Algal Research 71 (2023) 103084

Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

Extraction of fatty acids and cellulose from the biomass of algae *Durvillaea antarctica* and *Ulva lactuca*: An alternative for biorefineries

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ARTICLE INFO

Keywords:
Seaweed
Sub-Antarctic Chilean algae
Ultrafine fiber
Lipids

ABSTRACT

Algae have cellular structures, rich in polysaccharides, proteins, lipids, vitamins and minerals. In addition, fatty acids are known for their benefits to human health, such as in treating blood pressure, diabetes, and obesity. These properties determine the algal biomass value as a raw material for different applications. One of the polysaccharides present in algae and is still little explored is cellulose, an important material for numerous technological applications. In this study, *Durvillaea antarctica* and *Ulva lactuca* algae were used as raw materials for the production of a cellulosic-based materials combining alkaline treatment, bleaching and freeze-drying. The samples were analyzed by XRD, ^{13}C-CP-MAS-NMR, FT-IR, SEM, TEM and TGA techniques. XRD analysis showed that the material obtained presented crystallinity of above 60 %. FT-IR revealed that the methodology was effective in obtaining cellulose. SEM and TEM images exhibited a morphology consisted of cellulose fibers.

1. Introduction

Macroalgae cultivation has emerged among the world aquaculture sectors due to the demand for blue biotechnology and the transition to a low-carbon economy. The cultivation of macroalgae has grown exponentially, reaching an increase of almost 10 % per year [1]. The term "algae", etymologically, is used for a group of taxonomically unrelated organisms, including cyanobacteria, eukaryotic microalgae and macroalgae. Macroalgae are divided according to their physiological and biochemical characteristics, which can be: red algae (Rhodophyta), green algae (Chlorophyta) and brown algae (Ochrophyta) [2]. Their cell walls are composed of complex networks of biopolymers, cellulose as the skeleton, fibrous parts, and a matrix of specific polysaccharides, in addition to proteins, lipids, vitamins, and minerals. These components are what determine their value as a raw material for different applications [3,4].

Macroalgae are recently attracting much interest from several industry sectors [5]. However, only 50 % of the 72,500 species of algae identified were studied. Thus, the potential of algae technologies for a wide range of applications is indisputable. Proteins, carbohydrates, lipids and fatty acids are the major components of algae, corresponding to approximately 40 % of the total mass of the algae [6].

Fatty acids are normal-chain monocarboxylic acids having the carboxyl group bound to an alkyl, saturated, or unsaturated long chain. They are divided into saturated (SFA), monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA). Fatty acids are recognized for their various benefits related to human health, being used in the treatment of blood pressure, diabetes and obesity, among others [7]. Thus, algae are precursors of essential lipids, such as linoleic acid, which are not present in the human body. Studies describing the acid extraction of algae samples have already been reported, however, no studies regarding the use of macroalgae, such as *Durvillaea antarctica* and *Ulva lactuca* are

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https://doi.org/10.1016/j.algal.2023.103084
Received 16 August 2022; Received in revised form 28 March 2023; Accepted 31 March 2023
Available online 5 April 2023

reported [7,8]. Moreover, algae samples have the potential to be used as raw material for obtaining cellulose, which is also a research field that can be more investigated [9].

Cellulose can be found in plants, marine animals, marine biomass, fungi, bacteria, and invertebrates, among others. Being one of the most abundant biopolymers, the extraction of these materials occurs in different forms, including fibers, microfibers, microfibrils, nanofibers, and nanocrystals [10]. Cellulose from algae was described for the first time in 1885. Since then, it has received great attention mainly due to its economic advantage. The extraction of fibers from algae has been considered a great alternative in the context of environmental maintenance, with support for growing market demand in the most varied areas [11]. Thus, this study aims to collaborate with studies on the extraction of fatty acids and cellulose from macroalgae, using *Durvilae antarctica* and *Ulva lactuca* collected in the sub-Antarctic region.

2. Materials and methods

2.1. Collection and pre-treatment of algae biomass

Durvillaea antarctica and *Ulva lactuca* biomass were collected in Chile, sub-Antarctic region (53° 07′ 33″ S 71° 21′ 12″ W) in august of 2018. After collection, the algae samples were prepared as described by Santos et al. [12] and oven-dried at 35 °C for 24 h. Then, the samples were grounded in a knife mill and stored at 20 °C in a package free of moisture and light, these processes took approximately 2 h. The general information of algae collection, individuals stored for exsiccate and morphological identification under specified numbering were carried out in the herbarium of the Laboratory of Antarctic and sub-Antarctic Marine Ecosystems. In the next steps, all reagents were used without further purification and purchased from Sigma-Aldrich.

