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Optimization of Biomethane Yield of *Xyris capensis* Grass Using Oxidative Pretreatment

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Abstract: Biogas production from lignocellulose feedstocks has become an acceptable energy source globally due to their availability and economy. Lignocellulose materials have a complex arrangement that hinders digestion during the process. Therefore, applying the pretreatment process to lower the recalcitrant properties is required to utilize the full potential of the feedstock. This study, therefore, examines the influence of the oxidative pretreatment on the microstructural arrangement and biomethane yield of *Xyris capensis*. Piranha solution was prepared using H_2O_2 and H_2SO_4 at 100, 95:5, 85:15, and 75:25% of H_2O_2:H_2SO_4, respectively, and *Xyris capensis* grass was soaked in the prepared solution. The pretreated and untreated feedstocks were examined under the scanning electron microscope (SEM) to study the effect of the pretreatment on the microstructural arrangement. The effect of the pretreatment on biomethane yield was investigated during anaerobic digestion in a laboratory-scale batch digester at a mesophilic temperature (37 °C). The SEM analysis shows that the oxidative pretreatment method significantly affects the substrate's microstructure, and the pretreatment's severity depends on the percentage of H_2SO_4 added. A biomethane yield of 174.41, 188.61, 192.23, 207.51, and 139.71 mL CH_4/g VS_{added} was observed, and the yield was increased by between 24.84 and 48.52% compared to the untreated substrate. Therefore, applying oxidative pretreatment using low-cost H_2O_2 is a clear method of improving the biomethane yield of lignocellulose feedstocks.

Keywords: anaerobic digestion; lignocellulose material; *Xyris capensis*; oxidative pretreatment; microstructural arrangement; biomethane

Citation: Olatunji, K.O.; Madyira, D.M. Optimization of Biomethane Yield of *Xyris capensis* Grass Using Oxidative Pretreatment. *Energies* **2023**, *16*, 3977. https://doi.org/10.3390/en16103977

Academic Editor: Byong-Hun Jeon

Received: 11 March 2023
Revised: 1 May 2023
Accepted: 7 May 2023
Published: 9 May 2023

1. Introduction

The global energy requirement is rapidly increasing, necessitating green energy to supplement the energy requirements [1]. It has been envisaged that energy requirements will rise by 30% by the year 2040, and the effect of fossil fuel combustion on the ecosystem will increase if the main energy source by then is fossil fuels. This has necessitated the need to source alternative energy that is sustainable, renewable, and economical [2]. Substituting fossil fuels with clean, sustainable, and renewable energy generated at low cost with little harmful environmental effect will be vital to sustainable growth globally [3]. Renewable energy generation from organic wastes through anaerobic digestion is a clear means due to its accessibility, cost, and methane yield potential [4]. Anaerobic digestion occurs when biodigestable organic materials are degraded by microorganisms without oxygen to release biogas. This is a natural process that can be regulated such that the gases released can be captured and usable. Microbes present in the anaerobic digestion process break down the organic matter and release biogas which is a mixture of methane (60–70%), carbon dioxide (20–30%), and some other gases in traces. Biogas generated from the anaerobic digestion process is an attractive alternative energy source because of the high calorific value of methane [5].

There are several feedstocks that have been identified with good potential feedstock for biogas production, but lignocellulose materials have been gaining prominent attention recently [6,7]. The main reasons that make lignocellulose feedstocks acceptable are their high biogas production potential and fertilizer production and they require low energy input [8]. Lignocellulose from agricultural residues and energy grasses represents vital feedstock for clean energy through anaerobic digestion, which is also a crucial component of the circular economy [9]. Lignocellulose feedstocks are made up of cellulose, hemicellulose, and lignin that are firmly attached. This three-dimensional arrangement hinders biodegradation during the hydrolysis stage of anaerobic digestion, resulting in low gas yield and a longer retention period. Therefore, lignocellulose feedstock pretreatment before anaerobic digestion is required to improve biogas and methane yield. Different studies have examined the influence of various pretreatments to degrade the microstructural arrangement of lignocellulose feedstocks to release organic matter and improve microorganisms' access to the feedstock [1]. Pretreatment methods have been studied widely and are classified as mechanical, biological, chemical, thermal, nanoparticle additives, and combined. It was observed that different pretreatment methods have varying effects on lignocellulose feedstocks, which necessitates the research for optimum conditions for individual feedstocks for each pretreatment method [10]. The chemical pretreatment method is one of the most widely studied because of its effectiveness and capacity to enhance the digestion of complex lignocellulose materials [11]. This method is classified into acidic, alkali, oxidative, ozonolysis, organic solvent, ionic liquids, carbon dioxide explosion, etc., depending on the process and chemicals used [10].

