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Case Report

Direct analysis of valuable by-products in cork wastewater

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ABSTRACT

Cork sector plays an important economic role in several Mediterranean regions whose manufacturing process consists of several stages involving waste generation, mainly industrial water or cork boiling wastewater (CBW). These waste products have traditionally been considered as simple pollutants, but CBW contains interesting compounds for recovery, however, their chemical characterization is long, difficult and expensive due to the high organic load. This work studied an advanced valorization of CBW through a sequential process. In a first step, a wide range of phenolic compounds were analyzed in CBWs, identifying the most interesting ones for commercial purposes. Furthermore, the phenolic fraction was separated by green techniques and the supernatant studied to detect and quantify remained by-products, highlighting low molecular weight polyphenols together with significant concentrations of carbohydrates made up of glucose, galactose and arabinose among others. In conclusion, we propose a methodology that offers a quick and efficient way to analyze the most important by-products in CBWs and a design of a recovery and purification process by eco-friendly and efficient techniques.

1. Introduction

Cork oak landscapes extend over an area of over 2.1 million hectares in seven countries: Portugal, Spain, Algeria, Morocco, Tunisia, Italy and France. Cork is the outer bark of this tree (*Quercus suber*) and it can be regenerated after each stripping. It is a natural material with very useful properties (durable, resilient, elastic, light, etc.), whose production performs a key role in the economy of several Mediterranean regions: total world exports in 2017 were over 1400 million € and the Iberian Peninsula accounted for over 80% of these exports [1]. The main compounds present in cork are: suberin (22.7–41.0%), lignin (22.0–30.0%), polysaccharides such as cellulose and hemicelluloses (18.2–33.1%) and extractables: waxes and phenolic compounds, with a range of 11.9–16.2% [2].

The cork industrial process includes a stage in which cork planks are immersed in boiling water during 1 h in order to improve their physico-chemical characteristics. Cork boiling wastewater (CBW) is a dark liquid containing suspended solids (up to 0.9 $kg{\cdot}m^{-3}$) and high chemical oxygen demand (COD) with up to 11.5 $kg{\cdot}m^{-3}$ due to the total phenolic compounds content with up to >1 $kg{\cdot}m^{-3}$ [3–11]. So far, some phenolic compounds have been detected and quantified in CBWs highlighting gallic acid, ellagic acid, protocatechuic acid, vanillic acid, esculetin and vanillin [12,13]. Due to the toxicological properties of these effluents and the high volumes produced, from 140 to 1200 $L{\cdot}ton^{-1}$ cork [13], the uncontrolled discharge of these untreated effluents can cause serious damages to the environment. Therefore, these effluents currently constitute one of the most serious problems for the cork industry and they must be treated before being discharged into public waterways through sophisticated treatments, which increases the costs of the process enormously.

A wide range of proposed treatments for this wastewater can be found in the bibliography: ultrafiltration (UF) and/or nanofiltration (NF) [3,7,14]; microfiltration-ultrafiltration-nanofiltration [12]; flocculation/flotation [15]; ozonization combined with other treatments [4,6,16]; photo-Fenton [9,17,18]; biodigestion [13]; combination of advanced oxidation technologies [19], sonication [20]; electro-assisted processes [21] and thermal wet oxidation processes [22]. However, these treatments require significant operational expenses and, in many cases, the use of chemical reagents with the consequent environmental risks.

Nevertheless, there are several compounds extracted during the boiling cycle, with useful properties to be used in several industries, so their recovery would generate an added-value to cork sector. At the same time, a good yield of depuration can be achieved due to the fact that these compounds account for most of the organic pollution in CBWs. By these reasons, CBWs are a promising source of value-added by-

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products by implementing the concept of biorefinery. Currently, this concept is beginning to be studied for CBW although not in a comprehensive way.

