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Eggshell Calcium Nanoparticles: A Sustainable Approach to Boost Biogas Production from Tofu Liquid Waste

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Abstract

This study explored enhancing biogas and methane production from tofu liquid wastewater (TLW) by adding calcium nanoparticles. Eggshell calcium nanoparticles (ECN) in the form of nano $Ca(OH)_2$ were introduced to improve the degradation process. Chicken eggshells were calcinated at 1000 °C to create $Ca(OH)_2$ particles, followed by milling to yield ECN. Characterization using X-ray diffraction (XRD) confirmed the presence of $Ca(OH)_2$ in the ECN, while scanning electron microscopy (SEM) revealed the irregular morphology of the particles. Energy-dispersive X-ray spectroscopy (EDS) analysis showed calcium and oxygen as the primary elements. To investigate the effect of ECN in enhancing biogas and methane production, we evaluated 3 levels of ECN concentrations during anaerobic fermentation of TLW: 2.5 g/L, 5 g/L. and 7.5 g/L. We observed that adding ECN of 5 g/L during anaerobic digestion improved biogas production. Further, at this concentration, the methane concentration on the biogas was 64%, while on the control samples (without ECN) was only 0.09%. These findings suggested the benefit of ECN supplementation during anaerobic digestion of TLW for biogas production.

Introduction

Tofu, a staple food in many Asian cultures, is produced from soybeans through a process that generates a significant amount of liquid waste. This byproduct, known as tofu liquid waste (TLW), poses a challenge due to its high organic content and acidic nature [1].

TLW, if improperly disposed of, can have detrimental effects on the environment. Its high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) can deplete oxygen levels in waterways, harming aquatic life. Additionally, the acidic pH of TLW can disrupt the delicate balance of freshwater ecosystems [2], [3], [4].

Despite its potential negative impacts, TLW also presents an opportunity. Research has shown that this waste stream holds potential for various applications [5]. The organic matter in TLW can be converted into biogas, a renewable energy source. TLW can be used as a fertilizer with proper treatment due to its nutrient content [6].

Reutilizing the TLW is expected to improve the sustainability of the tofu industry. However, the methods for treating TLW and possibly utilizing the resulting products from TLW reutilization still need to be explored and optimized.

Biogas production from liquid waste offers a promising avenue for converting waste into a clean energy source. Anaerobic digestion is a promising technology for converting food wastewater into biogas [7], including TLW. Getting more biogas out of anaerobic digestion is crucial for it to be a viable alternative energy source. This efficiency is critical to reducing our carbon footprint and transitioning to a low-carbon economy. Turning organic waste into energy and valuable products helps us achieve this goal, effectively recycling these materials into the system. However, simply increasing biogas output is not enough. We need to consider the energy needs of the entire process. Pretreating some organic waste can improve its breakdown in the digester, but this might require special equipment and extra energy, potentially making the whole process unsustainable [8]. Recent advancements focus on speeding up the initial breakdown stage, also known as the hydrolysis step, using methods like heat [9], [10], mechanical processes [11], [12], [13], ultrasound [14], [15], [16], or even electrical pulses. However, the success of this new technology hinges on balancing increased biogas production with the energy required for the pretreatment itself. Another approach is adding specific materials to the digester, like conductive materials, adsorbents, trace elements, or enzymes, to enhance waste degradation [17], [18], [19], [20], [21], [22], [23]. These materials could escape the digester and harm the environment if they contain contaminants [7], [24]. For that, careful consideration is required before introducing materials to the digesters.

Liquid waste, including tofu processing wastewater, often exhibits an acidic nature with a low pH. This acidic environment can harm methanogenic bacteria, the key players in biogas production, through anaerobic digestion [25], [26]. They thrive in a slightly alkaline environment, typically with a pH ranging from 6.8 to 7.5. Thus, maintaining a specific optimal pH level for the microbes responsible for biogas generation is one of the bottlenecks in the waste-to-energy process from liquid waste.

