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Organic fraction of municipal solid waste for the production of L-lactic acid with high optical purity

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ABSTRACT

The organic fraction of municipal solid waste (OFMSW) is an abundant biowaste with great potential in the bioeconomy model. Previous reports have demonstrated that OFMSW hydrolysates are good substrates for lactic acid (LA) production. However, LA can exist in two enantiomeric forms (L- and D-) and most commercial LA applications require a high enantiomeric purity, typically of the L-isomer. Due to natural occurring bacteria in the waste, a mixture of D- and L-LA can form in the substrate, reducing the final enantiomeric purity of the product and limiting its commercial application. In the research reported in this article, hydrolysates from OFMSW were evaluated for the production L-LA with high enantiomeric purity. Firstly, a pre-treatment with monopolar electrodialysis membranes was implemented to remove the unfavourable D-LA in the hydrolysate. This step allowed the reduction in LA concentration and subsequent fermentations of the hydrolysate resulted in enantiomeric purities over 98%. At the pilot scale, a fermentation of the pre-treated hydrolysate, by *B. coagulans* A166, resulted in a final LA concentration of 61.1 g L^{-1} and a yield of 0.94 g g^{-1}. The downstream of the process resulted on a LA recovery of 51.5% and a L-LA optical purity of 98.7%.

1. Introduction

The term 'organic fraction of municipal solid waste' (OFMSW) describes the heterogeneous organic wastes derived from urban areas (Abudi et al., 2016). Although their composition can vary, in general, these biowastes contain high levels of carbohydrates, proteins and lipids, making them an interesting substrate for biotechnological applications (Pleissner and Lin, 2013; Uçkun Kiran et al., 2014). Therefore, instead of being incinerated, composted or used in biogas production (Burnley et al., 2011; Grosso et al., 2010), the residues have been utilised, solely or in combination to other waste streams and/or nutrients, for hydrogen, ethanol, butanol amongst other bio-based products (Abudi et al., 2016; Kannengiesser et al., 2018; Matsakas et al., 2017).

In our previous work, we explored the production of lactic acid (LA) from OFMSW (López-Gómez et al., 2019). LA is an important building block, with a wide range of applications (Alves de Oliveira et al., 2018), that can exist in the L- and D-enantiomeric forms. However, a high enantiomeric purity is crucial when LA is intended to be used for high-value applications, such as in the production of the biopolymer polylactic acid (PLA), which typically requires purities over 98% (Alves de Oliveira et al., 2018; Jem et al., 2010; Klotz et al., 2016). Furthermore, since D-LA can cause metabolic problems its utilization is restricted in the food, pharmaceutical and agrochemical industries. Unlike in its chemical synthesis, which yields a racemic mixture of the D- and L-enantiomers, various microorganisms possess homofermentative pathways that synthesize only one isomer and thus, biochemical production of LA is widely preferred (Alves de Oliveira et al., 2018).

The need for a cost-efficient and more sustainable production of L-LA with high enantiomeric purity has pushed research towards the utilization of inexpensive renewable resources. Many studies have already shown that L-LA with high optical purity can be produced from various waste and by-product streams like coffee pulp and mucilage (Neu et al., 2016; Pleissner et al., 2016), food waste streams (Demichelis et al., 2017; Pleissner et al., 2017a), defatted rice bran (Alexandri et al., 2018) and sugarcane bagasse hemicellulosic hydrolysate (Alves de Oliveira et al., 2019a,b), using

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Abbreviations

D-LA	dextro-lactic acid
H1	coarse filtrated hydrolysate
H2	microfiltrated hydrolysate
H3	hydrolysate after electrodialysis
HMF	hydroxymethylfurfural
LA	lactic acid
L-LA	levo-lactic acid
N_{Total}	total nitrogen
OFMSW	organic fraction of municipal solid waste
P	productivity
P_{exp}	productivity during the exponential phase
PLA	polylactic acid
P_{max}	maximum productivity
P_{Total}	total phosphorus

Bacillus coagulans. *B. coagulans* strains present many advantages over other LA producing bacteria, due to their ability to grow at high temperatures (optimum 52 °C), on different carbon sources while having low nutrient requirements. To this end, fermentation of OFMSW using *B. coagulans* for high optical purity L-LA would be a promising alternative for the sustainable exploitation of this waste stream.

Although studies available in the literature regarding the conversion of OFMSW into LA are scanty, they have shown that OFMSW contain a mixture of mainly LA producing bacteria able to proliferate and produce LA (Probst et al., 2013). Nonetheless, being a mixed culture, the production of LA is prone to low yields and racemic mixtures of D- and L-LA (Demichelis et al., 2017). As explained by Probst et al. (2015), although there is a good potential for the production of LA, the purification and synthesis of products with high optical purity still needs to be addressed. This was confirmed by López-Gómez et al. (2019) who determined that depending on the collection system of OFMSW, hydrolysates contained a racemic mixture of D- and L-LA in concentrations from 5 to 20 g L^{-1} approximately. As a result the maximum LA optical purity achieved was only 93% which would hinder its use for some specific applications. Therefore, the research reported in this article aimed to explore the possibility of utilising OFMSW for the fermentation of LA with high enantiomeric purity and, additionally, to carry out the required steps for its purification. After its chemical characterisation, OFMSW hydrolysate samples were pre-treated for the removal of LA produced by natural occurring bacteria. Following that, the hydrolysates were used in lab scale experiments and a screening was carried out for the selection of the most appropriate microorganism. Results obtained at the lab scale were used as the basis to conduct fermentations at the pilot scale to provide further insights on the performance of the fermentation. Following that, a downstream process based on electrodialysis was carried out for the purification of LA.

