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Comprehensive modeling of photo-fermentation process for prediction of hydrogen production

*Leila Akbari, Behrooz Mahmoodzadeh Vaziri**

Department of Chemical Engineering, Quchan Branch, Islamic Azad University, Quchan, Iran

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ABSTRACT

Hydrogen production via modern technologies and without using fossil fuels has been found considerably important recently. Photo-fermentation is introduced as one of the most effective methods without high risk for bio-hydrogen production. In this study, comprehensive modeling and simulation of bio-hydrogen production is carried out through photo-fermentation process. In this way, different applicable models are considered to predict the kinetics of microbial growth. Also, new modified mathematical models are particularly proposed for photo-fermentation to forecast the specific growth rate of microorganisms, substrate consumption and hydrogen production rates. Various combinations of the models are applied and predictions of the models are validated by experimental data related to the growth of *Rhodobacter Sphaeroides* on malate as the substrate. The combination, entitled as *MVA1*, is introduced as the best one to predict kinetic factors in photo-fermentation. The presented models can be used as an excellent starting point to accomplish experimental and industrial works.

Introduction

Nowadays about 83 percent of the United States of America's energy demand and 78 percent of Europe's energy demand are provided from fossil fuels like oil, natural gas and coal. As the demand for energy is increasing all over the world, natural sources of energy will be rapidly consumed in near future. This limitation on the availability of fossil fuels and also the concern about greenhouse gas emissions and other pressing environmental issues over the use of fossil fuels has caused the governments lean towards other clean fuels such as hydrogen gas [1,2].

Many scientists perceive hydrogen gas as the future fuel because of its non-polluting features and its being environmentally safe. It does not contribute to the greenhouse effect and when it is combusted, it only produces water with no fine particles, hydrocarbons, carbon dioxide or carbon monoxide [3,4]. Moreover, hydrogen has a high gravimetric energy density of 122 kJ/g, which is almost 2.5 to 3 times greater than that of conventional fossil fuels, such as petroleum (44 kJ/g), natural gas (52 kJ/g), coal (40 kJ/g), and ethanol (26.5 kJ/g) [5]. Furthermore, hydrogen is an important energy carrier and could be applied to fuel cells for generation of electricity [6].

A major doubt over the use of hydrogen as a clean energy alternative is the way it is produced. The current hydrogen gas production is unfriendly as it is being generated from fossil fuels through thermo-chemical processes, such as hydrocarbon reforming, coal gasification and partial oxidation of heavier hydrocarbons. However, H_2 may be produced via photo-synthetic or fermentative processes. Fermentative H_2 production is more adequate than a photo-synthetic one [7,8].

* *Corresponding author.*
E-mail addresses: vaziri@iauq.ac.ir, behrouz.vaziri@gmail.com (B. Mahmoodzadeh Vaziri).
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Bio-hydrogen production by microbial fermentation to convert organic compounds into H_2 has attracted increasing global attention, owing to its potentials for inexhaustible low-cost, environmentally friendly, renewable source of clean energy and the ability to use organic wastes in order to eliminate pollution [7,9]. Studies on bio-hydrogen production have been focusing on bio-photolysis of water, using algae and cyanobacteria, photo-decomposition of organic compounds by photo-synthetic bacteria and dark fermentation from organic compounds with anaerobic [7].

Among the various bioprocesses of hydrogen production, dark and photo-fermentation are the main methods of producing biological hydrogen:

Dark fermentation produces hydrogen via biodegradation of organic compounds (usually carbohydrates) under anaerobic conditions in the absence of light. The main co-products in dark fermentation are butyrate and acetate [10,11]. A lot of heterotrophic bacteria can ferment carbohydrates under anaerobic condition to produce H_2, volatile fatty acids (VFA) and CO_2 [6].

