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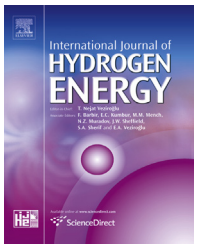

Kinetic analysis of biohydrogen production from complex dairy wastewater under optimized condition

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ABSTRACT

Present work describes a kinetic analysis of various aspects of biohydrogen production in batch test using optimized conditions obtained previously. Monod model and Logistic equation have been used to find growth kinetic parameters in batch test under uncontrolled pH. The values of μ_m, K_s, and X_m were 0.64 h^{-1}, 15.89 g-COD L^{-1}, and 7.26 g-VSS L^{-1}, respectively. Modified Leudeking-Piret and Michaelis–Menten equation corroborates a flux of energy to hydrogen production pathway and energy sufficiency in the system. Modified Gompertz equation illustrates that the overall rate and hydrogen yield at 15 g-COD L^{-1} was higher compared to a dark fermentation of other wastewaters. Besides, Andrew's equation also suggests that since the higher value of K_I (19.95 g-COD L^{-1}), k (255 mL h^{-1} L^{-1}) was not inhibited at high S. The experimental results implied that the entire products during the fermentation process were growth and substrate degradation associated. The result also confirms that the acetate and butyrate were substantially used for hydrogen production in acidogenic metabolism under uncontrolled pH.

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1. Introduction

The increased concerns of greenhouse gas emissions and other environmental issues thrusting research in the area of alternative fuels for sustainable development. A recent intensive research within the field of renewable energy has proven hydrogen as an optimal energy carrier and promising alternate fuel due to its non-polluting features [1]. However, a major doubt over the use of hydrogen as a clean-energy alternative is the way it is produced. The current hydrogen gas production processes *viz.* hydrocarbon reforming; coal gasification and partial oxidation of heavier hydrocarbons are unfriendly and contributing to the greenhouse effect [2].

Dark fermentation by microorganisms for biohydrogen production has attracted global attention, owing to its potential for operation at ambient temperature and atmospheric pressure [3,4]. Moreover, the process can be carried out on various organic wastes and wastewaters enriched with carbohydrates, thereby achieving sustainable low-cost biohydrogen production with concomitant waste stabilization. Biohydrogen production has been evaluated in many organic wastes, including waste molasses [5], dairy wastewater [6], sewage sludge [7] and so on. The hydrogen yields from these wastes differ due to their different organic composition, and the primary organic components in these wastes are usually carbohydrates and/or proteins [8].

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Nomenclature

μ	Specific growth rate, h^{-1}
μ_m	Maximum specific growth rate, h^{-1}
S_0	Initial substrate concentration, g-COD L^{-1}
S	Substrate concentration, g-COD L^{-1}
k_s	Half saturation constant of substrate, g-COD L^{-1}
X_0	Initial biomass concentration, g-VSS L^{-1}
X	Biomass concentration, g-VSS L^{-1}
X_m	Maximum attainable biomass concentration, g-VSS L^{-1}
t	Fermentation time, h
k	Hydrogen production rate constant, mL h^{-1}
$Y_{x/S}$	Maximum yield coefficient, g-VSS g-COD^{-1}
m_s	Maintenance coefficient, g-COD g-VSS^{-1}
ν	Specific substrate degradation rate, g-COD g-VSS^{-1} h^{-1}
ν_m	Maximum specific substrate degradation rate, g-COD g-VSS^{-1} h^{-1}
k_m	Dissociation constant
i	Represent product i.e., hydrogen, butyric acid and acetic acid, respectively
P_i	Products 'i' formed, mM L^{-1}
$P_{m,i}$	Maximum potential of product 'i' formed, mM L^{-1}
R	Hydrogen production rate, mM h^{-1}
R_m	Maximum hydrogen production rate, mL h^{-1}
$R_{m,i}$	Maximum rate of product 'i' formation, mM h^{-1}
λ_i	Lag phase of product 'i' formation, h
K_I	Inhibition constant, g-COD L^{-1}
dP_i/Xdt	Specific product 'i' formation rate, mM g-VSS^{-1} h^{-1}
α_i	Coefficient of growth linked product 'i' formation
β_i	Coefficient of non-growth linked product 'i' formation
Y_{Pi}	Yield of product 'i', mM g-COD^{-1}