2. Materials and methods

2.1. Substrate: OFMSW hydrolysates

OFMSW hydrolysates were kindly provided by IMECAL SA company (L'Alcúdia, Valencia, Spain). Based on previous reported results (López-Gómez et al., 2019), the hydrolysates used in this study were produced with batches of separately collected OFMWS from a municipal solid waste treatment plant in Valencia, Spain. Before the hydrolysis, the samples were screened to manually remove inert materials such as glass, plastics, stones, textiles, etc. Following that, a pilot hammer mill was used for homogenisation and finally the wastes were sterilized at 121 °C for 1 h in an autoclave. The solids load for the enzymatic hydrolysis was 20% and it was carried out for 72 h at 50 °C, 150 rpm. The pH was controlled at 5 by the addition of NaOH (20% w w^{-1}). The cocktail of enzymes, provided by Novozymes, is based on a mixture of cellulases and amylases and was developed particularly for OFMSW substrates. Samples were taken during the hydrolysis to quantify the liberation of sugars and the production of growth inhibitors. A total of 13 hydrolysate batches were prepared and High Pressure Liquid Chromatography (HPLC) (Coregel 87H3 7.8 mm × 300 mm column) was used for the quantification of sugars and organic acids.

2.2. Microorganisms and inoculum

All the strains used in this study were gram-positive, thermophilic and homofermentative L-LA producing bacteria, obtained from the strain bank of the Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB) in Potsdam, Germany. MALDI-TOF was used for the identification of the strains. Pre-cultures were carried out in MRS broth (Merck, Germany) supplemented with dolomite EVERZIT Dol 0.5–2.5 mm (Evers, Germany) as a buffer. Flasks containing the seed culture were placed in an orbital shaker at 150 rpm and 52 °C for 12–16 h.

2.3. Hydrolysate purification

A series of purification steps were implemented to removed the LA (racemic mixture of D- and L-) from the hydrolysate. In the first step i.e. coarse filtration, a filter bag with a pore size of 150 μm was used for the removal of larger solid particles. Following that a microfiltration was carried out with a cross-flow micro-filtration system (UFI-TEC, Germany), pore size 0.2 μm, at 1.5 bar and 15 °C, equipped with 4 TAMI membranes (TAMI Industries, France). Finally, LA was removed by monopolar electrodialysis, at 35 °C, 20 V and 3 A, using 11 cation exchange membranes and 10 anion exchange membranes Type IV (Fujifilm, The Netherlands).

2.4. Fermentations

2.4.1. Evaluation of the effects of the purification steps

Experiments in small scale bioreactors were performed to evaluate how the purification steps impact the fermentation potential of the OFMSW hydrolysate. Thus, 3 sets of fermentations were carried out, one with the coarse filtrated hydrolysate (H1), one with the microfiltrated hydrolysate (H2) and one with the hydrolysate after electrodialysis (H3). Fermentations were carried out, in duplicate, with 250 mL working volume, at 52 °C and 400 rpm, using an Eloferm multifermentation system (Biotronix GmbH, Germany). The pH was controlled at 6.0 with a solution of NaOH 20% (w v^{-1}). The bioreactors were inoculated with *B. coagulans* A166 (3% v v^{-1}) and samples were withdrawn every few hours (in most cases after 2 h intervals) for the quantification of sugars and LA.

2.4.2. Evaluation of various strains for the production of L-LA with high optical purity

A total of 13 strains were evaluated for the production of LA with high optical purity using the OFMSW hydrolysate after electrodialysis. Experiments were carried out under the same conditions as described in section 2.4.1. After the selection of the strain, an experiment was carried out to compare its performance when yeast extract (5 g L^{-1}) was added to the hydrolysate after electrodialysis.

2.4.3. Fermentations in 1 L bioreactor and pilot scale bioreactor

The OFMSW hydrolysate after electrodialysis, supplemented with yeast extract (5 g L^{-1}), was used for lab scale fermentation (1 L working volume) and pilot scale fermentation (23 L working volume) with the strain A166. The lab scale fermentation was carried out in a 2 L BIOSTAT bioreactor (Sartorius AG, Germany) whereas the pilot scale fermentation was carried out in a 72 L BIOSTAT UD bioreactor (B-Braun Biotech, Germany). Inoculum for the fermentation in pilot scale was prepared in a 1 L BIOSTAT bioreactor (Sartorius AG, Germany) with 700 mL working volume of the same hydrolysate medium. The fermentations were carried out at 52 °C, with constant agitation of 200 rpm and a pH of 6.0 regulated by the addition of NaOH 20% (w v^{-1}). Samples were withdrawn from the fermenters at various times, inactivated at 95 °C for 20 min and stored at −20 °C until the quantification of sugars and LA was performed.

