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Review

Effect of different pretreatments and their parameters on biogas production performance: A review

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Abstract: Energy supply is fundamental to modern society, yet its current reliance on fossil fuels is a major contributor to global warming. A transition to renewable energy is therefore critical, offering both climate mitigation and economic opportunities. Biogas is a particularly effective renewable source, addressing energy needs and waste management simultaneously by converting organic matter into clean fuel. Production occurs through a four-stage anaerobic digestion process, influenced by parameters such as temperature, pH, C/N ratio, retention time, mixing, and moisture. Pretreatment methods can significantly enhance efficiency and yield. For lignocellulosic materials, sodium hydroxide is a common chemical choice, while biological pretreatment offers a low-energy alternative. Among additives, zero-valent iron nanoparticles have shown considerable promise. This article aims to identify optimal conditions to make biogas production more cost-effective. Synthesized studies indicate that maximum biogas yield is achieved by: reducing feedstock particle size, maintaining an inlet concentration near 8%, applying a ratio of 25, ensuring neutral pH, and operating at mesophilic temperatures. A key finding is that pretreatment effectiveness is not universal; it is highly dependent on the specific feedstock and digestion conditions. In conclusion, biogas exemplifies the potential of renewables to create a more sustainable and resilient energy system. By optimizing its production, we can advance toward a greener future that reduces environmental impact while supporting economic growth.

Keywords: energy crisis; biogas; pre-treatment; optimal state; production; nanoparticles; anaerobic digestion

1. Introduction

The main cause of the energy crisis in society is the need to change the pattern of energy consumption and strive for sustainability. Despite the increasing energy demand, fossil fuel resources are depleting, and they currently account for approximately 85% of the world's primary energy consumption [1]. Fuel consumption occurs at a much faster rate than the time it takes for production and replenishment, leading to a rapid depletion of resources. Moreover, the use of these fuels results in the release of greenhouse gases, the most significant impact of which is the rising global temperature, posing a threat to human well-being. The consequences of this temperature increase can be multiple and devastating, necessitating society to take action to mitigate the upward trend.

With the growing human impact on the environment and the advancement of societal structures, waste management has become a crucial consideration. Inefficient waste disposal practices can result in unpleasant odors, pose risks to human health, and contribute to surface and groundwater pollution [2]. While there are various methods available for waste disposal, the most effective approach is to transform this challenge into an opportunity, aligning with the primary development policy in many countries. Anaerobic digestion (AD) has emerged as the most favorable and efficient method for waste management and addressing global warming concerns [3]. Considering its economic, environmental, and social benefits, anaerobic digestion stands out as the most promising solution [4]. Anaerobic digestion has significant potential due to its ability to utilize a wide range of resources and its minimal carbon emissions during the production process [5]. The process of anaerobic digestion can generate various forms of energy, including heat, electricity, and transportation fuel, utilizing renewable sources [6]. In general, biomass resources can be categorized into five main groups (**Figure 1**) [7]:

- Urban solid waste;
- Animal waste;
- Agricultural waste;
- Urban sewage;
- Industrial waste.

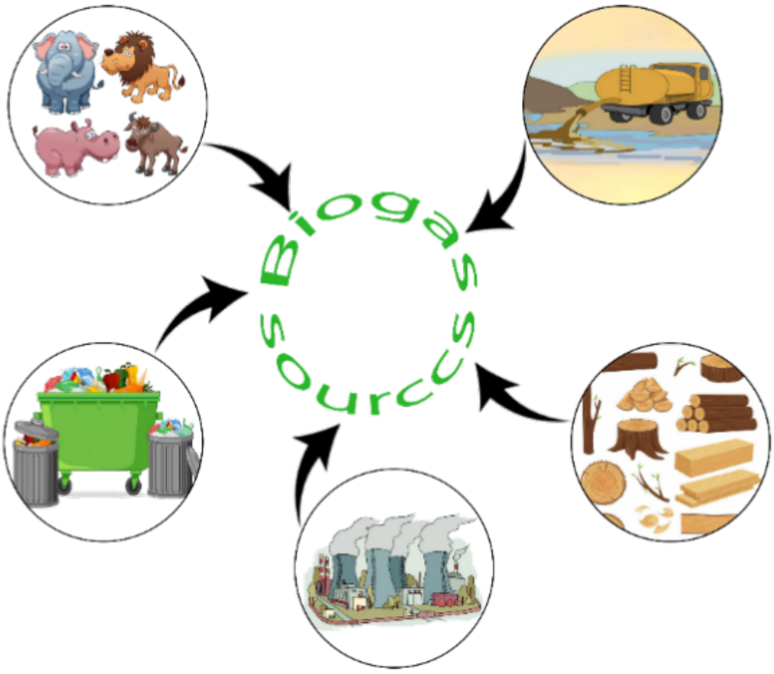

Figure 1. Biomass sources for biogas production.

The biogas industry has its unique characteristics in different parts of the world due to the availability of primary resources. Switzerland and Sweden primarily obtain a significant portion of biogas through the decomposition of wastewater. On the other hand, Denmark, Germany, and Great Britain utilize more food waste due to the abundance and accessibility of animal manure [8]. Lignocellulosic materials serve as one of the most valuable sources of organic materials for biogas production. These materials are widely available in agricultural and industrial wastes and represent a renewable resource that is more cost-effective compared to other organic materials.

Agricultural biomass undergoes a short time lag, resulting in a low biogas yield. To enhance its productivity and efficiency, pre-treatment is necessary before subjecting it to anaerobic digestion [9]. The digestion of cellulose in biomass is mainly hindered by factors such as the presence of lignin, cellulose crystallinity, and particle size [10].

To enhance the absorption of carbohydrates in lignocellulosic biomass during fermentation processes, it is crucial to decrease the rigidity of the cell fiber, leading to the breakdown of lignin and the hydrolysis of cellulose and hemicellulose. This ultimately results in the conversion of these components into polysaccharides and monomers. Consequently, pretreatments involving physical, chemical, or biological methods may be required to facilitate the hydrolysis of lignocellulosic constituents [11].

However, there is no consensus on the most appropriate type of pretreatment for lignocellulosic waste applications, as their effects may vary depending on the source [12]. The rate of biogas production is influenced by various factors including the type of pretreatment utilized, operating conditions, bed type, and AD parameters [13]. Other factors such as reactor type, feed material composition, concentration, temperature, pH, C/N ratio, residence time, stirring, and moisture percentage also impact the biogas yield [14]. The objective is to achieve the optimal biogas production rate while considering the aforementioned factors. The production cost of biogas can be reduced and made more economical by increasing the amount of biogas generated. Optimization techniques can lead to a 57% increase in biogas performance [15]. Therefore, it is essential to search for the ideal conditions and the best pretreatment methods to achieve the maximum yield of biogas.