2.2. Lipid extraction and fatty acid methyl esterification

The extraction of the lipid content of the algae samples was performed based on the modified methodology proposed by Bligh and Dyer [13] and a schematic representation of the procedures are shown in Fig. S1. Firstly, a solution containing 1 g of biomass in a 10 mL solution of 1:0.5 ratio of methanol: chloroform, and sodium sulfate (1.5 % w/v) was kept stirring for 30 min. Then, the samples were centrifuged at 2800 rpm for 30 min to separate the solids from the liquid phase (organic phase). Finally, solvents were removed from the organic phase using a rotary evaporator (Buchi, Switzerland) with a V-700 vacuum pump and a B-741 cooler.

The algae lipid extract was esterified and converted into fatty acids methyl esters (FAMEs) based on the B method proposed by Moss et al. [14]. The lipids extraction was performed by stirring under reflux at 80 °C for 8 min with 6 mL of methanolic solution of potassium hydroxide (2 % w/v). Then, 7 mL of boron trifluoride/methanol (14 % v/v) was added and maintained stirring and refluxing for further 2 min. The solution was then cooled to room temperature and 5 mL of an aqueous solution of sodium chloride (20 %, w/v) was added. The organic phase that contained the FAMEs was retrieved with 20 mL of hexane, filtered using anhydrous sodium sulfate, evaporated under vacuum, and dried under nitrogen flow.

2.3. Obtaining the cellulosic material

After the fatty acids extraction, the cellulosic material was obtained following the methodology displayed in Fig. S2, previously described by Paniz et al. [15]. Firstly, 5 g of biomass free of lipid content was added to 200 mL of deionized water for 3 h at 110 °C with the aid of a condenser to avoid the evaporation of water. Then, the sample was filtered and washed to remove the remaining salt. After the desalting step, a Soxhlet system was applied for 7 h at 120 °C, using 260 mL of a 2:1 (v/v) ratio toluene/ethanol solution, respectively. Then, the biomass was subjected to alkaline treatment with NaOH solution (5 % w/v) and bleached using $NaClO_2$ solution (0.1 M) adjusted to pH 4 with acetic acid. Both procedures were performed at 80 °C for 2 h. Finally, neutralization of the bleached material was carried out by filtration and washing with distilled water using a Büchner funnel with a porous plate (Laborglass, Brazil, type 1) with the aid of a vacuum pump. Cellulosic materials obtained from *U. lactuca* and *D. Antarctica* were named U-cellulose and D-cellulose, respectively.

2.4. Characterizations

The fatty acid obtained from algae biomass were analyzed by Gas Chromatography with Flame Ionization Detector (GC-FID; SHIMADZU QC-2010, Japan), according to the methodology reported by Santos et al. [12]. Dry weight percentage of lipids (%) was determined by measuring the total weight of lipids extracted in the Bligh & Dyer extraction proccess. The fatty acid content was obtained through a calibration curve in the concentration range of 0.625 to 20 mg mL^{-1} using a standard MIX solution of fatty acids (FAME 37-MIX, Supelco/USA) and a nanodecanoate as an internal standard (Sigma-Aldrich, USA).

The yield of cellulosic materials was investigated in dry weight, following the TAPPI T9 standard. Algae and cellulosic materials were characterized concerning functional groups on their surface through Fourier Transform Infrared Spectroscopy (FTIR; SHIMADZU IRspirit, Japan). The spectrum was performed with 45 scans in the range of 400 to 4000 cm^{-1} and a resolution of 4 cm^{-1}. Scanning Electronic Microscopy (SEM; JEOL JSM 6610, USA) and Transmission Electronic Microscopy (TEM; CM200 Philips, USA) were carried out to observe the surface morphology analysis of the samples. To assist in the interpretation of the molecular structure of the cellulosic materials, the chemical shifts were analyzed by Nuclear Magnetic Resonance (NMR; Agilent 500 MHz, model DD2), ^{13}C-CP-MAS, using a Magic-Angle Spinning (MAS) rate of 10 kHz and frequency of 125.69 MHz. Also, the spectrum was obtained with 20,000 scans, 0.8 ms of contact time, 2.55 ls pulse width, 35 ms acquisition time, and 2.5 s of recycling delay. Chemical shifts are reported relative to the signals of adamantane used as an external standard.

