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Challenges in Biochemical Engineering and Biotechnology for Sustainable Environment

Batch Kinetic Modelling of Hydrogen Production using Confectionery Wastewater

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Abstract: Hydrogen has been recognized globally as an energy carrier that fulfills all the environmental quality, energy security and economic competitiveness demands. Hence in the present study, batch experiments were performed to examine the influence of initial substrate concentration (1000 - 9000 mg COD/L) on hydrogen production. It was inferred that the maximum cumulative hydrogen production of 1825 mL was obtained at optimized conditions of 7000 mg COD/L, pH of 5.5. The experimental data were modelled using various kinetic models like the first order model, diffusional model and Singh model. Kinetic constants were evaluated to found out the suitability of these models. Among these models, Singh model was found to be the best suited with the experimental results. The higher R^2 value of Singh model indicated that initial substrate concentration played a major role in the hydrogen production process from the confectionery wastewater. In addition, the lower R^2 values of first order and diffusional models indicated the unsuitability of the model. From the present study, it could be concluded that confectionery wastewater could be effectively treated and used for hydrogen production as it is rich in carbohydrates.
Keywords: Confectionery wastewater, Hydrogen production, Batch kinetics.

Introduction

It is well known that organics like carbohydrates are the potential source for hydrogen production[1, 2]. The sustainability of fermentative hydrogen production is much dependent on the substrate used and it has been shown that the physical–chemical properties of the substrate strongly determine the overall efficiency of the process[3]. Hence, using the wastewater or solid wastes, it could be possible to generate hydrogen. Recently it was estimated that, only 26% of the wastewater generated is treated before letting out and the rest disposed untreated[4, 5]. Hence utilisation of these wastewaters as a potential substrate for hydrogen production has been drawing considerable interest in recent years as it addresses most of the criteria required for substrate selection viz., availability, cost, biodegradability, high organic loading possibilities, low nutrient requirements and positive net energy gain[6]. This provides dual environmental benefits in the aspect of wastewater treatment along with sustainable hydrogen generation. It is estimated that upto 20% reduction of global environmental problems can be achieved by utilizing the wastes and wastewaters[7].

Among the various types of industrial wastewaters, confectionery wastewater is rich in carbohydrates which would be ideal substrates for hydrogen producing anaerobic bacteria. In confectionery industry, approximately about 50-60 kilo liters/d of wastewater was generated which contains rich organic matters with higher chemical oxygen demand and biological oxygen demand[8]. Hydrogen production using wastewaters has gained more importance in the recent years and extensive studies has been carried using distillery, sago, pharmaceutical and synthetic wastewaters, whereas only little works have been carried out using confectionery wastewater[5].

Hence, the present research work has been designed to produce hydrogen from organic rich confectionery wastewater in batch reactor using selectively enriched anaerobic mixed culture under acidophilic conditions.

Materials and Methods

Substrate and inoculum

Confectionery wastewater was collected from leading confectionery units in Tamil Nadu, India and used as substrate. Inoculum was collected from anaerobically digested sludge in the confectionery wastewater treatment plant. The culture was heat treated at 110°C for 2 h in order to inactivate methanogens and to enrich hydrogen producing bacteria[9].

Batch experiments

Batch experiments were carried out using 250 mL Erlenmeyer flask. The effect of initial substrate concentration (1000, 3000, 5000, 7000 and 9000 mg COD/L) on hydrogen production was evaluated. After addition of inoculum, the batch reactors were sparged with nitrogen gas to generate an anaerobic environment. Initial pH was adjusted using 1N HCl or 1N NaOH. All the experiments were carried out in triplicate. The COD concentration and hydrogen production were monitored for every 6 h and continued until the attainment of concordant values.

Monitoring and analysis

The pH, chemical oxygen demand (COD) and hydrogen production were recorded daily and analysed according to the standard methods of APHA[10]. The hydrogen gas was determined using a gas chromatograph (Shimadzu, 221-70026-34, Japan) equipped with a thermal conductivity detector (TCD) and the column was packed with porapak Q column. Nitrogen was used as the carrier gas. The operating temperatures of the column and detector were 100ºC and 120ºC, respectively.

