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Enhancing Biogas Production from Lime Soaked Corn Cob Residue

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Abstract- This study assessed the impact of lime ($Ca(OH)_2$) soaking pretreatment on biomass digestibility and potential of biogas productions compare to untreated corn cob. Corn cob was soaked for different time of incubation, 7, 15, and 30 days. Scanning electron micrograph perceived destruction in the morphology of treated corn cob. The highest cumulative biogas of 360.5, 305.4, 218.6 NmL/gVS was obtained from 30, 15, 7 days pretreated corn cob respectively, which was 2-times higher than the cumulative biogas produced from the untreated corn cob 115.1 NmL/gVS. The best result for the methane yield (136.8 NmL/gVS) was obtained for 30 days soaking. The present study suggested that soaking with $Ca(OH)_2$ for longer time is effective for increasing digestibility of agriculture waste biomass and improving biogas production.

Keywords Anaerobic digestion, digestibility, biogas, corn cob.

1. Nomenclature

NmL/gVS= Normalized biogas in mL per gram volatile solid, CH_4 = Methane

OBA= Online Biogas App

MC= Moisture content, TS= Total solid, VS= Volatile solid.

2. Introduction

Waste is generating in large quantity around the world. This waste is a rich source of organic carbon and can be utilized for biogas production. The importance of this waste is getting attention as the fossil fuels are depleting continuously and releasing greenhouse gases which further increasing environmental problems [1, 2]. Agriculture biomass composed of three main components, hemicellulose, lignin, and cellulose. Cellulose is a carbon source containing long chains of glucose units. The outer surface is covered by hemicellulose which is heteropolymers of pentose sugars [3, 4]. Lignin is in the middle of the three component, and highly resistant to microbial degradation during the process of anaerobic digestion, thus and decreases the total yield of biogas [5]. Therefore a pretreatment of agriculture biomass is necessary to remove lignin and increase the anaerobic digestion process [6, 7]. Previously a number of chemical pretreatment are reported using high concentration of chemicals in acid treatment, alkalies treatment, ammonia fiber explosion, steam explosion auto hydrolysis, and microwave heating [6, 8]. Pretreatment with acid follow by enzymatic hydrolysis is also reported, however the process is costly, as high amount of enzymes are stringent conditions are required for the biomass hydrolysis [9].

Among the alkalies treatment, NaOH treatment is reported highly effective for increasing digestibility and lignin removal from biomasses [10]. However, this treatment process needs heating and high concentration of alkali which generates toxic by-products, and increase the overall cost of treatment process [11]. The advantage of lime ($Ca(OH)_2$) pretreatment is the low-cost of $Ca(OH)_2$ as compared to other alkalies. Secondly, it does not generate much inhibitors and can be easily recovered from hydrolysate by reaction with CO_2 during treatment process[12]. Soaking with $Ca(OH)_2$ did not need any thermal heating, so it is also beneficial for large scale development and energy output yield. The corn cob is a waste biomass of maize an important cereal crop grown in Pakistan. Thus, corn cob could be assessed as substrates for biogas production. Being an inexpensive pretreatment method, the current study focused to test the consequences of lime ($Ca(OH)_2$) pretreatment on structural properties of corn cob using scanning electron microscopy (SEM). Additionally, the effect of Ca(OH)2 soaking before and after treatment was compared for composition, biogas and methane yields of the corn cob.

3. Methodology

3.1. Lignocellulosic waste biomass

The corn cob was obtained locally (Faisalabad, Pakistan) after field harvesting and oven dried at 70°C for 24 h. The dried corn cob residue was ground up-to about 40 mesh size with a grinding machine. The powder samples were placed shelter in polyethylene plastic bags.