The thermal stability of the samples was evaluated by thermogravimetric analysis (TGA; SHIMADZU TGA 50, Japan) with a heating rate of 10 °C min^{-1} and an N^2 flow rate of 20 mL min^{-1}. The crystallographic planes of the samples were analyzed by X-ray diffraction (XRD; Rigaku ULTIMA IV, Japan) applying a Cu Ka radiation (k = 1.54 A°) at 40 kV, by scanning step over the range of 5–70°. Eq. (1) was used to infer the Segal crystallinity index [16].

$$\%crystallinity = \frac{(I_{cr} - I_{am})}{I_{cr}}.100 \quad (1)$$

where I_{cr} is the intensity of the crystalline phase and I_{am} is the intensity of the amorphous phase.

3. Results and discussions

3.1. Gas chromatography with flame ionization detector (GC-FID)

The total lipid content (dry weight) obtained was 5.43 ± 0.26 % and 3.32 ± 0.14 % for *U. lactuca* and *D. antarctica*, respectively, which were considerably higher than the value obtained for *U. lactuca* and *D. antarctica* performed by Ortiz et al. [17], which reached 0.3 % and 0.8 % of lipids content, respectively. Mateluna et al. [18], found 0.1 % of lipid content for *D. antarctica* and Roleda et al. [19] 1.32 % from *U. lactuca*. The high values obtained in this work can be explained by the high adaptation of macroalgae, which allows these organisms to inhabit many complex environments. The extreme environmental conditions of the sub-Antarctic region, such as low water temperature, limited

nutrient availability, high exposure to ultraviolet radiation, restricted photoperiod and high-water salinity, promote the development of survival strategies, altering their biochemical composition [20]. The activation of these secondary metabolites in macroalgae causes an increase in lipids, sterols, polysaccharides, amino acids, flavonoids, and terpenoids [20].

Tables 1 and 2, show the results of the GC-FID analysis performed on the extracts of the algae *Durvillaea antarctica and Ulva lactuca,* exhibiting a variation in the fatty acids content (%, dry weight). *U. lactuca* obtained a higher value of polyunsaturated fatty acids (62.75 %), while *D. antarctica* had a higher value of saturated fatty acids (84.91 %), which can be ascribed to their chemical composition that is directly related to the different species and algae growth conditions.

The SFA with the highest value content for both algae species was palmitic acid, which is in agreement with previous reports that evaluated the fatty acid content in algae collected in the Chile region [12,21]. The main PUFA present in the *U. lactuca* species were linolelaidic acid (18:2n6t), α-linoleic acid (18:3n3), and eicosadienoic acid (20:2n6). Similarly, previous reported studies also described a higher abundance of these PUFAs for algae of the species *Ulva* sp. [5], differently from the *D. antarctica* specie, which exhibited a minor concentration of this PUFA.

The content of PUFA is responsible for the strength of the algal structural membrane at lower temperatures [22]. In addition, factors such as exposure to solar irradiation and hyperosmotic stress can vary the concentration of PUFA [23]. Khotimchenko and Yakovleva [24] evaluated the lipid content in marine green algae *Ulva fenestrata* under different irradiance conditions and revealed that the concentration of palmitic acid, a compound with the highest concentration for both species of algae, presented higher values for the samples subjected to a more severe solar irradiation.

The class of PUFA with a high interest in human health is the *n*-3 essential, in this case, represented by linoleic acid, which is not synthesized by human organisms [25]. Studies of this class of PUFA show that they can be related to the reduction of the risk of heart disease [26] and cancer [27].

3.2. Cellulose extraction yield

After the extraction of fatty acids, the extraction of cellulose was performed. The cellulosic materials presented a sponge-like structure, with a yield of 0.97 ± 0.09 %, for D-Cellulose and 3.82 ± 0.13 % for U-Cellulose, related to the initial algal biomass. This yield is low compared to terrestrial plants. However, they can be harvested or grown in numerous aquatic environments (outdoors and indoors), with no need of an arable land. Also, algae have fast growth rates and can be harvested in shorter periods compared to terrestrial plants.

Thus, the yield of *U. lactuca* is in agreement with similar reports studies. Gomaa et al. [28] obtained a yield of 2.53 to 5.67 % (dry weight) for *U. lactuca* collected in the supralittoral region of Egypt, while Wahlström et al. [29] reached a yield of 2.2 % (dry weight) for the *U. lactuca* collected at the Vattenholmen, Sweden. These differences in cellulose yield might be related to the extraction procedures and environmental conditions in which the algae are exposed before being collected. Regarding *D. antarctica*, until now, no data related to cellulose extraction have been published. However, the results obtained from the TAPPI T9 standard, the cellulose content of *U. lactuca* and *D. antarctica* are 4.02 ± 0.16 % (dry weight) and 1.21 ± 0.02 % (dry weight), respectively. Paniz et al. [15], extracted cellulose from the macroalgae *Cystosphaera jacquinotii*, obtaining a yield of 4.62 % for a cellulose content of 5 %. This indicates that the extraction of cellulose from the macroalgae *U. lactuca* and *D. antarctica* after the extraction of fatty acids presents a satisfactory yield, in addition to greater use of the algae biomass potential.

