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Optimization of process parameters for catalytic conversion of solid bio-waste during thermophilic anaerobic digestion

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Abstract

Biomethanation is a process by which organic material is microbiologically converted under anaerobic conditions to biogas. Three main physiological groups of microorganisms are involved: fermenting bacteria, organic acid oxidizing bacteria, and methanogenic archaea. Microorganisms degrade organic matter via cascades of biochemical conversions to methane and carbon dioxide. Syntrophic relationships between hydrogen producers (acetogens) and hydrogen scavengers (homoacetogens, hydrogenotrophic methanogens, etc.) are critical to the process. Determination of practical and theoretical methane potential is very important for design for optimal process design, configuration, and effective evaluation of economic feasibility.

The present work is undertaken for generating bio-gas from food waste, kitchen waste, water hyacinth and Parthenium biomass separately using anaerobic digestion process. Attempts have been made to optimize various parameters viz. pH, temperature, volatile fatty acid (VFA), chemical oxygen demand (COD) in order to determine the most favorable condition for maximum biogas production from the different substrates. The biogas yields have been determined using batch anaerobic thermophilic digestion tests with a retention time of 55 days using biogas plant slurry and water treatment plant sludge separately as inoculum and bakhar, acetic acid and cow urine as catalyst. The methylotroph consortium present in the biogas slurry or water treatment sludge use the carbon source from methane for their growth due to which there is a significant change in methane production in different substrates under different conditions. The total biogas generated in the system over the experimental period was the sum of methane and carbon dioxide. Biogas produced from the decomposition of food waste produced a mixture of 65% methane and 24% carbon dioxide.

Keywords: solid bio-waste, thermophilic anaerobic digestion, VFA, COD, methane.

1. Introduction

In today's world, rapid urbanization and industrialization of the countries has led to increased rate of energy consumption. Renewable sources of energy has highly reduced for which there is rise in prices and has become difficult to avail. Biogas, a renewable source of energy, has a promising future and can be used in our long run. New research ideas for biogas production are simply based on Lignocellulosic feedstock. It is considered as an attractive raw material because of its availability in large quantities at low cost not only for the liquid transportation fuel but also for the production of chemicals and materials, i.e. the development of carbohydrate-based biorefineries. Besides terrestrial plants, aquatic plants are also a promising renewable energy resource. Water hyacinth, *Eichhornia crassipes* is such an aquatic plant. Other examples of lignocellulosic feedstock are straw, rice paddy, sugarcane plants etc.

The process of Biomethanation can be expressed in terms of anaerobic digestion is a biological process where organic material is decomposed by anaerobes in absence of air to yield methane rich biogas(Sarkar & Banerjee, 2013). The anaerobic digestion of solid waste leads to high degree of waste stabilization, low production of excess biological sludge, low nutrient(Girisuta, Danon, Manurung, Janssen, & Heeres, 2008) requirement and high production of methane gas as a useful by-product. The concept of biogas production has been applied since past 60 years as a part of domestic sewage treatment(Sarkar & Banerjee, 2013) and traditionally India has been based on dairy manure as feed stock and these Gobar gas plants have been in operation for a long period of time, especially in rural India.

1.1 Biomethanation Process

The whole process of Biomethanation can be divided in four conversion and degradation phases- hydrolysis, acidogenesis, acetogenesis and methanation(Boontian).The Hydrolysis Phase generally includes the hydrolase enzyme secreted by facultative and obligate anaerobes break down cellulose, carbohydrates, protein and fats into monomers. Lignocellulose and lignin degrade slowly and incompletely. The second stage , Acidogenic Phase primary comprise of the monomers produced on hydrolysis are degraded further, by those bacteria, into short-chain organic acids, C1–C5 molecules (e.g., butyric acid, propionic acid, acetate, and acetic acid), alcohols, hydrogen, and carbon dioxide. Intermediate hydrogen affects the fermentation products. Intermediate fermentation products are formed if the partial pressure of hydrogen is high enough(Boontian). The penultimate stage is Acetogenic Phase which generally includes the Acidogenic products of the previous phase serve as substrates for bacteria in the acetogenic phase. Homoacetogenic microorganisms of the acetogenic phase use exergonic H_2 and CO_2 to form acetic acid. Methanogenic bacteria grow concurrently with acetogenic bacteria. Short-chain organic acids and alcohols are converted to acetate. In the conversion of ethanol to acetate, carbon dioxide is used and acetate and hydrogen are produced. Acetate production decreases if

hydrogen partial pressure is great enough(Boontian).The last stage is Methanogenic Phase in which the methane production takes place under strict anaerobic conditions. Not all methanogenic bacteria degrade all substrates. It can be divided into acceptable substrates acceptable for methanogenesis into the following three groups:

