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Biochars from *Spirulina* as an alternative material in the purification of lactic acid from a fermentation broth

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ABSTRACT

In this study, *Spirulina* biochar obtained from fast pyrolysis was evaluated as an alternative to commercial activated carbon for lactic acid (LA) purification from a fermentation broth. Thermally (350 and 400 °C treatment of the biochar in N_2 atmosphere for 4 h) and chemically (KOH solution impregnation of the algal material and fast pyrolysis to obtain the biochar) activated *Spirulina* biochars were also tested. The biochars were previously characterized using SEM and FT-IR. Two purification methodologies were evaluated: filtration and stirring. The stirring method prove to be simpler, faster and chipper, with excellent purification results. All the evaluated biochars presented a performance comparable to that of activated carbon in the stirring methodology. *Spirulina* biochar and the KOH activated biochar were the once with the best results, with 92 and 82% LA recovery and 82 and 90% protein removal efficiencies, respectively.

1. Introduction

Lactic acid (LA), is an organic acid widely used in various industry sectors. In the pharmaceutical industry lactic acid can be used as a raw material in the production of cosmetics, ointment and lotion formulation; in the chemical industry it is used in the production of chemical bases and organic solvents and in the food industry it acts as acidulants, flavorings and emulsifiers [1,2]. Another major field of interest for lactic acid is the production of renewable and biodegradable plastics from polylactic acid (PLA). Polymers made from lactic acid have shown physical and mechanical properties comparable to plastics produced from petroleum, but with high biodegradability rates, such as food packaging and various plastic utensils [3–5]. In addition, PLA biopolymers, because they are bioresorbable, can be used in medicine, tissue regeneration, sutures, fracture fixation, bone replacement, cartilage repair, meniscal repair, ligament fixation and implants [6–8].

Lactic acid can be manufactured by both chemical and biotechnological synthesis through fermentative processes. The process of obtaining lactic acid by chemical synthesis is based on lactonitrile. Hydrocyanic acid is added to acetaldehyde in the presence of a base to produce lactonitrile, and this reaction occurs in liquid phase under high atmospheric pressure. Lactonitrile is recovered and purified by distillation and then hydrolyzed to lactic acid by the application of hydrochloric acid or sulfuric acid, producing ammonium salts and lactic acid. Production by chemical synthesis results in a racemic mixture of lactic acid [9].

On the other hand, fermentative processes (bacteria, fungi and yeast) are more advantageous due to the lower reaction temperatures and pressures (which means lower energy consumption) and the process is friendlier with the environment. In addition, fermentative production offers a great advantage in obtaining L (+) and D (−) optically pure lactic acid as well as DL lactic acid, depending on the strain selected for fermentation [10,11]. Approximately 90% of the total lactic acid produced in the world is produced by fermentation using bacteria [4,12].

For the production of lactic acid by fermentation process to be viable, it is necessary to achieve better operational conditions inside the reactor,

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reducing costs in the lactic acid purification and extraction stage. The technological barriers to low-cost lactic acid production are mainly in the process of recovery and purification of lactic acid from the fermentative medium. These two process steps represent approximately 50% of the total cost of lactic acid production and the reduction of this cost is one of the most important challenges of lactic acid production [11–14].

Several methodologies have been and are currently evaluated for lactic acid purification from fermentation broths (see Table 1).

In the conventional method of purification of lactic acid occurs calcium lactate precipitation, with esterification and hydrolysis through reactive distillation. It is an economic process, simple and reliable, but generates large amounts of $CaSO_4$, which is considered an environmental contaminant [26]. For this reason, it has sought alternative and ecologically correct methods for purification, as for example, methods involving adsorbents in general: activated carbon, ion exchange resins, etc.

