Anaerobic Co-Digestion of Canola Straw and Buffalo Dung: Optimization of Methane Production in Batch Experiments

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ABSTRACT

In several regions of the Pakistan, crop cultivation is leading to the production crop residues and its disposal problems. It has been suggested that the co-digestion of the crop residues with the buffalo dung might be a disposal way for the wasted portion of the crops' residue. The objective of present study was to optimize the anaerobic co-digestion of canola straw and the buffalo dung through batch experiments in order to obtain maximum methane production. The optimization was carried out in three stages. In first stage, the best canola straw to buffalo dung ratio was evaluated. In second stage, the best concentration of sodium hydrogen carbonate was assessedas the alkaline pretreatment chemical, whereas in the third stage most suitable particle size of the canola strawwas evaluated. The assessment criteria for the optimization of a co-digestion were cumulative methane production and ABD (Anaerobic Biodegradability). The results yield that anaerobic co-digestibility of the canola straw and the buffalo dung is obviously influenced by all the three factors of optimization. The maximum methane production was obtained as 911 NmL from the canola straw to buffalo dung ratio of 40:60, the alkaline doze of 0.6 g$NaHCO_3$/ gVS and canola straw particle size of 2mm. However, because of the higher shredding cost to produce 2mm sized canola straw, particle size 4mm could be the best canola straw particle size.

Key Words: Anaerobic, Co-Digestion, Canola Straw, Buffalo Dung, Methane Optimization, Alkaline Doze.

1. INTRODUCTION

Anaerobic digestion is a biochemical process that decomposes organic matter to biogas which mainly consists of carbon dioxide (CO_2) and methane (CH_4) by a concentrated action of several types of microorganisms. It is a well-recognized process that treats severalcategories of liquid and solid organic waste [1]. Production of biogas from agricultural waste is getting great significance as it offers substantial environmental benefits [2] and is asupplementary source of profits for crop growers. On the contrary, production of biogas from animal waste reduces the emissions of methane during storage of dung and also improves the fertilizer quality of the digestate. Most of the biodegradable matter in the animal dung is digested in the first stomach and in the intestine. Thus, animal dung has a lesser potential to produce biogas than the crop residues, but animal dung

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has high alkalinity which can be utilized in the co-digestion with the acidic crop residues like canola straw [3]. Moreover, biogas produced from the animal dung has less concentration of methane [4].

In several regions of the Pakistan, production of crop residues including banana plant waste, cotton gin waste, rice straw, canola straw, Sugarcane trash and cotton stalks is leading to a solids disposal problems [5]. It has been suggested that the co-digestion of the crop residues with the buffalo dung might be a disposal way for the wasted portion of the crops' residue [6]. Monetary efficiency of the successful anaerobic digestion process not only be governed by the investment and operating cost of the biogas plant, but also on the optimum methane production.

Production of methane from organic matter primarily depends on the content of substances that can be degraded into a biogas, while their composition and biodegradability are the key factors for the methane production [4]. Biomass from the crops chiefly contains cellulose, hemicellulose and lignin [7], out of these lignin is poorly degraded in anaerobic conditions. Hydrolysis is the rate-limiting step in anaerobic digestion of solid materials such as energy crops and crop residues [8]. Pre-treatments can be carried out either mechanically, chemically or biologically, or as combinations of these [9].The mechanical pre-treatment leads to a particle size reduction of the biomass, thus increasing the surface area of cellulose. Chemical pre-treatments are categorized as acidic, alkaline, oxidative, and ionic liquids pre-treatments. Among them, alkaline pre-treatments are efficient in altering the structure of lignin [10].

The objective of present study was to optimize the anaerobic co-digestion of canola straw and the buffalo dung through batch experiments in order to obtain maximum methane production. The optimization was carried out in three stages. In first stage, the best canola straw to buffalo dung ratio of was evaluated. In second stage, the best concentration of sodium hydrogen carbonate ($NaHCO_3$) was assessed as the alkaline pretreatment chemical, whereas in the third stage most suitable particle size of the canola strawwas evaluated. The assessment criteria for the optimization of a co-digestion were cumulative methane production and ABD.

2. METHODOLOGY

2.1 Optimization of Co-Digestion in Batch Experiments

The present study comprises of three stages optimization of the anaerobic co-digestion of the canola straw and the buffalo dung. The blocks diagram of the study is presented in Fig. 1. The optimization was carried out in three stages of the batch experiments i.e. canola straw to buffalo dungratio optimization, alkaline doze optimization and canola straw particle size optimization. In the first stage, the ratio of canola straw and buffalo dung was optimized, keeping the constant pH in all the batch assays and using the canola straw of size less than 1mm. The pH in all batch assays was maintained to 8.0 by adding the 2M $NaHCO_3$ solution. On the basis of volatile solids, six ratios of canola straw and buffalo dung were employed for optimization i.e. 10:90, 20:80, 30:70, 40:60, 50:50 and 60:40 and are designated as ratio R1-R6 respectively.

