Accepted Manuscript.

Regular article

Detoxification of chestnut burrs hydrolyzates to produce biomolecules

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ARTICLE INFO

ABSTRACT

Activated charcoal was proposed to detoxify the streams rich in carbohydrates generated after the acid hydrolysis of chestnut (*Castanea sativa*) burrs. Adsorption isotherms, kinetics and thermodynamics parameters were evaluated under different ratios of adsorbent/adsorbate (0.25–5.0 % w/v). Results showed that Langmuir equations fitted better the equilibrium sorption than the Freundlich isotherm, while pseudo-second-order reaction kinetics explained the reaction mechanism most effectively. An exothermic and non-spontaneous adsorption process was defined by negative enthalpies and positive free energies; meanwhile negative entropies showed the affinity of phenolic compounds for the adsorbent. Mid temperatures (30 °C) and higher amounts of charcoal (5.0 % (w/v)) stimulated the adsorption process, with a higher percentage of phenolic compounds removal (95.50 ± 0.03%). *Lactobacillus plantarum* CECT-221 was unable to consume raw hydrolyzates; however, it was capable to produce bacteriocins with antimicrobial activity against *Listeria monocytogenes* CECT-934, cell-bond biosurfactants and lactic acid on detoxified hydrolyzates in biotechnology processes carried out in Erlenmeyer flasks and 2 L stirred tank bioreactors.

1. Introduction

The concept of lignocellulosic waste includes the plant biomass that derives from agricultural, industrial or forestry activities. The yearly lignocellulosic waste production rate is approximately 200×10^9 tons, only 3% of which comes from non-food-based areas [1]. Lignocellulosic waste is mainly made up of cellulose, hemicellulose and lignin, although smaller amounts of other materials (including ash, proteins or pectins) can also be present [2]. Hemicellulose, the second major polysaccharide in lignocellulosic waste is comprised of heterogeneous polymers of pentoses (D-xylose and L-arabinose) and hexoses (D-glucose, D-mannose and D-galactose); although phenolic, uronic or acetyl groups can replace them [3].

Worthy of note among these lignocellulosic wastes is *Castanea sativa* Mill., one of Southern Europe's most economically important fruit crops, particularly on the northern side of the Mediterranean basin [4]; about 100 thousand tons of chestnut fruits go on the market in the EU each year, turning over around 200 million Euros [5].

An integrated lignocellulosic waste biorefinery seeks selective separation of the three main components [3], where the dilute acid hydrol ysis (prehydrolysis) emerges as the best economic option as the first stage of an integrated global strategy to generate interesting products [6]. Generally, prehydrolysis is performed with mineral acids such as H_2SO_4 or HCl, under different temperatures. The hemicellulose fraction is hydrolyzed into xylose and other sugars at a lower temperature than the cellulosic fraction [7]. However, various substances that are toxic/inhibitors or fermentation may result during the pretreatment of lignocellulosic waste. For instance, decomposition of lignin could originate phenolic compounds; dehydration of pentoses and hexoses could generate furfural and 5-hydroxymethylfurfural (HMF) respectively; and acetyl groups of hemicellulose could be hydrolyzed during acid pretreatment releasing acetic acid [8]. Thus, furans, several phenolic compounds and weak acids have shown negative impacts in cell grown and fermentation yields as a consequence of inhibition or modification of some of their metabolic activities [9]. The literature cites several detoxification methods as being successful at reducing these inhibitors. Neutralization and overliming, biological adaptation, extraction with organic solvents, ion-exchange resins and adsorption with activated charcoal are the most widely-used methods [10]. Comparing to other detoxification methods, activated carbon adsorption is cheaper

and easier to be employed and reutilized [11]. Activated charcoal shows interesting characteristics because its porous structure increases its surface area (ranges from 500 to 5000 m²/g) and therefore its adsorption capacity [12]. Furthermore, the wide spectrum of surface functional groups allows the adsorption of a wide range of compounds which includes heavy metals and phenolic compounds [13].

Lactic acid bacteria (LAB) are a heterogeneous group of microorganisms, whose common characteristic is the production of lactic acid as a product of their metabolism [14]. Lactic acid has several industrial applications, but some members of this group also produce other metabolites of interest such as bacteriocins and biosurfactants [15]. Besides, LAB are considerate as 'Generally Regarded as Safe (GRAS)' and are currently employed in food industry taking part of fermented foods [16]. However, its production is associated with high prices [16], therefore, for its industrial implementation is necessary to look for new processes that can reduce their cost. In this sense, the formulation of culture media from lignocellulosic residues could be an approach.

This work studies the adsorption isotherms and thermodynamic properties of phenolic compounds, present on acid-hydrolyzates from chestnut burrs, on commercial powdered charcoal to produce fermentable culture media. Detoxified acid hydrolyzates were subsequently used to produce lactic acid, bacteriocins and biosurfactants by *Lactobacillus plantarum*.

