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Analysis of the Biochemical Methane Potential (BMP) and batch reactor studies of primary sludge from a paper mill

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Abstract

The pulp and paper industry faces serious problems with regard to hazardous pollutants that are generated during its manufacturing process. The dewatered primary sludge (DPS) from the paper mill production process is the largest solid by-product of that industry and considered to be harmful for human beings and the environment. Since the anaerobic digestion has been widely used as a treatment method for organic waste and for the generation of methane gas, the anaerobic digestion of DPS with digester sludge has been looked closer by Biochemical Methane Potential studies (BMP), followed by batch reactor studies carried out on a larger scale. Thereby the anaerobic digestion with methane gas production was found to be a suitable method for paper pulp sludge treatment.

Keywords: paper mill sludge, anaerobic digestion, Biochemical Methane Potential (BMP), batch reactor studies

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1. Introduction

The pulp and paper industry faces serious concerns with regard to hazardous pollutants that are generated during the production of paper [1, 2]. As the largest solid waste product, the dewatered primary sludge (DPS) gives rise to great concern due to its toxic components that can be released through leachate, for instance on landfill sides. So, solid residues from the pulp and paper production are usually incinerated or dumped on landfills [3]. The Nagaon Paper Mill in Morigaon (Assam) produces around 100,000 tons of paper yearly, whereby most of the paper is exported to Iran, Sri Lanka or Egypt. Until now, the solid primary sludge from the primary waste water treatment has been dewatered mechanically and dumped in the local area around with negative impacts on environment and inhabitants. Due to the high content of organic matter and its high energetic potential, the anaerobic digestion of paper mill sludge has to receive closer attention and the treatment strategies of DPS from the pulp and paper industry should be reconsidered, as anaerobic treatment of biodegradable waste has already been widely used, owing to its environmental and energetical advantages [4]. In earlier studies, the biological treatment of secondary sludge from a Kraft Mill Process has often been researched [5]. Anaerobic digestion has also been carried out with Sulfite Process sludge for example [6]. Analysis on the Biochemical Methane Potential was done with mixed paper mill sludge and other materials [7]. However, this study´s aim was to find the best F/M ratio (TVS-based with wet material) for the anaerobic digestion of DPS, with digester sludge as inoculum and subsequent batch reactor studies.

2. Materials and methods

2.1 Dewatered primary sludge and inoculum

Samples of DPS were collected from the primary sludge storage of the Nagaon Paper Mill in Assam.

The samples were sent to the laboratories of IIT Guwahati and stored in a cooling device at 4°C in a cooling device. Digester sludge was collected from a nearby farm in Amingaon and used as inoculum for the BMP and batch reactor studies. All physical and chemical analyses were carried out in accordance with the American Standard Methods. The results of the initial characterizations of the DPS and digester sludge are shown in Table 1.

2.2 Biochemical Methane Potential studies

Biochemical Methane Potential studies are low-cost and space-saving methods which are carried out in small reactors to compare the results of different F/M-ratios. Thus, it is easily controllable because of

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Table 1 Initial characterization values of DPS from the Nagaon Paper Mill and Digester Sludge

Parameter	DPS	Digester sludge
TVS (%)	16.2	4.9
Na (ppm)	53.8	52.5
K (ppm)	47.6	71.3
Ca (ppm)	229.8	291.2
TKN (mg TKN/g)	0.2	0.9
VFA (mg/L)	100	937.5
SCOD (mg O_2/L)	853	6,400
Chlorin (g/L)	22	0
Phosphorus (mg/L)	114	465
pH	7.6	6.7
TCOD (g O_2/L)	-	42.5

the low reactor volume and it allows multiple experiments in a short period of time. The Biochemical Methane Potential studies were performed in duplicated glass bottles for F/M-ratios of 0 (control), 0.5, 1, 1.5 and 2. The glass bottles were filled with 200 mL of digester sludge and corresponding masses of DPS for all F/M-ratios. Nutrients, such as calcium chloride, ferric chloride, magnesium sulfate and phosphate buffer solution were added into the bottles. The bottles were filled with distilled water up to a volume of 500 mL and hermetically sealed with a cork. To insure anaerobic conditions, the residual oxygen was removed by the addition of nitrogen to glass bottles. During the experiments, the methane gas production was measured daily by the water displacement method wherefore the generated gas was fed into a sodium hydroxide solution, where carbon dioxide is absorbed and only methane gas is left over. During the experiments Volatile Fatty Acids (VFA), Soluble Chemical Oxygen Demand (SCOD), pH, ammonia and moisture content were analysed.