In the second stage, the best ratio of the canola straw and buffalo dung was further optimized for the alkaline doze, whereas the size of the canola straw was taken as less than 1mm. The second stage involves the selection of best concentration of $NaHCO_3$, which can be added as the pr-etreatment chemical. Literature revels that the biogas production of corn stalk, spruce and birch can be improved by employing alkaline dozing as a pretreatment method, which removes a part of the lignin and hemicellulose, and thus improves the efficiency of the anaerobic digestion process [11-12]. Six different quantities of $NaHCO_3$ were used based on the volatile solid content in the each reactor i.e. 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 $gNaHCO_3/gVS$ and are designated as doze D1-D6 respectively.

In the third stage, the best ratio of the canola straw to buffalo dung along with the best concentration of $NaHCO_3$ was used to optimize the canola strawparticle size. Particle size of the canola straw is one of the important factors that not only influence the anaerobic digestion process but also on the efficiency of the biogas plant. In present study, six different particle sizes of the canola straw were used i.e. less than 1, 2, 4, 6, 8, and 10mm and are designated as size S1 to S6 respectively. The size reduction of the canola straw was done by using the hammer mill along with the respected shredding plate of 2,4,6,8 and 10mm sizes, whereas the less than 1mm size was obtained by grinding 6mm particle sized canola straw through coffee grinder.