Within this framework, our research group has developed research lines for cork factories in order to apply green and innovative techniques to extract useful bioproducts (e.g. chemicals, biogas and fertilizers) from CBWs [12,23]. In this work, we have optimized an advanced valorization through a sequential process that was designed considering the concept of circular economy for minimizing the generation of wastes. In order to achieve these objectives, groups of useful by-products presented in crude CBWs were analyzed and recovered generating a more purified effluent which can be treated with green techniques, avoiding the use of chemical reagents. In this process there were two main steps:

1) Analysis of the main individual phenolic compounds present in crude CBWs in order to study their abundance, extraction capacity and feasibility of recovery.
2) Recovery of main phenolic compounds and carbohydrates from crude CBWs by using $Ca(OH)_2$ as a coagulant itself and not only as a way to adjust pH, according to a new methodology developed in our previous work [24]. Besides, a comprehensive characterization of phenolic compounds was carried out after the treatment and the results compared with untreated samples. In order to achieve a complete valorization and to study the extraction of other compounds, the monosaccharide composition in the clarified extracts (CBWTs) was also studied.

The final effluent presented a considerably reduction in its organic load, enabling a possible reuse by using less expensive and green treatments. Regarding the precipitates, they could be digested in order to obtain good yields of other by-products (biogas, fertilizers) according to our research lines [25]. Thus, nearly all the wastes can be recycled and generate added-value.

2. Materials and methods

2.1. Reagents

Reagents with PA, ACS and HPLC quality from Panreac and Sigma-Aldrich were used. The standards for the identification of phenolic compounds were gallic, protocatechuic, *p*-hydroxyphenyl acetic, *p*-hydroxybenzoic, vanillic, caffeic, syringic, *p*-coumaric, ferulic, ellagic and salicylic acids; vescalagin, castalagin, catechin, esculetin, epicatechin, vanillin, rutin-hydrate, myricetin, eriodictyol, naringenin, kaempferol, syringaldehyde, coniferyl aldehyde and sinapaldehyde.

2.2. Cork boiling wastewater

Three CBWs were generated under real industrial conditions by cork factories based in San Vicente de Alcántara (Spain). They were taken at different boiling times and amounts of boiled cork. All subsequent tests were carried out at laboratory scale, and their technology readiness level (TRL) is specified in section 3.4 below.

2.3. Coagulation/flocculation process

Crude CBWs were treated with increasing doses of calcium, with the following conditions, according to our previously optimized methodology [24]. The calcium was added as $Ca(OH)_2$ to achieve simultaneously the basicity of the medium and the coagulation of the organic load of CBWs. The doses were always in excess with respect to the concentration of phenolic compounds. They ranged from 800 to 1200 mg $Ca{\cdot}L^{-1}$. Samples were stirred for 5 min at 150 rpm and decanted for 24 h. In order to check if the amount of $Ca(OH)_2$ was right for every sample, a strong precipitation had to be observed after a decantation of 24 h (Fig. 1).

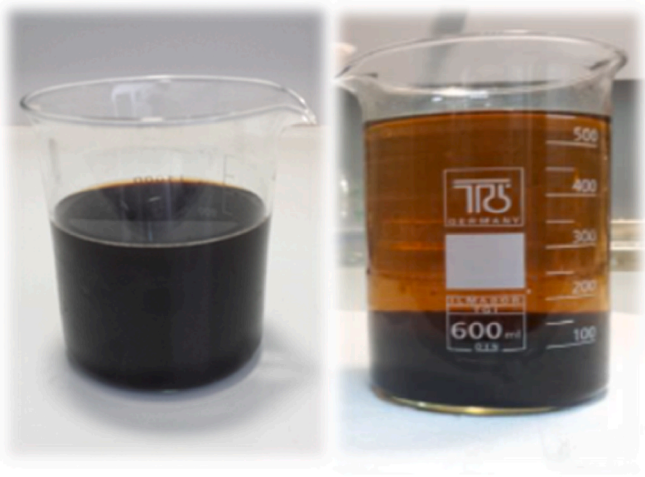


Fig. 1. Precipitation of phenolic compounds from crude CBW by using $Ca(OH)_2$. Left: CBW before to precipitation, right: CBW after to precipitation.

COD, total phenolic compounds and low molecular-weight phenolic compounds were studied in both crude samples and clarified ones in order to study the efficiency of the removal.

