 16, 17]. Additionally, the landscape value of wetlands is perfectly compatible with cork oak forests.

Until today, there is no study or research published for the treatment of CBW using CW systems. Thus, this investigation is a novelty and included the monitoring over a period of four years of the operation of a horizontal subsurface flow constructed wetland (HSF CW) microcosm-scale system planted with common reeds (*Phragmites australis*) and filled with light expanded clay aggregates (LECA), as support media for the plants and for biofilm development. The contribution of plants to the treatment was assessed by the comparison with an identical wetland unit without plantation (control bed). After this extended period of operation intended to maximize biomass development and acclimatization, which included stepwise increase of the organic load rate (OLR) up to 8.9 g COD/m^2/d, the assessment of the treatment capacity of the system was done by doubling the OLR to 16.4 g COD/m^2/d during 200 days.

14.1.2 Cork Boiling Wastewater Characteristics

CBW has an intense dark color, high concentration of organic pollutants, namely polysaccharides, phenols, polyphenolic compounds and cork extracts including polymerized tannins. Some of these compounds have high molecular weight (MW), as it is the case of tannins with 500 to 3,000 Da and when polymerized can reach up to 40 kDa [18]. The combination of these features results in poor bioavailability and biodegradability, increases the toxicity and ultimately restrains the feasibility of conventional biological processes for wastewater treatment discharge or reuse [10, 18, 19].

The most complete and recent published CBW characterization from different studies is presented in Table 14.1. These results show a great diversity of values for all parameters analyzed due to variations in specific water consumption, differences in the contamination levels and/or composition of the raw corkwood processed [1, 3–5]. For instance, the chemical oxygen demand (COD) and biological oxygen demand for 5-days incubation (BOD_5) concentrations range from 1,240–11,500 mg/L and 320–3,500 mg/L, respectively.

Table 14.1 Main characteristics of cork boiling wastewater from recent published literature.

Parameter[a] (units)	Vilara et al. [23]	Teixeira et al. [22]	Bernardo et al. [10]	Pintor et al. [29]	Santos et al. [21]	Gomes et al. [28]	De Torres-Socías et al. [28]	Marques et al. [11]	Fernandes et al. [30]
pH	7.50	4.6–6.2	4.70	5.0–6.5	5.42	5.81	7.2	5.8 ± 0.0	6.5 ± 0.5
Conductivity (mS/cm)	2.90		0.935	1.2			1.1	1.5 ± 0.1	0.70 ± 0.07
Turbidity (NTU)	30.3			58–84			163		
Abs 254 nm				0.97–1.17	0.395[b]	0.562[b]			0.43 ± 0.09[b]
Color	11,300[c]	Visible[d]	7,100[e]		0.118[f]	0.221[f]			0.08 ± 0.01[f]
SS (mg/L)		65–900		126	970		290		
COD (mg/L)	4,692	2,260–11,500	2,604	1,786–2,403	1,536	1,878	1,240	6,500 ± 100	2,041 ± 114
DOC (mg/L)	1,448			763–892	595		586		800 ± 71
BOD_5 (mg/L)	750	500–3,500	900	320–456	407	498			260 ± 52
BOD_{20} (mg/L)			1,225		554	684			474 ± 62
BOD_5/COD			0.35	0.18–0.19	0.26	0.27			0.13 ± 0.02
BOD_{20}/COD			0.47		0.36	0.36			0.23 ± 0.03
TN (mg/L)	308.8	60–200		21–58	15.33	17.02	27.8	40	20 ± 3
TP (mg/L)	10.3	20–60		17.7–19.9	6.46	5.85			
TPh (mg/L)	740[g]	1,000–3,500[h]	410[i]		110.3[i]	523[i]		1,200[g]	140 ± 20[i]
Tannins (mg/L)		850–1,700[i]	270[i]			399[i]			

[a] Abs: Absorbance, SS: suspended solids, COD: chemical oxygen demand, DOC: dissolved organic carbon, BOD_5: biological oxygen demand after 5 days incubation, BOD_{20}: biological oxygen demand after 20 days incubation, TN: total nitrogen, TP: total phosphorus, TPh: total phenols;
[b] for dilutions (1:50);
[c] Pt-Co units (at 400 nm);
[d] dilution (1:20);
[e] Hazen Units;
[f] Absorbance at 580 nm for dilutions (1:5);
[g] expressed as caffeic acid equivalents;
[h] expressed as gallic acid equivalents;
[i] expressed as tannic acid equivalents.

Beside the differences in the methodologies used to quantify color (Table 14.1), in all cases CBW samples had dark brownish color due to high concentration of corkwood extracts with high molecular size, namely of tannins. The quantification of these pollutants was made through the total phenols (TPh) analysis and less frequently includes tannin determination by the gravimetric method described by Makkar et al. (1993) [20]. The methodologies reported for TPh quantification involve several variations on the original procedure published by Folin and Ciocaulteu (1927), namely employ the Folin–Ciocalteau reagent solution, absorbance measurements at 765 nm, use of different compounds for calibration and then to express the overall concentration, namely gallic, caffeic and tannic acids [11, 21–25]. The major drawbacks of these methods are the low selectivity of the reagent solution, which reacts with any reducing substances in addition to phenols [25].

The majority of the research results published includes bioassays to assess biodegradability and, less frequently, the acute toxicity before and after the treatment to evaluate the environmental impact of the effluent discharge or, in the case of pretreatment stages, to evaluate the feasibility of the subsequent biological treatment. The most common biodegradability indices used are based on the ratio between the BOD and COD; the rapidly bioavailable fraction of the organics in the wastewater corresponds to the BOD_5 using non-acclimatized aerobic biomass or extended incubation up to 20-days (BOD_{20}) to account for the overall biodegradable fraction [10, 21]. According to some authors, values of BOD_5/COD ratios higher than 0.40–0.50 are required for effective biological treatment [26, 27]. Less frequently, the Zahn–Wellens test protocol (with 28-days incubation) was used to assess the ultimate biodegradability and the determination of the oxygen uptake rate (OUR) for the short-term biodegradability assessment [23, 28, 29].

To date, only one publication reported the number of total heterotrophic bacteria in CBW using serially diluted, spread on plate count agar with 48 hours incubation at 25°C and 50°C. These temperatures were selected taking into consideration the cooling of CBW from 100°C to ambient temperature. The bacterial enumeration at 25°C ranged from 3.8×10^4–1.8×10^7 colony-forming units (CFU) per mL and at 50°C were $<1 \times 10^1$–2.1×10^4 CFU/mL [7]. In any case, CBW has also low bacterial biodiversity, which is further reduced in the case of the isolation of cultures grown using phenolic compounds as selective carbon sources [7, 30].