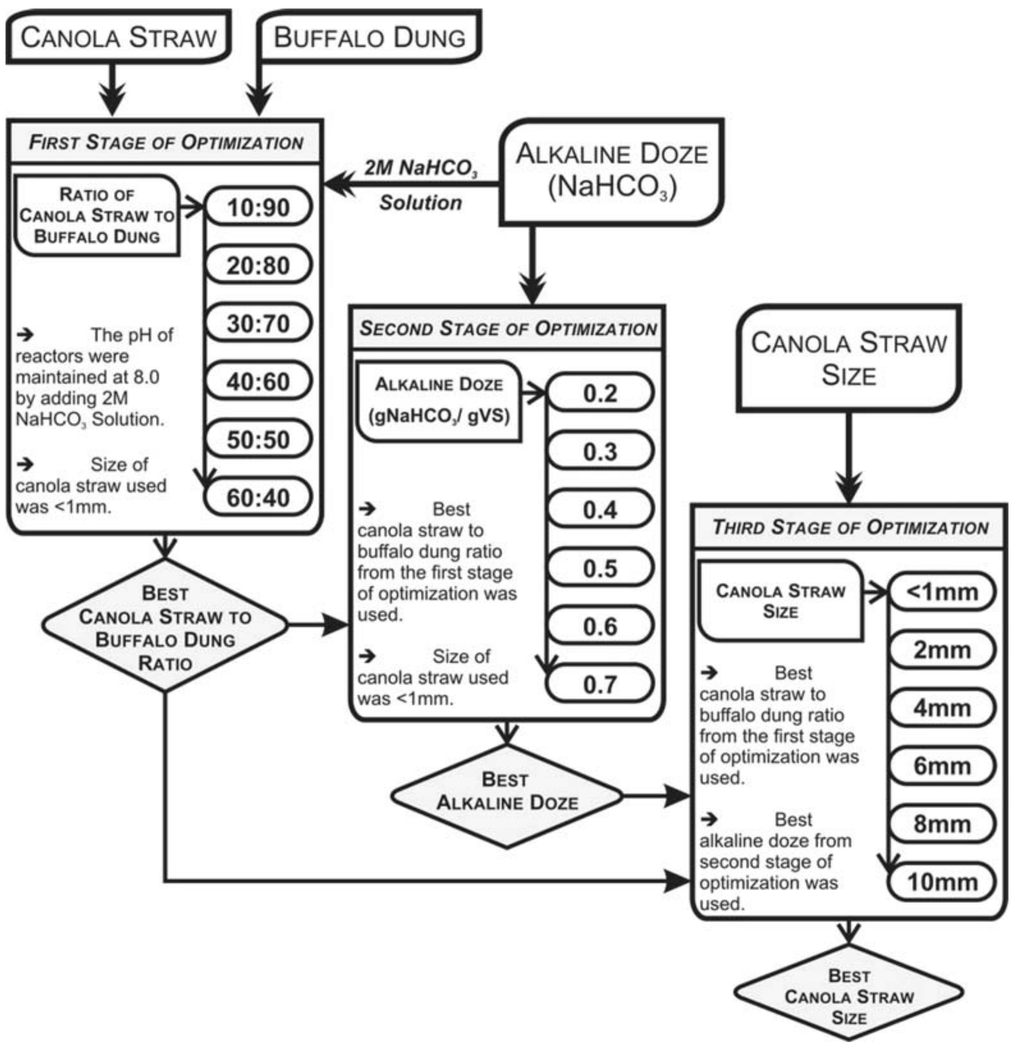


FIG. 1. BLOCKS DIAGRAM OF STUDY

2.2 Formulation of Batch Assays

The batch assays were run as duplicates on ampts AMPTS (Automatic Methane Potential Test System), and for statistical significance the average values were taken as the final results. The 500mL glass bottles were used as reactors and the BMP assays were performed at the temperature of 37±0.2°C, which is most favorable temperature to methanogenic microorganisms [13]. All reactors were charged with 5g of VS of the substrate (mixture of canola straw and buffalo dung) and 20 mL of inoculum. The inoculum was the digestate of the anaerobic reactor, which was treating buffalo dung at the temperature of 37±0.2°C. After wards, all reactors were filled up to 400 mL of volume with distilled water and were hermetically sealed with rubber stoppers. Before incubation, all reactors were purged with nitrogen gas, whereas $NaHCO_3$ was used as the buffer. The contents of the reactors were mixed intermittently through the electric motors, which run for 30 seconds after every 600 seconds. The methane was measured in NmL (normalized milliliters) [4], after absorption of the CO_2 through 3M NaOH solution [3].

2.3 Feedstock Characterization

The feedstock of the present study was the buffalo dung and the canola straw. Their weight percentages of the C (carbon), O (oxygen), H (hydrogen), N (nitrogen) and S (sulfur), pH values and percentages of MC (Moisture Content), TS (Total Solids) and VS (Volatile Solids) were determined as per standard methods as stated in previous study [3] and are given in Table 1. After reducing the size of the canola straw, its each designated particle size was analyzed for bulk density. The bulk density is a significant characteristic of any type biomass, which is directly related to the cost and storage of feedstock [14]. It also influences on the biomass handling system in any biological processes [15]. The bulk density of the different particle sized canola straw was determined by dividing the net mass of the straw by volume of the container. It was done by filling the known volume beaker with the canola straw and after tapping the beaker;it was weighedon electronic balance to obtain the net mass of the canola straw.

2.4 Anaerobic Biodegradability

The ABD was estimated by using Equation (1) [16], where ABD in terms of percentage, $BMP_{observed}$ is the biochemical methane potential observed during the period of incubation of feedstockin NmLand $BMP_{theoretical}$ is biochemical methane potential in NmL that can be theoretically achieved.

$$ABD = \frac{BM_{observed}}{BMP_{theoretical}} \times 100 \tag{1}$$

The $BMP_{theoretical}$ was estimated by employing the theoretical equation of Bushwell and Mueller Equation (2) [17]. According to Tchobanoglous, et. al. [18], Equation (2) assumes that the whole biodegradable material is converted into methane (CH_4), carbon dioxide (CO_2), ammonia (NH_3) and hydrogen sulfide (H_2S). In Equation (2), the subscripts a,b,c,d and e are the mole fractions of the elemental C,H,O,N and S respectively.

$$C_aH_bO_dN_dS_e + \frac{(4a-2c+3d-2e)}{4}H_2O \rightarrow \frac{(4a+b-3d-2e)}{8} CH_4 + \frac{(4a-b+2c+3d+2e)}{8}CO_2 + dNH_3 + eH_2S \tag{2}$$

TABLE 1. CHARACTERISTICS AND THEORETICAL BMP OF THE FEEDSTOCK

Feedstock	Weight Dry Basis (%)					pH	MC (%)	TS (%)	VS (% TS)	$BMP_{theoretical}$ (NmL/gVS)
	C	H	N	O	S					
Buffalo Dung	38.62	4.30	1.32	40.12	0.15	7.50	80.50	19.50	71.81	391
Canola Straw	43.44	4.73	0.44	39.75	1.02	5.40	6.56	93.44	90.81	439

Considering the atomic masses of C,H,O,N and Sin Equation (2), it can be modified as Equation (3), where $BMP_{theoretical}$ is the maximum theoretical methane potential in NmL and C, H, O, N and S are the weight percentages of the elemental carbon, hydrogen, oxygen and nitrogen respectively on dry basis.

$$BMP_{theoretical} = \frac{930 \times C + 2790 \times H - 350 \times O - 600 \times N - 175 - S}{C + H + O + N + S} \quad (3)$$

Moreover, for the anaerobic co-digestion of the canola straw and buffalo dung, the combined theoretical methane potential was estimated on the basis of their proportions added in the each pair of batch reactors.

3. RESULTS & DISCUSSION

3.1 Characteristics and Theoretical BMPof the Feedstock

The characteristics of the feedstock including the results of ultimate analysis on the dry weight basis; pH values, gravimetric analysis and their theoretical biochemical methane potentialsare given in Table 1. The $BMP_{theoretical}$ for canola straw was 439 NmL/gVS and for buffalo dung it was 391 NmL/gVS. The canola straw has about 11% higher $BMP_{theoretical}$ than to the buffalo dung because of the higher percentage of the elemental carbon in it.

The theoretical biochemical methane potential of the different ratios of the canola straw and buffalo dung used in the present study was calculated on the basis of their proportions and are given in Table 2. It was observed that as the canola straw fraction increased; the theoretical methane potential also increased. This is because of the higher percentage of elemental carbon in the canola straw.

