Effect of Alkaline and Photocatalysis assisted Alkaline Pretreatment on Characteristics and Biogas Production of Rice Straw

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Certified that the contents and form of the thesis entitled **“Effect of Alkaline and Photocatalysis assisted Alkaline pretreatment on Characteristics and Biogas Production of Rice Straw”** submitted by Ms. Mariam Sabeeh has been found satisfactory for partial fulfilment of the requirements of the degree of Masters of Science in Environmental Engineering

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LIST OF ABBREVIATIONS

Abbreviations	Description
AD	Anaerobic Digestion
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
CH_3COOH	Acetic Acid
CH_4	Methane
C/N ratio	Carbon to Nitrogen Ratio
COD	Chemical Oxygen Demand
CO_2	Carbon Dioxide
EDS	Energy Dispersive X-ray Spectroscopy
g	Gram
gVS/L	Gram of Volatile Solids Per Liter
h	Hour
H_2SO_4	Sulphuric Acid
H_2	Hydrogen
kg/m^3	Kilogram Per Cubic Meter
M	Molar Solution
mg/l	Milligram Per Liter
Nml CH_4/gVS	Normal Milliliter of Methane Per Gram of Volatile Solids

mm	Millimeter
$NaHCO_3$	Sodium Bicarbonate
NaOH	Sodium Hydroxide
Nml/gVS	Normal Milliliter (Volume at gas at standard temperature, pressure and without moisture content)Per Gram of Volatile Solids
NPs	Nanoparticles
OLR	Organic Loading Rate
R^2	Co-efficient of multiple determination for multiple regression
Rmax	Maximum Biogas Production rate
RS	Rice Straw
SEM	Scanning Electron Microscopy
TiO_2	Titanium Dioxide
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon
TS	Total Solids
VFAs	Volatile Fatty Acids

ABSTRACT

To overcome recalcitrant nature and investigate enhancement of biogas production of rice straw (RS), it was subjected to pretreatment under mild conditions. Alkaline pretreatment using sodium hydroxide (NaOH), photocatalytic pretreatment utilizing titania nanoparticles (TiO_2 NPs) and alkaline-photocatalytic pretreatment was used to disrupt the lignocellulose complex. As compared to raw RS, maximum biogas and methane enhancement due to alkaline pretreatment was observed for 1.5% w/v NaOH pretreated RS which was 50 and 71% respectively. Photocatalytic pretreatment of RS at 0.25 g/L TiO2 increased biogas and methane yield by 30 and 36% respectively. However, maximum biogas and methane enhancement was observed for alkaline-photocatalytic pretreatment at 1.5% w/v NaOH- 0.25 g/L TiO_2 which was 74 and 122% respectively. Comparatively high enhancements were observed during alkaline-photocatalytic combined pretreatment due to increased cellulose and decreased lignin content. Moreover, the experimental data obtained from the experiments were validated using a non-linear kinetic model.

Keywords

Rice straw, Alkaline pretreatment, Titania nanoparticles photocatalytic pretreatment, Alkaline-photocatalytic pretreatment, Anaerobic digestion

1 INTRODUCTION

1.1 Background

Rapid increase in world population, advancement in technology and change in living standards have led to escalation of energy demand, which is expected to increase 56% by 2040 (US EIA, 2013). Conventional method of energy generation by utilization of fossil fuel has caused deadly consequences in terms of global warming and climate change. Moreover, depletion of affordable fossil fuel resources which is expected to occur by mid of century will create economic and political chaos. To battle with these foreseen consequences, renewable energy sources have to be explored. (Peter, 2018). Agricultural crop waste can be utilized as a sustainable and renewable source for biogas production due to abundant availability (Darmawan et al.,2018; Huzir et al., 2018). Rice straw is one of the most abundant source for second generation biofuel production as its global annual production was estimated to be 730 million metric tons in 2017 with variation in grain to straw ratio from 1:0.3 to 1:3 (Swain et al., 2019). However, its energy potential is lost as most of it is burnt to prepare land for wheat crop and to reduce labor cost creating environmental and human health concerns (Fang et al., 2017). To battle energy crisis, incorporation of rice straw residue for biogas production leading to bioenergy production, efficient waste management and subsequent generation of soil enriching digestate as a result of anaerobic digestion could be a viable option (Li et al., 2019; Raheem et al., 2016). Biochemical conversion to biogas through anaerobic digestion is economically viable and environmentally favorable as compared to other physicochemical and thermochemical methods as it is moderate and less energy intensive. A study reported energy output to input ratio to be 28.8 MJ/MJ for anaerobic digestion which was greater than other energy conversion technologies to other types of biofuels (Chandra et al., 2012b). However, one main barrier is the natural composition and complex structure of second generation biomass which generally consists of 15-20% lignin, 40-50% cellulose and 25-30% hemicellulose. Lignin is main component composed mainly of phenolic compounds which binds together hemicellulose and cellulose and runs throughout the three dimensional structure providing a protective sheath over hemicellulose and cellulose, giving resistance to microbial attack, rigidity and support to plant. Hemicellulose and cellulose collectively called holocellulose are polymers of sugars which are biodegradable and can be effectively utilized to produce biogas (Neshat et al., 2017; Sun et al., 2016).

1.2 Need for pretreatment

To break the barrier of lignin and expose holocellulose to degradation, pretreatment of rice straw is required. Pretreatment methods are mainly based on physical (grinding, milling, and extrusion), chemical (acidic, alkaline, advanced oxidation processes, organo solv) and biological (enzymatic, fungal, bacterial) processes, however, they can also be used in combination to disintegrate the complex structure. For anaerobic digestion, pretreatment option selected should avoid size reduction, preserve hemicellulose and cellulose while degrading and solubilizing lignin, generate relatively few inhibitors, minimize energy and chemical requirement and defend cost on downstream processing steps (Cybulska et al., 2019; Rabemanolontsoa and Saka, 2016). Chemical pretreatment has been proven to be highly effective in solubilizing hemicellulose and lignin content to recover sugars and carbohydrates under mild conditions and low inhibitors formation. Alkaline pretreatment using sodium hydroxide (NaOH) was proved to be most effective in lignin solubilisation along with small portion of hemicellulose and swelling of crystalline structure of cellulose increasing the surface area for microbial attack while reserving greater holocellulose content as compared to other chemicals (Menon and Rao, 2012; Paudel et al., 2017). Moreover, comparatively less inhibitors are generated which mainly include furfurals and phenolic acids, which are removed upon washing (Moradi et al., 2013).

Similarly, advanced oxidation process using titania photocatalysis for degradation of organics is preferred due to titania nanoparticles' (TiO_2 NPs) high photocatalytic activity, low toxicity, chemical stability and low cost which reserves its position to be an environmentally safe and economically viable photocatalyst. Titania photocatalysis has been extensively employed for treatment of wastewater containing organic pollutant, dyes and heavy metals like chromium and degradation of commercial lignin (Thiruvenkatachari et al., 2008). Degradation of natural lignin is however difficult but some efforts have been made in the past to depolymerize some natural and synthetic lignin sources with comparatively simpler structures like wood flour and rice husk into valuable products including vanillin, aldehydes, malonic acid, succinic and acetic acid (Do et al., 2017; Khaki et al., 2017). When titania nanoparticles are bombarded with wavelength less than 415 nm, hydroxyl and superoxide radicals are generated forming radical sites on substrate expediting the degradation process. Titania photocatalysis selectively cleaves β-O-4 bond of which 50% of lignin is constituted allowing access to compounds underneath which can be degraded to fine chemicals and fuels (Liu et al., 2019). However, studies on photocatalysis using titania on lignocelluloses are very few which have shown considerable degradation of microbial resistant lignocellulose structures and subsequent biofuel production (Corro et al., 2014; Yasuda et al., 2011).

In addition, an attempt for in depth investigation of impact on lignocellulose content and bio methane potential was carried out by pretreating rice straw with alkali assisted with titania nanoparticles' photocatalysis. The combined effect of photocatalysis with alkaline reactions are reported to be very few for real lignocellulose substrate. Niu et al. (2009) investigated the effect of alkali assisted photocatalytic pretreatment on rice straw biomass in which 3% NaOH and 2 g/L nano-TiO_2 were added to ground rice straw under UV light for 1 hour with reaction time of 22 hours resulting in 71.50% increase in cellulose and lignin removal of 18.50%. From this result, it is evident that alkaline pretreatment with photocatalyst assistance performed tremendously well in rendering cellulose for microbial consumption.

For comparing impact of alkaline, photocatalytic and alkaline-photocatalytic pretreatment of rice straw, there is a need to evaluate degradation of lignocellulose components and biogas production under mild pretreatment conditions.

1.3 Objectives of the study

In order to enhance biogas and methane production by degradation of lignocellulose complex of rice straw under mild pretreatment conditions and to compare the pretreatment impact of NaOH and Titania, following objectives were defined:

- To study the impact of alkaline (NaOH) pretreatment on characteristics and biogas enhancement of rice straw.
- To study the impact of titania (TiO_2) nanoparticles (NPs) photocatalytic pretreatment on characteristics and biogas enhancement of rice straw.
- To study the impact of titania (TiO_2) NPs photocatalysis assisted alkaline (NaOH) pretreatment on characteristics and biogas enhancement of rice straw.

1.4 Scope of the study

This study was conducted to evaluate impact of alkaline and photocatalytic pretreatment on rice straw under less energy intensive conditions. Its scope can be defined as follows:

- Substrate i.e. rice straw was obtained from a regional farm at district Faisalabad.
- Inoculum was a mixture of cow dung and anaerobic sludge. Cow dung was brought from local animal farm at Islamabad while anaerobic sludge was collected from sediments of constructed wetlands at NUST, Islamabad.
- For alkaline pretreatment, NaOH concentration were used in range of 0.5 to 2% w/v. Pretreatment was carried out on lab scale by putting NaOH solution and rice straw in Pyrex bottle which was then placed in a water bath.
- For photocatalytic pretreatment, a lab scale UV rays protection chamber was employed with UV bulbs of required wavelength. Rice straw was degraded in presence of titania nanoparticles in a beaker placed within the chamber. Titania doses of 0 to 1 g/L were used to investigate degradation impact.

- Effect of pretreatment was analyzed by characterization of raw and pretreated rice straw. Lab tests were carried out to determine lignocellulose composition, total solids, volatile solids and total kjeldahl nitrogen.
- Furthermore, lab scale anaerobic digestion of raw and pretreated rice straw was carried out in batch mode to evaluate enhancement in biogas production and methane yield of pretreated rice straw and associate the results with lignocellulose composition.
- This study was limited to studying lignocellulose content changes and enhancement in biogas production and methane yield of rice straw as a result of NaOH and titania pretreatment. The duration of experimentation was one year.

