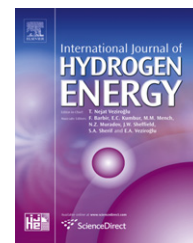


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Effects of biomass, COD and bicarbonate concentrations on fermentative hydrogen production from POME by granulated sludge in a batch culture

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ABSTRACT

Effects of three selected variables viz. biomass concentration, initial chemical oxygen demand (COD) concentration and initial bicarbonate alkalinity (BA) on biological hydrogen production from palm oil mill effluent (POME) using the granulated sludge in batch culture were investigated. The experimental results were analyzed and modeled using a central composite design (CCD) of response surface methodology (RSM). In order to carry out a comprehensive analysis of the biohydrogen production process, indicative parameters namely hydrogen yield (Y_H), specific hydrogen production rate (SHPR), and COD removal efficiency were studied as the process responses. Maximum hydrogen yield (124.5 mmol H_2 /g $COD_{removed}$) and specific hydrogen production rate (55.42 mmol H_2 /g VSS.d) were achieved at COD_{in} 3000 and 6500 mg/l, MLVSS 4000 and 2000 mg/l, and initial BA 1100 mg $CaCO_3$ /l, respectively.

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1. Introduction

One of the most important contributors to Malaysia's economy is palm oil industry. This industry generates large quantities of polluted wastewater commonly called as palm oil mill effluent (POME). It is estimated that 5–7.5 tonnes of water are required for each tonne of crude palm oil production; and more than 50% of the water ends up as POME [1,2]. Based on palm oil production industry in Malaysia, 15.2 million tonnes of POME were produced in 2005 alone [3]. The three main sources of POME are sterilization (36%), clarification (60%), and hydrocyclone (4%) units. Raw POME as

a colloidal suspension contained 95–96% water, 0.6–0.7% oil and 4–5% total solids [2,4].

Nowadays, fossil fuels are the primary source of global energy requirements, with their foreseeable depletion due to limited fossil energy resource. With respect to global environmental impacts due to the usages of this energy resource, such as greenhouse effect, ozone layer depletion and resource recovery, intensive search is going on worldwide for renewable and non-polluting energy source [5–16]. Hydrogen is an effective fuel with high-energy yield (122 kJ/g) which is 2.4, 2.8 and 4 times higher than energy yields of methane, gasoline and coal, respectively [17–23].

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Fermentation of agro-waste biomass using microorganisms is a promising approach for producing hydrogen which is known as the cleanest renewable energy. Fermentative hydrogen production is influenced by many factors such as inoculum, substrate, alkalinity, reactor type, organic loading rate, pH and temperature. Some aforementioned parameters have been studied before. Chong and coworkers [3] have investigated the effect of pH on hydrogen production from POME. The maximum hydrogen production and maximum volumetric hydrogen production rate were achieved at 3195 ml H₂/l POME and 1034 ml H₂/l h at pH 5.5 and 37 °C in temperature, respectively. Also, the maximum process stability in an anaerobic sequencing batch reactor (ASBR) for biohydrogen production from POME was studied by Prasertsan et al. [24]. At an organic loading rate (OLR) of 60 g/l d and hydraulic retention time (HRT) of 2 days, maximum hydrogen yield of 0.27 l H₂/g COD with a volumetric hydrogen production rate of 9.1 l H₂/l d were achieved. The most researches have been carried out investigating the effect of operational factors on fermentative hydrogen production. While in this research, the effect of process factors on biological hydrogen production is studied for estimation of optimum conditions.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables on the response [25–27]. RSM has an important application in the process analysis and optimization as well as the improvement of existing design. There have been several studies the interactive effect among the variables on the optimization of fermentative hydrogen production process to depict by using RSM. The effects of three variables (carbon to nitrogen (C/N) ratio, carbon to phosphate (C/P) ratio and iron concentration) in POME on fermentative hydrogen production using RSM have been studied in an anaerobic sequencing batch reactor operating [28]. The RSM results showed that optimal hydrogen production and chemical oxygen demand (COD) removal were at C/N ratio, C/P ratio, and Fe²⁺ of 74, 559, and 257 mg, respectively. Also, the RSM results indicated that optimum conditions for hydrogen production (306 ml H₂/g carbohydrate) were pH 5.69, 36 °C, and 92 g COD/l [29].

The efficiency of biohydrogen production is directly related to the optimal control of food to microorganism (F/M) ratio [30,31]. The metabolic and kinetic characteristics of microorganisms were affected by initial COD and biomass concentration ratio significantly [31,32]. There exists certain

disagreement on the optimal F/M ratio for fermentative hydrogen production. It has been demonstrated that in an appropriate range of F/M could increase the ability of hydrogen producing bacteria to produce hydrogen during fermentative hydrogen production, but F/M ratio at much higher levels could decrease it with increasing levels [31].

Fermentative hydrogen production processes produce bicarbonate alkalinity (BA) which could maintain the pH at favorable range for hydrogenesis activity. Therefore, in this study, the effects of three important process variables viz. initial COD concentration, biomass concentration and initial BA, on biological hydrogen production from POME in batch culture were investigated. The experiments were designed as central composite face-centered design (CCFD) using Design Expert® software (Stat-Ease Inc., version 6.0.8).

2. Materials and methods

2.1. Wastewater preparation

Raw POME samples were taken from SIME Darby Plantation Palm Oil Industry Sdn. Bhd., Nilai, Malaysia. The samples were transferred to the laboratory immediately and stored in a cold room (4 °C) before use. The characteristics of the raw and pre-settled POME are summarized in Table 1. This was used as the liquid medium in the batch fermentation study.

2.2. Seed sludge preparation

The inoculum for the batch fermentation was the granulated sludge obtained from a working upflow anaerobic sludge blanket-fixed film (UASB-FF) bioreactor operated at steady-state (HRT of 12 h, influent COD 25880 mg/l, and OLR of 51.8 g COD/l d) in our laboratory for biological hydrogen production from POME. The granulated sludge was withdrawn from the bottom part of the reactor.

2.3. Batch experiments

Experiments were performed in 163-ml serum bottles with 50 ml medium (experimental conditions as shown in Table 2) and sealed with butyl rubber stoppers and aluminum seals as shown in Fig. 1. The initial pH was adjusted to 5.5 using NaOH (3N) and HCl (3N). The medium was distributed anaerobically

Table 1 – Characteristics of raw and per-settled POME.

Parameters	Raw POME		Pre-settled POME	
	Amount	Standard deviation	Amount	Standard deviation
BOD ₅	22,500	±2150	19,400	±235
TCOD	49,800	±4250	28,800	±260
SCOD	21,950	±2320	17,140	±165
TSS	18,800	±1240	850	±21
TKN	430	±32	382	±3.5
TP	84	±7.5	84	±1.5
Oil and grease	4250	±62	1480	±13.8
pH	4.2	±0.2	4.2	±0.15
All in mg/l except pH.				

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