2.4. Chemical oxygen demand (COD)

COD was analyzed by COD reagents kits, digested in HI839800 COD Test Tube at 150 °C for 2 h. The absorbance was measured in a HI83099 COD Multiparameter photometer at 620 nm. All the consumables and equipment were supplied from Hanna Instruments.

2.5. Total phenolic compounds (TPC)

The total phenolic compounds (TPC) were determined by the Folin-Ciocalteu method described in Ref. [26]. CBW samples (2 vol) were mixed with 2 vol of Folin-Ciocalteu reagent (Merck KGaA, Darmstadt, Germany) and 40 vol of 7.5% (w/v) sodium carbonate. In the control tube, the sample volume was replaced by deionized water. The mixture was stirred gently and maintained in the dark and at room temperature for 60 min. After incubation, the absorbance was measured at 670 nm, using a UV/Vis Varian Cary-50 spectrophotometer (Palo Alto, CA, USA). Gallic acid (Sigma-Aldrich, Merck KGaA, Darmstadt, Germany) was used as standard and results were expressed as mg of gallic acid equivalents (GAE) per L of CBW sample.

2.6. Low molecular-weight phenolic compounds

Low molecular-weight phenolic compounds were studied by high performance liquid chromatography (HPLC) in both CBWs and treated ones in order to determine their variation before and after the proposed treatment for removal organic matter. They were analyzed on an Agilent 1200 liquid chromatograph instrument (Agilent Technologies, Santa Clara, CA, USA). The analyses were carried out using a column Poroshell 120 SB-C18 (100 mm × 4.6 mm x 2.7 μm, Agilent) and the compounds identified and quantified by a diode-array detector (255, 280, 305, 345 and 370 nm) and fluorescence detector (Ex = 275 nm, Em = 315 nm) according to the methodology described by Ref. [27], based on a direct analysis of the samples with a previous dilution and filtration by nylon filters.

2.7. Carbohydrate analysis

The study of carbohydrates was carried out only in clarified samples after the treatment with calcium, in order to study possible remained by-

products which can be extracted before the final treatment for depuration in order to optimize the valorization process. For monosaccharide analysis, CBWT samples were acid-hydrolyzed with 2 N trifluoroacetic acid at 120 °C for 1 h. Subsequently, the hydrolysates were dried under nitrogen stream, resuspended in distilled water and filtered through PTFE filters (0.45 μm). Monosaccharides were analyzed by high-performance anion-exchange chromatography/pulsed amperometric detection (HPAEC-PAD) in a LC 930 Compact IC Flex (Metrohm) chromatography system with an IC pulsed amperometric detector (Flex-iPAD). The chromatographic separation was carried out using a Metrosep Carb 2250/4.0 (Metrohm) analytical column and a Metrosep Carb 2 Guard/4.0 (Metrohm) guard column at 25 °C. The eluents used were a mixture of 1 mM NaOH and 1 mM sodium acetate (eluent A) and a mixture of 100 mM NaOH and 170 mM sodium acetate (eluent B). Sugars were separated with a flow rate of 0.6 mL·min^{-1} with the following chromatographic method: 100% eluent A (0–24 min), 100% eluent B (24.1–55 min), and 100% eluent A (55.1–75 min). For quantification, standard curves of rhamnose, fucose, arabinose, xylose, mannose, galactose, glucose, glucuronic acid and galacturonic acid commercial standards were used. Myo-inositol was used as internal standard.

3. Results and discussion

3.1. Characterization of CBWs

In crude CBWs, up to 22 phenolic compounds were detected and/or quantified (Table 1), highlighting significant concentrations of gallic (14.5–24.6 mg·L^{-1}), protocatechuic (13.7–28.8 mg·L^{-1}), ellagic (4.9–14.6 mg·L^{-1}) and vanillic acids (7.31.-15.61 mg·L^{-1}) together with and esculetin (0.8–3.2 mg·L^{-1}), syringic acid (4.4–4.9 mg·L^{-1}) and vanillin (0.4–4.8 mg·L^{-1}), what agreed in general terms with the results of other authors [13]. A remarkable aspect of the characterization was the presence of relative high concentrations of the ellagitannins castalagin (4.7–74.6 mg·L^{-1}) and vescalagin (27.3–251.1 mg·L^{-1}), despite of the possible thermal degradation caused by the boiler [28].

