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Anaerobic digestion of wastewater generated from the hydrothermal liquefaction of *Spirulina:* Toxicity assessment and minimization

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ABSTRACT

Previous studies demonstrate anaerobic digestion of hydrothermal liquefaction wastewater (HTL-WW) is significant to the sustainability of algal biofuel development for nutrient reuse and residual energy recovery. HTL-WW contains substantial amounts of residual energy but is toxic to anaerobes. With 6% HTL-WW converted from cyanobacteria (e.g. *Spirulina*), anaerobes were 50% inhibited. In this study, zeolite, granular activated carbon (GAC), and polyurethane matrices (PM) were used during a two-round anaerobic batch test with HTL-WW, and in the presence of each material, the total methane yields were 136 mL/g COD, 169 mL/g COD, and 168 mL/g COD, respectively, being 11%, 37% and 36% higher than the control. GAC was considered promising due to its highest methane yield of 124 mL/g COD at the second feeding, indicating a good recovery of adsorption capacity. The observed low methane production rates indicated the necessity for anaerobic process optimization. The physicochemical analysis of the digestates demonstrated that most of the compounds identified in the HTL-WW were degraded.

1. Introduction

Hydrothermal liquefaction (HTL) is a thermochemical process that converts organic compounds of the feedstock into biocrude oil, solid residues, aqueous products and gas products at 250–350 °C and 5–25 MPa [1]. The process is specially appropriated to convert wet substrates, such as algae (moisture content >90 wt%). Wet feedstocks can be treated directly by HTL without a drying process, and energy-dense oil products can self-separate from the aqueous products after HTL treatment [2].

Earlier studies reported that during the HTL process, only approximately 40% of carbon and 35% of hydrogen in algal feedstocks were converted into oil [3]. From 10% to 45% of the organic compounds present in the feedstock was converted into aqueous products [3,4]. In addition, Yu et al. [5] found that 65–70% of nitrogen in the algal feedstock was converted into water-soluble compounds. The extraction and recovery of carbon and nutrients from the aqueous products is paramount to improve the overall economic viability of the HTL process [6]. As previous studies have demonstrated, the Environment-Enhancing Energy (E2-Energy) system is an integration of algal wastewater treatment with HTL of algal biomass for bioenergy production, which provides synergistic recycling of carbon dioxide from the HTL gaseous product and the nutrients from the HTL aqueous product to support multiple rounds of algae cultivation [2,5,7].

The HTL aqueous product, henceforth called HTL wastewater (HTL-WW), is a high-strength wastewater with high concentrations

Abbreviations: ATA, anaerobic toxicity assay; COD, chemical oxygen demand; C/N ratio, carbon/nitrogen ratio; E2-Energy system, Environment-Enhancing Energy system; GAC, granular activated carbon; HTL, hydrothermal liquefaction; HTL-WW, hydrothermal liquefaction wastewater; I, percent inhibition; NH_4^+-N, ammonia nitrogen; PM, polyurethane matrices; RPA, total relative peak area; SCOD, soluble chemical oxygen demand; TCD, thermal conductivity detector; TN, total nitrogen; TOC, total organic carbon; TP, total phosphorus; TS, total solid; VFA, volatile fatty acid; VS, volatile solid; VSS, volatile suspended solid.

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of chemical oxygen demand (COD, 0.42–104 g/L), high concentrations of ammonia (1.86–7.07 g/L), and a wide variety of organic compounds. These compounds include sugars, alcohols, ketones, cyclic hydrocarbons, and various nitrogen-containing compounds [2,8–10].

Anaerobic digestion is a natural choice for the treatment of highly concentrated effluents, which proved feasible for the treatment of HTL-WW [9,11]. According to Ward et al. [12], anaerobic digestion produces a nutrient-rich digestate that is ideal for the cultivation of algal species. Thus, a closed loop for an integration system, such as the E2-Energy paradigm, can be realized based on the nutrients cycle in which algae can be cultivated in anaerobically treated HTL-WW, and then harvested and converted to produce more algal bio-crude oil. This system is anticipated to enhance the cost-effectiveness of the biocrude oil production and improve the feasibility and sustainability of algal biofuel production.

However, HTL-WW could be inhibitory or toxic to anaerobes due to its high ammonia concentrations or recalcitrant organic compounds (e.g., phenols), which limits the digestibility and biogas production [9]. Potential detoxification methods include adsorption, ozonation, and biological treatment with adapted or specialized microbes. Zeolite and activated carbon have a high degree of porosity, showing a great capacity for pollutant adsorption [13,14]. Moreover, Zhou et al. (2015) observed the positive effects of activated carbon in the anaerobic stabilization of HTL-WW converted from swine manure. On the other hand, microorganisms organized in biofilms showed better responses than suspended biomass when used in tests for acute and chronic toxicity [15]. Reticular polyurethane foam has a high specific surface area that can reach 2400 m^2/m^3 and a porosity of 97% [16]. Polyurethane foam has been widely studied as a support matrix to immobilize anaerobic biomass and as an isolation material to prevent the release of hazardous materials into the environment [17,18]. This material has been primarily used in fixed-bed reactors and provides adequate environmental conditions for biomass growth and retention.

