Co-Digestion of Petroleum Sludge and Buffalo Dung by Batch Anaerobic Digestion System

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ABSTRACT

Globally, the petroleum industry plays a very significant role in producing oil to fulfil the demand of the growing population. The improper management of abandoned quantity of petroleum sludge that is one of the byproducts of petroleum industry has posed many environmental as well as socio-economic issues in most of the developing countries. The petroleum sludge contains various toxic substances, like minerals, oil, and other chemicals which are very harmful for biotic as well as abiotic environment. Meanwhile, a huge quantity of livestock manure, especially buffalo dung, is produced in villages and burned as fuel after drying in open atmosphere for domestic application without any treatment which generates indoor air pollution. This study was formulated to analyze the biochemical methane potential of buffalo dung with petroleum sludge at different mixing ratios (i.e., 1:1, 1.5:0.5, and 0.5:1.5) through batch digestion system. The substrates were prepared and characterized before and after batch digestion by using standard methodology. The maximum methane was obtained as 268 Nml/gVS, followed by 326 Nml/gVS and 191 Nml/gVS at mixing ratios of 1:1, 1.5:0.5 and 0.5:1.5, respectively. The results and findings of the study indicated that the co-digestion of buffalo dung with petroleum sludge at mixing ratio of 1.5:0.5 through continuous batch digestion would be the best option to enhance methane production.

Keywords: petroleum sludge, animal dung, batch digestion, methane potential.

INTRODUCTION

Among all other industries, the petroleum industry plays a very important role to yield different type of products to fulfil the demand of overgrowing population in all over the world. The huge quantity of petroleum sludge (PS) is produced by various activities of petroleum industry including drilling activity, refinery, and production processing (Islam et al., 2015). The composition of PS is mostly contributed by varying quantity of waste oil, wastewater, chemicals, and mineral depending upon source generation. Approximately 2000 g/ton of crude oil is generated by the industries of the United States with generation of 4.5 million tons per year according to the study of (Aldemar et al., 2018; 2019). PS poses a serious threat on biotic as well as abiotic...
environments. There are various rules, regulations and policies like the environmental protection act and hazardous waste handling rules which play a very significant role in implementing strong policies for mitigating hazardous substances. The open dumping of PS causes the release of various toxic and carcinogenic substances into the environment. The improper storage, handling, and transport of PS affects fauna and flora on one hand. On the other hand, resources can be recovered from the PS because of containing hydrocarbons (Sompson, 2019). The natural environment has been seriously affected due to improper handling, treating and disposal of the PS as discussed in previous studies (Silva et al., 2017). The proper treatment of PS has become a very challenging issue among all other issues associated with the disposal of other types of waste like municipal solid waste, hospital waste etc., as PS contains aliphatic as well as aromatic hydrocarbons. The recovery of soil is a very difficult task because of the serious contamination by the very toxic constituents of PS. Normal treatment, including burning, heating for microbiological activities, is not suitable for the treatment of PS (Guanghua et al., 2016). The landfilling of the PS is objectionable and faces many strong obligations by many companies. Another treatment option is incineration which is not economical, and voice is raised by public living within the vicinity of plant because of greenhouse emissions, including furan and smallest materials from incineration plant (Gabriel et al., 2018). The physical and chemical treatment options of PS have created many environmental, socio-economic problems even at large scale. Another cost effective, and environment friendly option to achieve toxin degradation of PS is microbial bioremediation (Ali et al., 2019). The treatment of PS by anaerobic digestion (AD) is the best option for its safe disposal and methane generation. The single digestion of PS inhibits the process because of acidic nature of PS leading to lower methane production. To enhance methane yield and avoid inhibition, the addition of buffalo dung (BD) bears great importance because of the easy and economical availability of dung.