Our previous study [27] has shown that adding eggshell calcium nanoparticles (ECN) during the anaerobic digestion of palm oil mill effluent mixed with cow manure increased biogas production. For that, we explore the impact of supplementing tofu liquid waste with calcium nanoparticles derived from eggshells (ECN) on its conversion into biogas. We expect that calcium acts as a pH buffer, helping to regulate and maintain this optimal range, as a previous study on palm oil mill effluent indicated [27]. When added to the liquid waste, calcium compounds like calcium carbonate (limestone) or calcium hydroxide (lime) react with the free hydrogen ions present in the acidic solution. This neutralizes the acidity, raising the pH towards the desired level for efficient methanogenesis.

This paper reports on our recent study on using ECN during the anaerobic digestion of TLW. Therefore, we investigated the biogas production from TLW with and without the addition of ECNs. Three concentrations of ECNs were investigated in this study: 2.5 g/L, 5 g/L, and 7.5 g/L.

Experimental Method

Figure 1 illustrates the general process involved in this study: TLW preparation, ECN preparation, and biogas production.

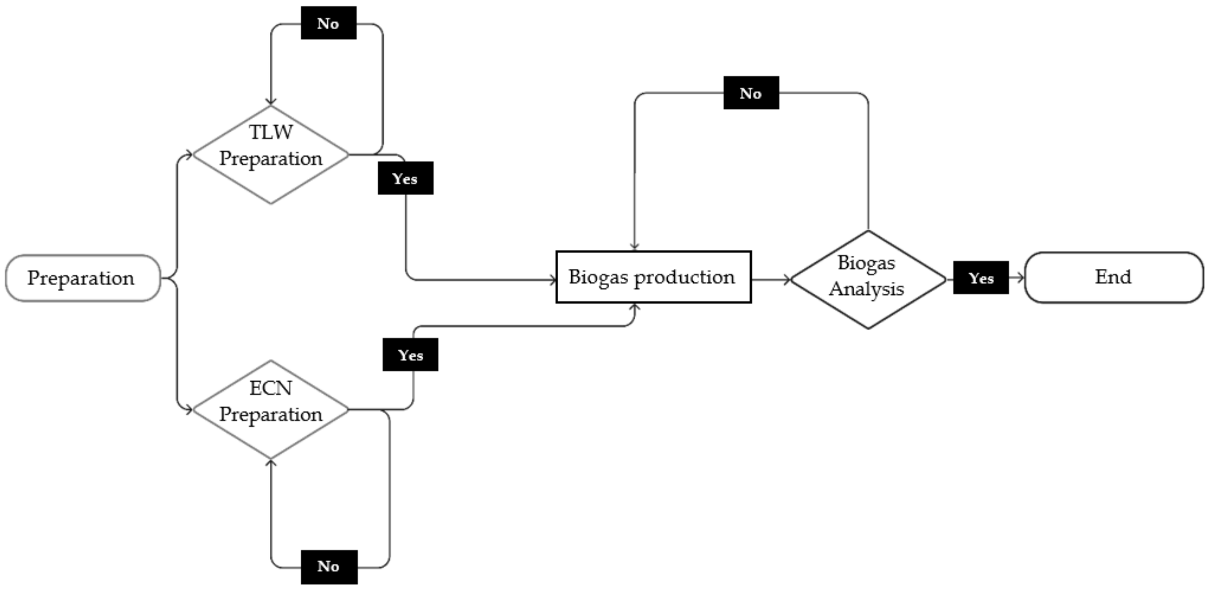

Figure 1. Flowchart indicating the process involved in converting TLW into biogas

Tofu Liquid Waste Preparation

Fresh Tofu liquid waste (TLW) was obtained from a commercial producer, Bandung Tofu Factory "Ashor," located in Cibanteng, Bogor, Indonesia. The use of an inoculum enhanced bacterial digestion. This inoculum was a probiotic produced from fermented coconut water. Commercially available fermented coconut water produced by CV. Tirta Herbal Sukses was used as it is.

Eggshell Calcium Nanoparticle (ECN) production from chicken eggshell

The ECN was produced following a previous study [27]. Figure 2 shows a flowchart indicating the process for producing eggshell calcium nanoparticles (ECN) from chicken eggshells (CES). Cleaned and dried chicken eggshells (CES) were weighed to determine their initial mass. The CES was then placed in a crucible and heated in a furnace at 1000 °C for 5 hours with a gradual temperature increase of 5 °C/minute. The resulting calcinated CES Eggshell Calcium (EC) particles were ground into a fine powder using a mortar. The mass of the CES powder was measured again after calcination. The calcinated EC particles would react with moisture in the air to form $Ca(OH)_2$ [19].

