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ADVANCES IN RECOVERY OF HIGH-ADDED VALUE COMPOUNDS FROM ACID SULPHITE PULP PRODUCTION STREAMS

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SUMMARY

Recent studies on the industrial streams from acid sulphite pulping of *Eucalyptus globulus* wood (e.g., pulping liquor and bleaching effluents) revealed that they contain noticeable amounts of valuable underutilised biologically active substances, such as ellagic acid (EA) and β-sitosterol (BS). This study aimed to develop an industrially viable and ecologically sound approach for the recovery of high purity EA and BS from acid sulphite pulping streams. EA was recovered *via* selective crystallization from acidified sulphite spent liquor under optimized conditions (temperature and time of holding in a container of appropriate surface-to-volume ratio) without the use of organic solvents. The obtained crystals (yield of 0.25-0.44 g/L) were washed with acidified water (leading to *ca.* 85-95% of EA purity), dried and characterized by liquid and solid-state carbon nuclear magnetic resonance spectroscopy, mass spectrometry and wide-angle X-ray scattering. BS was recovered from the alkaline extract from sulphite pulp purification step by two-step acidification at pH 5 and pH 3 under pre-selected conditions, followed by fractionation of the formed precipitate with water-miscible organic solvents, having obtained best results (>90% of BS purity; yield of 70-210 mg/L) with methanol fractionation followed by BS crystallization induced via water addition (*ca.* 10% vol.).

Keywords: Acid sulphite pulp, *Eucalyptus globulus*, Ellagic acid, β-sitosterol,

INTRODUCTION

According to Confederation of European Paper Industries (CEPI) Portugal falls within the top three European wood pulp producers (CEPI 2021), being wood-based pulp and paper industry one of the largest industries in the country, contributing *ca.* 6% of total exports (SIT Nº 02 2023). Sulphite cooking, involving the treatment of wood under acidic conditions with aqueous solution of SO_2 in the presence of inorganic bases, is the second most important process after the sulphate (kraft) pulping for the production of cellulose pulp, with *Eucalyptus globulus* wood being a common raw material [1]. Nowadays sulphite pulping in Portugal is oriented exclusively to the production of dissolving pulp for the chemical processing, primarily for viscose production. The main side product of sulphite pulping is sulphite spent liquor (SSL), which besides spent pulping reagents also contains dissolved degraded sulfonated lignin (lignosulfonate) and hydrolysed sugars [2]. SSL is usually burned to recuperate energy and chemicals or used in several applications as surfactant or as chemical feedstock [1]. However, SSL is also known to contain phytochemicals such as ellagic acid (EA). In fact, *Eucalyptus globulos* wood contains noticeable amounts of EA (*ca.* 1100 ± 600 mg/kg) which distributes after cooking between SSL and unbleached cellulosic pulp (*ca*. 50/50). Other abundant extractives, such as phytosterols (645.0 ± 10.0 and 516.7 ± 17.0 mg/kg for free and conjugated compounds, respectively, with BS being the predominant specie in *E. globulus* [3]) are largely concentrated in the sulphite pulp [4]. Since bleaching of sulphite pulp encompasses an alkaline purification extraction stage, which allows leaching of significant amounts of residual lignin, hemicelluloses and extractives (including EA and phytosterols) [4], the alkaline extract (AE) from bleaching stage is another effluent containing EA and sterol derivatives, whose composition and structures are still unknown. Both, EA [5] and phytosterols (PS) [6], have been widely recognised as bioactive molecules that have many potential applications in health and food related industries. In particular, EA and EA derivatives are drawing an increasing interest towards extensive technical and biomedical applications. The latter ones include possible antibacterial,

antifungal, antiviral, anti-inflammatory, hepato- and cardioprotective, chemopreventive, neuroprotective, anti-diabetic, gastroprotective, antihyperlipidemic, and antidepressant-like activities among others [5]. PS have topped with evidence of having beneficial effects in healthy subjects and applications in food, cosmetic and pharmaceutical industries.

