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Investigating Kinetic Parameters in the Anaerobic Digestion of Sugarcane Bagasse

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ABSTRACT:

Lignocellulosic biomass has sufficient organic matter to convert into biogas. Abundantly available biomass such as bagasse has the potential to be an alternative renewable energy resource. However, lignin poses a hindrance to their biodegradation through anaerobic digestion which can be fixed by chemical pretreatment. Anaerobic digestion of chemically pretreated bagasse co-digested with cow dung at a mesophilic temperature in a batch mode process was studied in the present work. Bagasse was pretreated at normal room temperature by soaking it with different concentrations (w/w) (2%, 4%, and 6% concentration) of NaOH. After that slurry was prepared by co-digesting bagasse with cow dung in the ratio 1:2 and water in the ratio of 1:3 fed into four different one-liter digesters for biogas measurement. Gompertz Model was found to have consistency with results obtained from experimental studies as the maximum biogas production potential of 486.53 ml at a rate of 19.8629 ml/day which was found to be highest in the case of 4% NaOH pretreated bagasse.

1. INTRODUCTION

The increase in demand for energy and large dependency on fossil fuels has demanded researchers' attention towards alternate sources of energy. With the increase in population, the production of food crops also increases proportionally and so do the leftover crops infield[1]. Globally, around 140 BMT (billion metric tons) of biomass were produced from agriculture in the year 2019. In which maximum crop residue was found to be from sugarcane crops [2]. Over 1.9 billion tons of sugarcane were produced by 115 countries Globally in the year 2020[3]. India tops in the production of sugarcane as around 36.88 MMT of sugarcane was produced in the country in the year 2020-2021[3]. India tops in the production of sugarcane as around 36.88 MMT of sugarcane was produced in the country in the year 2020-2021[3]. India being an agriculture-based country produces an abundant amount of crop residues. Burning of crop residues in northern states of the country such as Punjab, and Haryana causes greenhouse gas emissions, resulting in air pollution[4][5][6].

Burning of 24% of 488 MT of crop residues in fields resulted in more than 800 Gg of Particulate emission, 211 Tg of carbon dioxide emissions, 58 Gg of elemental carbon, and 239 Gg of organic carbon emissions were added to the atmosphere in the year 2017. These crop residues have the potential to generate 120 TWh of power, production in India [7]. Most abundantly available crop residues such as bagasse, rice, wheat, oat straw, etc. can be efficiently used to recover bioenergy from these residues via anaerobic digestion techniques [8][9]. Anaerobic digestion of organic waste to attain clean and green energy is found to be the most sustainable approach worldwide[10][11]. The anaerobic digestion is the biochemical pathway of energy conversion that involves four steps. The first step, hydrolysis, of the anaerobic digestion process, was found to be a rate-determining step as reported in various studies[12][13]. However, microorganisms involved in further steps are key to the anaerobic digestion process[14]. However, lignin present in this organic waste poses a recalcitrance to biomass degradation through anaerobic digestion. Therefore, the lignocellulosic matrix needs to be disintegrated by different pretreatment techniques[15][16]. So, physical pretreatment of biomass followed by other different chemical pretreatment methods was found to be favorable for the efficient production of biogas[17][18].

