Energy Conversion and Management 119 (2016) 142–150

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Ultrasonication pre-treatment of combined effluents from palm oil, pulp and paper mills for improving photofermentative biohydrogen production

Pretty Mori Budiman, Ta Yeong Wu *

Chemical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form 21 March 2016
Accepted 23 March 2016
Available online 19 April 2016

Keywords:
Palm oil mill effluent
Photofermentation
Pulp and paper mill effluent
Ultrasound
Rhodobacter sphaeroides
Wastewater reuse

ABSTRACT

The improvement of batch photofermentative biohydrogen production was investigated using ultrasonication pre-treatment on a combined effluent of palm oil and pulp and paper mills. The effects of the amplitude (30–90%) and ultrasonication duration (5–60 min) were investigated in terms of their influences on the biohydrogen yield and chemical oxygen demand (COD) removal. The recommended ultrasonication parameters were found at the higher ranges of amplitude and duration (A70T45). Using A70T45 ultrasonication, the production of biohydrogen at 30 °C could be enhanced up to 8.72 mL H_2/mL_{medium}, with a total COD removal of 36.9%. During pre-treatment at A70T45, an energy input of 775 J/mL was supplied to disintegrate complex compounds into simpler structures. As a result, an increase in the soluble organic matter concentration was achieved, which led to enhanced biohydrogen production. On the other hand, the lowest biohydrogen yield (4.67 mL H_2/mL_{medium}) and total COD removal (28.8%) were obtained in the control without pre-treatment. The enthalpy of the photofermentation process was estimated to be 141.1 kJ/mol with a threshold temperature of 30.9 °C based on a modified Arrhenius approach.

1. Introduction

The prospect of replacing fossil fuels with hydrogen as an energy source has been widely investigated by researchers [1–3]. With the gradual development of fuel cell technology, many studies have suggested that hydrogen has a high potential to replace fossil fuels because of its clean combustion product and the high energy content [1]. Among the existing production methods, biological hydrogen production has emerged as a more sustainable approach compared to thermo and electro-chemical processes, mainly due to its ability to use biomass and wastewater as renewable energy sources and the application of the process at ambient temperature and pressure [2,3].

Photofermentation is known to be one of the most favorable biological approaches to produce biohydrogen because of its high theoretical conversion yield, absence of oxygen-evolving activity, possibility of using a wide range of light, and ability to reuse waste materials as substrates [4]. However, the low biohydrogen yield and low conversion efficiency have limited the practical feasibility of biohydrogen production. In photofermentation, biohydrogen was produced by the nitrogenase-catalyzed photodecomposition of organic compounds by photosynthetic bacteria or purple non-sulfur bacteria, such as *Rhodobacter sphaeroides* [5]. In a nitrogen-deficient environment, these bacteria are capable of reducing protons into hydrogen gas using extra energy [3]. In the past, wastewater was diluted with water or a defined medium before it was reused as a substrate in a photofermentation process. For example, Eroğlu et al. [6] reported the successful reuse of olive mill wastewater diluted with water to a concentration of 4% (v/v) as a photofermentation substrate to produce biohydrogen at up to 16 mL H_2/mL_{medium}. However, a very low light conversion efficiency of 0.12% was obtained in this process [6]. Similar biohydrogen productions were also reported by Seifert et al. [7] and Suwansaard et al. [8]. Seifert et al. [7] achieved a biohydrogen yield of 2.2 mL H_2/mL_{medium} with 1.7% light efficiency, whereas Suwansaard et al. [8] obtained 1.1 mL H_2/mL_{medium} with 1.07% light efficiency. In their study, Seifert et al. [7] diluted brewery wastewater up to 10% (v/v) with Biebl and Pfennig mediums. Despite the advantages of the photofermentation process, the high energy requirement during the nitrogenase-catalyzed reaction and the low hydrogen production efficiencies have become major concerns in industrial applications.

* Corresponding author.
E-mail addresses: wu.ta.yeong@monash.edu, tayeong@hotmail.com (T.Y. Wu).

http://dx.doi.org/10.1016/j.enconman.2016.03.060
0196-8904/

In this study, palm oil mill effluent (POME) and pulp and paper mill effluent (PPME) are mixed and reused as a combined photofermentation substrate to produce biohydrogen by using purple non-sulfur bacteria, namely, *R. sphaeroides* NCIMB 8253. Typically, POME is treated using a ponding system [9], but this treatment method accumulates large amounts of sludge, causes an uncontrollable release of greenhouse gases, requires a large area of land and results in the lowest utilization of renewable resources [10]. On the contrary, high contents of organic acids, carbohydrates, lipids, minerals, protein, and nitrogen have led to the successful reuse of POME as a growth and production medium for various microorganisms [11,12]. However, dilution was necessary to reduce the turbidity of the POME for encouraging the growth of photofermentative bacteria [13]. Furthermore, Budiman et al. [14] reported that the highest biohydrogen yield of 4.67 mL H_2/mL_{medium} could only be obtained after 25% (v/v) POME was combined with PPME as a diluting agent. To reduce the water consumption, the reuse of PPME as an alternative diluting agent was introduced due to the lighter color of this effluent in both the present and previous studies [13,14]. The pulp and paper mill industries are widely known to consume a large amount of water in their manufacturing process, with an estimated 60 m^3 of wastewater generated for each ton of paper produced [15]. In Malaysia, a local board and paper mill is estimated to generate 25,000 m^3/day of effluent [16]. The reutilization of POME and PPME as a combined substrate was expected to produce biohydrogen in a sustainable manner and at the same time remove contaminants from the effluent before it is discharged into waterways.