The bulk density of the canola straw for its different particle size is given in Table 3. The bulk density ranges from 364-109 kg/m^3 for particle size less than 1-10mm. Moreover, there is an inverse linear relationship between the bulk density and the particle size of the canola straw with coefficient of determination (R^2) of 0.94. The coefficient of determination was calculated as stated by Sahito, et. al. [19].

3.2 Best Canola Straw to Buffalo Dung Ratio

The cumulative methane productions and their flow rates at different canola straw to buffalo dung ratio are shown in Fig. 2. The maximum methane production was observed as 845 NmL for ratio R4 (40% canola straw and 60% buffalo dung) followed by 823.4, 814.9, 814.7, 783.9 and 723.3 NmL for ratios R5, R6, R3, R2 and R1 respectively. The highest flow rate was observed as 65 NmL/day for ratio R5 followed by 62, 57, 54, 47 and 46 NmL/day for ratios R4, R3, R2, R1 and R6 respectively.

TABLE 2. THEORETICAL BMP OF THE DIFFERENT RATIOS OF CANOLA STRAW TO BUFFALO DUNG

Canola Straw to Buffalo Dung Ratio (% VS/%VS)	R1	R2	R3	R4	R5	R6
	10:90	20:80	30:70	40:60	50:50	60:40
$BMP_{theoretical}$ (NmL/5gVS)	1980	2004	2027	2051	2075	2099

TABLE 3. BULK DENSITY OF DIFFERENT PARTICLE SIZE OF CANOLA STRAW

Particle Size of Canola Straw	S1	S2	S3	S4	S5	S6
	<1mm	2mm	4mm	6mm	8mm	10mm
Bulk Density (kg/m^3)	364	303	215	185	118	109

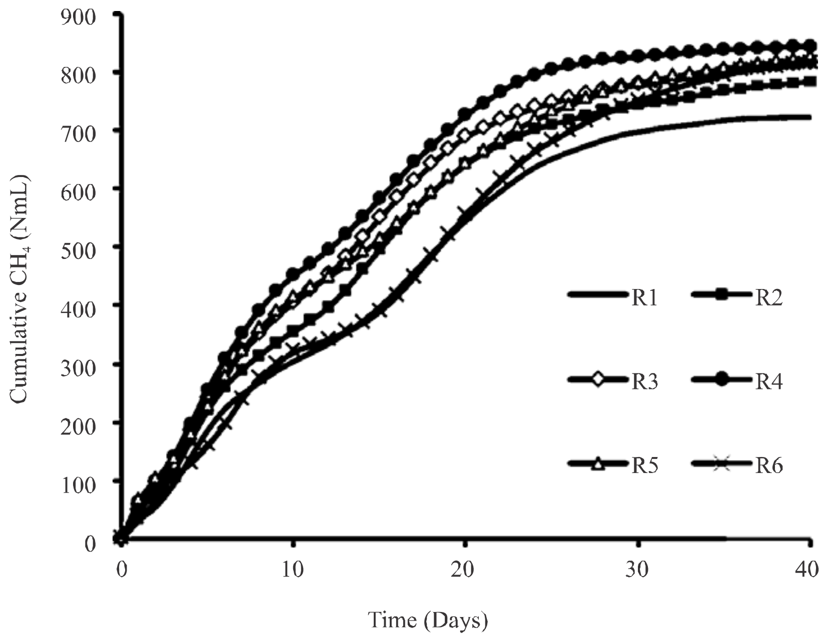
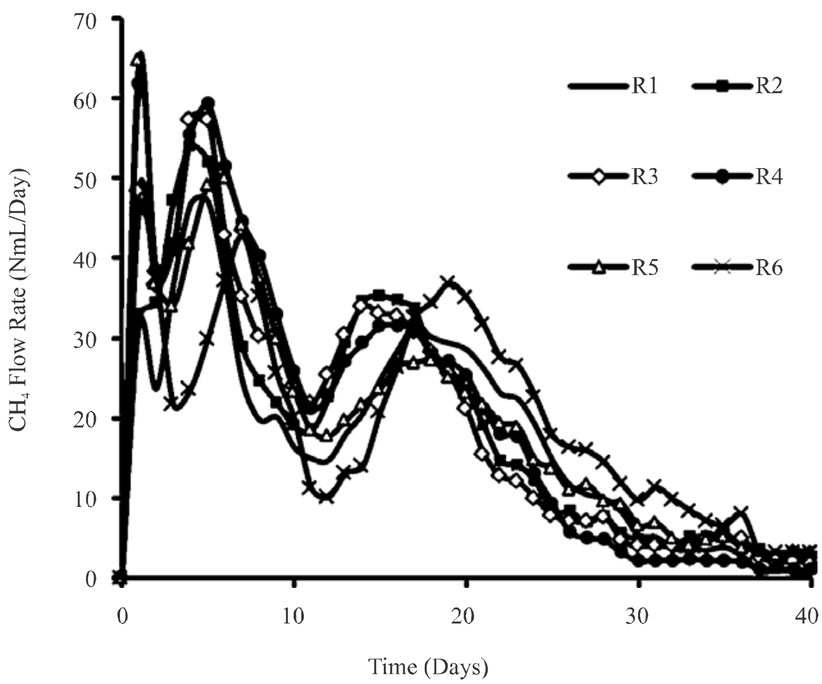