Table 1
Detailed composition of the respective fatty acids (% d.w.) in the algae samples.

Fatty acid	*U. lactuca*	*D. antarctica*
Tridecylic acid (13:0)	0.43	3.30
Myristic acid (14:0)	0.56	4.42
Palmitic acid (16:0)	21.51	63.36
Palmitoleic acid (16:1n7)	ND	1.40
Stearic acid (18:0)	2.27	13.83
Oleic acid (18:1n9c)	10.60	9.61
Linolelaidic acid (18:2n6t)	14.72	0.78
Linoleic (18:2n6c)	2.90	ND
A-Linoleic (18:3n3)	19.19	ND
Eicosadienoic acid (20:2n6)	18.65	ND
Arachidonic acid (20:4n6)	ND	1.65
Eicosapentaenic acid (20:5n3)	1.67	0.94
Other	7.49	0.70

Table 2
Result of the content of the respective classes of fatty acids for the *U. lactuca* and *D. Antarctica* samples.

Fatty acids	*U. Lactuca*	*D. Antarctica*
Saturated	25.01	84.91
Monounsaturated	12.23	11.01
Polyunsaturated	62.75	4.07

3.3. Ray – X diffraction (XRD)

Fig. 1 presents the XRD patterns of the crystal structure and the crystallinity index of the algae biomass and cellulosic materials. In the diffractograms referring to alga biomass, peaks corresponding to the impurities and untreated raw marine algae, at approximately 32°, 45° and 56° were observed [15,29]. The diffraction peaks in the cellulose samples are equivalent to the diffraction peaks of crystalline cellulose, confirming that the proposed methodology was effective. The cellulose derived from both *U. lactuca* and *D. antarctica* presented a main peak between 20° – 23° referring to the plane (110), sustaining the presence of crystalline regions [29]. Thus, the diffraction peak at 45° observed for the U-Cellulose sample, might be related to impurities corresponding to sodium chloride [15]. The crystallinity indexes for U-cellulose and D-cellulose were 68.17 % and 62.39 %, respectively, indicating that the methodology for obtaining cellulose after alkalinization and bleaching treatments as possible, removing non-cellulosic polysaccharide components. The lower crystallinity index for the D-cellulose sample may indicate the presence of non-cellulose compounds, which can be confirmed by 13C-CP-MAS, FT-IR and TGA.

3.4. FT-IR Spectrum

The FTIR spectrum for the *U. lactuca* and *D. antarctica* and the respective cellulosic materials are shown in Fig. 2. All samples present a shoulder in the range of 3500–3000 cm^{-1} and 1635–1655 cm^{-1}, which indicates the presence of stretching and bonding O—H groups. The *U. lactuca* and U-cellulosic material suffered a slight modification in the region from 3402 cm^{-1} to 3382 cm^{-1}, indicating a change from O(2) H···O(6) to O(3)H···O(5), probably caused by the alkaline treatment [30]. Also, all samples showed a peak at 2926 cm^{-1} related to the presence of asymmetric stretching of C—H bonds on –CH, $–CH_2$, and $–CH_3$ groups [31,32]. The band at 1654 and 1655 cm^{-1} in the algae indicate the presence of C═N imine/oxime stretching and the bands in the range of 1420–1440 the presence of O—H bending carboxylic acid and C—F fluor compound. In addition, algae samples do not displayed bands related to the presence of hemicellulose. Thus, a broad shoulder between 1092 and 1029 cm^{-1} might be hiding the presence of hemicellulose in the sample, which can be confirmed through the thermogravimetric analysis [15].

The FT-IR spectrum shows a difference in the range between 1200 and 800 cm^{-1}, since the cellulosic material presents characteristics marked bands [33] while the untreated algae present several weaker