2.3 Batch reactor studies

Batch reactor studies are carried out after Biochemical Methane Potential studies to confirm the application of the best F/M-ratio in larger scale. Additionally, the batch reactor studies provide information about the retention time. During the Biochemical Methane Potential studies discussed in the previous section, the F/M-ratio of 1.5 showed the highest TVS-reduction and gas production rate. Thus, this F/M- ratio of 1.5 was assumed to represent the best balance for the anaerobic digestion of DPS with digester sludge as inoculum. Similar to the Biochemical Methane Potential studies above, the batch reactor experiments were carried out in sealed flasks, but on a larger scale. Accordingly, 100 mL of calcium chloride, ferric chloride, magnesium sulfate and 200 mL of phosphate buffer solution were added and the bottles were diluted to 10 L. Samples for the analysis of VFA, SCOD, pH, ammonia and sulphate concentrations were collected on the initial day, on day 1, 2, 4, 6, 8, 10 and afterwards on every 4^{th} day, until the end of the experiment at about 60 days.

2.4 Kinetic study

The cumulative methane gas productions of the Biochemical Methane Potential and of the batch reactor studies with an F/M- ratio of 1.5 were fitted by a three-parameter Gompertz-model [8] with R Statistical Computing software. The modified Gompertz-model is defined as follows:

$$Y = M \times \exp\left\{-\exp\left[\frac{R_m \times e}{M}(\lambda - t) + 1\right]\right\} \qquad (1)$$

where Y represents the cumulative methane gas production, t is the time, M is the methane gas production potential (mL CH_4), R_m is the maximum methane production rate (mL CH_4 d-1), λ is the lag phase time (d) and e is Euler's constant and equal to 2.71. The unknown equation variables M, R_m and λ were adjusted by non-linear least-squares regression of the pairs of experimental data (Y, t).

3. Results and discussion

3.1 Biochemical Methane Potential

1) Methane gas production

The primary objective of this study is the DPS treatment with a simultaneous methane gas production. Figure 1 shows the methane gas production during 30 days of Biochemical Methane Potential studies. Figure 1 illustrates that the highest methane gas production of 140 mL/d is achieved on day 3 for an F/M-ratio of 1.0. Furthermore, the highest fluctuations are observed for an F/M- ratio of 1.0. Figure 1 reveals also a low-gas production level for an F/M-ratio of 0 (control) and for an F/M-ratio of 0.5, but an increasing gas production for F/M-ratios higher than 1.

Figure 2 indicates the cumulative methane gas production during the Biochemical Methane Potential studies. Corresponding to Figure 1, the control- and F/M-ratio = 0.5 - experiments show the lowest methane gas production after 30 days.

Although the F/M-ratio of 1.0 has the highest methane gas production rate on the initial days, the F/M ratio = 1.5 - curve reaches the highest volume of 1,970 mL after 30 days.