Oxidative pretreatment uses oxidizing agents such as hydrogen peroxide (H_2O_2), iron chloride ($FeCl_3$), and oxygen or air to disintegrate the lignin and hemicellulose portion of lignocellulose materials to improve the hydrolysis of organic contents during anaerobic digestion [12,13]. During oxidative pretreatment, oxidizing agents such as per-acetic acid or hydrogen peroxide can be dissolved in water and poured on lignocellulose feedstocks. Oxidative pretreatment aims to partially disintegrate hemicelluloses and delignification of the feedstock [14]. The main challenges of this process are the damage to a significant portion of hemicelluloses and making them unavailable during anaerobic digestion [15]. Different oxidizing agents were experimented with on agricultural residues, and the methane yield was increased by 23–30% [16]. Oxidative pretreatment using H_2O_2 was investigated on sorghum bicolor stalk, and it was noticed that the lignin portion was reduced by 73% and hemicellulose by 42%, and the cellulose availability was increased by 23%. It was also observed that the methane yield increased by 56% compared to the untreated substrate and 65% compared to the feedstock pretreated with H_2SO_4 [17].

Xyris capensis is a perennial (but annual on a few occasions) herbaceous rush-like plant of 60–300 mm in height that can be found in clumps. It is a widespread species with no identified threats and is regarded as the least concern, and it is considered not to be at risk of extinction any moment soon [18]. This grass belongs to the family of yellow-eyed grass. It has about 280 species that can be found in Africa, subtropical America, Asia, Australia, and a few species in China. *Xyris capensis* stems are mainly used for beer strainers production and mats weaving locally [19]. The stem of this grass can be classified as lignocellulose material because of its carbohydrate content [20]. It can be considered a potential feedstock for biogas generation if the stem's sugar content can be accessed. In that case, it will serve as a promising feedstock for the hydrolysis stage during anaerobic digestion and thereby release a high yield of biogas. Therefore, there is a need to investigate the potential of this economically abundant feedstock for biogas generation. Nevertheless, suitable pretreatment methods need to be applied in order to make it accessible to anaerobic digestion bacteria [21]. Limited research has examined the influence of the oxidative pretreatment method on biogas and methane yield on the readily available *Xyris capensis*. This necessitated establishing the effect of oxidative pretreatment on *Xyris capensis*, which is missing in the literature. Studying the influence of the oxidative pretreatment technique on *Xyris capensis* will assist in establishing the most effective pretreatment conditions for

energy recovery from this economically important feedstock. This study is thereby aimed at investigating the influence of oxidative pretreatment on the microstructural arrangement of *Xyris capensis* using scanning electron microscopy (SEM) and biomethane yield. The results will present the appropriate oxidative pretreatment condition for *Xyris capensis* and will also present baseline information for further studies on the anaerobic digestion of lignocellulose feedstocks.

2. Materials and Methods

2.1. Substrate Collection

Xyris capensis grass was sourced locally in the Limpopo province of South Africa. The substrate was dried at atmospheric temperature to 15.38% moisture content, chopped into smaller sizes (4–8 mm), and kept in well-ventilated conditions in the laboratory at 4 °C for further use. The feedstock was then analyzed in the laboratory for lignin, cellulose, hemicellulose, total solids, ash content, volatile solids, carbon, nitrogen, and sulphur following the Association of Official Analytical Chemists (AOAC) standard procedure [22].

2.2. Inoculum

Stabled inoculum from an anaerobic digester where food waste and livestock manure were co-digested at mesophilic temperature was collected and used for this study. The sample of the inoculum was also analyzed for total solids, ash content, volatile solids, and elemental compositions by using the same procedure as the substrate. The inoculum was kept in the laboratory at room temperature for the experimental setup.