The calcinated EC particles were subjected to a milling process for 1 hour at a speed of 700 rpm to achieve nanoparticle dimensions. This milling treatment reduced the particle size of the calcinated CES powder, resulting in eggshell calcium nanoparticles (ECN) and an increase in its surface area. A larger surface area promotes enhanced biogas production using the ECN powder as an additive.

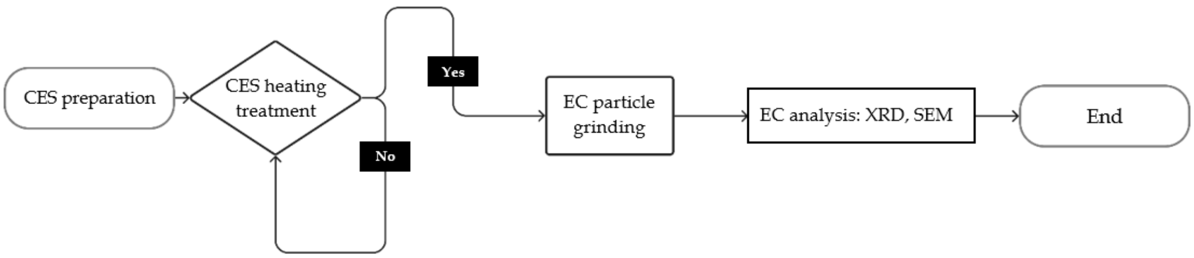

Figure 2. The flowchart indicates the process of producing eggshell calcium nanoparticles (ECN) from chicken eggshells (CES).

Biogas Production

The study employed four samples of a mixture of TLW, inoculum, and eggshell calcium nanoparticles (ECN) in $Ca(OH)_2$. ECNs were added to each digester in varying amounts and concentrations. These four samples were evaluated for biogas production. One sample served as a control, while the remaining three were supplemented with ECN and subjected to milling treatment at concentrations of 2.5 g/L, 5 g/L, and 7.5 g/L, respectively. Table 1 outlines the treatment types for the samples to be used. Figure 3 illustrates the experimental set adapted from a previous study [27], [28].

Table 1. Composition of Tofu Liquid Waste (TLW) and Eggshell Calcium Nanoparticle (ECN) Treatments.

Sample code	Composition
Control	0.1 L inoculum + 0.4 L TLW
2.5 NP	0.1 L inoculum + 0.4 L TLW + 2.5 g/L ECN
5 NP	0.1 L inoculum + 0.4 L TLW + 5.0 g/L ECN
7.5 NP	0.1 L inoculum + 0.4 L TLW + 7.5 g/L ECN

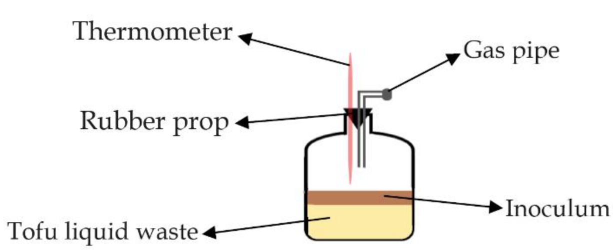

Figure 3. Experimental setup for anaerobic digestion of tofu liquid waste, adapted from the previous study [27], [28]

Each solution sample listed in the table was thoroughly stirred until a uniform mixture was achieved. Stirring was carried out daily using a magnetic stirrer for 30 minutes per sample. The stirred samples were then stored at room temperature for a predetermined duration. Following the storage period, biogas volume measurements were performed. Concurrent with daily stirring using a magnetic stirrer, the temperature and pressure of each sample were also measured daily using a thermometer and barometer, respectively. These daily temperature and pressure measurements enabled the estimation of the gas production rate.

