

# METHANOGENESIS FROM DAIRY WASTEWATER STIMULATED BY ELECTROLYSIS

Shrishail A.Manganure<sup>1</sup>, Kirankumar S. Daddenavar<sup>2</sup>, G.M.Hiremath<sup>3</sup>

<sup>1</sup>M.Tech student, Civil Engineering Department, Basaveshwar Engineering College, Bagalkot.

<sup>2</sup>M.Tech student, Civil Engineering Department, Basaveshwar Engineering College, Bagalkot.

<sup>3</sup>Associate Professor, Civil Engineering Department, Basaveshwar Engineering College, Bagalkot.

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**Abstract** - The treatment of dairy wastewater using Controlled Expanded Granular Sludge Blanket (EGSB) reactor (R1) and HEGSB reactor with the addition of electrodes (R2) has been carried out in this study. Initially, the granulation was carried out in batch reactors and the accelerated granulation was achieved on 21<sup>st</sup> day with addition of chitosan, methanol, nutrients etc. The reactors R1 and R2 were loaded with 9 L active granular sludge, The electrodes were installed in the reactor sludge bed and a voltage of 1.7-6.0 V was applied resulting in water electrolysis. Liberated hydrogen and oxygen from electrolysis process. The oxygen created micro-aerobic conditions, which facilitated hydrolysis of dairy wastewater and reduced the release of hydrogen sulfide to the biogas. A portion of the hydrogen produced electrically escaped to the biogas improving its combustion properties, while another part was converted to methane by hydrogenotrophic methanogens, methane production of 25.45 L/L/d. At an Organic Loading Rate (OLR) of 3.2 Kg COD/m<sup>3</sup>/day with 12 h Hydraulic Retention Time (HRT), hybrid EGSB showed higher methane production of 25.45 L/L/d, at the applied voltage of 6 volts and current of 0.012 ampere.

**Key Words:** Hybrid EGSB reactor, Batch reactor, Anaerobic digestion, Methane production.

## 1.0 INTRODUCTION

Water is essential for all domestics, industrial and agricultural purpose. Industrialization plays an important role in developing countries. The industries utilizes huge amount of water for many purpose during operation period. The water utilized by the industries was discharged as wastewater. During industrialization, dairy industries were also developed a lot. Now dairy industries are found everywhere, because dairy industries produce daily essential products. Dairy industry is also one of those industries which utilizes huge amount of water and discharges wastewater.

The dairy wastewater is having high Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) which degrades very quickly and creates heavy odor nuisance. Table 1. shows the characteristics of dairy wastewater. If this wastewater discharged as untreated, it causes serious environment pollution problems and adversely affects on human health (Bharati S.S. and N.P.Shinkar, 2013). The dairy wastewater can be treated efficiently through biological

treatment methods. Wastewater treatment becomes costlier due to the energy required to treat and recycling it to reduce fresh water demand (Bharati S.S. and N.P.Shinkar, 2017). The heavy investment of money and high energy is better if a valuable byproduct recovered. The anaerobic reactors are most efficient in biological treatment with the valuable byproduct like biogas.

**Table 1 Dairy wastewater Characteristics**

Parameter	Values
Color	White colour
pH	7.0-7.69
COD	1296-1600mg/l
BOD	745-817 mg/l
Total solids	1194 mg/l
Chlorides	630 mg/l

Expanded granular Sludge Bed (EGSB) reactor is a modified UASB reactor with recirculation. Hybrid Expanded Granular Sludge Bed (HEGSB) reactor is an upgraded form of the EGSB reactor with electrodes. This study includes the treatment of dairy wastewater through EGSB (R1) and HEGSB (R2).

## 2.0 MATERIALS

### i. Inoculum

Inoculum was prepared from batch reactors after 21 days of achieving accelerated granulation by mixing active sludge, which was obtained from UASB reactor treating sugar mill wastewater of EID Parry India Ltd, at Naynegali, Hungund taluk, septic tank sludge and cow dung in the proportion of 1:1:1.

### ii. Substrate

The experiment work was carried out by using dairy wastewater as a substrate which was collected from KMF Dairy industry at Bagalkot and it was stored in deep freezer at 4°C.

### iii. Chemicals Required:

The different chemicals required for the Hybrid EGSB reactor operation.

#### a. Macro nutrients and Micro nutrients:

The micro nutrients were added as per the reference paper (Tartakovsky and Bourque, 2011).