2.3. Pretreatment

Oxidative pretreatment was carried out using Piranha solution, and the solution was prepared as reported by Shrivash et al. [23] with slight modification after it was discovered that the first trial burnt off the entire feedstock. A total of 75 g of ice cube was put in a 500 mL beaker, and H_2O_2 and H_2SO_4 were added, as shown in Table 1. The mixture was stirred continuously to form a homogenous solution. The chopped *Xyris capensis* (4–8 mm) was then soaked in the prepared solutions in a ratio of 1:10 of solid to liquid. The beaker with its contents was then placed on a magnetic stirrer for two hours at 200 rpm set at 90 °C, as reported in previous studies [24,25]. After the treatment exposure time, 10% of NaOH was added to stop further substrate oxidation and warm distilled water was added as an anti-solvent to prevent further reaction. The pretreated *Xyris capensis* was filtered using filter paper and washed with tap water until a neutral pH of 7 was achieved. The pretreated substrate was then dried in an oven set at 60 °C for 6 h and kept in zip-lock bags for laboratory analysis and anaerobic digestion.

Table 1. Oxidative pretreatment conditions of *Xyris capensis*.

Treatment	H_2O_2 Concentration (%)	H_2SO_4 Concentration (%)
A	100	0
B	95	5
C	85	15
D	75	25
E	Control	Control

2.4. Structural Characterization of the Substrate

The influence of the pretreatment method on the microstructural arrangement of the pretreated and untreated *Xyris capensis* was investigated. Scanning electron microscope (SEM) (VEGA 3 TESCAN X-Max, Brno-Kohoutovice, Czech Republic) was used to ascertain the effect of oxidative pretreatment on the morphological arrangement of the substrate.

2.5. Experimental Setup

The biomethane potential of oxidative pretreated and untreated *Xyris capensis* was studied on a laboratory scale according to European standards using Automatic Methane Potential Test System II (AMPTS II) at mesophilic temperature [26]. The 500 mL digester reactor bottles were charged with 400 g of stable inoculum. Equation (1) was used to calculate the quantity of substrate added to each digester as prescribed by VDI 4630 [26]. The mass of substrate added to the digester was calculated using volatile solids (VS) of the substrate and inoculum (2:1), and the experiment was carried out at a temperature of 37 ± 2 °C. The experiment was duplicated twice, and two digesters with only inoculum were run parallel, and its gas yield was used to correct the biogas released. The gas yield from the parallel digester was deducted from other digesters with both substrate and inoculum. AMPTS II software was supplied with the following information before the commencement of the experiment. Flush gas for carbon dioxide removal was set at 10%, stirring time was set at 60 s and 60 s off time, and the mixer speed of 80% was maintained throughout the digestion process. Methane yield was predicted to be 60% [27], and a headspace of 100 mL was maintained for all digesters. The anaerobic condition was set in the digester when nitrogen gas purged oxygen off the system before connecting the silicon pipes to the digester. Sodium hydroxide (0.56% NaOH) was used to remove the carbon oxide from the gas released from the digester using 100 mL bottles. Silicon pipes from the digesters were connected directly to the carbon dioxide removal unit that contains a 75 mL NaOH solution. Another silicon pipe was connected from the carbon dioxide unit to the third unit, where the volume of biomethane released was recorded. The system consists of a gas chromatograph device that analyzes the gas released and provides the composition of the gas released. The process was stopped after 24 days when it was discovered that the daily gas yield was less than 1% of the total yield.

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

where M_s = mass of the substrate (g), M_i = mass of inoculums (g), C_s = concentration of substrate (%), C_i = concentration of inoculum (%) [26].

3. Results and Discussion

3.1. Physicochemical Properties of Xyris capensis and Inoculum

The physicochemical characteristics of *Xyris capensis* are illustrated in Table 2. It can be observed from Table 2 that the total solids (TS) and volatile solids (VS) of the substrate are 84.62 and 95.00%, respectively. The result of the VS indicates a higher organic matter available for biogas production, which is a sign of promising potential feedstock. Compared with other lignocellulose feedstocks, groundnut shells 91.27% [28], dairy manure (84.7 ± 2.4%), rice straw (74.9 ± 0.2%), and corn straw (75.05 ± 0.3%) [29], it can be observed that the substrate has a higher potential for biogas production. It indicates a high buffering capacity for microorganisms during the anaerobic digestion of *Xyris capensis*. It has been observed that the anaerobic digestion process's biogas and methane yield depends on the feedstock's volatile solid [30]. Higher TS, conversely, can hinder sufficient compaction of the substrate inside the digester and promote anaerobic digestion at the digester outlet [31]. TS of 28–40% are often regarded as the ideal for optimal anaerobic digestion. The TS of the feedstock and inoculum were higher than the required standard of 30 and 98% of substrate and inoculum; therefore, water was added to the substrate and inoculum to lower the TS to the acceptable standard [26].