Activated carbon has being reported as an adsorbent for solutions clarification and purification [27–29], due to his abundant surface functional groups and high surface-to-volume ratio [30,31]. In this context, biochar appeared as a low cost, renewable and ecological alternative as adsorption material in replacement of commercial activated carbon, which 45% of the worldwide supply is produced from coal, a non-renewable source [32]. Biochar is one of the three biomass pyrolysis products. During pyrolysis studies, bio-oil is the product that has received most attention, but now biochars are also extensively studied [33–35]. Many studies proved that biochars have lots and different active sites, most of them oxygen-containing functional groups [36]. Regarding to broth purification, it is known that the adsorption of sugars and proteins on activated carbon it is much greater than the adsorption of lactic acid [37]. Also, the process is easy to handle, has low cost and can be performed in any laboratory.

In the present work, biochar obtained from fast pyrolysis of *Arthrospira patensis – Spirulina* was evaluated as adsorption material in the purification process of lactic acid obtained through bacterial fermentation. *Spirulina* was extensively studied as pyrolysis biomass source for bio-oil production in order to achieve biofuels [38–41]. The purpose of this study is to take advantage of biochar formed during *Spirulina* pyrolysis and which is the secondary product of the process. Different treatments of both the starting material and the carbon obtained in the purification of lactic acid have been evaluated.

2. Materials and methods

2.1. Reagents

Arthrospira patensis – Spirulina was commercially acquired and used without further treatment. KOH was directly purchase from Biopack and use to prepare an aqueous solution 7% KOH (w/v). Commercial activated carbon (CAC) was purchase from Sigma-Aldrich and used as reference material. *Bacillus coagulans* arr4 was isolated from *Ruta graveolens* rhizosphere (São Paulo, Brazil) and used to LA production.

2.2. Lactic acid production and broth characterization

Exponential fed-batch culture was used to obtain the fermentation broth. The feed rate (F) was calculated as previously reported [42]. The fermentation fed batch were performed in a INFORS HT fermenter. The temperature and agitation were 50 °C and 100 rpm, respectively, and the pH was kept constant at 6.5 by adding a solution of $Ca(OH)_2$.

A N_2 flow of 0.5 mL/min was added for 12 h to maintain anaerobic conditions during fermentation. Fermentation started with around 109 g/L of sucrose, a concentration that does not inhibit the microorganism, according to preliminary studies; 30 g/L of yeast extract and 5 mL/L of salts of GYP medium, that consists of (g/L): $MnSO_4$ (2.0), $MgSO_4$ (40.0), NaCl (2.0), and $FeSO_4{\cdot}7H_2O$ (2.0). The feed solution contained 900 g/L of granulated sugar and 1% of yeast extract, and started at 10 h of fermentation and lasted 6 h and 30 min, adding to the reactor 930 mL of this feed solution. Centrifugation of the broth was performed at 7000×*g* at 20 °C for 10 min to remove some cell debris and non-soluble impurities from fermentation. The broth was characterized, for which the content of LA, sucrose, total proteins and pH was determined.

To determine the production of the optical isomers of lactic acid, a high-performance liquid chromatograph was used, equipped with an ultra-violet detector at 254 nm, Chirex 3126 Phenomenex column (150 × 4.6 mm) eluted with 1 mM of copper sulfate II in aqueous solution as a mobile phase, flow of 1 mL/min and temperature of 26 °C. The proportion of enantiomers is 80.71% L-(+) LA and 19.29% D-(−) LA.

2.3. Biochar production

A fixed bed fast pyrolysis reactor was used, previously reported [43–45]. The amount of 1 g of *Arthrospira patensis – Spirulina* was placed in ceramic boat and introduced into a quartz tubular reactor when all the reaction conditions such as pressure, temperature and flow of transport gas (ultra-dry nitrogen) have been achieved. At the opposite side of the reactor, a condensation trap and a vacuum pump are connected to the system. The reaction took place at 300 °C for 20 min, with a nitrogen flow of 0.2 mL s^{-1} and a vacuum of 50–100 mTorr. Once the reaction was finished, the system pressure was compensated and the reactor was allowed to cool. The solid product (BC-Sp) was removed, weighed and washed with distilled water.