Analysis

The ECN powder underwent characterization using scanning electron microscopy (SEM) Hitachi, SU-3500 at an accelerating voltage of 20 kV and X-ray X-ray diffractometer (XRD) RIGAKU, SMARTLAB using CuKα (1.541862 Å) at 40 kV and 30 mA techniques. SEM characterization revealed the morphology and particle size of the powder. EDS characterization enabled the determination of the elemental composition and mass percentages of the elements present in the sample. XRD characterization was employed to identify the phases, crystallite size, and lattice parameters of the ECN powder.

The daily temperature and pressure data obtained from the measurements serve as a basis for determining the gas mole. The ideal gas law, represented by the equation PV = nRT, is employed to calculate the biogas mole. In this equation, P represents the pressure (N/m^2 or Pa), V represents the biogas volume obtained, n represents the number of particles (mol), and R represents the ideal gas constant (0.082 atm.L/mol.K). Biogas produced would increase the height of the liquid in the digester. By measuring the height of liquid on each day and knowing that the initial volume of liquid was 500 mL, we can calculate the volume of the biogas produced as:

$$V_{biogas\ produced} = V_{liquid\ observed\ at\ particular\ day} - V_{liquid\ initial} \quad (1)$$

The generated biogas underwent analysis using a Shimadzu 8A TCD gas chromatograph to quantify the methane (CH_4) concentration within the biogas. This gas chromatography apparatus utilizes argon (Ar) as the carrier gas, an activated carbon column as the stationary phase, a column temperature of 100 °C, and a gas flow rate ranging from 40 to 70 cc/min.

Result and Discussion

Eggshell Calcium Nanoparticle (ECN) production

Calcination involves heating a substance to an elevated temperature below its melting point to eliminate volatile components. Eggshells comprise 94% calcium carbonate, 1% calcium phosphate, 1% magnesium carbonate, and the remaining portion is organic matter [29]. Chicken eggshells undergo calcination to remove organic compounds and protein fiber layers. The calcination temperature typically employed for eggshells falls within the 900 to 1100 °C range. The chemical reaction that transpires during the eggshell calcination process is as follows.

$$CaCO_{3(s)} \xrightarrow{heat} CaO_{(s)} + CO_{2\,(g)} \quad (2)$$

Chicken eggshells (CES) underwent calcination at 1000 °C for 5 hours within a furnace, employing a heating rate of 5 °C/min. The mass of the CES post-calcination was lower than that of the pre-calcination CES, attributed to the release of organic matter and the expulsion of CO_2 from $CaCO_3$ because of the applied heat. We observed mass loss percentage for c.a 46% (Fig 4). CES mass lost was calculated as:

$$CES\ mass\ lost\ (\%) = \frac{mass\ of\ CES_{before\ calcination} - mass\ of\ CES_{after\ calcination}}{mass\ of\ CES_{before\ calcination}} \times 100\% \quad (3)$$

CES mass loss indicates the success of the decomposition of calcium carbonate ($CaCO_3$) in the eggshell into calcium oxide (CaO). The CES's color changes from light brown to light white after calcination, confirming the decomposition of calcium carbonate to calcium oxide [30].

