

Methanogenesis from Distillery Spentwash Stimulated by Addition of Elemental Metals

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ABSTRACT: The work presented in the study, treatment of distillery spent wash using Expanded Granular Sludge Blanket (EGSB) reactor (R1) and EGSB reactor with the addition of elemental metals (R2) (i.e. Iron and Manganese). In the start-up period, the granulation was carried out in batch reactors and the accelerated granulation was achieved on 21st day with addition of chitosan, aluminium sulfate, methonal, nutrients etc. The operations of the reactors were observed for their performance. To start with, the reactors R1 and R2 were first loaded with 9 L activated granular sludge, at an Organic Loading Rate (OLR) of 2.3 KgCOD/m³/day with 24 h Hydraulic Retention Time (HRT). Observations were made on pH, Chemical Oxygen Demand (COD) efficiency, effluent Volatile Fatty Acids (VFA), effluent Alkalinity and methane generation. pH of effluent varied from 6.5 to 8.10 in R1 and in R2 from 6.5 to 7.95. VFA/Alkalinity ratio varied from 0.39 to 0.15 in R1 and 0.36 to 0.10 in R2. Thus it is proved that R2 is more efficient compared to R1. On 62nd day, at an OLR of 38.40 KgCOD/m³/day in R1 and R2, COD removal efficiencies were 81.40% and 85.20% and methane production 2.61 L/L/day and 3.78 L/L/day respectively. The performance in methane production in EGSB reactor with elemental metals (R1) was much better than EGSB reactor (R2) (i.e. of the order of 1.45 times).

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

I. INTRODUCTION

Water is essential for human and environmental health. The water has two dimensions of its availability in terms of its quantity and quality. The quality of the water at source determines the environmental health and water quality at delivery point determines the human health. The industrialisation has created water stress in terms of its quantity and quality. When society industrialized, it generates huge amount of waste that leads to damage the quality of environment, human health. [1].

In North Karnataka region, among the different industries, sugar and distillery industries effluents are highly concentrated and acidic in nature having pH 4 to 4.3. Hence these effluents are to be treated and disposed properly. To treat and manage these types of effluents different treatment methods were practiced. Aerobic and anaerobic treatment processes are two different biological methods. Aerobic treatment method demands oxygen for the treatment whereas in anaerobic process treatment takes place in absence of oxygen. [2]. In related to the physical and chemical treatment methods the biological treatment method is found to be the best, because, it can handle high COD (Chemical Oxygen Demand) and BOD (Biochemical Oxygen Demand). [3]. Generation of spent wash/wastewater is increasing day by day; hence treatment is necessary before releasing into the environment. Through Anaerobic Digestion (AD) treatment can be achieved along with energy production. [4]. Nowadays industries are opting to incineration whereas during incineration process nutrients are lost therefore AD gained importance throughout the world.

Through anaerobic digestion certain works have been carried out in EGSB reactor such as treatment of Palm oil, the COD removal efficiency was of the order of 91% whereas methane generated was only 46 %. [5] while methanogenic activity is affected Volatile Fatty Acids (VFA) and concentration of propionic acid was increased to 900 mg/L resulted in lowering methane generation. [6]. Addition of heavy metals such as iron and manganese enhance the generation of methane through anaerobic process. This study focuses on the overview for the optimization of the AD process by addition of elemental metals to increase methane generation, along with removal of organic material ensuring high efficiency.

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II. RELATED WORK

Hiremath. G. M and Soraganvi. V., (2015) performed study on accelerated granulation in the EGSB reactor. In this study chitosan and aluminium sulfate were used for accelerating granulation at a OLR of 4 kgCOD/m³/d. Spherical granules of average diameter of 2 mm were observed on 21st day.

Tapas N et al., (2002) the study is carried out on resource recovery from molasses distillery by wastewater management. The spent wash coming out as effluent is highly acidic (pH 4-4.3) with high concentration biochemical and chemical oxygen demand (BOD: 52-58, COD: 92-100 kg/m³) and suspended solids (2-2.5 kg/m³). Biogas is generated from raw spent wash in an anaerobic fixed film reactor.