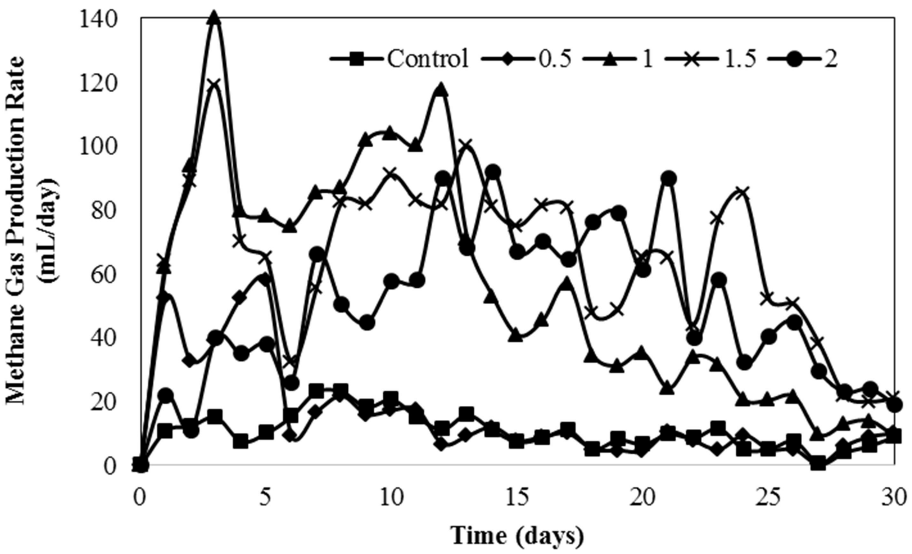

Figure 1 Methane gas production rate during Biochemical Methane Potential- experiments for different F/M- ratios of DPS and digester sludge

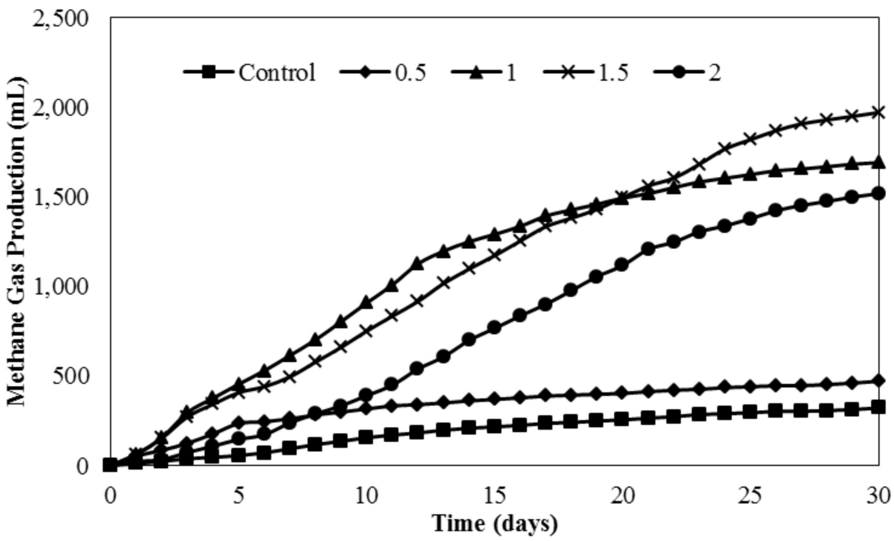

Figure 2 Cumulative methane gas production during Biochemical Methane Potential- experiments for different F/M- ratios of DPS and digester sludge

2) Total Volatile Solids

The loss of mass from the anaerobic digestion process was determined by the degradation of TVS. Generally, gas production and TVS reduction are dependent on the biological activities of inoculum inside the reactors. Figure 3 shows the steady decrease of TVS over the experimental time frame of 30 days. The highest TVS reduction rate occurs between day 14 and day 21 for F/M-ratio of 1.5. Here, highest TVS content was always determined for the F/M-ratio of 2.0.

3) Volatile fatty acids

The dominating acids during the anaerobic digestion are acetic acid, propionic acid and butyric acid. The generation and removal of acids in the anaerobic digestion process is an indicator for the gas production inside the reactors, but increasing concentrations of acids also causes a reduction of pH. For this reason, pH was always maintained between 6.5 and 7.5 through the addition of a 1 N sodium bicarbonate solution. The concentration curve of volatile fatty acids during the anaerobic digestion of paper mill sludge with digester sludge is shown in Figure 4. The highest concentration of volatile fatty acids was achieved with an F/M-ratio of 2.0. However, the experiments with an F/M-ratio of 1.5 showed an efficient balance between acid generation and consumption.