(i) Acetoclastic Methanogenesis: Acetate \rightarrow CH₄ + CO₂

(ii) Hydrogenotrophic Methanogenesis: H₂ + CO₂ \rightarrow CH₄

(iii) Methyltrophic Methanogenesis: Methanol \rightarrow CH₄ + H₂O

1.2 Water Hyacinth and it's characteristics

Water hyacinth (*Eichhornia crassipes*) is a monocotyledonous freshwater aquatic plant, belonging to the family Pontederiaceae, related to the lily family (Liliaceae) and is a native of Brazil and Equador region(Kunatsa & Mufundirwa, 2013). It is also a well known ornamental plant found in water gardens and aquariums, bears beautiful blue to lilac colored flowers along with their round to oblong curved leaves and waxy coated petioles. Water hyacinth is considered as a noxious weed in many parts of the world as it grows very fast under favourable conditions. It can achieve a growth rate of 17.5 metric tons per hectare per day(Kunatsa & Mufundirwa, 2013). There is a great discrepancy among policy makers, environmental agencies and research scientists on the way to control this invasive species and the practical benefits that can be obtained. Previous studies depicts that,(Bhattacharya & Kumar, 2010) an ideal bio fuel producing crop must have the following attributes, notably, the naturally grown vegetation, preferably perennials, Rich in cellulose with low lignin content per unit volume of dry matter, easily degradable, should not compete with arable crop plants for space, light and nutrients, resists pests, insects and disease, not prone to genetic pollution by cross breeding with cultivated food crops. Water hyacinth is low in lignin content (10%) and contains high amounts of cellulose (20%) and hemicellulose (33%)(Bhattacharya & Kumar, 2010). In plants, lignin (composed of phenylpropanoid groups) acts as a polymer around the hemicellulose microfibrils, binding the cellulose molecules together and protecting them against chemical degradation. Lignin cannot be converted into sugars. Thus, it is not practical in biofuel production. Their degradation is a high-energy process. Water hyacinth has low lignin, which means the cellulose and hemicellulose are more easily converted to fermentable sugar thus resulting in enormous amount of utilizable biomass for the biofuel industry (Fig. 1)(Bhattacharya & Kumar, 2010).

Table 2. Characteristics of water hyacinth

Parameters	Results
Proximate Analysis	
Moisture	86.1
Ash(dry basis)	2.24
Volatile Matter(dry basis)	7.59
Fixed Carbon	4.07
CHN Analysis(by weight)	
Total Carbon	39.3
Hydrogen	5.91
Nitrogen	2.32

2.2. Chemicals Used

All the chemicals(Girisuta et al., 2008) that are used are not in the pure form. Inoculum is used in two different types, Gobar gas plant sludge and Sewage Plant sludge, each of 20gm in 10gm substrate. Three catalysts that are used, 2.5 gm Bakhor (Rice-beer cake), 0.6ml of Acetic acid and 2.5ml Cow's Urine(Sarkar & Banerjee, 2013). 250ml water is used to prepare different solutions. Sodium hydroxide is used in case, to adjust the pH. Concentrated sulphuric acid is used with a measurement of 2.5ml, 400ml distilled water and 5-6drops of phenolphthalein indicator each time for measuring the VFA concentrations.

2.3. Experimental Details

The experiment was carried in a semi-batch digester. In total, 14 conical flasks of 500ml capacity were used along with same number of drilled corks, pipes, thermometer, pH paper, distillation unit, Methane Gas analyzer. A total of 14 conical flasks were distributed in two categories:

- (i) Seven were incorporated with Gobar gas plant sludge, out of those seven, two were treated with Bakhor, two were treated with acetic acid, two were treated with cow's urine and one was kept as a control where no catalysts was applied.
- (ii) Other seven were incorporated with Sewage Plant sludge, out of those seven, two were treated with Bakhor, two were treated with acetic acid, two were treated with cow's urine and one was kept as a control where no catalysts was applied.

For the two cases i) and ii), the control and one out of each catalyst pair was taken every day for measurement of temperature and pH and measurement of VFA concentration once a week, while the other one is kept aside for 20-30 days(Boontian) until methane gas was produced.