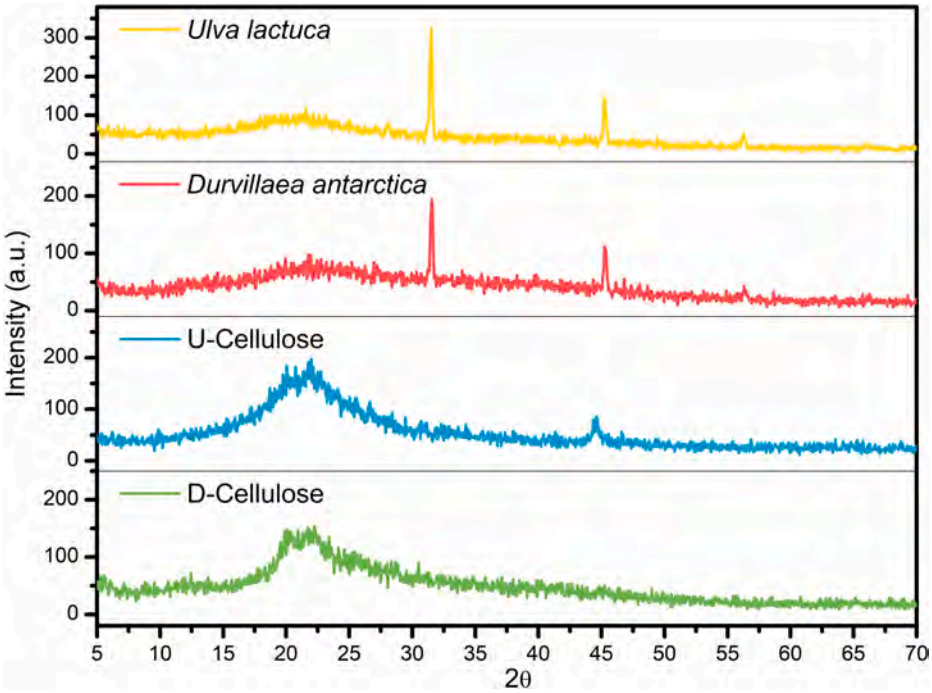

Fig. 1. Diffractograms of algae samples and cellulosic materials.

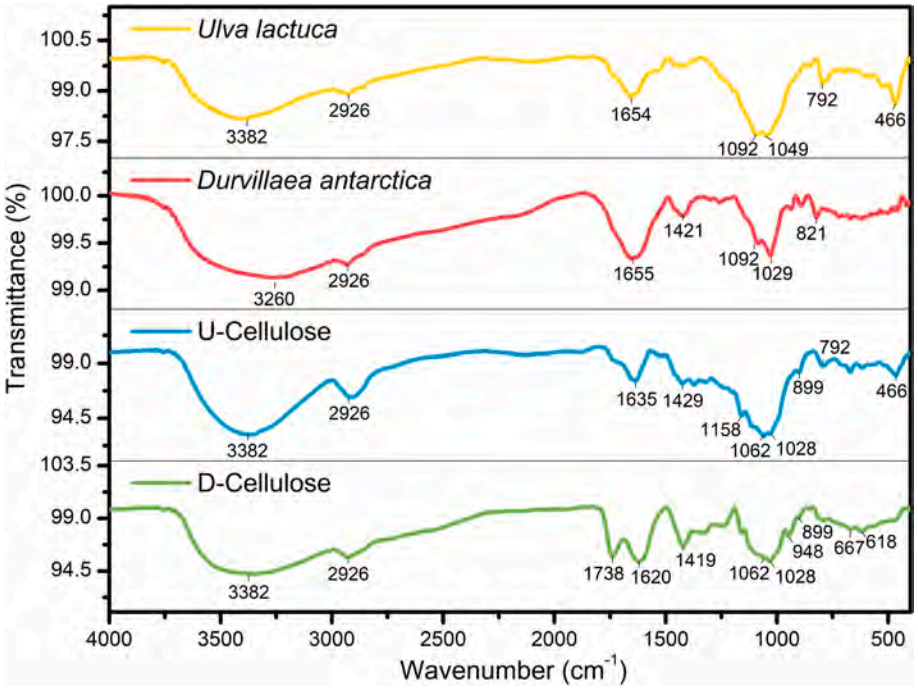

Fig. 2. The FT-IR spectrum of algae samples and cellulosic materials.

and mixed bands, which are characteristic of non-cellulosic compounds [34]. Furthermore, bands at 899 cm^{-1}, 1158 cm^{-1}, 1062 cm^{-1} and 1028 cm^{-1} represent, in cellulosic materials, the presence of β-glycosidic linkages between the anhydroglucose rings in the cellulose, asymmetric stretching of COC at the β-glucosidic linkage, CO skeletal vibration, and CO bond stretching, respectively [33]. These four bands were not all identified in the FT-IR spectra of untreated algae, since the cellulose is surrounded by several other non-cellulose materials [15].