The co-digestion of BD with biodegradable substances is the best economical way of biogas generation. As the co-digestion of different organic waste with each other balances the nutrients and accelerates the AD process, leading to more methane generation (Hamed et al., 2019). Moreover, the literature reveals that cow dung, cattle manure/BD, and poultry manure were found suitable co-substrates with PS for biogas recovery (Ismail and Jasim, 2022). However, this study was chosen due to the higher quantity of BD compared to other types of waste nearby oil fields for economic justification. The outdoor burning of BD is also dangerous and releases various gases, which deteriorates the air quality and thus promotes unsustainability. Its proper utilization into valuable product is the need of current time for promoting sustainability within the area. From animal farming, the flow of BD into water body during the rainy season causes various impacts by polluting the water quality. Therefore, effective management of BD plays a very significant role to reduce non-point source of water pollution. The biogas generation from organic waste has become a driver to maintain socio-economic and sustainable energy source for improving health level (Asha et al., 2019). In the anaerobic digestion process, conversion of organic substances, such as animal manure, agriculture residue, food waste, and sewage sludge, takes place in major four steps, i.e. hydrolysis, acido genesis, acetogenesis and methanogenesis. The biogas produced by the AD process is composed of mainly methane and carbon dioxide in the absence of oxygen (Mona et al., 2019). The focus of the present study is to assess the methane potential of PS with BD at different mixing ratios. The biogas generated from codigestion of PS and BD is used as fuel for most of the remote areas, where the availability of natural gas is very short, and people are facing shortage of gas during winter season. Not only this but the disposal problems of PS could be resolved to some extent leading to sustaining environment for flora and fauna. The results of this study also contribute to the decision making process and putting forward an alternative energy source to bridge the gap between the supply and demand of energy and reduce the risk of hazardous PS disposal.

**MATERIAL AND METHODS**

Following major steps were performed in detail to investigate the methane generation potential of buffalo dung and byproducts of petroleum industry (i.e., petroleum sludge) through biochemical methane potential test system (BMPTS) at different mixing ratios.
Sample collection

Two types of substrates were collected from different destinations to run the digestion system. One was BD and second was PS which were collected from animal form within the vicinity of Jamshoro and petroleum industry, respectively. To run the digestion system successfully, the inoculum plays a very important role in speeding up the digestion process. The inoculum was effluent of continuous anaerobic digestion which is under running condition and situated within the surrounding of Hyderabad district.

Sample analysis

Various characteristics, such as elemental and proximate analysis, pH, total alkalinity (TA), and volatile fatty acids (VFA) of substrates and inoculum before and after digestion system were investigated by using standard methodology (Korai et al., 2016; Sahito et al., 2013, Zhang et al., 2013). The pH, TA and VFA before and after BMP test of samples in duplicates were analyzed by proper mixing of dried substrates with distilled water at ratio of 1:5 for 15 minutes (Zhang et al., 2013; Sahito et al., 2013). The assessment of carbon, hydrogen, nitrogen, oxygen, sulfur is called elemental analysis. The values of all elements were taken from literature. In turn, the assessment of moisture content (MC), total solids (TS), volatile solids (VS) and ash content (AC) was called proximate analysis. For proximate analysis, duplicate samples of each substrate were prepared and placed in an oven to dry at 105 °C for 24 hours. Then, the final weight of sample (i.e., after oven drying) was subtracted from the initial weight of sample (i.e., before oven dry) for MC and TS analysis. After oven drying, the samples were placed in a muffle dryer at 550 °C for 2 hours to analyze VS and AC, as determined by previous studies (Korai et al., 2016, Sahito et al., 2013; Zhang et al., 2013).

Biochemical methane potential test system

The biochemical methane potential (BMP) test of PS and BD was performed at lab scale by using semi-automatic methane potential test system (SMPTS), as illustrated in Figure 1. The reactor bottles were provided from both sides of SMPTS. The reactor bottles were equipped with inlet and outlet valve for receiving and outgoing biogas generation during anaerobic digestion process of substrates. Out of the total capacity (i.e., 500 ml) of reactor bottles, 100 ml was left empty for biogas accumulation. In turn, 400 ml volume of reactor was filled with water, substrates, and inoculum. Three mixing ratios of BD and PS (i.e., 1:1, 1.5:0.5 and 0.5:1.5) were fed into reactor bottles in duplicate form. For adjusting the favorable condition of reactors, the alkaline substance (sodium bicarbonate) was used in all reactor bottles. The amount of nitrogen was also

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Figure 1. Semi-automatic methane potential test system
supplied into reactor bottles to displace oxygen in bottles for providing anaerobic conditions in all reactors (Korai et al., 2018 a, b; Sahito et al., 2013). Three ratios were selected to determine the methane potential of substrates at different ratios. In the first ratio, equal proportion of both substrates were selected, the quantity of BD was increased in the second ratio; In turn, the quantity of PS was decreased, and the quantity of BD and PS was decreased and increased in the third ratio, respectively. Moreover, these ratios were selected to observe the effect on methane potential of substrates.