2. Biogas

Biogas is the gas generated during the anaerobic digestion of biomass waste, including animal waste, plant residues, sewage, urban and human solid waste, industrial waste, and agricultural waste [16]. The anaerobic digestion process involves four stages in which different bacteria interact with each other [17]. These stages include hydrolysis, acidogenesis, acetogenesis, and methanogenesis. First step: To harness the energy contained within biomass, it is necessary to first convert long molecular chains into smaller units or monomers that can be easily decomposed by bacteria. This process, known as hydrolysis, involves breaking down these chains and dissolving smaller molecules in a solution. Hydrolysis plays a crucial role in anaerobic digestion as it is the initial step in converting complex organic molecules into simple sugars, amino acids, and fatty acids [18].

The second stage involves the biological process of acidogenesis, which leads to the further decomposition of the remaining components through the activity of acid-producing bacteria. During this stage, certain components from the previous stage, such as acetate and hydrogen, can be directly utilized by methanogens. However, there are also volatile fatty acids (VFAs) with longer chain lengths than acetate, which require conversion into compounds that are directly usable by methanogens. The acidification stage exhibits a rich microbial diversity. During the process of hydrolysis, a majority of the bacteria involved also contribute to acidification. Additional bacteria from the genera Enterobacterium, Streptococcus, and Eubacterium are also involved in the acidification process [19]. It is important to maintain a pH level above six during acidification to optimize the conversion process [20].

Third stage: During the steatogenesis phase (stratigraphy), the steatogenic bacteria interact with newly formed compounds, resulting in the production of acetic acid, carbon dioxide, and hydrogen. Microbial species such as Clostridium, Syntrophus, Syntrophomonas, and Syntro-bacteria have been found to contribute to the osteogenesis process [19]. Fourth stage: In the methanogenesis stage, methanogens utilise the by-products generated from the preceding stages (acetic acid, carbon dioxide, and hydrogen) and convert them into methane, carbon dioxide, and water [17]. Methanogenesis is sensitive to pH levels, with optimal conditions occurring between 6 and 8.5. This process involves two distinct groups of bacteria: hydrogenotrophic bacteria, which facilitate the anaerobic oxidation of hydrogen, and acetoclastic bacteria, which facilitate the anaerobic conversion of acetic acid, resulting in the production of methane and carbon dioxide [21]. The synergistic interaction between the acidogenic bacteria and methanogens renders the entire biogas production process thermodynamically efficient [22]. **Figure 2** illustrates the four stages of biogas production.

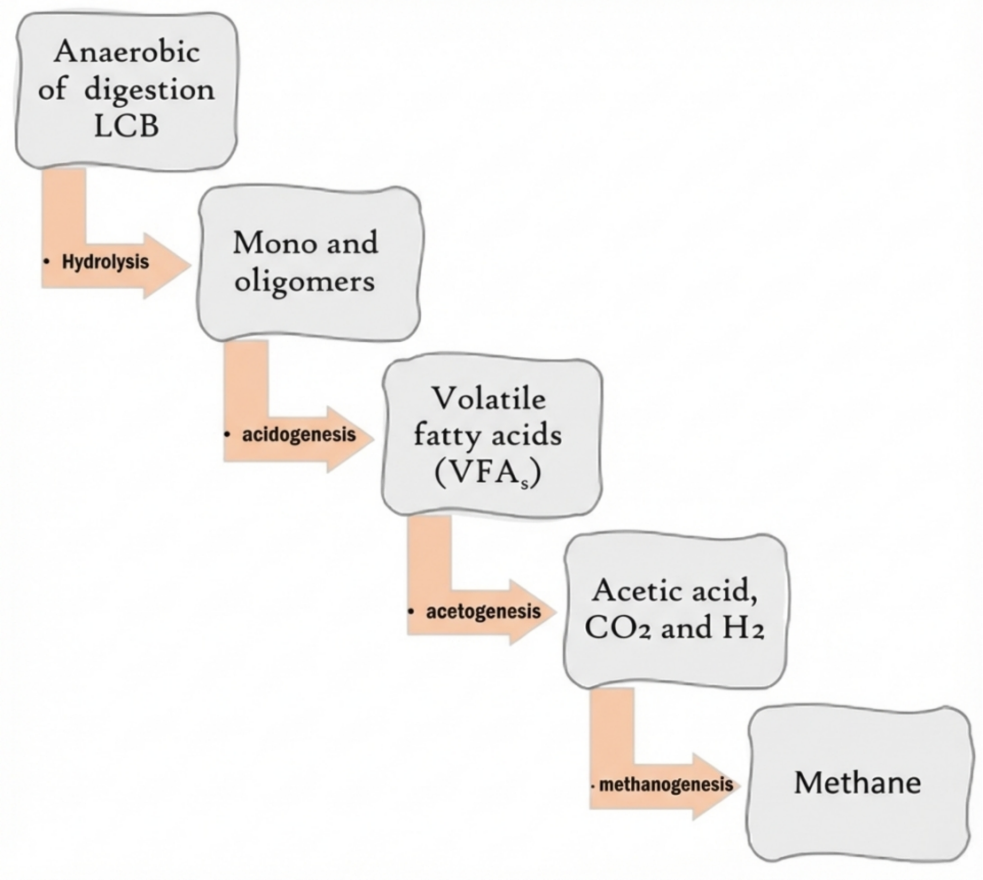

Figure 2. Wood lignocellulosic biomass (WLB) degradation processing.

The components of biogas include H_2O, N_2, O_2, H_2S, NH_3, and CO_2 [23]. The composition of biogas typically consists of 50–70% methane and 30–50% carbon dioxide [24]. This renewable energy source is produced from abundant raw materials, making it a cost-effective option with significant economic value [25]. Additionally, the waste generated from the anaerobic digestion process serves as fertilizer, enhancing agricultural fertility while reducing the need for chemical pesticides [26].

2.1. Biogas applications

Biogas serves as a versatile energy carrier with critical applications across multiple sectors, underpinning its role in the transition to a sustainable energy system. Its primary uses can be categorized into three key areas: power generation, thermal energy production, and the provision of renewable fuel. When purified to biomethane (typically >95% methane content) through upgrading processes, biogas becomes fully compatible with existing natural gas infrastructure. This allows for its direct injection into the national gas grid. Consequently, biomethane can be utilized for household and industrial heating, electricity generation in gas-fired power plants, or as a high-quality vehicle fuel in the form of compressed natural gas (CNG). A distinct advantage of biomethane is its storability, which provides essential flexibility to balance supply and demand within the energy system [27].

