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EFFECT OF SILICON OXIDE NANOADDITIVE ON BIOGAS AND METHANE YIELD OF ANAEROBIC DIGESTION OF COW DUNG AND SHEEP DUNG

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Abstract

Anaerobic digestion of animal waste is a promising approach for renewable energy production, but enhancing its efficiency remains a challenge. This study investigates the effect of silicon oxide nanoadditive on the biogas and methane yield of anaerobic digestion using cow and sheep dung as substrates. Previous research suggests that nanoadditives can improve microbial activity and enhance biogas production. However, limited studies have focused on the specific impact of silicon oxide nanoadditive on biogas quality and methane yield, particularly using cow and sheep dung as feedstock. Cow and sheep dung samples were collected and subjected to anaerobic digestion with and without the addition of silicon oxide nanoadditive. Biogas composition including methane, carbon dioxide, hydrogen sulfide, and carbon monoxide was analyzed using gas chromatography. Addition of silicon oxide nanoadditive increased methane content in cow dung biogas from 64.9% to 65.7% and in sheep dung biogas from 59.3% to 60.2%. This enhancement suggests improved microbial activity and organic matter breakdown. The nanoadditive also reduced carbon dioxide content, indicating more efficient carbon conversion to methane. Additionally, it mitigated hydrogen sulfide content, particularly in sheep dung, improving overall gas quality. Silicon oxide nanoadditive shows promise in enhancing biogas quality and methane yield from cow and sheep dung. The findings highlight the potential of nanoadditives in optimizing anaerobic digestion processes for renewable energy production. Further research is recommended to optimize nanoadditive concentrations and assess long-term effects on anaerobic digestion performance. This study contributes to understanding the role of nanoadditives in improving biogas production from animal waste, advancing sustainable energy solutions.

Keywords: Silicon Oxide, Nanoadditive, Biogas, Methane, Anaerobic Digestion, Cow Dung, Sheep Dung.

Introduction

Anaerobic digestion (AD) is a widely practiced process for converting organic materials by a variety of microbial species in the absence of oxygen into biogas, with potential applications in waste treatment and renewable energy production (Achinas *et al*. 2020), through the addition of a second digestion stage (Nekhubvi *et al.* 2024) Anaerobic digestion is a crucial technology for sustainable waste management and renewable energy production (Uddin *et al.* 2021; Kumar *et al.* 2020; Chen *et al.* 2005; Labatut *et al.* 2018). It offers significant environmental and economic benefits by reducing waste, conserving resources, and reducing greenhouse gas emissions (Uddin *et al.* 2021). However, its potential for energy recovery from organic waste is not fully realized due to operational issues and process instability (Kumar *et al.* 2020). The technology's ability to destroy complex organic matter in wastes and provide pollution prevention, waste conservation, sustainable energy, and nutrient recovery makes it a key method for waste reduction and renewable fuel recovery (Chen *et al.* 2005) and a key player in the circular economy (Sevillano *et al.* 2021). Anaerobic digestion's robustness allows for the conversion of food waste into methane, which can be used for heat and electricity generation (Labatut *et al.* 2018). Despite the challenges, the technology's potential for sustainable waste management and renewable energy production is significant. However, challenges such as slow process kinetics and poor stability have prompted the exploration of complementary technologies, including microbial electrochemical systems, to enhance AD performance (Zakaria *et al.* 2020). This process can be optimized through the acceleration of syntrophic interactions and methanogenic reactions, which can be achieved through process chemistry (Anukam *et al.* 2019). AD has evolved beyond its traditional role in biogas generation, with applications now including waste remediation, bioenergy generation, and the treatment of micropollutants (Khanal *et al.* 2021).