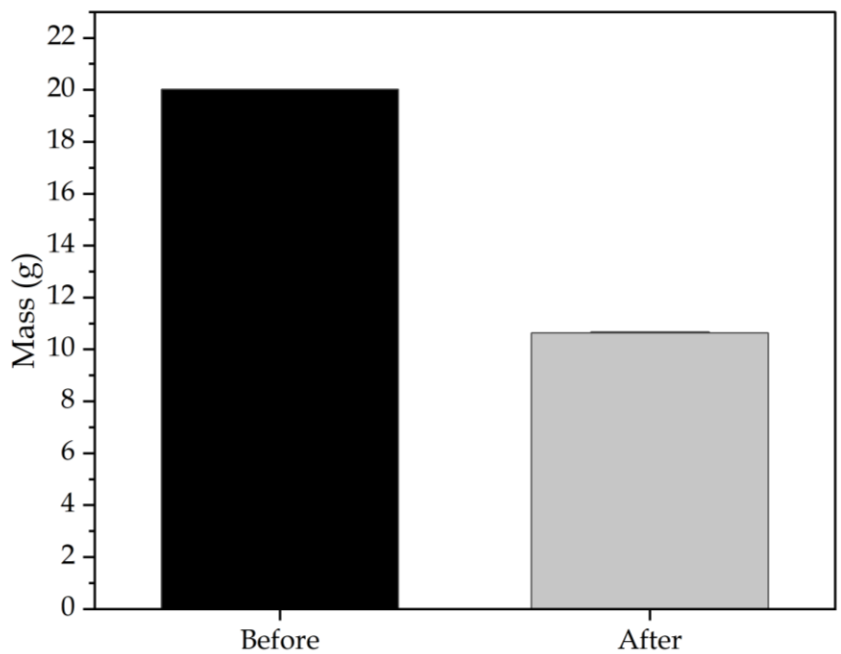

Figure 4. Mass of CES before and after calcination. Percentage mass loss: 46.88 ± 0.12%

The X-ray diffraction (XRD) spectrum of the calcinated and ECN powder was acquired using CuKα radiation (λ = 1.54056 Å) at 2θ angles ranging from 10° to 90° (Fig 5). The XRD pattern of this ECN sample was successfully matched with the XRD pattern for $Ca(OH)_2$ as listed in the Joint Committee on Powder Diffraction Standards (JCPDS) under no. 04-0733. This indicates that calcium carbonate, the main constituent of eggshell [31], has been successfully converted into calcium oxide through thermal treatment [32]. However, the diffractogram showed peaks corresponding to the calcium hydroxide ($Ca(OH)_2$) rather than calcium oxide CaO. The presence of $Ca(OH)_2$ in the XRD diffractogram is likely due to the hygroscopic nature of CaO. Since CaO readily absorbs moisture from the air, it can easily convert to $Ca(OH)_2$ before or during the XRD analysis. The XRD pattern of the ECN is presented in Figure 5. The

2θ angles observed for the sample closely align with those reported in the JCPDS database for $Ca(OH)_2$. A detailed comparison of the 2θ angles corresponding to the XRD peaks of the ECN sample with those in the JCPDS database for $Ca(OH)_2$ is provided in Table 2.

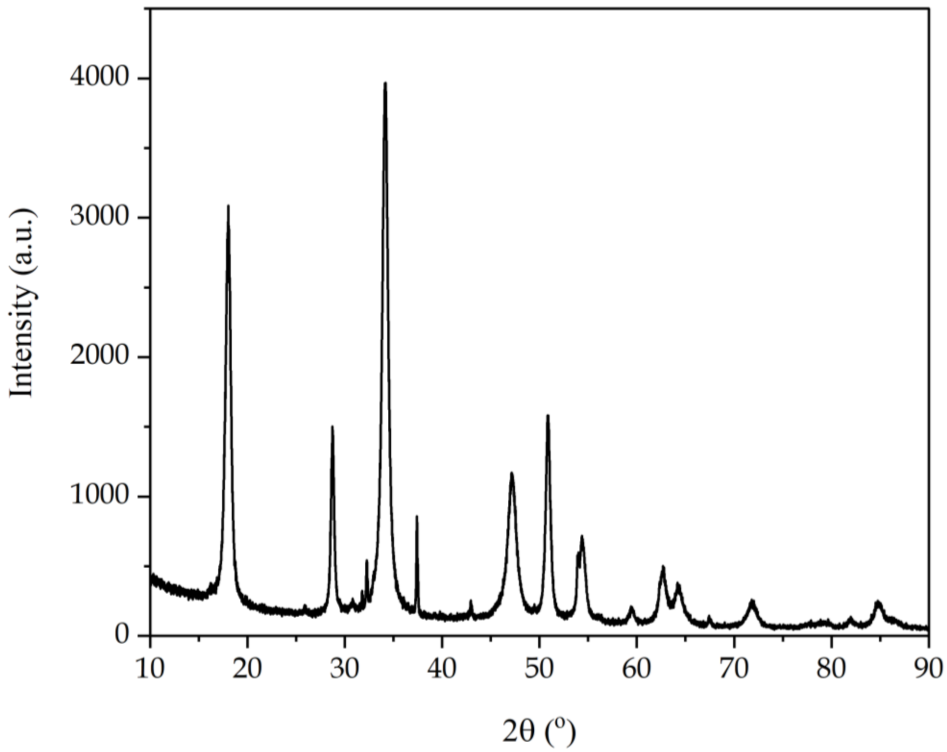

Figure 5. XRD diffractogram of ECN (Eggshell Calcium Nanoparticle)