Hitherto, the quantification of the organic pollutants in CBW includes more than 50 compounds with concentration ranging from 0.22–2.00 mg/L for the syringic acid up to 238.7 mg/L for the ellagic acid. However, research results published for CBW treatment (in mg/L) were limited to phenolic acids, namely gallic (2.46–103.70), protocatechuic (0.38–71.10), caffeic (2.14), vanillic (2.00–8.00), *p*-cumaric (4.10), ferulic (6.00–7.70) and ellagic (2.92–238.70) [11, 21, 31, 32]. Some of these compounds are also present in other agro-industrial wastewaters, namely from olive mills (OMW), wine-distillery, wood debarking and coffee processing [11, 33]. The potential for recovery and valorization of these by-products as promising sources of renewable chemicals is high due to their bioactive properties and extended range of potential uses, namely as antioxidants, anti-inflammatories, anti-carcinogenics and inhibitors of enzymes with activity related to several diseases, but this has not yet been explored [25, 34].

The anaerobic digestion of CBW raises the opportunity to recover energy and resources through biogas production and concentration increase of compounds from the benzoic acid family (i.e., gallic, protocatechuic, vanillic and syringic acids), highlighting the potential for added value to CBWs [11]. The use of ionizing radiation (gamma radiation) also increased the concentration of phenolic compounds and antioxidant capacity [34]. Another opportunity for CBW valorization is the replacement of the vegetable extracts used in the tanning industry by nanofiltration (NF) concentrates [19, 22]. Overall, all of these approaches have the potential to enhance the environmental and economic sustainability of the cork manufacture industry but until today they have not yet been implemented on a real scale.

14.2 Cork Boiling Wastewater Treatment

Despite the significant investment in innovation to create new cork products and to improve the quality of those already sold, especially to ensure close to complete elimination of organic contaminants, namely of the chlorophenols (such as 2,4,6-trichloroanisole) to prevent damage of the organoleptic quality of the wine during the storage period, in most factories CBW treatment still limited. In fact, the CBW disposal has only progressed from direct discharge into public water-courses without any treatment, or after retention basins to allow for equalization, homogenization and partial evaporation, to the application of coagulation–flocculation as a pretreatment stage, followed by discharge into municipal wastewater treatment plants [7, 28, 35–37]. However, the acceptance of cork products and the profitability of production and transformation activities can be increased if they are viewed as products with an environmental and sustainable character [1]. Therefore, technologies allowing for the reduction of water consumption and the mitigation of pollution discharged to water bodies are necessary and can contribute to this goal.

The literature review showed a vast array of possibilities for CBW treatment, including physico-chemical processes, membrane separation technologies, biological treatments and treatment sequences. In most cases, several pretreatments options are applied to reduce the suspended solids (SS) concentration (between 23–59%), in addition to COD removal (between 43–70%) [19, 31, 32, 38–40]. Besides the removal of gross solids, which is critical for membrane technology performance, oxidation is often used to increase the biodegradability and reduce the toxicity, so that subsequent biological treatment can be successfully applied and, in one case, to enhance the performance of ultrafiltration (UF) membranes in a wide range of molecular weight cut-offs (MWCOs), from 4 to 98 kDa, through fouling reduction [6, 21, 24].

However, it should be taken into account that sequential treatments, through combination of physico-chemical processes or of chemical and biological oxidation, present an additional difficulty for an efficient operation of a large-scale plant. Moreover, it is necessary to ensure that the chemical oxidant and the biological culture do not come in undue contact with each other [12, 28].

Next, the results published for CBW treatments are revised and categorized according to the methodology used, i.e., physico-chemical processes, membrane separation, biological treatment and sequential treatments (Tables 14.2–14.5).

14.2.1 Physico-Chemical Treatment

The physico-chemical processes applied to CBW can be divided into those requiring the consumption of reactants, namely coagulation–flocculation, chemical oxidation and anodic oxidation, and those using membrane technologies (MTs). However, the large variations of CBW characteristics (Table 14.1) make difficult the direct comparisons.

As summarized in Table 14.2, coagulation–flocculation processes consume reactants to adjust the pH and to promote the formation of flocs, allowing the transformation of non-settleable solutes into

Table 14.2 Literature review results for treatment of CBW with physico-chemical processes.

	pH		Color		COD		TPh		
Treatment method	**IN**	**OUT**	**IN**	**Rem (%)**	**IN (mg/L)**	**Rem (%)**	**IN (mg/L)**	**Rem (%)**	**Reference**
Coagulation-Flocculation									
(200 mg Fe^{+3}/L)	5.6	7.2			2,280	53	380[d]	89	[41]
(166 mg Al^{+3}/L)	5.0[a]				3,047	54	381[d]	82	[8]
(100 mg Chitosan/L)	2.9[a]				2,469[b]	17	958[e]	26	[32]
(200 mg Chitosan/L)	3.0[a]					25		45	
(Fe^{3+} added up to 20 mg/L)	7.2	3.1			1,170[c]	43			[42]
	6.6	2.6			1,780[c]	70			
(Fe^{+3} added up to 20 mg/L)	2.8[a]				1,240	61			[9]
(Fe^{+2} added to 20 mg/L)						45			
Fenton-Oxidation									
(10.6 g H_2O_2/L; H_2O_2:Fe^{2+} weight ratio of 1:5)	3.2[a]				5,000[c]	87			[29]
Photo-Fenton									
(13.64 g H_2O_2/L; H_2O_2:Fe^{b} = 1:8.3 weight ratio; Irradiation time = 10 min)	3.2[a]				2,100[b]	66			[43]
Solar Photo-Fenton									
(20-80 mg Fe^{3+}/L; 4.36 g H_2O_2/L)[g]	2.6–2.8[a]	2.8			1,786–2,404	65	352[d]	95	[29]
		2.9				91		81	
([Fe^{3+}] set to 20 mg/L; 750 mg H_2O_2/L; irradiation time 377 min)	2.6–2.8[a]				1,240	59			[28]
([Fe^{3+}] set to 20 mg/L; 780 mg H_2O_2/L; irradiation time 435 min)					480[c]	52			

Ozonation									
($O_{3,app}/COD_i = 0.32–1.64$)	~5.3	2.7–3.6			~1,900	19–48	~290[d]	65–80	[42]
($O_{3,app}/COD_i = 2.90–3.60$)	4.8				~1,600	42–69	~305[d]	80–94	[35]
$O_{3,app}/COD_i = 0.27–2.63$	3.3[a]	2.2–2.7	0.554[h]	70–87	1,878	15–53	523[d]	66–83	[24]
	5.8	3.3–5.4		57–91		16–59		60–82	
	10.0[a]	4.0–6.3		59–92		25–62		38–75	
AOP									
50 mg O_3/L + 0.34–3.40 g H_2O_2/L	4.8				~1,600	76–80	305[d]	95–98	[35]
(0.82 g O_3/L + 0,6 g H_2O_2/L; Oxidation Time = 11 h)	7.0[a]	5.1			480[c]	14			[28]
	10.0[a]	6.4				33			
Anodic Oxidation									
BDD electrodes Na_2SO_4 = 0–1,5 g/L; current density of 30 mA/cm[b]; Oxidation time up to 8 h)	6.5		0.080[h]	>50	~2,000	>74	140[f]	>80	[44]

