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Methane potential and anaerobic treatment feasibility of *Sargassum muticum*

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HIGHLIGHTS

- Methane potential of the algae *S. muticum* ranged from 166 to 208 mL CH_4/gVS.
- Alga grinding was not necessary for continuous digestion.
- Accumulation of toxic compounds was not observed at least up to 80 gTS/L.
- Up to 0.26 L CH_4/L d were obtained at loading rates of 3.2 gTS/L d.
- Accumulated non-biodegradable solids is the main efficiency limit of digesters.

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ABSTRACT

The aim of this research was to study the feasibility of anaerobic digestion of the alga *Sargassum muticum* with special attention to its biodegradability, potential toxicity caused by its salt content, alga components and intermediate process compounds, and potential limitations to continuous treatment. Specific methane potential (SMP) for three samples of *S. muticum* collected from the Galician coast (Northwest Spain) at different seasons ranged from 166 to 208 mL CH_4/gVS while accumulation of toxic compounds was not observed at alga concentrations of up to 100 gTS/L, except for one of the samples in which inhibition started at 80–100 gTS/L. Continuous digestion is feasible at alga concentration up to 100 gTS/L with methane production rates ranging from 0.14 to 0.26 L CH_4/L d at organic loading rates of 3.2 gTS/L d, but SMP dropped to 113–159 mL CH_4/gVS.

1. Introduction

Today most of the naturally produced and harvested algal biomass is an unused resource, in some cases incorporated into compost and spread on fields as enriching agents, but it is mainly dumped or left stranded to decompose on the coasts creating environmental problems (Bruhn et al., 2011; Nielsen and Heiske, 2011). Anaerobic digestion may be economical for methane production from algal biomass generated either during wastewater treatment or harvested from eutrophic water bodies. Methane conversion of whole algae or combined biodiesel and biogas production produces the highest energy output (Bohutskyi et al., 2014). Furthermore, after anaerobic digestion, digested seaweed can be used as a fertilizer, soil conditioner, sorbent or in other environmental applications.

The genus *Sargassum* is widely distributed and common in the Indo-Pacific region with 335 species and many ethnobotanical uses (Marquez et al., 2014). Although *Sargassum muticum* is a naturally growing algal on the Asian coast, it is an aggressive invasive species on European coasts, and harvesting has been suggested as a control strategy. Its uses range from aquaculture to alginate, antioxidant production or environmental uses as heavy metal sorption (Lodeiro et al., 2004; González-López et al., 2012; Marquez et al., 2014). Biogas production was another potential use of *S. muticum* biomass as earlier reported by Bird et al. (1990) and Chynoweth (2005). Seaweed species as *Sargassum* spp., *Turbinaria* spp., *Hydroclathrus* spp., *Caulerpa* spp., and *Ulva* spp. allow sustainable biomass supply for methane fermentation in the Philippines, even in household biogas digesters of rural communities (Marquez et al., 2014).

The anaerobic digestion of marine macroalgae biomass could meet two currently important needs, the mitigation of eutrophic effects and the production of renewable energy. Because of the

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abundance of seaweed biomass, harvesting and conversion can be highly desirable and convenient, chiefly for countries with long coastlines or eutrophic environments (Migliore et al., 2012). Langlois et al. (2012) performed a life cycle assessment for methane as a biofuel from the anaerobic digestion of seaweeds in European countries and concluded that seaweed could become competitive with terrestrial feedstock for biofuel production in the near future. The main benefits were obtained for greenhouse gas emissions, fossil fuel depletion, ozone depletion and marine eutrophication prevention as compared to natural gas as a fossil fuel reference.

Continuous algae digestion was carried out in one step CSTR using algae as the sole substrate (Briand and Morand, 1997; Hinks et al., 2013) or by co-digestion (Nielsen and Heiske, 2011; Schwede et al., 2013a) with farm waste or other wastes mainly at mesophilic temperatures but also at psycrophilic and thermophilic temperatures (Zamalloa et al., 2012; Kinnunen et al., 2014). Two-step anaerobic digestion systems have also been experimented with aiming to optimize the digestion process through a first step of hydrolysis followed by a second step consisting of a high rate methanogenic digester (Vergara-Fernández et al., 2008; Nkemka and Murto, 2010).

Several key obstacles to biogas production still remain, such as low biodegradability of algae biomass, potential toxicity caused by ammonia release, and potential toxicity caused by the presence of sodium and sulfate (or sulfide from sulfate reduction) for marine species (Briand and Morand, 1997; Sialve et al., 2009; Nkemka and Murto, 2010; Nielsen and Heiske, 2011; Bohutskyi et al., 2014; Kinnunen et al., 2014). Other inhibiting phenomena may be those caused by heavy metals, tannins, furanic and phenolic compounds and polyphenols (Nkemka and Murto, 2010; Jard et al., 2013; Monlau et al., 2014).

