Effect of Elemental Metals on Methanogenesis by Treating Dairy Wastewater

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Abstract - *The work presented in the study, treatment of dairy wastewater using control reactor (R1) and EGSB reactor with elemental metals (i.e. Iron 4g/L and Manganese 20 g/L) (R2). In the startup period, the granulation was carried out in batch reactors and the accelerated granulation was achieved on 21st day with addition of chitosan, aluminium sulfate, nutrients, etc. Initially, the reactors R1 and R2 were loaded with 9 L active granular sludge, at an Organic Loading Rate (OLR) of 1.6 kgCOD/m³/day with 24h Hydraulic Retention Time (HRT) with the 4m/h of up-flow velocity. On 60th day, at an OLR of 3.2 kgCOD/m³/day, R1 and R2 showed methane production 16.64 L/L/day and 23.29 L/L/day respectively. Addition of iron and manganese resulted in enhancing hydrolysis, VFA reduction and methanogenesis. EGSB reactor with elemental metals (R2) showed methane production of the order of 1.45 times than control EGSB reactor (R1).*

Key Words: Granulation, Anaerobic digestion, Elemental metals, EGSB reactor, Methane production.

1. INTRODUCTION

Human and Environmental wellbeing basically requires water. The industrialization has made water problem as far as its amount and quality. At the point when society experiences industrialization, it changes over enormous measure of water into waste after its use what makes harm the environment condition.

Dairy industry is additionally one of those industries which deliver the basic items. Dairy industries are discovered everywhere throughout the world. The dairy industry can be separated into a few production segments. Irrespective of the product, every processing plant has a segment where milk is delivered and stored.

1.1 Dairy wastewater

Dairy effluents decompose rapidly and deplete the dissolved oxygen level of the receiving streams immediately resulting in anaerobic conditions and release of strong foul odors due to nuisance conditions. Table1. shows characteristics of dairy effluent. The casein precipitation from waste which decomposes further into a highly odorous black sludge at certain dilutions the dairy waste is found to be toxic to fish also. Dairy effluent contains soluble organics, suspended solids, trace organics. They do decrease, promote release of gases, cause taste and odor, impart color or turbidity and promote eutrophication.

Table -1: Characteristics of dairy industry wastewaters

Sl.NO	Parameter	Value in mg/l, expect pH & Color
1	pH	7.0-7.69
2	Color	Whitish
3	Total solid	1194
4	BOD	745-817
5	COD	1296-100
6	Chloride	630

2. MATERIALS

i) Inoculums

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: Dairy wastewater collected from Nandini Dairy Industry, Bagalkot. The tests such as pH, Total Solids, COD and BOD have been conducted for the characterization of dairy wastewater.

iii) Chitosan: For accelerated granulation, chitosan was used as polymer and added at the rate of 2 mg/gm of total solids present in the sludge [G.M.Hiremath & Veena S.S.].

iv) Glucose: While mixing different types of sludges, methanogenic bacteria were not habituated to the particular food, therefore to grow bacteria in anaerobic conditions, glucose was fed as a carbon source.

v) Chemicals : The various chemicals required for the reactor operation and analysis of parameters are distinguished as macro nutrients and micro nutrients.

a. Micro nutrients and Macro nutrients

The micro and macro nutrients were added as per the study carried out by B. Tartakovsky et al.

Nitrogen: The amount of requirement is dependent upon chemical composition of bacterial cell. Composition of influent nutrients is not taken into account. Assuming that nutrients present in the influent available for the bacterial about in the range COD: N: P = 350:5:1 [G.M.Hiremath & Veena S.S.].

vii) Elemental metals

Based on the literature survey, number of metals, for example, copper, nickel, zinc, cadmium, chromium, lead, manganese and iron were utilized as a part of the reactors to upgrade the anaerobic processing to boost biogas generation. Apart from manganese and iron metal every other metals exhibits toxicity. Typically, methanogens are not specifically making utilization of biological acids till they were degraded into acetic acetate by syntrophic acetogenic microscopic organisms.