2 LITERATURE REVIEW

This chapter enlightens about application of anaerobic digestion to lignocellulose and previous studies conducted regarding pretreatment of lignocellulose biomass and their impact on biogas production.

2.1 Introduction to lignocellulose biomass

Lignocellulose biomass is profusely existing resource with global annual production of more than 200 billion metric tons (dry) per year (Beringer et al., 2011). Main types of biomass are agricultural residues, forest residues and dedicated energy crops. It is comprised of cellulose (35–50%), hemicellulose (20–35%), and lignin (10–25%), in addition to minute proportions of inorganic and organic compounds like lipids, proteins and extractives (Ghaemy et al., 2019). However, the amounts of these constituents vary depending upon specie, source, type, growth condition and maturation. Cellulose is a vital component of all plant cells making it one the most abundant renewable polymers on Earth. Cellulose exists in d-glucose subunits, linked by β-1,4-glycosidic bonds. Cellulose fibrils are mostly independent and weakly bound through hydrogen bonding. Hemicellulose is a complex carbohydrate structure that consists of different polymers like pentoses (like xylose and arabinose), hexoses (like mannose, glucose and galactose) and sugar acids. Hemicellulose has a lower molecular weight than cellulose, and branches with short lateral chains that consist of different sugars, which are easy hydrolysable polymers. Hemicellulose serves as a connection between the lignin and the cellulose fibers and gives the whole cellulose–hemicellulose– lignin network more rigidity. Lignin is, after cellulose and hemicellulose, one of the most abundant polymers in nature and is present in the cellular wall. It is an amorphous heteropolymer consisting of three different phenylpropane units (p-coumaryl, coniferyl and sinapyl alcohol) that are held together by different kinds of linkages. The main function of lignin is to give plants structural support, impermeability, and resistance against microbial attack and oxidative stress. The amorphous heteropolymer is also non-water soluble and optically inactive. All these make the degradation of lignin very tough. Although both cellulose and hemicellulose are easy to be degraded according to their chemical structure, the microbes require access from degradation of lignin so that the biodegradable content is exposed.

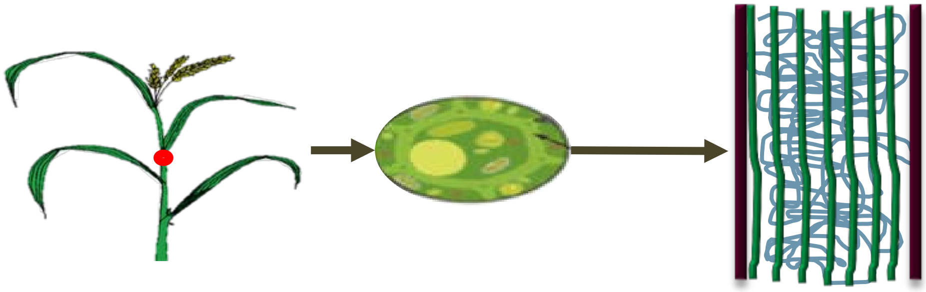


Figure 1: Lignocellulose structure of agricultural biomass

The AD of lignocelluloses generates energy-rich methane gas. The yield of methane per unit area is often utilized to decide energy productivity of a specific feedstock and is likely to vary significantly with different species, maturity, location and application of water and nutrients etc. (Yang et al., 2013). The Biochemical Methane Potential (BMP) test is mainly used to test the anaerobic digestibility of organic substrates. Low yield of quality biomass suitable for AD is another issue. For this, deciding high energy yielding specie and applying appropriate inputs during cultivation and increasing resistance to filed attack by pests and diseases is being utilized (Sims et al., 2006). Moreover, due to the complex structure of lignocelluloses, its conversion to biogas is challenging. Thus, the rigid structure encapsulated by lignin, cellulose and hemicellulose has to be disrupted by an appropriate, effective, economic pretreatment method to decrease retention time in digester, increase biogas yield and decrease lag time so that microorganisms can easily assimilate cellulose and hemicellulose as substrate and convert it into useful methane gas (Kumari and Singh., 2018).

2.2 Pretreatment Techniques

Common pretreatment techniques falling under the categories of physical, chemical, physiochemical and biological function differently to break the structure of lignocelluloses. Due to which different products, byproducts and yields are obtained. Moreover, every pretreatment has its advantages and disadvantages so selection should be made on the basis of available resources, cost effectiveness and intended use of substrate. One main drawback is associated cost which is not only of the chemical or equipment but also the loss of lignocellulose biomass, post treatment handling and cleaning and generation of waste stream. To cater this, studies and approaches have been done on developing low cost treatment options, conditions requiring less chemical and machinery, recovery of generated by products and high value co products like lignin and protein and chemicals from waste stream along with economic assessment (Kumari and Singh., 2018, Carrere et al., 2016). The following table describes the associated advantages and disadvantages with commonly employed pretreatment techniques (Kumar and Sharma, 2017).

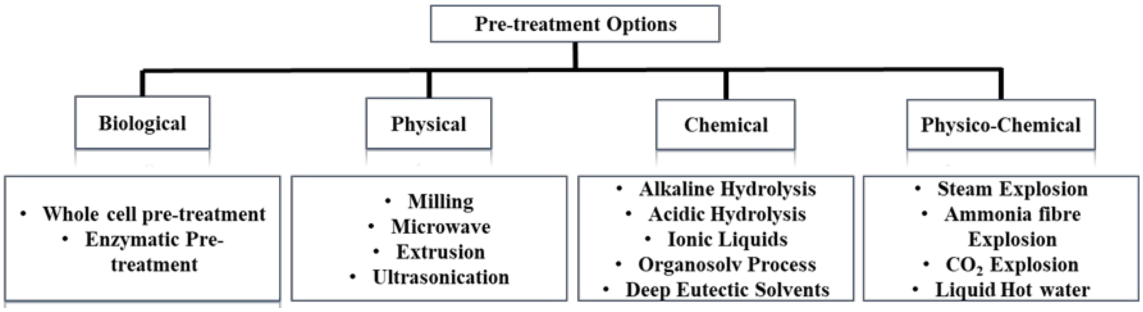


Figure 2: Selection of pre-treatment

An economical and effective pretreatment should meet the following criteria:

- Effective delignification.
- Preservation of hemicelluloses and cellulose.
- Avoiding production of inhibitory compounds that can be inhibit the activity of hydrolysis enzymes and fermenting microorganisms.
- Cost effective and consume less energy.
- Minimizing the cost of size reduction for substrates
- Minimizing the cost of material of construction for pretreatment reactors

Table 1 Effect of pretreatment on lignocellulose degradation of biomass

Biomass	Pretreatment	Conditions	Lignin removal (%)	Hemicellulose removal (%)	Cellulose recovery (%)	Reference
Wheat straw	Thermal	180°C, 1 h	15	23	31	Rajput et al., 2018
Rice Straw	Alkali	1% NaOH, 35°C, 3 h	15	30	27	Shetty et al., 2017
Rice straw	Fungal	Pleurotus ostreatus, 30 days	24	15	10	Mustafa et al., 2016
Rice Straw	Extrusion with alkali	3% NaOH, 35°C, 48 h	26	11	5	Zhang et al., 2015
Sunflower straw	H_2SO_4	20%W/W,121°C, 1 h	15	17	3	Antonopoulou et al., 2015
Bamboo residue	Kraft pulping	160°C, 70 min	95	55	43	Huang et al., 2015
Coffee pulp	Photocatalysis	10%Cu/TiO2, sunlight, 7 h	41	-	-	Corro et al., 2014

Table 1 shows the impact of various pretreatment types that have been studied over the last five years for breakdown of complex lignocellulose matrix. Different researchers have opted different techniques to break down lignin, cellulose and hemicellulose to expose and conserve the contents required for required bio fuel production.

2.3 Anaerobic Digestion

Anaerobic Digestion is a process carried out by a consortia of microorganisms by degrading the organic matter in the absence of oxygen and rendering biogas and resultant digestate as end products (Di Maria et al.,2014). On the basis of main chemical reactions playing a part, anaerobic process is divided into four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. These four steps are carried out by a sequence of microorganism and creating different end products at the end of each step. The steps are illustrated in figure given below (Li et al., 2011):

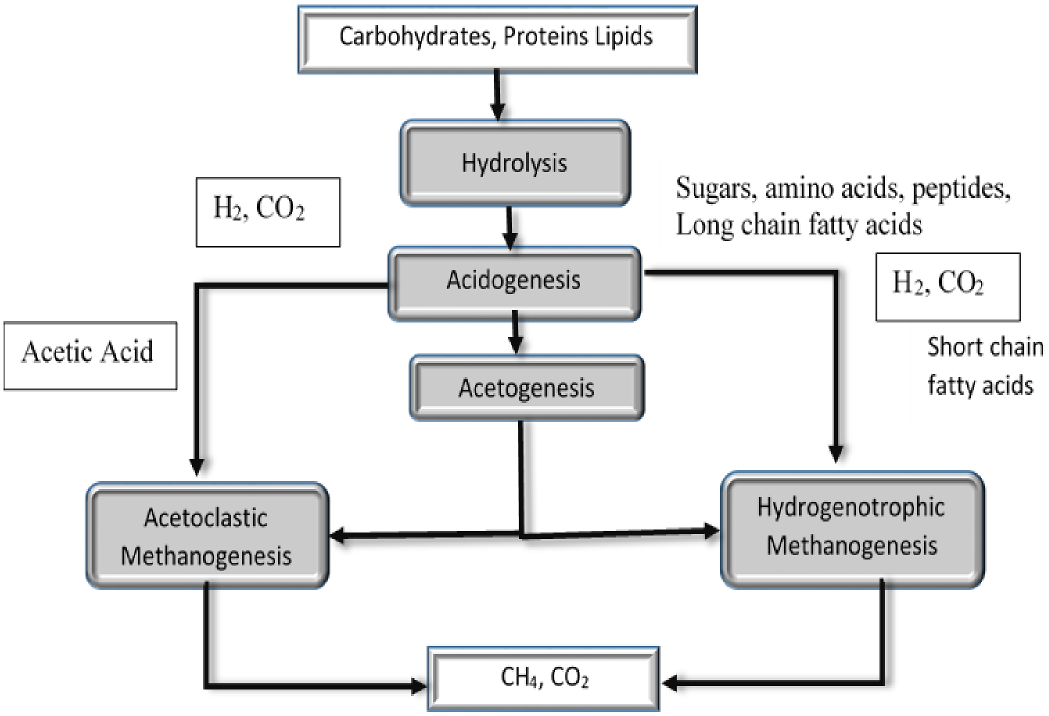


Figure 3 Anaerobic metabolism process

2.3.1 Hydrolysis

Hydrolysis is the first step converting in which polymeric compounds, of which biomass is constituted, is broken down into smaller units i.e. soluble oligomers and monomers. It is an extra cellular process and is important prior to acidification steps as it prepares substrate for bacteria responsible for acidification as fermentative bacteria can't assimilate complex organic matter directly into cell bodies. Responsible enzymes for the step are cellobiase, xylanase, amylase and cellulose for breakdown of carbohydrates into sugars i.e. monosaccharides, protease is responsible for converting proteins to amino acids whereas lipase stands responsible for degradation of lipid to long chain fatty acids and glycerol (Schön, 2010). It is often considered a rate limiting step when anaerobic digestion of lignocelluloses is considered because of its highly packed, cross linked and crystalline structure and coverage of digestible holocellulose with lignin. Due to this reason, a pretreatment step is anticipated to rupture crystalline structure of lignocellulosic biomass (Hendriks & Zeeman, 2009).