2.5. Downstream and purification

Fig. 1 shows the flow diagram of the process. The units (*b*),(*c*),and (*d*) correspond to the pre-treatment of the hydrolysate carried out as described in section 2.3. After fermentation (*e*) the broth was inactivated and afterwards microfiltrated (*f*) as described in section 2.3 but at 5 °C. Following that, a nanofiltration step (*g*) was performed (150–300 Da cut-off) at 30 bar with an UFI-TEC crossflow nanofiltration system (UFI-TEC, Germany). Calcium and magnesium ions were then removed in a column (*h*) packed with a PUROLITE S950 acid chelating resin (Purolite, Germany). After softening, the electrodialysis was carried out in 2 steps using 11 cation and 10 anion exchange membranes Type II (Fujifilm, The Netherlands). The monopolar step (*i*) was finished when the conductivity of the filtrate was below 1 mS cm^2, whereas the bipolar step (*j*) was stopped when the conductivity of the filtrate was below 2 mS cm^2. The acid stream obtained was then decolorized (*k*) using an adsorbent resin MACRONET™ MN-502 (Purolite, Germany). Following that cation (*l*) and anion (*m*) exchange chromatography were performed using resins RELITE EXA 133 and RELITE EXC 08 (Resindion S. R. L., Italy), respectively. Finally, vacuum distillation (*n*) was used to concentrate the product at 55 °C, −1 bar and 350 rpm (Büchi Labortechnik, Germany). A detailed description of the downstream process can be found in Neu et al. (2016).

2.6. Analytical assays

A detailed description of the methods for the quantification of sugars, LA, ions, total nitrogen, total biomass and total cells can be found in Neu et al. (2016). Analytical essays for the quantification of sugars and LA concentration and LA enantiomeric purity were carried out as detailed by Alexandri et al. (2018).

During the hydrolysis, high Pressure Liquid Chromatography (HPLC) (Coregel 87H3 7.8 mm × 300 mm column, Chrom Tech, USA) was implemented to measure the release of sugars and the formation of furfural and 5-HMF. During the fermentations, quantification of sugars and LA was carried out via HPLC (Dionex, USA) and a Eurokat H column (300 mm × 8 mm x 10 μm, Knauer, Germany). An aqueous solution of 5 mM H_2SO_4 was the mobile phase at a flow rate of 0.8 mL min^{-1}. The detection of the components was achieved using a refractive index detector (RI-71, Shodex, Japan). Likewise, optical purity of the samples was performed using HPLC (Dionex, USA) with a Phenomenex Chirex 3126 column (150 × 4.6 mm ID, Phenomenex, USA) at 30 °C coupled to an ultraviolet detector. In this case, Cu_2SO_4 flowing at 1 mL min^{-1} was the mobile phase.

The total number of cells was determined with a THOMA cell chamber (Glaswarenfabrik Karl Hecht GmbH & Co KG, Germany) whereas the number of colony forming units was used to determine the number of living cells as described in Alexandri et al. (2018).

3. Results and discussion

3.1. Composition of the hydrolysate

An initial characterisation of the substrate was fundamental to determine the amount of sugars available and the total concentration of LA. Results for the analysis of the 13 batches of OFMSW hydrolysate have been reported in López-Gómez et al. (2019). On average, hydrolysates showed a sugar content above 70 g L^{-1}. Glucose was the predominant sugar with an average value of 55.41 ± 2.01 g L^{-1}, followed by xylose with 10.13 ± 1.2 g L^{-1}. As indicated by Nwobi et al. (2014), the mild conditions of enzymatic pre-treatments avoid the formation of inhibitory compounds which are typically produced in harsh thermochemical pre-treatments. This was confirmed by the samples analysed in this study which did not show the presence of inhibitory compounds such as furfural and 5-HMF.

Nonetheless, LA was detected in every sample with an average concentration of 5.69 ± 0.88 g L^{-1}. The presence of LA is the result of a variety of naturally occurring bacteria, mostly *Lactobacillus* spp., in the OFMSW (Probst et al., 2013). Analysis of the LA enantiomeric

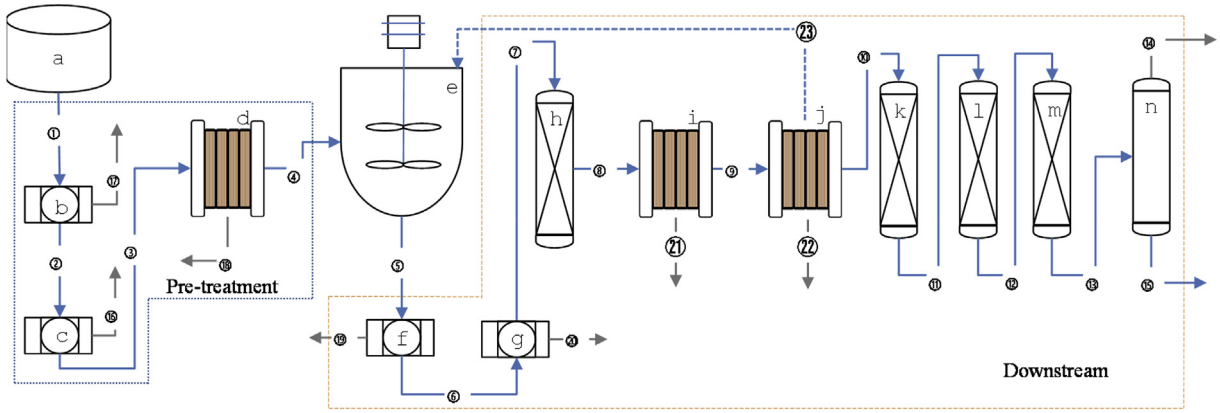

Fig. 1. Process flow diagram of the production of LA with high enantiomeric purity from OMSW hydrolysate. (a) hydrolysate tank, (b) coarse filtration, (c) microfiltration, (d) monopolar electrodialysis, (e) fermentation, (f) microfiltration, (g) nanofiltration, (h) softening column, (i) monopolar electrodialysis, (j) bipolar electrodialysis, (k) decolourisation column, (l) anion exchange column, (m) cation exchange column, (n) distillation.