3.5. Solid-state nuclear magnetic resonance – ^{13}C-CP-MAS

The ^{13}C-CP-MAS-NMR spectra for the cellulosic materials obtained from *U. lactuca* and *D. antarctica* are shown in Fig. 3. U-cellulose presents the typical signals of carbon associated to the anhydroglucose units of cellulose at 105.7 ppm (C1), 89.8, and 84.6 (C4), a large signal centered at 75.7 ppm (C2, C3 e C5) and 65.5 and 63.8 ppm (C6) [35]. Although the chemical shifts assigned to amorphous cellulose are more intense in C4 and C6 at 84.6 and 63.8, respectively, signals at 89.8 and 65.5 corresponding to crystalline cellulose were also detected, which is in

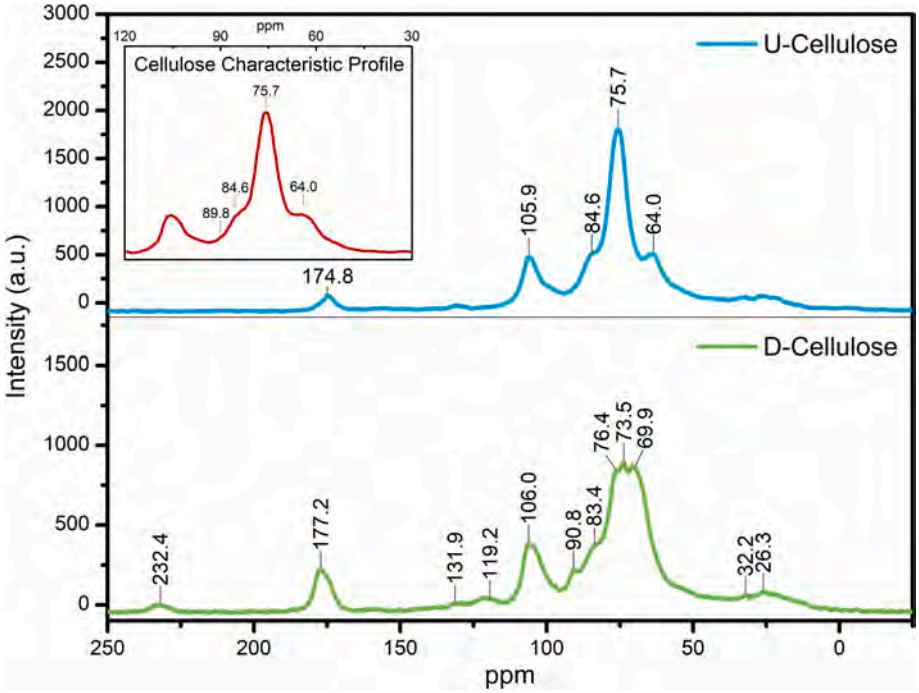

Fig. 3. NMR C13 spectra of the cellulosic materials.

agreement with XRD results [35]. On the other hand, in the cellulose spectrum of *D. antarctica*, the signal assigned to C1 is clear, nevertheless, the signals between 100 and 50 ppm are more complex, suggesting an overlapping of the signals from the cellulose with the other *D. antarctica* components, like polysaccharides, lipids, and proteins [17]. Other signals between 10 and 30, and at 130, 175, and 230 ppm, could be attributed to the resonance of aliphatic carbons, double bonds, carbonyl and carbonyl of organic acids, respectively [36]. These observations are consistent with the Infrared results, in which a band at 1738 cm^{-1} could be attributed to CO from esters [37].

3.6. Thermogravimetric analyses

Fig. 4a–b shows the TGA thermogram of the algae and the cellulosic materials obtained from *U. lactuca* and *D. antarctica*, respectively. It was noticed that the cellulosic materials from both sources exhibited greater thermal stability than their algae precursors. Weight losses of 30 and 53 were observed for the U-cellulose and D-cellulose, respectively, suggesting the presence of other non-cellulosic materials in D-cellulose structure, as previously indicated in the XRD analysis. The lower thermal resistance for algae samples is related to the presence of impurities with low molecular weight, which can generate active sites that accelerate the thermal degradation. These results indicates that the process was efficient in eliminating most of the impurities present in the algae samples [15].

The TGA and DTG profiles of algae samples displayed three well defined stages. For the cellulosic materials two different temperature ranges were observed. The first stage for all samples occurred at approximately 100 °C, corresponding to the evaporation of moisture adsorbed in the fibers and high volatile compounds [15,38]. The second stage of weight loss for *U. lactuca* and U-cellulose occurred at 230 °C and 322 °C, respectively. For the alga sample, this peak is related to the degradation of hemicellulose, cellulose, triglycerides, and other related compounds [39]. The greater thermal stability of cellulose indicates that most of the hemicellulose and other compounds were eliminated during the synthesis [40]. The *D. antarctica* sample presented a similar behavior, with peaks at 256 °C for the algae sample and 348 °C for cellulosic material. The third stage of weight loss for the algae samples occurred between 500 and 950 °C, indicating a very complex process of solid decomposition [39].

