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Integration of fermentative biohydrogen with methanogenesis from fruit–vegetable waste using different pre-treatments

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ABSTRACT

Fruit–vegetable waste was subjected to three different pre-treatments to enrich the two-stage biofuel production potential. The fluorescence excitation–emission matrix (EEM) spectra coupled with parallel factor (PARAFAC) analysis and fluorescence regional integration analysis were utilised to investigate dissolved organic matter degradation during two-stage fermentation process. The results showed that compared with that of alkali and enzyme pre-treatments, the acid pre-treatment resulted in the maximum biogas production rates and proportion in the hydrogenogenic stage (10.11 mL/h, 41.2% hydrogen) when combined with the methanogenic process (4.67 mL/h, 76.1% methane). In addition, the analysis of soluble metabolites composition indicated that both ethanol- and butyric acid-type fermentation processes had taken place as a result of acid pre-treatment, whereas only butyric acid-type fermentation resulted from alkali and enzyme pre-treatments. The PARAFAC analysis modelling of the EEM spectra revealed three fluorescent components in the effluents of three fermentation stages and assumed that the projected characteristic value may be used as a rapidly obtained indicator for substrate degradation and system stability of a two-stage biofuel production process.

1. Introduction

Fruit–vegetable waste (FVW) is the most abundant organic resource produced from food markets and households. Reports have estimated that the annual yield of FVW is more than 100 million tons in China [1]. However, FVW treatment options are limited in China due to regulations and the availability of suitable techniques. Concerns over vermin attraction, odour, leachate production and greenhouse gas emissions have led to many highly putrescible waste streams, such as FVW being disposed to landfills [2]. Due to its high biogas potential, fermentative hydrogen production is a promising energy-saving and energy-producing process for pre-treating and degrading highly putrescible waste streams, such as FVW [3–5].

Sequential hydrogen and methane processes are more efficient than independent hydrogen processes. In the former, hydrogen can be recovered during hydrolysis and the decomposition of complex substrates, such as proteins, carbohydrates and lipids, into smaller units. The latter require longer hydraulic detention times and produce methane [6]. In a two-stage process, the residual substrates from the first stage can be reduced at the second-stage to yield an energy conversion ratio of 89% [7].

Dissolved organic matter (DOM) is the most active component in the anaerobic fermentation process, and its chemical and structural characteristics are most likely to affect its biodegradation [8]. As a simple, sensitive and non-destructive technique, fluorescence excitation–emission matrix (EEM) spectroscopy is often used to trace the composition and biogeochemical cycling of DOM [9,10]. However, the EEM spectra of DOMs in fermentation effluent are composed of various types of overlapping fluorophores, which can be very difficult to interpret. Parallel factor analysis (PARAFAC) can decompose fluorescence signals into underlying fluorescent phenomena and accurately quantify them by fluorescence regional integration (FRI) analysis [11]. Guo et al. [8] observed the changes in the fluorescent components that occur in the DOM of a swine fermentation slurry through fluorescence spectroscopy using a PARAFAC analysis. Thus, the combination of EEMs and PARAFAC is a powerful tool in the assessment of DOM dynamics during the two-stage anaerobic fermentation process. Most of the challenges involved in developing a two-stage fermentation process

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concern the initial hydrogen-producing stage. Additional pre-treatment processes are necessary to improve the availability of carbohydrates from FVW to hydrogenogens. To date, the effects of various pre-treatment methods have been systematically investigated [12–14]. In contrast, few studies have analysed the metabolic mechanism of FVW in response to different pre-treatments using a combination of EEM and PARAFAC analysis.

The objectives of this study are evaluated three pre-treatments for FVW by the biogas energy productivity, soluble metabolites characteristic and present an integrated substrate degradation and stability evaluation method based the structural characteristics of DOM using EEM spectra with PARAFAC analysis. The kinetics of the two-stage process were analysed to determine important parameters, such as the maximum hydrogen/methane production rate, lag time during the process and varied soluble metabolite composition in response to pre-treatment.

2. Materials and methods

2.1. Materials

FVW was collected from a market in Beijing, China. The characteristics of FVW are shown in Table 1. The FVW was composed of (w/w basis) lettuces (40%), lemon (40%) and grape (20%). The larger chunks of FVW were chopped into small pieces measuring approximately less than 5 mm in length and width.

2.2. Seed microflora

The microflora (piggery anaerobic digested residues, PADRs) were enriched from an anaerobic reactor used for treating pig manure. Before being used, the PADRs were diluted by an equal volume of distilled water and then sieved through a 100-mesh sieve to remove stones, sand, and other coarse matter. The characteristics of the PADRs were as follows: a pH of 7.8, a total COD (TCOD) of 59.09 g/L, a total solids (TS) content of 21.2%, a volatile solids (VS) content of 9.95%, a suspended solids (SS) content of 19.1%, a volatile suspended solids (VSS) content of 9.15% and a gravimetric moisture content of 78.8%.