purity revealed a racemic mixture of D- and L-LA (50:50). Thus, an average sample of OFMSW hydrolysate would contain approximately 2.55 g L^{-1} of D-LA which represents a problem if a product with high optical purity is required. The vast majority of industrially produced PLA is obtained from L-LA with optical purities above 98% (Jem et al., 2010; Kunasundari et al., 2013). Considering an OFMSW hydrolysate sample, initially containing 70 g L^{-1} of sugars, fermented by a homofermentative LA producer, even with a 100% sugar conversion and a yield of 1 g g^{-1}, a maximum final LA concentration of 75.11 g L^{-1} would be achieved. From that, 2.55 g L^{-1} correspond to the D-LA initially present in the sample and to a final enantiomeric purity of around 97%. Hence, even in a scenario with optimal conversions the optical purity of the product would be below the desired threshold for the production of PLA with high optical purity (Inkinen et al., 2011; Jem et al., 2010).

3.2. Hydrolysate purification

The separation of LA enantiomers has been a topic of research for some time (Boonpan et al., 2013; Huang et al., 2018), however, an economically feasible method to achieve it is still unavailable. Therefore, in this study, a series of purification steps were carried out to remove the total LA initially present in the OFMSW hydrolysate. The separation was carried out in three main steps: coarse filtration, microfiltration and electrodialysis. Table 1 shows the average composition (from 2 batches) of the hydrolysates before and after the purification steps. As seen in the table, the concentrations for the sugars remained stable after every step. LA concentration was successfully pulled down from 5.70 ± 0.01 to 0.89 ± 0.89 g L^{-1}. Naturally, there was also a reduction in the content of nutrients most noticeable after electrodialysis. The total nitrogen content went down from a concentration of 3953 ± 34 mg L^{-1} in the raw hydrolysate to a concentration of 1731 ± 04 mg L^{-1} in the hydrolysate samples after electrodialysis. Furthermore, all the other ions saw a reduction in their concentration of more than 95%. The effect in this decrease is clearly demonstrated in the fermentation profiles shown in Fig. 2.

Final LA concentrations were approximately 60, 56 and 54 g L^{-1} as shown in Fig. 2a, b and c, respectively. Although, it may appear that H3 had a lower titre, it is important to consider that the initial concentration of LA was only about 2.8 g L^{-1} compared to 7.6 and 8.5 g L^{-1} h^{-1} for H1 and H2. Glucose was completely consumed in all the experiments and final values for the residual sugars were 14.8, 11.6 and 10.9 g L^{-1} for H1, H2 and H3 respectively. Additionally, it is apparent that there was a reduction of around 4 h in the lag phase after the microfiltration step. Furthermore, there was an evident difference in the fermentation rate between H3 and the other two fermentations. While there is a clear exponential phase in the curves for H1 and H2, lasting approximately 10 h in both cases, it took H3 about 22 h (from the time the reduction in sugars was firstly noticeable) until the value of residual sugars was again stable. Congruently, the value for maximum productivity (P_{max}) was only 4.40 ± 0.00 g L^{-1} h^{-1} for H3 compared to 5.67 ± 0.32 and 7.89 ± 0.02 g L^{-1} h^{-1} for H1 and H2 respectively. Values for global productivities (P) were calculated from the inoculation time until the beginning of the stationary phase. P values were 2.95, 2.98 and 2.09 g L^{-1} h^{-1} and yields 0.91, 0.97 and 0.89 g g^{-1} for H1, H2 and H3, respectively. It is reasonable to assume that the reduction in the concentrations of nitrogen and other nutrients, resulting from the electrodialysis step, was responsible for the slowdown in H3. Nonetheless, the experiments proved that the hydrolysate was able to support the growth of bacteria even without the addition of any extra nutrients. As expected, the final LA enantiomeric purity was only 92.75 and 92.50% for the fermentations with H1 and H2. On the other hand, the pre-treatment carried out to produce H3 allowed achieving a final L-LA of 98.25% after the fermentation.

3.3. Screening of the hydrolysate with various L-LA bacteria

A screening of various isolates was carried out using the hydrolysate after electrodialysis. Table 2 shows the strains tested, their internal code, from where they were obtained/isolated and summarizes the results of yield, productivities, LA titre, residual sugars fraction and final enantiomeric purity for the fermentations. The value of productivity during the exponential phase (P_{exp}) was calculated using the values of LA only during the exponential period of growth. Graphs for the fermentation profiles can be found in the supplementary material.

Yields higher than 0.90 g g^{-1} and final LA concentrations over 50 g L^{-1} were observed for most of the strains. In general, the strain A166 was amongst the best in terms of productivities and yields and it also showed the maximum value for L-LA purity at 98.6%.