Marcos von S and Carlos Aaugasto d L C., (2005) expresses on factors affecting and narrated about nutrients required for anaerobic digestion. The amount of nitrogen content with high yield coefficient follows, COD: N: P = 350:5:1 or C: N: P = 130:5:1, the required quantity of phosphorus around 1/5 to 1/7 of that established for nitrogen. Most of the microorganisms use sulfide a source of sulfur. Sulfur is necessary for synthesis of proteins. In general sulfur and phosphorous seem to be required in the same amount. Design considerations were decided for the design of EGSB reactor.

Joo-Hwa T et al., (2006) studied on bio-granulation methods to treat different wastewater. To form granules in anaerobic reactor more number of conditions has to be satisfied. As yet, no model is describing the entire anaerobic granulation process correctly. Physical, chemical and biological factors which influence granulation should be integrated.

Yinghong Feng et al., (2014) conducted experiment on enhancement of anaerobic degradation of activated sludge through adding elemental iron. The lower hydrolysis acidification in the anaerobic process will lead to restrict the sludge digestion. Addition of iron metal will improve the anaerobic digestion process with hydrolysis acidification. The results shown that addition of iron will enhance the process by increase in protein degradation by 21.9% and 37.3% in volatile fatty acids. By the addition of metal will help in production of more acetate acid compared to propionate acids. The more number of hydrogen consuming acidobacterial and hydrogenotrophic methanogens will help in increase in production of methane by 43.5%.

Yiwen Liu et al., (2015) studied on improvement in the methane generation by methane potential rather than hydrolysis from activated sludge. Slower hydrolysis and low methane potential results in limited methane generation from sludge. In these study different forms of iron metal is used such as iron powder, clean and rusty scrap for methane generation from sludge. By experimental study both clean and rusty iron showed enhance in the methane generation compared to iron powder.

Sen Q et al., (2015) studied on enhancement of methanogenic activity by addition of manganese metal to wastewater. Adding up of elemental manganese (4g/L) helps to increase in methane production by 3-5 times and also addition of manganese in the process results in more acetate utilization and reduction in the propionate generation. In the methanogenesis stage manganese metal acts as electron donor from carbon dioxide. The addition results in 96.9% methane generation which is 2 times more than actual (46.6%).

III. METHODOLOGY

The reactors were operated in two phase, first phase as batch reactor where granulation was taken place. In the batch reactor of 2 litres capacity the screened, non granulated sludge was fed, which is mixture of sludge from UASB reactor, septic tank and cow dung. The macro and micro nutrients along with methonal and chitosan were added to the reactors. The batch reactors were initially fed with glucose as a feed. pH was maintained between 7-7.5. Observation was carried out for COD removal efficiency and pH.

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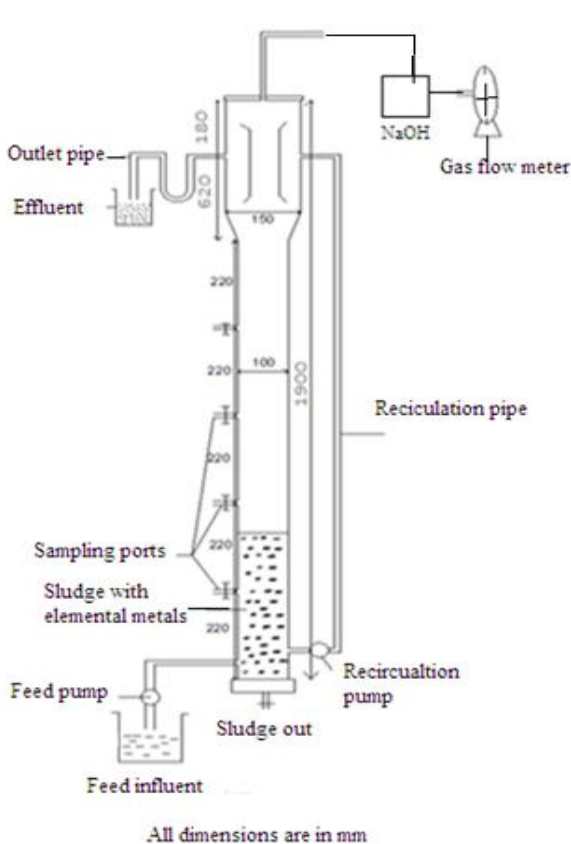
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Figure 1. After 21 days of observation granulation occurred in the reactors as showed in below Figure, mean size of granules were of 1.5-2 mm. The same granulated sludge was fed into the EGSB reactors.