[a] pH after adjustment;
[b] values for total organic carbon (TOC) concentration;
[c] after CBW pre-treatment;
[d] expressed as caffeic acid equivalents;
[e] expressed as gallic acid equivalents;
[f] expressed as tannic acid equivalents;
[g] using cork bleaching WW as source for H_2O_2 (at 7.7 g H_2O_2/L) results for end of solar-photo-treatment;
[h] Abs at 580 nm for samples dilutions of 1:10;

Table 14.3 Literature review results for treatment of CBW with membrane separation technology.

Membrane(pore size or MWCO)	Operational conditions(1)	Color		COD		TPh		Reference
		IN	Rem (%)	IN (mg/L)	Rem (%)	IN (mg/L)	Rem (%)	
MF								
DUR-0.65 (0.65 μm)	$\Delta P = 0.45–2.3$ bar; $Lp = 860$ L/m^b/h/bar;	0.114^b	47–83	4,290	17–39	761^c	21–48	[39]
DUR-0.10 (0.10 μm)	$\Delta P = 0.45–2.3$ bar; $Lp = 248$ L/m^b/h/bar;		60–85		19–41		26–48	
UF								
Bio-300K (300 kDa)	$\Delta P = 0.35–1.8$ bar; $Lp = 769$ L/m^b/h/bar;	0.114^b	66–83	4,290	24–39	761^c	26–49	[39]
Bio-300K (300 kDa)	$\Delta P = 0.75$ bar; $Lp = 769$ L/m^b/h/bar;	0.020^b	83	2,670	7	197^c	16	[45]
Bio-10K (100 kDa)	$\Delta P = 0.75–1.80$ bar; $J_{v(initial)} = 86–147$ L/m^b/h;		95		29		41	
GR40PP (100 kDa)	$\Delta P = 1–3$ bar; VRF = 4; $Lp = 60$ L/m^b/h/bar	0.059^b	64	1,536	45	110.3^d	37	[21]
– (91 kDa)	$\Delta P = 3$ bar; $Lp = 106$ L/m^b/h/bar	5,700^e	66	2,285	45	360^d	46	[10]
GR51PP (50 kDa)(6)	$\Delta P = 1–3$ bar; VRF=4; $Lp = 52.5$ L/m^b/h/bar	0.022^b	24	851	45	69.4^d	48	[21]
– (45 kDa)	$\Delta P = 3$ bar; $Lp = 56$ L/m^b/h/bar	5,700^e	91	2,285	52	360^d	65	[10]
– (25 kDa)	$\Delta P = 3$ bar; $Lp = 37.8$ L/m^b/h/bar	7,100^e	93	2,604	62	410^d	68	
GR61PP (20 kDa)^g	$\Delta P = 1–3$ bar; VRF=4; $Lp = 26.6$ L/m^b/h/bar	0.016^b	50	686	24	31.6^d	20	[21]
– (13.6 kDa)	$\Delta P = 3$ bar; $Lp = 34.8$ L/m^b/h/bar	5,700^e	95	2,285	68	360^d	75	[10]

GR81PP (10 kDa)[h]	ΔP = 1–3 bar; VRF=4; *Lp* = 13.5 L/m[b]/h/bar	0.008[b]	13	520	26	28.8[d]	42	[18]
– (3.8 kDa)	ΔP = 3 bar; *Lp* = 2.5 L/m[b]/h/bar	5,700[e]	97	2,285	74	360[d]	82	[10]
– (1.2 kDa)	ΔP = 3 bar; *Lp* = 1.4 L/m[b]/h/bar		99		90		90	[10]
NF								
NF270 (400 Da)	ΔP = 3 bar; VRF>7; *Lp* = 11 L/m[b]/h/bar; $J_{v(initial)}$ = 3.6 L/m[b]/h		>99	2,260–11,500	>96	1,000–3,000[i]	>96	[22]
CK (150–300 Da)	ΔP = 10–30 bar; VRF = 2; *Lp* = 6.5 L/m[b]/h/bar; $J_{v(initial)}$ = 21–61 L/m[b]/h	0.114[b]	99	4,290	96	760[(3)]	98	[45]
DK (150–300 Da)	ΔP = 30 bar; VRF = 2; *Lp* = 4.6 L/m[b]/h/bar; $J_{v(initial)}$ = 73.1 L/m[b]/h		98		93		96	
NF90 (~150Da)	ΔP = 15 bar; VRF>7; *Lp* = 7 L/m[b]/h/bar; $J_{v(initial)}$ = 2.3 L/m[b]/h		>99	2,260–11,500	>99	1,000–3,000[i]	>99	[22]
– (125 kDa)	ΔP = 3 bar; *Lp* = 5.2 L/m[b]/h/bar	5700[e]	~100	2,285	95	360[d]	92	[10]

[a] ΔP = transmembrane pressure, Lp = permeability to pure water and Jv(initial) = initial permeate flux with CBW;
[b] Abs at 580 nm for samples dilutions of 1:10;
[c] tannic content;
[d] expressed as tannic acid equivalent;
[e] Hazen Units;
[f] results for operation with the permeate from GR40PP (MWCO of 100 kDa);
[g] operation with the permeate from GR51PP (MWCO of 50 kDa);
[h] operation with the permeate from GR61PP (MWCO of 20 kDa);
[i] expressed as gallic acid equivalent.

Table 14.4 Literature review results for treatment of CBW with biological processes.

