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Supplementing pineapple pulp waste with urea and metal ions enhances biogas production.

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Abstract: *Pineapple is a tropical plant with an annual global production of 2,33,33,886 tonnes as of 2012 (FAO official website).Pineapple pulp waste is one of the major waste material that is produced by pineapple processing industries. It is a high carbon containing waste, so needs nitrogen supplementation for production of biogas both efficiently and in a cost effective manner. In this study, we have tested the effect of urea supplementation in varying concentration and found that 2 % urea is the most optimum for production of biogas which yields 19 % more biogas than the control. Various metal ions also showed stimulatory effects in enhancing biogas from pineapple pulp waste. Ferric, Zinc, Cupric, Nickel, Cobalt were found to be stimulatory. Out of these, Cobalt was found to be more effective than other metal ions with 7.5 % more biogas compared to the control. Various metal ions in combination proved to be more stimulatory than individual addition of metal ions with an enhanced yield of 8.6 % higher than the control.*

Keywords: *Pineapple pulp waste, Anaerobic Digestion, Biogas, Urea supplementation, Metal ions, Cost effective.*

I. Introduction

The world is suffering from energy crisis due to limited amount of non renewable fuels, at the same time, the demands for fossil fuels and conventional energy are increasing day by day. All efforts should be made to tap renewable energy sources available on the planet to propel the economies in future. Energy is the backbone for the economic growth of a country. India's diverse climate ensures availability of all varieties of fresh fruits & vegetables. It ranks second in fruits and vegetables production in the world, after China. As per National Horticulture Database published by National Horticulture Board, India during 2012-13 India produced 81.285 million metric tonnes of fruits and 162.19 million metric tonnes of vegetables.

Annually, India produces approximately 14 lac tonnes of pineapple which makes it the sixth largest producer of pineapple in the world. During processing, around 20-30 % of the wet weight of the fruits will be discarded as processing waste. Due to their nature and composition, they deteriorate easily and cause foul smell leading to environmental pollution [1]

Anaerobic digestion is the biological degradation by a complex microbial ecosystem of organic and occasionally inorganic substrates in the absence of an organic source. There are four metabolic stages involved in the production of methane using anaerobic digestion process. First, the particulate organic matters undergo hydrolysis by extracellular enzymes to convert polymers into monomers. Then the soluble organic matter and the products of hydrolysis are converted into Organic acids, alcohols, hydrogen and carbon dioxide by acidogenic bacteria. Then, the acetogenic bacteria convert the products of acidiogens into acetic acid, hydrogen and carbon dioxide. Finally, methanogenic bacteria are responsible for methane production from acetogen products. The main advantage in using anaerobic digestion is the production of biogas, which can be used for steam production, heating, cooking and generation of electricity [2], [3], [4]. The slurry, which is a byproduct of the digestion can be used as a bio-fertilizer or soil conditioner.

The anaerobic digestion as a biological process, is strongly dependent on the environmental conditions [5] such as temperature, pH, nutrients content, carbon/nitrogen (C/N) and carbon/phosphorus (C/P) ratio, presence of inhibitors, type of substrate, microelements availability, particles size, etc.

Fruits and vegetable wastes are excellent substrates for biomethanation [6],[7],[8][9],[10],[11]. Approximately 35 % of pulp waste is generated from pineapple canning industries annually [12]. In general finely ground waste products produce more biogas due to large surface area of contact with bacteria. [13].

II. Materials and Methods

2.1 Production of biogas from pineapple pulp waste supplemented with urea: Pineapple pulp waste was collected from a local juice bar and was washed three times with water to remove residual sugars. 200 grams of

pineapple pulp waste was mixed with 35 grams of fresh cow dung (Inoculum) and then it is mixed with 500 ml of water, the whole mixture is made up to a final volume of 700 ml and the resulting slurry was poured into a 1 liter conical flask which was closed by one holed rubber stopper and the flask was placed in a water bath filled with water with a constant temperature of 35^{o} C. The initial pH of the slurry in all the cases was recorded as 7.5. In order to ensure mechanical stability, especially as the water level in the water bath were higher than the level in the flask, it was attached to a rugged clamp and the supporting strand. The fermentation gases (biogas) were quantitated using water displacement system, this setup was used as the positive control.

A similar setup was made with 35 grams of cow dung mixed thoroughly with 500 ml of water and made up to a final volume of 700 ml which was used as a negative control.

Five different conical flasks were used to make fermentation media with 200 grams of pineapple pulp waste along with 35 grams of fresh cow dung and urea in the range of 1 to 5 grams added to the respective flasks. Gas production was monitored using water displacement method.

