Demonstration of Hybridized Processes for Waste to Energy under Partial Photocatalytic Processes

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Abstract. The present study reveals the carbon recovery potential from municipal solid waste (MSW) and wastewater by proximate physico-chemical analysis for the purpose of renewable energy production. MSW with cow dung (FS1) and wastewater (FS2) showed a C: N ratio of 43:1.2 and 16:0.8 respectively, which indicates significant carbon recovery potential. Cumulative methane production rates with different ratios of feed stocks were tested through batch scale bioreactors. Maximum cumulative methane yields of 346 ml and 367 ml were obtained under biomethanation processes with mixed ratios of 3:1 and 2:2 respectively for duration of 48 days. The effect of photocatalytic processes on the final methane yield under visible light source was studied by incorporating a suitable photocatalyst in the headspace of the bioreactor. Quantification of methane production rate was carried out by liquid displacement method and the accuracy was compared with the GC method using photocatalyst incorporated bioreactor.

1. Introduction

The total estimated methane and carbon dioxide emission to the atmosphere is approximately $525 \times 10^6$ tons per year by inappropriate management of municipal wastes and this rate is increasing by approximately 1 percent per year [1-5]. Recycling carbon contents in the municipal wastes by sustainable methane production is highly beneficial in terms of GHG emission and fuel crisis [6-8]. However, sustainable and efficient recycling of carbon contents from the municipal wastes is under development and more efforts are required to develop novel technologies. The existing conventional technologies for the conversion of waste into fuel have some limitations such as deficient yield, low quality, comparatively high cost, unclear mechanism and so on [9]. Conventional carbon recycling techniques like biomethanation used for the conversion of waste into energy have resulted only 60-65% of methane yields along with 35-40% carbon dioxide and other byproducts in the final biogas stock. The presence of carbon dioxide and other byproducts in the final biogas stock along with deficient performance suppress the practical application at large scale. In recent days, due to the scarcity and availability of fossil fuels, scope of sustainable production of methane as renewable fuel from municipal wastes by various routes has gradually increased. Many studies have explained the possible mechanism, simulations of quantum chemicals, experimental observations and principles for improved methane yield. TiO$_2$ is well recognized due to several advantages like nontoxic, higher redox potential, chemically/thermally stability, abundantly availability and relatively cheapness [10-11]. In addition, searching and identification of alternative reducing agents from renewable sources for.
the sustainable and effective conversion of carbon dioxide into methane and other hydrocarbon fuels is an important task. Potential carbon recovery from municipal wastes and intensification of methane production rate by hybrid photo-bioreactors could tackle the energy crisis and environmental problems of GHG.

2. Materials and Methods

2.1. Materials
About 5-10 kg of freshly disposed of municipal solid waste was collected from central market (Devaraja Urs Market) in Mysore City using polythene bags. As obtained solid waste was consisted with a varieties of organic substances such as fruit bunches, rotten fruits, vegetable, packing leaves, flowers, fibers, shells and nut, decomposed millets and floor, spoiled food, mushroom, packing maters, packing papers, waste generated during cleaning and sweeping, etc. About 10 L of wastewater was collected from the inlet of municipal wastewater treatment plant at Kesare, Mysore using polythene cans. Cow dung was also collected, dried and stored in an air-tight polyethylene bag then it was used as an inoculating substrate to feed the bioreactors. About 5 kg of municipal solid waste was taken and grinded along with ≈ 2.5 kg cow dung into fine slurry (FS1) under overhead homogenizer (Remi RQM-122R). Physico-chemical characterizations of homogenized slurry (FS1) and raw municipal wastewater (FS2) were expressed by proximate content of total solids (TS), volatile solid (VS), carbon to nitrogen (C: N) ratio, crude fibers, crude protein, crude fat, ash content and moisture content, using standard analytical methods [12].