The conversion of biogas into electricity via internal combustion engines, gas turbines, or fuel cells represents one of its most widespread and rapidly growing applications globally. This pathway delivers significant environmental benefits by simultaneously displacing fossil fuel-based power and mitigating greenhouse gas emissions. Crucially, it captures methane—a potent greenhouse gas—that would otherwise be released from the anaerobic decomposition of organic waste, thereby contributing to climate change mitigation and improved waste management.

Biogas can be used directly for thermal applications in boilers, furnaces, or in combined heat and power (CHP) systems. In such processes, a substantial portion of the biogas's chemical energy is efficiently converted into usable heat for industrial processes, space heating, or drying applications [28]. Direct thermal use, especially when implemented near the production site, offers a highly efficient and cost-effective energy solution. In summary, the diverse applications of biogas transform it from a simple waste treatment technology into an integrated, circular solution that addresses energy security, waste valorization, and environmental sustainability concurrently.

2.2. Characteristics of biogas

The calorific value of biogas is 0.8 times that of natural gas, and it diffuses in the air at a rate of 40 cm/s [24]. The calorific value and flammability of biogas depend on the methane content; if the amount of carbon dioxide exceeds 50%, biogas will not be flammable [25]. Removing carbon dioxide is the most costly stage in biogas production. As the CO_2 content increases, the amount of CH_4 decreases, resulting in a decrease in the calorific value and flame stability of biogas. When used directly, this can lead to issues such as unstable combustion and low heat intensity [26].

Biogas has a thermal energy content of 36.7 MJ/m^3. When converted into electricity using existing engines, it can yield approximately 2 kW of electricity per cubic meter [27]. Methane gas, which is obtained from biogas, possesses a high octane number and low carbon content. As compared to fossil fuels, it remarkably reduces the emission of pollutant gases [28].

2.3. Types of anaerobic fermentation digesters

There are various factors to consider when selecting a digestion method, including the execution environment, retention time, properties of the raw material, and available equipment [29]. In terms of removing organic matter, two main methods are commonly used: aerobic digestion and anaerobic digestion. Aerobic digestion results in the production of water and carbon dioxide as byproducts. On the other hand, anaerobic digestion (AD) produces methane, carbon dioxide, and a small amount of other gases. The proportions of these gases can vary depending on the type, properties, and quantity of the raw material [30]. Anaerobic digestion can be further categorized into solid (HS-AD) digestion and liquid (L-AD) digestion.

In solid-state anaerobic digestion, the dry matter content is typically above 15%, while in liquid-state anaerobic digestion, it is less than 10%. It has been observed that the production of methane increases significantly in the case of liquid digestion [31]. Comparing the liquid anaerobic digestion mode to the solid anaerobic digestion mode, the amount of methane produced is 13.6% higher in the former, which can be attributed to the optimal carbon-to-nitrogen (C/N) ratio in the liquid mode. However, it is worth noting that the hydrothermal slurry anaerobic digestion (HS-AD) method offers advantages over the liquid anaerobic digestion (L-AD) method, including smaller reactor dimensions, lower cost, minimal nutrient loss, reduced water consumption, and lower maintenance cost [32]. Anaerobic digestion can be conducted using either a single-stage or a two-stage process. In the single-stage method, all the necessary processes for methane production, as well as the destruction of organic compounds, are carried out in a single stage. On the other hand, the two-stage process involves the hydrolysis of organic compounds and the production of volatile fatty acids and H_2 in the first stage, followed by the production of methane in the second stage.

It has been observed that under both aerobic and anaerobic conditions, the hydrolysis process is more efficient when conducted in a two-stage system. This enhanced efficiency leads to an improved yield of methane [33].

When loading substances into the digester, it is possible to use a single material or a combination of multiple materials. However, a digester tends to be more efficient when loaded with several materials. This is because the efficiency of the digestion process increases, leading to accelerated degradation rates [34–36].

3. Types of biogas production digester models

3.1. Biogas production device with buoyancy gas chamber

This type of storage system, commonly referred to as the ”Indian model,” utilizes a floating cap tank to store gas. The tank moves up and down in response to changes in gas pressure, ensuring a consistent output pressure. However, this system requires regular maintenance, and ensuring a proper seal on the tank is crucial. Additionally, this model is not well-suited for cold regions due to high-temperature loss from the gas storage tank.

3.2. Biogas production device with fixed tank

This is known as the Chinese model, which has gained importance and efficiency due to its underground location. It offers advantages such as space-saving, minimal space requirements, heat stabilization, and resistance to cold regions.

3.3. Ideal conditions for the growth of bacteria and enzymes

Bacteria are the main factor in biogas production and it is necessary to provide optimal conditions to accelerate the process and increase the amount of biogas produced. Critical variables in biogas power plants include temperature, pH, C/N ratio, retention time, mixing, moisture percentage, particle size, digestion concentration microbial activity, hydrolysis rate, and biomass degradation degree [37].

3.3.1. Temperature

Temperature is a crucial factor in anaerobic digestive as it impacts enzyme activity and methane production yield [38]. Significant temperature drops, exceeding 2 degrees Celsius, have a decisive effect on gas production [39]. Rapid temperature fluctuations disrupt bacterial activity [40]. When the temperature falls below 30 °C, the digestion environment becomes acidic. Conversely, when the temperature surpasses 60 °C, the activity of microorganisms involved in digestion decreases and eventually ceases. The most optimal temperature from both technical and economic perspectives is the mesophilic temperature range, as it promotes stability in the digester [41]. Research has shown that the highest methane production occurs under mesophilic conditions [42]. Increasing the temperature in the anaerobic digestion (AD) process of biomass can lead to an increase in methane production [43]. Temperature plays a critical role in the separation and decomposition of solid materials, with better decomposition occurring at thermophilic temperatures compared to lower, cold-loving temperatures [44].