Results and Discussion

Effect of initial substrate concentration on hydrogen production

Initial substrate concentration is one of the important parameters in hydrogen production because of its significant effect on bacterial growth and hydrogenase activity[5, 11]. For the different initial substrate concentrations of 1000, 3000, 5000, 7000 and 9000 mg COD/L, the steady state COD removal efficiencies were 77, 94, 96, 98 and 86% respectively, by the end of 72 h with constant initial pH of 5.5 at 32±2°C (Fig. 1). The corresponding cumulative hydrogen productions were 600, 1325, 1565, 1825 and 915 mL (Fig. 2). It was observed that the COD removal efficiencies and the hydrogen production increased with an increase in initial substrate concentration from 1000 to 7000 mg COD/L. Further increase of initial substrate concentration from 7000 to 9000 mg/L, decreased the COD removal efficiency and the hydrogen production to 86 % and 915 mL, respectively. Thus, a maximum of 98% COD removal efficiency and cumulative hydrogen production of 1825 mL was attained at 7000 mg COD/L. At the lower initial substrate concentration, reduction in the accumulation of the acidic fermentation products led to higher hydrogen production from 600 to 1825 mL.The lower COD removal efficiency of 86% and cumulative hydrogen production (915 mL) at higher initial substrate concentration of 9000 mg COD/L might be due to the accumulation of liquid fermentation products which had resulted in the over-acidification of bacterial growth. This in turn had inhibiting the fermentation process[9, 12].

The steady state effluent pH was 4.6, 4.5, 4.2, 4 and 3.5 respectively. The effluent pH of 4.6 to 4 at initial substrate concentration levels from 1000 to 7000 mg/L indicated the acid production by acidogenic bacteria which favoured the hydrogen production[13]. The lower pH at higher initial substrate concentration might be due to the accumulation of VFA and so micro organisms could not perform fermentation at this pH due to rate limiting steps in anaerobic digestion process like hydrolysis[14].

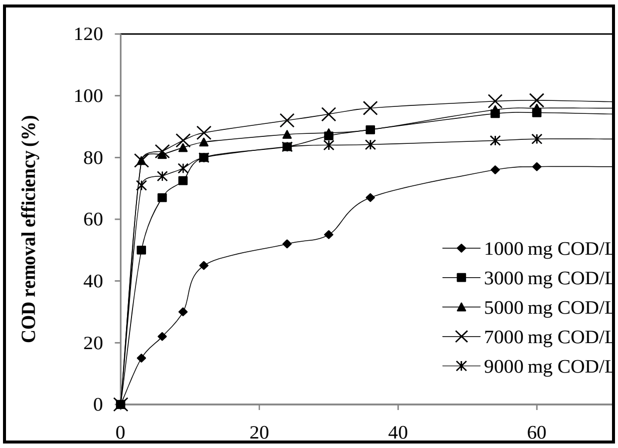


Fig. 1 Effect of time on COD removal efficiency at various initial substrate concentrations

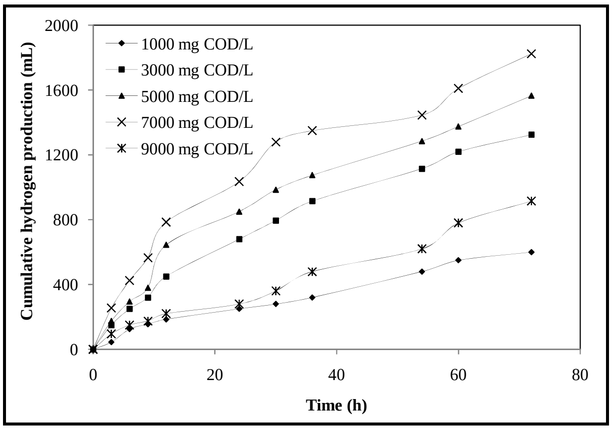


Fig. 2 Effect of time on cumulative hydrogen production at various initial substrate concentrations

Batch kinetics of hydrogen production

The first order model

Table 1 Kinetic parameters of the tested models

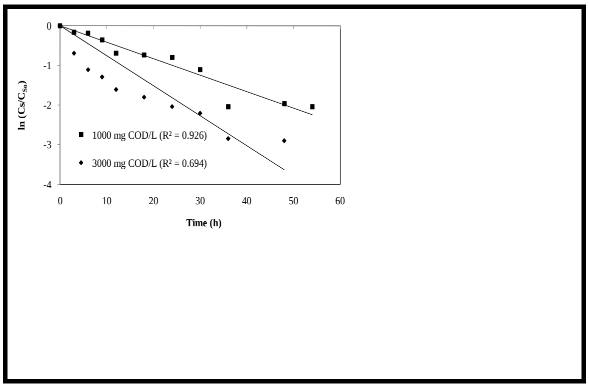
Kinetic model (1/d)	Initial substrate concentration (mg COD/L)				
	1000	3000	5000	7000	9000
The first order model (k_1)	0.041	0.075	0.083	0.108	0.059
The Singh model (k_2)	0.301	0.534	0.769	0.859	0.863
The diffusional model (k_3)	0.338	0.31	1.107	1.45	1.23

The basic linear equation of first order model is given in Eq. (1)

$$\ln\left(\frac{S}{S_o}\right) = -k_1\, t \qquad \text{(Eq. 1)}$$

where, S, S_o = substrate concentration at effluent and influent respectively, k_1 = first order rate kinetic constant ($time^{-1}$), t = time (h)

The first order rate kinetic constant (k_1) was calculated from the Fig. 3. k_1 was found to increase with increase in initial substrate concentration from 1000 to 7000 mg COD/L and decreased at 9000 mg COD/L (Table 1). The determination of coefficient, R^2 values indicated that the model was unfit for the prediction of the system. This might be owing to the nature of substrate and inoculum used. The present work was in agreement with the work of Mullai[15].