Dairy wastewater (DWW) has a good potential for hydrogen production when being treated anaerobically. A DWW thought to be complex in nature due to presence of lipids along with carbohydrate and protein compounds make it a recalcitrant substrate for anaerobic digestion [6]. The dark fermentation of DWW for hydrogen production is a complex process and is greatly influenced by many factors such as substrate concentration, reactor configuration, pH, temperature, oxidation-reduction potential and nutritional requirement [9]. Therefore, the optimization of fermentation conditions, particularly nutritional and environmental parameters are of primary importance for the sustainable bioprocess development [10].

Previously, the factors affecting hydrogen production from complex DWW by dark fermentation in batch test were optimized using response surface methodology integrated with the desirability function approach [11]. The experiments were conducted in a 125 mL serum bottle containing 100 mL reaction mixture comprising of DWW and anaerobic sludge. The effects of process variables *viz.* substrate concentration, pH, COD/N ratio, and COD/P ratio, on yield and specific rate of biohydrogen production were studied in batch test. It was found that, the selected parameters had a profound impact on biohydrogen production individually, squared, and interactively. The maximum hydrogen yield (13.54 mmol H_2 g-COD^{-1}) and specific hydrogen production rate (29.91 mmol H_2 g-VSS d^{-1}) were achieved at optimum conditions of substrate concentration, initial pH, COD/N ratio, and COD/P ratio as follows: 15.3 g-COD L^{-1}, 5.5, 100.5 and 120, respectively.

Till the date number of studies has reported the optimization of engineering parameters for biohydrogen production [12]. Additionally, various unstructured kinetic models have been proposed by different researchers to describe the effect of principle state variables, the behaviour of fermentation quantitatively, and design the bioreactors [13,14]. However, very few kinetic studies described the effects of optimized variables on substrate utilization, biomass growth, and product formation during batch fermentation [12–14]. Therefore, we attempted to analyse the batch kinetics of biohydrogen production from DWW using optimized conditions obtained previously. Therefore, there are two-fold objectives of the present study to enhance the understanding of hydrogen production from complex DWW as follows: (1) Use of various unstructured models to describe the kinetics of biohydrogen production by dark fermentation in a batch mode from complex DWW under optimized conditions. (2) A comprehensive kinetic analysis elucidating the effect of operational parameters on substrate utilization, biomass growth, and product formation rate under uncontrolled pH. The results from this study are expected to be helpful for understanding the behaviour of biohydrogen production process.

2. Material and methods

2.1. Dairy wastewater

Dairy wastewater collected from the Government Dairy Society, Nagpur, India was used as a substrate. After collection, a fresh wastewater was transferred immediately to the laboratory and stored at temperature 4 °C to avoid degradation. The characteristics of dairy wastewater were as follows: COD, 25,600 mg L^{-1}; BOD, 10,210 mg L^{-1}; SS, 590 mg L^{-1}; TDS, 1890 mg L^{-1}; TS, 2340 mg L^{-1}; pH, 7.2. The desired substrate concentration of DWW for dark fermentation, *i.e.*15.3 g-COD L^{-1}, was achieved by the addition of distilled water [11].

2.2. Seed and inoculum preparation

The anaerobic seed sludge used for this study was obtained from full-scale Upflow Anaerobic Sludge Blanket (UASB) reactor treating DWW located in Nagpur, India, and stored at 4 °C. The UASB is being operated at pH 6.8 and temperature of 35 °C to produce methane from the wastewater of dairy and food product production process. Prior to use, the anaerobic sludge was pretreated at 90 °C for 20 min (pretreatment was optimized previously [11]) to inactivate hydrogenotrophic methanogens and to enrich hydrogen producing bacteria (HPB).

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