Comparative analysis of the effects of different pretreatment methods on methane yield of groundnut shells

Kehinde O. Olatunji*
Daniel M. Madyira
Department of Mechanical Engineering Science,
Faculty of Engineering and the Built Environment,
University of Johannesburg, South Africa.
***Corresponding author: olaoladoke293@gmail.com**

Centre for Renewable and Sustainable Energy Studies

Abstract

Groundnut shells are one of the abundant lignocellulose feedstock with a high composition of lignin, hemicellulose, and cellulose. Cellulose is tightly embedded in the lignin and hemicellulose, leading to lignification and crystallization, high resistance to methanogenic bacteria, and more recalcitrant during anaerobic digestion. Therefore, an appropriate pretreatment method is required to break down the heterogeneous matrix and make the hemicellulose and cellulose accessible to microorganisms. This study investigates the effects of thermal, nanoparticle additives, and combined pretreatments on the methane yield of groundnut shells. Groundnut shells were pretreated using conventional heating at 100 °C for 30 min, addition of 20 mg/L of Fe_3O_4 nanoparticles and a combination of particle size reduction with 20 mg/L of Fe_3O_4 nanoparticles. They were subjected to anaerobic digestion in a lab-scale batch digester for 30 days at mesophilic temperature (37 °C). The result showed the cumulative methane yield of 31.07, 79.59, 98.01, and 23.69 ml/g VS_{added} for thermal, Fe_3O_4 additives, combined pretreatments, and untreated groundnut shells, respectively. This study confirmed that appropriate pretreatment methods improve the methane yields of lignocellulose feedstocks, and combined pretreatments released the highest methane yield. This result can be replicated at the industrial scale to establish its economic reality.

Keywords: Anaerobic digestion, lignocellulose materials, groundnut shells, pretreatment methods, methane yield.

1. Introduction

Waste and biodegradable, renewable materials have been reported to have the capacity to provide the global energy needs, and they have been producing a significant percentage of energy needs in recent years (Korbag *et al.*, 2020). The search for an alternate energy source to substitute fossil fuels because of its price increase and environmental challenges has recently been the primary research focus in the energy sector (Abdel-Shafy and Mansour, 2018). The production and application of renewable energies from readily available materials is another major concern in the energy sector. Substituting fossil fuels with biofuel has been regarded as one of the best options due to its biodegradability, non-toxic, lower pollution, and renewability (Gumisiriza *et al.*, 2017). Biogas is one of the brightest biofuels among the alternative sources identified because it is a second-generation biofuel that does not compete with food sources. Biogas is the product of the anaerobic digestion of organic materials in the absence of oxygen, and it is a composition of mainly methane, carbon dioxide, and other mixtures in traces

(Harasimowicz *et al.*, 2007). Lignocellulose materials are one of the biogas feedstock that offers attractive renewable origins and higher biogas production potential (Jekayinfa *et al.*, 2020). In several countries, especially developing countries, lignocellulose materials are abundant as residues from agricultural activities. Groundnut shells, wheat straw, rice straw, maize streak, sorghum stalk, cow dung, pig slurry, oil cakes, etc. are some of the agricultural residues that can be employed for biogas production (Dahunsi, Oranusi and Efeovbokhan, 2017; Ogunkunle, Ahmed and Olatunji, 2019; Kehinde O. Olatunji, Ahmed, *et al.*, 2022).

Lignocellulose feedstocks are rigid in structure and embedded in a carbohydrate polymer matrix enclosed mostly by cellulose and hemicelluloses. They are cross-linked and attached firmly to lignin. This complex arrangement is referred to as recalcitrance characteristics, which hinder the enzymatic hydrolysis of the feedstocks during anaerobic digestion (Pu *et al.*, 2013). Therefore, appropriate pretreatment is needed to break down the heterogeneous matrix, improve surface area and crystallinity, and unbundle the carbohydrate from their lignin association, thus improving enzymatic hydrolysis and subsequent biogas yield (Olatunji, Ahmed and Ogunkunle, 2021). Various pretreatment techniques have been experimented with and reported to be effective in feedstock pretreatment. They are categorized as biological, chemical, physical, nanoparticle additive, thermal, or a combination of two or more methods (Rabemanolontsoa and Saka, 2016). The morphological arrangement and resistance of each lignocellulose feedstock vary with pretreatment methods, which requires appropriate pretreatment methods depending on the characteristics of each feedstock (Karagöz *et al.*, 2012). The thermal pretreatment method is when the feedstocks are subjected to high temperatures. When the feedstock is subjected to high temperature, lignin and hemicellulose start to solubilize, and their characteristics and structural arrangement are ascertained by the branching groups of the hemicellulose (Olatunji, Ahmed and Ogunkunle, 2021). Wheat straw was thermally pretreated with conventional heating at 120 °C for 30 min, and the biogas yield was improved by 64.3%. On the contrary, maize stalks pretreated with conventional heating at 120 °C for 30 min showed no effect on the biogas released (Menardo, Airoldi and Balsari, 2012). Hydrothermal pretreatment of rice straw at 100 °C for 10 min improves the biogas yield by 204.35% (Luo *et al.*, 2019).