A viable method for the recovery of phytosterols from effluents of sulphite pulp production has never been projected. Conversely, the recovery of a phenolic mixture comprising EA, from *Eucalyptus* wood-based SSL of acid sulphite pulping, has been achieved by liquid-liquid extraction with different organic solvents [7]. However, no economically viable and technologically reliable methods of obtaining EA from industrial streams have been proposed. In this context, the present study assessed the recovery, purification and analysis of EA and sterol derivatives (mainly β-sitosterol) from SSL and AE effluents from acid sulphite pulping of *E. globulos* wood. The approach, proposed for the valorisation of these industrial streams, was fairly original and was never applied before.

EXPERIMENTAL

Material

The industrial sulphite spent liquors (SSL) after Mg-based sulphite acid sulphite pulping of *E. globulus* wood were supplied by Caima - Indústria de Celulose S.A. (Constância, Portugal). The SSL was collected from the last (7th) evaporation effect operated at *ca*. 70°C to remove free SO_2. The received SSL showed a pH value of 2.5–2.6 and the amount of dry solids of *ca*. 15% (w/w). The extract after the alkaline purification step (alkaline extract, AE) was collected from the washing press after the alkali extraction stage (E stage) and immediately cooled down to 30–40°C and neutralized by 10% (w/w) H_2SO_4 to pH 7. In total 10 SSL samples and 11 AE samples were collected in the period between 2018 and 2021, using same pulping and bleaching conditions and a similar wood source. All reagents used were of high quality (95-99%, w/w) commercial products supplied by: Aldrich-Chemie, Steinheim, Germany; Acros Organics, Geel, Belgium; and Sigma-Aldrich Chem. Comp. (Steinheim, Germany).

Crystallization of ellagic acid from SSL

In a typical trial, 6000–10000 cm^3 of *Eucalyptus* wood magnesium-based acid sulphite industrial cooking liquor were thoroughly mixed together and placed in sealed glass containers with known surface-to-volume (S/V) ratio. In the case of the experiments on the effect of S/V ratio and material of the holding container on the crystallization of EA, the samples were placed into laboratory glassware of different geometries (laboratory glass cylinders, flasks, beakers or separating funnels) or plastic containers (high density polyethylene or polyethylene terephthalate) and sealed using glass or polypropylene stoppers. The samples were stored at desired temperatures for predetermined time periods in ventilated ovens or refrigerators during various exposure times, depending on the experiment [8,9]. Thereafter, the solids were mixed with distilled water (1:10 vol. ratio), centrifuged again and the so-called unwashed sample dried in a vacuum oven at 30°C. Alternatively, the raw precipitates containing EA were dispersed in acidified (HCl, pH 2) water, centrifuged, and washed again two to ten times with distilled water (1:20 vol ratio), each time separating the solid *via* centrifugation. The final washed sample was dried in a vacuum oven as described above, weighted and the final yield expressed in grams per litre of SSL. All experiments were carried out in at least triplicate. The presence of EA was confirmed by gas chromatography coupled with mass spectrometry (GC-MS) and NMR spectra; wide-angle X-ray scattering was used to assess the crystalline structure of EA [8]. The analyses were carried out in random samples as described in the section below.

Crystallization of ellagic acid from AE

In a typical assay, 6000–10000 cm^3 of industrial alkaline extract after the first stage of the E-O-P bleaching line (alkaline extraction (E)-oxygen delignification (O)-hydrogen peroxide bleaching(P)) of acid sulphite pulp obtained from *E. globulus* wood by Mg-based acid sulphite cooking, were collected from the washing press at a temperature of approximately 70°C in a high-density polyethylene (HDPE) container. The extract was rapidly cooled to a temperature of 50°C and the initial pH of 10 was adjusted to 7 using 20% sulfuric acid (m/m). After cooling to 20°C the extract was acidified again to pH 5.0 and placed in a glass vessel with an S/V ratio of 0.67. After 24–120 h of exposure at 20°C, the formed

precipitate was separated from the extract by decantation followed by centrifugation. The rest of the protocol followed the steps described in the previous section, being all experiments performed in at least triplicate.