2.2. Experimental Setup
Six sets of laboratory scale bioreactors (BR1, BR2, BR3, BR4, BR5, and BR6) were used for biochemical methane production from the municipal wastes collected. About 1 L capacity of glass container (C1) was used to build a bioreactor with an air-tight lid. Glass container (C1) was connected to the gas collecting system attached to 500 ml containers (C2) and measuring jar. C1 and C2 were filled with feed stocks (mixture of municipal wastes) and alkaline solution (5M NaOH) respectively then methane production rate was measured through liquid displacement method [28-32]. All C1 containers were filled with 75% of feed stocks with different mixed ratios of FS1 and FS2. The different mixed ratios of FS1 and FS2 were maintained as 750:0, 600:150, 450:300, 300:450, 150:600, and 0:750 ml then fed into bioreactors BR1, BR2, BR3, BR4, BR5, and BR6 respectively. Neutral pH (6.5-8.5) was maintained in all feed stocks in the bioreactors using diluted sodium hydrogen carbonate (NaHCO₃). Nitrogen gas was purged through valve-I continuously over the headspace for a minute to remove oxygen traces to insure anaerobic condition then connected into gas collecting container. Before starting experiments, all the bioreactor’s connections were sealed into leak proof using rubber corks and Teflon tape. Each experiment was carried out under the room temperature (27-30°C) and methane production rate was measured on daily basis after the elimination of carbon dioxide from biogas stock by passing through the alkaline solution (pH>9) [13-14].

2.3. Partial Photocatalytic Process
The effect of partial photocatalytic process on final methane production rate was determined by incorporating a potential photocatalyst over the headspace of the new set of bioreactor container (C1) with the same conditions as BR3. Preparation of Mg doped TiO₂ wedge structures were carried out under sol-gel process using amorphous TiO₂ (Aldrich) as an initial precursor. During the preparation, 5 gm amorphous TiO₂ powder (Spectrochem, Pvt. Ltd, India) of 98 % purity was added into 25 ml 5M NaOH solution (Changshu Yangyuan Chemical, China) with constant stirring on the magnetic stirrer. About 0.1 g of Magnesium sulphate (SD fine-chem. Ltd. India) was dissolved in 1 ml of concentrated HNO₃ (Merck Pvt. Ltd. India) that gives Mg(NO₃)₂ and it was added into the homogeneous mixture drop wise as a source of Mg dopant. The resultant mixture was continuously stirred (250 rpm) for 3 days at room temperature and then dried in a dust free hot air oven at 50°C. Finally, obtained powder
was treated in a dust free muffle furnace using silica vessel provided with lid at 450 °C for 2 hours. Finally, it was quickly quenched to room temperature under cooling system to obtain desired functionalities. As obtained final product was characterized using powder X-ray diffraction (Rigaku Smart lab) and SEM (Shimadzu-8400S) techniques to confirm the obtained crystallinity and active surface morphology under sol-gel techniques. Mg doped TiO₂ wedge structures were used as an effective photocatalyst and photocatalyst wedge structures were coated on Teflon slides (1.5 × 6 cm) under screen printing technique and photocatalyst loaded Teflon slides were incorporated at headspace of the bioreactor using nylon tread. As incorporated photocatalysts were irradiated to visible light sources (Tungsten bulb, 15V, Philips) continuously and the effect of photocatalytic processes on the cumulative methane production rate was determined.

3. Results and Discussions

Proximate physico-chemical characterizations of mixed slurry of solid waste with cow dung (FS1), and raw municipal wastewater (FS2) are shown in Table 1. Feed stocks FS1 and FS2 used for carbon recovery by biochemical methane production processes showed a carbon to nitrogen (C:N) ratio of 43:1.2 and 16:0.8 respectively. Feed stock FS1 showed comparatively higher C:N ratios than raw municipal wastewater attributed by enormous contents of biodegradable organics and cow dung. Physico-chemical characterization of municipal wastes clearly indicated significant carbon recovery potential that could be attributed to the high level C:N ratios. C:N ratio is one of the major factors that influences the potential of methane yield in biomethanation and this makes it a vital parameter that is considered in enhancing the methane production from biogas feed stocks. It is very important to maintain the suitable substrate compositions for optimum operation of biomethanation reactor so that the C:N ratio should be remained within the desired level [13]. Physico-chemical analysis of both FS1 and FS2 feed stocks indicated existence of considerable amount of mainly carbon, volatile organic solid and moisture contents, which are the fundamental sustenance for anaerobic microorganisms for methane production under biochemical methanation [13-15]. Tremendous improvement in cumulative biochemical methane production rate from all the variants of organic waste may be attributed to this factor [15].

