MATHEMATICAL MODELING OF DISTILLERY WASTEWATERS BIOMETHANATION IN FLUIDIZED-BED BIOREACTOR

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Received 25 January 2010; received in revised form 3 April 2010

Abstract: An anaerobic fluidized- bed reactor was designed to treat distillery wastewaters for biogas generation using actively digested aerobic sludge of a sewage plant. The optimum digestion time was 8 h and optimum initial pH of feed was observed as 7.5 respectively. The optimum temperature of feed was 40°C and optimum feed flow is 14 L/min with maximum OLR was 39.513 kg COD m⁻³ h⁻¹ respectively. The OLR was calculated on the basis of COD inlet in the bioreactor at different flow rates. Maximum CH₄ gas concentration was 63.56 % (v/v) of the total (0.835 m³/kg COD m⁻³ h⁻¹) biogas generation, corresponding to 0.530 m³/kg COD m⁻³ h⁻¹ at optimum digestion parameters. Maximum COD and BOD reduction of the distillery wastewaters were 76.82% (w/w) and 81.65% (w/w) with maximum OLR of 39.513 kg COD m⁻³ h⁻¹ at optimum conditions respectively. The rate constant (k) was measured as 0.31 h⁻¹ in fluidized-bed bioreactor and followed a first order rate equation. The specific growth rate (Ç) was 0.99 h⁻¹ and maximum sp. growth rate (Cmax) was 1.98 h⁻¹ respectively. The bacterial yield coefficient (Ç) was determined as 0.319/kg COD m⁻³ h⁻¹ at optimum parameters. The studies also dealt with the mathematical modeling of the experimental data on biomethanation and suggested modeling equations relating to kinetic parameter (rate constant, k), maximum specific growth rate (Cmax) with respect to COD (substrate) removal. The mathematical model was also analyzed for hydrodynamic pressure (Δp) vs feed flow (µ) and hydrodynamic pressure (Δp) with respect to CH₄ gas yields. The linear and non-linear equations which fitted the models were obtained.

Keywords: Biomethanation, anaerobic, optimum condition, modeling

DOI: 10.3329/cerb.v14i1.4224

1. Introduction

The energy crisis of the early 1970s brought into sharp focus the vital importance of the extent biomass energy base in the face of destabilized global trade in fossil energy. Since the bulk of energy used in developing countries is in the form of biomass energy formal household consumption, the energy crisis has, in reality, became biomass energy crisis in those countries. Much of the present-day technology is fueled by biomass of carboniferous era. To a varying extent, this fossil biomass energy resource is supplemented all over the world by energy obtainable from extant biomass. A reassessment of conventional biomass energy production and conversion technologies is pertinent at this stage. The bulk of biomass energy is currently derived from vegetable and from agricultural crop residues [1–5]. Biogas production is of major importance for the sustainable use of agrarian biomass as renewable energy source. In a few instances, municipal wastes and such sources as peat form additional sources of biomass energy. A more possible alternative is to use of industrial cellulosic wastewaters, wastewaters and effluents to satisfy the ecological balances and pollution abatement [6–29].

Since the early 70s, anaerobic digestion of industrial waste-waters has gained considerably in importance. It is concluded that while the anaerobic fluidized- bed process has become an established technology for biomethanation of treatment of industrial waste-waters, further improvements can still be expected. Attached bacteria have the highest relative activities and are considered to have a more important role in anaerobic stabilization than the unattached portion [16–19]. Biomass concentration in the bottom part of the bed showed higher values than in the upper levels in the fluidized bed reactor. On the other hand, biofilm density increased towards the reactor bottom, wherein it showed the highest values. The assays indicated that total activity was higher in bioparticle sampled from upper reactor levels. This was explained by the lower biofilm density values in this zone and mass transfer limitation phenomena [16–19].

Perez et al [8] examined the effect of organic loading rate (OLR) on the removal efficiency of Chemical Oxygen Demands (COD) and total organic carbon (TOC) anaerobic thermophilic fluidized bed reactor (AFBR) in the treatment of cutting-oil wastewater at different hydraulic retention time (HRT) conditions. Acharya et al [9] studied on anaerobic digestion of wastewater from a distillery industry having very high COD and Biological Oxygen demands (BOD) was fed in a continuous upflow fixed film column reactor using different support materials such as charcoal, coconut coir and nylon fibers under varying HRT and OLR respectively.