4) Soluble chemical oxygen demand

The Soluble Chemical Oxygen Demand (SCOD) describes the amount of oxygen that is required for the chemical oxidation of soluble organic matter.

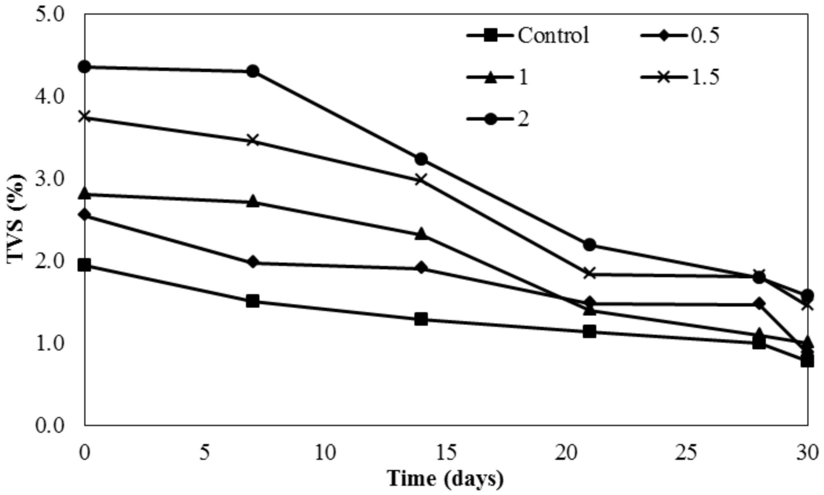

Figure 3 TVS during experiments for different F/M- ratios during Biochemical Methane Potential-experiments for different F/M- ratios of DPS and digester sludge

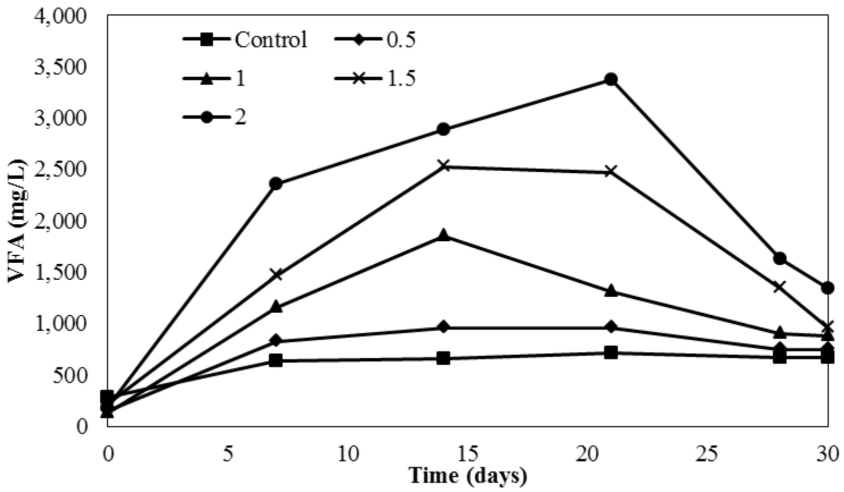

Figure 4 VFA during Biochemical Methane Potential- experiments for different F/M-ratios of DPS and digester sludge

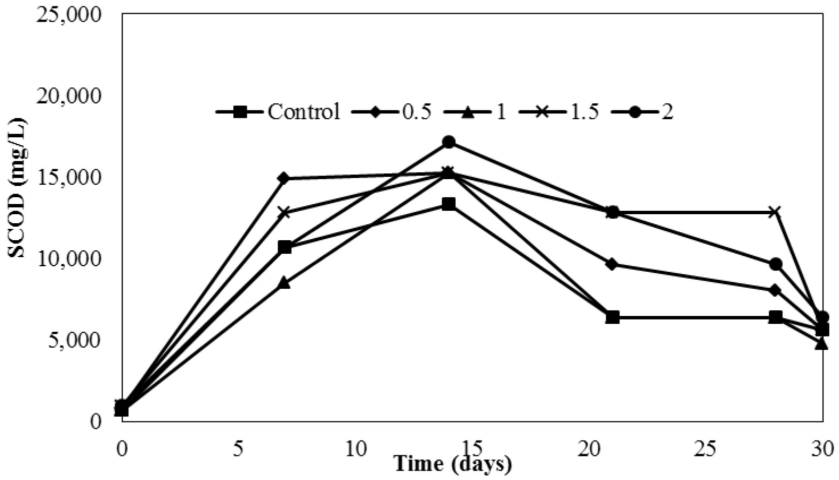

Figure 5 SCOD during Biochemical Methane Potential- experiments for different F/M- ratios of DPS and digester sludge