Recovery of β-sitosterol from AE

2000 cm^3 of industrial alkaline extract (AE) after the first stage of the E-O-P bleaching, previously cooled down to 30°C and adjusted to pH 7, was acidified to pH 5 using 20% sulfuric acid (w/w). After 24 h of exposure at room temperature (25°C), in glass containers (surface-to-volume (S/V) ratio of 0.67) sealed using glass or polypropylene stoppers or polymeric film (Parafilm®), the formed precipitate was separated from the extract by decantation followed by centrifugation [10,11]. Subsequently, the supernatant was further adjusted to pH 3 using 20% (w/w) sulfuric acid. After a second 24 h of exposure at room temperature (25°C) in the same glass container, the formed precipitate was once again separated from the extract by decantation followed by centrifugation. The obtained residue was successively fractionated under stirring with methanol (3×20 cm^3), centrifuging the sample after each extraction step and collecting the supernatant. Finally, 10% v/v of water was added to the combined methanolic extract to induce the precipitation of β-sitosterol, which was separated from the supernatant by centrifugation [10]. After washing with water at room temperature, in order to remove traces of methanol, the precipitate was dried at 30°C in a vacuum oven. Alternatively, 2000 cm^3 of industrial AE after the first stage of the E-O-P bleaching was stepwise acidified using the same procedure as described above, but the obtained precipitate formed from AE at pH 3 was fractionated 3 times with ethanol (3×20.0 cm^3) instead of methanol. The addition of 40% v/v of water to the collected ethanolic extract induced the precipitation of an insoluble residue, which was separated from the supernatant by centrifugation. The alkaline hydrolysis of this residue was carried out in methanol with sodium methoxide under the conditions described previously [4].

Analyses

GC-MS analyses were carried out according to previously published protocols [8,10]. Ash content in the samples was determined by calcination at 525°C according to ISO 1762:2015. Solid-state Cross Polarization - Magic Angle Spinning ^{13}C Nuclear Magnetic Resonance (CP-MAS ^{13}C NMR) spectra were registered on a Bruker Advance 400 spectrometer (magnetic field of 9.4 T) [8,10]. X-ray diffraction scattering analysis was carried out on a Philipps X'Pert MPD diffractometer using Cu-Kα source (λ = 0.154 nm) [8]. The images of EA crystals were recorded using bench scan electron microscope (SEM) TM4000Plus Hitachi (Hitachi Ltd, Tokyo, Japan) equipped with backscattered electrons (BSE) detector. The analysis of metals by ICP-AES was carried out as described previously [8]. Fourier transform infrared spectroscopy (FTIR) spectra were acquired using a FTIR System Spectrum BX (PerkinElmer, Massachusetts, USA), coupled with a universal attenuated total reflectance (ATR) sampling accessory [8]. Sugars analysis of the cellulose-containing residue was carried out using hydrolysate obtained by Saeman hydrolysis on a Dionex™ Integrion™ HPIC™ system (Thermo Fisher Scientific, Massachusetts, USA) [10].

RESULTS AND DISCUSSION

Recovery of EA from SSL

In this study was proposed the original approach for the isolation of ellagic acid from SSL via crystallization. Noteworthy that unlike other polyphenols, such as gallic acid or catechin, ellagic acid (EA) is poorly soluble in aqueous solutions [5]. This fact, together with a highly symmetrical chemical structure (Figure 1), allows to find the conditions for a selective crystallization of EA from the SSL of the acidic sulphite pulping of *Eucalyptus* wood [8]. The relatively low pH of the SSL (pH 2-3) favours EA crystallization, being below the pKa of the phenolic groups (pKa=5.42-6.76). Spontaneous crystallization of EA already occurs at room temperature and is essentially observed on the surface of the container in which it is placed (Figure 2). The dynamics of EA precipitation from SSL are temperature dependent and were studied at 6°C and 20°C for up to 696 h using glass recipients with the same area-to-volume (S/V) ratio (*ca.* 0.50). The amount of the precipitate formed at 6°C was *ca.* 30% greater than that formed at 20°C. However, the content of EA in precipitate formed at 20°C was

substantially higher than in the one obtained at 6°C. At lower temperatures, the solubility of other SSL constituents besides EA also decreases, leading to competitive co-precipitation with EA. Most of the precipitate was formed during the first 120 h; from 120 h onwards the increase in the amount was much less pronounced. The highest purity of EA was attained during first 24 h of SSL exposure [8].