The present investigations were undertaken for an effective anaerobic biomethanation of distillery wastewaters using aerobic activated digested sludge from sewage plant for biogas generation in fluidized- bed bioreactor. Attempts

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were made to optimize digestion time, initial feed pH, feed temperature and feed flow (OLR) to obtain maximum CH₄ gas generation and removal of COD and BOD of distillery wastewaters. The kinetics of anaerobic biomethanation of the distillery wastewaters with respect to COD removal in fluidized-bed bioreactor was also investigated. The studies dealt with the mathematical modeling of the experimental data on biomethanation and suggest model equations relating kinetic parameter (rate constant, k), maximum specific growth rate (µ_max) with respect to COD (substrate) removal [15–19]. The mathematical model was also analyzed for hydrodynamic pressure (Δp) vs feed flow (u) and hydrodynamic pressure (Δp) with respect to CH₄ gas yields.

2. Experimental

2.1. Collection of seed and suspension culture preparation

Actively digesting sludge was collected from the local aerobic sewage plant constitutes ideal “seed” material. It was transferred to suspension culture media and incubated at 30°C for 7 days in an incubator for sufficient bacterial population. The resulting methagenic bacterial cell suspensions were filtered through several layers of sterile absorbent cotton. The bacterial population was counted as 7.1 x 10⁸ numbers of cells per mL of the suspension culture [30]. This bacterial suspension culture was used for the present studies. The following constituents were used for suspension culture media preparation per liter: KH₂PO₄-20g, MgSO₄·7H₂O-5.0g, CaCl₂-1.0g, MnSO₄·7H₂O-0.05g, FeSO₄·7H₂O-0.10g, CaCl₂·6H₂O-0.10g, AlK(SO₄)₂·12H₂O-0.01g, Na₂MoO₄·2H₂O-0.01g.

2.2. Collection and analysis of distillery wastewater

The distillery wastewater was collected from indigenous source and stored in freeze at 4°C. The sample was analyzed for COD (95,785 mg/L) and BOD (72,655 mg/L) respectively.

2.3. Experimental setup

The experimental setup of fluidized-bed bioreactor (M/S Apex Innovations Ltd) is shown in Figure 1. The distillery wastewaters entered at the bottom and passed through the fluidized-bed bioreactor (volume: 0.0186 m³; column dia: 13×10⁻² m) and left from upward. The flow had a velocity sufficient to expand the bed without necessarily causing vigorous agitation, which resulted in complete mixing of the wastewaters and methagenic bacteria. The spherical glass particle (dia, 5x10⁻⁴ m; solid particle density, 2230 kg/m³) that allowed low energy requirements for fluidization, also, provided a good surface for biomass attachment (biofilm formation) and development. It was assumed that most particles had been covered with a thin biofilm of uniform thickness. Outlet digested feed was recycled to the feed tank (Figure 1). The biogas was collected in a gas holder (The gas holder is normally an airproof steel container that, by floating like a ball on the fermentation mix, cuts off air to the digester and collects the gas generate) fitted with a Flame-Ionization Detector (FID) for CH₄ gas analysis [30].

2.4. General method

Experiments were carried out in 50 L plastic tank containing 20 L of raw wastewaters as feed to be digested for biogas generation. Equal volumes (20 L) of suspension mixed methagenic bacterial culture as inoculum were added to the feed tank. 20 L of suspension culture media were added to the feed tank contents. The initial pH of feed in tank was maintained at 6.0 by using 0.1 N H₂SO₄ acid and/or 1 M CaCO₃ slurry. The temperature of the feed was maintained at 30°C by means of heating coil fitted with off-on temperature controller. The temperature of feed was measured by a thermocouple. The feed was pumped to fluidized-bed bioreactor form the feed tank. The initial feed flow was maintained at 10 L/min (OLR 28.224 kg COD m⁻³ h⁻¹) through a rotameter (Figure 1). After each operation, the digested feed was discharged through a valve.