Table 1
COD, concentrations of total phenolic compounds (TPC) and individual phenolic compounds quantified in CBWs samples. Values are means ± SD, n = 3 for COD and n = 2 for TPC and phenolic compounds.

(1)	CBW 1	CBW 2	CBW 3
Kg Cork boiled/m^3 boiler volume (M/V)	1275	1800	2100
TPC (mg gallic acid·L^{-1})	497.01 ± 0.13	768.10 ± 29	1035.05 ± 0.16
COD (mg O_2·L^{-1})	5247 ± 180	7440 ± 72	8870 ± 60
Gallic acid	14.50 ± 1.93	20.15 ± 1.28	24.61 ± 0.36
Protocatechuic acid	13.60 ± 1.62	24.51 ± 1.65	28.74 ± 0.09
Vescalagin	27.32 ± 0.64	251.07 ± 8.23	151.10 ± 1.68
Castalagin	4.69 ± 0.32	53.11 ± 8.28	74.58 ± 0.16
***p*-Hydroxybenzoic acid**	1.00 ± 0.25	2.05 ± 0.73	3.01 ± 0.23
Catechin	n.q.	n.q.	2.95 ± 0.10
Vanillic acid	8.45 ± 0.93	7.31 ± 0.60	15.61 ± 0.34
Esculetin	0.75 ± 0.41	3.19 ± 0.06	2.09 ± 0.20
Caffeic acid	n.q.	0.70 ± 0.14	0.67 ± 0.03
Syringic acid	n.q.	4.36 ± 0.46	4.92 ± 0.21
Vanillin	0.43 ± 0.05	4.78 ± 0.36	3.52 ± 0.27
***p*-Coumaric acid**	n.q.	n.q.	0.54 ± 0.04
Syringaldehyde	n.q.	0.70 ± 0.02	0.39 ± 0.18
Ferulic acid	n.q.	0.91 ± 0.05	0.76 ± 0.08
Ellagic acid	4.92 ± 0.96	13.19 ± 1.43	14.57 ± 1.52
Rutin-hydrate	0.75 ± 0.16	3.15 ± 0.10	n.q.
Salicylic acid	n.q.	0.58 ± 0.01	0.76 ± 0.03
Coniferyl aldehyde	n.q.	0.62 ± 0.11	n.q.
Sinapaldehyde	n.q.	0.44 ± 0.06	n.q.
Myricetin	2.37 ± 0.19	1.43 ± 0.27	3.03 ± 0.17
Eriodictyol	n.q.	1.28 ± 0.38	2.45 ± 0.19
Quercetin	n.q.	0.47 ± 0.07	0.87 ± 0.15
Kaempferol	n.q.	n.q.	0.60 ± 0.06

(1)Concentrations of individual phenolic compounds in mg·L^{-1}; n.q.: non quantified.

Considering that the samples have been generated from different companies and amounts of cork, the concentration of phenolic compounds is proportional to the increase of boiled cork per m^3 of boiler volume (M/V) but this extraction did not show a linear regression for most of the low molecular weight phenolic compounds (Fig. 2.A) and there are some of these compounds (vanillin and esculetin) whose extraction was lower as the M/V was increased. This process can be explained due to the saturation of the water, the quality of cork and little variations of its composition, together with the decrease in the extraction capacity as the amount of cork increases.

This slowdown in the extraction of phenolic compounds, or even a drop in the extraction of these molecules, when the amount of boiled cork increased was also observed by other authors [11]. According to these data, frequent changes of water will stimulate the optimum extraction of these phenolic compounds since water saturation is avoided. However, the extraction of polyphenols, particularly castalagin and vescalagin, was optimum when the ratio of M/V increases (for both ellagitannins up to >300% of increase and even a sharp rise of concentration for vescalagin for a M/V ratio of 1800), that is in contrast with most of low molecular weight phenolic compounds (Fig. 2.B).