**Theoretical biochemical methane potential anaerobic biodegradability**

Theoretical biochemical methane potential (TBMP), experimental bio-chemical methane potential (EBMP) and methane based degradability (MBD) of the substrates were obtained by using following Equations (Oran et al., 2011; Zhou et al., 2011; Sahito et al., 2016; Safar et al., 2019).

\[
TBMP = \frac{4a - b - 2c + 3d}{8} CH_4 + \frac{4a - b + 2c + 3d}{8} CO_2 + dNH_3
\]  

\[
TBMP = \frac{2790 \times H + 930 \times C + 350 \times O - 600 \times N - 175 \times S}{C + H + O + N + S}
\]  

\[
MBD(\%) = \frac{EBMP}{TBMP} \times 100
\]

**RESULTS AND DISCUSSION**

**Characteristics of the influent**

The characteristics of substrates at different ratios are given in Table 1. Initial characterization of substrates (biodegradable waste) is a very significant step of the AD process to understand the variation of various process parameters, such as volatile solids, pH, alkalinity, and volatile fatty acids at the end of the AD process. The accumulation of VFA and lower pH significantly affect the anaerobic process, resulting as in lower methane yield from the digester (Ali et al., 2018; Slopiecka et al., 2022).

In turn, the VFA/alkalinity ratio has been reported to be an important indicator for understanding the level of stable or unstable methanogenic phase of anaerobic digestion process (Calabrò et al., 2021; Issah and Kabera, 2020; Soomro et al., 2020). Therefore, the influent parameters were analyzed using standard methods.

Mainly, three different ratios of BD and PS, such as R1 (1:1), R2 (1.5:0.5) and R3 (0.5:1.5), were simulated in the laboratory. PS has serious impacts on biotic as well as abiotic environments. There are various rules, regulations and policies like the environmental protection act and hazardous waste handling rules which play a very significant role in implementing strong policies for mitigating hazardous substances. The open dumping of PS causes the release of various toxic and carcinogenic substances into the environment. Moreover, PS contains various toxic substances including heavy metals, dissolved solids, and sulfur compounds which pose an environmental risk (Kondaveeti et al., 2023; Hasan et al., 2024). The characterization of influent samples is given in Table 1.

**Methane potential of substrate**

The methane potential of co-digestion between BD and PS is of great importance to decide the suitable ratio between BD and PS substrates. To determine the optimum conditions for real bioreactor and maintain favorable environment for microbial ecology. The BMP tests were carried out on individual substrates, such as BD, PS and Blank and mixing ratios between BD and PS, named here as R1 (1:1), R2 (1.5:0.5) and R3 (0.5:1.5). Fig. 1 show the methane flow rate and cumulative methane production of individual substrates such as BD, PS and Blank for 41 days. The Blank represents the inoculum. In this study, the purpose of using inoculum (CSTR effluent) was to maintain active microbial consortia for stable AD processes, such as hydrolysis, acidogenesis,
acetogenesis, and methanogenesis. Therefore, an equal amount of inoculum was used in all co-digested bioreactors (i.e., R1, R2 and R3).

