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Kinetic model for an up-flow anaerobic packed bed bioreactor: Dairy wastewater treatment

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Kinetic studies of anaerobic digestion process of cheese whey were conducted in a pilot-scale up-flow anaerobic packed bed bioreactor (UAPB). An influent COD concentration of 59419 mg/l was utilized at steady state condition. Logistic and Monod kinetic models were employed to describe microbial activities of cheese whey in an anaerobic digester. The hydraulic retention times (HRT) in the range of 6 to 24 h were investigated throughout the experiments. Lactose conversions were 58.5 and 99.4% for HRT of 6 and 16 h, respectively. The methane production rates were 6.57 and 3.25 l/h for HRT of 6 and 24 h, respectively. Monod biokinetic coefficients, K_s , μ_m and methane yield (Y_M) were 8.59, 7.63 (h⁻¹) and 0.11 (g methane/g lactose), respectively.

Key words: Anaerobic filter, UAPB, cheese whey, methane yield, kinetic model, monod, logistic.

INTRODUCTION

Dairy wastewater particularly cheese whey consists of high organic matters, mainly lactose, fat and protein. The enriched nutrients in cheese whey have created a suitable environment for *Lactobacillus* species to convert organic sources into methane via anaerobic process. Whey is considered as highly pollutant effluent with respect to COD level (60-80 g/l) (Mc-Hugh et al., 2006; Gannoun et al., 2008). There are number of biological treatment processes to treat dairy wastewater such as activated sludge system, anaerobic ponds and anaerobic digestion process (Demirel et al., 2005; Malaspina et al., 1996).

Anaerobic treatment process is an ideal technique for the bioconversion of cheese whey to biogas. In comparison to aerobic process, the system does not require aeration but generates biogas as energy source (Erguder et al., 2001; Gerardi, 2003).

Kinetic model which is used in design of bioreactor describes the performance of biological activities and the growth related to nutrients and organic sources exist in the living environment. Kinetic models are divided into structured and unstructured models. Indeed, intracellular products are multi-components which are followed by structured model. Any extracellular product which acts as enzyme and individually enhances the biochemical reactions may follow unstructured model (Liu et al., 2006; Najafpour, 2007; Bailey and Ollis, 1986).

The purpose of the present research was to investigate the performance of UAPB bioreactor for the treatment of whey. Three models were analyzed to find the suitability of the kinetic models for the bioconversion of whey. Monod and logistic models were used to predict the behavior of *Lactobacillus* species in the UAPB.

MATERIALS AND METHODS

Cheese whey

The cheese whey used in this study was obtained from "Gela Factory" (Amol, Iran), which used ultrafiltration process to produce cheese. The whey samples were provided from the factory in 20 I containers and daily transported to the laboratory, refrigerated and stored at 4°C to avoid acidification and changes of the chemical composition of the cheese whey. During the adaptation phase, diluted whey at pH 6.5 was fed into the reactor. Based on necessity of the experiment, various diluted solutions of cheese whey were prepared using distilled water. The feed pH was adjusted to 6.5, using a 6 M sodium hydroxide solution. The characteristic and chemical composition of cheese whey is shown in Table 1. The effluent possessed high COD content.

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| Characteristic | Unit | Value |
|------------------|------|---------|
| COD | mg/l | 60000 |
| Lactose | g/l | 50 |
| TS | g/l | 55 |
| VS | g/l | 49 |
| Proteins | g/l | 2.2 |
| Phosphate | g/l | 0.6 |
| Ca ²⁺ | g/l | 0.02 |
| рН | | 5.5-6.6 |

Table 1. The characteristic and chemicalcomposition of cheese whey.

Experimental set up

Figure1a presents the schematic diagram of the pilot scale UAPB bioreactor. The Plexiglas reactor was fabricated with an internal diameter of 19.4 cm and a height of 60 cm. The total volume of the reactor was 17.667 L. The column was packed with a seashell that is shown in Figure 1b. The void volume of the packed bed reactor was 65%. A 1000 ml funnel shaped gas separator was used to liberate the generated biogas from the effluent, and then the gas was led to the gas collector tank. The gas tank was a cylindrical glass pipe with an internal diameter of 80 mm and height of 1 m. The liberated gas was frequently measured at a constant HRT and the gas volume was recorded with respect to time. The gas tank was initially filled with water which was saturated by the displacement of water in the gas tank.

The UAPB reactor was operated at room temperature (25°C). Cheese whey as a suitable substrate was continuously fed to the reactor using a peristaltic pump (SR25 adjustable flow rate, Thomas, Germany). The feed was introduced from the bottom of the column and uniformly distributed through the column using a perforated plate. The effluent samples were collected from the top of the column in a 20 L polyethylene container.