Water displacement method for quantitation of biogas: Each of the respective media of volume 700 ml was poured into 1 liter conical flask closed with one holed rubber stoppers. The fermentation gases evolved as a part of the biochemical process (Methanogenesis) were conveyed through a rubber tubing to an inverted 1 liter conical flask closed with 2 holed rubber stoppers. The gas was collected at the top of the inverted conical flask, which displaced an equal quantity of water through rubber tubings to a measuring jar. The amount of water displaced in 24 hours is used for all further calculations.

2.2 Production of biogas from pineapple pulp waste supplemented with various metal ions: Pineapple pulp waste was washed three times with water to remove residual sugars. 200 grams of pineapple pulp waste was mixed with 35 grams of fresh cow dung (Inoculum) and then it is mixed with 500 ml of water. To it, 17.5 mg each of metal containing compounds were added. Five 1 liter conical flasks were used for this purpose which contained 17.5 mg of Ferric chloride, Cobalt chloride, Cupric chloride, Zinc chloride and Nickel chloride respectively. All these ion containing compounds were procured from Hi media laboratories Pvt.Ltd, Mumbai, India. The whole mixture is made up to a final volume of 700 ml. Each of the Flasks were closed with one holed rubber stoppers. The fermentation gases (Biogas) were quantitated using water displacement system.

2.3 Synergistic action of metal ions in enhancing biogas production: Pineapple pulp waste was washed three times with water to remove residual sugars. 200 grams of pineapple pulp waste was mixed with 35 grams of fresh cow dung (Inoculum) and then it is mixed with 500 ml of water. To a 1 Liter conical flask, 17.5 mg each of metal containing compounds were added. 17.5 mg each of Ferric chloride, Zinc chloride, Cobalt chloride, Nickel chloride and Cupric chloride were thoroughly mixed with pineapple pulp waste and cow dung and the whole mixture was made upto 700 ml. This fermentation media was allowed to ferment. The fermentation gases (biogas) were quantitated using water displacement system.

III. Results

3.1 Supplementation of pineapple pulp waste with urea: Carbohydrates in pineapple pulp represents upto 85 %, while the percentage of nitrogen is as low as 0.1 % of the total solid pulp waste. [14].

Since pineapple pulp contains less nitrogen and more carbon, it needs supplementation with easily soluble and cheap nitrogen source. In this aspect we have used urea to enhance the production of biogas from this industrial waste. Addition of urea in the range of 1 to 5 grams to 200 grams of pineapple pulp waste showed improved productivity of biogas compared to the control without urea.

Control showed a cumulative biogas production of 8182 ml, while the pulp waste with 1 gram, 2 grams, 3grams, 4 grams and 5 grams of urea showed a cumulative biogas production of 9,000 ml, 9,735 ml, 9,474 ml, 9,246 ml and 9,125 ml respectively over a period of 30 days. The highest production was achieved with 2 grams of urea with an output of 9,735 ml which is about 19% higher than the control. (As shown in fig.1)

3.2 Biomethanation of raw pineapple pulp waste with addition of various metal ions; Most of the metal containing compounds used in this study are readily available in bulk quantities and at cheaper rates. Various metal ions have got stimulatory effects on the yield of biogas from a particular substrate (10), in this context we have tested the effect of 0.0025 % of Cobalt, Copper, Iron, , Nickel and Zinc on the overall yield of biogas with pineapple pulp waste as the raw material, it has been found that cobalt (as cobalt chloride), copper (as cupric chloride), iron (as ferric chloride), nickel (as nickel chloride) and zinc (as zinc chloride) were found to be stimulatory with a cumulative yield of 8,795 ml, 8,218 ml, 8,595 ml, 8,463 ml and 8,297 ml over a period of 30 days. All were higher than the control without ions with a yield of 8,182 ml. The highest yield achieved was with Cobalt chloride with a yield of 8,795 ml, which was 7.5 % higher than the control. (As shown in fig.2)

3.3 Synergistic effect of various metal ions on biomethanation of raw pineapple pulp waste- Various combinations of metal ions have proved to be more stimulatory than individual metal ions in enhancing the yield of biogas from pineapple pulp waste. In this context, we have mixed 200 grams of pineapple pulp waste with 17.5 mg (w/v) each of Cobalt chloride, Ferric chloride, Nickel chloride, Zinc chloride and Copper chloride, which gave a cumulative biogas yield of 8,885 ml over a period of 30 days. The yield was about 8.6 % higher than the control without any metal ions. (As shown in fig.3)