Zero valent iron is a reducing metal. It was evaluated that essential iron enhances the hydrolysis and fermentation stage in the anaerobic procedure. Iron act as an electron donor for, changing over CO_2 to CH_4 through autotrophic methanogenesis [4].

$CO_2+4Fe^0+8H^+= CH_4+4Fe^{2+}+2H_2O$

Manganese is also a reducing metal, which is having comparatively similar physical and chemical properties as that of iron. Based on literature, manganese metal works as an electron donor for methane production from CO_2, due its better reducing nature it is more competent than iron. Manganese was consumed by methanogens to generate CH_4. The beneath response will indicate methanogenesis process with expansion of manganese[5].

$CO_2 + 4Mn^o + 8H^+ = CH_4 + 4Mn^{2+} + 2H_2O$

Iron (4 g/L) and manganese (20 g/L) metals are being used. Iron powder helps in hydrolysis and acidification, producing acetic acid and reducing the propionate acid, whereas manganese metal works in the range of hydrogenotrophic methanogens for the production of methane from CO_2.

3. METHODOLOGY

The anaerobic reactors were operated in two phases, first phase is granulation in batch reactor and in second phase two EGSB reactor were run, one is control reactor (R1) and other one is EGSB with elemental metals (R2).

3.1 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 as a carbon source. 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.

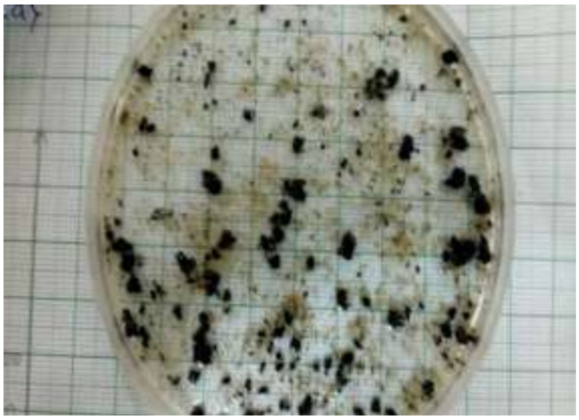

Figure 1. Granulation achieved on 21st day

3.2 Specific Methanogenic Activity Test

The analysis of specific methanogenic activity of the sludge has been conducted in the four flasks with different substrate concentrations (Sodium acetate) of 2mg/L, 4mg/L, 6mg/L and 10mg/L. The flask containing 4mg/L substrate showed the maximum methane gas production of 228 mL in 48 hours. Figure 3 shows the variations took place for each of the flasks with respect to the time.

Procedure for SMA test

i. Initially the volatile solids concentration existing in the sludge to be analyzed (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 pursing the test conditions at 30°C.

iii. The total conc. of the mixture (substrate, sludge & solution) must reach 2.5 g VS/L after the addition of nutrient & buffer solutions to the flask. Add the elemental metals Iron (20 mg/L of sludge) & Manganese (4 mg/L of sludge). The accumulation of contents must not cross the 70-90% of the flask volume.

iv. For the proper mixing of the contents a mixing device is used.

v. During the test period, note down the quantity of biogas liberated at every time interval (mL/hour). The methane concentration present in the biogas can be determined by passing the biogas through the alkaline solution (e.g. 5% NaOH) to arrest the carbon dioxide gas present in the biogas.

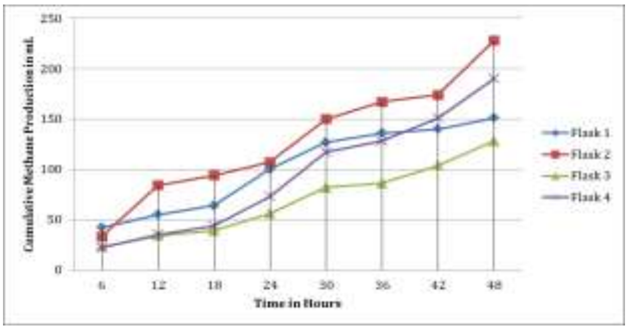

Figure 3 Methane Production Analysis by SMA test.