This study focuses on the characterization and quantification of the HTL-WW composition, with an emphasis on the toxicity to anaerobes, and explores methods for its detoxification. Thus, an anaerobic toxicity assay (ATA) was conducted to determine the level at which HTL-WW causes an adverse effect on the anaerobic digestion process. Two types of adsorbents, zeolite and activated carbon, were used to evaluate the toxicity reduction towards a microbial consortium during the anaerobic treatment of HTL-WW. In addition, polyurethane matrixes (PM) were also used to provide a suitable environment for the biofilm formation during the anaerobic digestion process of highly toxic HTL-WW.

2. Materials and methods

2.1. HTL process

The HTL process using *Spirulina* powder (from Cyanotech, Kailua-Kona, Hawaii, USA) as feedstock was conducted in triplicate in a 2 L stirred bench scale reactor (Parr Instrument Co., Moline, USA), according to the method by Pham et al. [13]. The reactor was filled with 600 g of feedstock at 20% solid content (80% water), sealed, and then purged three times with nitrogen to build up an initial pressure of 607–635 kPa to prevent water from boiling. The temperature was raised to 300 °C, maintained for 30 min and then rapidly cooled to room temperature (25–30 °C) using circulated tap water. The pressure during the process increased from 0.7 MPa to 8–9 MPa, and at the end, the pressure was 0.9–1 MPa. A typical temperature-pressure diagram under the HTL process is also available in supplementary data (Fig. S1). The gaseous product was vented, and the crude oil, solid residue, and wastewater were collected into sampling cups for separation. HTL-WW was separated from the crude oil and solid residue using a 1.0 μm pore size glass fiber filter. Filtered HTL-WW was used for the following analysis and experiments.

2.2. Anaerobic toxicity assay (ATA) of HTL-WW

An ATA was conducted to determine the potential toxicity of HTL-WW. The ATA was primarily based on the method and feedstock preparation proposed by Moody et al. [19] with one modification: acetate (1 mol/L) was utilized instead of glucose, according to Lisboa and Lansing [20]. They determined that compared with glucose, acetate as the standard feedstock produced more methane in the control bottles, facilitating the discernibility of the potential inhibition from the ATA. An inoculum and a standard feedstock were assayed without HTL-WW as controls and in combination with varying percentages of the HTL-WW as potential toxicants, as shown in Table 1. The inclusion ratios of HTL-WW were performed according to previous results obtained by Zhou et al. [21]. The inoculum from an anaerobic reactor treating secondary sludge was provided by the Urbana-Champaign Sanitary District (IL, USA) with total solids (TS) of 2.61%, volatile solids (VS) of 1.92%, and volatile suspended solids (VSS) of 18.6 g/L. Sludge addition was performed according to Angelidaki et al. [22]. The inoculum was degassed for 2–5 days until there was no significant methane production. Deionized (DI) water was added to the substrate to maintain a constant headspace volume in each bottle, while the headspace was sampled every day during the short testing period (6 days).

All ATA tests were performed in triplicate, with 50 mL of total liquid volume and 72 mL of headspace purged with nitrogen. Biogas production and methane content were measured daily. The volume and removal of biogas during the tests were measured and performed with glass syringes equipped with a 20-gauge needle. The methane content was determined by direct injection into the gas chromatography equipped with a thermal conductivity detector (GC-TCD) described in Section 2.4. The results were used to calculate the percent inhibition (I) of methane production for each substrate inclusion ratio using Eq. (1):

$$I = \left(1 - \frac{V_{CH_4} test}{V_{CH_4} Fed\ control}\right) * 100 \quad (1)$$

where V_{CH_4} *test* is the methane volume produced at the selected time for each potential toxicant percentage inclusion, and V_{CH_4}*Fed control* is the volume of methane produced at the selected time for the feed control. A negative value of "I" implies that the substrate enhances the methane production.

2.3. Effect of adsorption and biofilm on methane production enhancement

Anaerobic batch tests were assembled in 246 mL serum bottles with 100 mL of working volume and were performed in a 37 °C shaking incubation chamber. Each flask was initially supplied with 50 mL of inoculum sludge, 6.5 mL of HTL-WW and 43.5 mL basal medium [22]. Three types of conditions were tested, as shown in Table 2: the addition of 2 g/L zeolite, 2 g/L granular activated carbon (GAC, Calgon F-400), and 2 g polyurethane matrix (PM) [23,24]. The zeolites used were obtained from St. Cloud Mine (St. Cloud Zeolite, Winston, NM) and were preprocessed into a standard mesh size of 14 × 40. The materials were rinsed thoroughly with DI water until the turbidity was low; they were then soaked in 10% saltwater overnight and rinsed once more with DI water.

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