The production of biogas is significantly higher under thermophilic temperatures (55 °C) compared to cold temperatures (15 °C) [45]. This is because the endothermic digestion process leads to faster methane gas extraction, resulting in a shorter retention time. Therefore, thermophilic temperatures can be used in cases where there are limitations in the amount or size of the digester [46]. Furthermore, the inhibition of the system by ammonia in thermophilic digestion is less than in cryophilic digestion [47]. However, it's important to note that while there are several advantages to thermophilic conditions, they are more sensitive to environmental changes compared to mesophilic conditions [48]. Failure in the thermophilic process occurs when the temperature changes by more than one degree Celsius per day. To maintain stable anaerobic digestion, the temperature changes should be limited to less than 0.6 °C per day [38]. Additionally, biogas production is higher in mesophilic conditions compared to thermophilic conditions, attributed to the additional formation of volatile fatty acids [49].

3.3.2. pH and VFA

The optimal pH for biogas production is around neutral, ranging from 6.5 to 7.5. If the pH falls outside the range of 6 to 8, it can be detrimental to methanogenic bacteria and can lead to a decrease in biogas production [50]. It also hampers the production of biogas and results in the accumulation of more acids [40]. Acidification of the digester significantly hinders further conversion of organic materials [51]. A pH of 6.5 or lower causes a significant decrease in the activity of microorganisms [52]. When the pH drops below 6, the percentage of methane in biogas decreases to less than 50%, making it non-flammable [53]. If the pH level of the environment decreases to less than 5.5, the bacteria become inactive [54]. VFAs determine the pH of the environment and are one of the most important parameters affecting AD [31]. The number of bacteria can be controlled by acid-producing bacteria and pH control [55,56].

3.3.3. C/N ratio

The performance of anaerobic digestion is significantly influenced by the C/N ratio [57]. To ensure stable anaerobic digestion in the long term, it is important to maintain a balanced C/N ratio [31]. The optimal C/N value for anaerobic digestion of mixed waste can be achieved by mixing carbon-rich waste streams with nitrogen-rich substrates such as food waste (FW) and cow manure (CM) [58]. Studies have reported the ideal C/N ratio for anaerobic digestion to be in the range of 21–31 [59, 60]. Maintaining a C/N ratio of 25–30 is recommended to keep the solution at a neutral pH (pH = 7) and produce biogas with approximately 70% methane content [53]. Some researchers have suggested using a lower C/N ratio than the optimal value as it is more effective for biogas production [52]. If the amount of carbon (C) is lower than the desired level, excess nitrogen (N) is stored in the digester, resulting in toxicity to the bacteria. This can lead to a high mortality rate among the bacteria. On the other hand, if the amount of nitrogen is insufficient, the microorganisms will not be able to survive due to a decrease in the available food source. In one study involving anaerobic digestion of three organic materials (dairy waste, chicken manure, and wheat straw), it was found that the highest methane production occurred at a C/N ratio of 27.2, with a constant pH and low cumulative ammonia concentration [61].

3.3.4. Time left

The retention time in a biogas production system is directly related to the amount of biogas produced. A longer retention time and a high rate of organic compounds result in an increased methane yield. Typically, the recommended retention time in such systems is between 30 and 50 days [62]. Over time, the amount of biogas produced will increase, but at a decreasing rate. While the overall biogas production increases, it may not be economically efficient in terms of the energy and time invested due to the diminishing returns.

3.3.5. Mixing

The purpose of mixing materials in the digester is to distribute nutrients within the digester [63], prevent the accumulation of sediment in the loaded materials, achieve uniform temperature throughout the digester, prevent foam formation, and aid in the release of biogas from the materials [64,65]. Depending on the type of mixer used, the required energy for mixing can be reduced by up to 70% [66]. To enhance the methane production efficiency of biogas, some of the output material from the digester can be recycled back into the input [67]. Research has demonstrated that increasing the stirring speed results in a decrease in mixing time [68]. Paddle stirrers are suitable for very viscous fluid and are very common to avoid floating layers. In addition, paddle mixers with slow speed are more efficient in energy consumption compared to floating mixers with high speed [69].

3.3.6. Percentage of moisture

Changes in humidity levels have a direct impact on gas production [70]. For optimal anaerobic fermentation in a biogas system, the ideal solid concentration is around 7–9%. Increasing the total solids (TS) content by 2–8% can result in a higher biogas yield, while a TS of 10% or higher may lead to a decrease in biogas production. When the TS level reaches 8%, the performance can be 1.5 times higher compared to a TS level of 5% [46]. However, it's important to note that higher TS levels can lead to an increase in volatile fatty acids (VFA) and a slight decrease in methane yield.

3.4. Ammonia

Ammonia is produced through the biological decomposition of organic matter and is commonly found in two forms: NH+4 and free ammonia (NH_3) [71]. It serves as an important growth factor for bacteria, although high concentrations of ammonia can be toxic to them [72]. Ammonia plays a crucial role in balancing the C/N ratio, and it can significantly impact the performance of anaerobic digestion (AD) by neutralizing the volatile fatty acids (VFA) generated during the process [61, 73]. However, excessive ammonia levels can hinder biogas production, cause digestion failures, and result in the release of ammonia into wastewater [74].

3.5. Long fatty acids

Biodegradation of long-chain fatty acids (LCFA) is the step that determines the rate of anaerobic digestion. The rate of degradation is limited by the initial concentration of LCFA, and when the concentration is too high, anaerobic digestion can fail [75]. The inhibition of the system by saturated fatty acids becomes more intense as the number of double bonds and chain length increase [76]. Food waste contains a significant amount of fat, with a concentration of about 5 g/L [77, 78].

4. Pre-treatment of biogas

After applying the parameters mentioned by the researchers, pretreatment is employed to enhance the competitiveness of the anaerobic digestion process. This approach accelerates and boosts the production rate of the process by utilizing the decomposition of organic materials [79, 80]. Lignocellulose typically possesses a resistant structure, but with the application of pretreatment, it becomes feasible to hydrolyze cellulose and hemicellulose, resulting in the conversion of polymeric carbohydrates into fermentable monomers. The analysis further investigates the extent of biogas production [81]. Previous studies have shown that the implementation of pretreatment increases the methane yield of LBs and decreases the digestion period [82, 83]. Recent experiments have demonstrated that pretreatment techniques enhance the process of dairy manure fermentation, leading to a significant increase in biogas production (up to 2 to 3 times) [84, 85]. These pretreatment methods can be categorized into three main groups: physical (such as mechanical, thermal, and ultrasonic treatments), chemical (including acidic and alkaline methods), and biological pretreatment (involving the use of enzymes, fungal and microbial consortium pretreatment, microaerobic processes, and ensiling).