This test was conducted in view of the most extreme methane productivity rates (mLCH$_4$/gVS.h or gCOD-CH$_4$/gVS.d). The conversion of mLCH$_4$ into gCOD-CH$_4$ is done by Equations (1) and (2).

$$V_{CH4}=(COD_{CH4})\div K(t) \quad (1)$$

Where V_{CH4} = Volume of methane produced (L), COD $_{CH4}$ = Load of COD removed from the reactor and converted into methane (g COD), K (t) = Correction factor for the operational temperature of the reactor (g COD / L)

$$K(t)=(PK)\div[R(273+T)] \quad (2)$$

Where P=Atmospheric pressure (1atm), K=COD corresponding to one mole of CH_4 (64 gCOD / mole), R = Gas constant (0.08206 atm-L/mole-^oK), T=Operational temperature of the reactor (^oC)

3.3 Experimental setup of EGSB Reactor

In this study EGSB reactors were taken into consideration. The distinctive feature is that high up-flow velocity (4-10 m/h)[Lucas Seghezzo et. al.,]. Here the up-flow velocity of 4m/h was adopted. Increased velocity permits partial expansion of the granular sludge bed, improving wastewater to sludge contact as well as enhancing separation of small suspended particle from the sludge bed.

Figure 2 shows laboratory scale EGSB reactor. The similar type of reactor was fabricated. The effective volume of reactor is 18L. Opening of 18 mm at inlet, outlet, recirculation, gas outlet and sludge out arrangements were provided to avoid clogging action in the reactors. For the separation of gas, liquid and solid (GLS) separator was provided. Five numbers of sampling ports were provided along with the height of reactor at 220 mm c/c. The effluent pipe was placed such that, gas should not be escaped through it and inlet is provided at the bottom of the reactor, were influent was fed by peristaltic pump. The sludge outlet was provided at the bottom so as to remove excess sludge in the reactor. Gas collection outlet was provided at the top of the reactor and methane was measured by gas flow meter. The reactors were operated in the ambient temperature (27^{0}C to 35^{0}C).

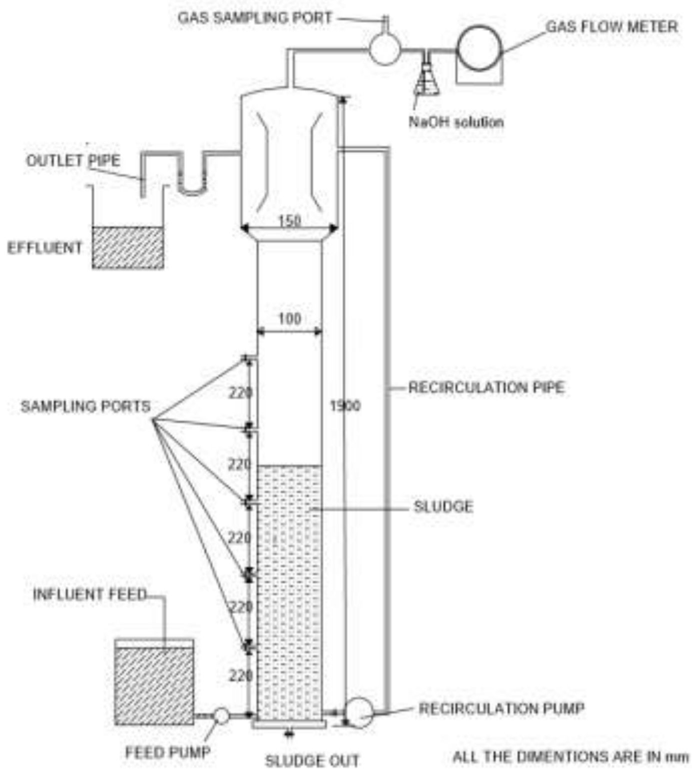

Figure 2 Expanded Granular Sludge Bed (EGSB) Reactor

4. RESULTS AND DISCUSSIONS

Effects of metal addition on hydrolysis rate and methane production rate.