2. Experimental

2.1. Chestnut burrs and chemical processing

Chestnut burrs, a seasonal waste, were collected from local cultivars (Vilardevós, Ourense, Spain) during the fall harvest in November 2018, dried at room temperature, milled and homogenized in one lot. The characterization of the raw material was carried out in a previous work [17], in which the acid hydrolysis pretreatment was optimized to maximize the release of sugars from the chestnut burrs. The chemical analysis showed the following composition: 10.97 ± 0.11% humidity, 0.90 ± 0.07% ashes, 20.61 ± 0.57% glucan, 19.26 ± 0.40% xylan, 5.79 ± 0.23% arabinan, 3.12 ± 0.32% acetyl groups, 20.04 ± 0.30 Klason lignin, 12.86 ± 0.25% extracts and 10.62 ± 0.66% acid-soluble lignin [17]. Hydrolyzates were obtained by optimized acid hydrolysis of ~~from~~ chestnut burrs with 3.52% H_2SO_4 liquid/solid ratio of 8 g/g during 30 minutes at 130 °C.

2.2. Adsorption studies

Acid hydrolyzates were neutralized with NaOH to a final pH of 6.0-6.5, and the liquors were detoxified with 0.25, 0.50, 1, 1.75, 2.5 or 5% (w/v) powder activated charcoal (Panreac AppliChem) at 30, 40, 50 and 60 °C under constant stirring at 150 rpm using orbital shakers (WY-100, Comecta s.a.). Samples were taken at different intervals, being the maximal at 12 h. The amounts of phenolic compounds (expressed as equivalent in gallic acid) adsorbed at 25 °C on the activated charcoal, and the adsorption yield were calculated using these equations:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{W} \tag{1}$$

$$\% Q_e = \frac{C_0 - C_e}{C_0} \cdot 100 \tag{2}$$

C_0 is defined as the initial concentration of phenolic compounds (g/L); C_e is the concentration of phenolic compounds at final time (g/L); Q_e are the phenolic compounds adsorbed in the charcoal (g/g); V is the volume of solution, while W is the weight of charcoal adsorbent used in each trial (g).

Samples of raw hydrolyzates and after the adsorption experiments were centrifuged, filtered and analyzed according to the analytical methods described in section 2.4. Independent experiments of adsorption were conducted in triplicate and its value was expressed as mean ± Standard Deviations (SD).

2.2.1. Isotherms of adsorption

Uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface are taken by the Langmuir isotherm model. The Equation for the Langmuir model has the following form [18]:

$$Q_e = Q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

Where Q_{max} is the maximum monolayer adsorption capacity (g/g) and the Langmuir coefficient K_L is a direct measure of the intensity of the adsorption process (L/g).

On the other hand, the Freundlich equation is exponential and assumes that as the adsorbate concentration increases, there is a corresponding increase in the concentration of adsorbate on the adsorbent surface [19]. Its form is the following:

$$Q_e = K_F C_e^{1/n} \tag{3}$$

Where

$$K_F = \frac{Q_{max}}{C_0^{\frac{1}{n}}} \tag{4}$$

K_F is a constant that indicates the adsorbent's relative adsorption capacity ($g^{1-(1/n)} \cdot L^{1/n} \cdot g^{-1}$); n is a constant that indicates the adsorption's intensity; and Q_{max} is the Freundlich maximum adsorption capacity ($g \cdot g^{-1}$).

2.2.2. Kinetic study

Lagergren's pseudo first order (Eq. 5) and a pseudo second order (Eq.6) were studied to determine the underlying mechanism of the adsorption process [12]:

$$\log(Q_e - Q_t) = \log Q_e - k_1 \cdot t \tag{5}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{6}$$

where, k_1 is the pseudo first-order rate constant of adsorption (h^{-1}), k_2 the pseudo second-order rate constants of adsorption (g/g·h) and Q_t is the adsorption capacity at time t (h) expressed in g/g.

2.2.3. Thermodynamics

The thermodynamic parameters enthalpy change (ΔH°), entropy change (ΔS°) and free energy change (ΔG°) thermodynamics were studied under different temperatures (30, 40, 50 and 60 °C). To calculate the equilibrium constants, the following equations were employed [20]:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{7}$$

where ΔS° is expressed in J/mol·K and ΔH° in J/mol·K. T is the absolute temperature in K and R is the universal gas constant (8.314 J/mol·K). Values for ΔS° and ΔH° were calculated using the slop and intercept of the linear plot of (lnK_D) vs. (1/T). K_D is the distribution coef

ficient of the adsorbate and can be expressed as:

$$K_D = \frac{Q_e}{C_e} \tag{8}$$

Additionally, the free energy of adsorption (ΔG) using the following equation:

$$\Delta G^0 = -RT \ln K_D \tag{9}$$

The adsorption process can be either spontaneous or non-spontaneous and thermodynamic parameters are used to indicate this. They also point to whether it is exothermic or endothermic.

2.3. Biotechnological application of hydrolyzates

The strain *Lactobacillus plantarum* CECT-221 was chosen to check if the hydrolyzates obtained are a suitable culture medium to recover biomolecules of industrial interest; meanwhile the bioindicator *Listeria monocytogenes* CECT-934 was used to evaluate the antimicrobial activity of cell-free extracts (CFE). *L. plantarum* and *L. monocytogenes* were grown in Man-Rogosa-Sharpe (MRS) and Brain Heart Infusion (BHI), respectively. Both strains were maintained in cryovials at -80 °C containing MRS or BHI broths, with 15% glycerol as cryoprotector [17]. For seed activation, one glycerol stock vial was used to inoculate 250 mL Erlenmeyer flasks containing 100 mL of MRS or BHI broths and placed into incubator shakers (Optic Ivymen System, Comecta S.A) at 30 °C and 150 rpm during 24 h for *L. plantarum* and at 35 °C and 150 rpm during 12 h for *L. monocytogenes.*

Fifty mL of two different culture media (MRS and detoxified hemicellulosic liquors supplemented with the MRS nutrients except glucose) were put in 250 mL Erlenmeyer flasks and sterilized in autoclave (Trade Raypa SL, Terrassa, and Barcelona, Spain) at 121 °C for 15 min and cooled at room temperature. *L. plantarum* pre-inoculum was added to 5% of the final culture volume and incubated at 30 °C and 150 rpm during 72 h. At certain intervals samples were taken to analyze the consumption of carbohydrates, and the production of bacteriocins and biosurfactants following the methods described in section 2.4. All the experiments were performed in triplicate.