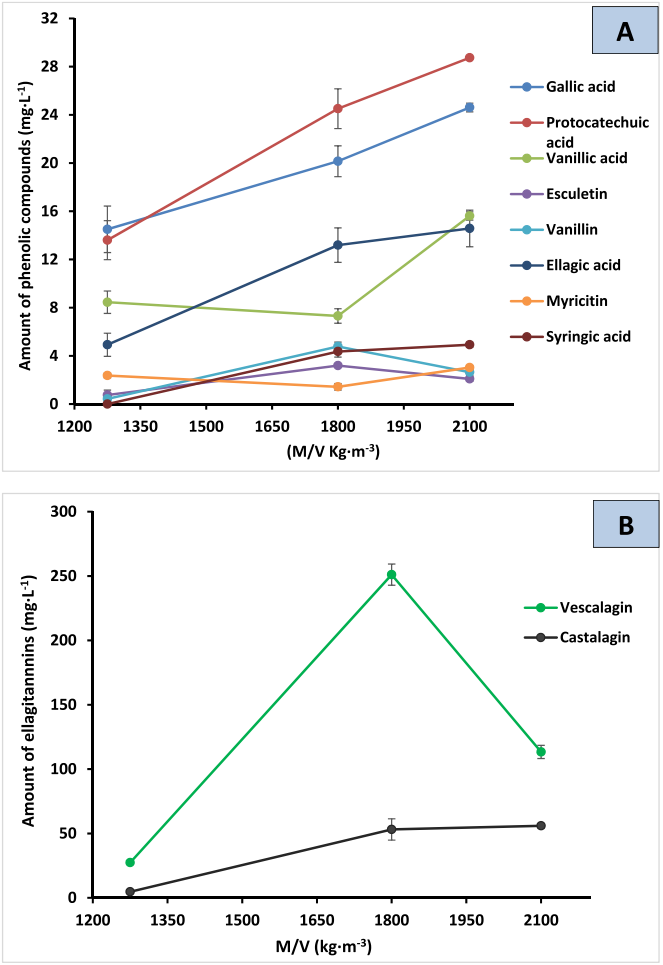


Fig. 2. Concentrations for the main low molecular weight polyphenols (A) and ellagitannins (B) presented in CBWs related to M/V. Values are means ± SD (error bars), n = 2.

Maybe, the reason of the differences in extraction of ellagitannins was their different chemical properties in relation to the other phenolic compounds, which can reduce their degradation (or maybe polymerization) processes that occurs due to the high temperature reached during the boiling [29].

Besides, it should also be taken into consideration that the concentrations of phenolic compounds in CBWs not only were related to M/V but they can also depend on the great heterogeneity of cork; cork composition differs significantly with the provenance and quality [30].

All these substances have properties which make them suitable to be used for several industrial sectors [31]. Indeed, vescalagin and castalagin have biological activities including antitumor and antibacterial effects [32], opening up a wide range of possibilities as possible nutraceuticals [33–35].

3.2. Coagulation/flocculation process

The calcium treatment in alkaline medium achieved average removal rates of 37.9% for COD and 82.9% for TPC and led to the precipitation of most of the phenolic compounds (100% for ellagic acid and esculetin, 97% for castalagin, >80% for gallic acid and vescalagin, and >70% for protocatechuic acid and myricetin) (Table 2, Fig. 3.A).