Treatment method (Main operation conditions)	pH		Color		COD (mg/L)		TPh (mg/L)		Reference
	IN	Final	IN	Rem (%)	IN	Rem (%)	IN	Rem (%)	
Activated-sludge (HRT=24-96 h; T = 20°C)	5.40 ± 0.20	7.89–8.55			~1,810	13–37	290 ± 60[a]	20–32	[6]
Fungal strains[b] (48 h batch incubation; 2 g/L of dry weight fungal biomass; T = 25°C)				−43–47	7,500 ± 500	49.5–58.9			[39]
Enriched cultures[c] (aeration rate = 0.2 (V/V); 15 days incubation; T = 25°C)	4.7–5.7				1,670[d]	~25	730[e]	~18	[7]
Self-bioremediation (bacterial immobilization into residual cork particles)								60–80	[30]
Anaerobic digestion (Batch incubation during 15–44 d with inoculum from OMW treatment at of 5 g VSS/L; T = 37°C)	7.20	7.67			3,000	40	553[a]	−63	[11]
		7.52			6,000	36	1,110[a]	−27	
HSF CW[f] (T = 18 ± 5 °C; HRT = 6.1 ± 0.6 d; HLR = 6.2 ± 0.6 L/m[b]/day; OLR = 16.5 ± 2.3 g COD/m[b]/day)	7.04 ± 0.25[g]	8.02 ± 0.35	0.109 ± 0.090 [h]	−111 ± 33	2,675 ± 289	62 ± 10[i]	116.8 ± 13.0 [e]	58 ± 7[i]	Present study

[a] Expressed as caffeic acid equivalent;
[b] 4 strains isolated from outer bark of cork oak trees and 2 for their ability to degrade lignin and to grow on phenol;
[c] selected for their ability to use tannic acid as single carbon and energy sources;
[d] values for TOC concentration;
[e] expressed as tannic acid equivalent;
[f] HSF – horizontal subsurface flow, CW – constructed wetland, HRT – hydraulic retention time, HLR – hydraulic loading rate and OLR – organic loading rate and the values presented corresponds to average ± standard deviation for n = 22;
[g] after pH adjustment;
[h] Abs at 580 nm for samples dilutions of 1:10;
[i] percentage of removals calculated through mass balance.

Table 14.5 Literature review results for treatment of CBW with sequential processes.

Treatment sequence	CBW			Removal (%)			Reference
	Color	COD(mg/L)	TPh(mg/L)	Color	COD	TPh	
O_3 (0.91 g/g COD; HRT = 6 h) → **Biodegradation** (Activated sludge with acclimatized biomass; HRT = 48 h)		1,900	290[a]		65	94	[6]
Biodegradation (Activated sludge with acclimatized biomass; HRT = 48 h) → **O_3** (0.85 g/g COD; HRT = 3 h)		1,800	250[a]		77	92	
Fenton → coagulation-flocculation (reactants for combined process Iron 0.06–11.2 g/L + H_2O_2 2–34 g/L)		3,500–3,900	480–580[a]		22–85	4–98	[9]
Fenton ($[Fe^{2+}]_{initial}$ = 1 g/l;$[H_2O_2]_{initial}$ = 5 g/L) → **Biodegradation** (Aerobes selected using tannic acid as sole carbon and energy source)		2,300 – 4,600[b]	660 – 780[c]		>90		[7]
Fenton ($[Fe^{2+}]_{initial}$ = 56–11,200 mg/L; $[H_2O_2]_{initial}$ = 2–34 g/L) → **Coagulation-flocculation** (NaOH added up to pH>10, 1 day sedimentation)		3,500 – 3,900	480 – 580[a]		22–85	4–98	[9]
Coagulation-Flocculation+Filtration (pH = 2.8; addition of Fe^{2+} or Fe^{3+} to have dissolved concentration of 20 mg/L + 75 µm pore size) → **Solar photo-Fenton** (1.9–2.4 g H_2O_2/L; irradiation time of 500–750 min)		1,170			45–90		[29]
		1,780					
Coagulation-Flocculation+Filtration (pH = 2.8; addition of Fe^{3+} to have dissolved concentration of 20 mg/L + 75 µm pore size) → **Solar photo-Fenton**(780 mg H_2O_2/L; irradiation time of 435 min)		1,240			52		[23]
Solar Photo-Fenton (pH = 2.6-2.8; 20-80 mg Fe^{2+}/L; H_2O_2 consumption 2.14–2.70 g/L provide from cork bleaching WW) → **Biodegradation** (Zahn-Wellens test with supply of nutrients, 28 days)		1,786 – 2,403	304 – 399[a]		65		[28]
O_3(0.05 g/g TOC) → **UF** (MWCO = 300 kDa; ΔP = 0.75 bar)	0.157[d]	4,400	897[e]	83	7	16	[39]
O_3(0.05 g/g TOC) → **UF** (MWCO = 10 kDa; ΔP = 1.25 bar)				95	29	41	
O_3(0.05 g/g TOC) → **UF** (MWCO = 5 kDa; ΔP = 0.75 bar)				91	24	31	

(Continued)

Table 14.5 (Continued)

Treatment sequence	CBW			Removal (%)			Reference
	Color	COD(mg/L)	TPh(mg/L)	Color	COD	TPh	
Sequences for the treatment of permeates							
MF(Pore size = 0.65 μm; Δ*P* = 0.75 bar) → $\mathbf{O_{3,appl}}$(0.05 g/g TOC)	0.157[d]	4,400	897[e]	98	82	94	[39]
MF(Pore size = 0.10 μm; Δ*P* = 0.75 bar) → $\mathbf{O_{3,appl}}$(0.05 g/g TOC)				96	83	97	
UF(MWCO = 300 kDa; Δ*P* = 0.75 bar) → $\mathbf{O_{3,appl}}$(0.05 g/g TOC)				96	87	98	
UF(MWCO = 300 kDa; Δ*P* = 0.75 bar) → **UV**				40	81	43	
UF(MWCO = 300 kDa; Δ*P* = 0.75 bar) → $\mathbf{O_{3,appl}}$(0.05 g/g TOC)+**UV**				98	97	100	
UF(MWCO = 300 kDa; Δ*P* = 0.75 bar) → **AOP** ($O_{3,appl}$ = 0.05 g/g TOC; $[H_2O_2]_{initia}$l = 34 mg/L)				99	98	100	
Sequences for the treatment of concentrates							
UF (MWCO = 100 kDa; Δ*P* = 1–3 bar; VRF = 4) → $\mathbf{O_3}$ ($O_{3,appl}$ = 0.7–1.3 g/L)	0.171[d]	3436	233[c]	90–97	59–69	88–92	[21]

[a] Expressed as caffeic acid equivalent;
[b] values for TOC concentration;
[c] expressed as tannic acid equivalent;
[d] Abs at 580 nm for samples dilutions of 1:10;
[e] tannic content.

coagulated settleable particles next removed as sludge. COD and TPh removals up to 70% and 89% were reported, but these results are strongly influenced by the type and dose of coagulant, coagulation mixing time and stirring rate, pH, ionic strength, nature and concentration of the organic compounds present in the solution [42]. Nevertheless, these processes are not an effective way for pollutant elimination, but they promote the concentration of the organics into chemical sludge, thus, further treatment is required before the final disposal (which is usually not considered).