FIG. 2. (a) CUMULATIVE METHANE



(b) METHANE FLOW RATE; (R1= 10:90; R2= 20:80; R3= 30:70; R4= 40:60; R5= 50:50; R6= 60:40)

FIG. 2. METHANE PRODUCTION AT DIFFERENT CANOLA STRAW TO BUFFALO DUNG RATIO

The graph between the different ratios of the canola straw to buffalo dung, $BMP_{observed}$ and ABD is illustrated in Fig. 3. The $BMP_{observed}$ was increasing from ratio R1 to R4 and then decreases up to R6. A similar trend was also observed for ABD. Moreover, the maximum ABD was observed as 41.2% for ratio R4 followed by 40.2, 39.7, 39.1, 38.8 and 36.5% for ratio R3, R5, R2, R6 and R1 respectively. As the maximum $BMP_{observed}$ and ABD were detected for ratio R4, thus ratio R4 was selected as the best ratio for the maximum production of the methane by the co-digestion of the canola straw and buffalo dung.

3.3 Best Alkaline Doze

The cumulative methane productions and their flow rates at ratio R4 for different alkaline dozes of $NaHCO_3$ are shown in Fig. 4. The maximum methane production was observed as 856.5 NmL for doze D5 (0.6 g $NaHCO_3$/gVS) followed by 805.2, 750, 743.5, 683.4 and 620.4 NmL for dozes D6, D4, D3, D2 and D1 respectively. The highest flow rate was observed as 67.3 NmL/day for doze D5 followed by 62, 56.9, 53.7, 52.2 and 49.8 NmL/day for dozes D3, D6, D1, D2 and D4 respectively.

The graph between the different dozes of $NaHCO_3$, $BMP_{observed}$ and its ABD is demonstrated in Fig. 5. The $BMP_{observed}$ was increasing from dozeD1-D5 and then decreases for doze D6. A similar trend was also observed for percentage ABD. Moreover, the maximum ABD was observed as 41.8% for doze D5 followed by 39.3, 36.6, 36.3, 33.3 and 30.2% for dozes D6, D4, D3, D2 and D1 respectively. As the maximum $BMP_{observed}$ and ABD were detected for doze D5, thus doze D5 was selected as the best alkaline doze for the maximum production of the methane through the co-digestion of the canola straw and buffalo dung.