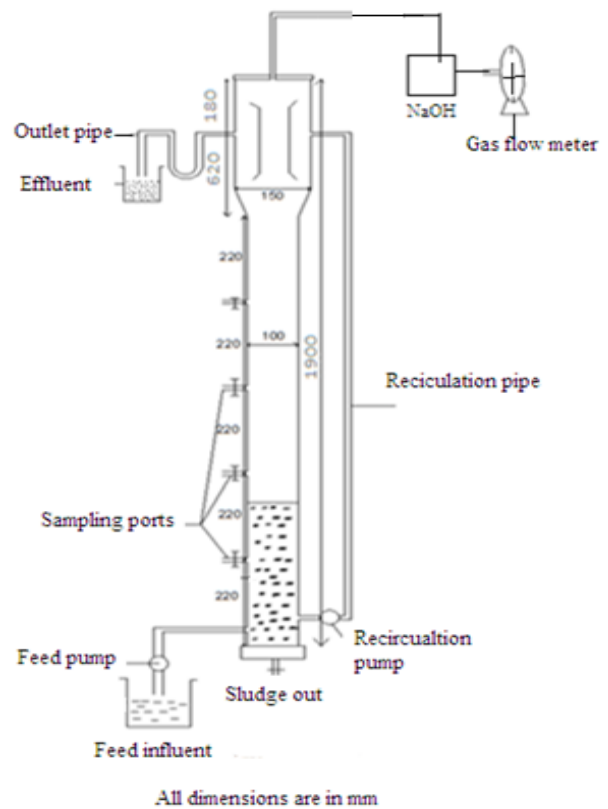
Figure 1. Granulation achieved on 21st day

Figure 2 (a) and 2 (b). In the second phase two laboratory scale EGSB reactors were fabricated as showed in below Figures using acrylic and PVC pipe of 100 mm diameter and overall height of 1900 mm.



(a)

Figure 2. (a) EGSB reactor with metals (R1)



(b)

Figure 2. (b) EGSB reactor (R2)

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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.

Table 1. The characteristics of distillery spent wash was analysed and parameters were listed below. Initially the concentration was maintained to 2300 mg/l of COD and maintaining the pH as 7 by using NaHCO₃. The reactors were operated in the ambient temperature (27^oC to 35^oC).

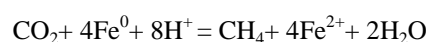
Table 1. Characteristics of Distillery Spent wash

Parameter	Values
Colour	Dark brown
pH	4.2-4.5
COD, mg/l	96400-105200 mg/l
BOD, mg/l	46000-55000 mg/l
Total solids, mg/l	86400-93600 mg/l
Chlorides, mg/l	3850-4200 mg/l
Sulphate, mg/l	3940-4340 mg/l
Total Nitrogen, mg/l	3940-4350 mg/l
Phosphorous, as P ₂ O ₅	780-1040 mg/l
Potassium	7900-8710 mg/l

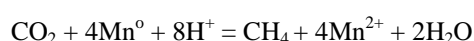
The activated sludge from the batch reactors was fed to the EGSB reactors about 1/2 of the volume of the reactor (9 L). This study was conducted to check the performance of EGSB reactors with and without elemental metals to treat distillery spent wash for varying feed COD concentrations with different HRT. The biogas generated was made to pass through NaOH solution wherein CO₂ was dissolved and methane flow through wet gas flow meter, was recorded.

Based on the literature review number of metals such as copper, nickel, zinc, cadmium, chromium, lead, manganese and iron were used in the reactors to enhance the anaerobic digestion to maximize biogas generation. Apart from manganese and iron metal all other metals exhibit toxic to the process. Reasons for the affect of heavy metals on process are concentration of metal, ionic form, metal species and quantity of biomass present in the digester. [10, 11]. Normally, methanogens are not directly making use of organic acids till they were degraded into acetate by syntrophic acetogenic bacteria. Methanol was added at start up for the enhancement of the growth of methanogenic bacteria. The addition of methanol is dependent upon the composition of the spent wash. [2].