2.3.2 Acidogenesis

At this stage, acid-formers or acidogenic bacteria convert the products of hydrolysis stage to volatile fatty acids (propionate, butyrate, acetate etc.), ketones, carbon dioxide, alcohols, aldehydes etc. This spontaneous breakdown route liberates high energy yield for microbes (Vavilin et al., 2008).

2.3.3 Acetogenesis

Acetogenic bacteria oxidize products of acidogenesis to formate, hydrogen, acetate and carbon dioxide. Acetic acid is the main product at this stage. The energy yield for acetogens is less which make them vulnerable to even slight changes in environment and are sow growing (Liu et al., 2017).

2.3.4 Methanogenesis

Acetotrophic and hydrogenotrophic bacteria known as methanogens are strict anaerobes. Under stabilized conditions, 70% methane comes from acetotrophic methanogens and 30% from hydrogen trophic methanogens (Angelidaki et al., 2011). Methane is produced by hydrogen trophic methanogens and synthrophic acetate oxidizing bacteria pathway. When conditions are favorable for methanogens, all the anaerobically biodegradable matter is converted to biogas leaving behind digestate with minute amounts of any intermediates (Schnürer & Nordberg, 2008).

2.4 Factors affecting anaerobic digestion

Since the whole process is governed by various organisms performing their duties at various stages, it requires a favorable requirement and is impacted by factors such as pH, alkalinity, temperature, inhibitors, nutrients, moisture content, VFAs and some operational parameters like residence time, mixing organic loading rate, substrate to inoculum ratio etc. (Chen et al., 2008; Weiland, 2010). Impact of these factors and parameters are described below:

2.4.1 Temperature

Temperature is a vital factor since it imparts its impacts on microbial growth and separation of gaseous products like methane and carbon dioxide from gaseous and liquid phases (Gerardi, 2003). A wide temperature range can be applied in AD process range i.e. psychrophilic (11-25 °C), mesophilic (35 to 40 °C), thermophilic (50 to 55 °C) and hyperthermophilic (> 55 °C) (Takashima et al., 2011). Thermophilic and Mesophilic range are the most adopted ones based based on available resources and time. Conventionally, mesophillic range is preferred for AD as problems related to instability, process failure and inhibition are associated with thermophilic range AD. (Labatut et al., 2014). Liu et al. (2017) concluded that higher temperature lead to more efficient conversion of corn stover to biogas as anaerobic digestion at temperature of 44°C gave off 16.6 to 42.4% higher biogas production that that produced at temperature of 35°C, 38°C and 41°C. Similar trend of increase in biogas production as a result of increase in temperature was report by Membere and Sallis (2018). They found that at anaerobic digestion temperature of 55°C, 18% to 23% increase in biogas production from microalgae was observed than at temperatures of 25°C, 35°C and 45°C.

2.4.2 pH, volatile fatty acids and alkalinity

Microorganisms in AD process require pH range of 6.5 to 8. Deviation form this range causes formation of intermediates which intoxicates the process (Weiland, 2010). Ammonium accumulation increases pH value while VFA accumulation decreases the pH . VFAs are precursors for methane production but their accumulation may inhibit methanogenesis as a result of the drop in pH (Chen et al., 2008). The accumulation of VFA will not always result in pH drop, due to the buffer capacity (alkalinity) of the system (Nges et al., 2012b). Begum et al. (2017) studied the effect of pH on digestion of leachate in a two stage anaerobic digestion reactor. It was observed that pH of 5.5 in the first reactor yielded 34% higher VFA production which resulted in 21% increased COD removal efficiency as compared to relatively acidic (3) and alkaline Ph (8) as they suppressed the activity leading to only dominant butyric acid production. Ravi et al. (2017) also compared pH values of 5.5 and 6 during acidogenesis phase of anaerobic digestion of vegetable waste and found that methane production was 8% higher when initial pH was set to 6 which was due to comparatively higher VFAs production.

2.4.3 Ammonia

Ammonium is released when protein-rich biomasses are degraded which generate biogas with high methane content. Thus they are considered suitable substrates for biogas production. However, they often lead to system disruptions as ammonia concentrations as low as 100-150 mg/L are proved to be inhibitory to an adapted AD process (Chen et al., 2008). The inhibition effect of ammonia is subjective to pH and temperature where increase in these parameters result in increased inhibition due to increased ammonia solubility. Ammonia in its free form passively enters the cell and disrupts proton balance or elevates pH of cytoplasm (Chen et al., 2008). Recent studies have shown that the acetoclastic methanogens are more prone to free ammonia toxicity wherein acetate is converted to CO_2 and H_2 by syntrophic acetate oxidizers to ensure continuance of methane production via the hydrogen trophic pathway (Manzoor et al., 2016). In a study by Yang et al. (2018), analysis of VFA production data in mesophilic and thermophilic reactors showed that ammonia inhibition primarily inhibits the process of methanogenesis and acetogenesis during mesophilic digestion while thermophilic digestion suffered only during the stage of methanogenesis. Moreover, when total ammonia nitrogen exceeded 2000 and 5000mg $NH4^+$-N/L in mesophilic and thermophilic reactors respectively, loss in methane production surpassed 20%. Peng et al. (2018) concluded that excess ammonia barred acetate metabolism leading to instability of anaerobic digestion process.

2.4.4 Mixing

Mixing augments the contact between microorganisms and organic matter to be degraded. It also influences release of gas entrapped in the form of bubbles in digester, heat transfer and particle size distribution (Kaparaju et al., 2008). For lab s ale digestion tests on batch mode, vigorous mixing for 2 to 3 minutes on daily basis are recommended to prevent formation of inactive layers as a results of gas formation which takes the substrate and inoculum with it to surface. Tian et al. (2015) observed that formation of floating layers in reactors can cause up to 88% decrease in daily biogas production which can effect energy efficiency and cost- effectiveness of the process. They also found that during anaerobic digestion of corns over in lab-scale CSTR, for OLR of 1.44, 1.78 and 2.11 g(TS) / L/ d, agitation should be provided after every 10 h, 6 h, and 2 h respectively. A study conducted on two-stage anaerobic digestion of palm oil mill effluent in continuous stirred tank reactor showed that agitation at 200rpm produced highest VFAs as compared to that produced using agitation of 25, 50 and 100 rpm. The high con centration of VFA caused comparatively higher methane production.

2.4.5 Moisture content

Water content is essential for all biochemical reaction as it carries out all the biological process in microorganisms, locomotion absorption of nutrient and mass transfer (Heiske et al., 2015). Alnakeeb et al. (2017) studied the effect of moisture content on anaerobic digestion of tomato waste from kitchen and found that biogas production was 17% higher at 99% moisture content than that produced at 94.4%. In another study, a mass diffusion model assessed the effect of moisture content on anaerobic digestion and proposed that low moisture content resists augmented mass diffusion due to accumulation of hydrolytic products (Veluchamy and Kalamdhad, 2017).

2.4.6 Inoculation

Inoculum is essential for AD process to decrease lag phase of biogas production as it contains consortium of microorganisms. Without inoculum, the process will take time to start. The digestate from biogas plants are widely utilized source of inoculum. (Li et al., 2011; Ye et al., 2013). Cordoba et al. (2015) compared rumen, sewage sludge and stabilized swine waste water as inoculums for anaerobic digestion of swine waste water. Sewage sludge gave off comparatively higher biogas production with low lag time due to diversity in microbial consortia. Dhamodharan et al. (2015) investigated the effect of different livestock dung (cow, rhinoceros, piggery, poultry and goat) on anaerobic digestion of food waste and found out that methane production was higher when cow and piggery dung were used as inoculum as the microbes in their guts efficiently degrade food waste.

2.4.7 Nutrients

For microbes to efficiently carry out AD process, sufficient amounts of micro and micro nutrients are required. Micro nutrients are directly linked to the biochemistry of methane production. Appropriate nutrient addition or enhancement balancing of carbon to nitrogen (C/N) ratio has been shown to noticeably improve the methane yield (Nges et al., 2012a; Takashima etal., 2011). Codigestion also aids in nutrient balancing (Brown &Li, 2013). In a study where addition of Potassium (K), Magnesium (Mg), Zinc (Zn) and Manganese (Mn) during anaerobic digestion of kitchen waste was studied, it was found that addition of these nutrients individually didn’t improve the process significantly in terms of biogas production. However, when they were added together in optimized amounts, increase in biogas production was significant (Wu et al., 2016). In another study, manure, whey and fish ensilage was combined to balance carbon to nitrogen ratio which resulted in 84% higher methane production (Liu et al., 2017).

2.5 Anaerobic digestion types based on mode of operation

Two types of processes are most commonly used to operate biogas plants namely batch digestion and continuous digestion. Both two are explained below:

2.5.1 Batch digestion

In batch digestion, the digesters are fed once with substrate, inoculum and water at the start with the addition of a buffer solution to encounter pH changes during the digestion and then closed for the whole retention time. The gas production is low at the start and gradually increased to a maximum and then decreased to a constant. Batch digestion gives high degradation of substrates than continuous digestion as the substrate spend more time in digester than in continuous digestion (Carrere et al., 2016).