A final experiment was carried out in a 2 L Braun Biostat bioreactor (Melsungen, Germany) under the same conditions of Erlenmeyers flasks, scaling the volume until 1800 mL of detoxified hemicellulosic sugars supplementation with the MRS nutrients (except glucose).

2.4. Analytical methods

2.4.1. Analysis of organic acids, carbohydrates and phenolic compounds

Before the analysis, samples were centrifuged at 2755 g for 15 min to remove cells or activated carbon from the hemicellulosic hydrolyzates. Then, the supernatants were filtered through 0.22 μm pore cellulose acetate membranes (Sartorious, Germany) and analyzed by High Pressure Liquid Chromatography (HPLC).

Quantification of organic acids (lactic and acetic) and sugars (glucose, xylose and arabinose) were done using an HPLC (Agilent, model 1200, Palo Alto, CA) equipped with a refractive index detector and an Aminex HPX-87H ion exclusion column (Bio Rad 300 mm × 7.8 mm, 9 m particles). Elution program was carry out during 23 min at 50 °C with a flow rate of 0.6 mL/min of 0.003 M sulfuric acid [21]. Total phenolic contents were determined by the Folin-Ciocalteu method [22] and results were expressed as equivalent in gallic acid, while furans (furfural and hydroxymethylfurfural (HMF)) were analyzed employing a reverse phase HPLC system (Agilent model 1200, Palo Alto, CA, USA) with UV-diode array detector and 4.6 × 150 mm Zorbax SB-Aq column (Agilent, Palo Alto, CA, USA). The elution program was carried out at 35 °C. Mixture of two solvents (A 2.5% formic acid aqueous solu-

tion (v/v) and B 100% methanol) composed the mobile phase at a flow rate of 1 mL/min. Five steps in elution profile were carry out: solvent A started at 100% for 35 min, then decreased to 52% during 5 min, continued using only solvent B at 16 min, returned solvent A to 100% at 4 min and finally, during 5 min the column was re-equilibrated before the next injection. UV detector at 276 nm was continuously measuring the elute [21].

2.4.2. Bacteriocin activity assay

Bacteriocins activity assays were carried out using CFE after adjustment to pH 3.0-3.5 with 5 M HCl to avoid the adsorption of bacteriocins to surface cells. Then, samples were centrifuged (3421 g for 10 min) and the pH was adjusted to 6.0-6.5 with 5 M NaOH to neutralize the effect of lactic acid. At the end, CFE was heated at 90 °C for 5 min and antibacterial activity was determined against *L. monocytogenes* by a photometric bioassay method following the protocol described by Rehaiem et al., [23].

2.4.3. Biosurfactants determination

To recover cell-bond biosurfactants, cells obtained after 72 h of fermentation were centrifuged (2755 g ×15 min) and washed twice with distilled water. Then, phosphate buffer saline at pH 7.4 was added in a 1/6 ratio (buffer solution/initial culture volume) with agitation at 150 rpm during 2 h at 30 °C. Afterwards, centrifugation was carried out to separate cells from supernatants, which contain biosurfactants. The Ring method test quantified the surface tension (ST) of supernatants at room temperature, by means of a KRÜSS Tensiometer (Hamburg, Germany) coupled with a 1.9 cm DuNoüy platinum ring [24].

3. Results and discussion

Lignocellulosic biomass is a source of compounds of interest, such as phenols, carbohydrates and proteins, among others. However, these compounds make up a complex network that makes it difficult to recover them. It is common for lignocellulosic material to be pretreated to fragment the structure and achieve higher performance in successive steps [9]. However, these pretreatments generate other streams or wastes that also need to be valorized. In a previous work [17], after the optimized acid hydrolysis two fractions were recovered, a solid fraction rich in lignin and cellulose, and a liquid fraction rich in carbohydrates from the hemicellulose. The solid fraction is where many of the scientific references are usually focused, since cellulose is a very versatile homopolymer, while the development of new techniques is allowing the valorization of lignin [25]. Therefore, this study is focus on the valorization of hemicellulosic liquors obtained after acid hydrolysis, and whose composition is as follows: 8.68 ± 0.05 g/L glucose, 15.42 ± 0.02 g/L xylose, 2.31 ± 0.03 g/L arabinose, 3.39 ± 0.18 g/L acetic acid, 0.57 ± 0.02 g/L furfural, 0.19 ± 0.00 g/L HMF and 1.99 ± 0.00 g/L phenolic compounds (expressed as equivalent in gallic acid).