Physical and chemical activations of the biochars were also studied to analyze the performance of this materials. For chemical activation, *Spirulina* was impregnated with 7% KOH (w/v) at 80 °C for 30 min, dyed and then pyrolyzed at 300 °C for 20 min. After pyrolysis, the biochar was washed with distilled water and dried (BC–KOH). For the physically activated carbons, BC-Sp was heated at 350 (BC-350) and 400 °C (BC-400) under N_2 atmosphere for 4 h.

Table 1
Different methodologies used in LA recovery from fermentation broth.

Purification method	Conditions	LA recovery efficiency	Ref.
Precipitation	Reflux of ammonium lactate with methanol and sulfuric acid. Filtration of ammonium sulfate and recovery of methyl lactate	~80% of methyl lactate	[15]
	Precipitation of lactate using $Ca(OH)_2$, Na(OH) and $NH_4(OH)$	65.4% with Na(OH) 64.6% with $NH_4(OH)$ 80.6% with $Ca(OH)_2$	[16]
Solvent extraction	Broth vortexed with ammonium sulfate and n-butanol. Separation with funnel and solvent evaporation	86%	[17]
	Ultrasonic solvent extraction with ethyl acetate and solvent evaporation	57%	[18]
Electrodialysis	Continuous electrodialysis fermentation with GC control of glucose	77%	[19]
	In situ fermentation and purification with bipolar membranes	86%	[20]
Nanofiltration	Composite polyamide nanofiltration membrane	32%	[21]
	Nanofiltration membrane, ion exchange and vacuum distillation	65%	[22]
Ion exchange resins	IRA-67 and IR-120	91%	[23]
	IRA-400 and IR-120	73%	[24]
	IRA-67	74%	[25]
Activated carbon	Commercial Activated carbon	69%	[25]

2.4. Biochars characterization

The morphological characteristics of the biochars were analyzed by a field emission scanning electron microscopy (FE-SEM) with a Jeol JSM 7500 F semi-in-lens detector, installed in the Advanced Microscopy Laboratory (LMA) of the Institute of Chemistry, of the São Paulo State University (UNESP), São Paulo, Brazil. The samples were previously metallized with a 20 nm layer of Au/Pd.

Specific surface area, pore volume and average pore size of the biochars were assessed by N_2 physisorption. The adsorption-desorption isotherms were obtained at 77 K using a Micrometrics ASAP 2010 instrument, with relative pressures between 0.001 and 0.998. Previously, the samples were maintained for 24 h under vacuum of 10 μPa, at 200 °C, in order to remove water and other physisorbed gases. Functional groups present on the surface of these materials were studied by FTIR, using an FT-IR microscope (Thermo Scientific™ Nicolet™ iN™10) in its reflection mode.

2.5. Purification experiments

For the purification of the broth, two sets of experiments were tested. The first purification technique evaluated, consisted of taking a 10 mL aliquot of the broth and subjected to vacuum filtration using a funnel with sintered glass plate (3.5 cm in diameter and 5.0 cm in height) containing 1 cm of height of carbon (about 1.3 g), similar to previous purification experiments [42]. Three filtrations of the same aliquot were performed; each with 2 washes of 10 mL of Milli-Q water. Between one filtration and the other, the carbon was dried 24 h in an oven at 70 °C. The experiments were carried out in duplicate, reporting the average of the two replicates with the standard error.

In the second designed experiment, 0.5 g of biochar, 5 mL of broth and a magnetic stirrer were placed in 50 mL centrifuge tubes. The mixture was allowed to stir at 21 °C for 24 h. Then, the mixture was centrifuged at 10,000×*g* for 20 min and the supernatant was removed. The solid material was washed two times with Milli-Q water of 3 mL each, separating the supernatant by centrifugation. The experiments were carried out in triplicate and results were expressed as mean of three replicates with the standard deviation.

Both the supernatant and the washes from the different experiments were analyzed for lactic acid and protein content.