Anaerobic digestion of organic waste produces biogas, which is primarily composed of methane and carbon dioxide, with small amounts of hydrogen sulfide, oxygen, ammonia, and nitrogen (Bedoić *et al.* 2018). The specific composition can vary, with typical ranges of 55-65% methane, 35-45% carbon dioxide, and 0.5-1.0% hydrogen sulfide (Yadav *et al.* 2014). Anaerobic digestion of organic waste, such as cow dung and water hyacinth, can produce biogas with a composition of 56.4% methane, 35% carbon dioxide, and 6.9% nitrogen (Uche *et al.* 2020). The use of hydrogen-assisted pathways and two-stage anaerobic digestion can enhance methane production and improve its proportion in the biogas composition (Silva *et al.* 2021). The composition of biogas from domestic waste through anaerobic digestion is 63% methane, 31% carbon dioxide, and 1% hydrogen sulfide, with a calorific value of 24.10 MJ/m3 (E.I *et al.* 2020). Biogas production takes place in an anaerobic digestion reactor which could be batch reactor, plug flow reactor or continuously stirred tank reactor. For this study, a laboratory scale CSTR was used because of its simplicity in design and operation, and its ability to provide greater uniformity of system parameters (Usack *et al.* 2012).

Nanotechnology has shown promise in enhancing the anaerobic digestion (AD) process. Chuenchart *et al* (2021) and Jeyakumar *et al* (2022) both highlight the potential of nanobubble technology and nanomaterials, respectively, in improving the efficiency of AD. These technologies can enhance substrate accessibility, enzymatic activity, and microbial activity, leading to increased biogas production. Baniamerian *et al.* 2019 further categorizes the types of nanomaterials used in AD, including zero-valent metallic NPs, metal oxide NPs, carbon-based nanomaterials, and multi-compound NPs. Goswami (2022) specifically discusses the use of nano-biochar as a sustainable catalyst in AD, emphasizing its role in enhancing biogas production and the need for further evaluation of its multi-functional roles. These studies collectively underscore the potential of nanotechnology in improving the AD process, with a focus on enhancing biogas production and process stability.

The objectives of the study on the effects of silicon oxide nanoadditive on anaerobic digestion and biogas production include assessing the impact of the nanoadditive on biogas yield, digestion efficiency, and microbial activity. The hypothesis being tested is that the addition of silicon oxide nanoparticles will enhance biogas production and improve the efficiency of anaerobic digestion processes.

The use of silicon oxide nanoadditive in anaerobic digestion (AD) processes has been shown to have a significant impact on biogas and methane production. Dehhaghi *et al.* 2019 and Ganzoury and Allam (2015) both highlight the potential of various nanomaterials, including silicon oxide, to enhance biogas production. The positive effects of these nanoadditives are attributed to their ability to stabilize the AD process, stimulate the growth of beneficial microorganisms, and improve biogas release. Furthermore, Hassanein *et al.*2021 and Ajay *et al.* 2020 emphasize the role of electro-conductive nanoparticles, which could include silicon oxide, in improving microbial degradation and promoting methane production. These findings suggest that the use of silicon oxide nanoadditive in AD processes has the potential to significantly increase biogas and methane production. Ajay *et al.* 2020 further emphasizes the role of nanoparticle additives in influencing AD, particularly through direct interspecies electron transfer (DIET) and conductive materials. Amo-Duodu *et al. (*2021) specifically discusses the application of metallic nanoparticles, which could potentially include silicon oxide, in increasing biogas production. These studies collectively suggest that the use of silicon oxide nanoadditive in AD processes can lead to improved biogas and methane production, although further research is needed to fully understand its mechanisms and potential environmental impacts.

A range of studies have explored the use of nanoadditives in anaerobic digestion processes, with a focus on their effects on microbial activity, methane yield, and process stability. Ajay *et al.* (2020) and Paritosh (2020) both highlight the potential of nanoadditives to enhance biogas production and improve biochemical activities, such as syntrophic, metabolic, catalytic, and enzymatic activities. Zhu *et al.* (2020) further supports these findings, noting the positive effects of metallic nanoparticles on gas production, effluent quality, and process optimization. However, the specific mechanisms behind these effects are not fully understood. Romero-Güiza (2016) provides a comprehensive review of inorganic and biological additives, including the promising role of iron in enhancing anaerobic digestion performance. These studies collectively suggest that nanoadditives, particularly metallic nanoparticles, have the potential to improve anaerobic digestion processes, but further research is needed to fully understand their mechanisms and optimize their use.