Zero valent iron is a reducing substance having different forms, such as iron powder, clean scrap and rusty scrap iron. It was estimated that elemental iron improves the hydrolysis and acidification phase in the anaerobic process. Elemental iron efficiently degrade the proteins and cellulose of the sludge and there is a significant increase in volatile fatty acids resulting in higher production of acetate acid and reduction in propionate acid while anaerobic digestion is under process during hydrolysis and acidification. Iron metal act as an electron donor for, converting CO₂ to CH₄ through autotrophic methanogenesis. [12, 13, 14].



Manganese metal is a reducing compound which involves similar physical, chemical characteristics as that of iron metal. Based on literature it was said that manganese metal acts as a electron donor for methane generation from carbon dioxide (CO₂), due its better reduction property it is more capable than iron. Manganese was consumed by methanogens to produce CH₄. The below reaction will show methanogenesis process with addition of manganese [15].



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In the study, iron and manganese 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 CO₂.

IV. RESULTS AND DISCUSSION

In first stage, granulation was carried out in the batch reactors. Glucose was added with COD of 1000 mg/l. Chitosan 2 mg/grams of VSS, methanol and micronutrients, aluminium Sulphate were also added [6]. The Granulation was achieved on 21st day of the study. The granulated sludge of 9 L was fed to EGSB reactors. One of the reactors was fed with elemental metals such as iron [20 gm/l of sludge] and manganese powder [4 gm/l of sludge] [8,9]. The study was carried out to observe the performance of EGSB reactors to treat distillery spent wash for varying COD concentrations with different HRT. During this study, observations were recorded for various parameters such as pH, VFA, Alkalinity, COD removal efficiency and methane production at regular interval.

Figure 3. Illustrates pH variation during operational period in both reactors. The influent pH was maintained to 7 by adding suitable amount of NaHCO₃. The optimal range of pH for methanogenic bacterial growth is in between 6.6-7.6. pH values less than 6.0 and more than 8.3 should be avoided . pH below 6 results in increase of acids and also slows up hydrolysis and acidogenesis activity. Hence pH was maintained between 6.6-7.6 in the effluent.

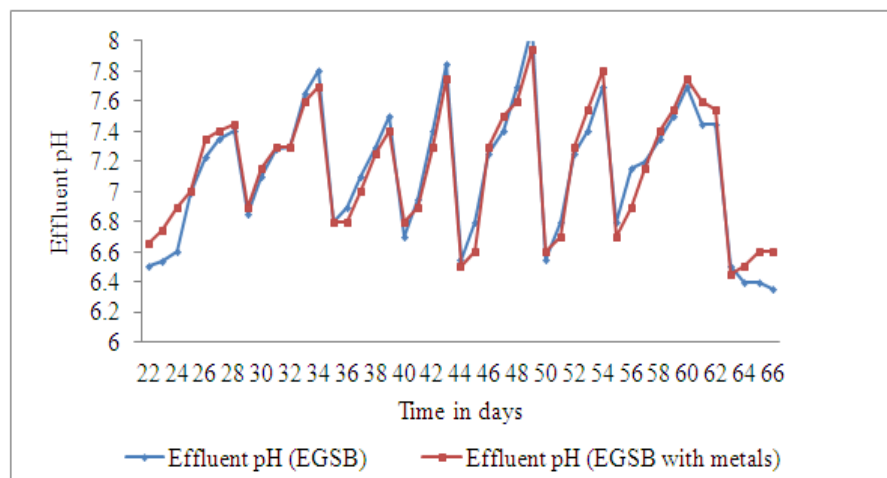


Figure 3. Effluent pH comparison

Figure 4. Shows the variation of influent feed concentration with HRT. The feed concentration of 2300 mg/L was kept in both reactors at 24h HRT and later it was changed to 4600 mg/L, 6900mg/L, 9600mg/L and HRT was varied to 12h,9h, 6h and 4h. The feed concentration was varied until the COD removal efficiency has reached steady state condition.