2.5. Effect of Digestion Time, Initial Feed pH, Feed Temperature and Feed Flow

The concentrations of CH₄ gas in the biogas were measured on a regular interval (2, 4, 6, 8, 10 and 12 h) of time and analyzed for COD and BOD in digested feed. The concentrations of CH₄ gas were measured at optimum digestion time (8 h) for various pH values (6.5, 7.0, 7.5 and 8.0) and analyzed for COD and BOD in digested feed. CH₄ gas concentrations were measured at optimum digestion time (8 h) and pH (7.5) for various temperatures (35, 40 and 45°C) and analyzed for COD and BOD in digested feed. CH₄ gas concentrations were measured at optimum time (8 h), pH (7.5) and temperature (40°C) for various feed flow (12 L/min, 14 L/min, 16 L/min and 18 L/min) and analyzed for COD and BOD in digested feed.

2.6. Analysis of methane

The analysis of biogas containing methane was carried out in the Flame-Ionization Detector (FID) [31]. The eluate coming from the column was mixed with hydrogen (the fuel) and then burned in a stream of air (the oxidant) to form
a combustible mixture in FID (M/S Ametek Process Instruments, Inc). The ignited mixture yielded a flame which provides the energy to ionize sample component in the eluate. The temperature (1800°C) of the air-hydrogen flame was used to ionize only carbon compounds. The positive ions thus formed during ionization in the flame were attracted to a negative “Collector” electrode and repelled by a positive “Repeller” electrode. The repeller electrode was either the metal burner or an electrode placed near the base of the flame. Upon striking the collector electrode, the positive ions cause a current to flow in the external circuit connecting the positive and negative electrodes. The current was amplified and recorded. The current flowing through the circuit was proportional to the number of ions striking the collector, which in turn was proportional to the concentration of sample CH4 gas entering the flame. It was calibrated by standard CH4 gas.

3. Results and Discussion

3.1. Effect of digestion time

The concentration and yield of CH4 gas were proportional to time. The concentration and yield of methane (CH4) gas increase with increase of time up to 8 h and then both decline (Figure 2). It was observed that maximum biogas yield from distillery wastewaters is 0.682 m3/kg COD m−3 h−1 at 8 h of digestion time (Figure 2). Maximum CH4 gas yields was 47.85 percent (v/v) corresponding to 0.326 m3/kg COD m−3 h−1 at time of 8 h (Figure 2) at temperature (30°C) and prevalent pressure (1393.265 kN/m2) in three-phase fluidized-bed bioreactor.

The removals of COD and BOD in the biomethanation of distillery wastewaters were 54.96 percent (w/w) and 57.65 percent (w/w) respectively at time of 8 h (Figure 3). After 8 h digestion time, the removal of COD and BOD from wastewaters was decreased and yields of biogas and CH4 was also declined. Therefore, digestion time of 8 h was optimum for biomethanation process in the fluidized-bed bioreactor. At the early stage of biomethanation, which coincided with lag-phase of bacterial growth, the removal of COD and BOD and yield of CH4 gas were very low. The transition of bacterial growth from the lag-phase to exponential phase led to a notable increase in CH4 gas yield, which proceeded with same until it reached maximum (0.326 m3/kg COD m−3 h−1) at optimum time of 8 h. It was evident from the Figure 2 that as the digestion time increased (>8 h), the yield of CH4 gas by the mixed methanogenic bacteria decreased due to death phase of bacteria.

3.2. Effect of initial feed pH

Initial feed pH was taken both in acidic and basic medium range. The increase in yields and concentrations of CH4 gas were observed with increase in initial pH of the feed upto 7.5 and then both were declined. It was observed that maximum biogas yield from distillery wastewaters was 0.718 m3/kg COD m−3 h−1 at feed pH of 7.5 at optimum digestion time (Figure 4). CH4 gas concentration was 52.36 percent (v/v) at feed pH of 7.5 with mixed mutualgenic bacteria (Figure 5). Maximum CH4 gas yields was 0.375 m3/kg COD m−3 h−1 at feed pH of 7.5 at temperature (30°C) and prevalent pressure (1393.265 kN/m2) in three-phase fluidized-bed bioreactor. With increase in feed pH (>7.5), the concentrations as well as the yield of CH4 gas were sharply decreased.