The characteristics of cow dung and sheep dung as substrates for anaerobic digestion are influenced by their microbial composition, carbon to nitrogen ratio, and potential for direct interspecies electron transfer. Cow dung, for example, has a favorable carbon to nitrogen ratio for microbial growth and a high carbon utilization rate, making it a suitable substrate for anaerobic digestion (Mutungwazi *et al.* 2022). However, the degradation of recalcitrant lignocellulosic components in cow dung can be promoted through co-digestion with lignin-poor co-substrates and various pretreatment methods (Li *et al.* 2021). The use of cow dung in anaerobic digestion can also be enhanced through the introduction of additives such as trace metals, carbon-based materials, and microbial cultures (Li *et al.* 2021). Similarly, sheep dung can benefit from co-digestion with other substrates to improve its carbon/nitrogen ratio and nutrient balance, as well as to increase the diversity of microbial communities (Ferdeș, *et al.* 2023). The potential for direct interspecies electron transfer in both cow dung and sheep dung can be further explored to enhance their performance in anaerobic digestion (Zhuravleva *et al.* 2022).

AD Process Parameters

A range of process parameters have been identified as crucial in the anaerobic digestion process. These include anaerobic conditions, temperature, system pH, volatile fatty acid content and conversion, availability of micro and trace nutrients, mixing, toxicity, solid retention time, volatile solids loading rate, and hydraulic retention time (Bajpai, 2017). In the context of dry anaerobic digestion, further research is needed to optimize parameters such as inoculum to substrate ratio, feedstock composition and size, liquid recirculation, bed compaction, and use of bulking agents (Rocamora *et al.* 2019). Monitoring and control of these parameters is also essential, with pH, alkalinity, gas production rate, gas composition, and volatile fatty acid concentration being key indicators (Björnsson, 2000). In the specific case of food waste anaerobic digestion, the intermediate alkalinity/partial alkalinity ratio has been proposed as a reliable indicator of process imbalance (Mei e*t al.* 2016).

Materials and Methods

Materials

The animal manure (cow dung and sheep dung) used for this study was obtained from Zungeru market, Niger State, Nigeria. Other materials and equipment include Continuously Stirred Tank Reactor (CSTR), Measuring cylinder, respirator, vertical stirrer (manually operated), Grant gas analyzer.

Analysis of the Substrate

The sample of animal manure (cow and sheep dung s) for this research was taken to the laboratory for analysis before the experiment and the following parameters were determined: Total solid (%), Volatile solid (%), Moisture Content (%)

Methods

Preparation of Silicon Oxide Nanoadditive

Producing silicon oxide nanoadditives involves a series of chemical and physical processes designed to create nanoparticles with specific properties suitable for enhancing anaerobic digestion. The detailed procedure for producing silicon oxide nanoadditives are highlighted below;

Materials and Equipment: Tetraethyl orthosilicate (TEOS), Ethanol, Ammonium hydroxide (NH_4OH), Deionized water, Magnetic stirrer, Ultrasonic bath, Centrifuge, Drying oven, High-purity nitrogen gas (optional), pH meter, Beakers, Pipettes.

Procedure

In a beaker, a solution was prepared by mixing ethanol and deionized water in a 4:1 ratio. To this solution, 20 ml of TEOS was added. Typically, a molar ratio of 1:4:16 (TEOS:NH_4OH:H_2O) was used. Ammonium hydroxide was carefully added to the mixture while stirring continuously, initiating the hydrolysis and condensation reactions necessary for silicon oxide nanoparticle formation. The pH of the solution was maintained between 9 and 10, monitored and adjusted using a pH meter.

The beaker was then placed on a magnetic stirrer, and the solution was stirred vigorously for about 2 hours at room temperature to ensure uniform reaction progression. The mixture was centrifuged at high speed (typically 10,000-15,000 rpm) for 30 minutes to separate the silicon oxide nanoparticles from the liquid phase, and the nanoparticle precipitate was collected.