2.5.2 Continuous digestion

In continuous digestion, substrate is fed 1-8 times on daily basis depends upon the type of substrate. The freshly fed substrate takes the place of the old fed material thus maintaining the constant digester volume so relatively less time is available for the substrate to biodegrade as compared to batch digesters. Continuous feed type process provides constant gas production as compared to batch digestion (Wei et al., 2018).

2.6 Alkaline pretreatment effect on lignocellulosic composition and biogas yield

Alkaline pretreatment utilizes bases NaOH, KOH, $Ca(OH)_2$ and NH_4OH to solubilize mainly lignin and partially hemicellulose and to some extent cellulose rendering the biomass more prone to microbial attack. In the past alkaline pretreatment has been mainly consumed in paper and pulp industry. The working principle of alkaline pretreatment is known to be cleavage of linkage between carbohydrate and lignin and saponification (Paudel et al., 2017). When these cross links are removed, porosity of substance increases along with a surface area leading to swelling of the crystalline structure decreasing the crystallinity and degree of polymerization. NaOH is the most widely used alkali and has been extensively studied to improve biogas production from lignocellulosic biomass including corn stover, wheat straw, sugarcane bagasse, rice straw, woody materials sunflower stalks, sludge, oil palm empty and fruit branches (Sun et al., 2016).

Table 2 Effect of alkaline pretreatment on lignocellulose changes in biomass

Biomass	Pretreatment	Conditions	Lignin removal (%)	Hemicellulose removal (%)	Cellulose recovery (%)	Reference
Rice Straw	Alkaline	2% NaOH, 37°C, 5 days	88	30	102	Khalid et al., 2019
Silver Grass	Alkaline	35°C , 3 hours	12	16	23	Fu et. al., 2018
Rice Straw	Alkaline	1% NaOH, 35°C, 3 h	15	-	27	Shetty et al., 2017
Rice Straw	Extrusion, alkaline	3% NaOH, 35°C, 48 h	26	6	5	Zhang et al., 2015
Rice	Alkaline	2% KOH,	35	45	75	Remli et

Straw	with autoclaving	121°C, mins				al., 2014
Barley straw	Alkaline with radio frequency heating	1% NaOH, 70°C, 20 mins.	11	13	25	Iroba et al., 2013

Various studies have proven alkaline pretreatment to be effective in disruption of lignocellulose complex and consequently increase biogas production and methane yield as shown in Table 2. It is evident from the table that moderate conditions of pretreatment incorporating lesser time duration and mild temperature causes effective degradation of lignocellulose complex.

Table 3 Effect of alkaline pretreatment on biogas and methane yield enhancement of biomass

Biomass	Pretreatment Conditions	Mode of Digestion	Increase in biogas yield (%)	Increase in methane yield (%)	Reference
Rice Straw	2% NaOH, 37°C, 5 days	Batch	57	60	Khalid et al., 2019
Wheat Straw	2% NaOH, 37°C, 5 days	Batch	-	15	Mancini et. al., 2018
Napier Grass	2% NaOH, 35°C, 24 h	Batch	-	21	Kang et. al., 2018
Corn Stover	5% NaOH, 25°C, 1 day	Batch	-	81	Feng et. al., 2018
Rice Straw	1% NaOH, 35°C, 3 h	Batch	37	59	Shetty et al., 2017
Rice Straw	8% $Ca(OH)_2$, 25°C, 72 h	Batch	36	-	Gu et. al., 2015

Disruption of lignocellulose complex and increase in biogas and methane production as a result has been reported in many studies as shown in Table 3. It can be observed that alkaline pretreatment even at mild and less energy consuming conditions led to increased biogas production than raw substrate.

Though alkali pretreatment has been proven effective in lignin removal and exposure of holocellulose, still water is needed to neutralize the pretreated substrate. In addition, the utilization of NaOH pretreatment might cause Na+ ion inhibition of AD processes, especially methanogenesis. Additionally, the disposal of Na+-containing effluent from. AD systems could lead to negative environmental impacts such as soil salinization and water pollution.

Chen et al. (2014) has developed an integrated NaOH pretreatment process that includes NaOH recycling to improve biogas yield from grape pomace and rice straw. This process could help to reduce the pretreatment and mitigate the potential environmental pollution caused by waste Na+ disposal. Moreover, the recovery of lignin degraded products from NaOH solution is also being explored including production of high-value products from bio refinery perspective.

2.7 Photocatalytic degradation and biogas production from lignocelluloses

Heterogeneous photocatalysis technology is one of the most preferred and adopted routes among advanced oxidation processes (AOPs) in which generation of highly reactive radicals degrade various hazardous or unwanted compounds. Basic principle of heterogeneous photocatalysis involves utilization of a light source (usually in UV or near UV range) which photo excites the semiconductor as the absorbed photon energy exceeds the band gap resulting in transfer of electron from valence band to conduction band creating a positive hole in valence band referred to as electron-hole pairs (EHP). The generated holes either oxidizes the target specie or water to produce reactive radicals which act as oxidizing species as well hydroxyl radical, superoxide and hydroperoxy radical. Widely accepted routes discussed in literature are summarized as follows (Colmenares et al., 2009; Liu et al., 2019):

$$\text{Photo excitation: Photocatalyst} + h\nu \rightarrow p^{+} + e^{-}$$

$$\text{Oxygen ionosorption: } e^{-} + O_2 \rightarrow O_2^{-}$$

$$\text{Degradation via generated hole: } p^{+} + \text{Organic} \rightarrow CO_2$$

$$\text{Ionization of water: } p^{+} + H_2O \rightarrow HO^{\cdot} + H^{+}$$

$$\text{Degradation via hydroxide radical: } HO^{\cdot} + \text{Organic} \rightarrow CO_2$$

Protonation of superoxides:

$$O_2^{\bullet-} + H+ \rightarrow HOO$$

The hydroperoxyl radical formed in has also scavenging properties similar to O2 thus doubly prolonging the lifetime of photo hole:

$$HOO\bullet + e- \rightarrow HO_2$$

$$HOO- + H+ \rightarrow H_2O_2$$

Both the oxidation and reduction can take place at the surface of the photo excited semiconductor photocatalyst. Recombination between electron and hole occurs unless oxygen is available to scavenge the electrons to form superoxides (O2 •−), its protonated form the hydroperoxyl radical (HO2•) and subsequently H_2O_2.

Widely used semiconductors are TiO_2, ZnO, ZrO_2, SrO_2 ZnS, Fe_2O_3, CdS, etc. Titania dioxide (TiO_2) is one of the most commonly used photocatalyst having three phases namely anatase, rutile and brookite. Anatase is preferred due to comparatively high photolytic activity low cost, commercial availability, low toxicity and photostability and band gap of 3.23 eV which enables its working in near UV region (Stucchi et al., 2015). Several studies have utilized TiO_2/UV as pretreatment technology to degrade organic contaminants in water and air. TiO_2/UV process has proved to be successfully pretreat paper mill effluent, black liquor, and olive mill waste and applications in air purification units. (Gaya and Abdullah 2008). Moreover, nano science has taken over a vast area of science and technology due to added benefits. In photocatalysis, Nano sized catalyst are being widely explored due to added benefits including decrease in recombination of electron hole pairs as the diffusing charge carriers quickly reach the surface of particle to be degraded and increase in surface area increases interaction of target particle with catalyst (Vorontsov et al., 2018).

Table 4 Effect of photocatalysis degradation on biomass

Biomass	Pretreatment	Conditions	Lignin removal (%)	Cellulose recovery (%)	Reference
Coffee	Photocatalysis	10%Cu/TiO2,	41	-	Corro et al.,

pulp		sunlight, 7 h			2014
Rice Straw	Alkali assisted photocatalysis	3% NaOH, 2g/L TiO2, 1 h	69		Niu et. al., 2009
Rice straw	Chemical assisted photocatalysis	TiO2/UV/H2O2	13	12	Chang et. al., 2018
Newspaper	Chemical assisted sonication	NaOH, ultra-sonication	80	-	Subhedar and Gogate, 2013

Effect of titania degradation in presence of UV light has been extensively studied on commercially available lignin however studies on natural lignocellulose biomass are few and the mechanism is still obscure. However, related research focused mainly on degradation of commercial lignin models to access the effectiveness of titania photocatalysis on lignin degradation whereas, commercial lignin has comparatively less complicated structure than native biomass. However, it is proven that titania photocatalysis degrades dominant B-O-4 bond in lignin which constitutes 63% of lignin by weight (Colmenares et al., 2009). Studies on photocatalytic degradation of lignocellulose waste are shown in Table 4. Results show that photocatalysis with titania in very minute amounts can cause effective degradation of recalcitrant lignin which encapsulates digestible and fermentable sugars and carbohydrates.

Table 5 Effect of photocatalytic degradation on biogas and methane yield enhancement of biomass

Biomass	Pretreatment	Conditions	Mode of Digestion	Increase in biogas yield (%)	Increase in methane yield (%)	Reference
Wheat Straw	Photocatalysis	1.5% (w/w) TiO_2 , 3 h	Continuous	25	37	Alvarado-Morales et. al., 2016
Coffee pulp	Photocatalysis	10%Cu/TiO2, sunlight, 7 h	Batch	24	-	Corro et al., 2014
Sugarcane Bagasses	Photocatalysis	1 g/L nano titania, 1 h	Batch	-	101	Jafari and Zilouei, 2016
Rice Straw	Nanoparticles and alkali	2%NaOH, 120ppm Fe nanoparticles	Batch	100	129	Khalid et al., 2019

Table 5 showns enhancement in biogas and methane production as a result of photocatalytic degradation of different substrates. The enhancement is obvious. Combined effect of alkali and photocatalyst pretreatment on degradation of lignocellulose has been seldom studied. The results of one such study conducted by Niu et al. (2009) can be seen in Table 5. From this result, it is evident that alkaline pretreatment with photocatalyst assistance performed tremendously well in rendering cellulose for microbial consumption.

2.8 Summary

Discussed literature proves that biogas production through anaerobic digestion of rice straw is a viable option to sustainably decrease the energy deficit. However, in order to effectively utilize the biodegradable holocellulose, there is a need to break lignocellulose complex and increase accessibility of microbes to hemicellulose and cellulose. Apart from various pretreatment options available, alkaline and photocatalysis have proven to be comparatively economic and environmental friendly, as the temperature and chemical requirement is relatively less. Moreover, their impact on disruption of structured matrix is also effective as application of these pretreatments have considerably increased biofuel production. So in an attempt to appraise the qualities of NaOH and titania, these were used in comparatively lesser quantities as compared to previous studies and under less energy intensive conditions to observe impact on biogas production. In addition, application of titania nanoparticles, to further reduce catalyst amount as compared to published literature, was investigated.