Reactor operation

The reactor was started with a 3 L seed culture contained anaerobic sludge which was originated from the waste-water treatment plant, Gela factory. In the packed bed bioreactor, to create sticky surface on seashells, 2 L solution of 1 g/l nutrient agar (Merck, Germany) was introduced from the top of the column for fast development of biofilm. In order to acclimate the sludge with cheese whey, the reactor was batchwise fed with diluted cheese whey (7000-20000 mg COD/I). For the first three days of operation, the bioreactor was continuously fed in full recycle mode. Then the feed tank was gradually loaded with fresh whey. Continuous feeding the reactor was started with an initial organic loading rate (OLR) of 0.66 g COD/(I.h) and HRT of 24 h. The HRT was maintained constant throughout the start-up period for duration of 5 days. The influent COD concentration was 15000 mg/l for the first 5 days, and then it was stepwise increased to 60000 mg/l (OLR = 2.47 g-COD/(l.h)) from 5 to 15 days of operation. The reactor was continuously operated for 65 days.

Analytical methods

COD was determined as described by Standard Methods (Elmitwalli and Otterpohl, 2007; APHA, 2005). Lactose and COD values were measured by spectrophotometer, UNICO 2100 (New Jersey, USA). A gas-tight syringe (Hamilton CO., Reno, Nevada, USA) was used to take sample from the gas sampling port. Gas chromatograph (Perkin Elmer, Auto system XL), equipped with thermal conductivity detector (TCD) and data acquisition system with computer software (Total Chrom) were used for gas composition analysis. A GC column, Carboxen 1000, with 100/120 mesh (Supelco, Park, Bellefonte, PA, USA) was used. The column temperature was initially maintained at 40°C for 3.5 min, followed by automatic temperature increase with a rate of 20°C/min till it reached to 180°C. The injector and detector temperatures were 150 and 200°C, respectively. The flow rate of carrier gas (He) was set at 30 ml/min.

RESULTS AND DISCUSSION

Reactor performance

The UAPB was continuously operated with HRT of 6 to 24 h. The biofilm was fully developed on the natural packing (seashell). Figure 2 shows substrate consumption profile (lactose) of the effluents and the cell density with respect to HRT. The lactose concentration was sharply reduced to about 0.5 g/l at HRT of 16 h. At any HRT of greater than 16 h, the profile was flattened. The cell dry weight of the fermentation broth was analyzed at various HRT. As the HRT increased the cell density was exponentially increased. At HRT of greater than 16 h, the cell growth had reached to stationary phase. The pattern for cell growth has exactly followed the substrate utilization which shows growth related model (Najafpour, 2007).

Several growth rate kinetic models were investigated. One of the models based on limited substrate consumption is the first-order reaction as follows (Raj and Anjaneyulu, 2005):

$$-\frac{dS}{dt} = k_s S \tag{1}$$

where k_S is the rate constant. Equation (1) is characterized as exponential growth and the substrate concentration profile with respect to HRT as followed:

$$S = S_0 e^{-k_s \tau} \tag{2}$$

where *S* is substrate concentration and S_o is the initial substrate concentration.

This model shows the exponential growth of the organism as the substrate is utilized. The logarithmic rate model for substrate utilization is given in equation (3):

$$\ln S / S_0 = -k_s \tau \tag{3}$$

Figure 3 depicted $\ln S/S_o$ vs HRT. The experimental data are very well fitted with the presented model (R² =0.99).



Figure 1. Schematic diagram of experimental set up: a. UAPB flow diagram. b. Fabricated pilot scale of the bioreactor.



Figure 2. Lactose consumption profile and cell growth curve with respect to HRT.

Monod growth kinetic model is considered as the functional relationship exists between the specific growth and the essential substrate is given by the following equation (Najafpour and Shan, 2003; Najafpour and Younesi 2007):

$$\mu = \frac{\mu_{\max}S}{K_s + S} \tag{4}$$

Here μ_{max} is the maximum specific growth rate and K_S is



Figure 3. Logarithmic rate model for substrate utilization.



Figure 4. Linearized double-reciprocal plot of the specific growth and substrate.

the Monod rate constant.

The linearized double- reciprocal plot of the specific growth and substrate; $1/\mu$ vs 1/S is shown in Figure 4.

The fitted experimental data showed that the biomass growth in the bioreactor has followed Monod kinetic model.



Figure 5. Riccati model for growth kinetics.

Another simple model was initially drawn from Malthus model which project the biomass growth that follows the exponential pattern. The following equation describes unstructured Malthus model (Najafpour and Yap, 2005; Najafpour, 2007):

$$\frac{dX}{dt} = f(X) = \mu X \tag{5}$$

Where μ is the specific growth rate and x represents the biomass concentration.