### iv. Chitosan

Chitosan was added as natural polymer to boost the sludge granulation of the order of 2mg/g of total solids.

(Boonyarit ,Nunta and kumjorn e, 2018)

### v. Glucose

During batch experiment, glucose was added as carbon source (food), which could be fermented to VFAs rapidly.

## 3. METHODOLOGY

### 3.1 To study granulation period in batch reactor

In the batch reactor of 2 litres capacity, the screened and non-granulated sludge from UASB reactor was fed along with septic tank sludge and cow dung in the ratio 1:1:1. The macro and micro nutrients along with chitosan were added to the reactors. The batch reactors were initially fed with glucose. pH was maintained between 7-7.5. Observation was carried out for COD removal efficiency and pH. Figure 1 shows the granules after 21 days, mean size of granules was 1.5-2 mm.



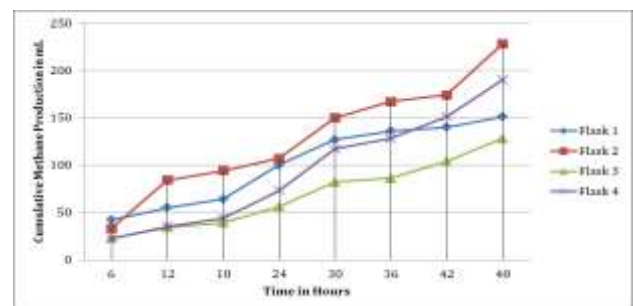
**Figure 1.0 Granulation achieved on 21<sup>st</sup> Day**

### 3.2 To evaluate of microbial activity (SMA Test)

- i. Volatile solids present in the sludge and to be analyzed for determination of their concentration [gVS/ L].
- ii. Reaction flask of 250-500 mL has been considered and the pre-determined amounts of sludge has been placed into the reaction flasks, before starting the test the sludge must be placed early 12-24 hours for pursuing the test conditions at 30°C.
- iii. Certain amount of the buffer and nutrient solution added to the reaction flasks, to obtained final mixture

concentrations (sludge + solution + substrate) around 2.5 gVS/L. 70 to 90% Volume of mixture should occupy volume of the reaction flask.

- iv. In the head space of the flask Oxygen present and it should be removed, before adding the substrate. By using gaseous nitrogen. Add the substrate to the reaction flasks, in the concentrations desired and it varying from 1.0-2.5 gCOD/L.
- v. After above procedure turn on the mixing devices in the reaction flask.
- vi. During test period (ml/hour) record the volumes of biogas produced at each interval of time.
- vii. Methane concentration determination can be made by adsorption of carbon dioxide gas present in the biogas, through its passes in a alkaline solution. (NaOH 5%).



**Figure 2.0 SMA Test, Cumulative Methane production Results**

According to the above figure 2 the total CH<sub>4</sub> production is determined from the substrate (sodium acetate) amount, at the end of the test for each of the flasks. The most accurate calculation of the activities should be done with the reaches of maximum slope flask 1 and flask 2, then percentage of substrate converted into methane an flask1, 97.01% and flask 2, 97.66%.

### 3.2 Experimental setup of EGSB reactors

The laboratory scale controlled EGSB (R1) and Hybrid EGSB reactor (R2) were fabricated using acrylic pipe of 100 mm diameter and overall height of 1900 mm. The reactor was supported by framed structure made up of mild steel. Inlet was provided at the bottom of the reactor with opening of 18 mm, one outlet has been provided at the top as the gas outlet and other as the outlet for the treated wastewater (effluent). For the separation of gas, liquid and solid (GLS) separator was provided. In HEGSB reactor (R2), zinc electrodes were installed with size of 10 cm x 6 cm. Figure 2. shows the laboratory scale HEGSB reactor (R2). During the process the voltage varies from 1.7 to 6.0V, these electrodes were connected to the DC regulated power supply. Micilns peristaltic pumps (model PP 30 EX 2C and PP 30 EX) were used for feeding and recirculation of dairy wastewater. The recirculation arrangement along the line of feed inlet was provided to maintain the desired up-flow velocity (4m/h). The up-flow velocity provides partial expansion of sludge bed. That improves the contact between sludge and the wastewater. Provision for sludge withdrawal was provided

at the bottom of the reactor. Gas collection outlet was provided at the top of the reactor and methane was measured by gas flow meter.