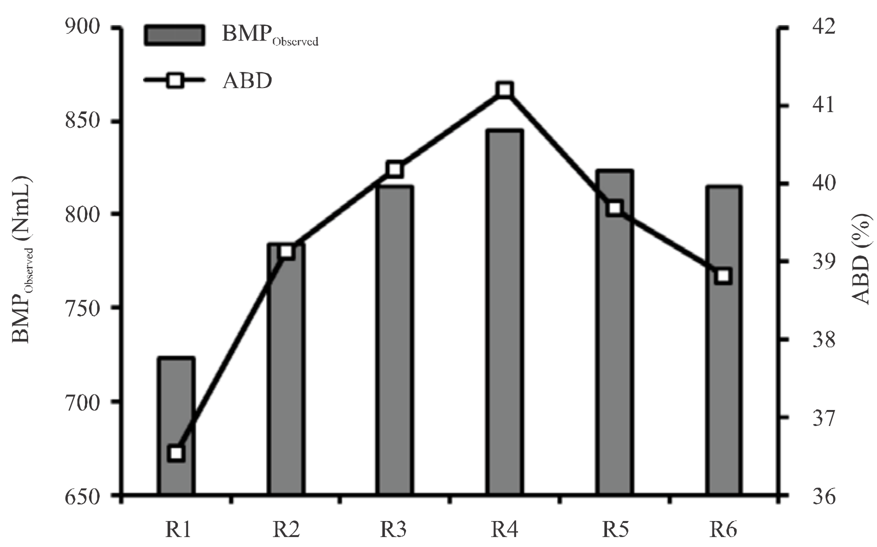
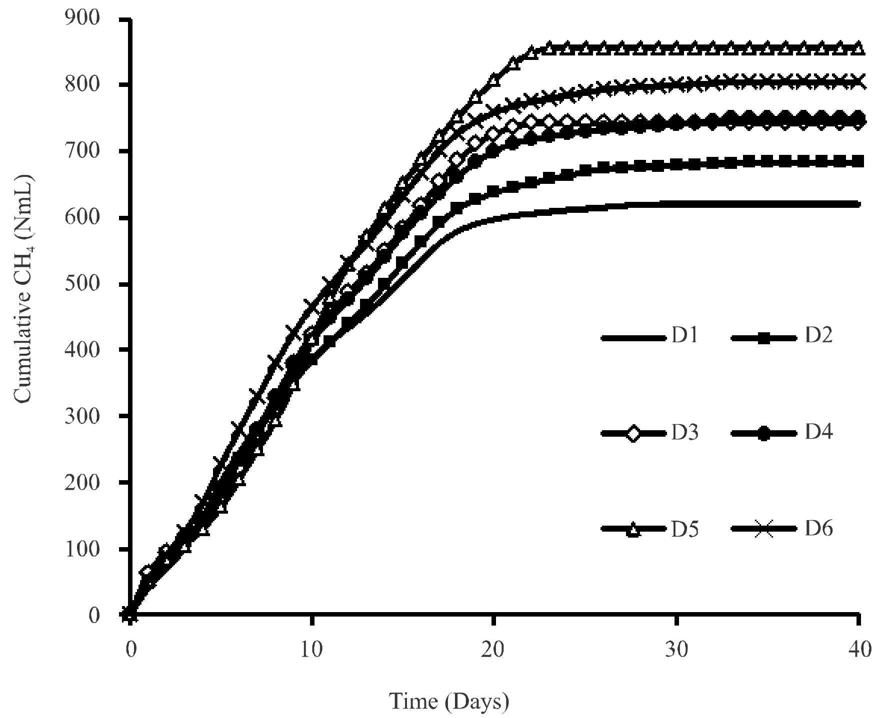
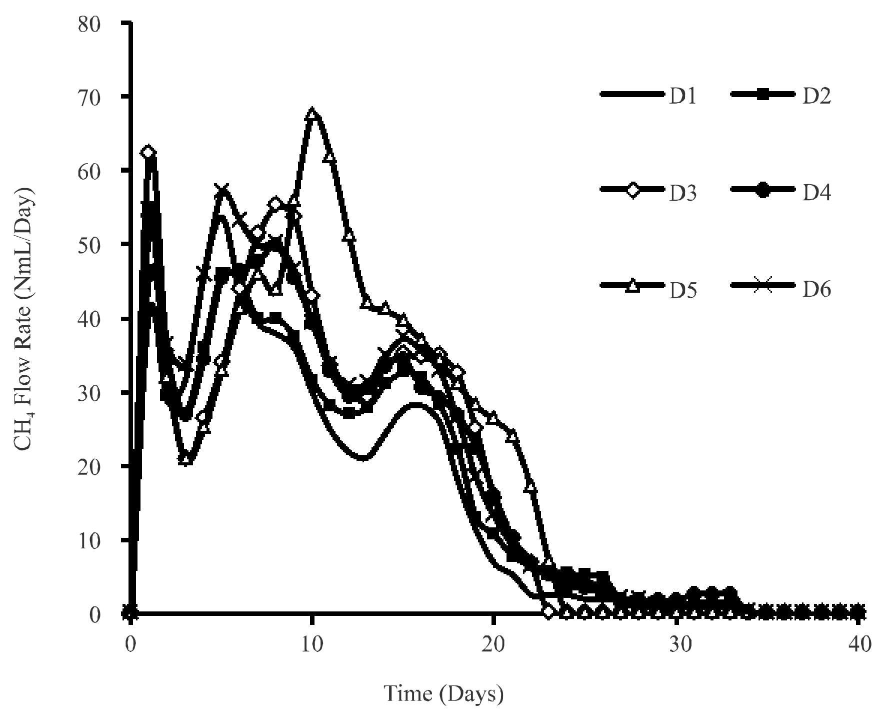


FIG. 3. COMPARISON OF BMP AND ABD AT DIFFERENT RATIOS OF THE CANOLA STRAW TO BUFFALO DUNG; (R1=10:90; R2=20:80; R3=30:70; R4=40:60; R5=50:50; R6=60:40)



(a) CUMULATIVE METHANE



(b) METHANE FLOW RATE; (D1=0.2; D2=0.3; D3=0.4; D4=0.5; D5=0.6; D6=0.7 $gNaHCO_3/gVS$)

FIG. 4. METHANE PRODUCTION AT DIFFERENT ALKALINE DOZE

3.4 Best Canola Straw Particle Size

The cumulative methane productions and their flow rates using canola straw to buffalo dung ratio R4 of and alkaline doze D5 for different particle sizes of the canola straw are shown in Fig. 6. The maximum methane production was observed as 911.3 NmL for particle size S2 (2mm) followed by 844.5, 804.7, 684.6, 637.5 and 633.5NmL for particle sizes S1, S3, S4, S5 and S6 respectively. The highest flow rate was observed as 100.2 NmL/day for particle size S2 followed by 98.7, 90.3, 68.6, 65.2 and 55.9 NmL/day for particle sizes S3, S1, S4, S6 and S5 respectively. Considering the previous study [3], the overall increase of the methane production from the canola straw keeping the ratio R4, alkaline doze D5 and canola straw particle size S2 has increased by 6% on the basis of VS. Furthermore, seeing the methane production from canola straw observed by Lehtomaki, et. al. [20] i.e. 240 NmL CH_4/gVS, present study yields 10% more methane production.