(The conical flasks were closed with drilled corks, after preparing the solution. Plastic pipes were incorporated through the corks in order to transfer the generated gas through the plastic pipe to

an enclosed cylinder filled with water. Anaerobic condition is a important factor for biomethanation as facultative and obligate anaerobes are responsible for this process.

(i)The optimum pH range and temperature range is (6.5-7.92) and (30-40°C) respectively, for mesophilic bacteria responsible for bio methanation[3].The pH of the experiment varied between 6.5 to 7.0 and the temperature varied between 31-33°C.

(ii)The normal concentration of VFA must not exceed 4g/l(Boontian). The VFA concentration for each set-up that was measured once a week varied between 1200mg/l to 4500mg/l. The whole VFA procedure was carried out in using standard precedures(Ganesh, Ramasamy, Gajalakshmi, & Abbasi, 2005).

(iii)After incubation for 20 days, the gas generated in the semi-batch digesters was measured by a methane gas analyser.

(iv) In the whole process the two types of sludge were used as a source of microbes(Girisuta et al., 2008). The loading rate i.e. substrate to inoculums ratio is maintained at 1:2.

2.4. Analytical Methods

The semi-batch reactor was run in mesophilic conditions. The pH of the slurry was measured using a digital pH meter having an accuracy of ± 0.01 pH unit while volatile fatty acid(VFA) was determined in accordance to the Standard Methods .

Volatile fatty acids (VFA) was analysed by distillation method followed by titration with 0.01N NaOH with a phenolphthalein indicator. Distilled water in all glass units of borosil design, was used for all purpose(Gotmare, Dhoble, & Pittule, 2011).

3.Results and Discussions

3.1 Component analysis of Water Hyacinth samples

The calculation of hemicellulose and lignin content was done on conducting the NDF and ADF method. The amount of calculated total cellulose , hemicellulose, lignin and ash content present in the Water Hyacinth biomass are be 25%, 35 %, 10%, 20% respectively. More detailed explanation of composition of water hyacinth is described in Table 1.

Table. 1 Compositional analysis of Water Hyacinth Biomass

Components	%Composition
Lignin	10
Cellulose	25
Hemicellulose	35
Ash	20
Nitrogen	03

3.2 Methane Gas Production

The production of biogas was observed after 3 weeks or after 25 days. Generally production starts between 20-35 days. Water hyacinth contains higher molecular mass compounds such as carbohydrates, proteins and lipids. Sewage sludge and Gobar gas sludge, as a source of inoculums, contains different species of microorganisms is suitably added to the water hyacinth substrate to boost up anaerobic decomposition stages. Low biomethanation rate can be easily detected if there are relatively high CO_2 and low CH_4 contents. It reflects that the digestion process has not yet reached active methanogenesis (Malakahmad, Zain, & Basri, 2012). Therefore, although biodegradability of substrate is a vital parameter for biomethanation, the presence of different groups of microorganisms is essential for substrate breakdown and anaerobic digestion. The ratio between food and microorganism (F/M) is an important factor in biomethanation process (Boontian; Malakahmad et al., 2012). When the bacteria grow, the protozoa will grow as well and the microorganisms in the system can be active very fast and hence produce gas.

3.3 pH Variation

Variation of pH for 4 samples of each sludge are given in the Fig.3.2.(a) and (b). The pH and temperature of the samples were measured in everyday for continuous 3 weeks. The average pH remained between 6.5 to 7.5. The pH variation could be categorized into three main zones. The first zone started from the first day till fifth day, which showed a drastic drop of pH. This is due to high development rate of volatile fatty acids and amino acids from lipids and protein breakdown during hydrolysis stage. The second zone started from the sixth till the eleventh day of the experiment. In the second zone, the pH was in the range of 6.8 to 7.2.