2.6. Lactic acid and protein quantification

For L (+)-LA and saccharose determination, High Pressure Liquid Chromatography (HPLC) was used. The equipment, Shimadzu Prominence brand equipped with UV detector and Refractive Index detector, was used with a Phenomenex Rezex ROA column (300 × 7.8 mm) using the conditions already described in previous work [14]. L (+)-LA was detected at 210 nm UV detection wavelength. The samples were previously filtered through a 0.2 μm cellulose acetate membrane. The mobile phase was prepared with Milli-Q water, filtered with funnel with sintered glass plate and 0.2 μm cellulose acetate filter, and sonicated for 10 min, with the aim of eliminating impurities and dissolved gases. L (+)-LA and saccharose calibration curves were performed to quantification.

Total protein quantification was performed using the Lowry method described by Peterson, with modifications proposed by Waterborg [46,47]. The reactions result in a strong blue color, whose absorbance was determined by UV Visible Spectroscopy at a wavelength of 550 nm.

Finally, the L (+)-LA recovery efficiency and protein removal efficiency of the purification methodologies were calculated using the equations below:

L (+) – LA recovery efficiency (%) = (final LA mass/initial LA mass) x100

Protein removal efficiency (%) = [(initial protein mass-final protein mass)/initial protein mass] x100

Table 2
- Characterization of bacterial fermentation broth.

Broth properties	
pH	7.07
LA ($g.L^{-1}$)	68.32
Proteins ($g.L^{-1}$)	3.39
Saccharose ($g.L^{-1}$)	0

3. Results and discussions

3.1. Broth characterization

The results of the characterization of the fermentation broth are summarized in Table 2.

The fermentation broth did not show dissolved saccharose, so purification focused on the elimination of proteins, that came mainly from cell debris and yeast extract that wasn't able to be eliminated in the centrifugation process. The pH value indicates that LA is present in the broth as lactate ($pKa_{LA} = 3.86$).

3.2. Biochar production and characterization

Biochars characterization was performed. Porosity of carbonaceous materials is one of the main parameter in the adsorption efficiency [48], so morphological characterization by SEM of the evaluated carbons was determined (Fig. 1).

Fig. 1 shows that all the studied biochars presented a heterogeneous surface, being BC-Sp the one with a reduced porosity, compared to the other samples. Different pore sizes and larger diameter channels were observed in the thermally activated carbons, BC-350 and BC-400. BC-KOH presented a very irregular surface, also with a high pore density.

The Brunauer-Emmet-Teller (BET) specific surface area and pore volume are presented in Table 3, provided through N_2 adsorption.

Surface area and pore volume increased with the thermal treatment at 400 °C, as expected [49]. BC-350 data was unable to determine with the equipment used in the analysis. In the case of BC-KOH it wasn't possible to measure, but based on the available bibliography, it is expected that the surface area and pore volume are much higher than untreated samples [35,50,51].

Functional groups present on the surface of the biochars were analyzed by Infrared Spectroscopy (Fig. 2).

All the biochars presented a peak at 3000-3600 cm^{-1} corresponding to O–H hydroxyl stretching of alcohols and phenols [36,52]. In BC-350 and BC-400 biochars, this peak decrease gradually with the increase of activation temperature and almost disappear in BC-400. This might be because the heat treatments reduce part of the functional groups presents in the surface, due to bonding destruction [49]. Peaks between 1040 and 1250 cm^{-1} can also been observed, corresponding to C–O stretching of oxygenated groups like alcohol, ester and phenol. In BC-KOH a peak between 1580 and 1740 cm^{-1} indicates the presence of C=O stretching from carboxylic acids [52]. This functional groups probably will interact with the components of the broth, allowing the purification of it.

3.3. LA purification

For purification experiments, vacuum filtration using commercial activated carbon (CAC) and *Spirulina* biochar (BC-Sp) was evaluated for the purification of LA. Results are shown in Table 4.