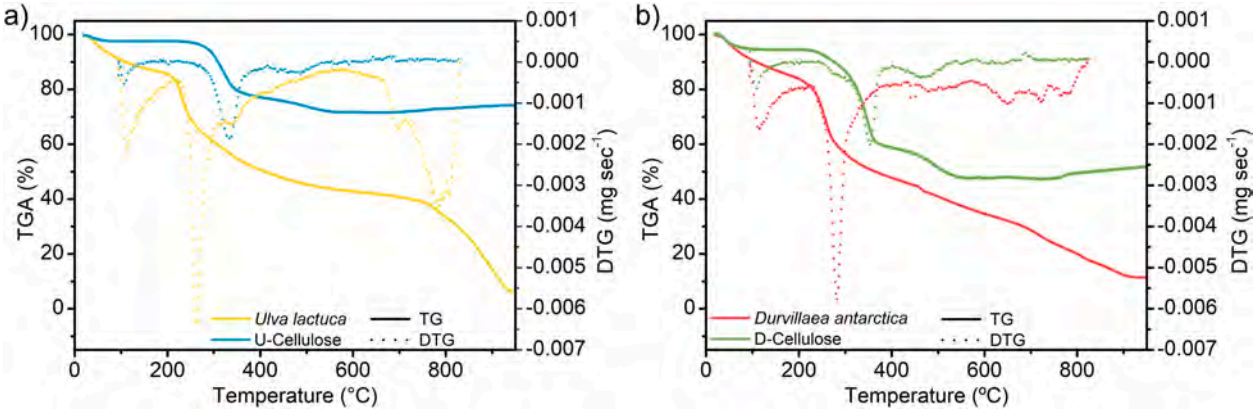

Fig. 4. Thermogravimetric analysis of algae samples and cellulosic materials.

3.7. Morphologic characterization

Fig. 5 shows the SEM images of the algae *U. lactuca* (Fig. 5a–c) and *D. antarctica* (Fig. 5d–f). It was verified a rough and inhomogeneous distribution of particles. On the surface of both samples, the presence of salt crystals was observed, which has already been reported in similar reported studies [15,40].

SEM images of cellulosic materials were present in Fig. 5g–j. The images show the presence of cellulose fibers clustered in a web-like structure [15]. This demonstrates that the methodology used in this work provided the breaking of hydrogen bonds and removed most of the non-cellulosic materials from the samples. Also, the presence of salt crystals on the surface of the samples was not noticed, indicating that the desalting step was efficient. According to the TEM image of the U-cellulose (Fig. 5k), the structure of the web-like fibers indicated the presence of nanofibers and ultrafine fibers. For the D-cellulose (Fig. 5l) revealed fibers with a diameter higher than 200 nm, being classified as ultrafine fibers. The morphology of U-Cellulose e D-Cellulose are in agreement with the results obtained for the cellulosic material of *Cystosphaera jacquinottii* using a similar methodology [15].

4. Conclusion

This work proposed an alternative for algae biorefinery through the extraction of fatty acids and cellulosic materials from the Chilean algae *D. antarctica* and *U. lactuca*. Regarding fatty acids, the *U. lactuca* sample proved to be rich in PUFA and the *D. antarctica* sample showed the highest SFA content. U-cellulose was obtained without traces of impurities, while the D-cellulose exhibited remaining compounds after extraction. Thus, the methodology proposed in this work was efficient in the extraction of ultrafine cellulose fibers, even after the extraction of fatty acids.

CRediT authorship contribution statement

Alaor Valério Filho: conceptualization, methodology, data curation, writing-original draft preparation, visualization, investigation. **Luiza Ribeiro Santana**: conceptualization, methodology, formal