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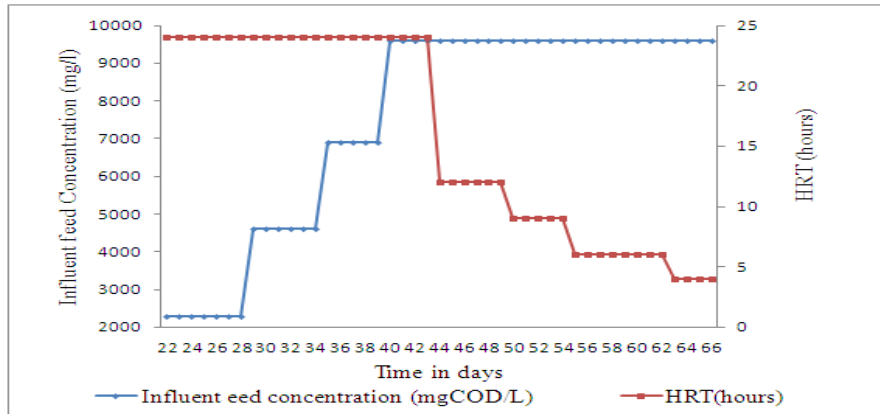


Figure 4. Variation of Influent feed concentration with HRT

Figure 5. Shows the variation of VFA/Alkalinity ratio with OLR and operational period. Higher concentration of VFA slower the methanogenesis, therefore the ratio of VFA/Alkalinity plays an important role in COD removal efficiency. When the ratio exceeds 0.4 methanogenic activity was stopped. Therefore optimum ratio should be less than 0.4. During operational period VFA/Alkalinity ratio was observed in between 0.1 to 0.32.

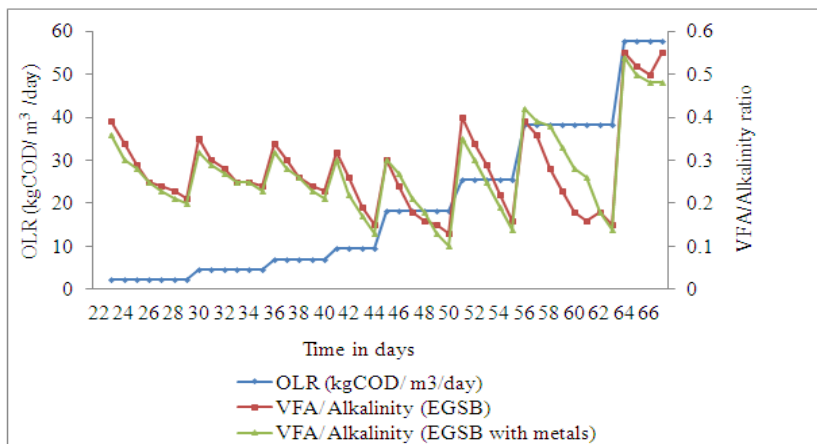


Figure 5. Variation of VFA/Alkalinity ratio with OLR.

Figure 6. During the start-up, the reactors were operated at HRT of 24h at an OLR 2.3 kg COD/m³/d. The treatment process was observed to reach maximum COD removal of 79.39% and 81.2% in EGSB and EGSB reactors with metals respectively. Similarly for HRTs of 12h, 9h, 6h and 4 h with varying OLRs of 4.6, 6.9, 9.6, 18.2, 25.6, 38.4 and 57.6 kgCOD/m³/d, COD removal efficiency were observed.

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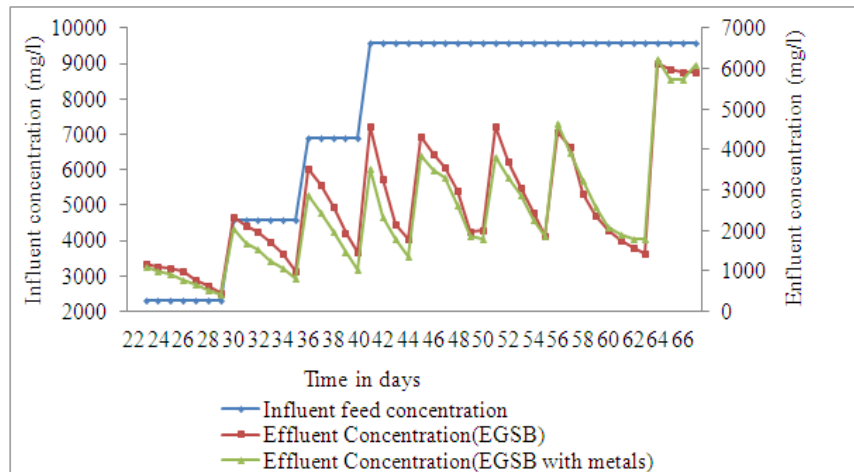