The graph between the different particle sizes of the canola straw, $BMP_{observed}$ and its ABD is demonstrated in Fig. 7. The $BMP_{observed}$ was increasing from particle size S1-S2 and then decreases up to particle size S6. A similar trend was also observed for percentage ABD. Moreover, the maximum ABD was observed as 44.4% for particle size S2 followed by 41.2, 39.2, 33.4, 31.1 and 30.9% for size S1, S3, S4, S5 and S6 respectively. Except of the particle size S1, it was established that as the particle size of the canola straw increases the $BMP_{observed}$ decreases. This is also in agreement with the study of Sambusiti, et. al. [9] that particle size 2mm produces more methane than to the particle size 1mm. Moreover, as the particle size of the canola straw decreases, it increases the cost of the grinding of the canola straw.The maximum $BMP_{observed}$ and percentage ABD were detected for particle size S2, thus particle size S2 isthe best canola straw particle size for the maximum production of the methane through the co-digestion of the canola straw and buffalo dung. On the contrary, because of its higher grinding cost to produce canola straw particle size of 2mm (particle size S2), the particle size S3 could be the best canola straw particle size.

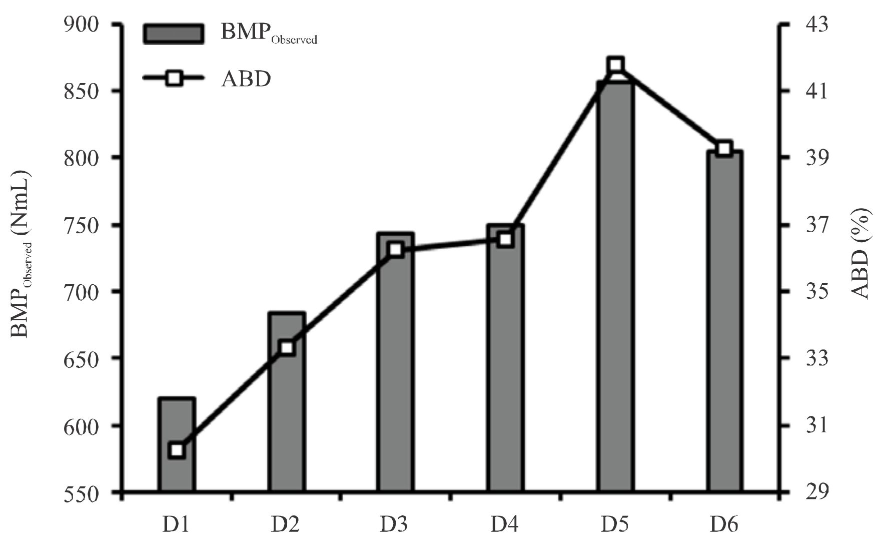
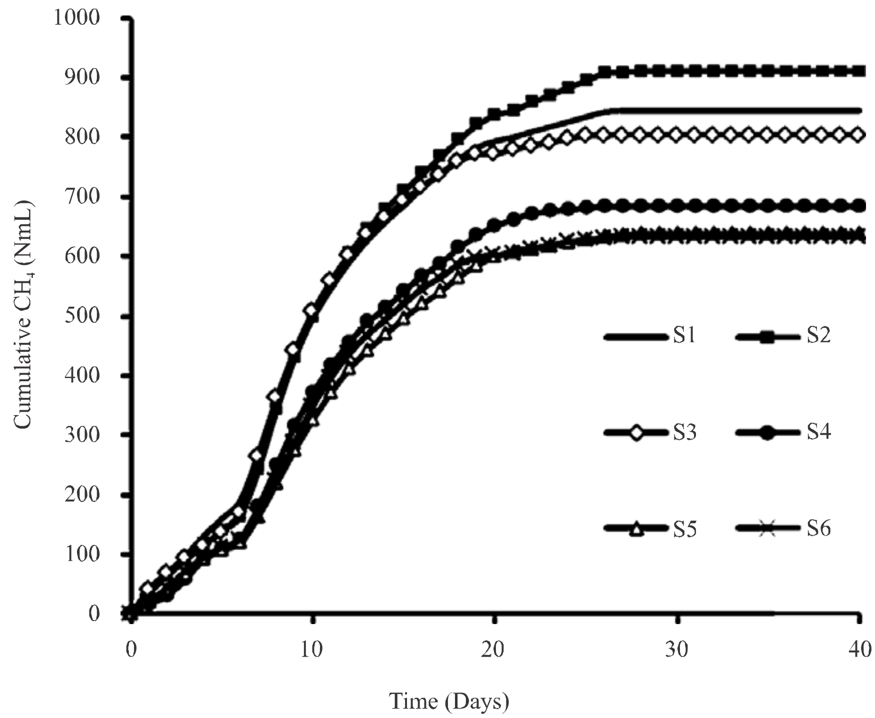
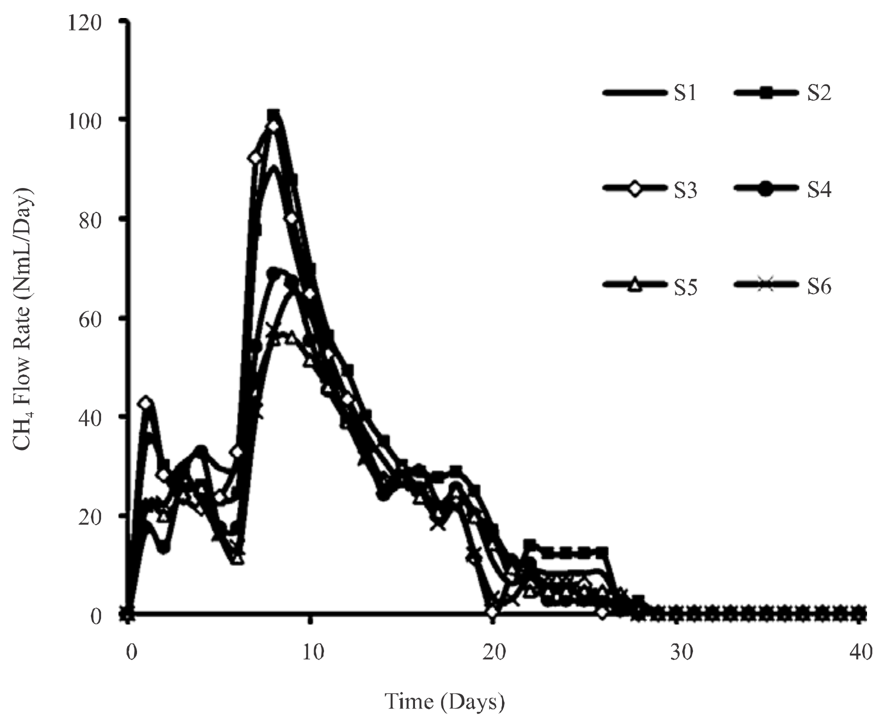