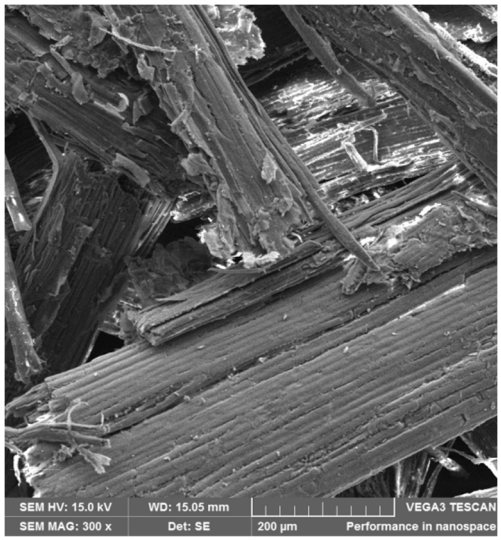
Table 2. Physicochemical characteristics of *Xyris capensis* and inoculum.

Parameters (%)	Substrate	Inoculum
Total Solids (TS)	84.62	19.12
Volatile Solids (VS)	95.00	91.67
Ash Content	3.76	7.85
Moisture Content	15.38	80.88
Nitrogen	1.48	1.23
Carbon	41.47	42.57
Hydrogen	5.38	5.50
Oxygen	46.15	0.60
Lignin	30.23	NA
Hemicellulose	19.45	NA
Cellulose	34.64	NA

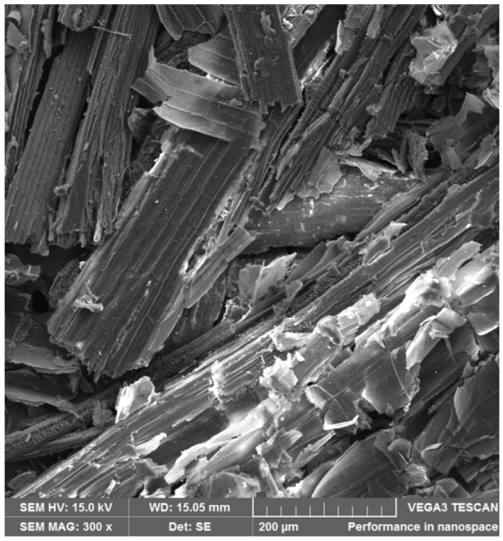
NA—Not Applicable.

3.2. Effect of Oxidative Pretreatment on Morphological Arrangement of Xyris capensis

A scanning electron microscope (SEM) was used to study the influence of oxidative pretreatment at different concentrations on the microstructural arrangement of the *Xyris capensis*. The images from the SEM analysis are presented in Figure 1, and it can be observed that oxidative pretreatment significantly affects the microstructure of Xyris capensis compared with the untreated substrate. This supports the previous study that observed that substrate pretreatment could alter the microstructure of lignocellulose materials [32]. The untreated *Xyris capensis* (Figure 1E) showed a compacted and fine bundle surface arrangement with several fiber layers that can restrict microbial activities during anaerobic digestion. After oxidative pretreatment, noticeable changes in the cell wall arrangement of the untreated one were observed, as shown in Figure 1A–D. The cell walls were degraded, and the original fine and rigid arrangement was broken and separated. Defibrillation and the coarseness of the substrate surface can be noticed to improve with the increase in the percentage of H_2SO_4. Noticeably, Figure 1D shows higher swollen fiber fragments on its surface. This can be linked to the ability of H_2SO_4 to break the cell walls and expose the hemicelluloses and celluloses of lignocellulose materials [33]. It is also important to note that due to the damage done to the structure of *Xyris capensis*, their internal tissues were exposed, making them easily accessible for the microorganisms' conversion. Generally, all the pretreated substrates showed an outstanding result. The images also showed partial lignin degradation and enhanced hemicellulose and cellulose availability, which agreed with a previous report on the influence of oxidative pretreatment on lignocellulose materials [34].