Variations of Fenton reaction, ozonation and advanced oxidation processes (AOP) are the most studied physico-chemical techniques for CBW treatment (Table 14.2). In this case, a mixture of oxidants, O_3 and H_2O_2, are applied alone or in combination with UV radiation to increase the amount of the highly reactive hydroxyl radicals ($OH^\bullet$). However, due to the lack of selectivity of oxidants, which is minimal for $OH^\bullet$, it is difficult to avoid their consumption in reaction with biodegradable organics or radical scavengers; the biocompatibility of the produced compounds is also difficult to estimate. Thus, most frequently, the oxidation extent is only the minimal to ensure the viability of the subsequent biological treatment. Moreover, the oxidant efficiency decreases with the dose; thus, it is necessary to carefully set the optimum oxidant dosage and to optimize the operational conditions (reactor configuration, increase of the mass transfer, temperature, reaction time, etc.) [12].

Fenton oxidation also takes advantage of the production of $OH^\bullet$ with high oxidant potential (2.08 V) resulted from the reaction of H_2O_2 with the catalyst (Fe^{2+}), which can be increased by exposure to UV radiation [12, 29]. The results reported were dependent on organic load (COD of 480–5,000 mg/L), oxidant doses (0.75–13.6 g H_2O_2/L), Fe^{2+} concentration, source of radiation and irradiation time. Despite the fact that most of the published results ignore the characteristics and amounts of sludge produced in Fenton oxidation, it is important to notice their magnitude, which in one case accounts for 176 mL/L of CBW with a water content of 96% [43, 45]. These processes allow an increase of the biodegradability from 0.18–0.27 up to 0.28–0.70, using the BOD_5/COD ratio for evaluation, and from 0.13 to 0.70 with the Zahn–Wellens test [28, 29, 43, 45]. Taking into account the process economics, the most interesting results were reported with 8.5–12.5 hours of solar irradiation and use of cork bleaching wastewater as source of H_2O_2 (at 7.7 g/L), which allows for COD and TPh removal of 65–91% and 81–91%, respectively. However, the strong color of the samples impaired any additional increases through irradiation and raised reaction times [29].

In ozonation trials, amounts of O_3 equivalent to $O_{3(appl)}/COD_0$ ratios of 0.27–3.60 were used to achieve color, COD and TPh removal of 59–92%, 15–69% and 38–94%, respectively [24, 35, 38]. Despite the pH of the sample and O_3 dose being critical parameters requiring optimization, the results reported show that ozonation is the best option for decolorization and that sample pH influences the extent of oxidation by molecular O_3 and by $OH^\bullet$, as for values below 5.5 the $OH^\bullet$ formed by ozone self-decomposition is suppressed [12]. The effect of pH (set at 3 and 10) and of O_3 dose ($O_{3(appl)}/COD_0$ ratios of 0.27–2.68) affected the BOD_5/COD ratio increase from 0.27 up to 0.44 and the toxicity reduction from 3.08 to 1.28 toxicity units (TU) (for Microtox) [24]. Other authors also reported significant increases of biodegradability from 0.13–0.60 up to 0.59–0.93 after ozonation [6, 35]. These results showed also that mineralization extension is not correlated with biocompatibility augmentation, because for close oxidant doses the COD removals were maximum at alkaline pH, but it was the large removal of TPh at acid pH that led to the highest increase of BOD_5/COD ratios and toxicity reduction [24].

The use of boron-doped diamond (BDD) anodes allowed the reduction of COD, dissolved organic carbon (DOC), TPh and color greater than 90%, and increase of the BOD_5/COD and BOD_{20}/COD ratios from 0.13 and 0.23 up to 0.59 and 0.72, respectively, after 8 h oxidation at current density of

30 mA/cm^2. However, to achieve conductivities that enabled anodic oxidation at the highest current intensities applied and to minimize the specific energy consumptions, addition of supporting electrolyte was required at 0.75 g/L of Na_2SO_4 [44].

Although MTs have a wide range of selectivity, from microfiltration (MF) having pore sizes ranging from 0.1 to 2 μm and operate at pressures below 5 bar to reverse osmosis (RO) requiring pressures in the range from 50 to 100 bar (seawater desalination) or of 15 to 50 bar (other applications), the presence of vegetal extracts covering a wide range of MW, as is the case of polyphenolic compounds having colloidal behavior, promotes severe membrane fouling, leading to a drastic permeate flux decline with operation time [10, 22, 31, 32, 42]. The other major drawback of MTs is the produced concentrates containing the pollutants rejected, requiring further treatment before final discharge; until now, the potential opportunities for valorization were limited to the reuse of NF retentates by the leather industry [19, 22]. Thus, for the remaining studies the alternative solutions for the concentrates were not presented.

Besides the differences in CBW characteristics and in the pretreatments used to remove gross SS, the comparison between the results presented in Table 14.3 is also difficult due to differences in experimental set-ups, membrane materials, module configuration, hydrodynamic and operational conditions. However, it is possible to assert that permeate flux and quality are correlated with membrane selectivity, usually reported in terms of MWCO. In any case, the results show that permeates obtained with lower MWCO membranes are less colored, have lower COD and TPh concentrations and are more readily biodegradable, which confirms that large MW compounds cause the strong color of CBW and are less available to undergo biodegradation [10, 21, 22].

All published results for operations with UF membranes having MWCOs of 4 up to 300 kDa, transmembrane pressures from 1 to 3 bar were performed after CBW pretreatment, which was not enough to prevent hydrophobic compounds, namely ellagic acid, to develop an adsorbed layer that increases membrane fouling and consequently leads to severe drops in permeate flux [10, 31, 32, 42]. The increase of selectivity with NF membranes raised the rejection of organic compounds, TPh and color above 92%, indicating that NF membranes have a very good ability to concentrate the pollutants and produce a permeate stream with characteristics close to those required for discharge or water reuse [10, 19, 22, 27]. In one case, it was suggested that about 86% of the CBW volume can be recovered for reuse through NF membrane (MWCO of 125 Da). However, this wastewater was collected after the patented Symbios cork boiling process instead of the traditional procedure, which reduces the TCA formation [22].

14.2.2 Biological Treatment

Biological treatment options either in aerobic, anaerobic or sequential conditions can be successfully applied to the treatment of agro-industrial effluents with high concentration of phenolic compounds, thus with characteristics similar to CBW [12]. Beside the aforementioned CBW features restraining biological treatment, the unbalanced composition (C:N:P ratio) should be noticed and the fact that 56% of the organic load comes from compounds with MW above 100 kDa [11, 21]. Thus, the results published for biological treatment (Table 14.4) are limited to conventional activated sludge inoculated with acclimatized biomass [6], use of enriched cultures of aerobic bacteria isolated from CBW samples with tannic acid as single carbon and energy source [7], fungal strains isolated from the outer bark of cork oak trees [46] and, more recently, anaerobic digestion [11]. In this last case, the authors claimed an effective contribution to the economic viability of the treatment process through reduction of the amount of sludge produced and recovery of the energy potential through methane production.