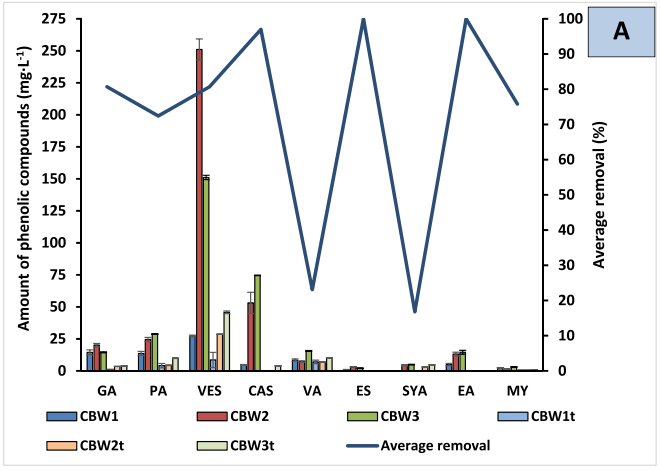
However, vanillic acid together with syringic acid presented a low removal compared to the other compounds (Fig. 3) and vanillin did not precipitate (Table 2). Regarding vanillin, it is remarkable that not only remained, but also there was a strong concentration of this molecule (13–458%) even if was presented in very low concentration (as in CBW1 sample). It is likely that there had been a degradation of complex phenolic compounds during the precipitation process, releasing vanillin as a result. Therefore, vanillin, syringic acid (>75%) and vanillic acid (>75%) remained in significant concentrations indicating that it would be interesting to design alternative processes for their recovery. That is also the case for ferulic acid, in which the efficiency of removal was lower than the rest of phenolic compounds.

Anaerobic digestion is a promising technology for the treatment of the organic effluents and for the simultaneous recovery of biogas (methane) and fertilizers (digestates). The documented research on

Table 2
COD, concentrations of total phenolic compounds (TPC), removal of COD and TPC and individual phenolic compounds quantified in treated CBWs samples (CBW_Ts). Values are means ± SD, n = 3. The phenolic compounds, esculetin, ellagic acid, rutin-hydrate, salicylic acid, sinapaldehyde, quercetin and kaempferol were not detected in the analysis and, therefore, were not included in the table.

(1)	CBW1 $_T$	CBW2 $_T$	CBW3 $_T$
Ca added (mg·L^{-1}) (2)	800	1000	1000
TPC (mg gallic acid·L^{-1})	118.05 ± 17.06	69.99 ± 1.26	168.09 ± 10.31
TPC removal (%)	76.2	90.9	83.8 .9
COD (mg O_2·L^{-1})	3325 ± 104	4955 ± 31	4775 ± 56
COD removal (%)	36.6	33.4	46.2
Gallic acid	1.06 ± 0.22	3.47 ± 0.05	3.88 ± 0.31
Protocatechuic acid	4.10 ± 1,70	4.38 ± 0.26	9.94 ± 0.27
Vescalagin	8.54 ± 5.94	28.63 ± 0.09	45.76 ± 1.04
Castalagin	n.q.	n.q.	3.90 ± 0.15
***p*-Hydroxybenzoic acid**	0.53 ± 0,07	0.78 ± 0.02	1.07 ± 0.08
Catechin	n.q.	n.q.	1.92 ± 0.51
Vanillic acid	7.02 ± 1.40	6.98 ± 0,27	10.11 ± 0.11
Caffeic acid	n.q.	0.58 ± 0.02	0.39 ± 0.01
Syringic acid	n.q.	2,99 ± 0.18	4.73 ± 0.12
Vanillin	2.40 ± 1.89	8.53 ± 1.29	3.99 ± 0.70
***p*-Coumaric acid**	n.q.	n.q.	0.71 ± 0.12
Syringaldehyde	n.q.	2.05 ± 0.45	n.q.
Ferulic acid	0.49 ± 0.03	0.94 ± 0.14	0.97 ± 0.03
Coniferyl aldehyde	n.q.	0.44 ± 0.02	n.q.
Myricetin	0.50 ± 0.01	0.50 ± 0.01	0.65 ± 0.05
Eriodictyol	n.q.	1.44 ± 0.06	2.40 ± 0.16

(1)Concentrations of individual phenolic compounds in mg·L^{-1}; 2) As $Ca(OH)_2$; n.q.: non-quantified.