The precipitate was washed several times with ethanol and deionized water to remove any residual reactants and by-products, using centrifugation after each wash to separate the nanoparticles from the washing liquids. The washed nanoparticle precipitate was then transferred to a drying oven and dried at 65°C for 4 hours to remove any remaining solvent and moisture.

Finally, a Scanning Electron Microscope (SEM) was used to ensure that the nanoparticles were within the desired size range (typically 10-100 nm) and possessed the appropriate surface characteristics for enhancing anaerobic digestion.

Measurements of Daily Gas Production Using Water Displacement Method

The water trough was filled with water trough, leaving enough space to submerge the gas collection cylinder. The graduated cylinder or gas collection bottle was filled with water completely. The graduated cylinder was carefully inverted in the water trough, ensuring no air bubbles are trapped inside. The open end was be submerged under water. One end of the rubber tubing was attached to the biogas outlet of the digester and the other end to the submerged mouth of the graduated cylinder. Soap solution was applied to the connections and watch for bubbles to ensure there are no leaks in the system. The biogas produced from the anaerobic digester was allowed to flow through the tubing into the graduated cylinder. The gas displace the water in the cylinder, causing the water level to drop. The gas collection was monitored. It was ensured that the graduated cylinder remains submerged in the water trough and that the gas is continuously collected. The volume of gas was recorded by reading the level of water displaced in the graduated cylinder on a daily basis for retention period of 30 days.

Results and Discussion

Continuously Stirred Tank Reactor (CSTR) biodigester was used for anaerobic digestion of cow dung and sheep dung improved with silicon oxide (SiO_2) nanoadditives for a retention period of 30 days. Biogas yield from anaerobic digestion of cow dung only, sheep dung only, cow dung with silicon oxide (SiO_2) nanoadditives and sheep dung with silicon oxide (SiO_2) nanoadditives were monitored.

Table 1: Physical properties of the substrate

Substrate	**Total Solid (%)**	**Volatile Solid (%)**	**Moisture** Content (%)
Cow dung	2.31	1.76	98.40
Sheep dung	2.52	1.58	98.20

