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Comparing pretreatment methods for improving microalgae anaerobic digestion: Thermal, hydrothermal, microwave and ultrasound

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HIGHLIGHTS

- The effect of thermal and mechanical pretreatments on microalgal biomass was compared.
- The highest biomass solubilisation was attained for thermal pretreatment (95 °C, 10 h).
- The highest methane yield increase (72%) was also attained for thermal pretreatment.
- Biomass solubilisation and methane yield increase showed a positive correlation.

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ABSTRACT

The anaerobic digestion of microalgae is hindered by its complex cell wall structure and composition. Thus, several pretreatment methods have been used for increasing microalgae anaerobic biodegradability. Since the methane yield depends on biomass characteristics, pretreatments should be compared using the same microalgal biomass. In this study, physical pretreatments including thermal (95 °C; 10 h), hydrothermal (130 °C; 15 min), microwave irradiation (900 W; 3 min; 34.3 MJ/kg TS) and ultrasonication (70 W; 30 min; 26.7 MJ/kg TS) were evaluated in terms of microalgae solubilisation and methane yield increase in batch tests. Organic matter solubilisation was improved in all cases, with the highest increase on soluble proteins, followed by soluble carbohydrates and soluble lipids. This was attributed to the macromolecular and cell wall composition of the main microalgae species composing the biomass, i.e. *Monoraphidium* sp. and *Stigeoclonium* sp. Furthermore, the methane yield was increased by 72% for thermal, 28% for hydrothermal and 21% for microwave pretreatments, whereas no significant increase was found for ultrasonication as compared to control. Outstanding results of the thermal pretreatment should be validated in prospective pilot-scale studies in order to quantify the potential increase in biogas production upon continuous operation.

1. Introduction

In the last decades microalgae production and processing for bioenergy purposes has been a trending topic of research. Most published literature in the field is focused on biodiesel and biogas generation. However, biodiesel production has high energy and economic impacts for drying the biomass and extracting the lipid content of microalgae cells. In fact, it has been shown that viable microalgae biofuel production in full-scale systems is only possible if all processes are optimised and integrated in a biorefinery approach [23]. Particularly, anaerobic digestion has been considered a crucial step for recovering energy from residual biomass after lipid extraction [22]. Anaerobic digestion is a consolidated technology, which may be also used for converting the whole microalgal biomass into biogas, without previous drying and extracting steps.

The drawback of microalgae anaerobic digestion relies on its complex cell wall structure and composition, which hampers the hydrolysis step. In this context, pretreatment methods have been applied for improving the methane yield and/or conversion rate of microalgae and other complex organic substrates [6,18]. Studies comparing the effect of different pretreatments on microalgae showed how intensive techniques involving high temperatures and pressures (170 °C and 6 bars) or high specific energies (100–130 MJ/kg TS) reached the highest methane yield increase [1,10], but they also require a high energy input.

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In our previous studies thermal, hydrothermal, microwave and ultrasound pretreatments were effective at increasing both biomass solubilisation and methane yield [15,16,19,21]. For each method, biochemical methane potential (BMP) tests were carried out under different pretreatment conditions in order to select the best ones based on experimental results (Table 1). However, from these studies it is not possible to elucidate which is the best pretreatment technique, since microalgal biomass was not the same in all of them. Indeed, when microalgal biomass is grown in high rate algal ponds (HRAP) treating wastewater, a spontaneous mixed culture of microalgae and bacteria is produced. This biomass varies over time due to many factors, such as environmental conditions (e.g. solar radiation, temperature and precipitation), wastewater composition (e.g. presence of bacteria and toxic compounds) and occurrence of microfauna (e.g. rotifers) [14]. Species variation together with the fact that microalgae biodegradability depends on the characteristics of the cell structure and composition, calls for pretreatment methods comparison using the same microalgal biomass.

Therefore, the aim of this study was to compare different mechanical and thermal pretreatments in terms of biomass solubilisation and methane yield increase in BMP tests using the same microalgal biomass. Thermal, hydrothermal, microwave and ultrasound pretreatments were applied under the best conditions found in previous experiments (Table 1). Biomass solubilisation was evaluated in terms of total organic matter solubilisation (i.e. volatile solids) and soluble proteins, carbohydrates and lipids (i.e. fatty acid methyl esters (FAME)) concentration. BMP tests were used for evaluating the digestion rate and methane yield improvement after each pretreatment.