Table 1. Proximate physico-chemical characterizations of municipal wastes which are used as feed stocks for biochemical methane production

| Physico-chemical characteristics | Mixture of solid waste and cow dung (2:1 ratio) | Raw municipal wastewater |
|----------------------------------|-----------------------------------------------|--------------------------|
| pH                               | 7.2                                           | 5.9                      |
| Temperature                      | 28                                            | 29                       |
| C/N ratio                        | 35.9                                          | 22.85                    |
| Nitrogen                         | 1.2                                           | 0.7                      |
| Total Carbon                     | 43                                            | 16                       |
| Total solid                      | 69.80                                         | 12.50                    |
| Moisture content                 | 30.20                                         | 87.50                    |
| Volatile solid                   | 73.50                                         | 6.50                     |
| Ash Content                      | 7.80                                          | 6.00                     |
| Crude Fat                        | 2.11                                          | 1.55                     |
| Crude Protein                    | 11.00                                         | 1.20                     |
| Crude Fibres                     | 20.00                                         | 0.33                     |
| COD                              | >5000                                         | 3200                     |

In the bioreactors BR1, BR2, and BR3 lag phases were observed till ⁹th, ⁷th, and ⁴th days respectively but in the bioreactors BR4, BR5 and BR6, methane production was commenced in the
first day (within 24 hrs) only. Such observations could be attributed to the different mixed ratios of feed stocks and their degree of predigesting potential under anaerobic conditions [16-18]. Due to the presence of pre-broken organic substances (pre-lag phase) in the municipal wastewater with higher ratios could lead into shorter lag phases in the bioreactors BR4, BR5 and BR6 than BR1, BR2, and BR3. In all of the bioreactors, maximum methane production rate was observed between the 16-28th days and figure 1 illustrates the daily methane production rate in the bioreactors with different mixed ratios of feed stocks. The cumulative methane production rate in the bioreactors with different mixed ratios of feed stocks for a period of 48 days can be seen in figure 2A and maximum cumulative methane production rate recorded was in the range of 181-367 ml. However, the cumulative methane production rate was differed significantly based on different mixed ratios of feed stocks FS1 and FS2 (Figure 2A). Maximum cumulative methane production rate was observed in the bioreactors BR2 and BR3 due to appropriate and high level of C:N ratio, volatile organics, moisture, and other substances required for anaerobic methanogenic microorganisms in the feed stocks. Cumulative methane production rate was not considerably progressed in the bioreactors BR1, BR2, BR3, BR4, BR5, and BR6 after 45, 43, 43, 38, 35, and 35 days respectively due to lack of available carbon contents and other sustenance in the feed stock for the growth of methanogenic bacteria. Analysis of variance in the bioreactors with different ratios of feed stocks indicated that there is a significant difference between the methane production rates in the individual bioreactor (Figure 2B).