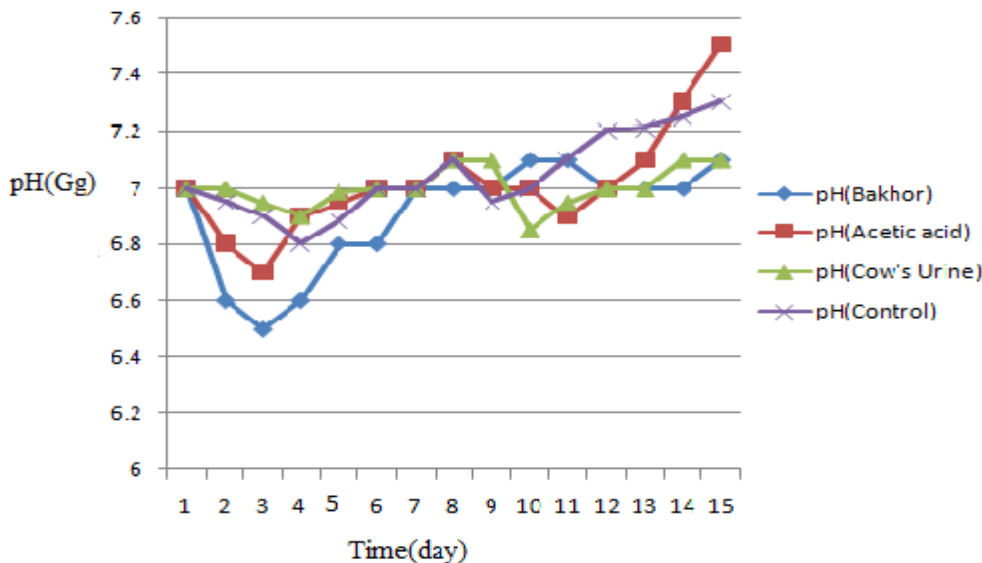


Fig.3.2.a) pH variation with time of GobarGas samples

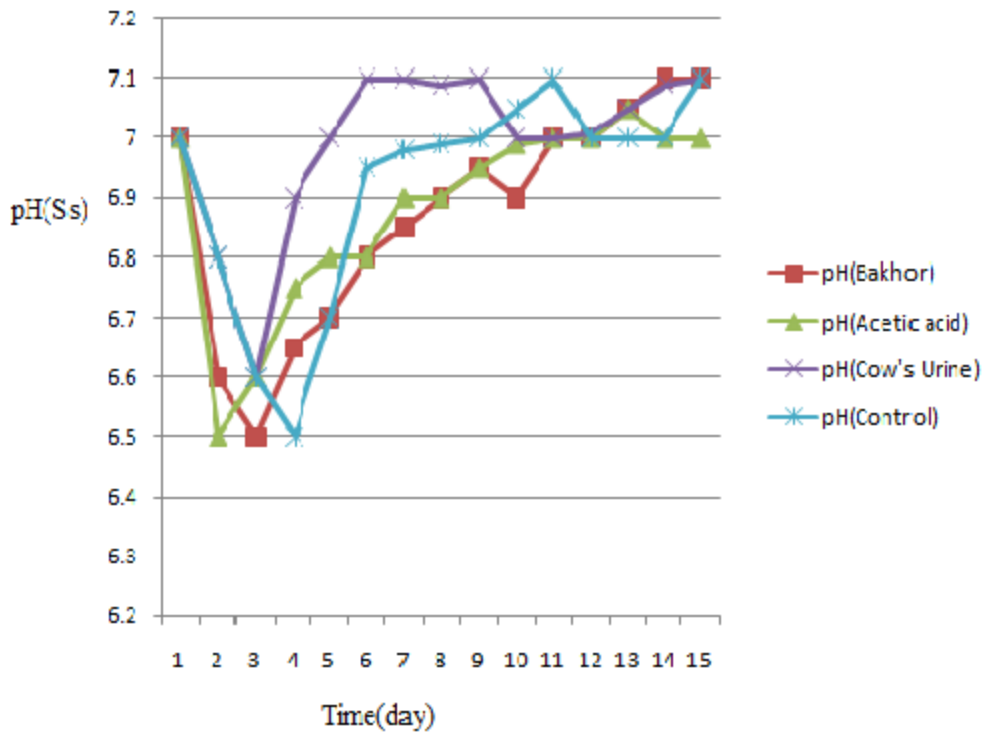


Fig.3.2.b) pH variation with time of Sewage Sludge samples

This is due to the development of $\text{CO}_3\text{H}\text{NH}_4$ from CO_2 and NH_3 , which were produced during the acidogenesis stage (Malakahmad et al., 2012). The percentage of $\text{CO}_3\text{H}\text{NH}_4$ caused the increase alkalinity of the samples. Due to this, any differences in the volatile fatty acid content did not affect the pH value. The third zone started on the twelfth till the last day of the experiment. In this zone, it was found that the pH value of the samples started to increase. This is due to the development of $\text{CO}_3\text{H}\text{NH}_4$ continuing while no more volatile fatty acid was produced. The pH observation results are in agreement with studies conducted earlier (Feng et al., 2009).