Ultrasonication is an irradiation of ultrasound with frequency beyond the normal hearing range of humans (>15–20 kHz). It has been widely used as a green technology to treat various wastewaters with higher degradation rates and shorter reaction times compared to conventional methods [17,18]. Wu et al. [18] described the advantages of using ultrasound technology as an environmentally friendly, compact and low-cost wastewater treatment option. Ultrasonication is expected to decompose complex organic pollutants in the effluent due to the formation and collapse of high-energy cavitation bubbles [19]. This phenomenon will lead to the disruption of cell wall structures, reduction of particle sizes, increase in material porosity and increase in the bioavailability of organic matter because of the breaking down of lignocellulosic materials [20,21]. Recent studies have shown that the use of ultrasound to pre-treat lignocellulosic biomass could enhance the production of biogas during the bioconversion process. For example, an application of ultrasound technology with an energy input of 182.21 kJ led to an increase in the biohydrogen production rate by a factor of 5.1 during the photofermentation of PPME [22]. Similarly, Oz and Uzun [23] reported that the application of ultrasound at 0.4 W/mL for 10 min prior to the anaerobic digestion of olive mill wastewater increased the production of biogas and methane by up to 20%. Both studies reported that the bioenergy yield was improved due to the remarkable increase of bioavailable organic matter. However, no study was found using ultrasonication to pre-treat a combined effluent from two industries for improving biohydrogen production through a photofermentation process. It was hypothesized that ultrasonication would help solubilize the organic matter in the combined effluents. Thus, the supplementation of nutrients was not necessary to boost biohydrogen production due to the abundance of bioavailable foods.

In this present study, ultrasound irradiation was applied on the combined effluent prior to the photofermentation process. Two parameters, namely, amplitude (30–90%) and ultrasonication duration (5–60 min), were investigated to develop the optimum ultrasonication scheme to enhance biohydrogen production. To evaluate the efficiency of ultrasound in the pre-treatment of combined effluent, the values of cumulative biohydrogen production, light efficiency, maximum biohydrogen production rate, total chemical oxygen demand (COD_{total}) and soluble chemical oxygen demand ($COD_{soluble}$) were determined. In addition, kinetic and thermodynamic analyses of the proposed photofermentative biohydrogen production were performed to determine the enthalpy and the threshold temperature of the photofermentation.

2. Materials and methods

2.1. Purple non-sulfur bacteria

Biohydrogen was produced using *R. sphaeroides* NCIMB8253. Bacteria were cultivated on agar slants and incubated for 24 h under 4000 lux illumination (WalkLAB Digital Lux meter, Trans Instrument Pte. Ltd., Singapore) with a temperature of 30 °C. Then, they were maintained and preserved in a chiller at 4 °C.

2.2. Collection of raw effluents

POME and PPME were collected from local production mills, namely, Seri Ulu Langat Palm Oil Mill Sdn. Bhd. and Muda Paper Mills Sdn. Bhd., respectively. The characteristics of these two effluents are shown in Table 1.

2.3. Ultrasonication pre-treatment

An attempt to improve the biohydrogen production was conducted by introducing ultrasonic pre-treatment onto the combined effluents, consisting of 25% and 75% (v/v) of POME and PPME, respectively, prior to the sterilization stage. Ultrasonic irradiation was performed using a QSonica Q700 Sonicator (QSonica LLC.,

Table 1
Raw POME and PPME characteristics.

Parameter	POME	PPME	Control*
pH	4.3 ± 0.3	6.15 ± 1.3	7.00 ± 0.25
Turbidity	67,500 ± 1910 NTU	4700 ± 141 NTU	16,450 ± 636 NTU
Total chemical oxygen demand	84,450 ± 19,500 mg/L	2716 ± 125 mg/L	22,900 ± 849 mg/L
Total suspended solids	19,610 ± 7900 mg/L	841 ± 878 mg/L	5559 ± 100 mg/L
Total soluble carbohydrate	27,500 ± 2250 mg/L	353 ± 18.94 mg/L	12,330 ± 6.56 mg/L
Total nitrogen	650 ± 300.00 mg/L	3.70 ± 3.65 mg/L	170.5 ± 2.12 mg/L
C/N ratio	6.54 ± 3.43	128 ± 22	8.41 ± 0.16
Heavy metal content			
Fe	70.7 ± 1.65 mg/L	0.50 ± 0.01 mg/L	18.35 ± 0.64 mg/L
Zn	7.53 ± 1.07 mg/L	0.12 ± 0.01 mg/L	2.01 ± 0.21 mg/L
Mn	6.47 ± 1.43 mg/L	0.09 ± 0.01 mg/L	1.72 ± 0.09 mg/L
Mg	1144 ± 7.00 mg/L	3.28 ± 1.08 mg/L	289.5 ± 2.12 mg/L
Al	334 ± 22.65 mg/L	33.43 ± 1.10 mg/L	109 ± 4.24 mg/L

* Control was a combined POME (25%, v/v) and PPME (75%, v/v) substrate with the initial pH adjusted to neutral and without undergoing ultrasonication pre-treatment.