After the treatment with both carbons, a decrease in the color was observed, achieving with CAC an almost clear solution. Applying a single filtration and their corresponding washes, it was possible to eliminate a moderate amount of protein, with high recovery rates of LA when BC-Sp and CAC were used as adsorbents. Subsequent filtrations managed to

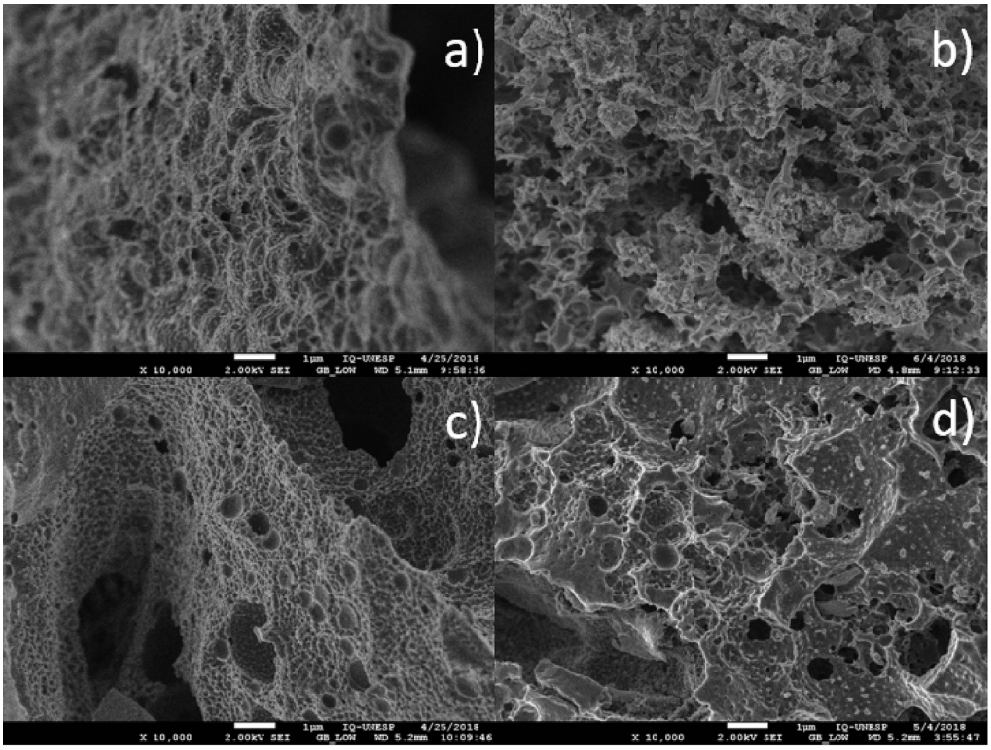

Fig. 1. - SEM images of the studied biochars: a) BC-Sp, b) BC-KOH, c) BC-350, d) BC-400.

Table 3
Surface area and pore volume of the studied biochars.

Sample	S_{BET} ($m^2.g^{-1}$)	Pore volume ($cm^3.g^{-1}$)	Average pore size (nm)
BC-Sp	2.2 ± 0.1	0.0019	3.40
BC-350	–	–	–
BC-400	4.0 ± 0.2	0.0032	3.22

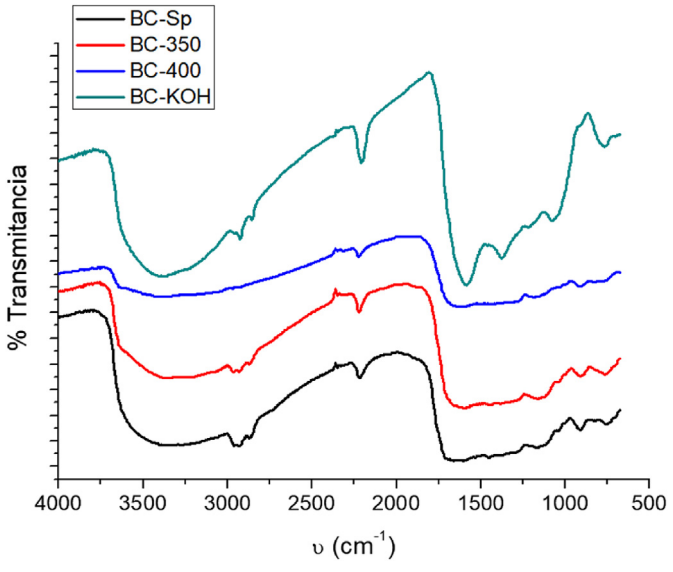

Fig. 2. - FT-IR spectrums of the studied biochars.

eliminate greater amounts of protein, resulting also in a loss of recovered LA. Considering that the time spent in the filtrations was high (1 h a day for 3 days) due to the compaction of the carbon inside the funnel and the drying times of the material, we decided to dismiss this test for the evaluation of the remain biochars.