The lattice parameters of the ECN sample were calculated using the Cohen Method [33] based on the obtained XRD pattern. According to JCPDS data No. 04-0733, the crystal structure of $Ca(OH)_2$ is hexagonal with lattice parameter values of a = b = 3.589 Å and c = 4.916 Å. These values correspond to the accuracy of 99.93% and 99.97, respectively, to those of JCPDS data No. 04-0733. We also calculated the crystallite size using Scherrer formulae (Table 2). Figure 6 shows the morphology of ECN obtained from SEM characterization. We observed that the ECN exhibited homogenous agglomerated particles. The image processing using Fiji ImageJ confirmed the formation of ECN with the particle size in the 467– 1604 nm range. The Energy Dispersive X-ray Spectroscopy (EDS) showed that the ECN consists of 45.4% Ca and 46.7% O. This confirmed the presence of $Ca(OH)_2$.

Table 2. The crystallite size of ECN is based on Scherrer formulae.

2θ (◦)	Crystallite Size (nm)
18.02	19.20
28.71	24.93
34.12	13.41
50.81	18.12
54.40	19.23

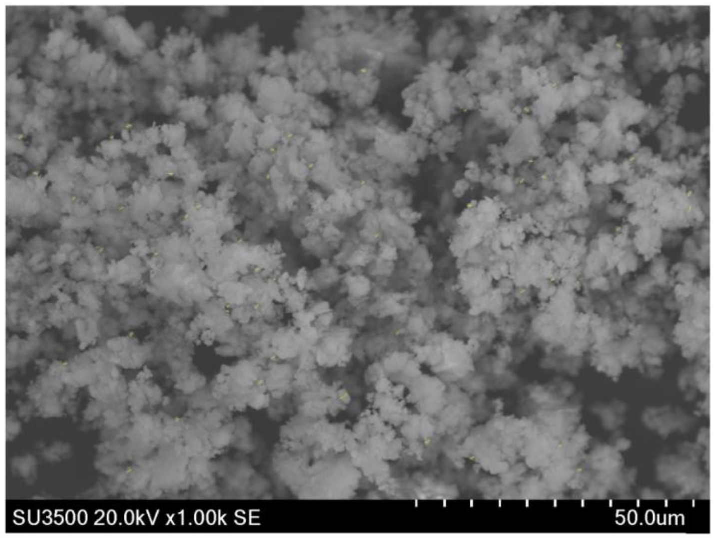

Figure 6. SEM Images of ECN with 1000x magnification

Biogas Production

Tofu production generates a significant amount of liquid waste. While traditionally disposed of, this wastewater holds hidden potential. It turns out that tofu liquid waste is rich in organic matter, making it a prime candidate for conversion into biogas through anaerobic digestion. Anaerobic digestion is a biological process where microorganisms break down organic material in an oxygen-free environment. When applied to tofu liquid waste, these microbes feast on the organic components, like carbohydrates, proteins, and fats. As they decompose this organic matter, they produce biogas, a mixture of gases primarily composed of methane (CH_4), carbon dioxide (CO_2), and smaller quantities of other gases. This process offers a sustainable solution for tofu waste management. Instead of polluting the environment, the waste is transformed into a valuable source of clean energy. Our study investigates tofu liquid waste (TLW) digestion using inoculum. We are particularly interested in evaluating the benefits of adding ECN to this process.