FIG. 5. COMPARISON OF BMP AND ABD AT DIFFERENT ALKALINE DOZES; (D1=0.2; D2=0.3; D3=0.4; D4=0.5; D5=0.6; D6=0.7 $gNaHCO_3$/gVS)



(a) CUMULATIVE METHANE



(b) METHANE FLOW RATE; (S1<1; S2=2; S3=4; S4=6; S5=8; S6=10mm)

FIG. 6. METHANE PRODUCTION AT DIFFERENT CANOLA STRAW PARTICLE SIZES

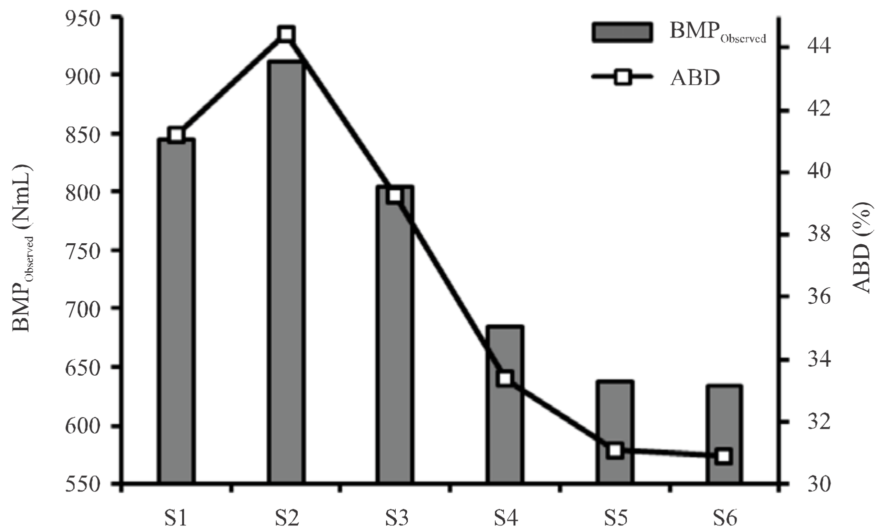


FIG. 7 COMPARISON OF BMP AND ABD AT DIFFERENT CANOLA STRAW PARTICLE SIZES; (S1<1; S2=2; S3=4; S4=6; S5=8; S6=10mm)

4. CONCLUSION

The present study was carried out to optimize the anaerobic co-digestion of canola straw and the buffalo dung. The optimization was carried out in three stages of the batch experiments i.e. canola straw to buffalo dung ratio optimization, alkaline doze optimization and canola straw particle size optimization. The results yield that anaerobic co-digestibility of the canola straw and the buffalo dung is obviously influenced by all the three factors of optimization. Considering the canola straw to buffalo dung ratio optimization, the ABD was in the range of 41.2-36.5%, while the maximum methane production was obtained as 845 NmL form the canola straw to buffalo dung ratio of 40:60 (R4). In view of the alkaline doze optimization, the ABD was in the range of 41.8-30.2%, whereas the maximum methane production was achieved as 856.5 NmL from the alkaline doze of 0.6g $NaHCO_3$/gVS (D5). In context to the canola straw particle size optimization, the highest cumulative methane production was achieved by utilizing the 2mm canola straw particle size (S2) i.e. 911 NmL, but because of its higher grinding cost to produce canola straw particle size of 2mm, particle size S3 (4mm) could be the best canola straw particle size.

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