3 MATERIALS AND METHODS

3.1 Feedstock and inoculum preparation

Rice Straw (RS) was collected from a field located in vicinity of Faisalabad Division in Punjab, Pakistan. It was then air dried for a week to reduce moisture content up to 10% followed by cutting and grinding. Ground rice straw was then passed through a sieve set to obtain particle size of around 1 mm which was then stored in air tight bags at room temperature. Inoculum used was a 1:1 mixture on dry weight basis of cow manure and anaerobic sludge. Cow manure was collected from an animal farm at Islamabad and anaerobic sludge consisted of sediments of constructed wetlands located at NUST, Islamabad. The inoculum mixture was incubated under mesophilic anaerobic conditions for a month under regular monitoring and degassing.

3.2 Preparation of titania nanoparticles

Titania nanoparticles (TiO_2 NPs) were prepared according to liquid impregnation (LI) method as described by Husnain et al. (2016). Following this method, 50 g of Titanium (IV) Oxide Anatase purchased from Daejung (Reagent Grade) was taken and added in 300 mL distilled water in a 1000 mL beaker. It was placed on a stirrer and was allowed to stir for 24 hours. The solution was then allowed to settle for another 24 hours followed by drying in an oven (Memmert, UNB-400, Germany) at 105°C for 12 hours. It was then crushed which was followed by calcination at 550°C in a muffle furnace (JSR, JSMF- 270H, Korea). The obtained powdered titania was allowed to cool down at room temperature in a desiccator. Size of nanoparticles was confirmed using Scanning Electron Microscopy (Tescan, Vega 3, Czech). SEM images showed that the prepared particles were relatively spherical in shape and uniform in size. Average size of prepared nanoparticles particles was in range of 47 to 60 nm. Energy dispersive X-ray spectroscopy linked with SEM indicated that there were no impurities in prepared nanoparticles and only titania and oxygen could be detected in range.

3.3 Pretreatment conditions

3.3.1 Alkaline pretreatment conditions

Rice straw was pretreated with NaOH concentrations of 0.5%, 1% 1.5%, and 2% w/v for 3 hours at solids to liquid ratio of 1:20 in 1 liter Pyrex bottles. The pretreatment was performed at 37°C in water bath (Memmert, WNB 7, Germany). After pretreatment, the mixture was filtered via Buchner Funnel and residue was washed with distilled water until the pH was neutralized. It was then dried at 60°C for 24 hours and was stored in air tight bags for further characterization and use in anaerobic digestion.

3.3.2 Photocatalytic pretreatment conditions

Photocatalytic pretreatment was performed at titania nanoparticles (TiO_2 NPs) doses of 0.1, 0.25, 0.5 and 1 g/L. Photocatalysis chamber consisted of 4 UV Lamps (4 x 100 watts) with spectrum range of 310 to 320 nm. Rice Straw (30 g) was placed in 1 liter beaker having 600 mL distilled water to maintain substrate to solvent ratio of 1:20. The required amount of titania was added to achieve the mentioned doses. To keep catalyst in continuous suspension and interacting with substrate surface, continuous stirring (120 rpm) was provided for the reaction time of 3 hours. After 3 hours, the suspension was taken out and washed with distilled water until filtrate became clear.

3.3.3 Alkaline-photocatalytic pretreatment conditions

For alkaline-photocatalytic pretreatment, all the concentrations of NaOH employed in alkaline pretreatment were used in combination with all the doses of titania nanoparticles used in photocatalytic pretreatment for further probing the impact on holocellulose. To maintain solids to liquid ratio of 1:20, 30 g rice straw was taken in 1 liter beaker and 600 mL solution having desired concentrations of NaOH and titania was added into it. The suspension was placed in UV chamber for 3 hours at 37°C and 120 rpm. Pretreated substrate was washed with distilled water until the filtrate was clear and its pH was 7.

3.4 Anaerobic digestion setup and design

Lab scale anaerobic digestion (AD) in batch mode was carried out for pretreated and raw rice straw to investigate the impact of pretreatments. On the basis of results of lignocellulose composition, all concentrations and doses used for individual alkaline and photocatalytic pretreatment were selected for AD while out of alkaline-photocatalytic pretreatment doses, combinations of all titania doses with 1.5% w/v NaOH which were used for AD on the basis of the obtained holocellulose content. Using 10 gVS/L organic loading and 75% working volume, 300 mL serum bottle reactors were filled with substrate and inoculum in ratio of 1:1 on gVS basis (2.25 gVS substrate and 2.25 gVS inoculum) while remaining volume was filled with distilled water. Sodium bicarbonate solution (1M) was added to the mixture till the pH reached 7.0 + 0.1. The reactors were then covered with rubber septa and sealed with aluminum caps by crimping. Nitrogen (N_2) gas was passed through headspace of digesters for 2 minutes by creating two ports in rubber septum with the help of syringes. The reaction bottles were then placed in an incubator (Velp Scientifica- FOC 120E Cooled Incubator, Italy) under mesophilic conditions at 37°C for 45 days. The reactors were manually mixed for 2-3 minutes daily and their biogas volume was recorded to calculate daily and cumulative biogas yield. Reactor bottles were prepared for raw and pretreated rice straw in triplicate. A set of blank reactors was also run alongside other reactors under same conditions to remove endogenous biogas production error from inoculum.

3.5 Analytical methods

Total solids (TS) and volatile solids (VS) were determined following ASTM standard method (ASTM, 2015). Total Kjeldahl Nitrogen (TKN) of the feedstock and inoculum was determined in accordance with APHA standard methods (APHA, 2017). Lignin, cellulose and hemicellulose contents were determined by chemical method as described by Li et al. (2004). Total Organic Carbon (TOC) was determined using formula suggested by Adams et al. (1951);

Organic carbon (%) = $\frac{VS\ (\%TS)}{1.8}$

To assess reactor stability before and after AD, samples were taken to analyze pH, VFA and alkalinity according to APHA standard methods (APHA, 2017). Effect of pretreatment on solids removal was also done by determining TS and VS before and after AD. Daily biogas volume was determined by water displacement method and was corrected to report results at normal temperature and pressure conditions. Methane content was analyzed at 20th, 30th and 40th day of digestion using Gas Chromatograph (Shimadzu, GC 2010 plus, Japan) with a thermal conductivity detector equipped with Molecular sieve 5A PLOT (Porous layer open tubular) column with Helium and Nitrogen as carrier gases.

3.6 Statistical analysis

All the experiments including the analysis of physical and chemical parameters of raw and pretreated substrate and inoculum were carried out in triplicate. Standard deviation was also determined. Single factor ANOVA (Analysis of variance) within confidence interval of 95%, was applied using Microsoft Excel to assess the impact of pretreatment on cumulative biogas yield.

Modified Gompertz model was applied to get kinetic model fitting of measured biogas production using the equation (Mu et al., 2006; Orozco et al., 2013):

$$y(t) = H_m . exp\left\{-exp\left[\frac{R_m . e}{H_m}(\lambda - \mathrm{t}) + 1\right]\right\}$$

Where y(t) is cumulative biogas production with respect to “t” (NmL /g VS) , Hm is maximum biogas potential (NmL /g VS), Rm is maximum biogas production rate (NmL /g VS /d) , e is Euler’s function taken as 2.72, **λ** is lag time (days) and t is anaerobic digestion time in days.

4 RESULTS AND DISCUSSIONS

4.1 Characteristics of rice straw and inoculum

Table 6 gives characteristics of rice straw and inoculum. TOC and TKN of rice straw and inoculum indicate that C/N ratio is very high for rice straw (150) and extremely low for inoculum (15.86). Very high C/N ratio of rice straw might have been adjusted by addition of inoculum rendering the mixture suitable for AD. Rice straw had comparatively higher volatile solids than inoculum. This is due to pre-incubation of inoculum. Yu et al. (2019) characterized cow dung for anaerobic digestion and found that TS, VS, TOC and TN were 23.89%, 62.87%, 32.89% and 1.89% respectively.

Table 6 Characteristics of rice straw and inoculum

Parameters	Rice Straw	Inoculum
Total Solids (%)^a	91.32 ± 0.25	12.55±2.05
Volatile Solids (%)^b	85.52 ± 0.01	57.96±1.54
Total Kjeldahl Nitrogen (%)^b	0.33 ± 0.03	2.03 ±0.77
Total Organic Carbon (%)^b	49.61 ± 0.04	32.20±1.99
Lignin (%)^b	19.70 ± 0.12	ND
Cellulose (%)^b	41.65 ± 1.04	ND
Hemicellulose (%)^b	37.30 ± 1.00	ND
Extractives (%)^b	2.30 ± 0.20	ND

^{a} On wet basis; ^{b} On dry basis; ND, not determined

Hemicellulose and cellulose, collectively known as holocellulose serve as food for microbes during AD. It constituted 78.95% of dry biomass which shows high potential for biogas production. Castro et al. (2017) characterized rice straw and found that it was composed of 17.5% lignin, 23.8% hemicellulose and 35.3% cellulose. The lignocellulose contents of rice straw vary throughout the world on basis of soil type, nutrient availability and time of crop harvesting (Arundale et al., 2015).