4.1. Mechanical pretreatment

Mechanical pretreatment is commonly employed before chemical and microbial pretreatment to achieve a synergistic effect [86]. Mechanical pretreatment involves crushing, which has two positive impacts on digestion performance. Firstly, it enhances methane production efficiency by expediting the reaction, primarily through an increase in specific surface area, thereby facilitating the digestion of LBs [87]. Secondly, it improves biomethane production efficiency by breaking down the complex structure and altering the morphology of LBs, including crystallinity, thus enhancing LBs' biodegradability [88]. For instance, researchers observed a 43% increase in methane yield by reducing the particle size of ley crop silage from 2 to 0.125 mm [88]. In a study, it was found that the consumption rate coefficient doubled when the average particle size decreased from 2.14 mm to 1.02 mm [31]. This indicates that reducing particle size can increase the biodegradability of LBs. When particle size is smaller, the digestion time is shortened, resulting in faster decomposition [89]. However, excessive mechanical pretreatment (such as excessive particle size reduction) may not favor methane production due to the accumulation of VFAs. This can lead to a deterioration in digestion performance [90] and a negative net energy output [88]. Another study reported a proportional decrease in methane production with a decrease in particle size of sunflower seed processing waste. The highest methane yield was observed when the particle size was between 1.4 and 2.0 mm [91].

4.2. Chemical pretreatments

Chemical pretreatments are commonly employed for the digestion of LBs [92]. These pretreatments mainly involve alkaline and acid treatments. Alkaline pretreatment aims to reduce cellulose crystallinity and lignin content by means of hydrolysis, consequently enhancing the porosity of LBs. This increased porosity facilitates the digestion process by microorganisms, making it the most widely utilized pretreatment method [87]. Typical chemical pretreatments include the addition of reagents such as ammonia fiber explosion, CO_2 explosion, as well as acidic and alkaline separation [93]. **Figure 3** illustrates the mechanism of alkaline pretreatment on LBs. The decomposition of LBs is challenging due to the presence of two crucial chemical bonds. The first bond is the hydrogen bond between lignin and polysaccharides, while the second bond is the ether-ester bond between hemicellulose and cellulose. These bonds are broken by OH produced by the alkaline precursor, which leads to easier decomposition of LBs [87].

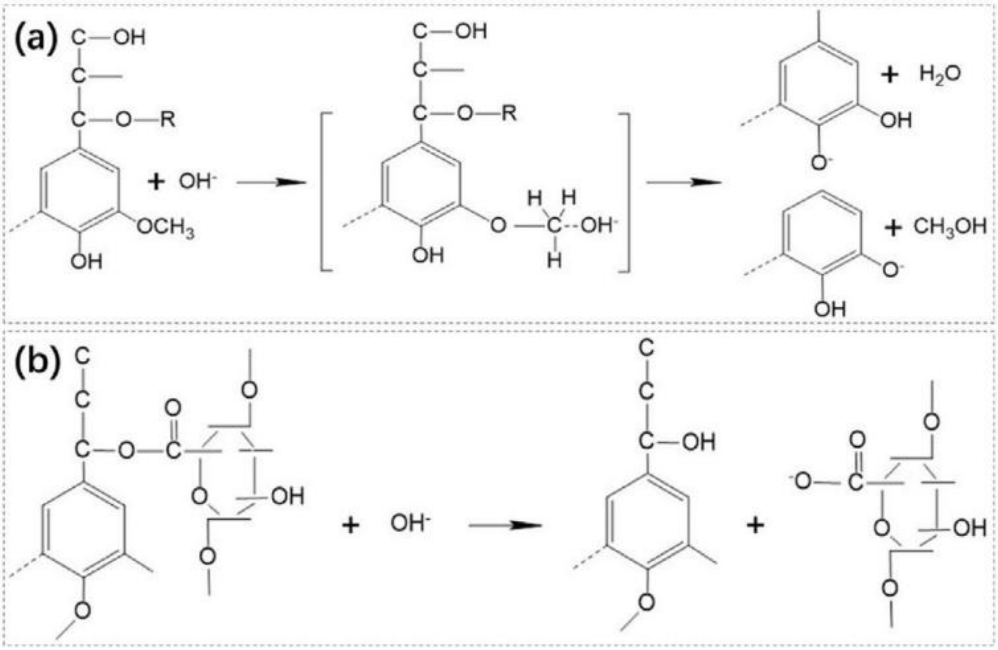

Figure 3. Mechanism of alkaline pretreatment: **(a)** Reaction mechanism between lignin and OH; **(b)** Reaction mechanism between lignin complex and OH [89].

After applying a pretreatment of 10% CaO, researchers observed an 11.99% increase in methane production [94]. For the acid peeling method, sugarcane bagasse was treated with hydrochloric acid (HCl 0.63 M) for a reaction time of 6.4 min at a temperature of 136 °C. After 30 days of incubation under mesophilic conditions (35 °C), 122.2 mL $CH_4.g^{-1}$ biomass was obtained [95]. Bases such as NaOH, potassium hydroxide (KOH), calcium hydroxide ($Ca(OH)_2$), or ammonium hydroxide (NH_4OH) help increase the porosity of the materials and reduce the degree of lignin polymerization [96]. This leads to the dissolution of lignin and makes hemicellulose more susceptible to enzymatic attack by microbes, resulting in a higher rate of biogas production [96,97]. Alkaline pretreatment using sodium hydroxide (NaOH) is one of the most widely used thermochemical methods for pretreating lignocellulosic biomass [98]. During anaerobic digestion (AD), lignin can be a potential inhibitor to microorganisms. For instance, when the dissolved lignin concentration reaches 1.0 g/L, the hydrolysis efficiency can decrease by 25% [99]. Zhu et al. reported a significant increase in biogas yields, up to 57%, with an 8% NaOH pretreatment at 175 °C. The removal of lignin was considered the main contributing factor to this improvement [100]. Silica is another factor that inhibits the digestion of cellulosic materials [101, 102]. After NaOH pretreatment, the silica content was reduced by 88.7%, resulting in increased biodegradability of lignocellulosic biomass [86]. In another study, the pretreatment of raw materials with NaOH showed improved efficacy compared to untreated raw materials. reported a 111.6% increase in methane production from wheat straw pretreated with NaOH (4% NaOH at 37 °C for 120 h) [103].