The limitations of biological treatment were well illustrated by the results reported for an activated sludge system operated at hydraulic retention times (HRT) of 24–96 h, which allowed only limited removals of 13–37% and 20–32% for COD and TPh, respectively [6]. Even the use of enriched microbial cultures taken from retention basins used to collect CBW, did not increase the bioavailability of the organic compounds, namely of the polyphenols. Therefore, the authors concluded that biodegradation needs to be preceded by Fenton oxidation to increase the total organic carbon (TOC) removal up to 90% [7]. Four fungal strains isolated from cork bark and another two selected due to their ability to degrade a large variety of persistent environmental pollutants, were incubated with CBW and after 5 days incubation the reductions of COD and color were of 48–62% and up to 47%, respectively. In any case, the values of EC_{50}-5 min for the Microtox bioassay showed a decline of toxicity ranging from a ten-fold decay up to complete loss [46]. Aerobic bacteria collected from CBW storage pounds and selected for their tolerance against phenol and chlorophenols were immobilized onto residual cork particles. The results reported for an overall of 16 strains isolated were limited to the removal of TPh (60–80%) and very dependent on experimental conditions (pH, temperature, nutrient addition, aeration, etc.) [30].

Regarding the anaerobic treatment of CBW, the absence of lag phase with biomass adapted to OMW, led to the conclusion that organic compound bioavailability limitations prevailed over the microbial consortium inhibition or toxicity, because colored compounds in CBW are not biodegradable but their presence does not affect the removal of the colorless fraction [11]. After 11–15 days' incubation period, the COD removals were 36–40% for CBW with 3 and 6 g COD/L. Besides the limited COD reduction, the methane yield was of 0.126–0.142 L/g COD added or 0.315 to 0.394 L/g COD removed. In addition, the authors suggested that the phenolic fraction, the dark colour and the remaining COD can only be removed through electrochemical processes, which will reduce the energy outcome of the combined treatment [11]. According to previous research, several genera of aerobic and anaerobic microorganisms can degrade phenolic compounds but chlorophenols are hardly degraded due to the high stability of the carbon-halogen bond [31].

In summary, in most cases, one single treatment stage is not enough to ensure the fulfillment of the environmental requirements for wastewater discharge or reuse and sequential treatments are required.

14.2.3 Sequential Treatment

The remediation of industrial wastewaters with a wide variety of pollutants and of concentrations, which is the case with CBW, is a complex problem. Thus, when the possibilities and capabilities of the available conventional treatments are not adequate to achieve the desired reclamation, sequential approaches are required (Table 14.5). The most common objective of the first stage of treatment based on chemical oxidation is the increase of the bioavailability and biodegradability of the pollutants, rather than mineralization [6, 7, 24].

The sequences of chemical oxidation followed by biodegradation are interesting because they limit the amount of reactants below those used for single stage treatment, allowing for the reduction of operational costs for COD removal of 65–90% [12]. In these cases, the percentage of mineralization should be minimal, to avoid unnecessary expenditure of chemicals and energy, but excellent process optimization is required. Most AOPs lower the pH of the wastewater due to the generation of organic acids, or the best results are achieved at pH values out of the range necessary for biodegradation (i.e., pH of 6.5–7.5), as it is the case of pH around 3 for Fenton or 9 for ozone, being necessary neutralization before biological treatment [12].

The results reported in Table 14.5 for treatment sequences including MTs can be divided in those using oxidation to improve the performance of MF (0.1 and 0.65 μm) and UF (MWCO of 5 to 300 kDa) membranes, through complete removal of the ellagic acid, previously associated with permeate flow decay with time of operation, or to improve permeate quality [32, 39, 40]. In the case of a 10 kDa membrane, the initial permeate flux increased 25% with pre-ozonation, which also yielded removal of color and tannins in the range of 80–90% and of COD around 40%. However, permeates post-ozonation procedures were more efficient in terms of the overall removal of COD, color and tannins, which were above 82% with both MF membranes [40]. Only for one study combining a 100 kDa membrane and ozonation, the characteristics and volumes of permeate and concentrates were provided. Taking into consideration the volumetric reduction factor (VRF = 4), 25% of the CBW volume process corresponds to a concentrate stream with a COD of 3,436 mg/L, TPh of 233 mg/L and Abs at 580 nm of 0.171 (dilution 1:10). The remaining volume was a permeate stream with COD of 851 mg/L, TPh of 69 mg/L and an absorbance at 580 nm of 0.042 (color); which corresponded to reductions of 45%, 37% and 64%, respectively [21].

The results for sequences of physico-chemical treatments still depend on the amount of reactants and energy consumed, which can be reduced using the solar photo-Fenton process already successfully implemented with other wastewaters, namely from wineries, pesticide and dyeing industries. In this context, the most interesting results were reported for the integration of solar photo-Fenton with biodegradation using cork bleaching wastewater as source for H_2O_2, with COD removal up to 65% [29].

14.3 Constructed Wetland Technology

CWs is an established technological solution for domestic and municipal wastewater treatment [13, 14]. They are considered internationally as an attractive, green alternative to conventional wastewater treatment methods for small and medium size communities [15]. The success of these eco-tech systems in providing high efficiency rates for the treatment of these wastewaters, enabled the investigation of their use for various industrial effluents. Today, a wide range of advances in wetland technology relates to industrial applications, such as effluents from the textile industry, food processing industry, wineries, oil and gas industry, etc. Especially wastewater generated from small-scale industrial facilities in rural areas represent a technical and economic challenge. Usually these contain high concentrations of organics, nutrients and heavy metals. Effective treatment with conventional methods, which include combinations of chemical, physical and biological processes is not always economically feasible. Moreover, the operation of such conventional treatment facilities can also be challenging and costly. From this point of view, CWs can be not only an effective but also a cost-effective treatment solution [14].

Wetland technology has already been introduced in Portugal. Various design configurations have been applied in the country, but the most widely used system in Portugal is the Horizontal Subsurface Flow (HSF) CW, as in most European and Mediterranean countries, for applications of domestic wastewater treatment. The substrate medium is essential for plant establishment, growth and development of the biofilm. Problems with substrate clogging are common, and its causes are still under investigation, while the search for new, appropriate materials is still ongoing. It is assumed that clogging is related to the characteristics of the substrate medium, the excessive growth of biomass, the retention and accumulation of organic solids, the precipitate formation and the development of rhizomes and roots [13, 47]. Light-expanded clay aggregates (LECA) have been presented as alternative substrate media to reduce the clogging problem and increase the treatment capacity, since they present both higher porosity and specific surface area, which allow for a good biofilm adhesion and a high hydraulic conductivity [48].