3.2. $Ca(OH)_2$ Soaking

Corn cob residue (50 g/L) was soaked in 100 mL of 0.5% of $Ca(OH)_2$ and was kept for 7, 15 and 30 days incubation time. The control sample of corn cob residue was immersed in 100 mL of distilled water without $Ca(OH)_2$. The experiment was run in the triplicate. After soaking time, the corn cob residue was collected and was washed with tap water several times with cheese cloth. The solid residue was dried at 70°C for 24 h. Change in lignin content was calculated using National Renewable Energy Laboratory (NREL) procedure [13]. Reduction in total weight of the samples were calculated at the end of each soaking time. Weight loss was measured in percentage, the final weight of corn cob was minus from the initial weight as such,

$$\text{Dry weight loss (\%)} = \frac{C1 - C2}{C1} \times 100$$

C1= initial weight
C2= final weight

3.3. Scanning Electron Microscopy (SEM)

The untreated corn cob, 7, 15, and 30 days of 0.5% $Ca(OH)_2$ soaked samples were subjected for Scanning Electron Microscopy (SEM) (JSM-7800F PRIME, JEOL's USA). Images of the untreated corn cob, 7, 15, and 30 days of 0.5% $Ca(OH)_2$ soaked were fixed on a black carbon tape and sputter with gold palladium and analysis of SEM was done using magnification range of 1k, 2k and 3k um to show the effect of pretreatment from samples morphology as describe earlier [14].

3.4. Biomethane Potential Test (BMP)

The BMP was carried out by mixing 2-gram substrate as a starting material. Untreated corn cob and 7, 15, and 30 days 0.5% $Ca(OH)_2$ soaked treated corn cob samples were prepared. The 20 mL of active inoculum of anaerobic digester plant was used as inoculum. A total working volume of media was 50 mL in each serum bottle. The pH was adjusted to 7.5 and then all the bottles were airtight with rubber cork and aluminum crimp caps. A control inoculum without a substrate and the substrate without inoculum were included. The batch assay was started **37±1°C incubation** temperature after N_2 gas flushing for 4 min. All the bottles were manually mixed and daily biogas volume was determined by water displacement method for 40 days. The CH_4 content of the biogas was evaluated using GFM406 – multichannel portable gas analyzer. The GFM is a hand-held portable gas analyzer which accurately detects CH_4, $C0_2$, H_2S and other gases composition in biogas sample.

The raw data of daily biogas volume and CH_4 composition obtained for untreated corn cob and 7, 15, and 30 days 0.5% $Ca(OH)_2$ soaked samples were analyzed using OBA (https://biotransformers.shinyapps.io/oba1/). This biogas package software (R package) calculates cumulative methane, cumulative biogas and daily rate of methane using a standard Eq.1 [15].

$$Vb = \frac{P \times Vh \times C}{(RT)} \tag{1}$$

Where
Vb = is the volume of daily produce gas (mL)
P= is the absolute pressure difference (kPa)
Vh= is the volume of head space (mL)
T = is absolute temperature in (K)
C= gas molar volume (22.14 L mol^{-1}) at 273.15 K and 101.325 kPa),
R= 8.314 L kPa k^{-1} mol^{-1} is universal gas constant

4. Results

4.1. Composition and $Ca(OH)_2$ soaking effect

The effect on the compositions of corn cob before lime treatment (initial value) and after treatment is listed in the (Table 1). Corn cobs are a lignocellulosic biomass composed of hemicellulose, cellulose and lignin. The percent composition of each constituent may be vary depending upon the variety, growth and analysis parameters. Corn cob was composed of 19% lignin, 30% hemicellulose, and 42% cellulose determined by using the protocol and methodology as described by Sluiter *et al.* 2013 [13]. The compositions of A soaking pretreatment method with 0.5% of $Ca(OH)_2$ was assessed for the measurement of lignin removal percentage and dry weight loss. The highest loss of lignin was 57.8±1% and maximum loss of dry weight was 33±1% after 30 days of soaking incubation as shown in the (Table1).

Table 1. Effect of $Ca(OH)_2$ soaking on composition of corn cob

Conditions (soaking)	Lignin content	Lignin loss (%)	Total weight loss (%)
Initial	19±1	0	0
7 days	16±1	15.7±2	12±1
15 days	12±1	36.8±1	23±2
30 days	8±1	57.8±1	33±1

4.2. Scanning Electron Microscopy

The effect of incubation time on corn cob were compared to see the surface degradation and morphological changes. The $Ca(OH)_2$ remove lignin from the substrates and make it swollen to increase it digestibility. This degradation effect can be seen in the images of scanning electron microscopy. The $Ca(OH)_2$ soaked solid residues of corn cob clear displayed degradation and visual distortion on their surfaces as can be seen in (Fig. 1). The SEM micrographs confirmed the impact of $Ca(OH)_2$ soaking in Fig. 1 (B), (C), (D), as compare to control (A). The intensity of the $Ca(OH)_2$ soaking treatment on corn cob surfaces increased with the incubation period. Fig. 1 (B) is 7 days, Fig. 1 (C) is 15 days, and Fig. 1 (D) is 30 days $Ca(OH)_2$ soaked sample. The prolong incubation time clearly indicating effect and severity of degradation. The images visibly displayed ruptures in the waxy structure in each sample.