3.1. Detoxification of hydrolyzates with activated charcoal

Clays, siliceous materials, zeolites, chitin, chitosan and peats are materials used as adsorbents, but only resins and activated charcoal find industrial applications [26]. However, the use of activated carbon has a handicap, the continuous accumulation of adsorbates in the surface reduces its adsorption capacity, causing a loss of its efficiency and appearing a new solid waste (spent charcoal). Usually, it is incinerated or dispose in landfills causing environmental problems [27], but currently, a wide range of techniques such as chemical, electrochemical, microbiological, wet oxidation, steam or microwave-assisted have demonstrated the possibility to regenerate spent charcoal [28]. For all this, and based on its proven efficacy by adsorbing phenolic compounds, activated carbon was selected for this study. Preliminary as-

says carried out with *Lactococcus lactis* subsp. *lactis* CECT 4434, *Lactobacillus pentosus* CECT 4023 and *Lactobacillus plantarum* CECT 221, revealed the unsuitability of raw hydrolyzates for microbial growth, therefore making necessary their detoxification [17].

There are many references to adsorption of microbial inhibitors in activated charcoal in the bibliography. For instance, removed ~95% of inhibitors from acid hydrolyzate of oat hull by treatment with 5% activated charcoal ~~[20]~~. Brito et al., [29] also removed ~91% phenolic compounds in palm press fiber hemicellulosic hydrolyzates after treatment with 5% (w/v) activated charcoal. Meanwhile, Mateo et al., [6], decreased the phenolic compounds present in olive tree pruning residue hydrolyzates by 81% using 2% charcoal. In our case, the adsorption of phenolic compounds increased gradually during the whole period evaluated, and with the percentage of charcoal added, from 48.47 ± 3.84 % with 0.25% (w/v) to 95.50 ± 0.03% with the highest concentration of charcoal (5.00 % (w/v)) at 12 h (see Table 1).

3.1.1. Adsorption isotherm study

Two commonly-utilized empirical isotherm models, Langmuir (Eq. 2) and Freundlich (Eq. 3) were assayed to evaluate the adsorption procedure of phenolic compounds on charcoal. Table 2 summarizes the isotherm parameters. Results indicated that the adsorption process fit better with Langmuir model (R^2 = 0.84) than the Freundlich model (R^2 = 0.81). Each model was obtained assuming a particular surface type: the Langmuir model ideally assumes a total homogenous adsorption surface, while the Freundlich isotherm assumes a surface that is highly heterogenous [30].

The maximum monolayer adsorption capacity (Q_{max}) at pH 6.5 and 25 °C was 0.21 g/g, similar to the values reported by Gupta et al., [12] who obtained a maximum monolayer adsorption capacity of 0.25 g/g for phenolics removal of acid hydrolyzate from corncob on charcoal at pH 7.0 and 30 °C. Lee and Park [18], from simulated hydrolyzates reported values of 0.20 g/g for 5-hydroxymethylfurfural; 0.23 g/g for furfural; 0.29 g/g for 4-hydroxybenzoic acid and 0.34 g/g for vanillic acid, meanwhile Soleimani et al., [20] achieved values between 0.08 and 0.34 g/g depending on the operational conditions of temperature and pH, during the removal of phenolics from oat hull hemicellulosic hydrolyzates.

Table 1
Percentage of phenolic compounds removed by adsorption on different activated charcoal charges at 25 °C

| Time (h)	0.25%	0.50%	1.00%	1.75%	2.50%
0	0.00	0.00	0.00	0.00	0.00
2	33.22 ± 1.93	37.77 ± 0.65	52.06 ± 0.03	59.56 ± 0.72	73.72 ±
4	33.93 ± 1.98	38.35 ± 1.38	53.66 ± 0.43	59.74 ± 0.93	75.05 ±
6	38.13 ± 0.58	44.19 ± 0.01	60.19 ± 1.65	63.06 ± 2.66	76.56 ±
8	42.81 ± 3.48	46.65 ± 0.34	62.16 ± 0.68	64.00 ± 2.56	77.97 ±
10	43.35 ± 3.60	52.14 ± 2.22	67.49 ± 3.97	69.99 ± 2.10	81.38 ±
12	48.47 ± 3.84	55.90 ± 0.29	69.10 ± 3.90	71.99 ± 1.42	82.91 ±

Table 2
Isotherm parameters at 25°C of phenolic compounds adsorption on activated charcoal.

Langmuir model			Freundlich model		
Q_m (g·g^{-1})	K_L (L/g)	R^2	K_F (g$^{1-(1/n)}$ L$^{1/n}$ g^{-1})	n	R^2
0.21	2.29	0.84	0.23	1.15	0.81

3.1.2. Kinetic study

The adsorption isotherms were plotted in Fig. 1 and classified as L type according to the classification of Giles [31] due to the nature of the curves, with an initial downward curvature as a consequence of the decreased availability of active sites. Using the highest dose of charcoal (5% w/v) the percentage of phenolic compounds adsorbed was 90.47 ± 0.36 % after only 2 h, increasing slightly afterwards, up to 95.50 ± 0.03 % after 12 h. However, under the lowest adsorbent percentage (0.25 % w/v), the maximum percentage achieved was 48.47 ± 3.84 %, the increment being gradual during the whole period evaluated (12 h). The fast-initial phase observed in all cases is explained by the high availability of adsorption sites on the adsorbent surface and, consequently, the elevated driving force for the mass transfer; meanwhile, the reduced stage is a consequence of the reduced number of available sites [12].