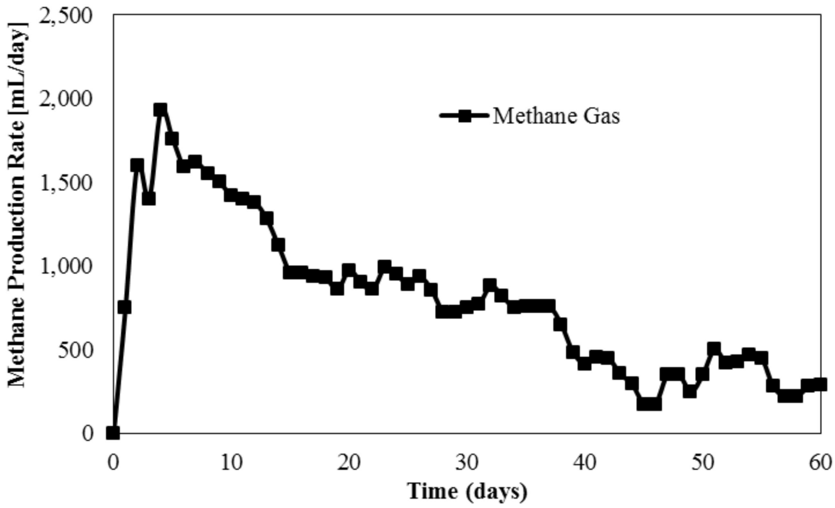

Figure 6 Methane gas production rate during the batch reactor experiment of DPS and digester sludge

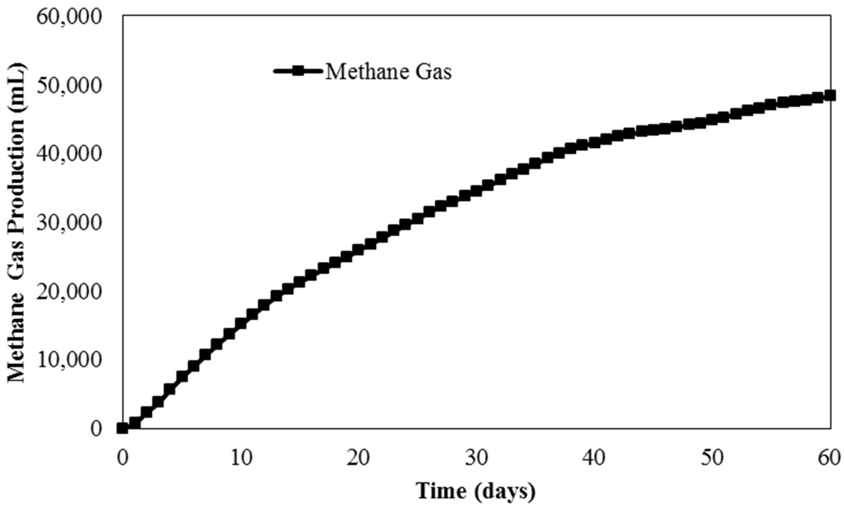

Figure 7 Cumulative methane gas production during batch experiment of DPS and digester sludge

During the anaerobic digestion processes, SCOD usually increases at the beginning and decreases at the end of an anaerobic digestion process.

Figure 5 indicates the concentrations of SCOD measured in the Biochemical Methane Potential studies. As expected, the concentration of Soluble Chemical Oxygen Demand is initially increasing and decreasing afterwards. The highest concentration of SCOD with approximately 18,000 mg/L was determined for an F/M-ratio of 2.0.