Subsequently, the purification of broth was performed by the stirring technique using CAC, Bc-Sp and the activated biochars BC-KOH, BC-350 and BC-400. The results are shown in Table 5.

In this case, the broth color also decreases after treatment, but not with the same efficiency as the vacuum experiments. Regarding the purification, all the biochars evaluated had very good recovery values of LA and protein elimination. This could be due to two main factors: the fact that LA, being present as a lactate, had a negative net charge, which generated an electrostatic repulsion with the biochars, also negatively charged [35,53,54], thus allowing its separation from proteins; and longer contact time between the broth and the biochar, which may have favored the adsorption of the proteins to the biochar surface [33,34,55].

BC-Sp managed to recover almost the total LA present in the broth, but the ability to eliminate proteins was regular. BC-KOH allowed to retain a higher percentage of proteins. This turned out to be the biochar that showed a behavior similar to CAC, managing to separate a high percentage of LA from proteins. BC-350 and BC-400 had the lowest performance for LA purification.

According to these results, the functional groups may have a major effect in the purification of LA than porosity. With BC-Sp and BC-KOH, major interactions are established between the functional groups and the proteins in the broth, which gives better protein removal percentages. With the thermally activated biochars, the increase in the activation temperature diminish the number of functional groups in the surface [49], resulting in a decrease in the interactions between BC-350 and BC-400 and the proteins, hence in a reduction in the efficiency of purification.

4. Conclusions

In the present work, it was decided to use biochars for the purification of LA on bacterial fermentation broth. Of the methodologies evaluated, stirring proved to be the simplest, fastest and most efficient option in the recovery of LA and protein elimination, compared to the vacuum filtration technique. The morphological characterization carried out by SEM

Table 4
- Purification of broth by vacuum filtration using *Spirulina*-derived carbon BC-Sp and CAC as adsorbents.

Carbon	Stage	LA (g)	Proteins (mg)	LA recovery efficiency (%)	Protein removal efficiency (%)
	Initial broth	0.66	33.94	–	
CAC	1st filtering	0.60 ± 0.05	4 ± 2	121 ± 8	80 ± 5
	Wash 1	0.18 ± 0.01	1.5 ± 0.3		
	Wash 2	0.011 ± 0.007	1.06 ± 0.02		
	WAD	0.011 ± 0.004	0.71 ± 0.09		
	Total	0.80 ± 0.05	7 ± 2		
	2nd filtering	0.309 ± 0.003	1.3 ± 0.2	70 ± 2	84 ± 1
	Wash 1	0.15 ± 0.01	2 ± 1		
	Wash 2	0.005 ± 0.001	2 ± 2		
	WAD	0.007 ± 0.004	0.07 ± 0.07		
	Total	0.466 ± 0.004	5.3 ± 0.5		
	3rd filtering	0.101 ± 0.002	1.67 ± 0.06	29 ± 2	88 ± 3
	Wash 1	0.086 ± 0.005	2.1 ± 0.9		
	Wash 2	0.003 ± 0.001	0.1 ± 0.1		
	Total	0.189 ± 0.004	3.9 ± 0.9		
BC-Sp	1st filtering	0.461 ± 0.03	13 ± 2	99 ± 9	52 ± 4
	Wash 1	0.15 ± 0.01	3.0 ± 0.5		
	Wash 2	0.045 ± 0.006	0.5 ± 0.5		
	WAD	0.003 ± 0.001	0 ± 0		
	Total	0.66 ± 0.04	16 ± 1		
	2nd filtering	0.29 ± 0.04	2.76 ± 0.09	62 ± 1	89 ± 1
	Wash 1	0.09 ± 0.04	0.99 ± 0.04		
	Wash 2	0.023 ± 0.004	0.06 ± 0.06		
	WAD	0.009 ± 0.009	0 ± 0		
	Total	0.41 ± 0.02	3.808 ± 0.002		
	3rd filtering	0.12 ± 0.03	1.5 ± 0.1	27 ± 1	95 ± 1
	Wash 1	0.06 ± 0.02	0 ± 0		
	Wash 2	0.003 ± 0.003	0.1 ± 0.1		
	Total	0.18 ± 0.01	1.6 ± 0.2		

