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Effects of process, operational and environmental variables on biohydrogen production using palm oil mill effluent (POME)

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ABSTRACT

A batch study for biohydrogen production was conducted using raw palm oil mill effluent (POME) and POME sludge as a feed and inoculum respectively. Response Surface Methodology (RSM) was used to design the experiments. Experiments were conducted at different reaction temperatures (30–50 °C), inoculum size to substrate ratios (I:S) and reaction times (8–24 h). An optimum condition of biohydrogen production was achieved with COD removal efficiency of 21.95% with hydrogen yield of 28.47 ml H_2 g^{-1} COD removed. The I:S ratio was 40:60, with reaction temperature of 50 °C at 8 h of reaction time. The study showed that a lower substrate concentration (less than 20 g L^{-1}) for biohydrogen production using pre-settled POME was achievable, with optimum HRT of 8 h under thermophilic condition (50 °C). This study also found that pre-settled POME is feasible to be used as a substrate for biohydrogen production under thermophilic condition.

Introduction

In the past 15 years, lot of past research focussed on producing biohydrogen using different types of wastewater; namely municipal wastewater, agricultural wastewater, and beverages wastewater [1–4]. This is possibly due to the fuel crisis resulting from fossil fuel resource depletion [5]. Other than the fuel crisis, the combustion of fossil fuel will also lead to the emissions of toxic materials, which is responsible for many environmental problems [6]. In addition to that, it will indirectly contribute to other consequences such as the increase of greenhouse gases (GHGs), the rising of sea levels, the impact on climate change, and the diminishing biodiversity [7].

One of the plausible resources for the biohydrogen production in Malaysia is from the treatment of palm oil-based industry's wastewater as this industry is among the world's biggest palm oil exporter [8]. Regardless of its many useful products, there are some harmful aspects associated with the

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production. Tons of wastewater that is produced every day, namely palm oil mill effluent (POME), can endanger the environment. The biogas that is produced from POME during anaerobic treatment is a thoughtful challenge resulted from the current production processes [5,9].

POME is categorized as a very high contaminating wastewater that contains a biochemical oxygen demand (BOD) of 25,000 mg L^{-1} and chemical oxygen demand (COD) of 69, 500 mg L $^{-1}$ [10]. Some other properties contains in POME that may harm the environment include glycerine, dissolved oil and fatty acids, crude oil solids and any other soluble material [11]. Therefore, direct discharge into the land is not encouraged. According to the Department of Environment Malaysia, in conjunction to the Environment Quality Act 1974, POME must be treated before it is directly released into the environment [12]. Since raw POME normally is discharged at 80–90 °C, therefore several researchers reported that treatment of POME can be done whether in mesophilic or thermophilic conditions [13–15]. Some other studies have been suggested for the treatment of POME. This includes by using evaporation ponds; applying thermal, physicochemical, and biological treatment. For that wastewater to be treated by biological means, its BOD/COD ratio needs to be greater than 0.5 [16] Moreover, biological treatment is also preferable due to its cost effectiveness as compared to chemical treatment.

Production of biogas from POME is widely known by using anaerobic digestion. Since its potential of treating wastes while producing renewable energy, it has become the most studied technology. Anaerobic digestion is a process where organic materials are decomposed in a condition where there is no oxygen present and useful biogas is produced, simultaneously. There are three stages of reactions involved in anaerobic digestion. The first stage is hydrolysis, followed by acidogenesis and lastly methanogenesis [17–19].

Hydrolysis is a process where complex organic compounds are converted (hydrolyse) by fermentative bacteria to simple monomers such as fatty acids, monosaccharides and amino acids. Next, in acidogenesis process, these simple monomers included sugars will be degraded further to acetate, hydrogen (H_2) and carbon dioxide (CO_2) [16]. Acetate, H_2 and CO_2 will be the precursors for methane production in methanogenesis process.