2. OBJECTIVES

Physical pretreatment of lignocellulosic biomass helps to disintegrate the matrix thus increasing the surface area for microorganism attack[19]. Various physical pretreatments such as milling, grinding, steam explosion, ultrasound, and microwave radiation are found in literature representing in enhancement of biogas production after physical pretreatment [20][21][22]. For instance, reducing rice straw size to 1 cm and followed by 4% NaOH pretreatment resulted in higher biogas production as compared to 0.075 M of acetic acid [23].In another study, NaOH-pretreated corn straw was found to produce 73.4% higher biogas production as compared to untreated corn straw [24]. Bagasse pretreated with 0.5 M solution of sodium sulphite at 100 ^{0}C resulted in the highest biogas production as compared to sodium carbonate and sodium acetate[25]. NaOH pretreatment of bagasse was found to be more efficient as compared to $Ca(OH)_2$ [26]. Another study on comparative analysis of three different pretreatment methods namely: Organsolv pretreatment, NMMO (N-Methylmorpholine N-Oxide) pretreatment, and NaOH pretreatment of wheat straw reported that alkaline pretreatment was found to be most effective in lignin removal, dissolution of hemicellulose takes place maximum by organosolv pretreatment method whereas NMMO didn't show any impact on lignin and hemicellulose structure [27]. Alkaline pretreatment with KOH, Ca(OH)2, and NaOH are the most frequently used alkalis for the pretreatment of lignocellulosic biomass, having mild pretreatment conditions for longer duration was found to be effective after alkaline pretreatment [28]. As alkaline pretreatment of lignocellulosic biomass makes it swollen and porous due to the solubilization of hemicellulose and/or restructuring of lignin[29].

Kinetic study of microbial activities of enzymes and biochemical pathways during the anaerobic digestion process can help understand the process, to optimize the biogas production [30]. Some authors proposed two models to study the kinetics of biodegradable waste; the first-order kinetic model was found to be fit for hydrolysis and needs to be modified for hard degradable waste. The Contois kinetic model and surface colonization were found to be fit for a wide variety of organic matter biodegradation and hydrolysis was the rate-limiting step [31]. However, the model did not provide any information regarding production, potential, lag phase period, and maximum rate, during biogas production. A kinetic study on hydrogen production and methane production from food waste reported that the cone model was best suited for hydrogen production whereas the Gompertz-modified model was found to be suitable for methane production [32]. The kinetic study of KOH-pretreated wheat straw reported maximum biogas production with a minimum lag phase period after 2% KOH pretreatment[33]. A kinetic study of biogas production from bananas and cassava reported that cassavas resulted in higher biogas production as validated by the Gompertz equation[34]. The Gompertz model provides best-fit results for biogas production from waste date palm fruits as compared to the first-order model and surface model[35]. The modified Gompertz Model to predict the growth rate of bacteria in the anaerobic digestion process is frequently used by various researchers to validate the biogas production from different feed materials [36][37][38]. Several operational conditions such as carbon-to-nitrogen ratio, temperature, pH, solids concentration, hydraulic retention time (HRT), etc. significantly affect the anaerobic digester performance[39][40][41][42].

The present study aims to study the kinetics of the biodegradation of NaOH-pretreated bagasse through anaerobic digestion. The evaluation was conducted based on the kinetic parameters obtained using a modified Gompertz model.

3. METHODS

3.1 Material Collection

Bagasse used in this work was collected from a jaggery-making unit situated in the Village of Mohali district, Punjab India, which was discarded as waste after extracting juice from it and sundried to reduce the moisture content. The dried bagasse was then physically pretreated with the grinding machine to reduce its particle size. Cow dung used as inoculum in this study was collected from village Dhanas, Chandigarh.

3.2 Chemical Pretreatment

Firstly, physically pretreated bagasse was soaked in (2%, 4%, and 6%) NaOH (w/v) solution at 25^{0}C temperature for round the clock. Chemical pretreatment of bagasse involves three steps as shown in Figure 1. In the second step, pretreated bagasse was then washed with water to neutralize the pH as it should maintained in the range of 6.5 - 7.5 to have optimum biogas production. After that, it was sundried to make it moisture-less and stored in an airtight container.

Figure 1. NaOH pretreatment of bagasse

3.4 Analytical Methods

For the characterization of bagasse total solids concentration, volatile solids, moisture, and ash content were determined by using the standard ASTM method [43]. The carbon and nitrogen elements present in bagasse and cow dung were measured by using a CHNSO elemental analyzer [44]. As carbon-to-nitrogen (C: N) ratio plays a crucial role in optimum biogas production. The high C: N ratio may result in the faster consumption of nitrogen by acidogenic bacteria than methanogenic bacteria thereby adversely affecting biogas production[45][46]. The compositional analysis of bagasse was carried out using the Soxhlet extraction method [47][48].