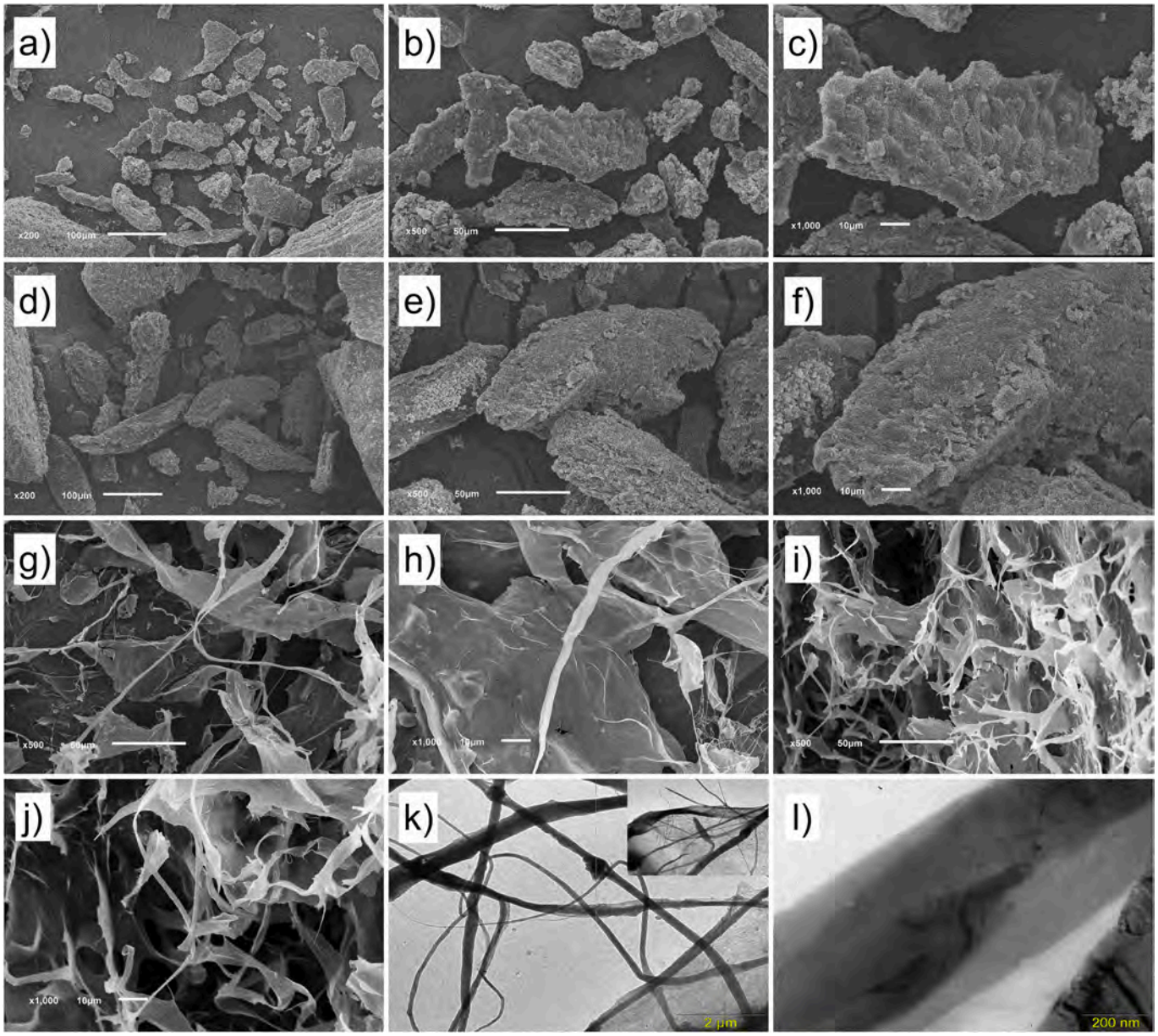

Fig. 5. SEM images of algae: *U. lactuca* (a–c), *D. antarctica* (d–f), U-cellulose (g,h) and D-cellulose (i,j). TEM images of U-cellulose (k) and D-cellulose (l).

analysis, investigation. **Naiane Garcia Motta** conceptualization, methodology, formal analysis. **Luan Ferreira Passos**: conceptualization, methodology, formal analysis**. Silvana lnes Wolke**: conceptualization, methodology, formal analysis. **Andrés Mansilla**: writing-review & editing, investigation, data curation. **Maria Soledad Astorga-España**: writing-review & editing, investigation, data curation. **Emilene Mendes Becker**: writing-review & editing, investigation, data curation. **Claudio Martin Pereira de Pereira**: writing-review & editing, investigation, data curation. **Neftalí Lenin Villarreal Carreño**: 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.

Data availability

Data will be made available on request.

Acknowledgments

The authors would like to thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES - Finance Code 001/ process number Print 88887.310585/2018-0). The Project ANID/BASAL FB210018, LMA-IQ-UNESP for TEM images. The CNANO-UFRGS for Solid State CP-MAS ^{13}C NMR and the invaluable technical support, and the LLipBio-UFPel for the FT-IR analysis. This project was also partially funded by the Cape Horn International Center project (CHIC- FB210018) and the Inova Clusters Tecnológicos Project, Innovat Hub B^3, from Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS - registration number 22/2551-0000840-2).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.algal.2023.103084.

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