3.4. Effect of the addition of yeast extract in the fermentations

Likewise, in the fermentation with H3, during the screening, the consumption of sugars and production of LA occurred at a slower rate than in the fermentations in which the hydrolysate was only microfiltrated, with P_{max} values around 75–80% lower. Therefore, prior the experiments in the lab and pilot scale bioreactors, an experiment was carried out to evaluate how the addition of yeast extract could enhance the productivities. Parallel fermentations

Table 1
Variation in the composition of the OFMSW hydrolysate after the purification steps. As seen, LA was completely removed in one experiment and partially removed (85%) in the second one.

Step	Concentration (g L-1)					
	Glucose	Disaccharides	Xylose	Arabinose	Lactic acid	Acetic acid
Raw hydrolysate	52.66±0.2	6.51±0.0	10.16±0.0	1.13±0.0	5.70±0.0	2.28±0.2
Coarse filtration (H1)	50.45±1.6	7.79±0.4	09.99±0.3	1.28±0.0	6.54±0.5	4.91±2.0
Microfiltration (H2)	52.68±1.8	7.42±0.7	10.18±0.4	1.30±0.0	6.68±0.5	4.71±2.2
Electrodialysis (H3)	55.07±0.7	7.43±0.5	10.62±0.0	1.36±0.1	0.89±0.9	n.d.

Step	Concentration (mg L^{-1})								
	N_{Total}	P_{Total}	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH^{4+}-N
Raw hydrolysate	3953±03	459±20	1853±01	322±2.9	16±0.1	1354±12	2114±02	171±03	894±0.1
Coarse filtration (H1)	3298±20	437±12	1840±26	320±14	17±0.1	907±6.8	2151±20	167±01	595±3.4
Microfiltration (H2)	2016±18	427±14	1803±30	297±09	17±0.1	850±4.7	2071±20	159±01	565±4.2
Electrodialysis (H3)	1731±04	23±2.6	10±2.6	10±1.7	1±0	84±2.3	90±5.8	1±0.1	6±0

*n.d.: not detected.

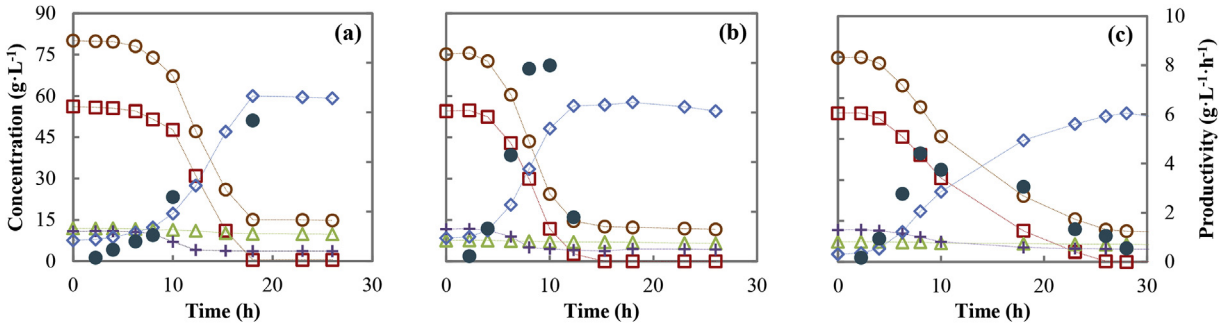

Fig. 2. Variation in the concentration of total sugars (○), glucose (□), disaccharides (△), xylose (+), lactic acid (◊) and productivity (●) for the fermentations of OFMSW hydrolysate samples after (a) coarse filtration-H1, (b) microfiltration-H2 (both from López-Gómez et al. (2019), published in https://doi.org/10.1016/j.bej.2019.107251, licensed under CC BY NC ND (https://creativecommons.org/licenses/by-nc-nd/4.0/) and (c) electrodialysis-H3, using *B. coagulans* A166.

Table 2
Results for yield, maximum productivity, overall productivity, LA final concentration and optical purity for the screening of 13 LA producing strains.

ID	Isolated from	Yield[a] ($g\,g^{-1}$)	P_{max} ($g\,L^{-1}\cdot h^{-1}$)	P ($g\cdot L^{-1}\cdot h^{-1}$)	P_{exp} ($g\cdot L^{-1}\cdot h^{-1}$)	LA ($g\cdot L^{-1}$)	Residual sugars fraction	L-LA%
A20	DSM 2314	0.93	4.34	1.85	2.32	56.5	0.16	98.6
A116	Mulberry	0.90	3.56	1.63	2.00	55.3	0.14	98.0
A120	Mulberry	0.96	3.66	1.47	2.09	54.5	0.09	98.7
A166	Fresh hemp mass	0.94	4.00	1.92	2.01	53.8	0.12	98.6
A183	Grass silage	0.88	3.60	1.66	1.65	55.4	0.11	97.7
A300	Foliage (rotted)	0.84	3.44	1.77	1.89	49.6	0.15	97.8
A432	Press juice alfalfa + dandelion	0.92	3.63	1.31	1.71	56.2	0.06	98.5
A516	Horse manure	0.92	3.47	1.54	1.72	51.8	0.14	98.3
A541	Olive remains Israel	0.91	3.84	1.63	2.02	54.4	0.13	98.1
A547	Ground sunflower seeds	0.92	4.43	1.87	2.00	54.6	0.17	98.4
A562	Sugar beet	0.87	4.76	1.61	1.74	52.3	0.10	95.7
A585	Algae	0.84	4.00	1.65	1.85	52.0	0.14	97.2

