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A comparison of treatment techniques to enhance fermentative hydrogen production from piggery anaerobic digested residues

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ABSTRACT

To accelerate the start-up process and enhance the efficiency of a hydrogen production system, piggery anaerobic digested residues (PADRs) were subjected to several different treatment methods to enrich the hydrogen-producing bacteria. Eight treatment methods were performed on the PADRs, including acid, alkali, heat, drying, ultrasound, aeration, sodium 2-bromoethanesulfonate (BES), and chloroform. The best method was found to be drying at 60 °C for 48 h, which maximised the total biogas production and the hydrogen fraction without causing any methane production. The volatile fatty acids (VFAs) found after the drying treatment were acetate and butyrate, which together accounted for 91.9% of all VFAs, indicating that butyric acid fermentation was established. Due to the drying treatment, the metabolites produced from the biodegradable DOM were utilised more rapidly, more completely, and with the least amount of hard-degradation organic matter content obtained, according to EEM fluorescence spectra. This drying treatment offers a promising method to¹ improve bio-hydrogen production.

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1. Introduction

Due to diminishing fossil diesel reserves and their concomitant environmental consequences, there is a pressing need to develop non-polluting, renewable energy sources. Compared with traditional energy sources like fossil fuels, hydrogen is a promising energy candidate because of its high 122 kJ/g energy yield; additionally, its sole combustion product is water vapour instead of dangerous greenhouse gases. Hydrogen can be

obtained by biological, thermochemical, and electrochemical processes. Known as less polluting and less energy intensive than other options, the biological production of hydrogen is the most environmentally friendly route and offers an opportunity to use renewable resources sustainably [1].

Biological processes for hydrogen production include the biophotolysis of water, dark anaerobic fermentation, and the photofermentation of organic matter [2,3]. Among the various biological hydrogen production methods, dark fermentative

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hydrogen production is widely recognised as a practical and applicable method with a high production rate, converting organic waste into environmentally sound materials [4]. However, the current fermentation method used to produce hydrogen has major drawbacks, such as low hydrogen productivity, lengthy retention times, and expensive feedstock. To improve the bio-hydrogen production efficiency and stability of a continuous hydrogen production system, it is important to develop treatment methods that inhibit the activity of hydrogen-consuming bacteria and enrich hydrogen-producing bacteria [5].

Based on the physiological differences between hydrogen-producing and hydrogen-consuming bacteria, various treatment methods have been investigated by researchers in half-scale and lab-scale plants, including heat, alkali, acid, chemical, and ultrasonic methods [6–8]. Enrichment by heat treatment is the most common technique to screen for hydrogen-producing bacteria [9]; it eliminates non-spore forming and hydrogen consuming microorganisms such as methanogens and initiates spore germination in *Clostridia* by altering their germination receptors. However, high temperatures can also kill beneficial microorganisms that play a positive role in the anaerobic fermentation process. Chemicals such as 2-bromoethanesulfonic acid and chloroform can also be used to eliminate methanogens [10]. There are disagreements about the best treatment method to enrich hydrogen-producing bacteria. Akutsua's [11] experimental results show that different inoculum sources have specific bacterial structures and that even the best treatment method cannot mimic these ideal structures.

Numerous trials have been conducted on the ideal seed for hydrogen production using different types of organic wastes, including waste activated sludge [12], anaerobic digester sludge [13], methanogenic granules [14], and anaerobic digested organic fractions of municipal solid waste [6]. Until now, the residues from the industrial anaerobic reactors that were used to treat pig manure have seldom been used as hydrogen producing inoculum sources, so here they were used to evaluate the effectiveness of various treatment methods for enriching hydrogen-producing bacteria. In fact, piggery anaerobic digested residues (PADRs) are an ideal substrate for anaerobic fermentation hydrogen production, containing a rich diversity of pro-hydrogen microbacteria, carbon sources, and nutritive elements. In this study, PADRs were used as the inocula to compare the efficiency of eight different methods of hydrogen producing bacteria enrichment: acid, alkali, heat, drying, ultrasonic, aeration, sodium 2-bromoethanesulfonate (BES), and chloroform treatments. The effects of the volatile fatty acid structural characteristics and the DOM EEM fluorescence spectra on the hydrogen production metabolic process, as well as the evolutions of the pH, the total organic carbon (TOC), the inorganic carbon (IC), and the total nitrogen (TN), were also investigated.

2. Methods

2.1. Materials

The PADRs were originally obtained from an anaerobic reactor used for treating pig manure. Before their use, 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 solid (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%.

2.2. Culture medium

The medium used for H_2 fermentation contained 10 g/L glucose as the carbon source and sufficient inorganic supplements, including NH_4HCO_3 (0.5 g/L), $NaHCO_3$ (6.72 g/L), K_2HPO_4 (0.5 g/L), $MgSO_4 \cdot 7H_2O$ (0.1 g/L), $FeSO_4 \cdot 7H_2O$ (0.5 g/L), $CaCl_2 \cdot 2H_2O$ (0.005 g/L), NaCl (4.0 g/L), yeast extract (2.0 g/L), peptone (2.0 g/L), and a trace element solution (1.0 mL/L).

2.3. Batch experiments

Batch experiments were performed in triplicate in 500 mL serum bottles that contained 200 mL of media, which were placed in a water bath with its vibrator rotating at 150 rpm at $37 \pm 1^\circ C$. Then, 30 mL of treatment sludge and the previously mixed medium were added to the bottle. The total volume was increased to 200 mL using distilled water, and the initial pH was adjusted to 6 using 2 M NaOH and 2 M HCl. The reactor's headspace was purged with nitrogen for 5 min to provide anaerobic conditions. Fermentation was deemed complete once no gas was produced for 48 h.

The acid treatment was performed by adding 1.0 M HCl to decrease the pH of the PADR solution to 2.0, where it was held for 24 h. Then, the solution was readjusted to a pH of 6.0 with the addition of 1.0 M NaOH. The alkali treatment was conducted by using 1.0 M NaOH to adjust the pH to 12.0, where it was maintained for 24 h. Then, the pH was readjusted back to 6.0 using 1.0 M HCl. The heat treatment was performed by immersing the experimental mixture in a boiling water bath for 15 min, followed by cooling. The drying treatment took place at $60^\circ C$ for 24 h to evaluate the influence of low temperature on the thermal treatment's effectiveness. In the aeration test, the PADR samples were aerated using an air pump for 24 h. The ultrasonic treatment was performed using an ultrasonicator (Branson, Danbury, CT, USA) operating at 42 kHz for 30 min. The chemical treatments were carried out by the separate addition of chloroform and BES into the PADRs (5 and 2.5% concentrations, respectively), maintaining those conditions for 24 h.

2.4. Analytical methods

The TS, VS, and pH were determined according to standard methods [15]. An elementary analysis was undertaken using the Vario EL element analyser (Elementar, Germany). 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 Gas Chromatograph) equipped with a thermal conductivity detector (TCD) and a 2 m high porous polymer bead-packed column.

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