4.2 Effect of pretreatment on lignocellulose composition of rice straw

Changes in lignocellulose composition of rice straw after pretreatment are shown in Table 7. For NaOH pretreated RS, an increase in cellulose content is observed due to degradation of lignin and hemicellulose. Maximum cellulose content was observed for 2% w/v NaOH pretreated rice straw closely followed by 1.5% w/v NaOH pretreated RS. However, maximum lignin solubilisation was observed for 1.5% w/v NaOH pretreated RS followed by 2% and 1% w/v NaOH pretreated RS. Moreover, maximum holocellulose content was also observed for 1.5% w/v NaOH pretreated RS i.e. 81.65% indicating presence of comparatively higher biodegradable matter for biogas production. Many studies have reported considerable changes in lignocellulose composition of rice straw during alkaline pretreatment (Gu et al., 2015; Khalid et al., 2019; Shetty et al., 2017; Zhang et al., 2015). Khalid et al. (2019) reported increase in cellulose content upto 70.6% and decrease in lignin content upto 1.2% by pretreating rice straw with 2% NaOH for duration of 5 days at 37°C. Low lignin content as compared to this study was due to increased pretreatment time. Effectives of 1% w/v NaOH pretreatment on rice straw composition was reported by Shetty et al. (2017). He observed considerable decrease in lignin and hemicellulose content causing exposure of cellulose which lead to increase in biogas and methane production. NaOH's degradation mechanism involves dilapidation of ester bonds and cleavage of glycosidic linkages in the cell wall matrix of lignocellulose leading to alteration of lignin structure, breakdown of lignin

Table 7 Changes in lignocellulose composition of rice straw for different pretreatments

Pretreatment		Lignin	Hemicellulose	Cellulose	Holocellulose	Lignin Decrease	Hemicellulose Decrease	Cellulose Increase
% w/v NaOH	g/L TiO$_2$	%				%		
Raw RS	-	19.70±0.124	37.30±1.00	42.4±1.04	79.70	0	0	0
0.5	-	19.11±0.46	32.13±1.25	45.12±1.35	77.25	3	14	6
1	-	17.99±0.89	23.41±0.9	54.99±2.04	78.40	9	37	30
1.5	-	15.14±0.33	25.45±0.28	56.20±0.40	81.65	23	32	32
2	-	17.57±1.63	20.79±1.21	57.11±1.74	77.90	11	44	35
-	0	19.60±0.86	36.54±2.62	42.55±2.19	79.09	0.5	2	0.5
-	0.1	19.25±0.45	36.77±0.22	42.98±0.43	79.75	2	1	1
-	0.25	17.79±0.45	31.07±0.9	48.41±1.54	79.48	10	17	14
-	0.5	19.08±0.24	30.73±0.53	47.59±1.07	78.32	3	18	12
-	1	19.48±0.71	30.26±0.45	46.86±0.75	77.12	1	19	10
0.5	0.1	15.22±2.65	25.95±0.71	56.56±3.72	82.51	23	30	33
0.5	0.25	15.56±2.45	19.89±0.83	59.45±4.44	79.34	21	47	40
0.5	0.5	9.47±0.58	21.33±3,04	61.33±2.92	82.66	52	43	45
0.5	1	10.79±0.06	26.5±0.79	60.39±0.71	86.89	45	29	42
1	0.1	9.54±1.09	20.73±0.7	68.71±1.81	89.44	52	44	62
1	0.25	11.82±0.57	12.66±1.77	72.54±1.93	85.20	40	66	71
1	0.5	9.75±1.48	11.95±2.37	74.70±0.88	86.65	50	68	76
1	1	9.25±0.27	17.11±0.96	71.59±0.71	88.70	53	54	69
1.5	0.1	16.93±4.16	14.17±1.61	66.53±5.34	80.70	14	62	57
1.5	0.25	6.61±0.75	9.17±0.35	82.09±1.10	91.26	66	75	94
1.5	0.5	70.3±1.33	9.99±1.59	81.10±2.52	91.09	63	73	91
1.5	1	8.64±0.17	15.01±2.66	74.86±2.86	89.87	56	60	76
2	0.1	10.38±3.36	13.36±2.53	73.88±4.18	87.24	47	64	74
2	0.25	7.88±0.83	10.28±0.99	79.98±1.25	90.26	60	72	89
2	0.5	9.08±1.40	11.42±0.53	79.32±1.09	90.74	54	69	87
2	1	6.37±0.34	13.24±0.31	78.31±0.82	91.55	68	64	85

hemicellulose complex and saponification which causes swelling and decrystallization of cellulose (Fu et al., 2018; Paudel et al., 2017).

In case of photocatalytic pretreatment, degradation of lignin and hemicellulose causing resultant increase in cellulose availability is obvious. Minimum lignin and maximum cellulose content was observed for rice straw pretreated with TiO_2 NPs dose of 0.25g/L. Lignocellulose composition of RS pretreated at dose higher than 0.25g/L TiO_2 show less degradation of lignin. This is because UV rays are reflected and blocked by excessive particles beyond a critical value of nanoparticles dose (Chang et al., 2018). Effective degradation of lignin via titania photocatalysis and subsequent production of degradation products have been reported by several studies (Alvarado-Morales et al., 2017; Chang et al., 2018; Kang and Kim, 2012). Chang et al. (2018) studied photocatalytic degradation of rice straw by 1% w/v TiO_2 and inorganic oxidant (H_2O_2) for three hours and found cellulose recovery of 12%, hemicellulose degradation of 9% and lignin degradation of 14%. In another study, detrimental effect of titania photocatalysis caused generation of lignin degradation products including vanillic and ferullic acids indicating breakdown of complex lignin structure (Alvarado-Morales et al., 2017). Studies conducted on different lignin model compounds to understand the kinetics of lignin degradation via titania photocatalysis suggest that radical reactions take place via radial species including hydroxyl ($^{\bullet}OH$) radical which is responsible for scission of β-O-4 bond which is the dominant bond composing 35 – 50% by weight of lignin.

In case of alkaline-photocatalytic pretreatment of RS, substantial decrease in lignin content caused enormous availability of cellulose and hemicellulose i.e. holocellulose for biodegradation. In combination with 1.5% w/v NaOH, lignin degradation increased till titania dose of 0.25 g/L and then decreased slightly. This can be due to change in pH as a result of NaOH addition and carboxylic acid production during photocatalysis which leads to change in surface charge of substrate and catalyst causing possible titania adsorption on RS (Alvarado-Morales et al., 2017). Increase in alkalinity causes increase in oxidation efficiency of titania according to a study (Colemenares et al., 2009). Highest degradation of lignin was observed for the combination of 1.5% w/v NaOH with 0.25 g/L TiO_2. Maximum lignin and hemicellulose degradation was 66% and 75% respectively while cellulose availability increased by 94%. Niu et al. (2009) reported lignin and hemicellulose degradation of 68% and 53% respectively, while cellulose increased by 88% during alkali (3% wt NaOH) assisted titania (2g/L) photocatalytic pretreatment of rice straw. The reason behind such detrimental impact on lignocellulose can be explained by combined effect of NaOH and TiO_2. Swelling of cellulose and lignin solubilisation by NaOH aided in titania’s interaction with solubilized monomer sugars which were comparatively easy to oxidize due to small molecule size caused by depolymerization and increased surface area due to swelling of cellulose.

Lignocellulose degradation results show that alkaline-photocatalytic pretreatment rendered high cellulose and hemicellulose i.e. holocellulose availability for biodegradation. Change in composition was comparatively much high as compared to individual alkali and TiO_2 NPs pretreated rice straw. This can reduce environmental stress in terms of low chemical use since same alkali dosage i.e. 1.5% w/v NaOH exposes comparatively less holocellulose (82%) than when combined with TiO_2 NPs which increase holocellulose up to 80.70, 91.26, 91.09 and 89.87% for combination of 1.5% NaOH with 0.1, 0.25, 0.5, and 1 g/L TiO_2 respectively.

4.3 Effect of pretreatment on biogas production of rice straw

Figure 4 shows cumulative biogas production for all types of pretreatments. Raw RS exhibited cumulative biogas yield of 483 Nml/gVS. In case of alkaline pretreatment, cumulative biogas production of 654, 665, 724 and 720 NmL/gVS was observed at concentration of 0.5, 1, 1.5 and 2% w/v NaOH. Biogas production increased for all pretreated substrate subject to exposure of cellulose and hemicellulose contents caused by delignification and partial solubilization of hemicellulose. Increase in biogas yield was maximum for 1.5% w/v NaOH followed by 2% w/v NaOH which was 50% and 49% higher than that produced by raw rice straw. 1% w/v NaOH pretreated RS showed 38% increase in biogas production. As reported by Shetty et al. (2017), biogas was increased by 37% at 1% NaOH pretreated RS under similar conditions while further increase in concentrations (2, 3, 4, and 5% NaOH) exhibited lower yields.

a

Higher concentrations have reported to suppress microbial activity due to increase in concentration of Na^+ ions which exert osmotic pressure on microbial cells leading to dehydration and inactivity in anaerobic systems. Analysis of variance (ANOVA) on biogas production form alkali pretreated RS showed significant increase for all concentrations with respect to raw rice straw ($p < 0.05$)