A recent interdisciplinary study in nanostructure science and technology has noticed that nanoparticles have the strength to revolutionize the structure of biogas feedstocks and enhance feedstock availability for enzyme attack (Ramakrishna *et al.*, 2018). Therefore, nanoparticles can be used to immobilize the enzymes and improve their activities during anaerobic digestion, and they are called nanocatalysts (Zdarta *et al.*, 2018). The study has shown that several nanoparticles can be reacted and/or absorbed with feedstock cell membranes and disintegrate them (Basso *et al.*, 2007). When fresh manure was pretreated with 20 mg/L of 7 nm Fe_3O_4, biogas yield was improved by 73%, and methane enhanced by 115.66% (Duc, 2013). But when the same fresh manure was pretreated with 1 mg/L of 28 nm Co, biogas and methane yield were improved by 71 and 45.92%, respectively (Abdelsalam *et al.*, 2016). The influence of ZnO was experimented with during the anaerobic digestion of sludge from UASB, and a 65% decrease in biogas was recorded (Duc, 2013). Fe_2O_3 additives on waste-activated sludge increase methane yield by 117% (Wang *et al.*, 2016), but applying ZnO on waste-activated sludge produces no effect (Mu *et al.*, 2012). The influence of nanoparticle additives during anaerobic digestion has a different impact on biogas and methane yields.

Groundnut shells have been reported to consist of cellulose, hemicellulose, and lignin, making it a complex organic polymer crystal structure (Kehinde Oladoke Olatunji *et al.*, 2022). Compared to sucrose and starch, which can be easily disintegrated into carbohydrates, lignin and hemicellulose present in groundnut shells are strongly embedded in the cellulose, leading to lignification and crystallization, which create a barrier to microorganisms' accessibility to cellulose and make the cell wall more recalcitrant during hydrolysis stage of anaerobic digestion. Therefore, appropriate pretreatment techniques are required to break down the heterogeneous matrix and partially eliminate the lignin content to improve the cellulose surface area and porosity. This assists in the degradation and transformation of groundnut shell feedstocks into biogas and methane yields (Olatunji, Ahmed and Ogunkunle, 2021). Nonetheless, few works of literature are available on the influence of pretreatment methods by thermal and nanoparticle additives and the methane yield of pretreated groundnut shells as a feedstock for anaerobic digestion. In this study, thermal pretreatment, nanoparticle additives, and combined particle size and nanoparticle additives were examined for considerable methane generation. The influence of pretreatment methods on methane yields released during anaerobic digestion was examined. Furthermore, the most effective pretreatment method was ascertained when methane released during anaerobic digestion was compared, which presents efficient technical assistance for the pretreatment methods to improve the anaerobic digestion of groundnut shells.

2. Materials and methods

Groundnut shells used for the experiment were sourced locally, and inoculum was collected from an existing biogas digester used to digest cattle dung and kitchen waste at ambient temperature. The thermal pretreatment method employed for this study is conventional thermal pretreatment (autoclaving), as reported by Bolado-Rodríguez *et al* (Bolado-Rodríguez *et al.*, 2016). The input variables for the study were temperature (°C) and exposure time (min). Autoclaving of groundnut shells was experimented with using a temperature of 100 °C for 30 min exposure time, the previously reported optimum pretreatment condition for groundnut shells (Kehinde O. Olatunji, Madyira, *et al.*, 2022). Dry groundnut shells were slurried for 5 min in deionized water in a solid: liquid ratio of 1: 10 w/w before autoclaving using the selected treatment conditions. At the expiration of the exposure time, the mixture was allowed to cool down to room temperature. The slurry formed was filtered and oven-dried at 45 °C for 24 h. the sample was then cooled and kept in a plastic bag at 4 °C for physicochemical analysis and anaerobic digestion. Another batch of groundnut shells was subjected to particle size reduction with a hammer mill with a varying screen size of 6 mm. The particle size was selected based on the previous recommendation by earlier researchers (Jekayinfa *et al.*, 2020).