[a] Calculated from the fraction of sugars consumed.

were carried out in duplicate, one with the hydrolysate after electrodialysis (Fig. 3a) and one with the same hydrolysate but supplemented with yeast extract (Fig. 3b). In a previous report, Neu et al. (2016) showed that the performances of *B. coagulans* could be enhanced 4–5 times by the addition of 5 $g\,L^{-1}$ of yeast extract. The same pre-culture was used for both fermentations and as seen, a similar lag phase of around 11 h could be observed. Nonetheless, the positive effect of the addition of yeast extract is evident after the 11 h mark. The fermentation with the supplementation of yeast extract exhibited a sharper variation in the sugars and LA concentrations. Glucose concentration went from 60 $g\,L^{-1}$ at t = 12 h to only 3.7 $g\,L^{-1}$ at t = 28 h and the LA concentration increased from 4.9 to 58.6 $g\,L^{-1}$ during the same period. In essence, the addition of yeast extract brought a reduction in the fermentation time of around 14 h compared to Fig. 2c. By contrast, the fermentation without yeast extract showed a decrease in the glucose concentration from 60.9 to only 34.7 $g\,L^{-1}$ during the same period. Naturally, the addition of yeast extract also resulted in an increase in both P_{max} and P with corresponding values of 4.56 $g\,L^{-1}\,h^{-1}$ and 2.78 $g\,L^{-1}\,h^{-1}$ compared to 4.00 $g\,L^{-1}\,h^{-1}$ and 1.92 $g\,L^{-1}\,h^{-1}$ in the fermentation without yeast extract. Thus, lab and pilot scales fermentations were performed using the OFMSW hydrolysate supplemented with yeast extract. Nonetheless, experimental work must be carried out in the future to find an inexpensive replacement for the nitrogen source.

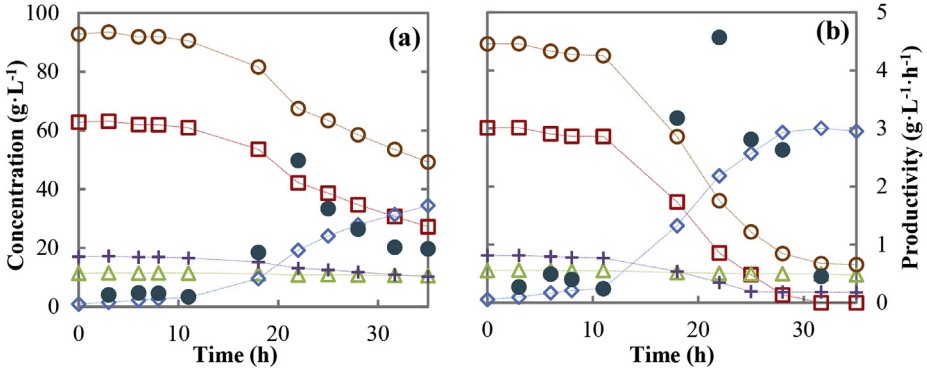

Fig. 3. Effect of the addition of yeast extract (5 $g\,L^{-1}$) on the fermentation of OFMSW hydrolysate after electrodialysis. Variation in the concentration of total sugars (○), glucose (□), disaccharides (△), xylose (+), lactic acid (◊) and productivity (●) for the fermentations of OFMSW hydrolysate samples (a) without the addition of yeast extract and (b) with yeast extract (5 $g\,L^{-1}$) using *B. coagulans* A166.

3.5. Lab and pilot scale fermentations

Fig. 4 shows the profiles for the lab (Fig. 4a) and pilot (Fig. 4b) scale fermentations of the OFMSW hydrolysate, after electrodialysis and supplemented with yeast extract (5 g L^{-1}), by *B. coagulans* A166. Initial sugar contents were above 80 g L^{-1} from which glucose showed a concentration of approximately 50 g L^{-1}, lower than in all the previous experiments. Oppositely, xylose had a concentration of about 25 g L^{-1} a value considerably higher than in the previous fermentations in which xylose varied from 7.6 to 17.5 g L^{-1}. Due to the nature of the substrate, variations of this type between batches are difficult to avoid.

As observed in Fig. 4a' and 4b', after 6 h of fermentation, biomass nearly doubled from 2.61 to 4.71 g L^{-1} and from 2.48 g L^{-1} to 4.85 g L^{-1} at the lab and pilot scale experiments respectively. It was also during this period that the productivities rapidly increased reaching P_{max} values of 6.05 g L^{-1} h^{-1} at the lab scale and 6.38 g L^{-1} h^{-1} at the pilot scale. After 6 h, productivity values started to decrease. Values of P and P_{exp} were 2.73 g L^{-1} h^{-1} and 3.73 g L^{-1} h^{-1} for the lab scale fermentation and, similarly, 2.68 g L^{-1} h^{-1} and 3.63 g L^{-1} h^{-1} for the pilot scale. Final LA concentrations reached 61.4 and 61.1 g L^{-1}, with yields of 0.97 and 0.94 g g^{-1}, in the lab and pilot scale respectively. In both cases, glucose was completely consumed after 17 h. The strain was able to consume xylose and glucose simultaneously, however, unlike in the case of glucose, consumption of xylose ceased without being completely depleted. Finally, enantiomeric purities for both fermentations were over 98.5% of L-LA.