CWs have not been tested yet for CBW treatment, which means that – to the best of the authors' knowledge – the project presented in this chapter is the first attempt to investigate the feasibility and the potential use of wetland systems for this agro-industrial wastewater source. However, CWs have been tested in effluents with a similar composition to that of CBW, mainly in wastewater containing a high organic load and phenol concentration. Such wastewater sources are olive mills [49–52], pulp and paper industry [53, 54], wineries [55, 56], coffee processing [57] and contaminated groundwater with refinery effluents and petrochemical industry effluent [58]. As reported in a review paper by Stefanakis and Thullner [59], various designs and wetland types have been tested with wastewater containing phenolic compounds. Although it has been proved that CWs have the ability to remove phenols from water, even at high concentrations, it is not yet clear whether discharge standards can be reached. However, the feasibility of CW systems in phenol removal seems to be a proven case, despite the need for further studies to evaluate the removal capacity. Hence, the present project aims at investigating the efficiency of microcosm-scale wetland units for the treatment of CWB, which also contains high levels of phenolic compounds.

14.3.1 Experimental Setup of Microcosm-Scale Constructed Wetlands

A long-term investigation was conducted to assess the performance of a microcosm-scale CW for the treatment of CBW. Two HSF CWs were used in the laboratory. Each wetland unit was a rectangular PVC container (15.0 cm wide, 34.8 cm long and 14.3 cm deep), filled with LECA (Figure 14.1). The porosity of LECA was initially measured and found to be 38.3% One unit was planted with common reeds (*Phragmites australis*) (CWP) and the other was left unplanted (CWC) and used as control unit. The planting took place in May 2012, followed by a commissioning period, during which synthetic wastewater with 300 mg COD/L was introduced to the two beds before the start of loadings with CBW. The maximum water level was at 9.8 cm, corresponding to an initial void volume of 1.961 L.

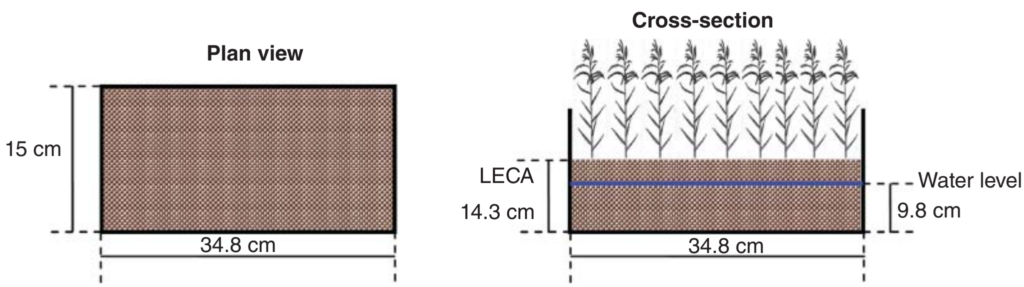

Figure 14.1 Plan view and cross-section of the lab-scale Horizontal Subsurface Flow Constructed Wetlands.

For more than four years the adaptation and acclimatization of the plants and biofilm development were carried out through six gradual increases of the OLRs from 2.55 to 8.87 g COD/m^2/d. Each phase ran until steady results for COD and TPh mass removal rates (MRR) were achieved; thus, the length of each phase varied according to the OLR increase, season and CBW characteristics. This long and carefully conducted acclimatization process was intended to overcome the difficulties resulting from the CBW complex composition, with low bacterial enumeration and metabolic biodiversity [7, 30].

The operating conditions of both bioreactors were set taking into consideration the COD of the CBW collected in an industrial plant located in the Portalegre district (Portugal) at the outlet of an equalization and homogenization tank, and by adjusting the feed flow rate supplied by two peristaltic pumps working in intermittent mode (15 min each operation hour). The characteristics of the CBW samples were in the range of those previously presented in Table 14.1, namely 2,028–3,237 mg COD/L and 89.5–135.1 mg TPh/L. The pH of the raw wastewater was set to 6.5–7.5 (with a mean value of 7.04 $\pm$ 0.25). The unbalanced C:N:P ratio of 100:1:0.4 was not adjusted to the reference value of 100:5:1 for aerobic biodegradation, i.e., the lack of nitrogen and phosphorus was not corrected. The feed flow rate of both pumps was measured weekly at least twice and adjustments were made when necessary to ensure steady values for the OLR. Both bioreactors were placed indoor in a laboratory of the Chemical Department of the University of Beira Interior (Covilhã-Portugal), in order to avoid excessive temperature variations, but ensuring at the same time plenty of natural light. The inside temperatures were maintained near 20°C through the regulation of a thermostatic device for a room temperature of 18 $\pm$ 5°C.

14.3.2 Experimental Results

The results reported in Table 14.4 (last row) were obtained with a mean OLR of 16.5 g COD/m^2/d during an operation period of 200 days (from 25 January to 11 August). According to CBW COD concentration, an HRT close to 6 days was ensure through adjustment of the inflow rates; thus resulting in the variation of the hydraulic loading rate (HLR) between 5.8–7.8 L/m^2/d. This high HRT was required because of the positive correlation between HRT and treatment efficiency and operation stability, highly recommended for wastewaters of bio-recalcitrant nature as it is the case of CBW (Table 14.1).

Due to the small size of the CWs used, the evaporation (EV) and evapotranspiration (ET) were important in all seasons. In the CWP, the ET values of 2.22 $\pm$ 0.84 L/m^2/d were above the values obtained with the CWC (1.17 $\pm$ 0.32 L/m^2/d) and these differences could be correlated with plant activity. Despite the contribution of plants to water losses, thus increasing the HRT, the significant development of plant roots biomass during successive growth cycles over four years resulted in the rise of the bed height from the initial value of 14.3 cm up to 20 cm; which corresponds to reduction of the void volume and offset the ET influence on operational conditions. Since the CWs were placed indoors, plants were not harvested and they maintained green leaves even during cold seasons, but after spring and until autumn the plants' height and leaves presented the highest development. It is worth mentioning that after several growth cycles with CBW, the plants never showed any toxicity signs and the expansion of roots also confirms their excellent physiological condition.

The removal efficiencies of COD and TPh were calculated through mass balance and expressed in percentages. This option was considered best suited to evaluate performance removals than the calculations based on concentration, because of the significant values of the EV and ET. However, the values of water loss calculated through mass balance and presented here for the planted unit of 35.7 $\pm$

13.6% are commonly reported for operations with small-scale CWs under warm climatic conditions, being a consequence of the so-called “oasis” effect which restrains the outflow volumes [48, 60]. The color removals reported in Table 14.4 are for the difference between the inflow and outflow values. In this case the correction of the water loss allows decolorization improvement from –111 ± 33% up to –28 ± 32%, which means that the color is higher in the outflow than in the inflow. This drawback of the biological treatments with CBW was also previously reported, namely for anaerobic and aerobic conditions, and it was correlated with the high MW of the pollutants contributing to color, which have also low bioavailability [6, 10, 11, 21]. On the other hand, a very high variability of this parameter was observed; this can be due to the physical process contribution to decolorization, namely sedimentation, precipitation and adsorption, which are reversible processes sensitive to the variation of operational conditions. Similar variability was observed for the CWC, with –25 ± 21%.