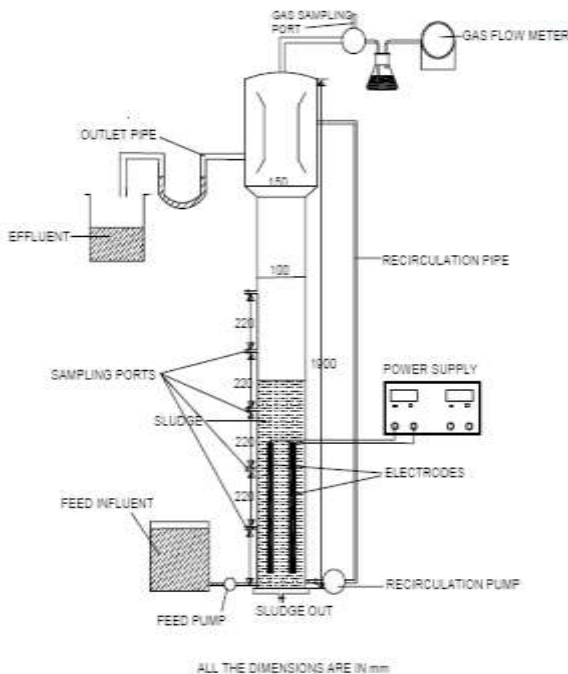


Figure 3.0 Hybrid EGSB reactor

#### 4. RESULTS AND DISCUSSION

In this study, both R1 and R2 reactors were operated simultaneously, to check the effect of water electrolysis on methanogenesis at reactor R2. Due to water electrolysis, electrodes liberate hydrogen and oxygen. The liberated Hydrogen may combine with carbon dioxide in presence of hydrogenotrophic methanogens forming methane gas ( $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ ). Similarly liberated oxygen may create micro-aerobic condition, that may combine with hydrogen sulphide gas forming sulphates, ( $O_2 + H_2S \rightarrow SO_4^{2-}$ ). The followings are the comparative results of R1 and R2 on treating dairy wastewater.

Higher concentration of VFA slower the methanogenesis, therefore the ratio of VFA/Alkalinity plays an important role in COD removal efficiency. Therefore optimum ratio should be less than 0.4. During operational period VFA/Alkalinity ratio was observed in between 0.1 to 0.32. Figure 4 shows the VFA/Alkalinity ratio with respect to OLR.

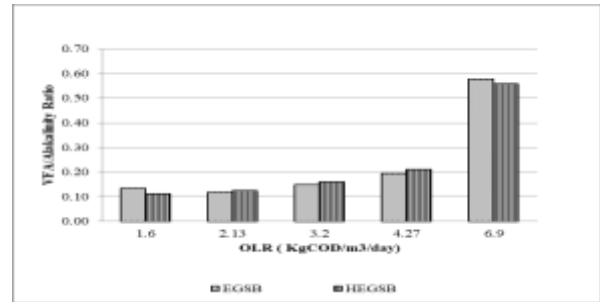


Figure 4.0 OLR v/s VFA/Alkalinity Ratio

In the Figure 5, R1 and R2 showed peak COD removal efficiencies of 90.42% and 87.40% respectively at OLR 3.2 kg COD/m<sup>3</sup>/day.

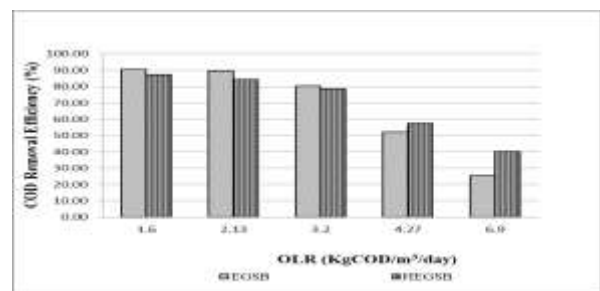


Figure 5.0. COD Removal Efficiency VS OLR

At 24h HRT, Organic Loading Rate (OLR) 1.6 kg COD/m<sup>3</sup>/day and up-flow velocity of 4 m/h improved mixing condition and helped to improve BOD removal efficiency. The figure 6 shows the BOD removal efficiency of reactor R1 and R2 were 88.29% and 89.91% respectively.