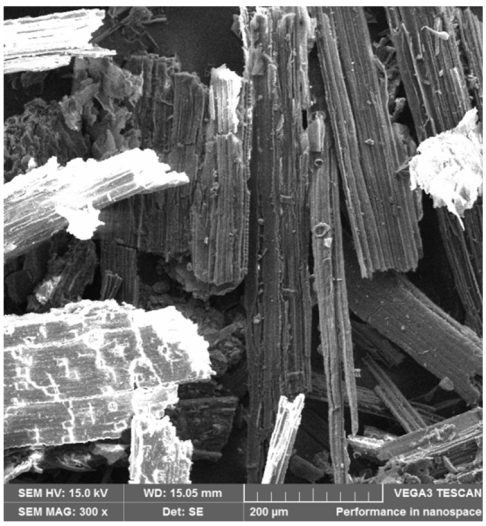


(**A**)

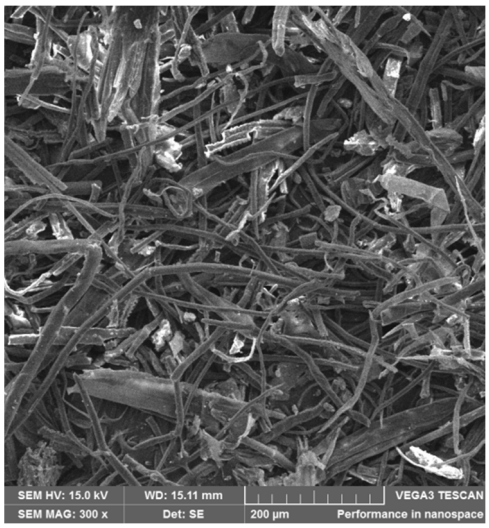


(**B**)

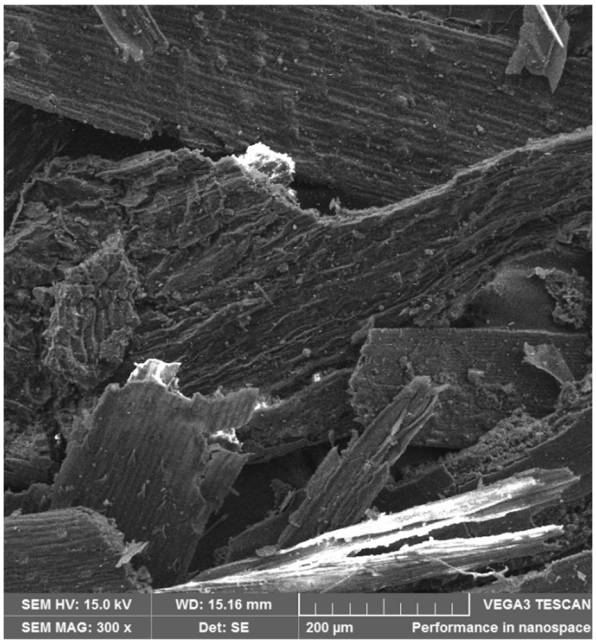
Figure 1. *Cont.*



(**C**)



(**D**)



(**E**)

Figure 1. SEM images of oxidative pretreated and untreated *Xyris capensis*: (**A**–**D**) pretreated with oxidizing agent, and (**E**) untreated *Xyris capensis*.

3.3. Effect of Oxidative Pretreatment on Daily Biomethane Yield of Xyris capensis

The daily biomethane released from the anaerobic digestion of oxidative pretreated and untreated *Xyris capensis* is presented in Figure 2. It can be observed that treatments A, B, and D followed the same pattern, and treatments B and E also followed a similar pattern. It can be inferred that the biomethane start-up was improved by oxidative pretreatment. All the treatments started biomethane production on the second day, and treatment A produced its highest peak (32.64 mL CH_4/g VS_{added}) on day 2. This indicates that pretreatment conditions for treatment A could have removed or redistributed the substrate's lignin portion, and the hemicellulose and cellulose are accessible for the methanogenic bacteria activities at the early stage of digestion. Other treatments were noticed to release their optimum biomethane yield within a retention time of 4 to 8 days. The daily biomethane highest peaks of 30.23, 14.93, 27.30, and 13.99 mL CH_4/g VS_{added}, were for treatments B, C, D, and E, respectively, and at retention times 7, 5, 4, and 8 days. The result shows that treatments A, B, and D comprise four different peaks that are not noticeable in treatments