To monitor the initial stages of biogas production, we measured the air pressure within the reactor daily. This data was then used to calculate the mole of biogas produced. For calculating the moles of biogas, we used the measured pressure (P), the biogas volume (obtained by subtracting the volume of the solution a particular day with the initial volume, the ideal gas constant (R = 8314 J/kmol K), and the measured temperature (T) in the ideal gas law equation:

$$n = \frac{pV}{RT} \quad (4)$$

Figure 7 shows the daily pressure of the reactor for a total of 30 days. The presence of ECN in the digester seemed to boost gas production. Pressure readings for the first few days were similar across all samples. There was a dip in pressure between days 3 and 10, suggesting a decrease in gas production, as seen in other studies [23]. Interestingly, pressure rose significantly from day 23 onwards, especially in samples with ECN. This suggests renewed gas production. For example, pressure in sample 5 NP increased from day 2 to day 29, while pressure in the control sample stayed the same. Overall, the pressure variations after day 10 suggest improved conditions for bacteria growth, particularly in samples with ECN. This is further supported by the higher pressure observed in all ECN samples by day 29, indicating more gas production.

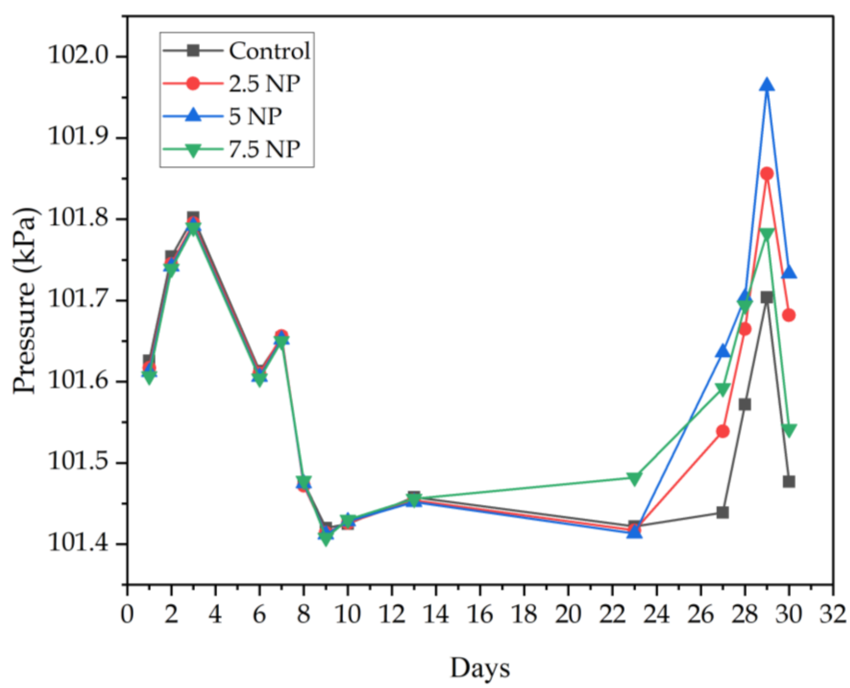

Figure 7. Pressure measured on the reactor from day 1 until day 30

We observed that the pressure was significantly dropped on the 30th day. Therefore, to evaluate the mole of biogas that was produced, we only compared the delta of mole of the 1st and the 29th day. The delta mole of the 1st day is calculated as the difference of the mole on the 1st day with that of the 0th day. At the same time, the delta mole of the 29th day is calculated as the difference between the mole on the 29th day and that of the 0th day. Figure 8 shows this data.

