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Hydrothermal post-treatment of digestate to maximize the methane yield from the anaerobic digestion of microalgae

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ABSTRACT

As an alternative to applying the hydrothermal treatment to the raw algal feedstock before the anaerobic digestion (i.e. pre-treatment), one considered a post-treatment scenario where anaerobic digestion is directly used as the primary treatment while the hydrothermal treatment is thereafter applied to the digestate. Hydrothermal treatments such as wet oxidation (WetOx) and hydrothermal carbonization (HTC) were compared at a temperature of 200 °C, for initial pressure of 0.1 and 0.82 MPa, and no holding time after the process had reached the temperature setpoint. Both WetOx and HTC resulted in a substantial solids conversion (47–62% with HTC, 64–83% with WetOx, both at 0.82 MPa) into soluble products, while some total chemical oxygen demand–based carbon loss from the solid-liquid phases was observed (20–39%). This generated high soluble products concentrations (from 6.2 to 10.9 g soluble chemical oxygen demand/L). Biomethane potential tests showed that these hydrothermal treatments allowed for a 4-fold improvement of the digestate anaerobic biodegradability. The hydrothermal treatments increased the methane yield to about 200 L_{STP} CH_4/kg volatile solids, when related to the untreated digestate, compared to 66 L_{STP} CH_4/kg volatile solids, without treatment.

1. Introduction

Microalgae can be an attractive feedstock for biogas production as it contains biodegradable compounds such as carbohydrates (4–57% of total solids (TS)), lipids (2–40% of TS) and proteins (8–71% of TS) (Prajapati et al., 2013). These compounds can be converted into methane. However in practice, the methane yield from anaerobic digestion (AD) of algae (0.1–0.4 L_{STP} CH_4/g volatile solids (VS) (Marsolek et al., 2014; McGinn et al., 2012)) is much lower than the methane potential based on the theoretical yields of cellular components, estimated at 0.42, 0.50, and 1.01 L_{STP} CH_4/g, for carbohydrates, proteins and lipids, respectively (Guiot and Frigon, 2012). A number of factors may contribute to the lower than anticipated methane yield. Cellulose and pectin are the main components of the cell walls of algae, and such rigid cell walls resist hydrolysis (Passos et al., 2015). Non-hydrolysable aliphatic biopolymers called algeanans are also present in the outer wall of many green microalgae (Schwede et al., 2011). Moreover polyphenols, found commonly in brown algae, inhibit alginate lyase activity and methane production during anaerobic digestion of algae (Marsolek et al., 2014). Hence it is desirable to apply thermal treatments to the raw algae before anaerobic digestion, to disrupt the structure of algae, increase the availability of substrates, and hereafter improve the biogas yield (Keymer et al., 2013; Ometto et al., 2014; Ortega-Martinez et al., 2016).

Thermal treatment increases the solubilization of particulate organic fractions and the hydrolysis of the polymeric organic molecules. Heat disrupts the hydrogen bonds in crystalline cellulose and lignocellulose complexes. The temperature used in thermal pretreatment methods can range from below 100 °C, at atmospheric pressure (0.1 MPa) to up to 300 °C at higher pressure. Amongst them, the hydrothermal treatment refers to technologies involving reactions carried out in an aqueous solvent at elevated temperatures (above 100 °C), with the subsequent increase of pressure (Rodriguez et al., 2015). Hydrothermal technologies can be broadly categorized into two main groups, oxidative and non-oxidative techniques. Wet air oxidation is representative of the oxidative techniques, and it is usually carried out at high temperatures in the presence of an oxidant. Non-oxidative techniques are undertaken without the addition of oxidants, at a lower temperature (<200 °C) such as in thermal hydrolysis, or at higher temperatures such as in hydrothermal carbonization (Hii et al., 2014).

Wet oxidation (WetOx) can break down the large polymers and convert them to low molecular weight biodegradable compounds

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(Malik et al., 2014) with air or oxygen as oxidant (Collado et al., 2013) at 125–320 °C and 0.1–6 MPa (Padoley et al., 2012). The wet oxidation has been reported to have significant advantages over other thermal treatment technologies such as lower production of toxic degradation products, decrease of cellulose crystallinity, and high delignification potential (Arvanitoyannis, 2010).

Hydrothermal carbonization (HTC) is operated at 180–280 °C for a few minutes up to several hours without oxygen (Wirth et al., 2015). Biomass is heated in water under autogenous pressures and produces a carbonaceous fraction (hydrochar) (Sabio et al., 2016). The dissolved organic products (e.g. fatty acids, soluble proteins) and nutrients (e.g. NH_4^+, P, K^+) from the HTC can be used as substrate and nutrients for anaerobic digestion (Erdogan et al., 2015).

Instead of applying the hydrothermal treatment to the raw feedstock before AD (i.e. pre-treatment), one can consider a post-treatment scenario where AD is directly used as the primary treatment of the raw algae while the hydrothermal treatment is thereafter applied to the digestate. The anticipated advantages of such a post-treatment approach are: (1) to save energy as thermal treatment energy is spent only to recalcitrant compounds, what the solid digestate is in essence (as opposed to conventional pre-treatment where both easily biodegradable and recalcitrant compounds use the treatment energy indistinctly, and unnecessarily in the case of the biodegradable ones); (2) to improve the overall methane yield by recycling the liquid products recovered from the thermally treated digestate back to the digester; and (3) to reduce the digestate volume. Fig. 1 is illustrating the post-treatment concept (B) in comparison with the conventional AD scheme with pre-treatment (A).