Table 3 shows the dynamic parameters of phenolic compounds adsorption on activated charcoal at 25 °C. The correlation coefficients resulting from the equations show that the pseudo-second-order model provides a better description of the kinetics of the adsorption of the adsorbates on charcoal. The basis for this is the supposition that the rate-limiting step could be chemical sorption or chemisorption entailing valency forces through sharing or exchange of electrons between sorbent and sorbate [32]. This finding agrees with previous research works in different areas. For instance, using the pseudo-second-order model [12] gave a better explanation of the adsorption of fermentation inhibitors that were produced as the acid hydrolysis of corncob took place in activated charcoal, while Mahardika et al., [33], using wastewater effluents, also explained the adsorptive removal of phosphorus in granular activated carbons impregnated with amorphous ferrihydrite.
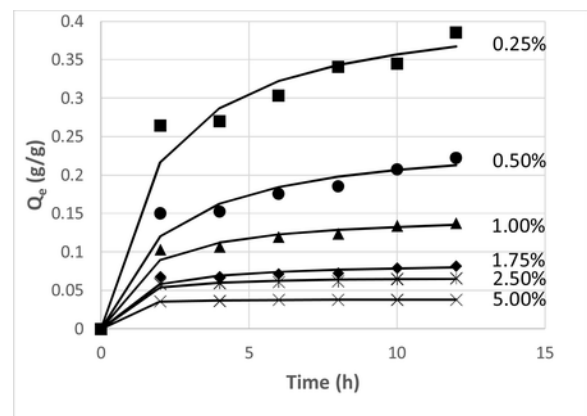
Fig. 1. Kinetic curves of adsorption for phenolic compounds from the acid hydrolyzate of chestnut (*Castanea sativa*) burrs at 25 °C.

Table 3
Dynamic parameters of phenolic compounds adsorption on activated charcoal at 25 °C.

Charcoal (%, w/v)	Pseudo First Order kinetics			Pseudo Second Order kinetics		
	k_1 (h^{-1})	Q_e (g/g)	R^2	k_2 (g·h^{-1})	Q_e (g/g)	R^2
0.25%	0.09	0.60	0.90	0.95	0.47	0.97
0.50%	0.08	0.44	0.88	2.14	0.24	0.97
1.00%	0.14	0.34	0.94	7.56	0.14	1.00
1.75%	0.14	0.28	0.86	11.86	0.09	0.99
2.50%	0.13	0.22	0.80	27.50	0.07	1.00
5.00%	0.23	0.16	0.89	146.10	0.04	1.00

3.1.3. Thermodynamics

To more clearly explain the features of phenolic compounds adsorption in charcoal, the thermodynamic parameters enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) were calculated and the results listed in Table 4.

Enthalpies values obtained ranged between -2.79 and -20.25 KJ/mol. Negative values indicate that the adsorption of phenolic compounds in charcoal is exothermic and a certain quantity of heat is evolved as the metal ion binds on the surface of adsorbent [34]. Similar negative enthalpies have been observed during the adsorption of microbial inhibitors brought about by the acid-catalyzed hydrolysis of oat hull in activated carbon [20]; the removal of phenol in date seed carbon [35]; and the adsorption of fermentation inhibitors generated during the acid hydrolysis of corncob in activated charcoal [12]. Negative enthalpies were also obtained when phenol was removed from wastewater by employing other absorbents based on sawdust [36] or date seed carbon [35]. Moreover, a physisorption process can be pointed out as the responsible mechanism in this study, since physisorption processes have adsorption energies <40 KJ/mol [34]. This process is a physical adsorption where intermolecular forces, such as Van der Waals, play their part without meaningful changes in the electronic orbital patterns of the species. Since the energy of interaction between the adsorbate and adsorbent has the same order of magnitude, no activation energy is required, and consequently low temperatures favor the adsorption process [20]. This is corroborated with our experimental values since the percent of adsorption decreased with increasing temperatures (Table 5), for instance, from 52.36 ± 0.00% at 30 °C to 32.49 ± 0.05 % at 60 °C using 0.25 % (w/v) charcoal, indicating that the process is exothermic. The decrease in adsorption with higher temperatures can be partly related to the weakening of the attractive force between phenolic compounds and charcoal, and partly as a consequence of the enhancement of thermal energies of the adsorbate; therefore, making the links between phenolic and charcoal too insufficient to hold the adsorbed molecules [35,36].

Additionally, free energy was positive in all cases, indicating the non-spontaneity of the adsorption process. This parameter increased from 2.07 KJ/mol al 30 °C to 4.56 KJ/mol at 60 °C with the lowest amount of adsorbent (0.25% w/v of charcoal), and from 2.34 KJ/mol at 30 °C to 4.13 KJ/mol at 60 °C using the highest value (5%w/v of charcoal). This fact also reinforced the idea of the negative effect that the temperature showed over the efficiency of adsorption.

Furthermore, entropies ranged between -21.04 and -73.04 J/mol·K, indicating the affinity of phenolic compounds for the adsorbent employed in this work, which led to diminishing disorder in the system [20]. These authors also obtained similar values with ΔG° between 1.78 and 5.45 KJ/mol and ΔS° between -34.83 and -100.18 J/mol·K, during the adsorption of phenol on activated carbon.