Overall, if the water loss of 14.4 ± 7.5% is reported by Albuquerque et al. (2009) [60] for a real-scale HSF CW operation (surface area of 773 m^2) with similar characteristics in a very close location and temperature (18.4 ± 9.2°C), it is possible to anticipate a great improvement of the outflow color, COD and TPh concentration. For this case scenario, the average characteristics of the outflow can be estimated to be: a pH close to neutrality, color of 0.196 for the Abs at 580 nm (dilution 1:10), COD of 1,357 mg/L and TPh of 68.4 mg/L; which clearly exceeds the legal requirements for discharge and indicates the need for post-treatment or the reduction of the OLRs.

The occurrence of environmental conditions appropriate to anaerobic or aerobic metabolism can be assessed through measurements of redox potential (Eh) in the middle of the beds; oxidative conditions require values bigger then +100 mV, reductive conditions for values less than –100 mV and the intermediary values can be classified as anoxic conditions [61, 62]. According to the wetland design, the oxygen required for aerobic degradation can be provided by diffusion, convection and oxygen emission from the macrophyte roots into the rhizosphere. However, it was this last source of oxygen that made the difference between CWC and CWP for the availability of oxygen, considering that for *P. australis* plants the reported value of oxygen input rate found in the literature is 0.02–12 g/m^2/d [61]. Thus, the increase of COD and TPh removals in the CWP system corresponds to additional available oxygen and to high metabolic diversity.

The measurements (in the middle of the beds) of Eh in the CWP were always above those of the CWC, with measurements between –61 to +56 and –117 to –75 mV, respectively. Thus, these conditions allowed for enhanced aerobic biodegradation, which increased close to the exit of the CWP where the Eh measurements were closer to oxidative conditions with –35 to 154 mV. However, the oxygen availability was still limited compared to the organic load in both units. In any case, the oxygen availability at the planted unit was always more than those of the control unit. It is also important to mention that root growth followed plant development, and also had a positive contribution to the performance by providing additional surface area for biofilm development with different characteristics than the LECA material and with variable oxygen availability.

Previous results reported for CWs systems suggest that a multitude of bacterial metabolisms can take place at the same time in different locations of the wetlands according to oxygen concentration and availability, namely aerobic respiration, denitrification, sulfate reduction and methanogenesis, etc. [49, 63]. The amount of oxygen released by plants into their immediate root environment is still a controversial issue, and subject of debate because multiple factors are involved in its calculation, namely the HRT. The assessments of oxygen transfer rate are lower than that reported in literature for estimations based on mass balances and theoretical stoichiometric calculations (from 5.4 to 22 g O_2/m^2/d) [17, 61].

As expected from past experience, the treatment performance of the CWP was always higher than the unplanted unit [15, 17, 58]. The COD mean reduction was of 62% (values in the range from 44 up to 79%), which corresponded to an MRR of 10.2 ± 2.6 g $COD/m^2/d$. The average values for the CWC were of 48 ± 9% and 6.9 ± 2.1g $COD/m^2/d$, respectively. The removal efficiencies for the TPh were of 41 ± 6% and 58 ± 11% for MRRs of 0.25 ± 0.05 and 0.41 ± 0.10 g $TPh/m^2/d$ for the unplanted and planted units, respectively. The results obtained by the CWP system are compared with other biological treatment alternatives in Table 14.4. With the exception of decolorization, the removals of COD and TPh in the CWP system are clearly higher than those reported for other methods. Moreover, the HRT of 6 days set for the CWP operation is in between the values of the activated sludge system and those of the anaerobic digestion of 1–4 and 15 days, respectively [6, 11].

The assessment and comparison of the phenolic compound removals reported here for the CWP unit is relevant but problematic to achieve, because it was difficult to find wastewaters with characteristics close to CBW and CW operations with values in the range of the OLR experienced by us. Stefanakis et al. [58] studied the application of HSF CW to the treatment of groundwater contaminated with phenol and m-cresol, corresponding to OLRs of 0.62 and 0.08 $g/m^2/d$ respectively, and reported removals higher than 84%. For CWs with the same configuration but a more close context, with aerated and non-aerated coffee processing wastewater, for OLR of 0.52 and 0.66 g $TPh/m^2/d$ and HRT of 12 days, removals were reported of 72 and 66%, respectively; which correspond to MRRs in the range of 0.37–0.44 g $TPh/m^2/d$; thus in agreement with our results [57].

The extended range of microbial metabolisms after a long period of acclimatization to wastewater characteristics had a positive contribution to TPh removal. However, even taking into consideration the water loss through ET, the COD mean concentration was only reduced from 2,675 to 1,009 mg/L (ranging from 670–1,545 mg/L) and the TPh concentration from 116.8 to 47.9 (ranging from 29.6–74.5 mg/L), which is still above the legal requirements for water discharge or reuse. Thus, further downstream treatment is necessary to reduce the remaining organic load, which has low bioavailability and biodegradability.

The most frequently mentioned constraints of HSF CWs operations, namely the significant land requirements, the lack of performance under cold climatic conditions and the limited removals of N and P [14, 61, 63], are anticipated to be overcome because most of the cork processing units are located in the Iberian Peninsula, thus under the warm climate typical of the Mediterranean region and large land areas are available. Finally, the less efficient removal of N and P by comparison with COD and BOD are not relevant issues in this effluent because of their low initial content and plant uptake.

14.4 Conclusions

The preservation of the cork oak natural ecosystem forest is closely dependent on the valorization of cork products, namely the stoppers used in wine bottles, which has a significant contribution for the economic viability of the cork supply chain. However, to ensure the consumer's preference for cork, it is necessary to enhance the sustainability and eco-efficiency of the manufacture stages, especially by reducing the amount of water and pollution generated during the transformation process. The application of Constructed Wetland systems in the treatment of CBW was tested for the first time, using microcosm-scale beds. After a long-term experimental run under varying pollutant loads, it was found that CWs can contribute to the reduction of the impacts resulting from post-harvest stages as an environmentally friendly technology, which can be easily integrated into the urban or agricultural landscape, in addition to low construction and operation costs. The CW systems with the horizontal subsurface flow configuration showed good treatment performance, namely for COD and TPh removal, which were higher compared to respective results of other biological treatment methods. This project is the first positive outcome regarding the use of wetland technology for CBW treatment, which enables the scaling up for the implementation of a full-scale wetland facility.

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