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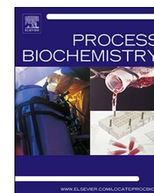

Metabolism and kinetic study of bioH_2 production by anaerobic sludge under different acid pretreatments

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ABSTRACT

This study presents results pertaining to bioH_2 production carried out in batch experiments under different inorganic acid pretreatments of sludge. The sludge was collected from an anaerobic digester and was subjected to different acid (H_2SO_4, H_3PO_4, HNO_3, and HCl) pretreatments at pH 3 for 24 h. The results showed that electron equivalent balance closure was within −12 to +10% for all experiments; the portion of electrons as bioH_2 fluctuated from 16% to 25%. H_2SO_4 pretreatments significantly increased H_2 yields to 3.3 mol H_2/mol glucose followed by HNO_3, HCl, and H_3PO_4 pretreatments which averaged 2.5 ± 0.5. Enthalpy (ΔH°) and Gibb's free energies (ΔG°) fluctuated from 120.5 to 192.7 (kJ/mol) and from −2.2 to −5.9 (kJ/mol). The modified Gompertz was assessed and determined that the maximum bioH_2 production potential, 1551 mL and maximum rate of bioH_2 production, 303 mL/h occurred using the H_2SO_4 pretreatment.

1. Introduction

At present, fossil fuels are responsible for about 80% of global energy demand [1]. Oil and natural gas are finite resources, and the combustion of these fossil fuels contributes to air pollution and the greenhouse effect [2]. High electrical-conversion efficiency (≈55% in a H_2 fuel cell) and the carbon-free nature of H_2 when extracted from non-fossil fuel resources makes H_2 a good alternative to fossil fuels in the future [3].

The biological methods for H_2 production (bioH_2) are more environmentally friendly and less energy intensive than thermochemical and electrochemical processes due to the capacity of these systems to utilize sunlight and organic wastes (biomass) as substrates. In addition, bioH_2 does not contain CO and H_2S which are catalyst poisons in fuel cells applications [4]. The bioH_2 production occurs through the active use of different microorganisms under the appropriate conditions; it is controlled by the action of hydrogen-producing enzymes such as hydrogenase and nitrogenase following specific metabolic pathways. The main bio-process technologies for bioH_2 production can be classified as biophotolysis of water, photobiological hydrogen production, dark hydrogen fermentation, hybrid systems using photosynthetic and fermentative bacteria, and hybrid system using biomethane production followed by steam methane reforming [5,6].

Dark fermentation is a biological process performed in anoxic conditions with bacteria grown in the absence of light sources to produce H_2 from carbohydrate rich substrates. The anaerobic degradation of carbohydrates by heterotrophic microorganisms has several important advantages such as high rates of H_2 production and continuous H_2 production (during day and night) [7,8]. In fermentative processes using carbohydrates, hydrogenase-mediated metabolisms are preferred over nitrogenase-mediated due to their higher fermentative bioH_2 yields and lower metabolic cost [7,9].

The two catabolic steps involved in bioH_2 production include pyruvate decarboxylation to acetyl-CoA which generates reduced ferredoxin (Fd), a direct electron donor for proton reduction to H_2 gas by *Clostridium sp.*; and H_2 production via formate cleavage by facultative anaerobes, such as *Enterobacter* and *Klebsiella* [3]. In anaerobic fermentative bioH_2 production from organic substrates, bacteria use protons (H^+) as their final electron acceptor and energy conservation occurs only through substrate-level phosphorylation [3,10]. The internal electron carriers are $NADH_2$ or Fd [10]. While 15% of the electrons are transferred to biomass growth, around 60% of electrons goes to the

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products – acetate, butyrate, ethanol, lactate, propionate, and others [11]. By fermentation of 1 mol of glucose, the highest bioH_2 yield that can be obtained using mesophilic bacteria is 4 mol H_2 but the previous study demonstrated that in the mesophilic fermentation, the practical yield of H_2 was limited to around 2 mol H_2 [10,12]; which represents up to 25% of relative portion of the end products.

Providing large amounts of active and stable inoculum is a key challenge for bioH_2 production in large scale. Different pretreatment methods have been applied to enrich bioH_2 production inoculum by eliminating methanogens, homoacetogens (hydrogen-consuming bacteria), and sulfate reducing bacteria [13,14]. Some of the pretreatment methods are including thermal pretreatment, alkaline pretreatment, acidification and ultrasonic pretreatment [15]. However, there still exist disagreements regarding the best pretreatment method to maximize bioH_2 production because of the variations in substrates or operating conditions. Substrates include anaerobic digested sludge, waste activated sludge, compost, cow dung, corn stover and food processing wastewater [2,12,16,17].

The emphasis of this study is to evaluate the effect of anaerobic sludge acidification on metabolism and kinetic study of bioH_2 production during glucose fermentation. Different strong inorganic acids were used as pretreatments to enhance fermentative bioH_2 production. The effect of pretreatment on soluble end products (SEP)including acetic, propionic, butyric, formic, lactic acid (fatty acids) and acetone, methanol and ethanol (solvents), reaction stoichiometry without cell synthesis, thermodynamics of bioH_2 production, volume of bioH_2 production, and bioH_2 yield were determined. In addition, the modified Gompertz equation was used to describe the cumulative bioH_2 production during the batch experiments.