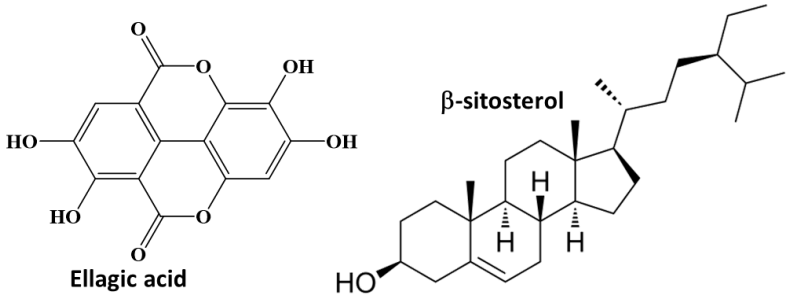

Figure 1. Chemical structures of ellagic acid and β-sitosterol.

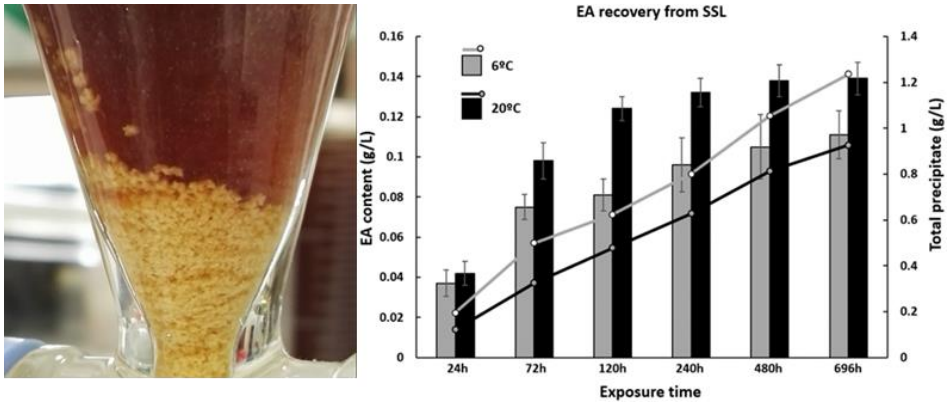

Figure 2. EA crystals on the surface of glass vessel used for the crystallization (left) and temperature effect on EA recovery from SSL showing the amount of total precipitate (line) and the content of EA (bars) [8].

A more detailed study on the temperature effect was carried out for 24 h, in the range of 10–90°C, using glass vessels with S/V ratio of 0.63 (Figure 3). In general, both the amount and the purity of EA, precipitated from SSL, has steadily increased with temperatures up to 80°C, while a decrease was observed at 90°C. The observed features can be explained not only by enhanced solubility of EA in the temperature range of 20–80°C, at which point saturated solution promotes the self-assembly of EA molecules, but also by a simultaneous improvement in the solubility of interfering concomitant substances (e.g., carbohydrates and LS). Some decrease in EA-containing precipitate at temperatures above 80°C may be related to a resulting lower EA solubility and increased fluctuations near the container's wall surface, which hinder EA nucleation from a system with no pre-existing crystalline matter. The purity of EA crystals, precipitated at exposure to 80°C, reached *ca.* 55% being increased to *ca.* 85% after washing with acidified distilled water. The final yield at the 80°C for all the samples, reaching at least 85% of EA content, was in the range of 0.25–0.44 g/L.