Sodium is known to be the inhibitory component of salt in the anaerobic process, when inhibitory concentrations vary from 2.3 to 27 g/L (Feijoo et al., 1995), important adaptation and antagonism effects being reported. It was also shown that ammonia inhibition started at 1.3 gNH_3-N/L for non-adapted sludge but at higher concentrations of 3–4 g/L for adapted sludge, and even up to 7 gNH_3-N/L are tolerated depending on the sludge pre-adaptation and pH (Soto et al., 1991). Furthermore, sulfur inhibition on methanogenic bacteria was reported for digestion of substrates having sea salt levels (Soto et al., 1991). Although ammonium and sulfur inhibition during anaerobic digestion of algae biomass was reported (Tartakovsky et al., 2013; Kinnunen et al., 2014), more concern exists about sodium toxicity (Lakaniemi et al., 2011; Schwede et al., 2013b; Santos et al., 2014).

Previously published results reported a low specific methane potential (SMP) of *Sargassum* ssp. ranging from 120 to 190 mL CH_4/gVSS (Bird et al., 1990; Chynoweth et al., 2001) while Jard et al. (2013) found the lowest methane potential (130 mL CH_4/gVS) for *S. muticum* among ten macroalgae studied. Low carbohydrates content, high content of insoluble fibers (which are difficult to degrade) and high levels of polyphenols (which are potential inhibitors in anaerobic digestion) were cited as the main reasons for low methane yield from *Sargassum* biomass. Available studies are scarce, and methane yields were usually obtained from batch assays, which could not discern inhibition situations (Jard et al., 2013).

The objectives of the present work were (i) to obtain the specific methane potential for three samples of *S. muticum* collected from the Galician coast (Northwest Spain) at different seasons, (ii) to identify the conditions for absence of process inhibition, and (iii) to assess the operation conditions of continuous digesters treating *S. muticum* biomass. For these purposes, batch and semi-continuous assays at different alga concentrations and organic loading rates were used.

2. Methods

2.1. Algae samples

Three samples of *S. muticum* (SM1, SM2 and SM3) were collected on the coast of A Coruña (Northwest Spain) at different seasons of the year. Algae samples were air dried (about 15% of moisture content) and conserved at ambient temperature. Before using them for anaerobic digestion experiments, algae samples were oven dried at 105 °C until they were a constant weight. Two of the algae samples were finely ground (SM1 and SM2, particle size below 3 mm), while the other (SM3) was only chopped to about 10 mm size.

2.2. Anaerobic batch assays for SMP determination

Batch assays were carried out in glass bottles of 500 mL while the liquid assay volume was 450 mL. A plastic tube connected the assay bottle to an inverted Marriotte flask of 250 mL, which contained an alkaline solution (2.5% of NaOH), so CO_2 was absorbed into the alkaline solution and the generated volume of CH_4 was measured as the displaced liquid volume (Soto et al., 1993). 75 mL of an anaerobic sludge coming from a full scale digester treating sea fish canning wastewater was used as inoculum for all assays, being the concentration into the assays 2.7 gVSS/L. Two series of anaerobic assays with different initial algae concentration of 5 and 10 gTS/L as substrate were carried out. All assays were carried out in duplicate, including blank and methanogenic activity control assays. A volatile fatty acid (VFA) mixture (acetic acid, 2 g/L; propionic, 0.5 g/L and n-butyric, 0.5 g/L) was used as substrate for the control assays, while blank assays contained inoculum but no substrate. 100 mg/L of $Na_2S \cdot 9H_2O$ and Na_2CO_3 at a ratio of 1 g/gTS of alga were added to each assay at the beginning, in order to obtain an anoxic medium and sufficient buffer capacity, respectively. Diluted HCl and NaOH solutions were used to regulate initial pH to the range of 7.0–7.1. Macro and micro nutrients were added only at the beginning of the assays (feed 1) in the amounts usually indicated for anaerobic digestion batch assays (i.e. 1 mL of each macro and micro nutrient stock solutions per L of assay medium, the composition detailed by Ferreiro and Soto, 2003), except for the methanogenic activity control assays, in which nutrients were added again in the 5th feed.

SMP of each substrate sample was obtained from the final cumulative methane production after subtracting the blank value, and dividing by the amount of dry alga fed.

2.3. Semi-continuous anaerobic digestion experiments

Through successive feeds of alga as substrate, batch assays were converted to semi-continuous digesters. This procedure aimed to provide operating conditions close to those of continuous treatment digesters, by increasing the effective concentration step by step. During feeds 2–4, dry algae substrate was added at the same amount of 5.0 gTS/L (C1) and 10 gTS/L (C2), while for feeds 5–7 the amounts added were 10 gST/L (C1+) and 20 gTS/L (C2+), as indicated in Table 1. Following this procedure, the average organic loading rate (OLR) reached during the second part of the study (feeds 5–7) was in the range of operation of semi-continuous and continuous reactors. Before adding the substrate of a new feed, the pH in the media was regulated to the range of 7.0–7.1 by adding diluted HCl solution.

Semi-continuous algae digestion was evaluated through maximum and average volumetric methane production rate (MPR) as well as substrate (TSS and VSS) removal and VFA and soluble COD accumulation.