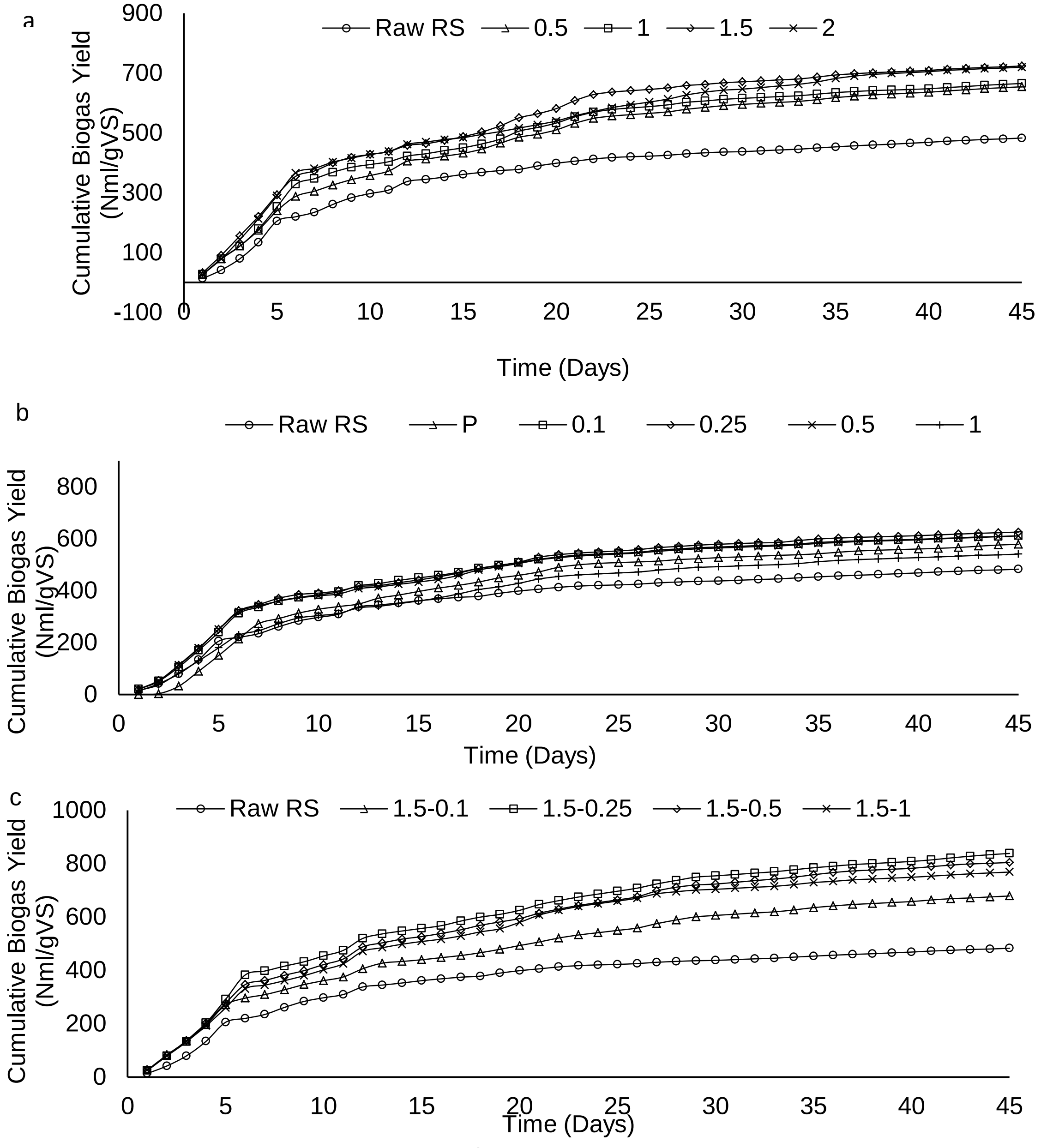


Figure 4 Cumulative biogas production from (a) NaOH (%w/v) pretreated RS (b) TiO2 (g/L) pretreated RS and (c) NaOH-TiO2 (% w/v- g/L) pretreated RS

Cumulative biogas production of 581,612, 626, 611 and 581 NmL/gVS was observed for rice straw pretreated with photolysis, 0.1, 0.25, 0.5 and 1 g/L TiO_2 respectively. Maximum biogas production was reported to be 30% higher than raw RS. At titania dose of 0.1, 0.25 and 0.5 g/L, biogas enhancement was significant ($p<0.05$) but at 0 (P) and 1g/L, increase was insignificant ($p > 0.05$) as compared to raw rice straw. Insignificant increase at higher dose is due to less degradation at titania dose above critical value of 0.25 g/L, causing reflection and blocking of ultraviolet (UV) rays due to presence of excessive titania particles (Chang et al., 2018).

If the trend of alkali and TiO_2 NPs pretreated RS is compared, alkali pretreated RS produced higher biogas yield. Comparison of biogas yield from optimum doses for alkaline pretreatment i.e. 1.5% w/v NaOH and photocatalytic pretreatment i.e. 0.25g/L TiO_2 shows 1.15 times higher biogas yield at 1.5% NaOH than 0.25 g/L TiO_2. The difference is attributed to attack mechanism of NaOH and TiO_2 on lignocellulose matter giving off different holocellulose content for microbial degradation. Titania photocatalysis assisted degradation is limited to surface activity and known for depolymerization of lignin under mild conditions (Alvarado-Morales et al., 2017). NaOH mediates glycosidic side chains and ester leading to lignin removal and swelling of structure causing increased porosity and surface area availability for microbial attack. It also degrades acetyl and different uronic acid substitutions on hemicellulose which are known to limit biodegradability of sugars by causing hindrance to enzyme accessibility. This extra function by NaOH causes comparatively higher degradation leading to higher holocellulose content and biogas and methane production (Loow et al., 2016).

Alkaline-photocatalytic pretreatment increased the biogas production manifold as compared to untreated, alkali and TiO_2 NPs pretreated RS. The maximum biogas yield was 838 NmL/gVS for dose of 1.5% NaOH-0.25g/L TiO_2 while lowest yield was 679 NmL/gVS for 1.5% NaOH-0.1 g/L TiO_2. Ultimate biogas yield for 1.5% NaOH-0.25 g/L TiO_2 was 74%, 16% and 34% higher than raw, 1.5% NaOH pretreated and 0.25 g/L TiO_2 NPs pretreated RS respectively. High degradation with alkaline-photocatalytic pretreatment can be explained by combined behavior of NaOH causing lignin solubilisation and partial hemicellulose degradation followed by further disintegration of molecular structure by titania nanoparticles, as described in section 3.2. One-way ANOVA indicated significant increase ($p<0.05$) in biogas production in case of alkaline-photocatalytic pretreatment as compared to raw rice straw.

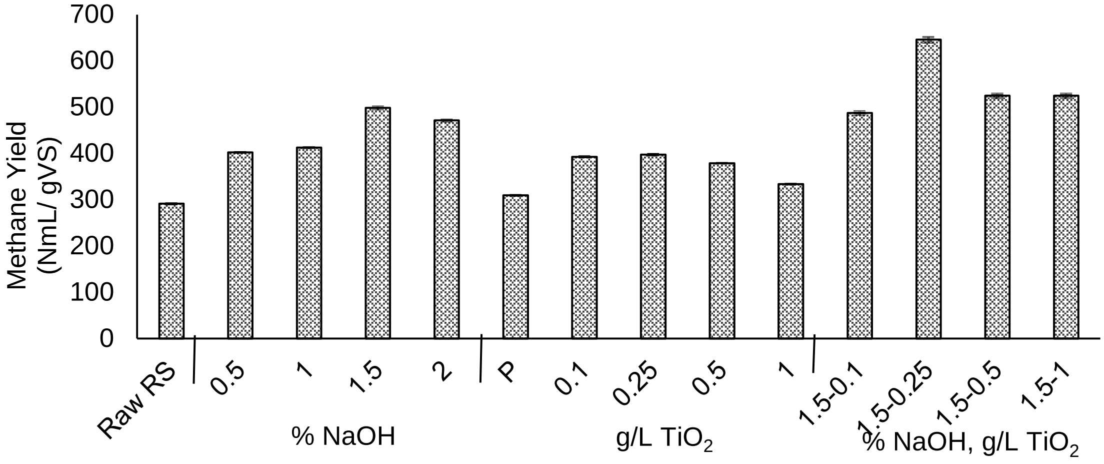
4.4 Effect of pretreatment on methane yield of rice straw

Methane yield of raw and pretreated rice straw is shown in Figure 5. Methane yield of raw RS was 291 Nml/gVS. Alkaline pretreated RS produced methane yield of 402, 413, 498 and 471 NmL/gVS at 0.5, 1, 1.5 and 2% w/v NaOH respectively. Maximum methane yield enhancement of 71% was observed at 1.5% w/v NaOH followed by 62% for 2% w/v NaOH pretreated RS. Decrease in methane yield for 2% w/v NaOH pretreated RS can be attributed to inhibition effect caused by Na^+ ions on methanogens which, in spite of having more cellulose content availability in 2% NaOH pretreated RS, led to decrease in methane yield (Hierholtzer and Akunna, 2012). Studies on alkaline pretreatment of lignocelluloses conclude positive impact on methane yield (Shetty et al., 2017; Khalid et al., 2019; Zhang et al., 2015). Shetty et al. (2017) reported 70.94% and 48.45% increase in methane yield for 1% and 2% w/v NaOH pretreated rice straw, respectively. Khalid et al. (2019) reported 60.39% increase in methane yield than control for 2%w/v NaOH pretreated rice straw.

For TiO_2 NPs pretreated rice straw, highest methane yield of 397 Nml/gVS was observed for 0.25 g/L dose of titania which was 36% greater than raw RS. Further increase in dose resulted in decrease in methane yield which might be due to reasons associated with light dispersion above a critical dose and low consequent photocatalytic activity. Degradation of wheat straw and subsequent methane yield was studied by Alvarado-Morales et al. (2017) who observed 37% increase in methane yield by application of photocatalysis using 1.5%w/w TiO_2 for 3 hours. Studies on titania assisted photocatalytic degradation on natural lignocellulose for enhancing bioethanol and enzymatic hydrolysis have also shown its ability to effectively degrade the complex matrix and make available the precursors for formation of bioethanol and other related products (Chang et al., 2018; Kang and Kim, 2012).

Figure 5 Methane yield of raw and pretreated rice straw

In case of alkaline-photocatalytic pretreatment, highest methane yield of 645 NmL/gVS was obtained at the combined dose of 1.5% w/v NaOH-0.25 g/L TiO_2, which was 122% higher than raw RS. As compared to individual alkaline and photocatalytic pretreatment, most of the doses of alkaline-photocatalytic pretreatment exhibited significantly enhanced methane yields. High methane yield is due to extremely low recalcitrant lignin content and high sugars i.e. hemicellulose and



cellulose due to excessive degradation caused by combined effect of NaOH and titania photocatalysis. Combined effect of alkali and titania photocatalysis hasn't been explored sufficiently. However, a study conducted by Niu et al. (2009) reported combined effect of alkaline and photocatalytic pretreatment on rice straw hydrolysis. The study affirmed the high exposure of holocellulose due to delignification and swelling by NaOH assisted by photocatalytic degradation of exposed area, to be the reason behind enhanced hydrolysis.

4.5 Biogas production data validation for raw and pretreated rice straw

The results of kinetic model fitting by Modified Gompertz Model are shown in Table 8. The correlation coefficients exceeded 0.994 for all the pretreatments. It is evident from results that experimental values of biogas production match well with model predicted values.

Pretreatment	R_m (mL /g VS /d)	P_b (NmL /g VS)	λ (days)	R^2
Raw RS	63.33	482.03	1.85	0.9987
0.5% w/v NaOH	64.77	654.23	1.50	0.9986
1% w/v NaOH	76.43	663.95	1.42	0.9986
1.5% w/v NaOH	78.14	723.84	1.03	0.9987
2% w/v NaOH	69.08	719.80	1.11	0.9957
0 g/L TiO_2	60.30	528.11	1.73	0.9980
0.1 g/L TiO_2	74.49	611.85	1.18	0.9985
0.25 g/L TiO_2	72.77	625.91	1.4	0.9977
0.5 g/L TiO_2	69.51	611.08	1.28	0.9972
1 g/L TiO_2	50.39	541.03	1.46	0.9985
1.5% w/v NaOH, 0.1 g/L TiO_2	71.17	678.79	0.59	0.9992
1.5% w/v NaOH, 0.25 g/L TiO_2	93.04	838.34	0.42	0.9996

1.5% w/v NaOH, 0.5g/L TiO_2	79.19	804.54	0.61	0.9994
1.5% w/v NaOH, 1 g/L TiO_2	76.66	768.47	0.71	0.9995

Table 8 Kinetic parameters of Modified Gompertz model for raw and pretreated rice straw

Among three pretreatment types, the shortest lag time was observed for alkaline-photocatalytic pretreatment and biogas production rate for the same pretreatment was higher as compared to alkali and TiO_2 NPs pretreated rice straw. This is due to high microbial access to increased content of holocellulose made readily available as a result of pretreatment. Rice straw pretreated with 1.5% NaOH-0.25g/L TiO_2 gave maximum cumulative biogas production and daily production rate with the shortest lag time. Kinetic models are mathematical expression used to related measured response with time under specified environmental condition. Modified Gompertz model is one such expression used to predict biogas production under certain conditions and determine critical process parameters (Gil et al., 2006). Many studies concluded modified Gompertz model to be one of the most suitable kinetic model to predict and study changes associated with biogas production during anaerobic digestion (Deepanraj et al.,2015; Rajput et al.,2018). Rajput et al. (2018) compared modified Gompertz model, transference and logistic function and concluded that modified Gompertz model gave

best fitted results for biogas production from thermally pretreated wheat straw.