The overall methodology adopted in the study is shown in the process flow diagram of Figure 2.

4. RESULTS

4.1 Characterization

Waste-derived fuel characterization can be carried out by performing the proximate analysis of bagasse. Moisture content, ash, volatile matter, and total solid content present in biomass play a critical role in evaluating the fuel characteristics. As biomass weight increases without any increase in its heating value in the case of wet biomass. Ash adds to the weight without releasing any heat during combustion

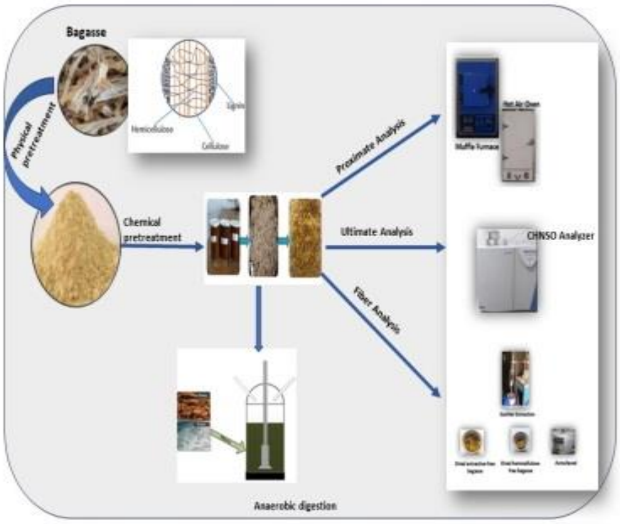

Figure 2. Process flow diagram anaerobic digestion of bagasse

Table 1 shows the result of the proximate analysis of untreated and pretreated bagasse. Total solids matter and volatile solids present in bagasse were found to be above 90% and 78% respectively representing that sufficient solids are present in it for bioenergy conversion. The moisture content of untreated and pretreated bagasse was found to vary from 5.21% to 8.49% after NaOH pretreatment. The proximate analysis results were found to be comparable with the literature[49].

Table 1 Proximate analysis

Bagasse	Pre-treatment			
	Untreated	2% NaOH	4% NaOH	6% NaOH
Moisture	5.21	7.29	8.49	6.14
Total solid	94.79	92.71	91.51	93.86
Volatile Solid	84.31	82.13	76.31	79.39

The carbon-to-nitrogen ratio as measured by CHNSO elemental analyzer was found to be 59.61:1 for bagasse and 23.8:1 for cow dung. Co-digestion of bagasse with cow dung helps to reduce carbon to nitrogen ratio of bagasse to 29.98:1 which lies in the range required for optimum biogas production as per studies performed by Dioha et., al., 2013 [46].

4.2 Compositional analysis

The bagasse was composed of 41% cellulose, 32.3% hemicellulose, and 19.5% lignin as measured by the method adopted by Ayeni et. al[47]. The results obtained from fibre analysis of bagasse were found to be comparable with the literature[50]. The NaOH pretreatment of bagasse resulted in an improvement of cellulose by 17-46 % with a decrease in hemicellulose and lignin by 21-46% and 22-57.4% respectively with an increase in NaOH pretreatment concentration which was comparable with the results obtained by Maryana et al., 2014 after alkali pretreatment of bagasse for bioethanol production[51]. From Figure 3 it can be observed that as the cellulose content of bagasse increased the lignin content decreased, thus resulting in a lower Lignin to Cellulose (L/C) ratio with increased concentration of NaOH pretreatment.

