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Optimised biogas production from microalgae through co-digestion with carbon-rich co-substrates

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HIGHLIGHTS

- Mono-digestion of *Arthrospira platensis* was stable at a low OLR of 1 g VS L^{-1} d^{-1}.
- Co-digestion with carbon-rich feedstock increased process stability.
- Co-digestion with beet silage resulted in highest methane yields of 404 L_N kg^{-1} VS.
- Co-digestion with brown seaweed allowed stability up to an OLR of 4 g VS L^{-1} d^{-1}.
- The suitability of the feedstock C:N ratio to predict process stability is limited.

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ABSTRACT

Microalgae can be used to upgrade biogas to biomethane and subsequently be digested for biogas production. However, the low C:N ratio of species such as *Arthrospira platensis* may cause ammonia inhibition and low process stability during anaerobic digestion. This study investigates co-fermentation of *A. platensis* with carbon-rich co-substrates (barley straw, beet silage and brown seaweed) at a C:N ratio of 25 to enhance biomass conversion. No synergistic effects on biomethane potential could be proven in batch fermentation tests. However continuous digestion trials showed significantly improved process stability. Mono-digestion of *A. platensis* was stable only at an organic loading of 1.0 g VS L^{-1} d^{-1}. The optimum process co-digested *A. platensis* with seaweed and achieved stable operation at an organic loading of 4.0 g VS L^{-1} d^{-1}. Co-digestion of microalgae and seaweed can be effectively applied to integrated coastal biomethane systems.

1. Introduction

The global energy demand associated with social and economic development and improvement in human health and standard of living is steadily rising. Fossil fuel consumption accounts for the majority of global anthropogenic greenhouse gases, turning climate change into one of the great challenges of the 21st century (EC, 2009). The production of biogas as a renewable energy carrier via anaerobic digestion has been shown to significantly contribute to the mitigation of greenhouse gas emissions when replacing traditional fossil fuels (Cherubini et al., 2009). A versatile spectrum of supply and usage of biogas as an energy carrier, including for electricity and heat production, the possibility for flexible demand-driven energy supply, and use as a transport fuel, makes biogas a valuable source in future renewable energy mixes.

A large variety of wet organic feedstocks including energy crops, agricultural and livestock residues, and industrial organic wastes can be converted to biogas via anaerobic digestion (Allen et al., 2016). The use of aquatic algal biomass for biogas production is a promising alternative to land-based biomass resources. Algae have many advantages such as: high biomass productivity; a more continuous biomass supply as compared with terrestrial plants; no competition for agricultural land; and its potential application in wastewater treatment (Lakaniemi et al., 2013). Another promising approach is the use of microalgae for biofixation of carbon dioxide, which may be integrated into biogas production systems (Xia et al., 2015). Biogas usually contains 25–50% carbon dioxide; this can be captured by microalgae via photosynthesis, simultaneously

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facilitating microalgae growth and biogas upgrading. Upgraded biogas with a methane concentration greater than 97% is suitable for substitution of natural gas and may be injected into the gas grid or compressed and used as transport fuel (Bauer et al., 2013). The yield of microalgal biomass can be further deployed as feedstock for the anaerobic digestion process. One disadvantage of direct feeding of biogas to microalgae cultivation systems is the accumulation of photosynthetically produced oxygen in the upgraded gas mixture. To overcome this problem, Xia et al. (2015) suggest an indirect biogas upgrading system, comprising carbon dioxide capture by carbonate solution and its use as carbon source with carbonate regeneration by microalgae. However, such system would require halophilic microalgae strains that are capable to grow under high pH conditions (Xia et al., 2015).

The prokaryotic cyanobacteria *Arthrospira platensis* (also referred to as *Spirulina platensis*), which is traditionally classified as microalgae, occurs naturally in saline environments and can be cultivated at high salt concentrations and pH values of 8.0–9.5 (Murphy et al., 2015). Previous studies on methane production from *A. platensis* indicate that medium to high specific methane yields of 293–358 $L_N\ kg^{-1}$ VS can be obtained (El-Mashad, 2013; Mussgnug et al., 2010). Thus, *A. platensis* is potentially suitable to be deployed in an integrated anaerobic digestion and indirect biogas upgrading system with carbonate/bicarbonate cycle (Xia et al., 2015). However, further information on optimal process conditions for anaerobic digestion of *A. platensis* is necessary to develop such a system.

Mono-digestion of microalgae has been shown to be difficult. Sialve et al. (2009) indicated high protein concentrations of 46–63% in *A. platensis* biomass. Extensive protein or nitrogen content leads to low C:N ratios (Ward et al., 2014). The degradation of proteins during the anaerobic digestion process results in a substantial release of ammonia, which induces inhibition of acidogenic bacteria and methanogens (Ward et al., 2014). Unionised ammonia–nitrogen and ionised ammonium–nitrogen accumulate within the fermenter liquid in equilibrium dependent on pH and temperature. The unionised ammonia–nitrogen is known to be especially toxic since it can diffuse passively through cell membranes and cause proton imbalance and potassium deficiency (Ward et al., 2014). Ammonia inhibition usually leads to volatile fatty acid (VFA) accumulation; total VFA concentrations above 4000 $mg\ L^{-1}$ can result in reduced methane production or complete process failure (Drosg, 2013).