3.2 Batch reactor studies

1) Methane gas production

The methane gas production of the batch reactor experiment carried out over a time span of 60 days is shown in Figure 6.

The highest methane gas production value of 1,930 mL/d is obtained on the initial days. Subsequently, the methane gas production rate decreases more or less monotonously, reaching a value of 750 mL/d on day 29 and fluctuating around that value up to day 38, before decreasing further afterwards, with a minimum of around 200 mL/d on day 46.

The last peak of the gas methane gas production rate is observed between days 50 and 52. On the last days of that experiment, the methane gas production reaches a more or less constant rate.

The cumulative gas production of batch experiment reaches a value of 48.3 L after 60 days, as illustrated in Figure 7.

2) Volatile fatty acids and soluble chemical oxygen demand

The course of the VFA-concentrations of the batch reactor experiment shown in Figure 8 (top panel) indicates that VFA initially increases and decreases to 750 mg/L after day 10, whereby small fluctuations appear on day 8 (1. progression).

A second peak of VFA with a concentration of 1,010 mg/L (2. progression) is observed on day 30. The VFA-curve increases slowly at the very end of the experiment to a value of 1,080 mg/L on day 60

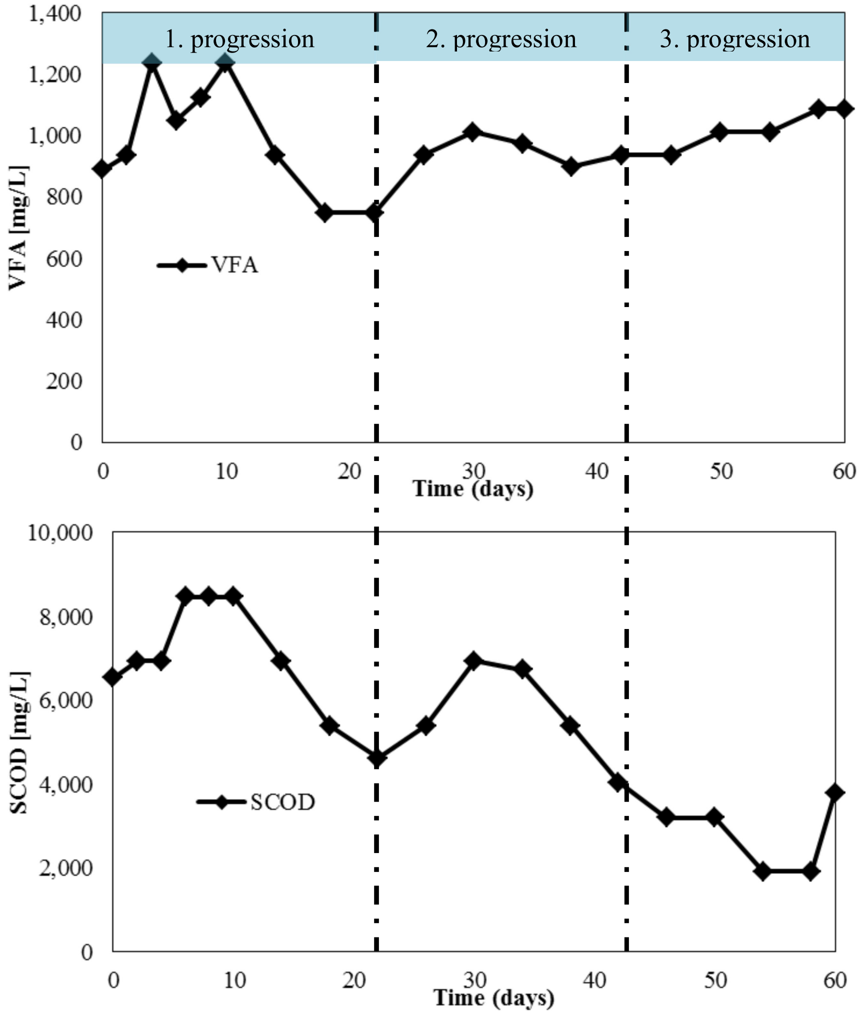

Figure 8 VFA (top panel) and SCOD (lower panel) during the batch reactor experiment of DPS and digester sludge