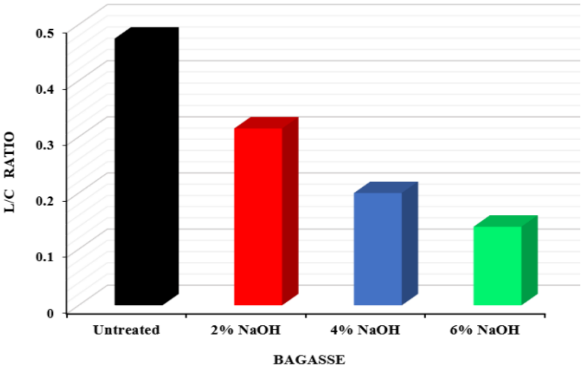

Figure 3 L/C ratio of bagasse

4.3 Kinetic study of anaerobic digestion

The microbial activity in the anaerobic digestion process can be evaluated by assessing the kinetics of substrate consumption. The kinetic model was reported to be a very useful tool for optimizing the co-digestion process and determining the rate of biogas production. The Gompertz model was used in this present work. Cumulative biogas production from batch digesters was assumed to correspond to methanogenic bacteria growth rate as given below[52]:

$$(t) = A * exp\ \{-\exp\ [\ \mu e\ (\lambda - t)/\ A + 1]\ \} \qquad (1)$$

where cumulative biogas (Methane) production (ml) obtained is represented by Y(t), production potential (ml) of biogas is represented by A, μ represents the maximum biogas production rate (ml/d), e is a mathematical constant having a value equal to 2.718282, and λ represents the lag phase period, and t represents the period of biogas production (day). The kinetic parameters A, μ, and λ of the modified Gompertz equation were analyzed using non-linear regression in MS Excel solver.

Figure 4(a) shows biogas production from the experimental study and Gompertz-model values for native (untreated) and 2% NaOH pretreated bagasse. It has been observed that from the experimental study, 403 ml after 2% NaOH pretreatment which higher as compared to native bagasse resulting in 325 ml of biogas. Similarly, Fig 4(b) and Fig. 4(c) represent the experimental and model values of biogas production for 4% NaOH pretreated bagasse and 6% NaOH pretreated bagasse respectively. It has been found that 482 ml of biogas production was obtained from the experimental study after 4% NaOH pretreatment whereas 369 ml of biogas production was observed after 6% NaOH pretreatment. It has been found that the highest production was from 4% NaOH pretreated bagasse followed by 2% NaOH pretreated, 6% NaOH pretreated, and untreated bagasse as can be seen from Figure 4(d).

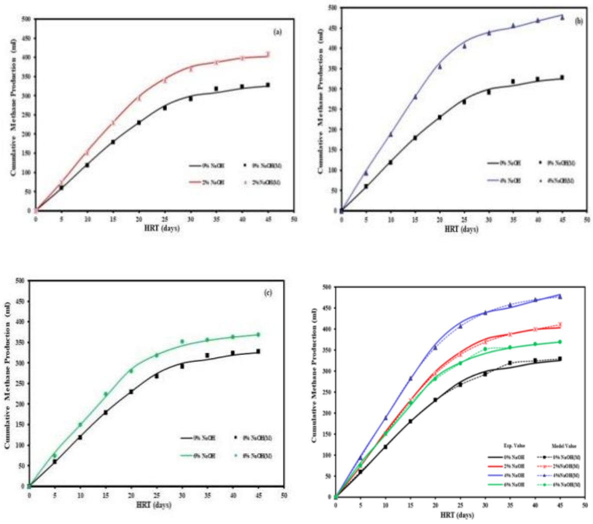

Figure 4 Kinetic study of biogas production (a) 2% NaOH (b) 4% NaOH (c) 6% NaOH (d) Comparative of NaOH Pretreatment

Table 2 shows the various kinetic parameters obtained from the Gompertz modal. The coefficient of correlation (R^2) was found to be 0.99 for all the test groups of bagasse as seen in Table 2 representing that Gompertz-model fitted well with the experimental study. The highest production potential of 486.5279 ml of biogas at a rate of 19.8629 ml/day in the lag phase period of 0.4842 was obtained after 4% NaOH pretreatment of bagasse

which was found to be the maximum among all the groups of bagasse as in case of experimental study. The biogas production rate in pretreated bagasse varied between 14.1789-19.8629 ml/day with a time lag phase period of about 0.4 after each pretreatment of bagasse.