In this study, in reactors R1 and R2, pH 7 was maintained at ambient temperature (30-35^{0}C). Compared to reactor R1, the R2 reactor shown higher efficiency in COD removal, Methane production, BOD removal and controlling the formation of VFA's. Because of addition of iron might serve as acid buffer to maintain favorable condition for methanogens that might resulted in enhancing hydrolysis and optimizing VFAs and as per Sen Qiao et al. manganese metal is assumed as an electron donor to produce CH_4 from CO_2 that might be enhanced the methane production. The followings are the comparative results of R1 and R2 at the maintained conditions on treating dairy wastewater.

VFA and Alkalinity

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.

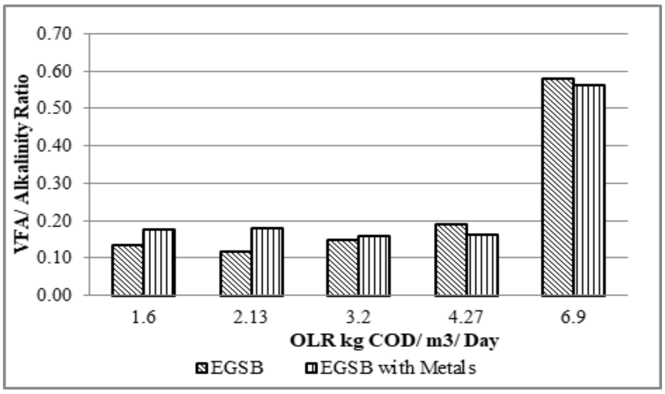

Figure 4 OLR v/s VFA/Alkalinity Ratio

COD Removal

In the Figure 5, R1 and R2 showed peak COD removal efficiencies of 90.42% and 85.25% respectively at 3.2 kg COD/ m^3/day.

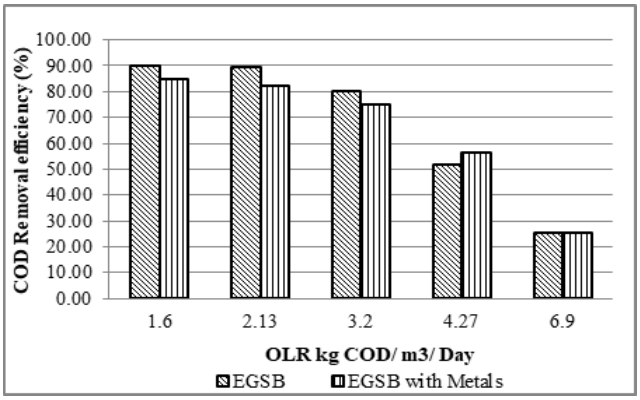

Figure 5 COD Removal Efficiency (%) with OLR.

Methane production

Elemental iron improved hydrolysis and acidification in the anaerobic process where proteins and cellulose were degraded. Apart from this, it acted as electron donor for converting CO_2 to CH_4 through autotrophic methanogenesis. Similarly manganese metal also behaved as that of iron metal. At an OLR of 3.2 kg COD/m^3/d. In Figure 6 R2 showed methane production of 23.29 l/d compared to R1 16.64 l/d.