It was also observed that a maximum COD removal in the biomethanation process of distillery wastewaters was 63.80 percent (w/w) at feed pH of 7.5 (Fig. 5). A maximum BOD removal from distillery wastewaters was 66.72 percent (w/w) at feed pH of 7.5. Then, the removals of COD and BOD decreased beyond optimum (7.5) pH. Therefore, initial feed pH of 7.5 was the optimum for maximum yield of CH4 gas and removal of COD and BOD from distillery wastewaters in a fluidized-bed bioreactor in biomethanation process. Variations in pH of the feed resulted in changes in the activity of
the mixed methogenic bacteria and hence the bacterial growth as well as the CH₄ generation. Methagenic bacteria were very active over a certain pH range. When pH differed from the optimal value (>7.5), the maintenance energy requirements increase that lead to decrease in bacterial population and biogas yields [32].

3.3. Effect of feed temperature

The effect of feed temperature on anaerobic biogas and CH₄ gas generation from distillery wastewater in fluidized-bed bioreactor is shown in Figure 6 and 7 respectively. The feed temperature was in the mesophilic range. With increase in temperature, the yields and concentrations CH₄ gas increased up to feed temperature of 40°C and then both decreased. The biogas yield from distillery wastewaters was 0.741 m³/kg COD m⁻³ h⁻¹ at feed temperature of 40°C at optimum conditions. The concentration of methane gas was 57.26 percent (v/v) at feed temperatures of 40°C. CH₄ gas yield in fluidized-bed bioreactor was 0.424 m³/kg COD m⁻³ h⁻¹ at optimum temperature (40°C) and prevalent pressure (1393.265 kN/m²) in three-phase fluidized-bed bioreactor.

Figure 6: Effect of feed temperature on biogas and methane yield

Maximum COD removal in the biomethanation of the distillery wastewaters was 69.83 percent (w/w) at feed temperature 40°C. Maximum BOD removal in the biomethanation of distillery wastewaters was 74.45 percent (w/w) at temperature 40°C. With increase in feed temperature (> 40°C), CH₄ gas yields and the removal of COD and BOD from distillery wastewaters declined as well. Therefore, feed temperature of 40°C was the optimum for maximum yield of methane gas and removal of COD and BOD from distillery wastewaters in a fluidized-bed bioreactor in biomethanation process. Temperatures below the optimum (<40°C) depressed the rate of metabolism of bacterial cells. At higher temperature (>40°C), the growth rate decreased and thermal death occurred [32]. At higher temperature (>40°C), death rate exceeded the growth rate, which causes a net decrease in the concentration of viable bacterial populations [32] with lower generation of CH₄ gas as well as COD and BOD removal.

3.4. Effect of feed flow

The OLR was calculated on the basis COD inlet in the reactor only with different feed flow. With increase in feed flow, the yield and concentration of CH4 gas increased up to 14 L/min and then both decreased. It was noticed that biogas yields in anaerobic fluidized-bed bioreactor was 0.835 m³/kg COD m⁻³ h⁻¹ at feed flow rate of 14 L/min at optimum biomethanation conditions (Figure 8). The concentration of CH₄ gas was 63.56 percent (v/v) at feed flow of 14 L/min (Figure 9). CH₄ gas yields in anaerobic fluidized-bed bioreactor was 0.530 m³/kg COD m⁻³ h⁻¹ at feed flow of 14 L/min at optimum temperature (40°C) and prevalent pressure (1708.264 kN/m²) in three-phase fluidized-bed bioreactor. With increase in feed flow (>14 L/min), the yield and concentration of methane gas were declined.