3.3. Temperature Variation

The temperature of the samples varied between 30-33°C (Boontian). This temperature range is the optimal for biogas production. The methanogens are mainly facultative and obligate anaerobes are mesophilic in nature. These microorganisms are active at temperatures 30°C to 40°C. A temperature below 30°C would have inhibited the whole process, as the mesophilic bacteria are not active, as well as there would be a reduction in the methane gas production.

3.4. Volatile Fatty Acids

The variation of VFAs with time of 4 samples of each of the two sludge are given in the fig.3.4.a) and b). The maximum limit of total VFA concentration should not exceed 4000mg/l (Boontian). The VFA concentration of all the samples was within the limit.

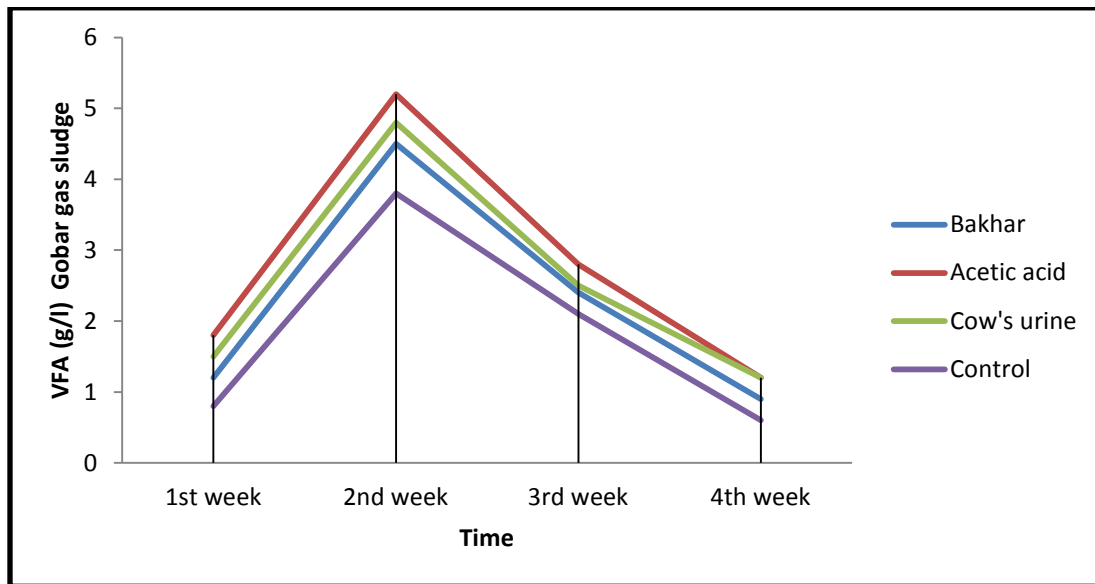


Fig. 3a VFA concentration variation with time of Gobar gas sludge samples.