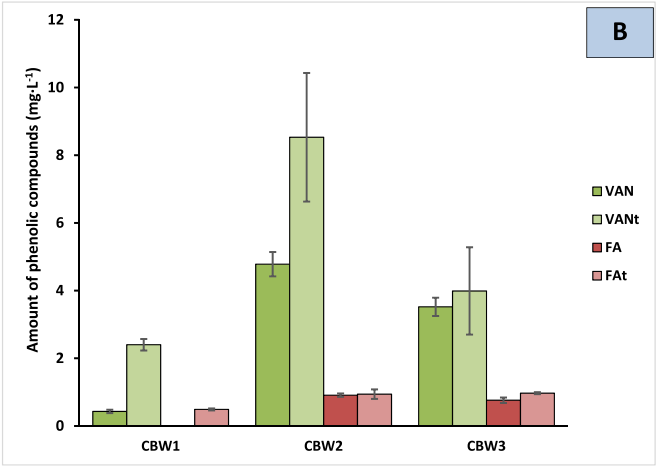


Fig. 3. A. Precipitation of the main phenolic compounds after the treatment with calcium and average removal. Values are means ± SD (error bars), n = 3. GA, gallic acid; PA, protocatechuic acid; VES, vescalagin; CAS, castalagin; ES, esculetin; VA, vanillic acid; EA, ellagic acid; My, myricitin, B. Main phenolic compounds that remained in treated samples. VANt, vanillin; FAt, ferulic acid, compared with their concentrations in non-treated CBW samples: VAN and FA.

anaerobic treatment/valorization performed with CBWs requires several inoculums [13,36] and also highly polluted CBWs in order to improve the process. Regarding the precipitates obtained from CBWTs, they can be digested using innovative co-substrates such as microalgae together with pig manure and prickly pear in order to produce biogas and fertilizers, according to research developed in our laboratory [25]. Thus, the purification process was optimized by generating by-products which can be used for the same industry (biogas) or sold for other market niches.

The final effluent was quite clarified and contained less organic load, which makes it suitable to be treated by green techniques such as photo-Fenton (due to its low turbidity) and sonication, avoiding an excessive use of chemical reagents.

3.3. Carbohydrates

Once most of phenolic compounds were precipitated, up to >580 mg·L^{-1} of total sugars in average were detected and quantified in clarified CBWs (Fig. 4). Most abundant monosaccharides were glucose (161.7–365.2 mg·L^{-1}), galactose (50.3–72.5 mg·L^{-1}), arabinose (32.0–50.4 mg·L^{-1}), mannose (31.7–44.2 mg·L^{-1}) and xylose (18.3–21.3 mg·L^{-1}) pointing to the presence of great amounts of glucans, such as cellulose, a major polysaccharidic component of cork oat

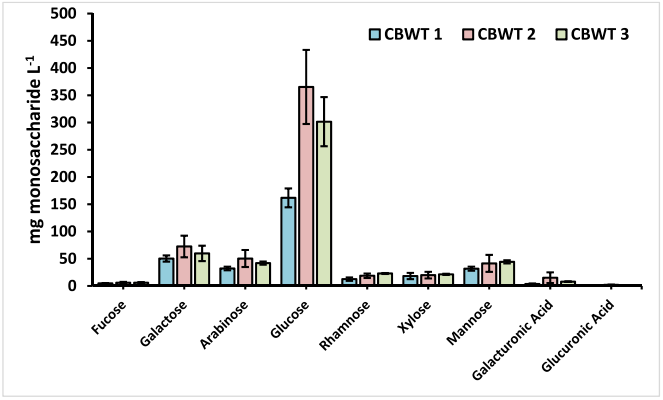


Fig. 4. Monosaccharide quantification in clarified effluents after calcium precipitation (CBWTs). Monosaccharides from CBWTs were released by a TFA hydrolysis procedure. Values are means ± SD (error bars), n = 3. Fuc, fucose; Gal, galactose; Ara, arabinose; Glc, glucose; Rha, rhamnose; Xyl, xylose; Man, mannose; GalU, galacturonic acid; GlcU, glucuronic acid.

phellem [37,38].

Moreover, although it has been described that most abundant hemicelluloses are xylans [37], the presence of higher amounts of mannose in clarified CBW suggest the presence of mannans. The presence of arabinose and galactose, and in a lesser extent, rhamnose and galacturonic acid suggest the presence of pectic polysaccharides or arabinogalactan proteins [39,40]. However, fucose and glucuronic acid were detected only at trace amounts. These data pointed to an enrichment of cellulose, hemicelluloses and pectin polysaccharides in the clarified extracts.