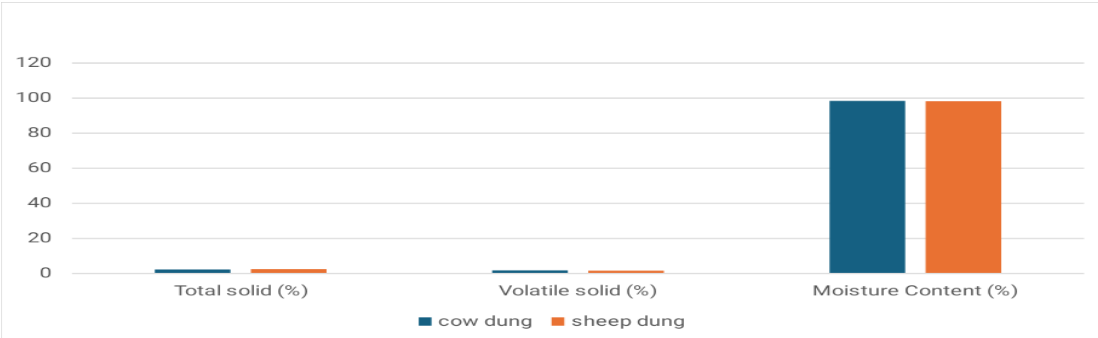

Figure 4.1 Physical properties of the substrate

From table 1, it was observed that Cow dung has a slightly higher total solids content of 2.52% compared to sheep dung of 2.31%. This indicates that cow dung has more overall solid material per unit weight, which includes both organic and inorganic matter. The higher total solids content in cow dung suggests that it may have a greater potential for biogas production, assuming similar efficiency in the digestion process, because it contains more material that can be converted into biogas. The volatile solids content, which represents the organic matter, is also higher in cow dung (1.76) compared to sheep dung (1.58). This is important because the volatile solids are the portion of the total solids that contribute to biogas production during anaerobic digestion. The higher volatile solids content in cow dung suggests that it has more organic material available for microbial digestion and biogas generation. The percentage of volatile solids in the total solids is slightly higher for cow dung (approximately 69.84%) compared to sheep dung (approximately 68.40%). This indicates that a larger fraction of the total solids in cow dung is organic and thus available for biogas production. The close percentages suggest that both types of dung have a high proportion of organic matter relative to their total solid content, making them both suitable for biogas production. The differences in total and volatile solids between cow dung and sheep dung can be attributed to variations in the animals' diets and their digestive processes. Cows and sheep have different feeding habits and digestive systems, which affect the composition of their manure. Cows typically consume larger quantities of fibrous plant material, which may contribute to the higher total and volatile solids content in their manure. It further shows that cow dung has a higher VS content than sheep dung, which implies that cow dung has more biodegradable organic matter available for anaerobic digestion. This suggests a potentially higher biogas yield from cow dung compared to sheep dung. Both substrates have very high moisture content, which is beneficial for anaerobic digestion. The slightly higher moisture content in cow dung could make it slightly more suitable for microbial processes, though the difference is minimal. High moisture content is advantageous for the anaerobic digestion process as it ensures that the substrate remains in a slurry form, which is easier to mix and process in the digester. Both cow dung and sheep dung have high moisture content (above 98%), making them ideal for anaerobic digestion. The slight difference in moisture content (98.4% for cow dung and 98.2% for sheep dung) is unlikely to have a significant impact on the overall process efficiency. Both substrates have high moisture content and low total solids, making them suitable for wet anaerobic digestion processes. The primary difference lies in their volatile solids content, which makes cow dung a somewhat better substrate for biogas production.

Table 2: Carbon Content and Calorific Value of the Substrate

SUBSTRATE	Carbon content (%)	Calorific value (kJ/kg)
Cow dung only	38.46	18,451.66
Sheep dung only	33.60	12,819.23