Equation (6) represents Logistic model which is induced by an inhibition factor for the population growth rate. Assuming that the inhibition is second-order with respect to cell density (x^2), then the equation becomes:

$$\mu = \mu_m \left[1 - \frac{X}{X_m} \right] \tag{6}$$

Where x_m is the maximum biomass concentration in g.l⁻¹ and μ_m is maximum specific growth rate in h⁻¹. Substituting Equation (5) into (6) and upon integrating gives a sigmoid variation of cell dry weight (*x*) as a function of time. The expression for cell dry weight known as Riccati is obtained (Najafpour and Yap, 2005; Najafpour et al., 2004):

$$x = \frac{x_0 e^{\mu_m t}}{1 - (x_0 / x_m) \cdot (1 - e^{\mu_m t})}$$
(7)

This model shows that the cell dry weight (x) is indepen-

dent of substrate concentration. Equation (7) may represent both exponential and stationary phases. The Riccati equation presented above does not predict the death phase of the microorganisms after the stationary phase. To predict the death phase of bacteria, equation (8) is expressed as follows (Pazouki et al., 2008):

$$x = \frac{x_0 e^{\mu_m t}}{1 - (\frac{x_0}{x_m})^2 (\frac{\mu_m}{k + \mu_m})(1 - e^{(k + \mu_m)t})}$$
(8)

Where k is a constant value which is associated with the promotion or decline of cell population in the batch culture.

The positive value of k shows the promotion of the cell population whereas a negative value of k shows a decline in the cell population. Figure 5 shows the experimental data fitted with Riccati model given in equation (8) with R² of 0.98. Based on assumption stated above, inhibition was incorporated in Logistic model. Riccati was derived from Logistic equation with the concept of inhibition. Therefore, Riccati model also predicts any possible inhibition may exist in the bioreactor.

One of the important kinetic coefficients of anaerobic digestion process is methane yield (Y_M) which represents the performance of a reactor in terms of methane production. The organic removal rate is related to the rate of methane production as stated in equation (9) (Zinatizadeh et al., 2006; Metcalf and Eddy, 2003):

$$Q_M = Y_M Q (S_0 - S) \tag{9}$$

Where S_0 is the concentration of influent COD (g COD/l),



Figure 6. Methane production with respect to utilized substrate.

| Table 2. Kinetic parameters | , rate models with | and without inhibition. |
|-----------------------------|--------------------|-------------------------|
|-----------------------------|--------------------|-------------------------|

| Parameter | μ _m (1/h) | K _S (1/h) | ќ (1/h) | k (1/h) | R ² | Y _{CH4 /lactose} (I/g) |
|----------------------------|----------------------|----------------------|---------|---------|----------------|---------------------------------|
| Substrate utilization rate | - | - | 0.175 | - | 0.99 | - |
| Monod equation | 7.633 | 8.594 | - | - | 0.99 | - |
| Logistic equation | 0.1046 | - | - | 0.047 | 0.98 | - |
| Methane yield | - | - | - | - | 0.98 | 0.183 |

S is the effluent COD concentration and Q is the volumetric feed flow rate (I/day).

Equation (9) was plotted (Figure 6) using the experimental data and the value of 0.183 I CH₄ STP/g COD removed was obtained for Y_{M} . The kinetic parameters for several models are summarized in Table 2.

Conclusions

The present investigation reveals that the biogas production and treatability of the whey using the UAPB bioreactor as a novel film anaerobic bioreactor with high performance for handling the high organic load was successfully achieved. The use of UAPB reactor was a great strategy to achieve high COD removal efficiency in a short period of time. The reactor was very efficient in the treatment of diluted and high strength whey at high OLR and short HRT. High COD and Lactose removals of 94.5 and 99% at HRT of 16 h were achieved. The highest yield of methane production was achieved at HRT of 16 h and the maximum biogas volumetric production rate was as HRT of 6h.

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Abbreviation and Nomenclatures:

| UAPB | Up-flow anaerobic packed bed bioreactor |
|----------------|---|
| COD | Chemical oxygen demand, mg/l |
| HRT | Hvdraulic retention time. h |
| TS | Total solid, mg/l |
| TSS | Total suspended solid, mg/l |
| VS | Volatile solid, mg/l |
| VSS | Volatile suspended solid, mg/l |
| Ks | Monod rate constant, g/l |
| μ | Specific growth rate, h ⁻¹ |
| | |
| $\mu_{ m max}$ | Maximum specific growth rate, h ⁻¹ |
| Y _M | Methane yield, g/g |
| S | Substrate concentration, g/l |
| So | Initial substrate concentration, g/l |
| au | retention time, h |
| Х | Biomass concentration, g/l |
| X _m | maximum biomass concentration, g/l |
| Xo | Initial biomass concentration, g/l |
| k | Rate constant, h ⁻¹ |
| K' | Substrate utilization rate, h ⁻¹ |
| Q | Volumetric feed flow rate, I/day |

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