3.2. Biotechnological application of hydrolyzates

Considering the non-fermentability of *Lactobacillus plantarum* CECT 221 in raw hydrolyzates [17] and the extensive use of this microorganism in the industry together with other lactic acid bacteria like L. *lactis* or L. *casei* [37], detoxification processes for subsequent fermentations by *L. plantarum* were chosen. Although mechanisms of inhibition of phenolic compounds have not been certainty elucidated, interactions of these compounds with proteins of cell membrane could cause losses in K^+, glutamic acid, intracellular RNA or alteration in the composition of fatty acids [38]. Furthermore, weak acids, can produce intracellular acidification, energy drainage and accumulation of reactive oxygen species that affect to cell growth; and furans (furfural and HMF) can affect to enzymes related to central carbon metabolism, amino acid biosynthesis or cell organelles [9]. In a prior adsorption study, phenolic compounds concentrations in hemicellulosic hydrolyzates with charcoal loads of 1.75%, 2.5% and 5% w/v after 12 h were as follow: 0.56 g/L, 0.34 g/L and 0.09 g/L (expressed as equivalent in gallic acid). García-Ruiz et al., [38] observed that lactic acid bacteria present tolerance to phenolic compounds at concentrations between 0.15 g/L and 0.25 g/L, while values around 0.50 g/L showed toxic effects. Therefore, a maximum charcoal concentration (5% w/v) was chosen to carry out the detoxification before the fermentations due to the minimal concentration of phenolic compounds (0.09 g/L) founded, despite the loss in carbohydrates content. The use of charcoal 5% w/v meant a reduction in fermentable sugars, being xylose the most affected, with a 33% reduction in this work. Other authors also reported important losses of xylose when corn cob acid hydrolyzate was detoxified with activated charcoal [39]. For that reason, more research would be necessary to minimize these losses.

After detoxification, the hemicellulosic hydrolyzate from chestnut burrs containing 5.69 ± 0.16 g/L glucose, 9.47 ± 0.13 g/L xylose, 2.48 ± 0.03 g/L arabinose, 6.36 ± 0.12 g/L acetic acid and 0.09 ± 0.00 g/L phenolic compounds, was assayed as culture medium to produce biomolecules. Biorefineries pretend to integrate recycling biomass or wastes for sustainable production of high-valued bio-products throughout different technologies [40].

3.2.1. Lactic acid production

LAB are able to produce lactic acid, which has several applications in different market niches: food industry like additive, acidulant or inhibitor of sporulation of bacteria in fermented foods; pharmaceutical in cosmetics, anti-acne solutions or humectants and chemical to produce solvents and food packaging and many plastic utensils from (poly)lactic acid (PLA) [41]. It has been demonstrated that lactic acid production by fermentative route has numerous advantages compared to chemical synthesis: the use of economical substrates, relatively lower temperatures, lower energy consumption, more environmentally friendly [42], high purity and versatility of creating products with personalized features [14]. Lignocellulosic wastes not widely used yet in industrial production of lactic acid but these materials are expected to be postu

Table 4
Thermodynamic parameters of adsorption of phenolic compounds on activated charcoal.

Charcoal (%, w/v)	ΔH° (KJ/mol)	ΔS° (J/mol·K)	$\Delta G^\circ_{30°C}$ (KJ/mol)	$\Delta G^\circ_{40°C}$ (KJ/mol)	$\Delta G^\circ_{50°C}$ (KJ/mol)	$\Delta G^\circ_{60°C}$ (KJ/mol)
0.25%	-20.25	-73.04	2.07	2.67	2.65	4.56
0.50%	-2.79	-21.14	3.42	4.35	3.64	4.35
1.00%	-6.40	-35.76	4.22	5.19	5.08	5.42
1.75%	-3.30	-26.30	4.65	4.93	5.33	5.38
2.50%	-11.17	-50.04	3.98	4.40	5.27	5.35
5.00%	-14.32	-55.54	2.34	3.41	3.54	4.13

ΔH° = enthalpy; ΔS° = entropy; ΔG° = free energy.

Table 5
Percentage of phenolic compounds removed by adsorption on different activated charcoal charges at different temperatures.

	30 °C	40 °C	50 °C	60 °C
0.25%	52.36 ± 0.00	47.30 ± 0.00	48.20 ± 0.05	32.49 ± 0.05
0.50%	56.29 ± 0.06	48.49 ± 0.06	56.33 ± 0.03	50.99 ± 0.03
1%	65.23 ± 0.00	57.63 ± 0.00	60.17 ± 0.00	58.55 ± 0.03
1.75%	73.45 ± 0.00	72.51 ± 0.02	70.66 ± 0.00	71.48 ± 0.00
2.50%	83.73 ± 0.02	82.18 ± 0.02	77.85 ± 0.02	78.39 ± 0.02
5%	95.18 ± 0.00	93.11 ± 0.00	93.06 ± 0.00	91.84 ± 0.01

lated as a low-cost renewable carbon sources and their reuse is interesting to comply with legislation and environmental issues [14]. Therefore, the use of hemicellulose hydrolyzate from chestnut burrs as a fermentative base for lactic acid production, could be a key factor for relatively reducing costs and become more competitive this biorefinery process.