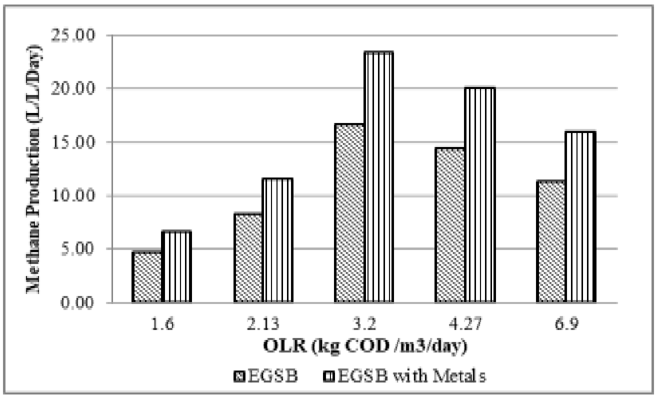

Figure 6 Methane Production with OLR.

Methane Yield

To enhance the methane yield, a limited aeration is enough in anaerobic digestion. Maximum methane yield of 0.27 was observed at OLRs of 1.6, 2.13 and 3.2.

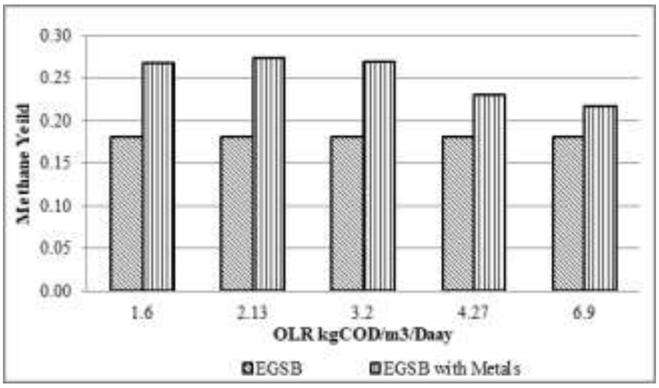

Figure 7 Methane Yield with OLR.

BOD Removal

At Organic Loading Rate (OLR) 1.6 kg COD/m^3/day, reactor R1 and R2 showed higher BOD removal efficiencies were 86.53% and 87.46% respectively. Similarly for different influent concentration BOD removal efficiencies were observed during operational period are shown in the Figure.8

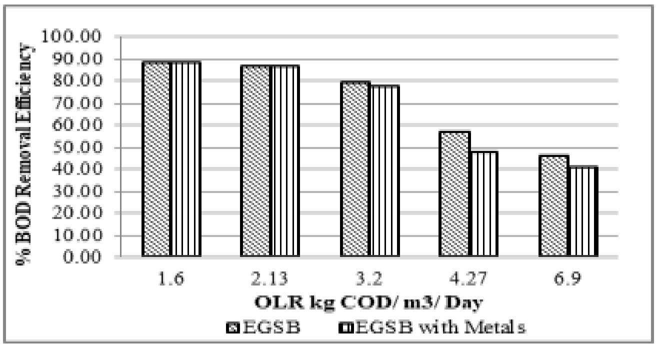

Figure 8 BOD Removal Efficiency (%) with OLR.

5. CONCULSIONS

Two laboratory scale EGSB rectors (with metals and without metals) were run to understand their possibility for treating dairy wastewater. Based upon the experimental results following conclusions were drawn,

i. Addition of chitosan has positive effect on sludge granulation. Granulation was achieved within a short period of 21 days in batch reactors.

ii. The startup times for both reactors have been minimized to 60 days.

iii. The organic loading rate has been optimized to 3.2 $KgCOD/m^3/day$ at 12h HRT.

iv. Addition of iron (4 g/L) and manganese (20 g/L) metals to the reactor (R2) showed higher COD removal efficiency and BOD removal efficiency when compared to controlled EGSB reactor (R1).

v. At the 12 h HRT on 3.2 kg $COD/m^3/day$ of OLR, methane production rate in the reactor (R2) shown 1.45 times higher than the controlled EGSB reactor (R1).

vi. The addition of Manganese resulted in decreasing the VFAs concentration by enhancing the acetoclastic methanogenesis. Whereas, the addition of Iron might helped in improving hydrolysis/acidification rate.

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