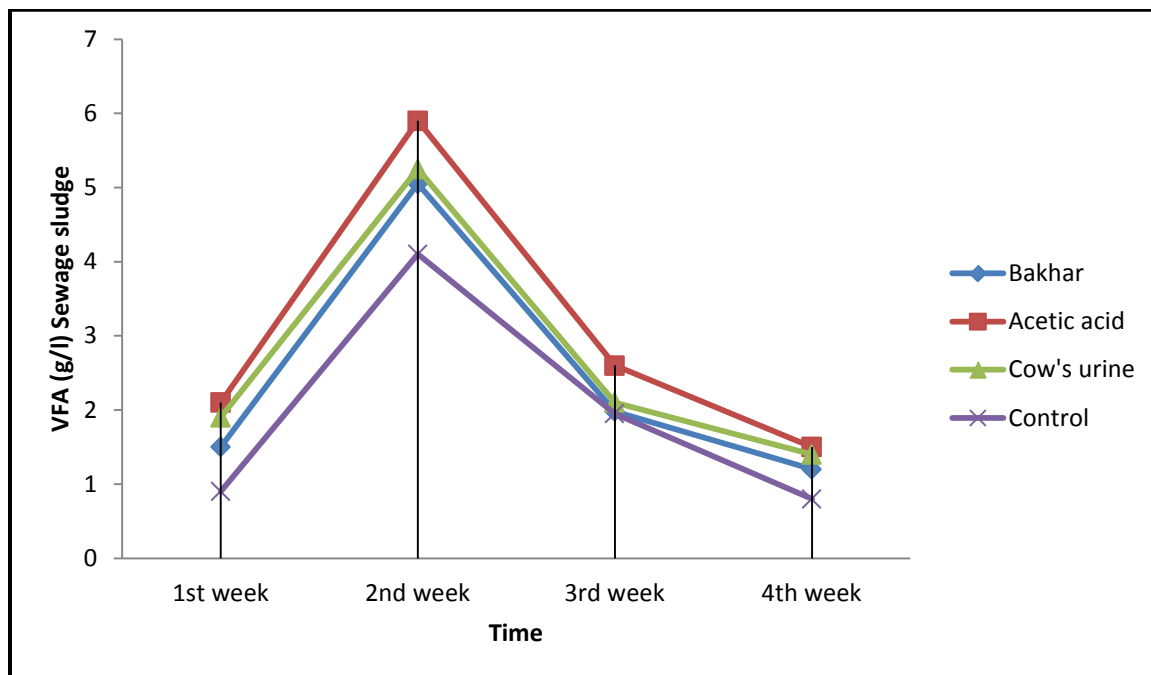
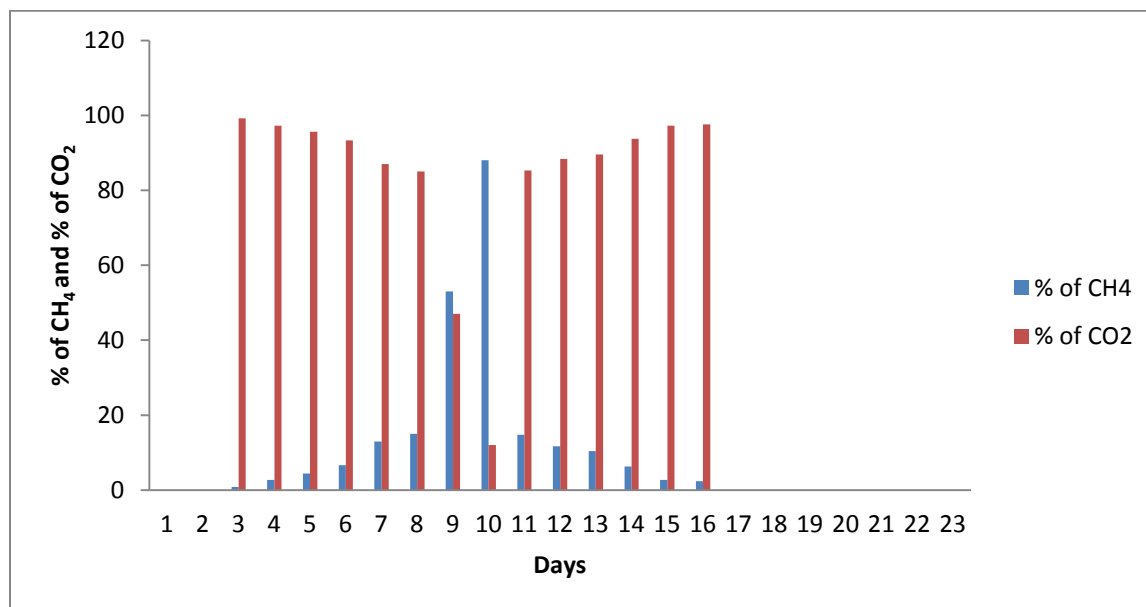


Fig. 3a VFA concentration variation with time of Sewage sludge samples

It may be seen from the figures that in all samples, except the acetic acid and control ones, the yield of VFA has climbed up in the second week and declined sharply in the third week.

METHANE PRODUCTION

Maximum amount of methane (CH₄) gas was found in water hyacinth substrate with gobar gas slurry using cow urine as bio-catalyst. The methane (CH₄) yield was found to be approximately 80%.



4. Conclusion

Anaerobic digestion of water hyacinth with Gobar Gas sludge and Sewage sludge was conducted under in semi-batch reactor to investigate the dependence of methane yield to water hyacinth substrate in combination with different catalysts. The VFA yields in the Bakhor and Cow's Urine samples was good enough ,which positively indicates that there was methane gas formation. In this process microbiological population is vital and boosts the methane generation rate. Along with this anaerobic conditions must be maintained properly otherwise aerobic conditions will inhibit the whole process. Water hyacinth samples may need some extra addition of water between the process, in case the sample becomes too dry. Obtained results in this study justify the importance of biomethanation process in any integrated solid waste management approach.

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