Figure 6. Influent v/s Effluent COD concentrations

Figure 7. Describes the performance of the anaerobic reactor can be observed by its COD removal efficiency. In the two reactors, COD removal efficiencies were compared to access performance. The COD removal efficiencies in the beginning was 48.04% and 52.15% in EGSB (R2) and EGSB with metals (R1) respectively when influent COD was 2300 mg/l. For the same influent, COD removal efficiencies were 79.39% and 81.20% respectively. Similarly for different influent concentration COD removal efficiencies were observed during operational period.

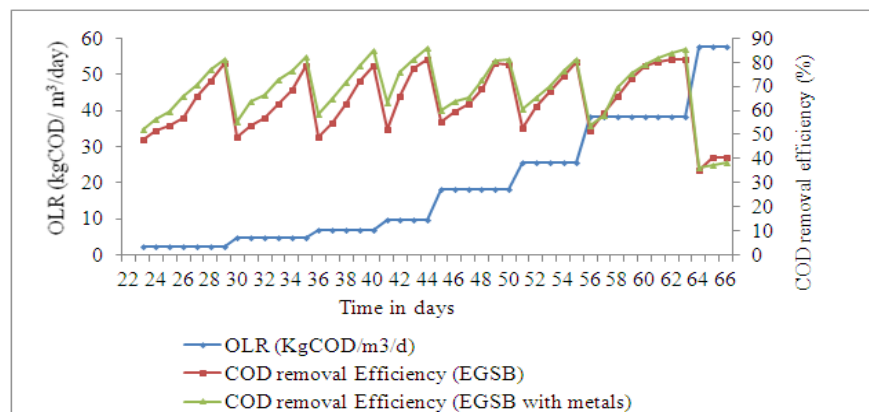


Figure 7. COD Removal efficiencies with OLR

Figure 8. Illustrates about the Methane production with addition of elemental iron, elemental iron improved hydrolysis and acidification phase in the anaerobic process where proteins and cellulose were degraded and there was significant increase in volatile fatty acids resulting in higher production of acetate acid and reduction in propionate acid. 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 38.40 kgCOD/m³/d EGSB with metals (R1) and EGSB (R2) have shown methane production of 3.79 L/L/d and 2.62 L/L/d respectively,

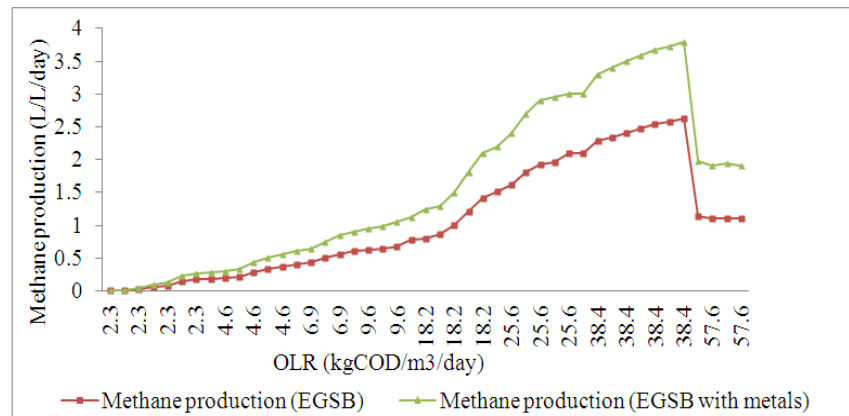


Figure 8. Methane production with OLR

V. CONCLUSION

Two laboratory scale EGSB reactors were run to understand their possibility for treating distillery spent wash. Based upon the experimental results following conclusions were drawn,

- i. By the addition of chitosan has positive effect on sludge granulation. Granulation was achieved within a short period of 21 days in batch reactors.
- ii. The start-up time for both EGSB reactors has been minimized to 62 days.
- iii. The OLR has been optimized to 38.4 KgCOD/m³/day at 6 h HRT.
- iv. COD removal efficiency in EGSB with metal (R1) is at higher side compared to EGSB (R2) reactor.
- v. Methane production rate in EGSB with metal (R1) is 1.45 times higher than that of EGSB (R2) reactor.

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