IV. Discussion

Pineapple pulp waste contains less proteins and more carbohydrates. Optimum biomethanation can take place at the C:N ratio of 25:1 to 30:1. If carbon is excess and nitrogen is low, due to over production of acid a low pH environment is created in the bioreactor. Usually no biogas will be produced if the pH is below 6.5. Since the methanogenic bacteria are very sensitive to pH, usually anaerobic digesters are maintained in the pH range of 7.5 to 8.5 under buffered conditions. Urea being a cheap organic nitrogen source can be used as a nitrogen supplement to increase the percentage of nitrogen in the fermentation broth. From the data, it is evident that supplementation with 2 % urea will yield 19 % more biogas compared to control, which is 9,735 ml.

Various metal ions play an important role as cofactors in methanogenic pathway which accentuate or enhance methanogenesis. Some are even essential for methanogenesis. Supplementation of metal ions will help to enhance biogas production and added revenue generation. From fig.2 it is evident that among the various metal ions supplemented (Fe, Co, Zn, Cu, Ni) Cobalt has been found to be very effective in the form of cobalt chloride at a concentration of 0.0025 % (w/v) with a yield of 8,795 ml, 7.5 % higher than the control.

Trace elements necessary for anaerobic digestion includes Fe, Co, Cu, Zn, Ni. These micronutrients are essential for microorganisms and also very essential for various enzymes. Acetate is the major precursor for methane production in anaerobic digesters and its utilization is the main rate limiting step in the anaerobic degradation of organic matter. Higher and faster conversion of acetic acid to methane by addition of Ferric chloride and Magnesium chloride has been observed in anaerobic digestion with 40 % increase in biogas production from fruit waste. Synergistic action of various metal ions was found to be more beneficial in enhancing biogas from pineapple pulp waste compared to individual usage of metal ions. From fig.3, it is evident that the combination of Ferric chloride, Cobalt chloride, Copper chloride, Zinc chloride, and Nickel chloride produced 8,885 ml compared to control which was 8,182 ml and it was also higher than cobalt supplemented fermentation medium which yielded 8,795 ml, which is 8.6 % higher than the control.

V. Conclusion

This study reveals that pineapple pulp waste alone is not a good substrate for methanogenesis, since its C:N ratio is not optimum for efficient production of Biogas. Easily assimilable and cost effective urea supplementation enhances biogas production from pineapple pulp waste. Similarly, supplementation of Iron, Cobalt, Copper, Zinc and Nickel were found to be stimulatory. Synergistic action of these metal ions further enhances biogas production from pineapple pulp waste.

Conflict of Interest

No conflict of interest declared.

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The relevant figures are numbered in the Arabic system and are provided below

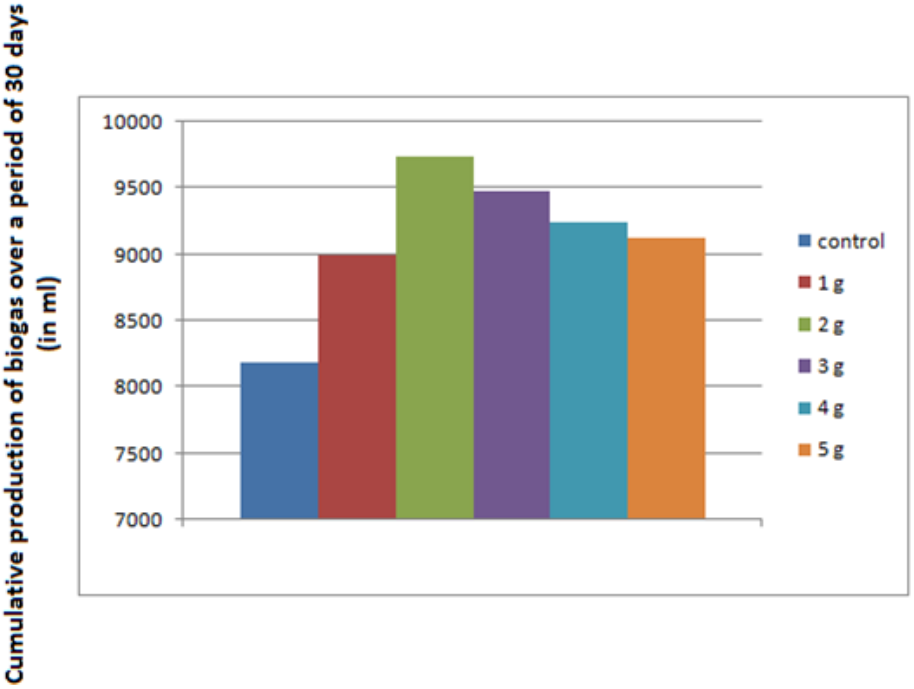

Figure 1- Supplementation of pineapple pulp waste with urea enhances the biogas production