Anaerobic digestion of groundnut shells was carried out on a laboratory scale as prescribed in European Standard (organischer Stoffe Substratcharakterisierung, 2016). Round bottom narrow neck flask bottles of 1-L served as the digester. This was connected to calibrated gas bottles that served as gas storage, and the gas was collected using the water displacement method. Ten digester bottles were fed with the recommended amount of stable inoculum, and the quantity of substrate added was calculated using equation 1. Two bottles were fed with thermally pretreated groundnut shells and denoted ‘A’, while another two bottles were fed with untreated groundnut shells and labeled ‘B’. Two of the remaining digesters were filled with groundnut shells reduced to 6 mm and labeled ‘C’, while another two digesters were fed with untreated groundnut shells and labeled ‘D’. The remaining two digesters were digested with only inoculum and served as a parallel experiment to ascertain the gas produced by the inoculum. The gas released by this set of the digester was removed from the gas released by digesters A – D. For digesters B and C, 20 mg/L of Fe_3O_4 (< 50 nm) was added as recommended by Abdelsalam et al (Abdelsalam *et al.*, 2016). As reported previously, this quantity of Fe3O4 was adopted due to its capacity to enhance biogas yield compared to other metal nanoparticles. All the digester bottles were carefully arranged in a thermostatic water bath preset at mesophilic temperature (37 ± 2 °C) and maintained the temperature throughout the experiment. The experiment was on for 30 days, and the following data were taken daily: time, temperature, pressure, gas volume, and the gas composition was taken at intervals depending on the volume of gas released using gas analyzer (Geotech, GA5000, Warwichshire, UK). The experiment was replicated twice as recommended and the digesters were shaken manually twice a day to break the scum and sediments formed. Gas yield was calculated as demonstrated in VDI 4630 as presented in equation 2 – 5 (organischer Stoffe Substratcharakterisierung, 2016).

$$M_s = \frac{M_i C_i}{2C_s} \quad (1)$$

Where: M_s = Mass of substrate (g), M_i = Mass of inoculums (g), C_s = Concentration of substrate (%), C_i = Concentration of inoculum (%).

Inoculum required is 80% of the reactor volume (organischer Stoffe Substratcharakterisierung, 2016).

$$Biogas\ yield\ (mlg^{-1}\ VS_{added}) = \frac{Biogas\ (Nml)}{Mass\ (g)} \quad (2)$$

$$Biogas\ (Nml) = Biogas\ (Nml) - Control\ (Nml)$$

$$Biogas\ (Nml) = Biogas\ (ml) X\ F$$

$$Gas\ Factor\ (F) = \frac{(P - P_{H_2O})\ x\ T_O}{(t + 273.15)\ x\ P_o} \quad (3)$$

Where F = Gas factor, P = Air Pressure, P_o = Absolute Pressure (1013.25 mbar), T_o = Absolute Temperature (273.15 K), t = Gas temperature (°C).

$$P_{H_2O} = y_o + a.e^{bt} \quad (4)$$

Where: y_o = -4.3905; a = 9.762 and b = 0.0521

$$Methane\ (mlg^{-1}\ VS_{added}) = \frac{biogas\ yield\ X\ CH_{4\ corrected}}{100} \quad (5)$$