Figure 8: Effect of feed flowrate on biogas and methane yield

Maximum COD removal in the biomethanation of the distillery wastewaters was 76.82 percent (w/w) at feed flow of 14 L/min. Maximum BOD removal in biomethanation of the distillery wastewaters was 81.65 percent (w/w) at feed flow of 14 L/min. With increase in feed flow (>14 L/min), CH₄
gas yield and concentrations and the removal of COD and BOD from wastewaters were decreased as well. Feed flow of 14 L/min was the optimum for maximum yield of CH₄ gas with maximum removal of COD and BOD from distillery wastewaters in a fluidized-bed bioreactor. Mechanical forces created by flowing fluids, hydrodynamic, and interfacial tension which can disturb the bacterial population to some extent [32]. In the three-phase fluidized-bed bioreactor, there exists a pressure difference between inlet and outlet of the feed. Increase in flow rates can disturb the elaborate shape of enzyme molecule of the bacteria to such a degree that denaturation of the protein occurred and deactivated the methanogenic bacterial growth. Therefore, the yields of CH₄ gas and removal of pollution loads decreased with increase in feed flow (>14 L/min) as well.

3.5. Analysis of Monod model with COD loading

The specific bacterial growth rate in presence of distillery wastewaters as substrate i.e. COD loading at different flow rates at optimum biomethanation conditions in three-phase fluidized-bed bioreactor is shown in Figure 10. The specific bacterial growth rate (µ) was determined by plotting growth rate against limiting substrate COD loading by using Monod Growth Model [32] as shown:

$$\mu = \mu_{max} \left( \frac{S}{K_s + S} \right)$$  \hspace{1cm} (1)

where, $K_s$ is limiting substrate COD loading at which the specific growth rate ($\mu$) was half of maximum growth rate $\mu_{max}$ i.e. $\mu = \mu_{max}/2$, at $K_s = S$ (upto linear portion of the curve). The model indicated a division between the lower concentration range, where was strongly (linearly) dependent on $S$, and the higher concentration range, where became independent of $S$ (curve portion of Figure 10); where, $S$ is the limiting substrate COD loading.

With increase in COD loading (OLR), the growth of bacteria increased (< 39.513 kg COD m⁻³ h⁻¹), then it decreased (>39.513 kg COD m⁻³ h⁻¹). The specific growth rate ($\mu$) was 1.18 h⁻¹ (upto linear portion of Figure 10) and maximum growth rate ($\mu_{max} = 2\mu$) is 2.36 h⁻¹ respectively. The kinetic parameter, $K_s$ was determined as 30.328 kg COD m⁻³ h⁻¹. The bacterial yield coefficient ($Y = X/S = $ maximum sp. growth of bacteria/COD consumed) was determined as 0.0395 kg COD m⁻³ h⁻¹ at optimum biomethanation parameters.

3.6. Kinetic model of fluidized-bed bioreactor

The kinetics of anaerobic biomethanation of the distillery wastewaters in three-phase fluidized-bed bioreactor was investigated. The first order rate equation was of the form:

$$-\ln\left(\frac{S}{S_0}\right) = kt$$  \hspace{1cm} (2)

where, $S_0$ and $S$ are COD consumptions at time=0 and at time $t$ respectively in kg COD m⁻³ h⁻¹.

A straight line (Figure 11) was obtained by plotting digestion time ($t$) against $-\ln\left(\frac{S}{S_0}\right)$. From Figure 11, the kinetic rate constant ($k$) was measured as 0.31 h⁻¹ in fluidized-bed bioreactor. Therefore, it followed the first order rate kinetics. Yield of CH₄ gas as against COD (substrate) consumption at different OLR is shown in Figure 12. With increase in COD consumption, the yield of CH₄ gas increases upto 0.530 m³/kg COD m⁻³ h⁻¹ (COD consumption 30.37 kg COD m⁻³ h⁻¹), then it declined though COD removal was increasing.

3.7. Substrate COD consumption at different flow rates (OLR) vs kinetic parameter (rate constant, $k$) plot

Substrate COD consumption at different flow rates (OLR) vs kinetic parameter (rate constant, $k$) plot is shown in Fig.13. $k$ is a measurement of the overall performance of the fluidized-bed bioreactor depends on COD consumption. $k$ has a maximum of 0.0219 h⁻¹ for COD consumption 30.37 kg COD m⁻³ h⁻¹ (Figure 13). The non-linear equation which fitted the curve of kinetic parameter ($k$) vs COD consumption is:

$$k = -0.0196S^2 + 0.1452S + 0.01321$$  \hspace{1cm} (3)
Substrate COD consumption vs maximum specific growth rate ($\mu_{max}$) is shown in Fig.14. $\mu_{max}$ showed a non-linear relationship with COD removal. $\mu_{max}$ is a measurement of the overall performance of the bacterial growth in three-phase fluidized-bed bioreactor and has a value of 2.58 h$^{-1}$ for COD consumption 30.37 kg COD m$^{-3}$ h$^{-1}$ (Figure 14). The non-linear equation which fitted the curve [15] of $\mu_{max}$ vs COD consumption is:

$$\mu_{max} = -0.0132S^2 + 0.1145S + 0.1125$$  \hspace{1cm} (4)