WAD: Wash after drying. Results expressed as mean ± SE, n = 2.

evidenced the heterogeneity in the surface of all the biochars studied. The activated biochars, either by physical or chemical methodologies, presented greater porosity, more irregular surface and the presence of channels, contrary to what was observed for BC-Sp. The study by IR Spectroscopy showed the effect of heat treatment on surface functional groups of BC-350 and BC-400, and their effect on protein removal efficiency. The BC-Sp and BC-KOH materials were the most efficient materials, since they presented a balance between the ability to purify LA and to eliminate proteins, recovering approximately amounts of LA greater than 92 and 88% respectively, parallel reducing the protein content approximately between values of 82 and 90%, respectively.

Table 5
- Purification of broth by stirring using CAC and *Spirulina*-derived carbons BC-Sp, BC-KOH, BC-350 and BC-400 as adsorbents.

Carbon	Stage	LA (g)	Proteins (mg)	LA recovery efficiency (%)	Protein removal efficiency (%)
	Initial broth	0.342	16.97	–	
CAC	Stirring	0.15 ± 0.04	0.4 ± 0.2	91 ± 7	94 ± 1
	1st wash	0.12 ± 0.02	0.2 ± 0.1		
	2nd wash	0.05 ± 0.02	0.3 ± 0.2		
	Total	0.32 ± 0.03	1.0 ± 0.2		
BC-Sp	Stirring	0.17 ± 0.02	1.2 ± 0.7	92 ± 9	82 ± 9
	1st wash	0.12 ± 0.02	1.2 ± 0.6		
	2nd wash	0.026 ± 0.006	0.6 ± 0.4		
	Total	0.31 ± 0.03	3 ± 2		
BC-KOH	Stirring	0.17 ± 0.02	0.6 ± 0.3	88 ± 3	90 ± 1
	1st wash	0.07 ± 0.02	0.7 ± 0.3		
	2nd wash	0.057 ± 0.009	0.4 ± 0.2		
	Total	0.30 ± 0.01	1.7 ± 0.1		
BC-350	Stirring	0.16 ± 0.03	0.9 ± 0.3	86 ± 8	85 ± 3
	1st wash	0.10 ± 0.02	1.0 ± 0.2		
	2nd wash	0.029 ± 0.002	0.7 ± 0.5		
	Total	0.30 ± 0.03	2.5 ± 0.6		
BC-400	Stirring	0.17 ± 0.01	1.7 ± 0.3	87 ± 3	75 ± 9
	1st wash	0.09 ± 0.02	2 ± 1		
	2nd wash	0.036 ± 0.006	0.4 ± 0.3		
	Total	0.29 ± 0.01	4 ± 2		

Results expressed as mean ± SD, n = 3.

CRediT authorship contribution statement

Roxana Verónica Piloni: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Visualization, Writing – review & editing. **Luciana Fontes Coelho:** Formal analysis, Resources. **Daiane Cristina Sass:** Supervision, Formal analysis, Writing – review & editing. **Mario Lanteri:** Formal analysis, Resources. **Maria Aparecida Zaghete Bertochi:** Resources. **E. Laura Moyano:** Conceptualization, Resources, Writing – review & editing, Visualization, Supervision, Funding acquisition. **Jonas Contiero:** Conceptualization, Methodology, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

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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