Figure 1. Daily methane production rates under biomethanation processes with different mixed ratios of feed stocks.
The effect of partial photocatalytic process on the methane production rate was evaluated using Mg doped TiO$_2$ flat wedge structures as a potential photocatalyst under visible light source. Well crystalline phases and flat wedge like structures of Mg doped TiO$_2$ photocatalysts was confirmed by powder X ray diffraction and high resolution SEM analysis respectively (Figure 3). Mg doped TiO$_2$ photocatalyst indicated well crystalline phase of anatase and rutile which are apparently stable and enhance the photochemical processes under visible light source [19]. Mg doped TiO$_2$ photocatalysts have flat wedge like morphology creating high surface area and porosity, which is quite suitable for enhancing the photocatalytic processes that enhances the intensification of methane production rate. The effect of photocatalytic processes on methane production rate is shown in figure 2C and it clearly indicated that methane production rate was significantly increased about 12±0.5% (from 367 to 414 ml) under photocatalytic process. Perhaps this was happened due to the presence of well crystallized and porous structure of Mg doped TiO$_2$ photocatalysts in the biogas stock (at headspace of bioreactor), which constituted with 30-35% CO$_2$ along with moisture contents and hydrogen traces. However, continuous emission of electrons under photocatalytic processes into carbon dioxide environment along with moisture and hydrogen are expected to reduce carbon dioxide into methane [48-50]. Apparently, Mg doped TiO$_2$ flat wedge structures with potential surface areas enhance the photochemical activities under visible light sources [12, 20] and it can be further utilized as an excellent photocatalyst by harvesting the natural sunlight as an alternative driving energy [19-20]. Moreover, maximum numbers of photocatalytic electrons productivity are also required along with hydrogen and moisture contents for the potential conversion of CO$_2$ into methane [21-22]. The continuous supply of electron population by photocatalyst and presence of hydrogen and moisture contents as reductant within the biogas stock also stimulate the conversion rate of CO$_2$ contents into methane. Besides, utilization of visible light as an alternative driving energy source emphasizes the sustainable route for intensification of methane yield during conversion of waste to energy. In addition, presence of Mg in the TiO$_2$ crystal structure inhibits the electron-hole recombination that would greatly increase the efficiency of photochemical reaction [23-24]. Beside, the photocatalytic reduction of CO$_2$ is also greatly influenced by incident light intensity, the specific surface area, chemical stability and fraction of light observed by photocatalyst [23-28]. However, the photocatalyst used in the study fulfilled the required criteria with the existence of positive synergy effect between anatase and rutile phases (Figure 3a), which tremendously intensify the photochemical reaction under the range of visible light [12-16]. Based on the above results and discussions, the photochemical mechanism of carbon dioxide reduction into methane in the presence of hydrogen and moisture under visible light is tentatively proposed. Intensification of methane production rate by photocatalytic conversion of carbon dioxide into methane under visible light source could be followed in the different pathways. However, methane production rate would be monotonically decreased with decrease in the
concentration of CO$_2$, H$_2$/H$_2$O in the biogas stock during photocatalytic intensification of methane yield.

Figure 3. Characterization results (a) Powder X-ray diffraction patterns of Mg doped TiO$_2$; (b) & (c) High resolution SEM images showing flat wedge like structures of Mg doped TiO$_2$ on Teflon slides.

The present study emphasizes the carbon recovery potential of municipal wastes for renewable energy production and intensification of cumulative methane production rate under hybrid bioreactor. Perhaps, intensification of methane yield has unique advantages under photocatalytic processes during the conversion of waste to energy under biomethanation that greatly decrease carbon dioxide emission into the environment. Alternative route of renewable energy production from municipal waste disturbing the environmental aesthetic is important for the sustainable development and keeping our environment clean.

4. Conclusion
The present research work revealed that potential carbon recovery from municipal wastes under biomethanation and municipal wastes showed maximum carbon nitrogen ratios up to 43:1.2 which is a vital parameter considered in enhancing the methane production from feed stocks. Maximum cumulative methane production rate recorded was the range of 181-367 ml for a period of 48 days and different mixed ratios of feed stocks indicated significant variation in the cumulative methane production rate. Sol-gel prepared Mg doped TiO$_2$ photocatalyst showed well crystalline phase of anatase and rutile along with wedge like structures, which greatly influenced the specific surface area, chemical stability and fraction of light observed by photocatalyst. Incorporation of photocatalytic process in the bioreactor indicated a significant intensification of methane production rate up to 12 $\pm$0.5 %. Such hybrid process not only intensifies the methane production rate but also offers an alternative way to produce the sustainable fuels using alternative driving energies like natural sunlight. However, more efforts are required for the development of novel multifunctional photocatalyst and potential hybrid photocatalytic-bioreactor designs to tackle energy crisis and environmental problems.

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