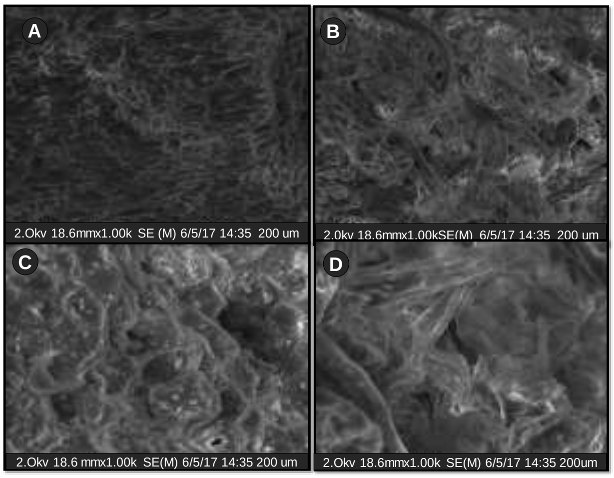

Fig. 1. Morphology of the corn cob before and after $Ca(OH)_2$ soaking. (A) untreated (B) 7 days treated (C) 15 days treated (D) 30 days $Ca(OH)_2$ soaked image with equal magnification.

4.3 Anaerobic digestion and biomethane potentia

Anaerobic digestion process is known for production of biogas from organic waste biomass. The volume of biogas is reported as the volume of biogas produced per gram volatile solid (VS) added for the specific substrate. The methane yield is calculated from the volatile solid (VS) of the substrate. The initial total solid of the corn cob was 85.5% and VS was 71.3%.

In this study, inoculum sample of a full-scale anaerobic digester was used. The inoculum was containing moisture content (MC) of 80.2%, 5.4% TS, and 3.2% VS. The highest methane (CH_4) concentration of the biogas was 50-55% for pre-treated corn cob and 35% for untreated corn cob respectively.

The 0.5% $Ca(OH)_2$ soaked samples for 7 days, 15 days, and 30 days were evaluated for biogas production compared to untreated corn cob. The highest daily biogas was 35 and 50 NmL/gVS from 15 days, and 30 days treated corn cob (Fig. 2). However, daily biogas was 27 and 15 NmL/gVS from 7 days treated and untreated corn cob (Fig. 2). Similarly, the highest daily volumetric methane was 18 and 20 NmL/gVS from 15 days, and 30 days treated corn cob (Fig. 2). However, daily volumetric methane was was 10 and 7 NmL/gVS from 7 days treated and untreated corn cob (Fig. 3). Although the maximum daily volumetric methane rate was 10.4 and 13.5 mL/gVS from 15 days, and 30 days treated corn cob while, 5.5 and 2.2 mL/gVS from 7 days treated and untreated corn cob (data not shown).

It was observed that; the daily volume of biogas and methane rate was 2 times higher in case of pretreated corn cob comparatively to untreated corn cob. In addition, lag phase of the daily volume of biogas and methane was minimum up to 48 hr of incubation and was longer in the case of untreated corn cob up to 7 days. The daily biogas and methane yield was maximum between 7-17 days of anaerobic digestion process. Routinely, the yield of biogas and methane slowly get down after 20 days of anaerobic fermentation process.

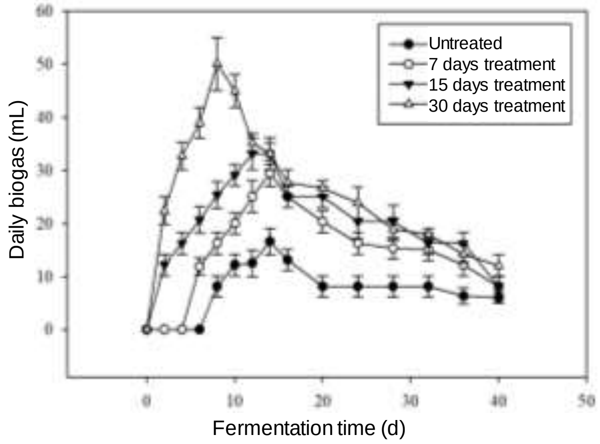

Fig. 2. Daily biogas (mL) of untreated, 7 days, 15 days, and 30 days 0.5% $Ca(OH)_2$ soaked corn cob, error bar indicates standard deviation among the triplicates samples.