Acidic pretreatment involves the addition of acid to the digester, and the acid used can include H_2SO_4, HCl, H_2O_2, and CH_3COOH. This pretreatment method is mainly targeted at dissolving hemicellulose, which is one of the components of lignocellulosic biomass (LBs). The acid breaks down the hemicellulose, resulting in significant changes in the biodegradation of LBs. However, it's worth noting that acidic pretreatment generally has lower performance compared to alkaline pretreatment, even when using the same molar concentration of acid. This is primarily because acidic pretreatment has a limited effect on the structure of LBs. The acids, whether organic or inorganic, convert the hydrogen bonds between cellulose chains into a completely amorphous state. As a result, the cellulose becomes more susceptible to breakdown into glucose.

In summary, while acidic pretreatment can be effective in dissolving hemicellulose, it may not have as significant an impact on the overall structure of LBs compared to alkaline pretreatment. **Figures 4** and **5** illustrate the steps involved in the hydrolysis of the rigid lignocellulosic structure into a simpler and more easily digestible form for microorganisms. The two figures show that the use of inorganic acids yields better results compared to organic acids, mainly due to their stronger nature.

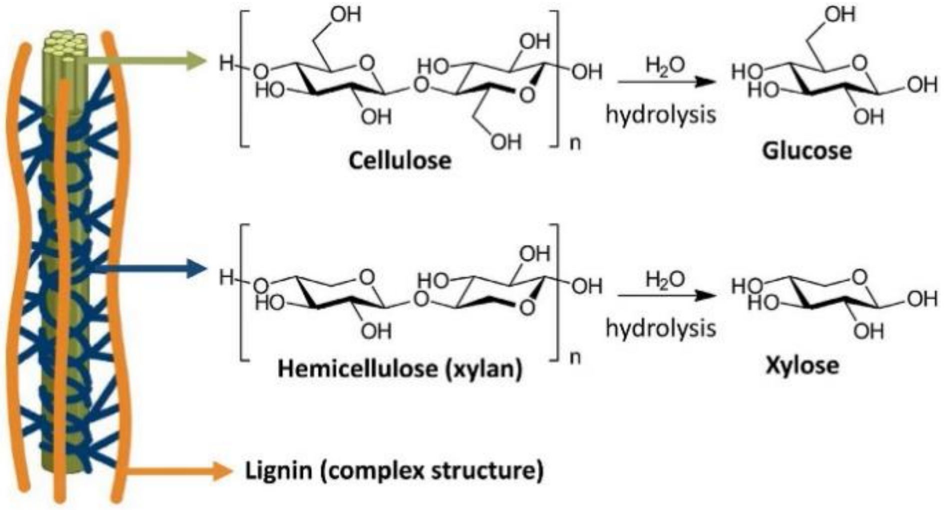

Figure 4. Simplified diagram of lignocellulosic structure and monomers formed after the combination of cellulose and hemicellulose hydrolysis [104].

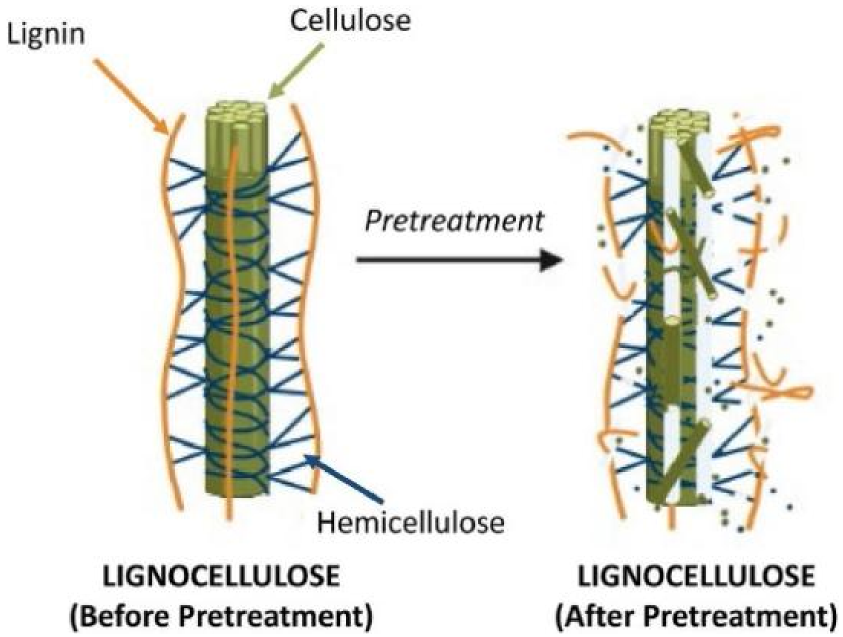

Figure 5. Simplified scheme of lignocellulosic structure disorder after pretreatment [104].

In a study comparing the effects of H_2SO_4, H_2O_2, HCl, and CH_3COOH pretreatments on rice straw, it was found that the biogas yield followed the order of 3% H_2O_2 > 2% H_2SO_4 > 2% HCl > 4% CH_3COOH. This indicates that pretreatment with hydrogen peroxide (H_2O_2) had the highest biogas production potential, followed by sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and acetic acid (CH_3COOH) respectively. However, it is generally observed that organic acid pretreatment at low concentrations may not yield satisfactory results in terms of biogas production. On the other hand, high concentrations of organic acid pretreatment can lead to the loss of a significant amount of dry matter, which can be detrimental to anaerobic digestion (AD) processes. This suggests that finding the right balance and optimal conditions for pretreatment is crucial for efficient biogas production from lignocellulosic materials [105].

4.3. Thermal treatment methods

Heat treatment is a process that involves applying heat to substrates, which leads to deflocculation of macromolecules. This deflocculation occurs due to the increased surface area of the substrates. As a result, the degradation of complex compounds is improved, leading to an increase in soluble organic matter. Additionally, heat treatment interacts with the microbial population, facilitating a greater conversion of organic matter to biomethane [106]. Some recent studies have suggested that anaerobic digestion may not be economically viable when thermal pretreatments are used [107]. However, it is possible to make anaerobic digestion profitable through a series of operations that include increasing energy efficiency, enhancing operational capacity, and utilizing technological advancements [108]. These measures can contribute to ensuring the economic feasibility of anaerobic digestion with thermal pretreatment.

Substrate thermal pretreatment methods such as autoclaving, hot water baths, ovens (hot air ovens), and microwaving are used to keep the substrate warm [109]. In hot water baths, ovens, and autoclaves, heat is transferred through hot water, hot air, and steam, respectively. The optimal temperature ranges for hot air, microwave, autoclave, and hot water bath are 90–170 °C, 140–200 °C, 90–175 °C, and 90–100 °C, respectively. All thermal pretreatments have a positive effect on the dissolution of lignocellulosic biomass (LBs). However, it should be noted that high temperatures above 150 °C can cause the decomposition of lignin into phenolic compounds, which are toxic to microorganisms in anaerobic digestion (AD) [86].