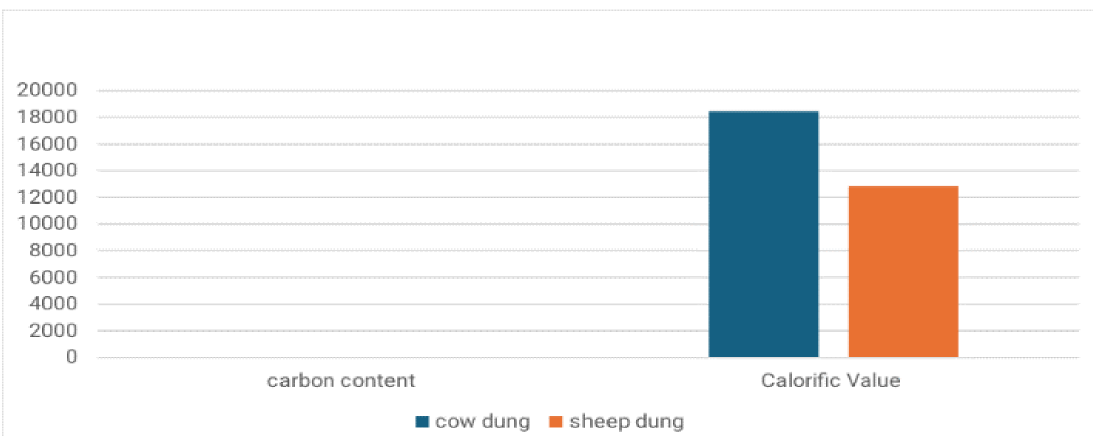

Figure 4.2: Carbon Content and Calorific Value of the Substrate

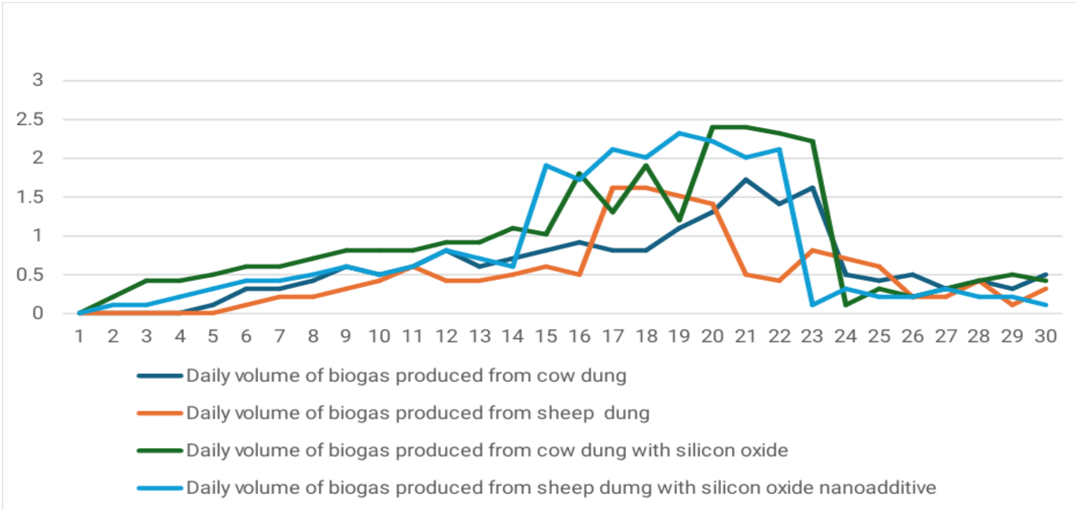

Figure 1: Graph of daily volume of biogas produced (m^3) against retention period (days)

Table 2 shows the carbon content and calorific values of cow dung and sheep dung. It was observed that Cow dung has a higher carbon content compared to sheep dung. This implies a greater amount of organic matter available for microbial conversion to biogas. Carbon is a primary element in the biochemical pathways that produce methane (CH_4) and carbon dioxide (CO_2) during digestion. The higher the carbon content, the greater the potential for biogas production, given that more carbon is available for conversion into methane. Therefore, cow dung is expected to have a higher biogas yield compared to sheep dung. The calorific value measures the amount of energy released during the combustion of a substrate. While anaerobic digestion doesn't involve combustion, the calorific value indicates the energy potential of the substrate, which translates to the energy available for biogas production. Cow dung has a significantly higher calorific value than sheep dung. This higher energy content means that cow dung has more potential energy that can be converted to biogas. Higher calorific value also suggests that the substrate can provide more energy per unit mass, which can improve the overall efficiency of the anaerobic digestion process. With 38.46% carbon content, cow dung has a rich organic matter composition, which is beneficial for the microbial activity in anaerobic digesters while With 33.6% carbon content, sheep dung also provides a substantial amount of organic matter, though less than cow dung. At 18,451.66 KJ/kg, cow dung has a high energy potential, suggesting a higher efficiency in biogas production. At 12,819.23 KJ/kg, sheep dung has a lower energy potential compared to cow dung, indicating a lower efficiency in biogas production. Given its higher carbon content and calorific value, cow dung is a more suitable substrate for anaerobic digestion in terms of both biogas production and energy efficiency, while still a viable substrate, sheep dung has a lower potential for biogas production compared to cow dung, given its lower carbon content and calorific value.

Table 3: Biogas Composition from the Substrate used in the Study

Sample	CO_2%	H_2S%	CO%	CH_4%
Cow dung	32.1	1.3	1.4	64.9
Cow dung + silicon oxide (30mg/l).	31.3	1.2	1.6	65.7
Sheep dung	37.2	1.7	1.8	59.3
Sheep dung + silicon oxide (30mg/l)	36.4	1.3	1.7	60.2