Table 2 Kinetic parameter constants of bagasse

Bagasse	**A (ml)**	**μ (ml/d)**	**Λ**	**R^2**
Untreated	334.6390	14.1789	0.4931	0.99
2% NaOH	415.5075	18.5143	0.4573	0.99
4% NaOH	486.5279	19.8629	0.4842	0.99
6% NaOH	375.1408	17.8568	0.4612	0.99

5. DISCUSSION

5.1 Key Findings of Study

Proximate analysis of bagasse represented that it has sufficient organic matter present in it to get attacked by microbes in the anaerobic digestion process. Mixing cow dung in ratio two helps to improve the carbon-to-nitrogen ratio to produce optimum biogas production. The alkaline pretreatment of bagasse at different concentrations of NaOH shows a significant effect on its chemical and physical properties after pretreatment. The cellulose content after each pretreatment concentration (i.e. 2%,4%,6% NaOH) as compared to untreated bagasse represents that chemical pretreatment helps to destroy the outer lignin layer making cellulose available for microbes' attack. With the increase in the concentration of NaOH pretreatment lignin deceased. As can be seen from Fig.3 2% NaOH pretreatment resulted in a decrease in L/C ratio as compared to untreated bagasse not found to be as much as effective as 4% NaOH and 6% NaOH pretreatment.

The various concentrations of NaOH pretreatment were compared with untreated bagasse. The pretreated bagasse samples have shown a higher production of biogas as compared with the untreated bagasse. The biogas production first peak was observed during the 5th to 10th day of the hydraulic retention period and maximum production takes place during the 30th to 35th day of HRT. After that saturation seems to be set as no major change in production has been observed. Among the different concentrations of NaOH pretreatment. 4% NaOH pretreatment resulted in the maximum yield of biogas. The 6% NaOH pretreatment resulted in lesser production as compared to the 4% NaOH pretreatment which may be attributed to the fact that greater solubilization of carbohydrates takes place at higher concentrations of NaOH pretreatment.

From the comparison of experimental and model data of bagasse, it has been observed that the Gompertz model also fits quite well for each experimental result in the case of bagasse. The analysis of kinetics parameters obtained from the Gompertz model represented that 4% NaOH pretreatment of bagasse has the highest biogas production potential and production rate among all concentrations used for pretreatment. The next higher concentration of 6% NaOH pretreatment represented in the decline of biogas production. The model values and the experimental study were seen to be following similar trends as 4% NaOH pretreatment biogas production potential was followed by 4% NaOH pretreatment and then 6% NaOH as observed from the experimental study.

6. CONCLUSION

The production of biogas depends on many factors such as temperature, carbon-to-nitrogen ratio, pH, volatile solids, etc. Therefore. Pretreatment is required to expose the maximum constituents of bagasse for the anaerobic digestion process. The alkaline pretreatment helps to increase the cellulose content by the destruction of the lignin structure. The pretreatment of bagasse with 4% NaOH concentration resulted in optimum biogas production as higher concentration shows a decline in production. The 6% NaOH pretreatment was found to be inefficient as compared to 4% NaOH and 2% NaOH pretreatment. The bagasse can be sustainably utilized as a renewable energy resource to get clean energy from biogas.

Most of the crop residues have lignocellulosic structure therefore effect of different chemicals such as Ca(OH)2, KOH, etc. can be analyzed on biogas production. In this study, cow dung was used as a medium to provide the microorganism however other sources of enzyme inputs can be analyzed. The use of chemicals also raises the cost of pretreatment so a comparative analysis of different pretreatment methods can be carried out. Further, studies are needed to explore the operating conditions, particle size, and chemicals used for pretreatment to get optimum biogas production.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of the paper.

Author Contribution

The authors confirm their contribution to the paper as follows: data collection, analysis and interpretation of results, draft manuscript preparation: Maninder Kaur, Proofreading, editing and concept: Sandeep Dhundhara. All authors reviewed the results and approved the final version of the manuscript.

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