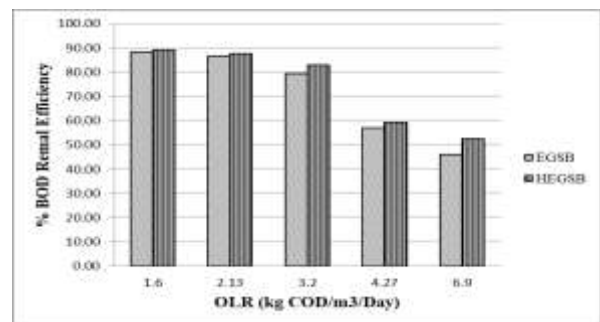
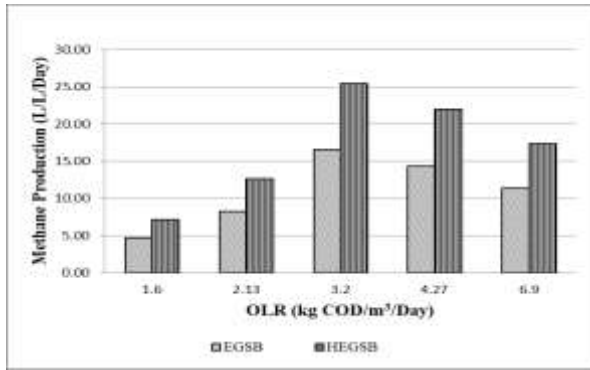


Figure 6.0 BOD Removal Efficiency vs OLR

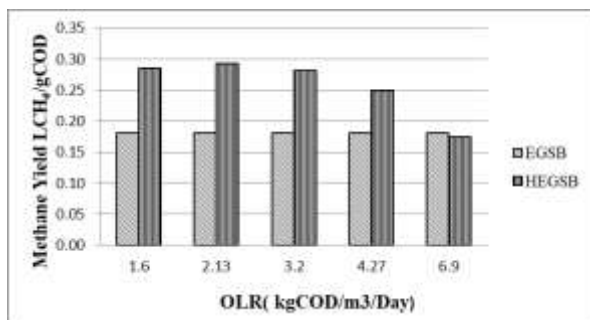
At OLR of 3.2 kg COD/m<sup>3</sup>/d, both R1 and R2 the reactor showed the higher methane production of 16.64 L/L/D and 25.45 L/L/D respectively. Due to electrolysis process in R2, the liberated hydrogen combined with CO<sub>2</sub> by producing more amount of methane gas that was amounted 1.53(53% higher) times more than EGSB, at 6 volts and 2 ampere current. Figure 7 shows the methane production of both reactors.



**Figure 7.0 Methane Production with OLR**

It is known that limited micro-aeration can enhance the methane yield in anaerobic digestion. The methane yield was calculated for the stable reactor operation using the formula shown below. Maximum methane yield of 0.29, was observed at an OLR of 2.13 kgCOD/m<sup>3</sup>/Day. Figure 8 shows the methane yield rate.

$$Y_{CH_4} = \text{Methane flow rate (L/d)} / \text{Liquid Flow rate (L/d)} \\ (\text{COD influent} - \text{COD effluent})$$



**Figure Figure 8.0 Methane Yeild with OLR**

## CONCLUSIONS

The performance of two laboratory scale anaerobic reactors EGSB and Hybrid EGSB reactor were investigated and compared for treatment of the dairy wastewater.

1. Addition of natural polymer (Chitosan) has positive effect towards granulation. Granules size of 1.5-2.0 mm was achieved 21 days in batch reactors.
2. Water electrolysis resulted in a continuous supply of hydrogen and oxygen. Hydrogen combines with carbon dioxide in presence of hydrogenotrophic methanogens forming methane gas, liberated oxygen increased the rate of hydrolysis of organic matter (Tartakovsky et.al.,2011) improved the COD removal efficiency and methane production. Further oxygen liberated, oxidised with H<sub>2</sub>S forming sulfates.
3. At 12 hours HRT, OLR of 3.2kg COD/m<sup>3</sup>/day HEGSB showed the optimum COD removal efficiency of 78.60% and BOD removal efficiency of 89.91%, methane production of 25.45 L/L/D , at the applied voltage of 6 volts and current of 0.012 ampere. HEGSB reactor

showed 1.53 times greater methane production than that of Controlled EGSB.

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