For a normal process of microbial fermentation, Hallenback and Ghosh (2009) reported that organic wastes only have about 7.5–15% of energy to be converted to hydrogen, whilst the rest will remain in volatile fatty acids (VFA), i.e. acetic acids (AA), butyric acid (BA), propionic acid (PA) and lactic acid (LA) [20]. VFA will then be converted to methane or any other suitable by-products through a process called methanogenesis [21]. A basic dark fermentation process can be simplified using equation below [22]:

$$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2 \quad (1)$$

Biohydrogen production from POME is not a new study in this field. O-Thong et al. (2008) in their study showed that under thermophilic condition (60 °C), a hydrogen yield of 4.2 L H_2 $L^{-1}{}_{waste}$ and COD reduction of 37% was achieved when using POME of 85 g COD L^{-1} [23]. Other studies reported a hydrogen yield of 4.5 L H_2/L_{waste} and a COD reduction of 40% using high concentration of POME (10–59.3 g L^{-1} COD) as substrate [24], a hydrogen yield of 0.27 L H_2 g^{-1} COD and 57% of a COD reduction under thermophilic condition [25] and 51.5 ml H_2 g^{-1} COD of hydrogen yield with 15.1% of a COD reduction using initial COD of 5–35 g L^{-1} COD at 55 °C [26], respectively.

Whether it is mesophilic and thermophilic in anaerobic treatment, both conditions give different impacts on the COD removal, biohydrogen production yield and rate of POME. Oh et al. (2003) in their study of effects of temperature (25–40 °C) on hydrogen production concluded the increasing of temperature from 25 to 36 °C also improved the cell growth rate and hydrogen production rate. They also reported that at 36 °C, maximum hydrogen yield was achieved (i.e. 2.49 mol H_2 mol^{-1} glucose) [27]. Chong et al. (2009) in their study using *Clostridium* sp. that extracted from the mixed cultures of POME anaerobic sludge reported that at 37 °C, total accumulated hydrogen gas was higher (i.e 3 L H_2 day^{-1}) [28]. Other study done by Lee et al. (2006) reported that temperature above 35 °C may inhibit the growth of the granular sludge [29]. Meanwhile, with thermophilic condition, Mamimin et al. (2015) reported that this condition is good for POME to be converted to H_2 as it has less variety of end-products, thermodynamic condition as well as has low inhibition of hydrogen partial pressure [30].

High production rate of hydrogen was produced in dark fermentation process but with low hydrogen yield [31,32]. The most recent batch study done by Norfadilah et al. (2016) used high concentration of raw POME as a substrate (initial COD concentrations were 32 g L^{-1} to 86 g L^{-1}), and they reported a COD removal of approximately 37% with the maximum hydrogen yield of 5.98 L H_2 L^{-1} -med at 10% POME sludge [33]. Additionally, a study done by Mohammadi et al. (2012) using pre-settled POME as substrate reported that the highest hydrogen yield calculated was 124.48 mmol H_2 g^{-1} COD removed with COD removal of 54.2% [34]. However, the study was done at low COD influent of 3 g L^{-1} COD – 10 g L^{-1} COD.

Based on the presented studies, most of the researchers were done at high substrate concentrations (>20 g L^{-1} COD). It is also understood that using high strength wastewater as a substrate in a mesophilic or thermophilic condition could increase the COD removal efficiency by increasing the rate of degradation along with the biogas production [15,35]. However, Poh et al. (2009) reported that in Malaysia, only mesophilic temperature conditions are conducted for anaerobic POME treatments [36].

Thus, this study was initiated to study biohydrogen production of POME in a dark fermentation process. Raw POME was used as a substrate and POME anaerobic sludge as an inoculum. The inoculum sizes (10:90–40:60), reaction times (8–24 h) and mesophilic to thermophilic conditions (30–50 °C) were varied to study their effects on biohydrogen production and its COD removal efficiency. For the optimization study, (RSM) was applied for hydrogen yield and COD removal efficiency. In this study, the substrate concentrations were varied from a low concentration of <20 g L^{-1} to high concentration of >20 g L^{-1} CODin.