3.4. Design of an innovative and green process of valorization for cork wastewater

According to these studies, a full advanced valorization of CBWs for the treatment of CBWs is proposed, whose scheme is presented in Fig. 5. We propose the combination of direct analysis of interesting compounds, treatment with calcium and biodigestion. This process can offer a great opportunity to integrate the concept of biorefinery for cork sector, enabling the circular economy.

In a first step, direct characterization studies of phenolic compounds that can be recovered would lead to the possibility to generate added-value for cork companies. The extraction can be performed by green techniques, with a minimum technology readiness level (TRL) of 4–5, such as the sequential extraction by membranes and the concentrates sent to the next step for their treatment [3,7,12,14].

A second phase consists in separating most of the organic load by precipitation through an efficient, green and cheap process with calcium added as $Ca(OH)_2$, achieving a clarified effluent and significantly reducing DQO and TPC and with a TRL scale of 4. Interestingly, some phenolic compounds such as vanillic acid and vanillin remained in the supernatant and can be recovered for using in several industrial sectors [41,42]. On the other hand, the supernatant also contents significant amounts of several sugars so it can be used for a possible source to obtain carbohydrate-based products such as plant biostimulants [43]. Besides, the precipitate is a promising source of biogas and organic fertilizers using a biodigestion process as it was quoted before [25] and taking account that this process has been tested with a TRL of 4–5 [13,25].

Once the useful by-products have been extracted, due to the fact that most of the organic load has been removed, further treatments which minimize the use of chemicals reagents by using UV radiation (photo-Fenton), sonication and other advanced oxidation processes (electrochemical oxidation, ozone based processes, etc.) could be applied in order to obtain a treated effluent suitable for reuse. All these treatments have been studied by several authors, achieving minimum TRLs of 4–6 [4,6]. Further research must be carried out to study and develop the suitable conditions to reach TRLs>6.

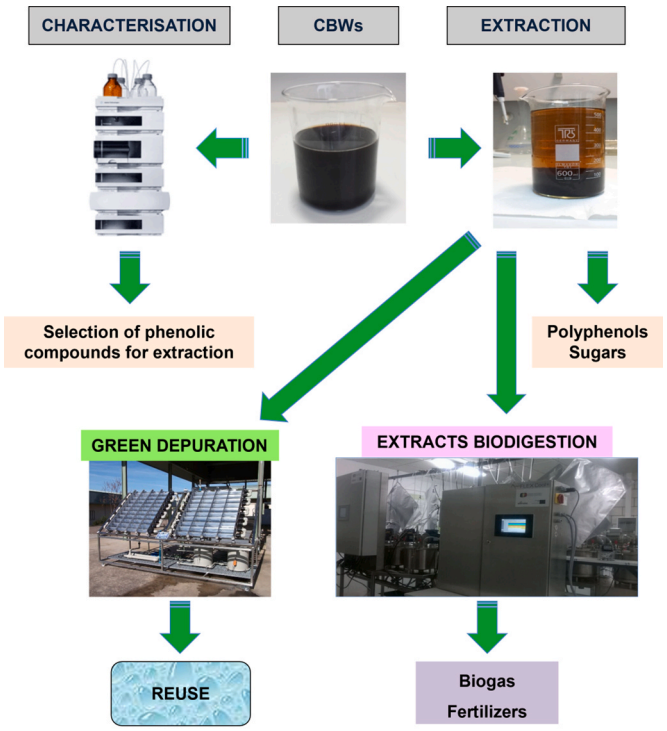


Fig. 5. Schematic design of an advanced valorization process for cork wastewater.

4. Conclusions

The direct analysis and proposed sequential separation of the compounds present in cork wastewater permitted the recovery of several useful by-products together with a significant depuration of the effluent, using green and not expensive techniques. These by-products have a potential use for several industrial sectors, generating an added-value for cork sector. In conclusion, the proposed methodology offers a quick and efficient way to analyze and extract most important by-products in cork boiling wastewater for future design of recovery processes and/or depuration techniques.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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