2. Material and methods

2.1. Inoculum and acid pretreatment

Inoculum was isolated from an anaerobic digester from the South Municipal Wastewater Treatment Plant (Tehran, Iran) and then screened via standard sieve #16 with 1.19 mm pore size (DG scientific production Co.) in order to remove large particulate materials. Before inoculation, in order to inhibit methanogenic bacteria and selection of bioH_2 producing bacteria, the pH of the inoculum was adjusted to pH 3 by using concentrated sulfuric acid (H_2SO_4), ortho-phosphoric acid (H_3PO_4), nitric acid (HNO_3) and hydrochloric acid (HCl).After 24 h, the pH was adjusted to 7 by adding mixture of NaOH and KOH (6 M) [18,19].

2.2. Batch experiments

Batch experiments to test for bioH_2 production were performed using 500 mL glass flasks containing 200 mL of pretreated inoculum and 200 mL of feed medium. Glucose was used as the sole substrate at 7.5 g/L (1 electron equivalent (e^- eq) glucose/L) and the composition of inorganic nutrients were used according to [20]. The batch experiments were conducted in duplicate experiments and average values are reported.All experiments were performed in a hot water bath (37 °C ± 0.2) at 150 rpm (360 s idle and 30 s mixing); for 55 h and anaerobic conditions were created by purging N_2 gas for 3 min and sealing with a crimp top rubber septum. The amount and composition of biogas, SEPs, residual glucose, chemical oxygen demand (COD), alkalinity and solution pH were measured according to [19].

2.3. Calculation

The stoichiometric reaction was used and is based on this fact that all e^- eq removed from the substrate (*e.g.* glucose) must be accounted for in the aqueous and gaseous fermentation products and in addition cell synthesis. In the first steps, the mass balance base on the e^- eq was carried out using Eq. (1).

$$e^-_{glu,in} = e^-_{glu,eff} + e^-_{SEP} + e^-_{H2} + e^-_{biomass} \tag{1}$$

where $e^-_{glu,in}$ is the e^- eq of influent glucose, $e^-_{glu,eff}$ is the e^- eq of residual glucose at the end of experiment, e^-_{SEP} is the e^- eq of soluble end products, e^-_{H2} is the e^- eq of the cumulative bioH_2 during incubation period, $e^-_{biomass}$ is the e^- eq of biomass growth during experiment. The accumulation of biomass was calculated by Eq. (2).

$$\Delta_{bimass}(mg/L) = (tCOD - sCOD)_{eff} - (tCOD - sCOD)_{in} \tag{2}$$

where tCOD is total COD (mg/L), sCOD is soluble COD (mg/L), and the chemical formula for biomass is assumed to be $C_5H_7O_2N$ [21]. The stoichiometric oxidation-reduction equations without cell synthesis were constructed using Eq. (3) as reported previously [3].

$$R_{bal} = R_a - R_d \tag{3}$$

where R_{bal} is the balanced reaction without cell synthesis, R_a is half reaction for electron acceptor and R_d is half reaction for electron donor. The half reaction for mixed electron acceptors in batch experiment was computed via Eqs. (4) and (5).

$$R_a = \sum_{i=1}^{n} e_{a,i} R_{a.i} \tag{4}$$

$$e_{a,i} = \frac{e^-_{eq,i}}{\sum_{i=1}^{n} e^-_{eq,i}} \quad and \quad \sum_{i=1}^{n} e^-_{a,i} = 1 \tag{5}$$

where $e_{a,i}$ is the fraction of e^- eq for i product of total e^- eq for SEPs plus H_2, $R_{a,i}$ is half reaction for i product, and $e^-_{eq,i}$ is e^- eq of i product. The balanced reactions do not include cell synthesis, but only the fermentation products. Hence, they represent the energy generating reactions [3].

After constructing the stoichiometric fermentation reaction of glucose, the Van't Hoff equation was used to estimate standard Gibb's free energy at 37.5 °C by obtaining the enthalpy change for each compound from the literature [22] via Eq. (6).

$$\ln\frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{6}$$

where K_1 is the equilibrium constant at temperature T_1, K_2 is the equilibrium constant at temperature T_2, ΔH° is the standard enthalpy change at 25 °C (kJ/mol), T_1 is standard temperature (298.15 K), T_2 is incubation temperature (310.65 K), and R is the ideal gas constant (0.008314 kJ/mol K)., The Gibb's free energy was computed according Eq. (7).

$$\Delta G^\circ_{f,37^\circ C} = -RT\ln[K_2] \tag{7}$$

According to [22], for various chemical species, the free energy was presented at standard pH equals to 7 and due to significant effect of solution pH, the Gibb's free energy in Eq. (7) was adjusted to Eq. (8).

$$\Delta G^\circ_{f,37^\circ C,pH} = \Delta G^\circ_{f,37^\circ C} + RT\ln[H^+] \tag{8}$$

where $\Delta G^\circ_{f,37\ ^\circ C}$ is Gibb's free energy at incubation temperature and at $[H^+]$ equal to 1 M (kJ/(e^- eq)), $\Delta G^\circ_{f,37\ ^\circ C,pH}$ is Gibb's free energy corrected by pH (kJ/(e^- eq)) and $[H^+]$ is proton concentration corresponding to pH value.

The previous study stated that the amount of produced pyruvate is equal to the used pyruvate and Eqs. (9)–(11) were used to calculate the residual amount of NADH [23].

$$\text{Residual NADH} = \text{Produced NADH} - \text{Used NADH} \tag{9}$$

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