4.4. Biological treatment methods

In addition to modifying the biomass structure, biological pretreatment methods have been shown to enhance methane yield through simultaneous digestion mechanisms [103]. This method offers several advantages, including low energy consumption [110] and environmental compatibility [111], which make it a promising approach.

Biological pretreatment can be achieved through microbial or enzymatic methods [86]. Microbial pretreatment is a commonly used approach, where fungi are capable of secreting cellulases, hemicellulases, and ligninase [112]. Enzymes play a crucial role in modifying the lignin structure (such as the guaiacyl/sinapyl ratio), increasing material porosity, reducing cellulose crystallinity, and altering hemicellulose structure [113].

4.5. Combined pretreatment

Combined pretreatment methods include both physical and chemical changes and are usually more efficient than physical pretreatment or chemical pretreatment.

4.6. Heat-alkaline pretreatment

Since mixed cultures have a greater ability to break down lignocellulosic enzymes compared to single cultures, they were initially considered more effective. However, studies have shown that the pretreatment time required for mixed cultures is much longer compared to physical or chemical pretreatment methods. Mixed culture pretreatments can take several days or even weeks, although some are shorter than monoculture pretreatments [114]. Furthermore, the microbial structure of mixed cultures can change over time, potentially reducing their degradation ability. The ultimate advantage of monoculture pretreatment over mixed culture pretreatment is the ease of controlling growth conditions in a monoculture [115]. Alkaline or thermal-alkaline pretreatments initially focus on lignin removal followed by hemicellulose breakdown. The extent of cellulose degradation depends on various factors including the pretreatment type, raw materials, and methodology employed. Thermal-alkaline pretreatment offers advantages such as high buffering capacity, dissolution of COD, and delayering, thereby enhancing the performance of the anaerobic digestion (AD) process. Previous research indicates that thermal-alkaline pretreatment at 150 degrees Celsius with 1% NaOH is a more viable and cost-effective option [13,116]. Thermochemical pretreatment, which combines thermal and chemical methods, has been recognized as a highly beneficial pretreatment approach [19].

5. Nanoparticles for biogas production

Many nanoparticles are added as additives to the process, which can generally be divided into three categories:

(1) Zero valent iron nanoparticles (ZVI);
(2) Metal nanoparticles and metal oxide;
(3) Carbon-based nanoparticles.

5.1. Nanoparticles of zero-valent iron (ZVI)

Iron, also known as zero iron, can enhance the hydrolysis process in anaerobic digestion by acting as an electron donor [117]. Iron nanoparticles are unstable and gradually release iron ions, thereby promoting the activity of methanogenic microorganisms [118]. The introduction of iron has been shown to stimulate and stabilize the anaerobic digester, leading to improved performance in biogas production [119]. However, it should be noted that while the addition of iron nanoparticles initially increased biogas production within the first 48 h, excessively high concentrations resulted in bacteria poisoning and ultimately led to a decline in biogas production [120]. The increase in biomethane production with the presence of iron nanoparticles can be attributed to the effect on the conditions of methanogenic microorganisms through the control of pH, the amount of volatile fatty acids, and the concentration of ammonia nitrogen [121].

5.2. Metal nanoparticles and metal oxides

Metals, as essential nutrients, play a crucial role in the efficiency and stability of agricultural biodigesters [122]. The incorporation of metal elements into anaerobic digestion can significantly enhance its performance. Apart from the essential elements found in food (N, O, H, and C), bacteria require metal elements such as metal ions (Al, Ca, Mg, K, and Na) and heavy ions (Ni, Zn, Cu, Co, Cr) to carry out aerobic processes [123]. Moreover, certain metal elements like Co, Cu, Fe, and Mo, and Ni can contribute to the stimulation and stabilization of anaerobic digestion for organic waste materials, even at low concentrations [124]. The addition of heavy metals such as Ni^{2+}, Zn^{2+}, and Cu^{2+} has been shown to improve the performance of the digester, with Ni^{2+} at 100 ppm yielding the best biogas production [125].

When the concentration of light and heavy metals is excessively high, it inhibits the system [38]. Zinc has a crucial role in enzymes and serves as a structural ion in the ester exchange factor, whereas copper is essential for coenzymes and biological electron transport [126]. In a study, the impact of four types of metal oxide nanoparticles (TiO_2, Al_2O_3, SiO_2, ZnO) on anaerobic digestion was examined, revealing that only ZnO had a detrimental effect on methane production, with no impact observed at low concentrations [127].

The increase in iron and zinc oxide nanoparticles and the decrease in cobalt oxide nanoparticles have a positive impact on methane production yield [128]. The researchers utilized Fe_3O_4 nanoparticles for anaerobic digestion of urban waste and determined the optimal dosage to be 75 g/L. They observed that if the nanoparticle dosage exceeds this amount, methane production will decrease [129].

5.3. Carbon-based nanoparticles

All compounds that contain carbon atoms in their structure are categorized as carbon-based nanomaterials, which are further classified based on their geometric structure. Graphene, fullerenes, and carbon nanotubes are significant examples of carbon-based nanoparticles used in various industries. Carbon nanotubes (CNTs) are nanometer-sized hollow tubes made up of carbon atoms, and they can exist as single-walled or multi-walled structures. Carbon nanotubes possess remarkable mechanical, absorption, electronic, and thermal properties, making them highly valuable in many industrial applications. Recently, they have also been explored for their potential use in biogas production, which is recognized as a branch of renewable energy.

Single-walled carbon nanotubes (SWCNTs) are cylindrical structures composed of a hexagonal lattice of carbon atoms. These nanomaterials play a crucial role in facilitating direct reciprocal electron transfer (DIET) in the anaerobic digestion (AD) process. Studies investigating the effects of SWCNTs on biogas production have observed an accelerated consumption of the loading materials, leading to a rapid release of biogas and a reduction in processing time. However, the methane production yield remains constant throughout the process [130].

Multiwalled carbon nanotubes (MWCNTs) consist of multiple layers of nested single-walled carbon nanotubes [131]. These nanomaterials have shown potential in enhancing biogas production through electron transfer to methanogenic microorganisms. Another successful approach for biogas production involves the use of ash-based nanomaterials. In a research study, the addition of ash particles with nano/micro dimensions (obtained from a municipal solid waste incinerator) to the anaerobic digestion (AD) digester resulted in a significant increase in biogas production [132].