The photo-fermentation process often utilizes VFA in addition to sugar as the substrate in the presence of light to produce hydrogen [10]. Photo-synthetic non-sulfur (PNS) bacteria are able to convert VFA to H_2 and CO_2 under anoxygenic conditions [12]. These species also have the ability to consume carbon sources such as glucose and sucrose rather than VFA for H_2 production. It is worth mentioning that different types of *Rhodobacter* species are the most well-known PNS bacteria which are used in photo-fermentation [13,14].

Generally, hydrogen production, using photo-fermentation is suitable since it proceeds in environmental conditions and wide variety of substrates, including agricultural and industrial wastes, have been utilized in this process [15]. However, low rate and inefficiency of this method are the most important disadvantages of producing hydrogen through fermentation. These shortcomings could be evaluated and eliminated by using applicable models and determining the optimal values of process key variables.

Various kinetic models have been developed and used to describe the progress of a batch photo-fermentative hydrogen production process [16,17]. The majority of these models are the conventional kinetic expressions. Evidently, these models are not able to evaluate the process kinetics accurately [18,19]. For instance, Monod, modified Monod and Michaelise-Menten models were widely utilized to describe the effects of substrate concentration on the rates of substrate degradation, bacteria growth and hydrogen formation. The conventional Luedeking-Piret model and its modified form were widely applied to predict the substrate consumption rate, and to describe the relationship between microbial growth rate and product formation rate. Gompertz model was widely used to express the progress of a batch fermentative hydrogen production process [20,21].

In the current study, some new kinetic models are proposed to establish the relationship among the hydrogen producing bacteria growth rate, the substrate consumption rate (SCR), and hydrogen production rate (HPR). Unlike the conventional models, the effect of all vital factors on process kinetics are considered in the adopted models. The descriptions of the presented models are comprehensively brought in section Modeling the photo-fermentation process.

Literature review

As mentioned above, the photo-fermentation process has recently attracted many scientists' attention. Despite the importance of the role of modeling in discernment of effective parameters and optimization of the process, most researchers have paid less attention to modeling of photo-fermentation. Consequently, few works have been done in this area. The followings are some of the papers published in the field of bio-hydrogen process modeling:

Gadhamshetty et al. [22] studied photo-fermentative bio-hydrogen production in 2008. They proposed kinetic models to predict cell growth, substrate consumption and hydrogen evolution. Exponential form of bacterial growth was used to describe biomass concentration. Their model package included various adjustable parameters which only some of these parameters were significant. The model predictions did not agree well with the experimental data specially for describing substrate consumption rate.

Wang and Wan [16] have summarized the various types of experimental design that includes one-factor-at-a-time design, factorial design, Taguchi design, Plackett-Burman design in 2009. Experimental design mainly involves various combination of different factor levels, which enables it to depict the interactions among different factors and more efficiently deal with a large number of factors.

Lo et al. [23] evaluated the performance of cell growth and photo-H_2 production using different carbon sources like acetate, butyrate, and lactate in 2011. The results showed that acetate was the most effective carbon source for photo-H_2 production. Conventional kinetic models were used to explain the relation among maximum specific growth rate, specific H_2 production rate and the substrate concentration. It also cleared that the dependence of cell growth rate and H_2 production rateon acetate and lactate can be described by Monod-type and Michaelise-Menten kinetic models respectively, whereas substrate inhibition kinetic model could be well when butyrate was used as the carbon source.

Sekoai and Kana [24] used a two-stage empirical modeling and optimization of bio-hydrogen production in 2013. A mixture design was utilized to determine the optimum proportions of agro-municipal waste mixture. The experimental data from the mixture design were applied to multiple regression analysis to fit a quadratic polynomial model that relates hydrogen production to the proportions of agro-municipal waste in the mixture. The optimum operational set points were studied for substrate concentration, pH, temperature and hydraulic retention time, using the box-behnken design. Experimental data obtained from the box-behnken design were applied to develop a second order polynomial equation to predict hydrogen yield. These experimental data were also used in multiple regression analysis to develop a quadratic model relating hydrogen production to the physicochemical parameters. Finally, their empirical models were subjected to the ANOVA, and the optimum