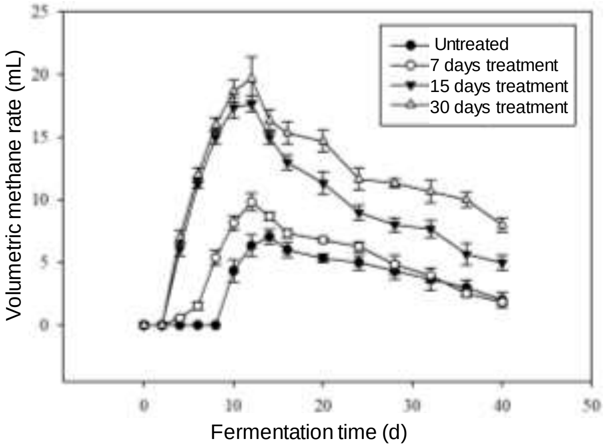

Fig. 3. Daily methane (mL) of untreated, 7 days, 15 days, and 30 days 0.5% $Ca(OH)_2$ soaked corn cob, error bar indicates standard deviation among the triplicates samples.

The cumulative biogas obtained from 0.5% Ca(OH)2 soaked samples for 7 days, 15 days, and 30 days was higher compared to untreated corn cob obtained. The best result was observed after 30 days of 0.5% Ca(OH)2 soaking with a cumulative biogas volume of 356.5 NmL/gVS. Similarly, a cumulative biogas volume of 218 and 305 NmL/gVS was obtained from 7 and 15 days 0.5% Ca(OH)2 soaked samples.

A lower cumulative biogas of 115.5 NmL/gVS was obtained from untreated corn cob. (Fig. 4).

The highest cumulative volume of methane for 0.5% Ca(OH)2 soaked samples for 30 days was 136.8 NmL/gVS. Similarly, a cumulative volume of methane of 44 and 104 NmL/gVS was obtained from 7 and 15 days 0.5% Ca(OH)2 soaked samples. A lower cumulative biogas of 27.5 NmL/gVS was obtained from untreated corn cob. (Fig. 5). The cumulative biogas obtained from the treated corn cob was increasing as the time of soaking was increasing from 7 to 30 days compare to untreated corn cob.

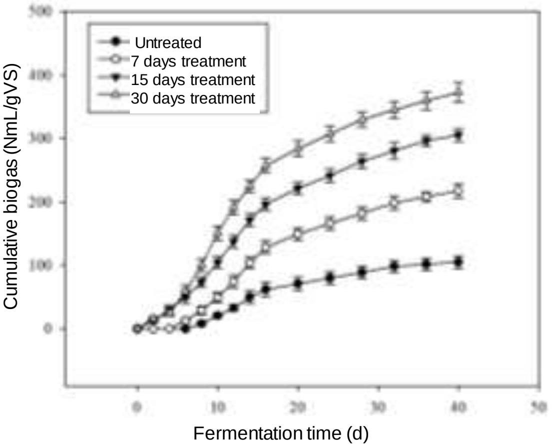

Fig. 4. Cumulative biogas (NmL/gVS) of untreated, 7 days, 15 days, and 30 days 0.5% $Ca(OH)_2$ soaked corn cob, error bar indicates standard deviation among the triplicates samples.

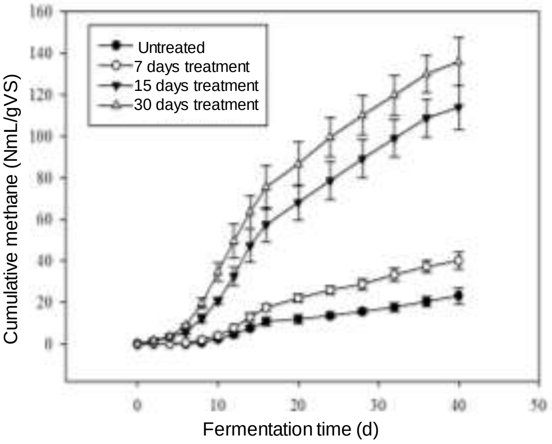

Fig. 5. Cumulative methane (NmL/gVS) of untreated, 7 days, 15 days, and 30 days 0.5% $Ca(OH)_2$ soaked corn cob, error bar indicates standard deviation among the triplicates samples.