2. Materials and methods

2.1. Microalgal biomass

Microalgal biomass consisted of a mixed culture of microalgae and bacteria mainly composed by green microalgae (*Stigeoclonium* sp. and *Monoraphidium* sp.) and diatoms (*Nitzschia* sp. and *Navicula* sp.) The biomass was grown in a pilot HRAP used for urban wastewater treatment. The experimental set-up was located outdoors at the laboratory of the GEMMA research group (Universitat Politècnica de Catalunya) in Barcelona (Spain). The HRAP received the primary effluent from a settling tank which had a useful volume of 7 L and a HRT of 0.9 h. The primary effluent was pumped to the HRAP, which consisted of a PVC raceway pond with a paddle-wheel for mixed liquor stirring. The HRAP had a useful volume of 470 L and was operated with a HRT of 8 days. Microalgal biomass was harvested from secondary settlers with a useful volume of 9 L and a HRT of 9 h. Following, biomass was thickened in laboratory gravity-settling cones at 4 °C for 24 h for reaching total solid (TS) concentration of 3.0% (w/w). Average characteristics of harvested biomass are summarised in Table 2.

Table 2
Microalgal biomass and inoculum characteristics. Mean values (standard deviation).

Parametre	Microalgal biomass	Inoculum
pH	7.23 (0.15)	7.36 (0.06)
TS (g/L)	31.49 (0.41)	33.24 (0.17)
VS (g/L)	20.19 (0.24)	22.76 (0.06)
VS/TS (%)	64.1 (0.32)	68.5 (0.15)
COD (g/L)	28.8 (0.40)	31.3 (0.26)
Proteins (%)	58 (4)	–
Carbohydrates (%)	22 (3)	–
Lipids (%)	19 (3)	–

2.2. Pretreatment methods

Four physical pretreatment methods were evaluated: thermal, hydrothermal, microwave irradiation and ultrasonication. Pretreatment conditions were selected according to our previous studies comparing different pretreatment conditions in BMP tests [15,16,19,21] (Table 1). All pretreatments were carried out in glass bottles of 250 mL containing 150 mL of microalgal biomass. On the whole, 2 L of the same harvested microalgal were used, which allows for comparison between pretreatment methods.

The thermal pretreatment was carried out in an incubator under continuous stirring at 95 °C for 10 h, and the hydrothermal pretreatment was performed in an autoclave at 130 °C and 1.7 bars for 15 min. Bottle caps were slightly loose. After reaching the target temperature, biomass was maintained under this condition during the whole exposure time and afterwards pressure was gradually released to reach atmospheric conditions.

The microwave pretreatment was carried out in a household type microwave (Samsung M1914, 2450 MHz frequency) with an output power of 900 W and an exposure time of 3 min. The applied specific energy (34.3 MJ/kg TS) was calculated according to Eq. (1)

$$\text{Specific energy (MJ/kg TS)} = \frac{\text{Power(W)} \times \text{Time(s)}}{\text{Sample weight (g TS)} \times 100} \quad (1)$$

Finally, the ultrasound pretreatment was evaluated using a HD2070 Sonopuls Bandelin Ultrasonic Homogenizer device, equipped with a MS 73 titanium microtip probe, working with an operating frequency of 20 kHz. Ultrasonication was performed with an output power of 70 W and an exposure time of 30 min. As for microwave pretreatment, the applied specific energy (26.7 MJ/kg TS) was calculated according to Eq. (1).

2.3. Organic matter solubilisation

The soluble organic matter content in pretreated and non-pretreated microalgal biomass was compared. On the one hand, the soluble volatile solids (VS_s) concentration was measured for evaluating the total organic matter solubilisation. On the other hand, proteins, carbohydrates and lipids solubilisation was analysed using as indicators the increase in soluble proteins (ON_s),

Table 1
Best pretreatment conditions for improving the anaerobic digestion of microalgal biomass grown in wastewater treatment algal ponds.

Pretreatment	Applied conditions	Best condition	VS solubilisation increase (%)	Methane yield	Reference
Thermal	Temperature (55, 75, 95 °C); exposure time (5, 10, 15 h)	95 °C; 10 h	20.6	170 mL CH_4/g VS (61% increase)	[15]
Hydrothermal	Temperature (110, 130 °C); exposure time (15, 30 min)	130 °C; 15 min	15.0	169 mL CH_4/g VS (39% increase)	[17]
Microwave	Output power (300, 600, 900 W); exposure time (1–9 min); specific energy (16–67 MJ/kg TS)	900 W; 3 min	7.6	209 mL CH_4/g VS (78% increase)	[16]
Ultrasound	Output power (50, 60, 70 W); exposure time (10, 20, 30 min); specific energy (21–65 MJ/kg TS)	70 W; 30 min	91	196 mL CH_4/g COD (33% increase)	[19]