Co-digestion of microalgae with carbon-rich feedstock has been proposed as a cost-effective and efficient approach to avoid ammonia inhibition (Ajeej et al., 2015; Sialve et al., 2009; Ward et al., 2014). This has mainly been investigated in batch anaerobic digestion tests in which significant increases in methane production up to 62% have been recorded (e.g. Fernández-Rodríguez et al. (2014), Olsson et al. (2014), Zhong et al. (2012)). A C:N ratio of 20–30:1 of the co-digestion mix is widely regarded as optimal for a balanced nutrient supply and prevention of ammonia inhibition (Ward et al., 2014).

The innovation in this study is that it is the first to assess the optimised conversion of *A. platensis* to biomethane through co-digestion with carbon-rich feedstock such as barley straw, beet silage and seaweed (macroalgae). Between 1.2 and 1.5 million tonnes of straw are harvested annually in Ireland; it is estimated that 80,000–320,000 tonnes of mainly barley and wheat straw could be available for energy production (Caslin and Finnan, 2010). Beets are a good option for crop rotations, taking advantage of existent knowledge and infrastructure gained in the production of sugar from beet in Ireland; this industry has closed in recent years (Allen et al., 2016). Furthermore, Ireland has a coastline of 5800–7500 km (dependent on high and low tide) with an abundant resource of, or potential to grow, seaweed, such as in multi-trophic aquaculture (Xia et al., 2015). Co-digestion of these co-substrates with *A. platensis* for biomethane production has not been reported in previous literature. The detailed objectives of the study are to:

- Assess the biomethane potential (BMP), specific methane yield (SMY) and the maximum organic loading rate (OLR) for stable mono-digestion of *A. platensis*.
- Investigate the performance of co-digestion of *A. platensis* with carbon-rich co-substrates in batch and continuous anaerobic digestion experiments.
- Analyse the SMY and the optimal OLR for co-digestion of *A. platensis* with barley straw, energy beet silage and brown seaweed at a C:N ratio of 25.

2. Materials and methods

2.1. Description of raw materials

Cyanobacteria *A. platensis* was investigated as feedstock in mono-digestion and co-digestion with straw, energy beet silage and seaweed. *A. platensis* was obtained as dried powder from blue-green Life Foundation Inc. (Lewes, DE, USA). Winter barley straw was harvested in July 2014 in Kinsale, Co. Cork and stored under dry conditions at room temperature until required for experimental use. Energy beets of the variety Gerty (KWS SAAT SE, Einbeck, Germany) were harvested in March 2014 in County Cork, in the South of Ireland. Whole beets were preserved by ensiling in 280 L cylindrical laboratory silos. Silos were equipped with a movable lid that allowed for the weighing down of the beets with a total mass of about 300 kg (equivalent to 0.11 $kg\ cm^{-2}$) in order to simulate pressures found in large-scale silos. Effluent formed during ensiling was drained every weekday. After a storage period of 225 days energy beets were removed from the silo, minced and frozen at −18 °C.

The brown macroalgae *Laminaria digitata* (seaweed commonly known as common kelp) was collected in West Cork in October 2014. *L. digitata* was washed with cold tap water to remove sand and impurities, cut and frozen at −18 °C. Particle size reduction of barley straw, ensiled energy beets and *L. digitata* was conducted consistently to a size of less than 5 mm using a heavy duty mincer (Buffalo Heavy Duty Mincer CD400).

Digestate from a commercial anaerobic digestion plant treating dairy slurry, grease and food waste under mesophilic conditions for biogas production was employed as inoculum for batch and continuous anaerobic digestion experiments (chemical characteristics: total solids (TS) 4.2%, volatile solids (VS) 2.5%, pH 8.1, total ammonical nitrogen (TAN) 1681 $mg\ L^{-1}$, organic acids 161.6 $mg\ L^{-1}$, conductivity 12.3 $mS\ cm^{-1}$, salinity 7.0 $g\ kg^{-1}$). Prior to experimental start-up, the inoculum was sieved through a 2 mm sieve and incubated for 7 days at 37 °C under anaerobic conditions in order to reduce residual gas production.

2.2. Chemical analyses

The TS contents of feedstocks and digestates were analysed by drying the samples at 105 °C for 24 h. VS contents were determined by burning the dried samples two hours at 550 °C. The contents of elemental carbon (C), nitrogen (N) and hydrogen (H) were measured using an elemental analyser with thermal conductivity detector (CE 440, Exeter Analytical, Coventry, UK). The TS and VS content and elemental composition of the energy beet silage was corrected for volatile organic compounds that were lost during oven drying including lactic acid, C2- to C7-volatile fatty acids, methanol, ethanol and propanol according to Weißbach and Strubelt (2008). Organic acids and alcohols were determined in