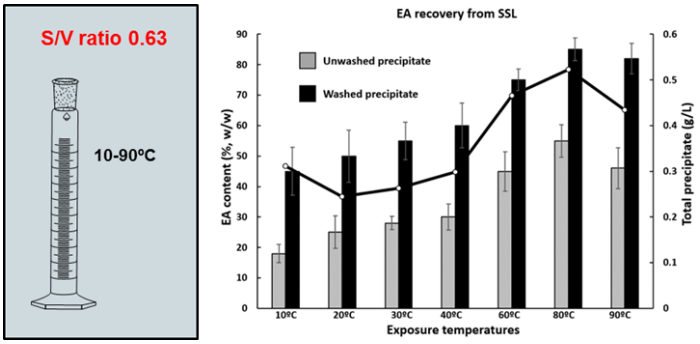

Figure 3. Temperature effect on EA crystallization from SSL in the range of 10-90ºC showing the amount of total precipitate (line) and the content of EA (bars).

The main contaminants of EA precipitated from SSL (carbohydrates, lignin, extractives and mineral salts) were found to be eliminated to a significant extent by washing EA crystals with acidified distilled water while stirring. This allowed reaching a purity of up to 95% with an acceptable level of metal contaminants (As, Cd, Pb and Hg), critically important for food and cosmetic applications [8].

It was also found that the degree of EA crystallization depends on specific area of the crystallizer due to the abundance of occurring nucleation centres. This was demonstrated by crystallization of EA from SSL using two types of glass vessels with different S/V ratios at 20°C for 24–696 h (Figure 4). Even a small increase in the S/V ratio (from 0.67 to 0.73) caused an increase in the precipitate with EA crystals, which occurred essentially at the surface. A clear dependence of EA crystallization yield (Y%) from SSL for 72 h was demonstrated in the S/V range of 0.5–2.0, which showed a logarithmic dependence ($Y,\% = 0.4336 \cdot Ln(S/V) + 0.5778$, $r^2 = 0.99$). Hence, S/V ratio have a crucial effect on the rate of EA crystallization from SSL, not completely disregarding the contribution of homogeneous nucleation.

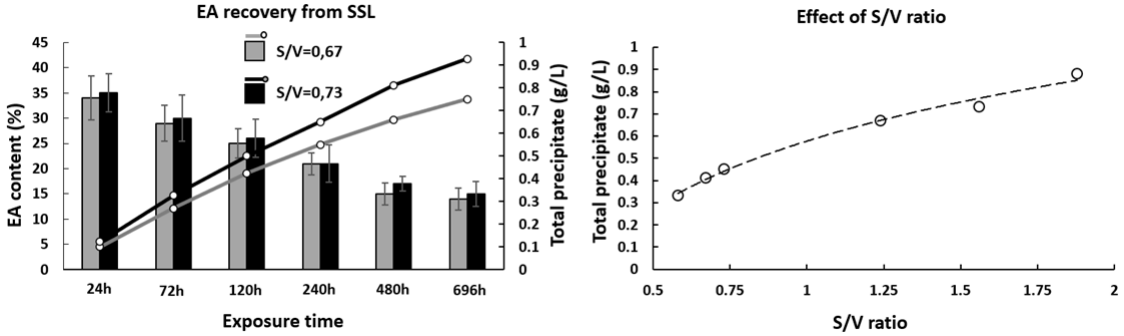

Figure 4. Effect of S/V ratio of a glass container on the dynamics of recovered EA from SSL and the composition of precipitate at 20°C (left image). The amount of precipitate formed in 72h as a function of S/V ratio of used glass vessels is shown in the right picture.

Albeit without controlling the morphology of the material of crystallizers, used as holding containers for EA crystallization from SSL, the importance of the vessel surface energy in nucleation activity was evaluated with four commercial materials: glass, stainless steel (inox) and plastic vessels (high density polyethylene (HDPE) and polyethylene terephthalate (PET)). All four containers of similar S/V ratio (*ca.* 0.5) filled with SSL were exposed to 25°C for 72 h. Plastics such as HDPE and PET have the lowest surface energy (γ_s) of *ca.* 30–40 mJ/m^2 while the highest belongs to stainless steel (> 100 mJ/m^2), being intermediate for borosilicate laboratory glass (*ca.* 50–70 mJ/m^2). The comparison between the container's material used for the EA crystallization clearly revealed the tendency of crystallized EA to increase with the diminishing in γ_s of the used container's material. Thus, the amount of crystallized EA and the purity of obtained precipitated matter was increased in the following order: plastic container > glass container > inox container. The purity of obtained EA after several washings with acidified water can reach as higher as 95% (w/w).