2.3. Experimental design

Acid and alkali pre-treatments were performed by mixing 10.0 g dry-weight FVW with 50 mL of dilute HCl (or NaOH) aqueous solution at 0.25% (or 1.0% (w/v)) concentration, and mixed for 24 h at 37 ± 1 °C in serum bottles. 10.0 g dry-weight FVW were mixed with 50 mL cellulase R-10 (Yakult, Japan) aqueous solution at 10 mg/L concentration and soaked for 48 h in serum bottles. The bottles were placed in an orbital shaker at 48 ± 1 °C since the optimal working condition for cellulase R-10 is: the pH level of 4.5–6.5 and the temperature of 45–60 °C. The mixture was then neutralised to pH 6.0 by the addition of 2.0 M NaOH (or HCl) after the pre-treatments.

The two-stage anaerobic fermentation of FVW that integrated the fermentation of biohydrogen and methanogenesis was carried out by varying the pre-treatment methods. Batch experiments were conducted using pretreated food waste as substrates (initial loading rate at 15 g VS/L) and performed in triplicate in 500-mL serum bottles. 25 mL PADRs were added to each bottle. The working volume was adjusted to 300 mL using distilled water. The bottles headspace was purged with nitrogen gas to provide anaerobic conditions. The serum bottles were placed in water bath with its vibrator rotating at 150 rpm at 37 ± 1 °C to provide better contact among substrates. Control bottles were also prepared using the FVW without any pre-treatment at the same time.

Each experiment included two stages, named hydrogenogenic stage (87 h) and methanogenic stage (300 h). In the hydrogenogenic stage, the initial pH was adjusted to 6.0 using 2 M NaOH or HCl. In the methanogenic stage (after 87 h, when no hydrogen production), the pH was adjusted to 7.5, and there was no need to adjust the pH condition during the following experiment process.

Table 1
The characteristics of FVW.

Parameters	Lettuces	Lemon	Grape	Mixed FVW
Moisture content (%)	93.32	83.92	86.61	88.95
Ash content (%)	18.34	3.42	1.40	9.84
Lignin (%)	36.79	21.57	21.65	33.75
Hemicellulose (%)	13.27	17.49	4.71	13.53
Cellulose (%)	7.46	9.85	0.78	7.04

2.4. Analytical methods

The TS, VS and pH were determined according to standard methods [15]. The total gas production was measured by the displacement of saturated brine solutions. The composition of the biogas (H_2, CH_4 and CO_2) in the reactor's headspace was analysed using a gas chromatograph (GC) (Perkin Elmer Clarus 500, New Jersey, USA) equipped with a thermal conductivity detector (TCD) and a 2-m high-porosity polymer bead-packed column.

The volatile fatty acids (VFAs) and ethanol concentration were determined using a GC equipped with a flame ionisation detector (FID) and a 30 m × 0.25 mm × 0.25 mm fused-silica capillary column (Agilent DB-VRX). Helium was used as the carrier gas at a flow rate of 1.2 mL/min and a split to a column flow ratio of 10:1. The injection temperature was 200 °C. The oven temperature was initially set to 40 °C with a holding time of one minute; the temperature was increased to 220 °C thereafter at a rate of 9 °C per minute.

2.5. Model analysis

The cumulative hydrogen or methane production during the batch experiments followed the modified Gompertz equation [16,17]:

$$H = P\left\{exp\left[\frac{R_m e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

where H is the cumulative hydrogen/methane production (mL), P is the hydrogen/methane production potential (mL), R_m is the maximum hydrogen/methane production rate (mL/h), e is 2.72, λ is the lag-phase time (h) and t is the incubation time (h). The corresponding values of P, R_m and λ for each batch were estimated using Origin 7.5, a scientific graphing and data analysis software program.

2.6. EEM spectra scan

Samples were collected from the initial fermentation broth after different pre-treatments at the end of the hydrogenogenic and methanogenic stages. The suspensions were centrifuged at 12,000 rpm for 10 min at 4 °C and filtered through a 0.45-μm membrane filter. Before fluorescence analysis was performed, the total organic carbon (TOC) was measured using a Shimadzu TOC-TNM analyser. All of the sample concentrations were similarly adjusted to make them mutually comparable. The final TOC content was approximately 8 mg/L. Fluorescence EEM spectroscopy was performed on each sample using a Hitachi F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at room temperature. The slit widths were adjusted to 10 nm for both the excitation