3. Results and discussion

3.1 Influence of pretreatments on daily methane yield of groundnut shells

The daily methane yield of groundnut shells pretreated thermally, Fe_3O_4 nanoparticle additives, and combined particle size reduction and Fe_3O_4 nanoparticle additive after 30 days retention time is shown in Figure 1. The Figure showed that thermal pretreatment produced the highest daily methane yield of 7.65 ml/g VS_{added} on day 2 of the experiment. This was followed by combined pretreatment and Fe_3O_4 nanoparticle additives. It can be noticed that all the pretreatments methods released higher daily methane yield compared to untreated groundnut shells. This result supports the earlier studies that appropriate pretreatment methods increase the methane yield of lignocellulose feedstocks (Zabed *et al.*, 2019; Olatunji, Ahmed and Ogunkunle, 2021). The result shows that the thermal pretreatment method released the highest daily yield; this can be traced to the ability of the heat to remove/redistribute the lignin portion of the feedstock and expose the cellulose and hemicellulose to enzymatic attack and lower the digestion time (Şenol, Erşan and Görgün, 2020). The daily methane yield from this pretreated substrate could be noticed to release their methane yield within the first 7 days of the experiment. This is because the pretreatment has solubilized the lignin portion of the substrate, positively affects the delignification and hemicellulose polymerization, and results in better biodigestibility (Bianco, Şenol and Papirio, 2021; Şenol, 2021). Treatments B and C also show improved daily methane yield compared to the control (treatment D) due to Fe_3O_4 nanoparticles piercing the substrate and making them accessible to methanogenic bacteria. Adding trace metals to the anaerobic digestion process provides some essential nutrients to the microorganisms, which helps them stimulate and stabilize the process (Romero-Güiza *et al.*, 2016; Xu *et al.*, 2019). The application of Fe nanoparticles lowers the hydrogen sulphide significantly and improves the methane yield (Su *et al.*, 2013). Treatment C, combining particle size reduction with Fe_3O_4 nanoparticle additives, shows better daily methane yield than a single pretreatment of Fe_3O_4 nanoparticle additives. This can be traced to the increase in surface area of the substrate after particle size reduction. It increases the level of attachment of the Fe particles on the substrate and, at the same time, increases the surface area for microbial activities (Lindmark *et al.*, 2012). Compared to other methods, the tendency for the thermal pretreatment to produce inhibitory compounds is very high, especially at higher treatment temperatures (Jiang *et al.*, 2015). But for the addition of the nanoparticles, the chances of having inhibitory compounds are very low when the appropriate quantity of the nanomaterials is used.

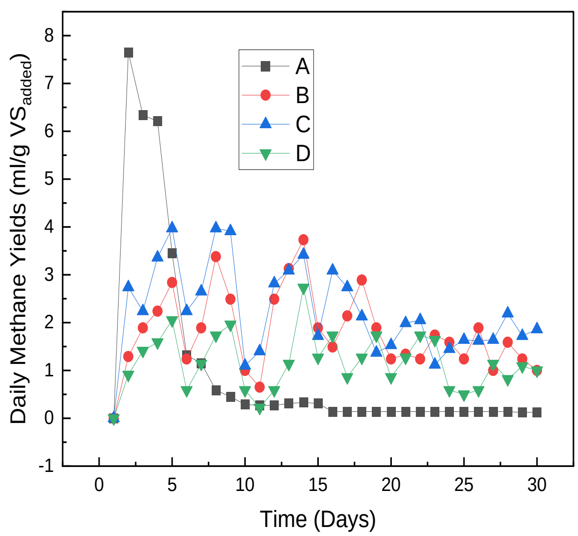

Figure 1: Effects of pretreatment techniques on daily methane yields of groundnut shells

3.2 Influence of pretreatment on cumulative yields of groundnut shells.

The cumulative methane yield of pretreated and untreated groundnut shells after 30 days retention period is illustrated in Figure 2. It can be observed that the methane yield are

31.07, 79.59, 98.01, and 23.69 ml/gVS$_{added}$ for thermal, Fe_3O_4 nanoparticle additives, combined particle size reduction with Fe_3O_4 nanoparticle additives, and untreated groundnut shells, respectively. There is a 31.15, 235.96, and 313.72% increase for thermal, Fe_3O_4 nanoparticle additives, and combined particle size reduction with Fe_3O_4 nanoparticle additives pretreatments compared to untreated groundnut shells. This result has shown that pretreatment methods can significantly improve the cumulative methane yield of groundnut shells. This is in line with what was observed when Safflower straw was pretreated thermally before biogas production (Hashemi, Karimi and Mirmohamadsadeghi, 2019). The methane yield increase was also recorded when rice straw was pretreated thermally under different temperatures (Luo *et al.*, 2019). The application of iron nanoparticles was also reported to enhance biogas and methane yields during the anaerobic digestion process (Abdelsalam *et al.*, 2016). Different researchers have experimented with the combination of two or more pretreatments methods during anaerobic digestion, and it was reported that the process increases the biogas and methane yields, which agrees with the findings of this study (Liu *et al.*, 2013; Dahunsi *et al.*, 2019; Korbag *et al.*, 2020).