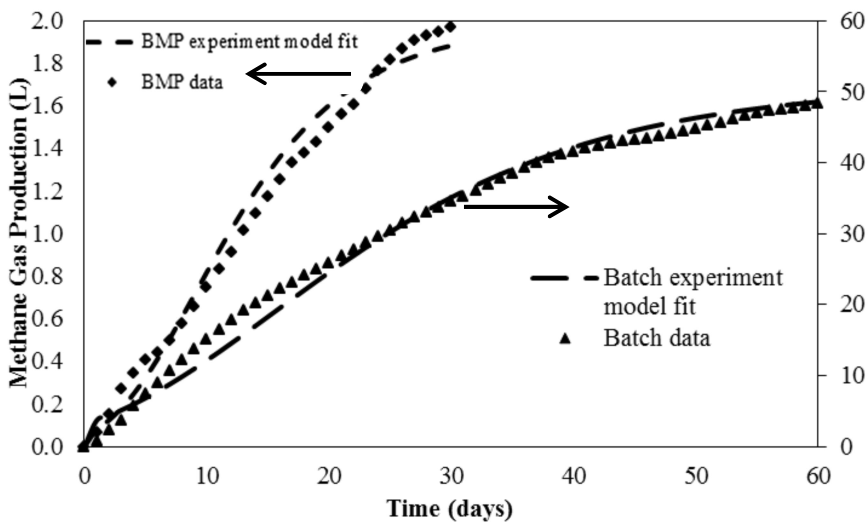

Figure 9 Modified Gompertz regression model fitted to the cumulative methane gas production data for the BMP- (left axis) and the batch reactor – experiments (right axis)

(3. progression). The lower panel of Figure 8 shows the course of the SCOD- concentration. Here, SCOD reaches a value of 8,462 mg/L on day 6, after which time it stays constant until day 10 (1. progression). Subsequently, the SCOD- concentration decreases to 4,615 mg/L by day 22. Similar to VFA, a second maximum is reached on day 30 (2. progression), after which time a rapid decrease of the SCOD concentrations follows (3. progression).

3.3 Kinetic study

The cumulative gas productions of the Biochemical Methane Potential (BMP) experiments (Figure 9, left axis) and of the batch reactor studies (Figure 9, right axis) were fitted by means of a nonlinear least squares approach implemented in the R software environment to the modified Gompertz kinetic equation by adjusting the corresponding parameters in that model (Eq. 1).

Using this approach, the standard residual error s of the fitted model to the observed data is calculated to s = 0.05 L CH_4, whereas the fitted kinetic parameters for the F/M = 1.5- ratio cases of the BMP- reactor experiment are calculated as M = 1.981 L CH_4, R_m = 0.104 L CH_4 d-1, and λ = 2.144 d. For the batch reactor experiments, the data fit of the Gompertz regression model provides kinetic parameters of M = 51.065 L CH_4, R_m = 1.263 L CH_4 d-1, and λ = 0.512 d, with a standard residual error s = 1.56 L CH_4.

4. Conclusions

Both the Biochemical Methane Potential experiments and the batch reactor studies show the feasibility for anaerobic digestion of primary sludge from the Nagaon Paper Mill. Based on the results of these two sets of experiments, anaerobic digestion can be considered as an interesting opportunity for the treatment of primary sludge, while generating, in addition, methane gas which can be used for different purposes. During the Biochemical Methane Potential studies, the highest cumulative gas production of 1,970 mL after 30 days and TVS reduction rate of 38.4% was achieved for an F/M-ratio of 1.5. In the batch reactor studies, the degradation process of primary sludge continued beyond 60 days and showed high fluctuations during the end of the experiment. However, an addition of nitrogen and pH adjustments should be further considered for the anaerobic digestion of paper mill sludge in future experiments. At the very end, the cumulative gas production was properly fitted by a modified Gompertz-regression model.

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