6. Analysis of technical, economic, and environmental effects

Pretreatment is vital for all types of biomass in biogas production, with cost being a significant factor. However, an economically viable and cost-effective pretreatment method is necessary. The primary challenge in biogas production is implementing a specialized pretreatment process to maximize biogas fuel production. This objective often involves mechanical pretreatment and optimizing associated parameters. However, at large industrial scales, mechanical pretreatment can incur high energy, operating, and maintenance costs, leading to increased overall biogas production expenses. Consequently, combined pretreatment approaches prove more economically feasible than single pretreatment methods for achieving efficient biogas production. Biological pretreatment is an environmentally friendly method, although its effectiveness is inferior to thermochemical pretreatments. Additionally, it is worth noting that zero-valent iron nanoparticles show great promise in enhancing biogas production. A summary of key pretreatment conditions, substrates, and corresponding biogas yields is given in **Table 1**.

Table 1. Summary of Key Pretreatment Conditions, Substrates, and Corresponding Biogas Yields.

Substrate	**Pretreatment method & key conditions**	**Effect on biogas/methane yield**
Ley crop silage	Mechanical: Particle size reduction (from 2 mm to 0.125 mm)	Increased methane yield by ~43%.
Wheat straw	Mechanical: Particle size reduction (average size from 2.14 mm to 1.02 mm)	Doubled the consumption rate coefficient, indicating increased biodegradability.
Sunflower seed waste	Mechanical: Particle size optimization (1.4–2.0 mm)	Highest methane yield was observed within this particle size range.
Wheat straw	Alkaline (NaOH): 4% NaOH at 37 °C for 120 h	Increased methane production by 111.6% compared to untreated straw.
Lignocellulosic biomass	Alkaline (NaOH): 8% NaOH at 175 °C	Increased biogas yields up to 57%, primarily due to lignin removal.
Lignocellulosic biomass	Alkaline (NaOH): General pretreatment	Silica content reduced by 88.7%, significantly increasing biomass biodegradability.
Various biomasses	Alkaline (CaO): 10% CaO pretreatment	Increased methane production by 11.99%.
Sugarcane bagasse	Acidic (HCl): 0.63 M HCl, 136 °C, 6.4 min reaction time	Yielded 122.2 mL CH_4 per gram of volatile solids (VS) after 30 days under mesophilic digestion (35 °C).

Table 1. *Cont.*

Substrate	Pretreatment method & key conditions	Effect on biogas/methane yield
Rice straw	Comparative Acidic: 3% H_2O_2, 2% H_2SO_4, 2% HCl, 4% CH_3COOH	Biogas yield order: 3% H_2O_2 2% H_2SO_4 2% HCl 4% CH_3COOH. Hydrogen peroxide pretreatment showed the highest potential.
Dairy manure	Thermal-Alkaline: 150 °C with 1% NaOH	Identified as a more viable and cost-effective pretreatment option, enhancing Anaerobic Digestion (AD) performance via high buffering capacity and COD dissolution.
Waste Flower Straw	Biogas Slurry Pretreatment	Enhanced biogas production characteristics in anaerobic digestion.
Pinewood	Mesophilic Aerobic Digestion (Biological)	An efficient and inexpensive biological pretreatment improving biogas production from highly-recalcitrant feedstock.
(General)	Thermal Pretreatment: Hot air (90–170 °C), Microwave (140–200 °C), Autoclave (90–175 °C), Hot water bath (90–100 °C)	All have a positive effect on dissolving lignocellulosic biomass. Caution: Temperatures 150 °C may degrade lignin into phenolic compounds toxic to AD microorganisms.
(General - Nanoparticles)	Additive: Zero-Valent Iron (ZVI) Nanoparticles	Enhances hydrolysis as an electron donor; stabilizes digester and improves biogas production. Optimal concentration is critical as excess causes bacterial inhibition.
Urban waste	Additive: Fe_3O_4 Nanoparticles at 75 mg/L	Optimal dosage for enhanced methane production. Dosages exceeding this level led to decreased methane yield.

7. Conclusion

Fossil fuel pollution, which supplies the largest amount of energy in the world, is the main factor in changing the energy source towards renewable energy. The primary sources of biogas are found in abundance in the world, and according to the geographical location and living conditions, its type is different. According to the two approaches presented, the source of biogas production is adopted. Several factors, including temperature, reactor type, input concentration, input material type, and mixing, impact biogas production. To optimize and increase the production rate, the addition of pretreatment materials that yield positive effects is often beneficial. However, it is essential to evaluate the economic efficiency of such pretreatments. The ultimate objective is to reduce the overall cost of the production process while creating favorable conditions for bacteria.

Temperature fluctuations can disrupt bacterial activity and even halt their metabolic processes. Extensive research indicates that the most favorable temperature conditions for efficient digestion and maximum biogas production are typically within the mesophilic range. Maintaining stable temperature conditions within this range is crucial for optimizing production yields. Mixing time is inversely related to the fermentation speed and plays a vital role in preventing sedimentation within the digester. The carbon-to-nitrogen (C/N) ratio, commonly found to be around 25 in various studies, is a key parameter influencing microbial activity and biogas production. While a small amount of ammonia is necessary for bacterial survival, exceeding the recommended threshold can lead to digestive toxicity and inhibit biogas production. It should be noted that the concentration and size of the loaded materials should not be too low or too high; Because it will disturb the digestion process. The economic efficiency parameter is a limiting factor that has a specific range and there is no economic value of production outside this range. Speeding up and increasing the amount of production, which is the main goal, can be strengthened by using pre-treatment. Pretreatment is the most common way to improve the AD efficiency of LBs.

Pretreatment is a process that breaks down the rigid structure of lignocellulose, converting it into fermentable monomers. This results in a reduction in the digestion period and a significant increase in biogas yield (2–3 times). While physical pretreatment is effective, it often requires high energy consumption, making it less cost-effective. Additionally, excessive reduction during physical pretreatment can lead to the accumulation of volatile fatty acids. On the other hand, chemical pretreatment is considered the most efficient method for enhancing AD efficiency. However, it has drawbacks such as potential secondary pollution and the production of toxins. Therefore, a careful balance between effectiveness and the associated drawbacks needs to be considered when selecting the appropriate pretreatment method. It has been observed that among chemical pretreatments, alkaline pretreatment exhibits the highest performance. Sodium hydroxide (NaOH) is a commonly used alkaline pretreatment in anaerobic digestion applications. Comparatively, acidic pretreatment shows lower performance than alkaline pretreatment when used at the same molar concentration.

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