5. Discussion

The anaerobic digestion of mentioned bio-waste (corn cob) could be used for biogas production. Maize is a cereal crop grown in Pakistan, it can be used for different purposes like eating, heating, burning, cooking and as an animal feeds. The Chaffs, cobs, and stalks of maize can be harvest as wastes biomass. The cobs and stalks are rich sources of lignocellulosic biomass composed of cellulose, hemicellulose, lignin along with other extractives [16]. This waste biomass can be directly processed for biogas production using animal dung as inoculum source, the waste biomass is converted into a mixture of methane 50-70% (CH4), 30-40% hydrogen (H2) and 30-40% carbon dioxide (CO2) anaerobically in a biogas digester [17]. However, the biogas yield is minimum, to increase the biogas yield, it is important to increase the digestibility of the waste biomass by removing lignin which acts as a barrier in energy production, therefore, the current study soaked corn cob with dilute lime at room temperature for different incubation time. The lime soaking significantly produce morphological degradation as can be seen in SEM micrograph (Fig. 1). The Fig. 1 shows that the degradation improves as we kept them for a longer period of time. A similar study, using alkali treatment of corn cob, reported a loose surface structure after treatment compares to the untreated sample in SEM micrographs. The study further suggested that these changes improve enzyme accessibility and digestibility [18]. Additionally, a considerable level of lignin reduction and weight loss was also observed (Table 1) from corn cob residue. This treatment later displayed significant enhancement in terms of biogas yield during biomethane potential process. In Fig. 2-4 the biogas yield enhanced with increasing the time of Ca(OH)2 soaking, the biogas potential is highest in case of 30 days' retention time than 15 and 7 days. Although the cumulative biogas is 2 times higher from the untreated corn cob residue (Fig. 4). The observations of the current study for biogas and methane yield is also supported by an earlier reported study. The author also shown improving digestibility, enhancing of biogas and methane yield after Ca(OH)2 pretreatment from rice straw [19]. Overall, the results of the present study suggested that dilute Ca(OH)2 soaking pretreatment might be an inexpensive treatment for waste biomass degradation compare to high alkali concentration treatment process combine with thermal heating to enhance biogas production.

It is proved that Ca(OH)2 remove lignin, minimize the degree of lignin polymerization in biomass, and open the chain of cellulose to enzymatic and microbial degradation during anaerobic digestion of corn cob [10, 20]. Soaking with dilute lime (Ca(OH)2), besides improve total biogas yield, additionally, are beneficial for releasing soluble sugar than high dosage alkali treatment [21]. To improve the process of anaerobic digestion, lignin removal of waste biomass with dilute lime (Ca(OH)2) soaking pretreatment might be considering to move forward from lab research to industrial scale process for less expensive biogas production. Further adjustment to an anaerobic process by co-substrate strategy can be proved as vital [22, 23]. The suitable design of anaerobic digester, generator, and optimization of conditions for anaerobic digestion process is also crucial for industrial-scale development [24, 25].

6. Conclusion

Pretreatment can improve the outcome of total biogas yield by removing the barrier to energy (lignin) from lignocellulosic biomass. After soaking corn cob with dilute lime (Ca(OH)2), the degradation effect was visible on the surface of treated corn cob samples. Moreover, lime soaking speeds up the process of digestion process by remove lignin from corn cob residue. The optimum biogas yield was obtained after 30 days of lime (Ca(OH)2) soaking. The cumulative biogas obtained from 30 days lime (Ca(OH)2) soaked sample was 2 times higher than the untreated corn cob. Notably, the initial lag period of anaerobic digestion was minimum in (Ca(OH)2) treated corn cob residue compare to untreated corn cob. The study highlights future progress in soaking of agribiomass with dilute (Ca(OH)2) as a potential strategy to be considered for increasing the cost-effectiveness of biogas production.

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Conflict of interest

The authors declare that they have no conflict of interest.

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