When the pretreatment methods were compared, thermal pretreatment showed the slightest improvement, followed by Fe_3O_4 nanoparticle additives, and the most significant improvement was recorded when the two methods were combined. The smallest improvement in cumulative methane yield of thermal pretreatments can be traced to the fact that hemicellulose has a higher percentage of amorphous and lower stable arrangement than cellulose, and thermal pretreatment influences hemicellulose mostly (Suryawati *et al.*, 2009; Ruiz *et al.*, 2012). Pretreatment of groundnut shells at higher temperatures can result in the removal of a certain percentage of hemicellulose, which will significantly affect methane yield. Groundnut shells mainly consist of xylan (Thota *et al.*, 2017), which digests quickly and positively influences biogas yield. Still, at higher temperatures, the amount of hydronium ions increases and behave like acid, resulting in the hydrolysis of hemicellulose (Suryawati *et al.*, 2009). The temperature significantly affects total sugar hydrolysates during pretreatment, and temperature increases, increasing the total sugar hydrolysates during the pretreatment process. This higher sugar concentration results from hemicellulose hydrolysis during the pretreatment and thus reduces the percentage of sugar available for biogas production.

Furthermore, hemicellulose hydrolysis releases acetyl groups that reduce the hydrolysate pH (Moniz *et al.*, 2013). Most biogas yield inhibitors like 5-hydroxymethylfurfural, furfural, and acetic acids are produced during the thermal pretreatment process, and their percentage is determined by temperature (Hashemi, Karimi and Mirmohamadsadeghi, 2019). Fe_3O_4 nanoparticle additives can be observed to improve the methane yield compared to thermal pretreatment of the nanoparticle to its ability to supply some important co-factors and enzymes that have been reported to induce and stabilize the biogas production process (Romero-Güiza *et al.*, 2016; Xu *et al.*, 2019). It was reported that Fe nanoparticle addition could reduce the hydrogen sulphide in the gas and enhance the methane released (Su *et al.*, 2013). Fe^{2-} /Fe^{3+} ion addition through Fe_3O_4 nanoparticles during anaerobic digestion could serve as growth supplements for methanogenic bacteria and enhance their activities (Abdelsalam *et al.*, 2016). The physicochemical properties of Fe_3O_4 have been observed to have magnetite and little amount of goethite, where magnetite releases bioavailable ions (Fe^{2-} and Fe^{3+} that have been reported as an important nutrient for methanogenic bacteria power generation (Nemr *et* *al.*, 2021). Hydrogenotrophic methanogenesis is enhanced by Fe_3O_4 by donating electrons or hydrogen development from the iron corrosion, which improves the methane released from carbon dioxide consumption as presented in equations 4 – 6 (Hu *et al.*, 2015; Xu *et al.*, 2019). Compared with other metal oxides that have been experimented with nanoparticle additives for biogas enhancement (ZnO, CuO, and CeO_2), this result produces a higher increase in methane yield (Duc, 2013; Otero-González, Field and Sierra-Alvarez, 2014). The result substantiates the previous report that 20 mg/L of Fe_3O_4 can improve the methane yield of lignocellulose feedstocks (Abdelsalam *et al.*, 2016).

$$CO_2 + 4Fe^o + 8H^+ \rightarrow CH_4 + 4Fe^{2+} + 2H_2O \quad (4)$$

$$Fe^o + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (5)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (6)$$