The implementation of the hydrolysate pre-treatment allowed for an important increase in the optical purity of L-LA, from 93% reported by López-Gómez et al. (2019), to 98.7%, a value above the market requirements (Castro-Aguirre et al., 2016). Additionally, a yield of 0.20 g_{LA} $g^{-1}_{dryOFMSW}$ was obtained after the fermentation step, only slightly lower than in our previous results in which a yield of 0.23 g_{LA} $g^{-1}_{dryOFMSW}$ was achieved (López-Gómez et al., 2019).

A product with high purity is critical because polymer grade LA is, virtually, the application with the upmost economic potential (Dusselier et al., 2013). In a recent report, published by 'Grand View Research', PLA dominated the LA market during 2018 with a revenue share of over 27.8% (Grand View Research, 2018), a trend that is forecasted to continue in the upcoming years. Furthermore, it is likely that due to the nature of OFMSW, its application in other fields such as in the food or cosmetic industries, in which the vast majority of non-polymer grade LA is used, can be difficult due to the consumers' perception of the product and laws that could restrict its use.

3.6. Lactic acid purification

An effective purification is critical for some specialised applications which require products with optimal specifications. In the case of PLA production for example, besides a high optical purity, the total amount of impurities should not exceed 0.05 mol % (Inkinen et al., 2011). Nevertheless, the developments of LA downstream and purification methods are still behind the achievements obtained in the up-streams processes (Alves De Oliveira et al., 2019a). This problem is highlighted by the fact that the downstream can account for 30–50% of the total cost of the process. Typically, separation at the industrial scale is carried out in a 2-steps process in which $Ca(OH)_2$ is firstly added to the fermentation broth resulting in a precipitate of calcium lactate. Following that, H_2SO_4 is used to separate the LA. However, a downside of this method is the formation of large quantities of $CaSO_4$ (gypsum), a low-value solid waste which, without properly disposal or recycling, can have negative environmental effects (Alves De Oliveira et al., 2019a; Komesu et al., 2017). Therefore, novel methods have been investigated to find a replacement for the purification of LA.

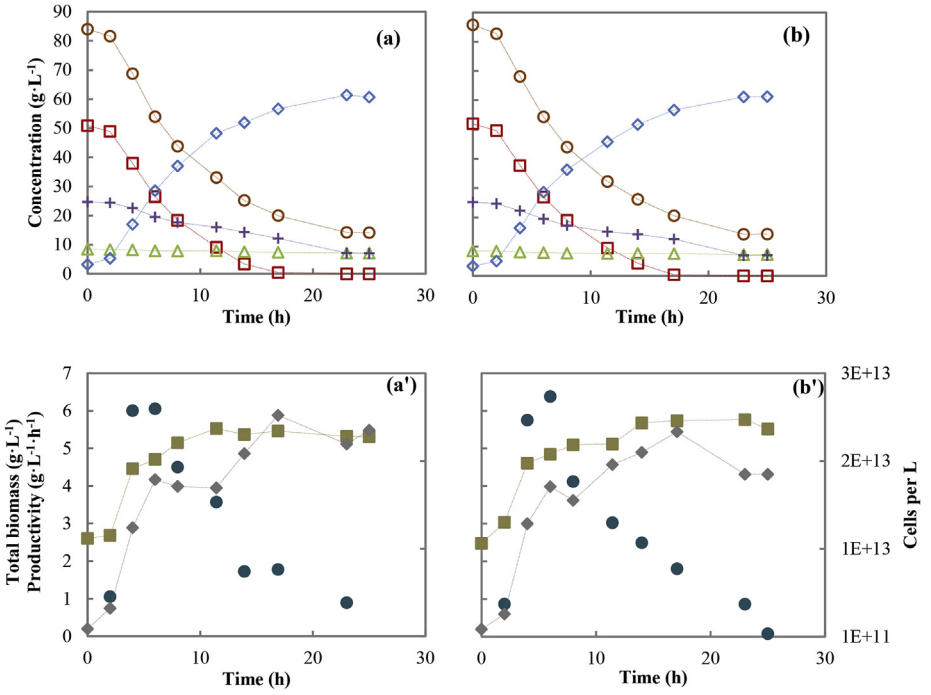

Fig. 4. Fermentations profiles at the lab (a,a') and pilot (b,b') scales of the hydrolysate after electrodialysis using *B. coagulans* A166. Variation in the concentration total sugars (○), glucose (□), disaccharides (△), xylose (+), lactic acid (◊), cells per L (♦), total biomass (■) and productivity (●).

Even though data in the literature regarding membrane electrodialysis for the separation of LA is scanty, it is an attractive alternative because the method does not produce harmful wastes, in can be easily scaled up and it allows for the recycling of chemicals (particularly the base for pH control) (Alves De Oliveira et al., 2019a).

A series of filtration steps followed by membrane electrodialysis were used in the reported experiments for the separation of LA. Fig. 5 shows the variation in the volume and concentration of ions and lactic acid after the fermentation and each downstream step. The numbers in brackets represent the stream of the process to which the samples were taken (see Fig. 1). The total volume of the fermentation broth was 26.7 L with a LA concentration of 59.1 g L^{-1}. By the end of the purification, the volume of the stream had been reduced to 1.13 L with 719 g L^{-1} of LA which corresponds to a total LA recovery of 51.5%.

