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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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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 5e7.5 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 95e96% water, 0.6e0.7% oil and 4e5% 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 [5e16]. 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 [17e23].

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 H_2/l POME and 1034mlH_2/l h atpH5.5 and 37 _C intemperature, 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 H_2/g COD with a volumetric hydrogen production rate of 9.1 l H_2/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 [25e27]. 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/N) 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 $Fe_{2þ}$ of 74, 559, and 257 mg, respectively. Also, the RSM results indicated that optimum conditions for hydrogen production (306 ml H_2/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 atmuchhigher 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 presettled 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 steadystate (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 into the serum bottles under nitrogen gas purging. The gas phase was also purged using nitrogen gas. The serum bottles were placed in a shaking incubator (DAIHAN LABTECH Co., Singapore) (120 rpm) at 38 _C. At 8 h interval, the composition of gas and liquid (H_2 percentage, volume of biogas produced, alkalinity and COD) were measured. The results after two days of fermentation were analyzed using analysis of variance (ANOVA) (Design Expert Software).

2.4. Experimental design and mathematical model

Results obtained from the previous experiments showed that BA was produced during anaerobic digestion of POME [33,34].

Fig. 1 e Serum bottles used for batch experiments.

Since one of the aims in this study was to determine the optimum initial BA which could maintain the pH at favorable range for hydrogenesis activity, therefore the range of BA was chosen from a minimum amount of 200e2000 mg $CaCO_3$/l. Nasr and coworkers [35] have found that the optimum range of F/M ratio for fermentative hydrogen production was 1e2 g COD/g VSS. Also the highest hydrogen yield was obtained at an F/M ratio of 1.24 g COD/g VSS from the range of 0.35e4.38 g COD/g VSS tested [31]. Hence, a wide range of food to microorganism (F/M) ratio from about 0.25 to 2.5 g COD/g VSS d was considered and examined as a criterion for determining the range of COD_{in} concentration (3000e10,000 mg/l) and biomass concentration (2000e6000 mg/l) in this study.

The statistical method of factorial design of experiment (DoE) eliminates systematic errors with an estimate of the experimental error and also minimizes the number of experiments [25,36]. In the present study,H_2 production fromPOME in batch culture was evaluated and optimizedemploying a central composite design (CCD) of response surface methodology (RSM). Themain and interactive effects ofCOD_{in} concentration, biomass concentration and initial BA on the process responses were explained. Table 2 shows the experimental conditions for fermentative hydrogen production from POME based on CCD design. The design includes of 2^k factorial points augmented by 2k (the number of variables) axial points and a center point. The levels of each variable vary from a low to high value, either numerically expressed in absolute values or coded as _1 (low) and 1 (high) with intermediate value of 0 (middle).

In order to evaluate the granular sludges performance in the hydrogen production, three responses were selected and the experimental results after two days under various process conditions are presented in Table 2. Three-dimensional plots were used to visualize the effects of the studied variables. The simultaneous interactions of the variables on the responses were also studied from these three-dimensional plots coefficients of the polynomialmodel were obtained using Eq. (1) [37].

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