Deepanraj et al. (2015) compared Gompertz model, logistics function and modified Gompertz model to predict kinetic parameters for anaerobic digestion of foodwaste and to study the effect of pH and total solids concentration. He also concluded modified Gompertz model to provide relatively perfect fit for biogas production as compared to Gmopertz model and logistic function.

4.6 Reactor stability under different pretreatments

Table 9 shows reactor stability parameters including pH, volatile fatty acids (VFA), alkalinity and VFA/Alkalinity. pH is one of the most considered stability parameter which shows the condition of anaerobic digestion process. The reactions brought by fermentative microbes in reactor varies with pH range of 4.0 to 8.5. However, methanogenesis takes place in neutral range i.e. 6.8-7.2 (Ye et al., 2013). In this study, at the end of experimental run, pH of all reactors were in neutral range. However, in case of buffer addition, pH might not be the only stability parameter because of enhanced resistance to pH change within the reactor due to the formation of VFAs (Björnsson et al., 2000). Alkalinity, which is the capacity of an aqueous solution to neutralize acids (Neshat et al., 2017), can be used as a parameter to judge the reactor’s stability. In this study, the alkalinity of all the reactors were above appropriate i.e. above 2000 mg/ L. VFAs produced during acidogenesis stage of anaerobic digestion are ingested by methanogens creating dynamic balance (Wang et al., 2016).

The suggested VFA values for a healthy AD system is <1500 mg/L (Neshat et al., 2017) and values of VFAs in all the reactors of the present study are within the recommended limits. It is evident from table that VFAs in reactors exhibiting high methane content and biogas yield are less than raw rice straw. It is clear from these values that comparatively higher amount of substrates were utilized in pretreated sample by methanogens to produce methane gas which also conforms to methane results.

Table 9 Reactor stability parameters as affected by different pretreatments

Pretreatment Doses		pH		VFA mg/L		Alkalinity mg/L		VFA/ Alkalinity	
NaOH %w/v	TiO_2 g/L	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Raw RS		7.1	7.1	111	839	1189	2956	0.09	0.28
0.50	-		7.3	123	389	1150	2517	0.11	0.15
1.0	-		7.1	228	356	1311	2672	0.17	0.13
1.5	-		7.2	133	339	1267	2617	0.11	0.13
2.0	-		7.6	139	320	1011	2283	0.14	0.14
-	0		7.1	117	722	1209	2750	0.10	0.26

-	0.1	7.1	110	578	1100	2583	0.10	0.22
-	0.25	7.2	150	550	1056	2611	0.14	0.21
-	0.5	7.4	166	633	1467	2528	0.11	0.25
-	1	7.1	244	617	1250	2361	0.20	0.26
1.5	0.1	7.3	261	339	1622	2333	0.16	0.15
1.5	0.25	7.3	156	328	956	2417	0.16	0.14
1.5	0.5	7.2	222	317	1189	2528	0.19	0.13
1.5	1	7.2	256	367	1478	2444	0.17	0.15

VFA/Alkalinity ratio is considered an important parameter in anaerobic digestion as the ratio tells about the relative amounts of VFA and alkalinity in digesters. The VFA/Alkalinity ratio for all the digesters was within optimum range i.e. <0.4 (Wang et al., 2016). Final VFA/Alkalinity ratio of raw RS show comparatively higher VFA yet to be ingested by methanogens than pretreated RS. Comparison of final VFA/Alkalinity ratios show similar values for alkaline and alkaline-photocatalytic pretreatment, while values were higher for TiO_2 NPs pretreated RS. This indicates high amount of VFA in case of TiO_2 NPs pretreated RS, still to be utilized by microbes which could have been left undigested due to delay caused by presence of comparatively high lignin content and less accessibility to holocellulose.

4.7 Effect of pretreatment on solids removal

Figure 6 shows total and volatile solids (TS and VS) removal for raw and pretreated rice straw. TS and VS removal for rice straw was 64% and 71% respectively. Volatile solids removal for untreated RS was higher as compared to previous studies by Khalid et al. (2019), Abudi et al. (2016) and Ye et al. (2013) reporting 63%, 51% and 58% VS removal respectively. In case of alkaline pretreatment, TS and VS removal were increased by 26 and 31% for 1.5% w/v NaOH pretreated RS. This concentration of NaOH also gave off highest biogas production due to least percentage of lignin and highest holocellulose availability.

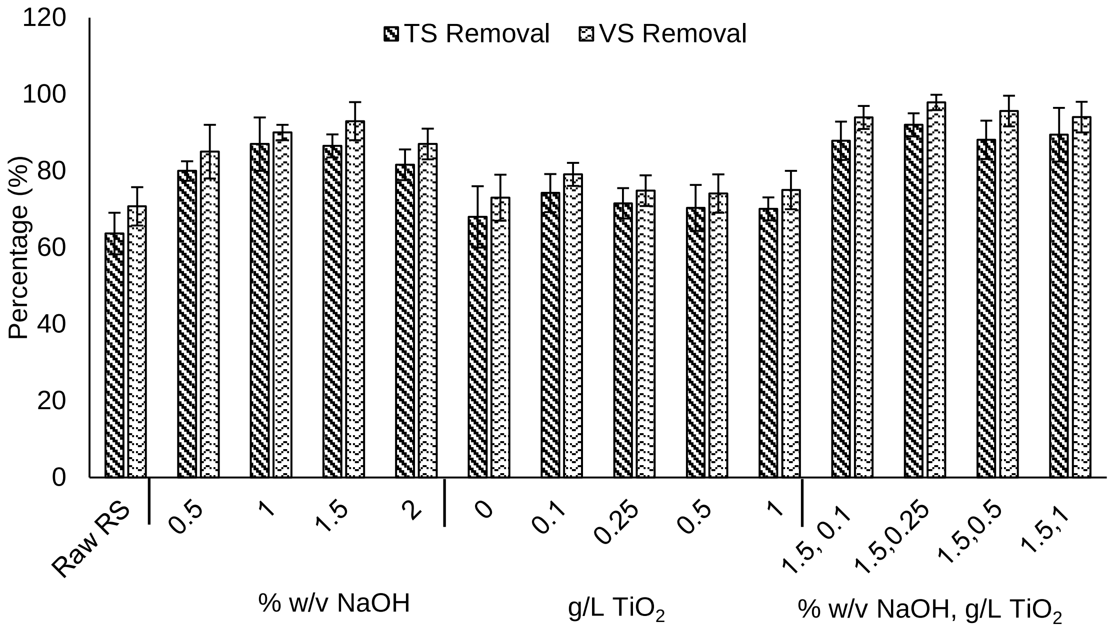


Figure 6 Effect of pretreatment of RS on solid removal during anaerobic digestion

In case of TiO_2 NPs pretreated RS, maximum solids removal was observed for dose of 0.25 g/L TiO_2, which also exhibited highest biogas yield among all doses of photocatalytic pretreatment. Rice straw pretreated with 0.25 g/L TiO_2 has comparatively less lignin and higher holocellulose content as compared to rice straw pretreated with other titania doses. In case of alkaline-photocatalytic pretreatment, TS and VS removal was higher as compared to individual alkaline and photocatalytic pretreatment. Highest TS and VS removal of 92% and 98% was reported for dose of 1.5% w/v NaOH-0.25g/L TiO_2 pretreated RS. Previous studies on pretreatment of lignocellulose for biogas production reported increase in volatile and total solids removal for pretreated substrates showing increased biogas and methane production (Chandra et al., 2012; Khalid et al., 2019). Khalid et al. (2019) reported TS and VS removal of 89 and 97% respectively for rice straw pretreated with 2% NaOH and dosed with 120ppm magnetite nanoparticles. Overall, TS and VS removal in three pretreatment case were in conformity with biogas and methane yield which shows that more volatile solids and total solids were converted to biogas and methane for pretreated substrates due to presence of high cellulose and low lignin content.

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

- In case of alkaline pretreatment, maximum holocellulose content and minimum lignin content was observed for 1.5% w/v NaOH pretreated RS. As a result of these changes in lignocellulose composition biogas production enhancement of 50% and methane yield enhancement of 43% was observed.
- Among TiO_2 NPs pretreated rice straw, 0.25 g/L titania pretreated RS showed highest biogas and methane production which was 30 % and 22% higher than raw RS. This increase was due to lignin removal of 10% and holocellulose content of 79.48%.
- Alkaline-photocatalytic pretreatment showed substantial degradation of lignocellulose complex as compared to individual alkaline and photocatalytic pretreatments. Methane production for RS pretreated at dose of 1.5% w/v NaOH- 0.25 g/L TiO_2 was 1.3 and 1.62 times higher than maximum methane production values for alkali and TiO_2 NPs pretreated RS respectively. Biogas and methane enhancement was 74% and 122% suggesting effectiveness of alkaline-photocatalytic pretreatment.
- Combined pretreatment with alkaline-photocatalytic dose of 1.5%w/v NaOH and 0.25 g/L TiO_2 was comparatively more effect in biogas and methane yield enhancement.

5.2 Recommendations

- Recovery of lignin from waste stream of alkaline pretreatment for further synthesis of lignin derived products
- Devise of easy chemical recovery methods
- Immobilization of titania for degradation of natural lignocellulose
- Investigate further enhancement in biogas production by co-digestion of pretreated rice straw with other substrates for example food waste, solid waste or sludge that could bring the C/N ratio within optimum range.

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