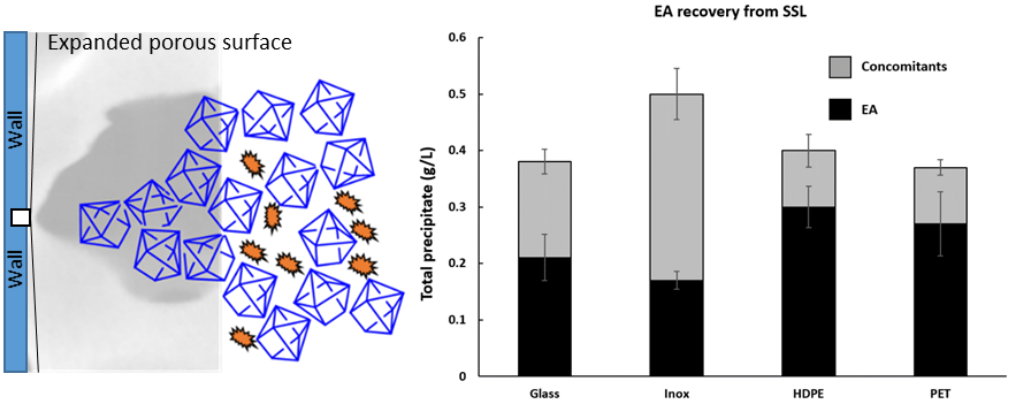

Figure 4. Schematic representation of EA crystallization from SSL on the surface of a glass vessel (left image). The crystalline EA in an expanded pore space is presented by blue polyhedron and the concomitants by brown spots. The container's material effect on the crystallization of EA from SSL at 25°C for 72 h (right picture).

Crystallization of EA from AE

Similar to the crystallization of EA from SSL, under the same conditions but for 24–120 h, the amount of precipitate from the neutralized AE at pH 5 grew for the first 48–72 h of exposure being further sealed for the longer exposure times [8]. Meanwhile, the amount and purity (*ca.* 10%) of EA in the precipitate remained similar and did not change much after washing. Evidently, sparingly soluble in water under weak acidic conditions (pH 5), the AE components readily co-precipitated with EA and could not be removed by washing with water. In fact, the residual lignin in the unbleached *Eucalyptus* sulphite pulp extracted in E stage is poorly sulphonated and has a relatively high molecular weight and low water solubility. In addition, the unbleached *Eucalyptus* sulphite pulp contains significant amounts of lipophilic extractives (*ca.* 0.3%), whose major part, especially fatty acids and triterpenoids, along with polyphenolics, are removed in the E stage [4]. These EA concomitants are only soluble in specific organic solvents. Therefore, the composition and concentrations of concomitants in aqueous solution affect the crystallization of EA from acidified solutions and its purity in precipitate. The attempts to improve EA isolation from AE at lower pH (pH 3–4) or at higher temperatures (40–80°C) were not successful [8]. The lowering of pH below five led to abrupt non-selective precipitation of AE components with EA content below 2% (w/w). The temperature increase, as high as 40°C, at pH 5 led to the co-precipitation of oligomeric/polymeric carbohydrates (e.g., β-cellulose) from AE, which hindered the recuperation of EA from precipitate. Therefore, the crystallization of EA from AE strongly competed with the precipitation of other dissolved/dispersed compounds, thus decreasing the purity of the target product. Accordingly, alternative approaches or the development of new purification schemes are needed for selective isolation of EA from AE.