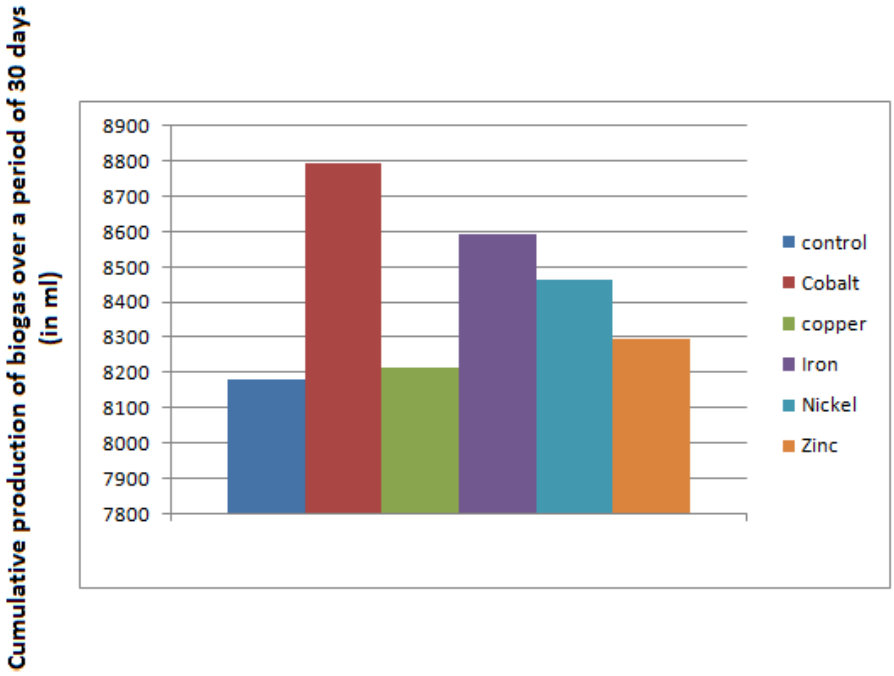

Figure 2- Biomethanation of raw pineapple pulp waste with addition of various metal ions

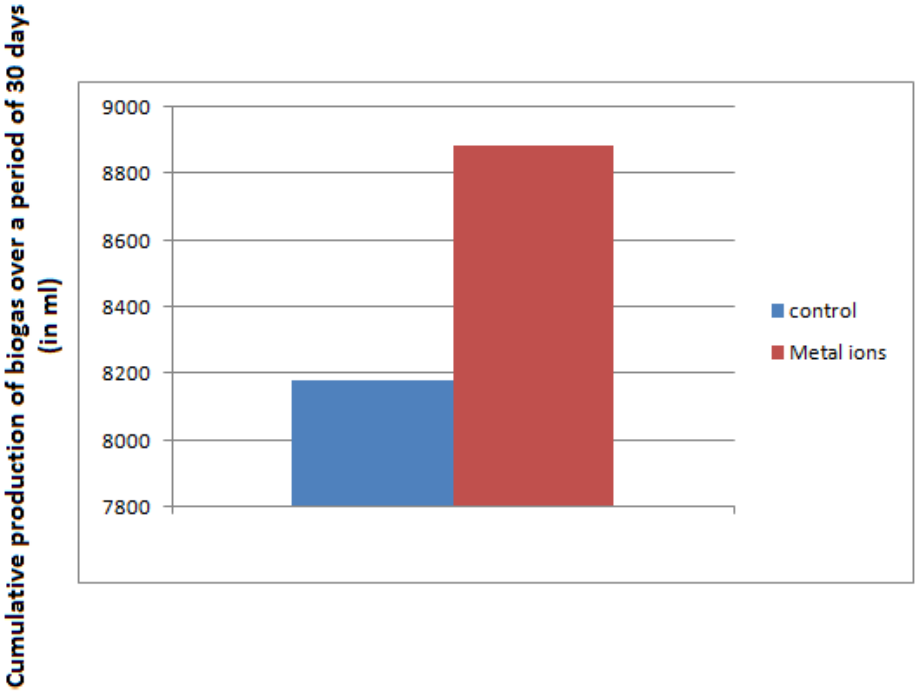

Figure 3- Synergistic effect of various metal ions on biomethanation of raw pineapple pulp waste