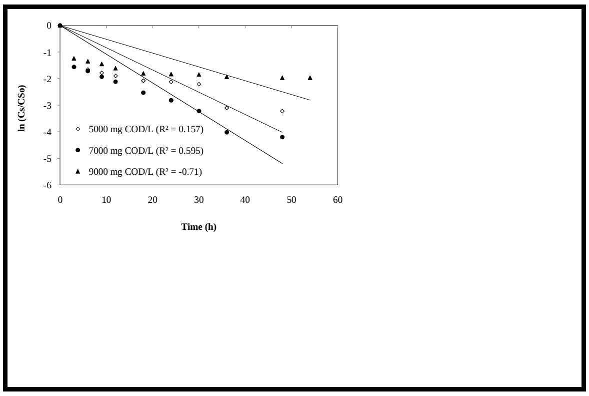


Fig. 3 The first order model

The diffusional model

$$\frac{dC_s}{dt} = -k_2 \left(C_s\right)^{0.5} \quad \text{(Eq.2)}$$

On integration, between the known limits Eq. (2) gives Eq. (3)

$$S^{0.5} - S_o^{0.5} = -0.5 k_2 t \quad \text{(Eq.3)}$$

where, S, S_o = substrate concentration at effluent and influent respectively, k_2 = diffusional model rate constant, t = time (h)

The kinetic constant was found to increase with increase in initial substrate concentration from 1000 to 9000 mg COD/L (Table 1). The R^2 values (Fig. 4) of the present study showed this model to be a poor fit. Similar results were obtained by Converti and team[16] during prehydrolysis of woody wastes. The model was best fit in the work of Mullai[15] during their study on pharmaceutical wastewater.