Combined pretreatment of particle size reduction with Fe_3O_4 nanoparticle additives (treatment C) showed the best methane yield from groundnut shells compared to other pretreatments (313.72%). This is because this method combines the strength of particle size reduction to improve methane yield with that of Fe_3O_4, increasing the effectiveness of the process. Particle size reduction enhances the lysis rate, which results in to increase in methane yield (Jekayinfa *et al.*, 2020). The process can be ascertained using the kinetic model of chemical reaction control recommended by Luo and Wu (Luo and Wu, 2021). If the anaerobic digestion process takes place evenly on the surface of the groundnut shells and at an equal rate, the rate of digestion can be represented by equation 7 (Luo and Wu, 2021). The substrate's surface area determined by the particle size reduction plays a vital role in the anaerobic digestion process. This result agreed with the previous report that observed nanoparticle additives pretreatment performs better when combined with other pretreatment methods (Zaidi *et al.*, 2019). When microwave pretreatment was combined with Fe_3O_4 during the pretreatment of microalgae, an increase in methane yield was observed (Nemr *et al.*, 2021). Combination of Fe_3O_4 with ultrasonic and ozone during the pretreatment of *Ulva intestinalis Livaneus* before anaerobic digestion was experimented with. It was reported that combined pretreatment produces higher methane yields compared to individual treatments (Nemr *et al.*, 2021). Combined pretreatment methods have been investigated and confirmed to enhance enzymatic hydrolysis of lignocellulose feedstocks and the corresponding methane (Olatunji, Ahmed and Ogunkunle, 2021). Particle size reduction enhances the surface area, polymerizes the feedstock, and the final cellulose crystallinity reduction (Pu *et al.*, 2013). It can be inferred from this study that particle size reduction increased the feedstock surface area of the feedstock, thereby increasing the available space for Fe_3O_4 attachment to the groundnut shells and enhancing hydrolysis and methanogenesis stages. Particle size reduction has been reported to improve lignocellulose materials' biogas and methane yields (Jekayinfa *et al.*, 2020). It was also reported that mechanical pretreatment methods could enhance biogas and methane yields of agricultural residues by up to 80% (Menardo, Airoldi and Balsari, 2012). Therefore, the ability of particle size reduction and nano additives was combined, and improve the methane yield drastically. Combined pretreatment methods are more effective in lignocellulose feedstocks, but they are more complicated compared to single pretreatment methdos.

$$V = -\frac{dm}{dt} = kAC^n \quad (7)$$

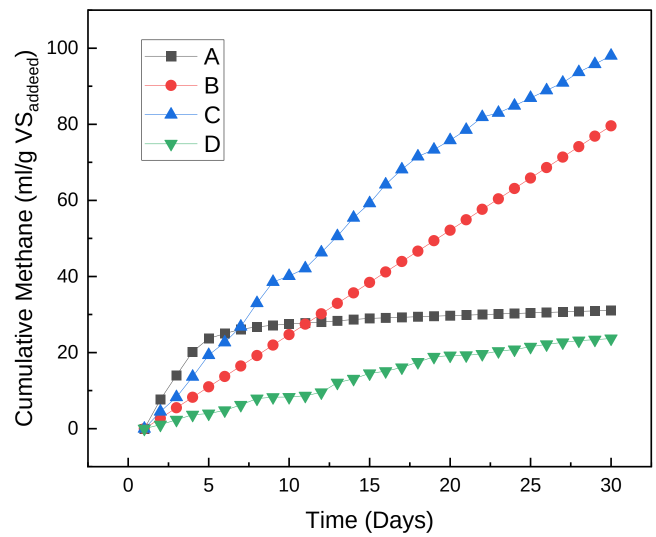

Figure 2: Effects of pretreatment techniques on cumulative methane yields of groundnut shells

Comparing these pretreatment methods considered in this study, it can be discovered that thermal pretreatment is capable of removing/redistributing the lignin portion of the groundnut shells and encouraging early biogas and methane yield compared to others. This has led to a shorter retention period during the anaerobic digestion process. But, the cumulative methane yield is low compared to other pretreatment methods. This may be due to the release of inhibitory compounds that lower methane yield during digestion. Anaerobic digestion of the single pretreatment of Fe_3O_4 nanoparticle additives released better methane yield than the thermal pretreatment method. This can be traced to the ability of the Fe_3O_4 to enhance the methanogenic bacteria activities and improve the biogas and methane yields. When particle size reduction was combined with Fe_3O_4 nanoparticle additives, it was discovered that the combined influence of both treatment methods produced the best yield. The possibility of having inhibitory compounds by Fe_3O_4 nanoparticle additives is minimal compared to thermal pretreatment. Although, appropriate selection of quantity and size of the particle during particle size reduction is critical to avoid over accumulation of volatile fatty acids that may hinder the methane yield.

4. Conclusion

This study shows that pretreatment methods can enhance the methane yield of lignocellulose feedstocks like groundnut shells. Thermal pretreatment can reduce the lag time compared to other pretreatment methods considered. Nanoparticles additives of Fe_3O_4 showed its biostimulating influence on the activities of methanogenic bacteria during anaerobic digestion of groundnut shells and improved the cumulative methane yields. Combined pretreatment produced the highest cumulative methane yield (98.01 ml/g VS_{added}) compared to the single (79.59 ml/g VS_{added}) pretreatment method. The finding from this study provides valuable information to enhance the energy recovery from groundnut shells.

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