It has been previously reported, that values for the recovery of lactic acid using electrodialysis can exceed 90% when define and semi-defined mediums are used (Pleissner et al., 2017b; Wee et al., 2005). However, lower values are reported in the literature when complex substrates had been employed for the fermentation. Neu et al. (2016), reported a recovery of 38% when coffee mucilage was used for the fermentations whereas Pleissner et al. (2016), reported a value of only 23%. In these two cases, as for the case reported in this article, the microfiltration and nanofiltration steps accounted for most of the losses during the purification. In this case, from the total LA losses, approximately 70% resulted from the microfiltration and nanofiltration steps. Similarly, 60% of LA was lost during those two steps in the process reported by Neu et al. (2016). Recently, a higher recovery of 62% has been reported when sweet sorghum juice was used for the fermentations (Olszewska-Widdrat et al., 2019). In that case, the purification did not include a microfiltration step, probably due to a low concentration of solids, which would explain the higher recovery. Nonetheless, the ultrafiltration step was accountable for about 20% of the LA losses.

The content of other ions was successfully reduced to only around 0.3 g L^{-1}, a value lower than in the previous mentioned cases (Neu et al., 2016; Olszewska-Widdrat et al., 2019; Pleissner et al., 2016). Likewise in those cases after distillation, sulphate ions were the most predominant with a concentration of 0.25 g L^{-1}. Overall yield of the process including the downstream was 0.10 $g_{LA}\ g^{-1}{}_{dryOFMSW}$. Even though, neither this work nor the cited articles focused on the downstream, undoubtedly, important improvements are necessary in this area to enhance the overall value of the process.

4. Conclusion

This is the first report in which OFMSW has been utilised for the production of L-LA with high enantiomeric purity. The hydrolysates obtained from such a cheap and abundant biowaste proved to be a good substrate for the bioconversion of LA. However, high optical purities could only be accomplished with a pre-treatment step (to remove D-LA) after which, fermentations carried out by several *B. coagulans* isolates successfully achieved enantiomeric purities over 98% L-LA. Scale up of the process was carried out and at the pilot scale, a fermentation of the pre-treated hydrolysate, by *B. coagulans* A166, resulted in a final LA concentration of 61.1 g L^{-1} and a yield of 0.94 g g^{-1}. The downstreamprocess resulted on a LA recovery of 51.5% and a purity of L-LA of 98.7%. Additional experimental work should be carried out to optimise the hydrolysate pretreatment stage, with perhaps investigations on alternative methods for LA removal. Moreover, further work on downstream optimisation is necessary to improve the performance of this critical stage of the process. Finally, future work should investigate the economic feasibility of the process and evaluate if the increased costs, due to hydrolysate purification, are compensated by the production of LA with higher enantiomeric purity.

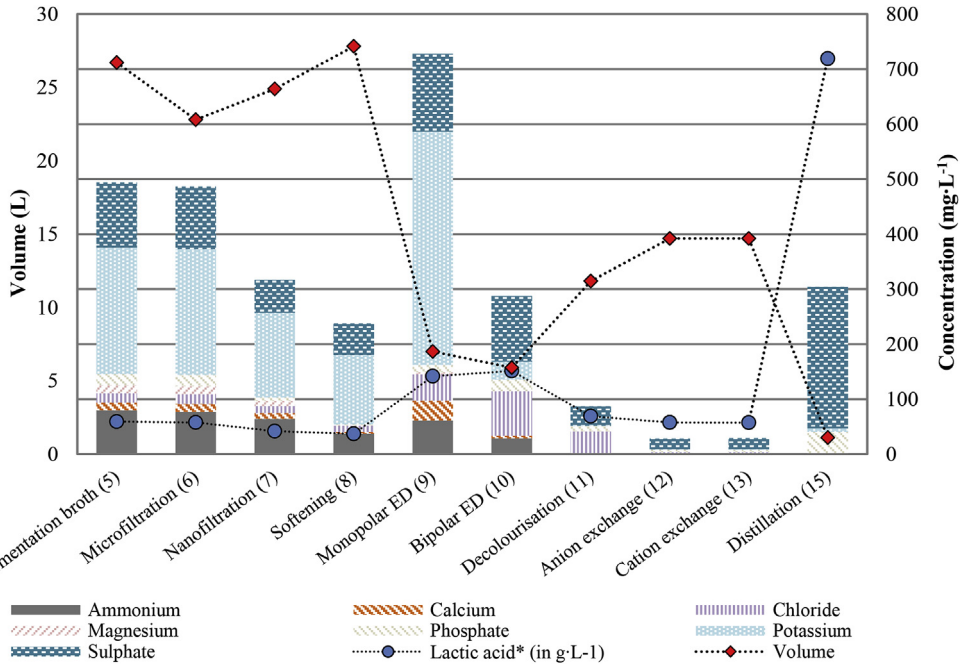

Fig. 5. Variation in the volume and concentration of ions and LA after the downstream steps. LA concentrations are given in g L^{-1}. The numbers in brackets indicate the streams from which they were taken in Fig. 1.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.119165.

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