Isolation of β-sitosterol and derivatives from AE

The significant part of extractives, present in *Eucalyptus* unbleached sulphite pulp, is removed in the alkaline purification E stage [4]. Accordingly, the alkaline extract contains not only released polyphenolic compounds, but also lipophilic compounds, mainly BS [4]. Accordingly, a novel process was developed for the highly selective isolation of BS from AE for the first time. The isolation scheme is presented in Figure 5. In the first step, the pH of the alkaline extract from stage E was adjusted to 5

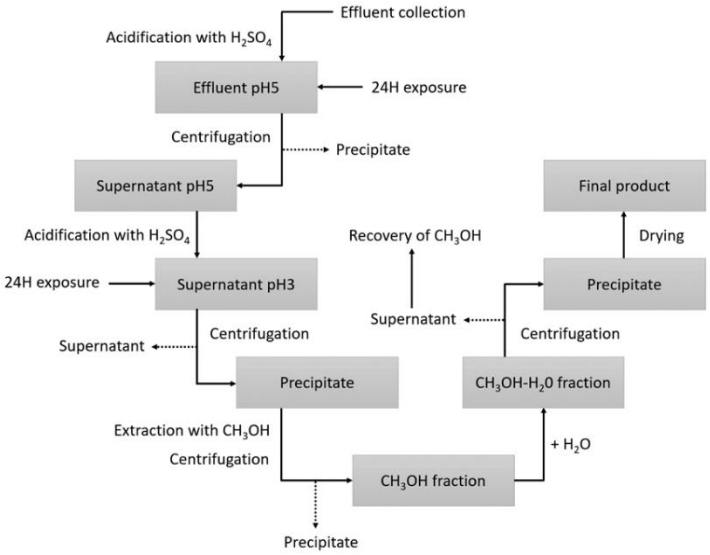

Figure 5. Schematic representation of the main steps comprising the developed process for the recovery of BS from E stage of the E-O-P bleaching line.

in order to eliminate the dissolved carbohydrates and polyphenolics. This precipitation step at pH 5 is temperature dependent [10] and when carried out in a glass container with surface-to-volume ratio (S/V ratio) of 0.67 at 60ºC for 24 h, causes the precipitation of the polysaccharides dissolved in the alkaline extract (*ca.* 0.43 g/dm^3), which was identified as β-cellulose by solid-state ^{13}C NMR. According to sugars analysis (glucose content), the purity of obtained cellulose was *ca.* 94%. However, if the same

operation on the precipitation at pH 5 is carried out in the glass container with the same S/V ratio and the same exposure time (24 h) but at lower temperatures (*ca.* 25°C), much less amount of precipitate was detected (*ca.* 0.15 g/dm^3). This was mainly attributed to the lower amount of precipitated cellulosic material and the presence of EA [10]. The increase in precipitate amount, registered for the longer exposure times at 25°C (up to 120 h), was much less significant. Precipitation at pH 5 had minimal influence on the quantity of BS-based final product recovered from the extract [10]. At the same time, the elimination of polyphenolic compounds (including EA) and polysaccharides from the effluent at pH 5 reduces the concomitants in the second precipitate at pH 3 and promotes purity of the target product. Subsequently, after separating the supernatant from the precipitate (pH 5), the former is further acidified to pH 3 giving rise to a sediment that contains β-sitosterol derivatives in its constitution (Figure 5). The preferred temperatures of this precipitation at pH 3 are between 20 and 30°C, while at higher temperatures the amount of precipitate decreased substantially. Thus, a solid obtained at 25°C (*ca.* 2.1 g/dm^3) was separated from the acidified extract and subjected to successive fractionation with a pre-selected organic solvent. The analysis of this precipitate by solid-state ^{13}C NMR clearly showed that besides lipophilic substances, showing intensive resonances at 10–40 ppm, it contained remarkable proportion of lignin (resonance of OCH_3 at *ca.* 56 ppm and aromatic carbons at 103–160 ppm) and of cellulose (resonance of C-6 at 63–66 ppm and C-2,3,5 at 70–78 ppm) (spectrum is not shown). The choice of organic solvent to dissolve the precipitate obtained at pH 3 determines the amount and purity of β-sitosterol present in the final product. The amount of solvent used in the fractionation must be minimal, in order to guarantee the saturation of the dissolved product and to avoid an evaporation step to remove the solvent excess. In this study, three successive fractionations of the precipitate were used with an organic solvent (liquid-to-residue ratio of *ca.* 5), combining the obtained fractions. The addition of small percentages of water as co-solvent (up to *ca.* 10%, which may be higher if the precipitation does not occur) to the extract obtained with the organic solvent induced sterol precipitation (Figure 5). Among examined water-miscible solvents (methanol, ethanol and acetone), the fractionation of the precipitate with methanol followed by crystallization with addition of water (*ca.* 10% vol.) gave the best BS purity (>90%) with yield of *ca.* 0.21 g/dm^3, quantitatively confirmed by GC-MS, with the main contaminant being a saturated analogue of the target compound, the sitostanol (*ca.* 4%) [10]. Among nonsteroidal lipophilic structures, only trace amounts of palmitic (16:0), linoleic (18:2) and cerotic (26:0) fatty acids were identified. The obtained product also showed characteristic patterns for BS in carbon and proton NMR spectra. Some other classes of extractives, undetected by GC-MS, could also be present [10].