The R3 bioreactor with BD and PS ratio of 0.5:1.5 showed rapid methane generation but limited to cumulative methane generation of about 191 Nml/gVS as shown in Fig. 2. However, the R2 bioreactor with BD and PS ratio of 1.5:0.5 produced methane gas of about 326 Nml/gVS. The comparison of both bioreactors indicates that R2 with 1.5:0.5 as a mixing ratio of BD and PS was found to be a suitable measure for higher methane yield. In terms of methane generation potential of individual substrates, the BD and PS produced about 133 and 116 Nml/gVS, respectively, as shown in Fig. 1. The higher methane yield in the R2 bioreactor than the R3 bioreactors may be attributed to the VFA/Alk ratio of co-digested feed as 0.32 and 0.43 respectively (Table 2). The literature reveals that the VFA/alkalinity ratio values ranging between 0.3 and 0.4 specify stable anaerobic digestion process with maximum yield of methane gas (Ciotola et al., 2014). The VFA of co-digested feed, another process parameter to be considered for the stability of anaerobic digestion process. The accumulation of VFA inhibits the growth of archaea community in the digester, thus reducing the methane yield (Ciotola et al., 2014). This could be one of the major reasons for the lower amount of cumulative methane generation in bioreactor R3, evident by higher VFAs in R3 effluent, as given in Table 2. The methane generation potential of anaerobic co-digestion of various substrates and co-substrates is further discussed in literature (Pilarska et al., 2023). The R1 bioreactor with an equal ratio between BD and PS produced the cumulative methane yield of about 268 Nml/gVS. In terms of methane gas yield, the R1 and R2 bioreactors showed similar behavior but variation in the maximum methane yield in a particular day. For example, bioreactor R1 produced 13.5 Nml/gVS on 11th day of AD process which was regarded as the maximum methane yield for bioreactor R1. In contrast, bioreactor R2 produced 17.0 Nml/gVS on 7th day of the AD process. The ratio value of 1.5:0.5 between BD and PS was found to be suitable ratio for early onset of methanogenesis in a real situation. The early onset of methanogenesis in AD process specifies the balance between

![Figure 2. Methane flow rate and cumulative methane potential of single substrate (Nml/gVS)](image)

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acid producing bacteria and methane producing archaea. The situation shows that a higher amount of BD with lower number of PS can provide a highest methane yield and energy benefits of co-digestion.

**Characteristics of effluent**

After 41 days of anaerobic digestion, effluents of bioreactors R1, R2 and R3 were characterized for the determination of MC (%), TS (%), VS (%), VFA, pH, Alkalinity and VFA/TA ratio, as given in Table 2. The parameters of effluent, such as VFAs, pH and alkalinity are used as the important indicators for the investigation of anaerobic digestion stability (Soomro et al., 2020). The higher concentration of VFAs (720 mg/l) in effluent taken from bioreactor R3 indicates less amount of cumulative methane production (191 Nml/gVS) which is the further indication of inhibition phenomenon due to higher amount of PS.

The results clearly indicate that higher proportion of PS during co-digestion with BD (0.5:1.5) would create an inhibitory phenomenon for the functional activities of bacteria and archaea in digester. In turn, co-digestion of substrates with high proportion of BD and less proportion of PS (1.5:0.5) will attain early onset of methanogenesis and maximum methane yield. Therefore, evidence of these experiments suggests higher proportion of BD and less proportion of PS to maintain bioreactor stability and avoid inhibitory phenomenon during co-digestion.

**Methane-based degradability**

The methane-based degradability of individual substrate is more important to investigate during co-digestion of two different substrates and its result is shown in Fig. 3.

To understand the methane flow rate and cumulative methane yield of co-digested substrates with different ratio values, the methane-based degradability of individual substrates such as BD, PS, Inoculum (Blank), and different ratios of BD and PS were measured, as shown in Fig. 3. The lower methane-based degradability of PS may be attributed to the presence of recalcitrant compounds such as hydrocarbon, creating unfavorable conditions for microbial ecology i.e. bacteria and archaea during AD process. This could be one of the reasons why bioreactor R3 with higher proportion of PS produced less methane gas compared to bioreactors R1 and R2. The methane-based biodegradability of individual substrates validates the results of cumulative methane yield.
CONCLUSIONS

Petroleum sludge is a waste product, produced from petroleum industries which is often used in open fires and brick kilns, causing a serious threat to human health and environment. In contrast, the use of PS as a co-substrate in anaerobic digestion process is an environment friendly option. In this study, different ratios of BD and PS (R1 – 1:1, R2 – 1.5:0.5, and R3 – 0.5:1.5) were prepared to investigate the methane generation potential of co-substrates by BMP Test. The results show that the methane potential of substrates was obtained as 268, 326 and 191 NmL/gVS at mixing ratios of 1:1, 1.5:0.5, and 0.5:1.5, respectively, in the batch digestion system. The results of this study suggest the co-digestion of buffalo dung and petroleum sludge with blending ratio of 1.5:0.5, as an optimum ratio to achieve maximum methane production. Further research is needed for the effectiveness of pretreatment of petroleum sludge before co-digestion to enhance methane yield through continuous digestion system.

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