3.7. Hydrodynamics of fluidized-bed bioreactor

The hydrodynamics of three-phase fluidized-bed bioreactor for CH$_4$ gas yield is shown in Figure 15 and 16. The maximum expansion of the bed was observed as 23.67 cm at optimum feed flow of 18 L/min (0.018 m$^3$/min) with optimum process parameters. It was observed that the increase of the bed expansion increases bacterial mass in the bioreactor. The hydrodynamic pressure ($\Delta p$, pressure difference between inlet and outlet of feed) were 1393.265, 1562.88, 1708.264, 1889.994 and 1974.802 kN/m$^2$ for corresponding fluid velocity of 0.01, 0.012, 0.014, 0.016 and 0.018 m$^3$/min respectively. The fluid velocity was plotted against $\Delta p$ in the three-phase fluidized-bed bioreactor (Figure 15). It was observed that the increase of the feed flow (fluid velocity) increases $\Delta p$ in the bioreactor. The linear relationship between $\Delta p$ vs feed flow ($u$) is:

$$u = 72.692(\Delta p) + 1352.00$$  \hspace{1cm} (5)

CH$_4$ gas yield was also plotted against $\Delta p$ (Figure 16). The non-linear equation which fitted the curve is:

$$Y_{CH_4} = -0.0154(\Delta p)^2 + 0.1378(\Delta p) + 0.04122$$  \hspace{1cm} (6)

where, $Y_{CH_4}$ is the CH$_4$ yield.
4. Conclusion

Generation of CH4 gas from distillery wastewaters in anaerobic fluidized-bed bioreactor using activated aerobic sewage sludge was an effective biomethanation process. The optimum digestion time was 8 h and optimum initial pH of feed was found to be 7.5 respectively. Optimum temperature of feed was 40°C. The optimum flow rate of feed in fluidized bed bioreactor was 14 L/min with OLR of 39.513 kg COD m⁻³ h⁻¹. The maximum expansion of the bed was observed as 23. 67 cm at optimum feed flow of 14 L/min. The maximum biogas yield in anaerobic fluidized-bed bioreactor was 0.835 m³/kg COD m⁻³ h⁻¹. The maximum concentration of CH4 gas at optimum biomethanation process parameters was found as 63.56 percent (v/v) in the anaerobic fluidized-bed bioreactor with mixed aerobic sludge bacteria. At optimum condition, maximum CH4 gas yield, COD and BOD removal were 0.530 m³/kg COD m⁻³ h⁻¹, 76.82 percent (w/w) and 81.65 percent (w/v) from the distillery wastewaters, respectively. A steady state was achieved with 76.82% COD reduction at OLR of 39.513 kg COD m⁻³ h⁻¹ (digestion time 8 h). The optimization of these parameters enabled a stable functioning of the process and allowed the application of high COD loading. The rate constant (k) was measured as 0.31 h⁻¹ in fluidized-bed bioreactor and followed a first order rate equation. The specific growth rate (µ) was 0.99 h⁻¹ and maximum sp. growth rate (µmax) was 1.98 h⁻¹ respectively. The bacterial yield coefficient (Y) was determined as 0.319/kg COD m⁻³ h⁻¹ at optimum parameters. It had been found that variation of kinetic parameter (k) with COD consumption and maximum sp. growth rate (µmax) followed a non-linear relationship with COD loading. The mathematical modeling was also analyzed for hydrodynamic pressure (∆p) vs fluid velocity (μ) and hydrodynamic pressure (∆p) with respect to CH4 gas yields. The linear and non-linear equations which fitted the models were obtained.

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