Table 3 shows the biogas composition produced from anaerobic digestion of the substrate with and without silicon oxide nanoadditive. Methane is the primary component of biogas that determines its energy content. Addition of silicon oxide nanoadditive increases the methane content of biogas produced from cow dung from 64.9% to 65.7%. This 0.8% increase suggests enhanced microbial activity or improved breakdown of organic matter due to the presence of the nanoadditive. Also, addition of the nanoadditive increases the methane content of biogas produced from sheep dung from 59.3% to 60.2%, a 0.9% increase. This indicates a similar beneficial effect of the nanoadditive as seen with cow dung, albeit starting from a lower baseline methane content. The silicon oxide nanoadditive increases methane content in both cow dung and sheep dung. The increase is slightly higher in sheep dung (0.9%) compared to cow dung (0.8%). This suggests that the nanoadditive is effective in enhancing biogas quality by increasing the methane yield. Carbon dioxide is a non-combustible component and lowers the calorific value of biogas. The CO_2 content decreases from 32.1% to 31.3% with the addition of the nanoadditive. This reduction in CO_2 is favorable as it suggests a more efficient conversion of carbon to methane. The CO_2 content decreases from 37.2% to 36.4% with the addition of the nanoadditive, showing a similar trend to cow dung. Both substrates show a reduction in CO_2 content with the addition of the nanoadditive. The reduction is marginal but significant, indicating a more efficient conversion process. H_2S is a corrosive gas that can damage equipment and reduce biogas quality. For cow dung, The addition of the nanoadditive reduces

H_2S content slightly from 1.3% to 1.2%. This is beneficial as it indicates a reduction in the presence of sulfur-containing compounds. While, for sheep dung, The addition of the nanoadditive reduces H_2S content more significantly from 1.7% to 1.3%, indicating a greater improvement in gas quality for sheep dung. The reduction in H_2S content is more pronounced in sheep dung than cow dung. This indicates that the nanoadditive may be more effective in reducing sulfur compounds in sheep dung, improving the overall quality of biogas. Carbon monoxide is a harmful gas, but its presence in biogas is typically low. The addition of the nanoadditive does not significantly affect the CO content for cow dung (remaining at 1.4%). For sheep dung, the CO content decreases slightly from 1.8% to 1.7%, indicating a minor improvement. The nanoadditive has a minimal impact on CO content. This suggests that while the nanoadditive improves methane yield and reduces CO_2 and H_2S, its effect on CO production is negligible.
The results further shows that cow dung has a higher baseline methane content (64.9%) compared to sheep dung (59.3%). This makes cow dung a more potent substrate for biogas production. The impact of the nanoadditive is slightly more pronounced in sheep dung, bringing its methane content closer to that of cow dung. However, cow dung with nanoadditive still produces higher methane (65.7%) compared to sheep dung with nanoadditive (60.2%). The reduction in CO_2 and H_2S is beneficial for both substrates. The more significant reduction in H_2S for sheep dung suggests a greater improvement in gas quality for sheep dung with the nanoadditive. The use of silicon oxide nanoadditives enhances biogas production and quality for both cow dung and sheep dung, with cow dung showing the highest overall performance.

Recommendations for practical applications and further investigation

Based on the results and discussion of the study on the effects of silicon oxide nanoadditive on anaerobic digestion and biogas production, several recommendations for practical applications and further investigation can be made:

- Implement the use of silicon oxide nanoadditive in anaerobic digestion systems to enhance biogas production and methane yield.
- Optimize nanoadditive dosage and application methods based on the specific characteristics of the feedstock and operating conditions of the digestion system.

- Explore the potential of using silicon oxide nanoadditive in commercial-scale biogas plants to improve overall process efficiency and profitability.
- Consider integrating nanoadditive treatments with other process optimization strategies, such as co-digestion of different feedstocks or biogas upgrading technologies, to further enhance biogas production and quality.

Further Investigation:

- Conduct long-term studies to evaluate the sustainability and stability of biogas production enhancement with silicon oxide nanoadditive over extended operational periods.
- Investigate the potential impacts of nanoadditive-treated digestate on soil health and nutrient cycling to ensure the overall sustainability of anaerobic digestion systems.
- Explore the underlying mechanisms through which silicon oxide nanoadditive influences microbial communities and enzymatic activities in anaerobic digestion processes.
- Investigate the potential synergistic effects of combining silicon oxide nanoadditive with other additives or pre-treatments to maximize biogas production and process efficiency.

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