Fig. 2a depicts the kinetics of fermentation performed in 250 mL Erlenmeyer flasks. Around 3 g/L of glucose and 2.5 g/L of xylose were consumed at 24 h, meanwhile lactic acid production reached 7.58 ± 0.67 g/L, which means a global volumetric productivity of 0.32 ± 0.03 g/L·h. Thereafter, sugars and lactic acid remained constant during 72 h. Afterwards, the same operational procedure was conducted in a higher-capacity system: a 2 L bioreactor (Fig. 2b). It can be seen that lactic acid concentration went up to 11.20 ± 0.22 g/L after 24 h and consequently the global volumetric productivity was 0.47 ± 0.01 g/L·h. However, these levels of lactic acid were smaller to those achieved with MRS broth (Fig. 2c) where 14.94 ± 0.46 g/L lactic acid were produced in the same period of time (24 h), increasing the productivity to 0.61 ± 0.02 g/L·h. Likely causes of this are the higher initial amount of glucose (17.20 ± 0.12 g/L) as the unique sugar, and the absence of fermentation inhibitors that allow glucose to be rapidly and efficiently consumed after 72 h.

3.2.2. Bacteriocin production

Bacteriocins are peptides, ribosomally synthesized, with antimicrobial activity against bacteria that are closely related [43]. L. monocytogenes is a human pathogenic strain that causes listeriosis, one of the most important foodborne infections, due to its great adaptive capacity to several environments and temperatures [44,45]. Beside lactic acid, L. plantarum is a strain characterized by produce one type of bacteriocin, called plantaricin [46], and as seen in Table 6 with antimicrobial activity against Listeria monocytogenes CECT-934. The inhibitory dose of 50% (ID_{50}) calculated for CFS after 48 h fermentation using the commercial culture medium MRS was 5.62. This value increased up to 6.13 and 6.65 when fermentations were performed with hemicellulosic hydrolyzates in Erlenmeyer flasks or 2 L bioreactors, respectively. The higher production of bacteriocins observed using the hemicellulosic hydrolyzates could be ascribed to stress factors. This is particularly more evident in the fermentation conducted in the bioreactor, where the shear stress due to the stirring is higher. Indeed, De Vuyst et al. [47] reported that bacteriocin production can be stimulated by manipulation of the cell environment, known as stress factors. Thus, the Lactobacillus amylovorus DCE 471 produces specific bacteriocin: amylovorin L471. Their generation was improved under unfavorable growth conditions which included low temperatures (30 °C) and the presence of ethanol (1.0 %, v/v) and oxygen (80%, v/v, air saturation), potentially toxic substances. There is also a possibility that bacteriocin expression are related to different concentrations of sucrose, lactose, glucose or other carbon sources [48]. For instance, they observed that L. lactis induced 50.0% higher bacteriocin expression reducing sucrose concentration from 12.5% to 0.14%. Vera et al. [15] observed that the highest concentration of sucrose assayed (2.0%) decreased the antimicrobial activity of L. lactis CECT-4434 regarding the lowest concentration (1.0%), concluding that the concentration of the carbon source, at
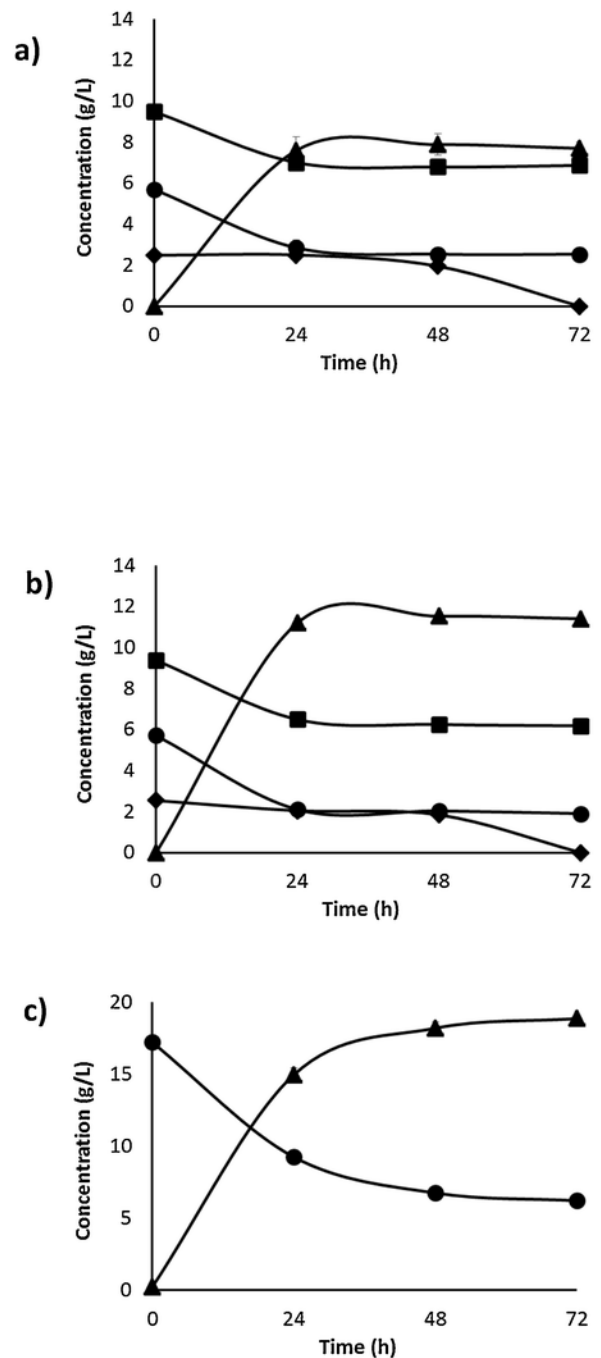
Fig. 2. Course with time for sugars consumption and lactic and acetic acids production by *L. plantarum* grown in hemicellulosic hydrolyzates detoxified with 5% (w/v) charcoal supplemented with the nutrients of MRS except glucose in experiments carried out using a) 250 mL Erlenmeyer flasks or b) 2 L Bioreactor. c) *L. plantarum* grown in MRS broth using Erlenmeyer flasks. Glucose (●); xylose (□); arabinose (♦) and lactic acid (▲). Standard deviations were calculated with values of triplicate experiments and they were included in graphics.