The objective of this study was to determine under which temperature, pressure and retention conditions the conversion of an algal solid digestate into liquid compounds would be maximized, then to compare WetOx and HTC under the optimal conditions as determined above, namely with respect to their impact on the biomethane potential improvement of the digestate after such a post-treatment.

2. Materials and methods

2.1. Feedstock

Mixed biomass was obtained from a 4 L-upflow anaerobic sludge blanket (UASB) reactor treating raw *Scenedesmus* microalgae at an organic loading rate (OLR) of 3 g VS/L reactor.d, under pH-neutral and mesophilic (35 °C) conditions (Tartakovsky et al., 2015); hence such a biomass is a mix of undigested microalgae and anaerobic alive and dead microbes. Liquid and solid fractions of the mixed biomass were separated by centrifugation (10,000 rpm at 10 °C for 10 min). The solid fraction (128 ± 1.5*g* TS/kg and 124 ± 1.5*g* VS/kg), referred to as algal solid digestate, served as the feedstock for this study and was stored at 4 °C until further use.

2.2. Pressure hydrothermal treatment

The algal solid digestate was treated using a 300 mL pressure vessel (PV) reactor (Series 4560 Mini Bench Top Reactor System, Parr Instrument Company, Moline, IL). Five grams of the digestate with 45 mL of demineralized water were transferred into the reactor. The system was tightly sealed to ensure no leakage. Oxygen or nitrogen gas was used to achieve the WetOx or HTC treatments, respectively. The PV reactor initial air content was flushed with the gas for 2 min. After that, all the lines of the reactor were closed and then the gas (N_2 or O_2) was supplied again so to reach the pressure initial setpoint (0.1, 0.69 and 0.82 MPa). The reactor was stirred using an impeller rotating at 150 rpm. The temperature reached the setpoint (120, 170 or 200 °C) at an average rate of about 10 °C/min, then kept at the temperature setpoint for a holding time of 60 min. At initial pressure of 0.1 MPa, the pressure continued to build up to 0.2, 0.8 and 1.5 MPa after 60 min, at temperatures of 120, 170 or 200 °C, respectively, and at initial pressure of 0.82 MPa, up to 1.3, 2.0 and 2.8 MPa, at temperatures of 120, 170 or 200 °C, respectively. Then the PV reactor was cooled down to 30 °C at an average rate of about 6 °C/min. The pressure decreased down to the initial pressure according to a similar profile to that of temperature. When the PV reactor was shut down right after the temperature had reached the setpoint, this is hereinafter referred to as a holding time of 0 min. Thereafter, the volume of the gas produced was released and measured at atmospheric pressure. The gas composition was measured by gas chromatography (H_2, O_2, N_2, CO, CH_4 and CO_2).

The treated digestate samples were then analyzed for TS, VS, suspended solid (SS), volatile suspended solid (VSS), total chemical oxygen demand (tCOD), soluble chemical oxygen demand (sCOD), according to the Standard Methods (Rice et al., 2012).

2.3. Biomethane potential (BMP) assays

The assays were performed in 500 mL serum bottles, as described previously (Frigon et al., 2013). Briefly, 5 g of raw algal

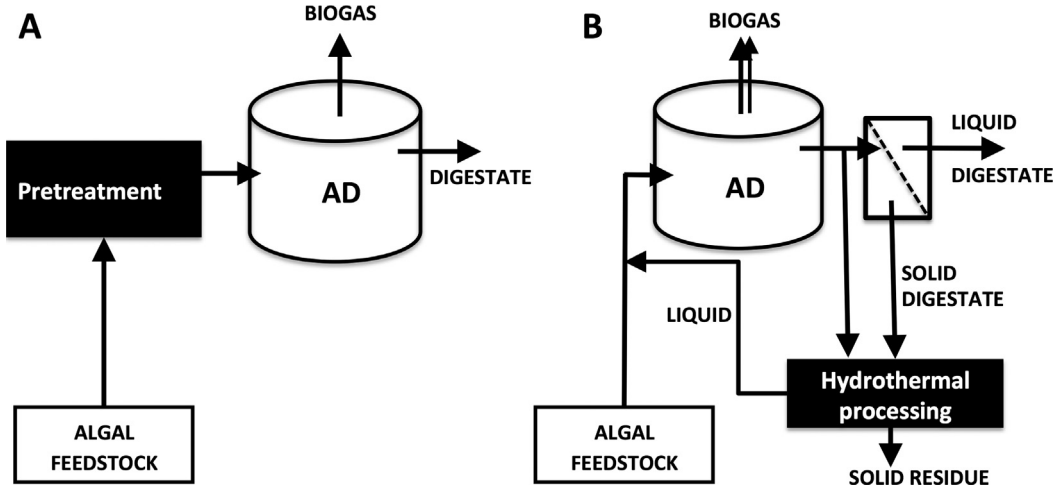

Fig. 1. Schematic illustration of the post-treatment concept (B) in comparison with the conventional anaerobic digestion (AD) approach with pre-treatment (A).

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