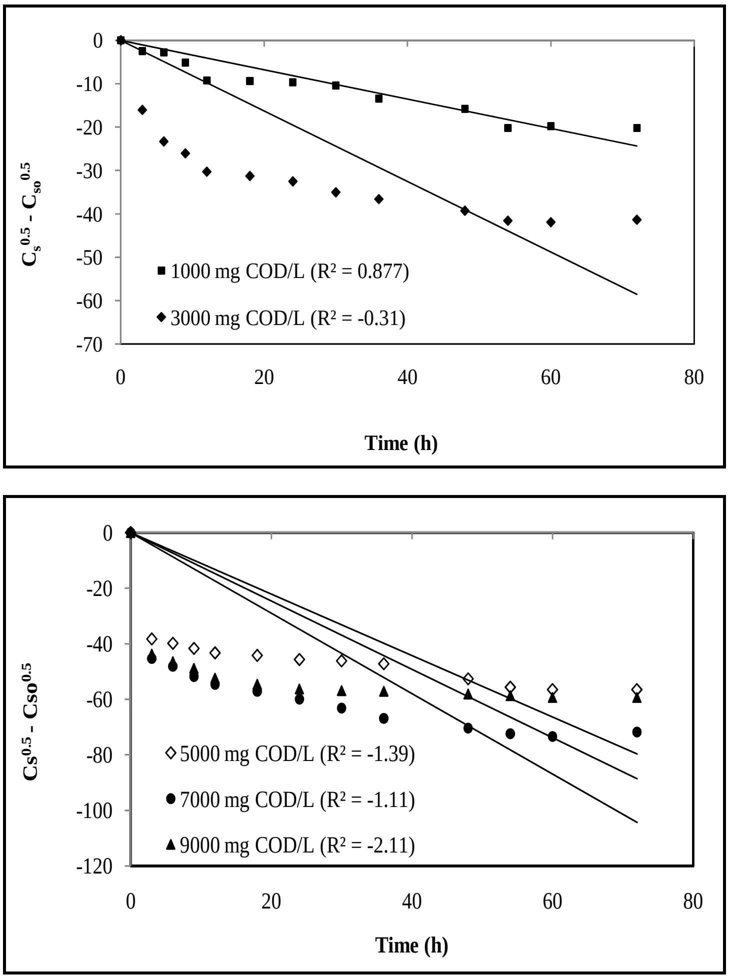


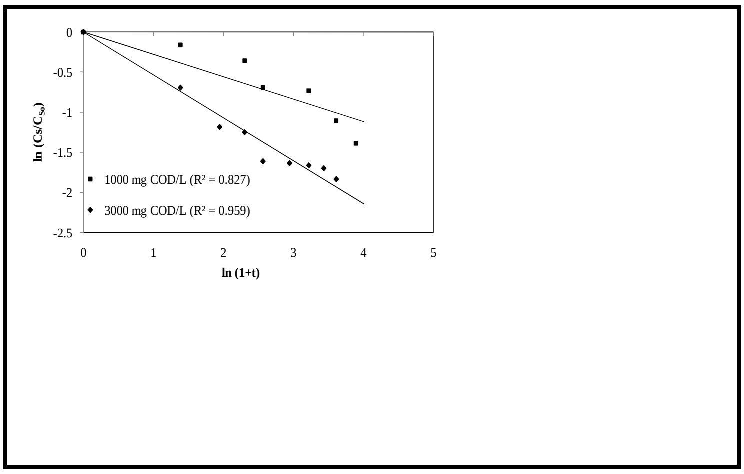
Fig. 4 The diffusional model

The Singh model

Modified version of the first order model as proposed by Singh and co-workers[17] is given in Eq. (4)

$$\ln \frac{S}{S_o} = -k_3 \ln (1+t) \qquad \text{(Eq. 4)}$$

where, S, S_o = substrate concentration at effluent and influent respectively, t = time (h), k_3 = rate constant of the Singh model.



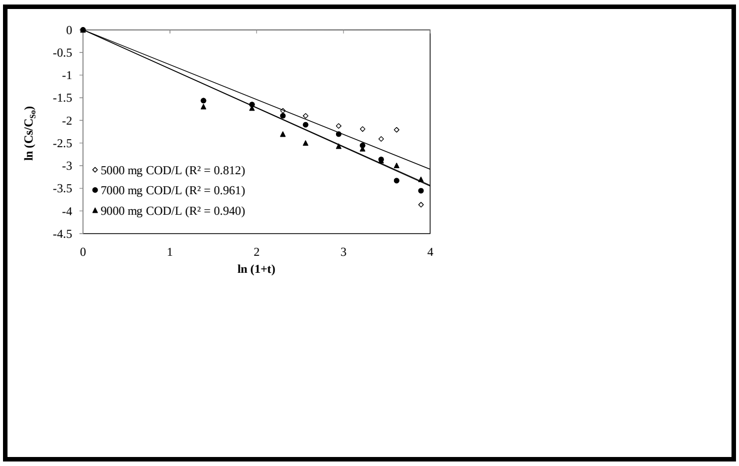


Fig. 5 The Singh Model

The rate constant, k_3 of the Singh model has been calculated from the slope of the Eq. (4) and Fig. 5. The obtained rate constant was given in the Table 1. For the various initial substrate concentrations like 1000, 3000, 5000, 7000 and 9000 mg COD/L, the corresponding R^2 values were 0.827, 0.959, 0.812, 0.967 and 0.940. The higher R^2 value at the optimum initial substrate concentration of 7000 mg COD/L, confirmed the aptness of this system. Also, the model finely predicted the substrate degradation for the production of hydrogen. The R^2 value indicated that initial substrate concentration played a major role in the hydrogen production process from the confectionery wastewater. For the first time, Singh model has been applied to study the performance of confectionery wastewater in hydrogen production. Alike, Singh et al.[17] and Converti et al.[16] stated that the model suited well with their works on degradation of cattle waste and woody waste respectively. In addition, Mullai[15] concluded that the model was not fitted well and reported that it might be due to the non – recalcitrant nature of the substrate used for the methane production.

Conclusions

Hence in the present study, batch experiments were performed to examine the influence of initial substrate concentration (1000 - 9000 mg COD/L) on hydrogen production. It was inferred that the maximum cumulative hydrogen production of 1825 mL was obtained at optimized conditions of 7000 mg COD/L, pH of 5.5. The experimental data were modelled using various kinetic models like the first order model, diffusional model and Singh model. Kinetic constants were evaluated to found out the suitability of these models. Among these models, Singh model was found to be the best suited with the experimental results. The higher R^2 value of Singh model indicated that initial substrate concentration played a major role in the hydrogen production process from the confectionery wastewater. In addition, the lower R^2 values of first order and diffusional models indicated the unsuitability of the model. From the present study, it could be concluded that confectionery wastewater could be effectively treated and used for hydrogen production as it is rich in carbohydrates.

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