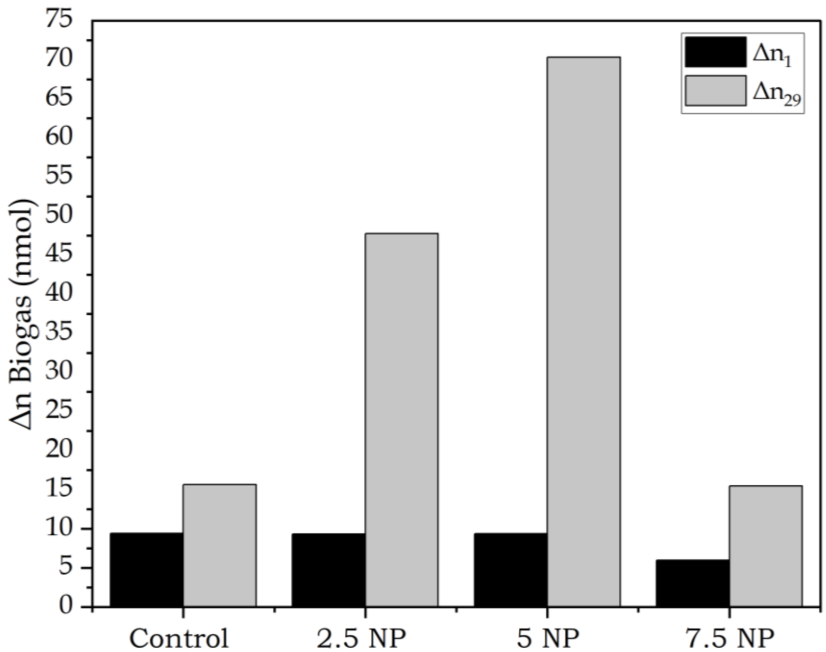

Figure 8. An additional mole of biogas is produced on the 1st day and 29th day of digestion

The addition of ECN powder significantly increased pressure and biogas production compared to the control group, as shown in Figures 7 and 8. Samples 5 NP showed the highest values, followed by 2.5 NP, 7.5 NP, and the control sample. These findings suggest that ECN promotes reactions between itself and the substrate, creating a more favorable environment for bacterial growth [27]. Other studies indicate that the benefits of calcium extend beyond simply raising the pH. Calcium also plays a role in strengthening the cell walls of methanogenic bacteria, improving their overall health and efficiency. Additionally, calcium can help mitigate issues like foaming disrupting the smooth operation of biogas digesters [35], [36].

Sample 5 NP, with the highest biogas volume, indicates that adding 5 g/L ECN to the substrate represents the optimal concentration for bacterial growth during biogas production using tofu wastewater and fermented coconut water probiotic solutions. The other two samples, 2.5 NP and 7.5 NP exhibited less optimal bacterial growth. This could be attributed to the inability of $Ca(OH)_2$ to effectively maintain a neutral pH in the substrate, resulting in a suboptimal environment for methanogenic bacteria. pH is crucial in anaerobic fermentation, influencing microbial growth and activity. Generally, a pH range of 6.6-7.5 is suitable for aerobic fermentation. When the pH falls below 6.5 or exceeds 8.2, methanogenic bacterial activity is hindered [37]. Therefore, a buffer with an appropriate concentration is necessary to maintain a neutral pH in case of acid addition, ensuring the overall process equilibrium remains stable [38].

By day 30, biogas production began to decline in all samples. This suggests that after 29 days, the substrate environment became less conducive for biogas production, eventually leading to a halt in biogas generation.

A correlation was observed between high biogas volume and high methane concentration. Methane concentration measurements were conducted only for the control sample and sample 5 NP. The procedure involved injecting gas into Duran bottles (sealed with rubber stoppers) and analyzing the gas composition using a gas chromatography instrument. These measurements aimed to determine whether ECN addition influenced the concentration of methane produced. The results are presented in Table 3.

Table 3. Methane concentration.

Sample	Methane concentration (%)
Control	0.09
5 NP	64.17

The addition of ECN was found to enhance methane production. The methane concentration in the control sample was 0.09%, while sample 5 NP exhibited a methane concentration of 64.17% of the total biogas volume on the last day of the experiment.

Conclusion

This paper reports on our recent study on using ECN during the anaerobic digestion of TLW. Therefore, we investigated the biogas production from TLW with and without the addition of ECNs. A 30-day anaerobic fermentation process was conducted to investigate biogas production from a mixture of tofu wastewater and probiotics (coconut water fermentation) supplemented with calcium eggshell nanoparticles (ECN) in the form of $Ca(OH)_2$. The addition of ECN resulted in a significant increase in both biogas and methane production. All samples treated with ECN powder exhibited higher biogas volumes than the control sample, in the following order: 5 NP, 2.5 NP, and 7.5 NP. This qualitatively demonstrates that ECN powder addition to the samples led to an increase in biogas volume. Sample 5 NP showed a remarkable methane concentration of 64.17%, far exceeding the control sample's methane concentration of merely 0.09%. Our findings indicate that calcium is critical in ensuring optimal conditions for biogas production from tofu liquid waste. By effectively buffering the pH and supporting the health of methanogenic bacteria, calcium paves the way for a successful and sustainable waste-to-energy conversion process. Developing biogas purification methods is suggested for future research.

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