a limiting level, may have played a part in the synthesis inhibitory substances similar to bacteriocin, likely due to the microorganism being exposed to a hostile or competitive environment. It must also be considered that antimicrobial activity must be mostly attributed to bacteriocins and not to the lactic acid produced, since hydrolyzates produced half amount of lactic acid in comparison to MRS broth.

Despite nisin continues being the most widely used bacteriocin and recognized as food additive for international organizations such as the World Health Organization (WHO)/Food Development Author-

Table 6

Lactic acid, bacteriocins and biosurfactants production under different fermentation conditions.

| | Time (h) | Hemicellulosic Hydrolyzate | | MRS |
		Erlenmeyer flasks	Bioreactor	Erlenmeyer flasks
Lactic Acid (g/L)	24	7.58 ± 0.67	11.20 ± 0.22	14.94 ± 0.46
Q_P (g/L·h)	24	0.32 ± 0.03	0.47 ± 0.01	0.61 ± 0.02
ID_{50}	24	5.68	4.67	4.65
ID_{50}	48	6.13	6.65	5.62
ID_{50}	72	5.94	6.34	4.66
$ST_{reduction}$	72	12.17 ± 0.29	11.17 ± 2.00	15.92 ± 0.48

Q_P: global volumetric productivity; ID_{50}: inhibitory dose of 50%; $ST_{reduction}$: surface tension reduction

ity (FDA) and the European Food Safety Authority (ESFA) [16], other bacteriocins, such as pediocins and Micocin®, are currently commercialized in Canada and USA [49]. These new additions could be the access to new commercialized products. The search for culture media to cut the prize of production could incentive more researches in the identification, purification and applications. For instance, the use of bacteriocins was tested alone or combined with other technologies such as pulsed electric field or other antimicrobial compounds (sodium acetate or sodium lactate) which improves biopreservation [37]. Besides, bacteriocins could be employed to produce bioactive food contact surfaces (such as stainless steel and rubber) to prevent undesired bacterial attachment (biofilms), and bioactive packaging materials (such as cellophane, polyethylene terephthalate (PET) and paper) to control the growth of spoilage bacteria and food-borne pathogens in foods and extend their shelf life [50,51]. Moreover, organoleptic properties of food can be improved through the use of bacteriocins [52].

3.2.3. Biosurfactant production

Biosurfactants are molecules generated by microorganisms able to reduce surface and interfacial tension of solutions and form emulsions because of their amphiphilic character [53]. Biosurfactants appear to have a promising future when using low-cost raw materials and optimized growth conditions to increase their production [54].

The presence of cell-bond biosurfactants was also observed (see Table 6) in the culture media, although the surface tension reduction ($ST_{reduction}$) decreased slightly from 15.92 ± 0.48 units using MRS, to 12.17 ± 0.29 units and 11.17 ± 2.00 units using the cheaper culture broth (hemicellulosic hydrolyzates) in Erlenmeyer flasks and 2 L bioreactors, respectively. However, it must be taken into account that the production of biomolecules (bacteriocins and biosurfactants) was not optimized, and only the ability to produce these substances was assessed. The production of biosurfactants depends on bacterial demands because there are complex regulatory mechanisms surrounding their biosynthesis; they are costly when their low yields are considered; and expensive substrates are needed to induce production [55].

4. Conclusions

Acid-hydrolysis of chestnut burrs releases some phenolic compounds that make unsuitable the culture broth formulated with crude hydrolyzates. Charcoal is an adsorbent capable of removing these compounds, and the efficiency of this adsorption increases with the increment in the amount of charcoal assayed. The adsorption equilibrium data of phenolic compounds on charcoal can be better fitted by Langmuir isotherm equation with a regression constant of 0.84 and the Langmuir pseudo-second-order model can better describe the kinetics of the adsorption of adsorbates. Thermodynamic parameters show neg

ative enthalpies and entropies and positive free energies, indicating an exothermic and non-spontaneous adsorption process. Under non-optimized conditions, detoxified acid-hydrolyzates from chestnut burrs were used by *L. plantarum* as economical culture media, to produce bacteriocins with antimicrobial activity against *Listeria monocytogenes* and cell-bond biosurfactants, in similar amounts to using commercial media. Besides, the benefits of using hemicellulosic hydrolyzates from chestnut burrs as culture media would increase simultaneously the production of lactic acid with no modification of the process which would undoubtedly be a more beneficial and commercially sustainable route for a larger scale biorefinery.

5. Declaration of Competing Interest

CRediT authorship contribution statement

Iván Costa-Trigo: Investigation, Visualization. **Patricia Otero-Penedo:** Investigation. **David Outeiriño:** Investigation. **Alicia Paz:** Methodology. **Ricardo Pinheiro de Souza Oliveira:** Writing - original draft. **José Manuel Domínguez:** Resources, Project administration, Writing - review & editing.

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