The same extraction procedure of AE precipitate at pH 3 was used to produce an ethanol extract, which then was mixed with water (*ca.* 40% vol.) to obtain a precipitate (*ca.* 0.33 g/dm^3 of AE) presumably containing BS [10]. However, the analysis of this precipitated matter revealed just trace amount of BS. At the same time, alkaline methanolysis followed by TMS-derivatization of obtained products revealed a noticeable amount of BS and fatty acid methyl esters (FAMEs) when analysed by GC-MS. A major part of β-sitosterol was also identified in the form of stigmasta-3,5-diene, a dehydration product of BS formed during the hydrolysis of sterol conjugates. The approximate amount of BS and its dehydration product was *ca.* 50% of identified compounds [10]. Among fatty acids formed in the alkaline methanolysis, linoleic acid was the predominant one, which agrees with existing information in the literature for conjugated sterols and fats of *E. globulus* [3]. Hydrolysis products of fats were also identified, including glycerol and a set of different FAMEs, among which hexadecanoic (16:0), 9,12-octadecadienoic (18:2), eicosanoic (20:0), tetracosanoic (24:0) and hexacosanoic (26:0) acid were detected. Thus, the product isolated from the ethanolic extract was mostly composed of fatty acid glycerides and conjugated sterols, with only small amounts of free sterols. These findings corroborate that BS, present in AE, exists in both its free and conjugated form, and that the solvent chosen for the extraction of the AE precipitate at pH 3 plays a decisive role in the composition of the final product.

CONCLUSIONS

Industrial streams of the production of sulphite dissolving pulp from *E. globulus* emerges as an underutilized source of high added-value compounds, such as EA and BS. In this study, for the first time, viable methods for the isolation of EA and BS from SSL and bleaching effluent were developed.

EA was recovered *via* selective crystallization from SSL under optimized conditions (temperature and time of holding in a container of appropriate surface-to-volume ratio) at a yield of 0.25-0.44 g/L with final products having up to 95% of EA purity. BS was isolated from the alkaline extract from sulphite pulp purification step by two-step acidification at pH 5 and pH 3 under pre-selected conditions, followed by fractionation of the formed precipitate with methanol BS was recovered from the alkaline extract from sulphite pulp purification step by two-step acidification at pH 5 and pH 3 under pre-selected conditions, followed by fractionation of the formed precipitate with water-miscible organic solvents. The resulting products with highest BS content (>90% of BS purity; yields up to 0.21 g/dm^3 of AE) were obtained during the extraction of the precipitate with methanol at temperatures between 20 and 30°C, followed by BS crystallization induced via water addition (*ca.* 10% vol.). When ethanol was used instead, BS was detected in minor quantities in the isolate, being fatty acid sterol esters and fatty acid glycerides the major constituents. After the recovery of EA and BS from industrial streams, the latter can be reintroduced into the conventional industrial process for energy and reagent recovery, thus creating no additional environmental impact. The processes fit perfectly within circular economy and biorefinery concepts, are adaptable to the large-scale industrial production of added-value products from industrial acid sulphite pulping streams and can represent an important profit for pulp companies.

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