C and E. Finally, the biomethane yield was observed to decline with small fluctuations until the biomethane yield released was minute. Treatment A produced the highest daily biomethane yield (32.64 mL/g mL CH_4/g VS_{added}), and the least biomethane yield of 13.99 mL CH_4/g VS_{added} was observed from treatment E (control). This can be linked to the ability of H_2O_2 and H_2SO_4 to break down the lignocellulose structure of *Xyris capensis* and make organic matter accessible for digestion. It can be observed that oxidative pretreatment using either of the treatment conditions considered in this study can enhance the daily biomethane yield of *Xyris capensis*. This supports what was reported in previous studies that pretreatment methods could improve the daily biomethane yield of lignocellulose materials [10,16].

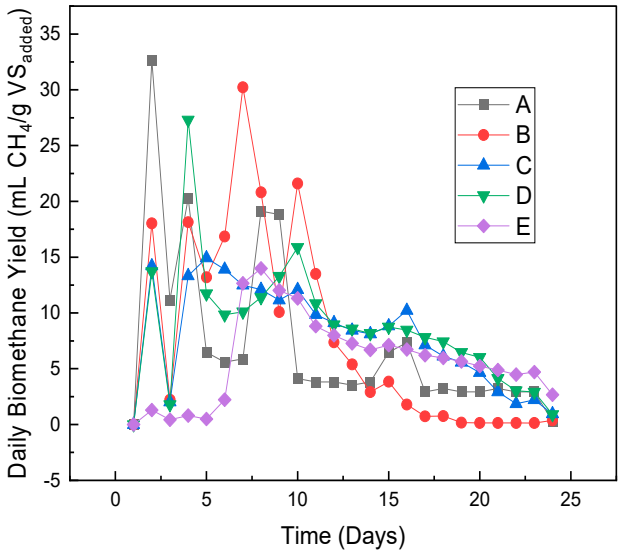


Figure 2. Influence of oxidative pretreatments on daily biomethane yield of oxidative pretreated and untreated *Xyris capensis*.

3.4. Effect of Oxidative Pretreatment on Cumulative Biomethane Yield of Xyris capensis

The cumulative biomethane yield released by the oxidative pretreated and untreated *Xyris capensis* at the end of 24 days is illustrated in Figure 3. The cumulative methane yield was 174.41, 188.61, 192.23, 207.51, and 139.71 mL CH_4/g VS_{added}, for treatments A, B, C, D, and E, respectively. When compared with the untreated *Xyris capensis*, it can be noticed that the biomethane yield was enhanced by 24.84, 35.00, 37.59, and 48.52% for treatments A, B, C, and D, respectively. It can be observed from Figure 3 that all the treatments showed a slow improvement at the start of the experiment, a significant improvement at the middle stage, and then started to flatten at the later stage of the digestion. Treatments A, C, and D showed a very close pattern from the start to the final stage of the experiment, while treatment B showed a sharp deviation at the mid-stage of the process. Combining H_2O_2 with concentrated H_2SO_4 produces highly activated and oxidizing peroxymonosulphuric acid (H_2SO_5) that can remove a trace amount of organic residues such as photoresist from the feedstock [35]. Depending on the preparation method, the prepared solution can have up to 5% peroxymonosulphuric acid. Treatment B behaves differently from A, C, and D because of the percentage of H_2SO_5 in the solution, which subsequently influences the biomethane yield during digestion. Treatment E, the control experiment, showed a clear difference from the rest, from the start to the final stage of the investigation. To investigate if oxidative pretreatment enhances the methane yield compared to the untreated substrate, Wilcoxon's rank-sum test was used to analyze the result of the methane yield [36]. The test was carried out using the methane yield of the untreated substrate as the benchmark yield and evaluated against the methane yield of each pretreated substrate at a 95% significance level. When the *p*-value is ≤ 0.05, there is a significant difference between the methane yield of untreated and pretreated substrates, but when the *p*-value is ≥ 0.05, there is no

significant difference. The results obtained from Wilcoxon's test showed that treatments A, B, C, and D have *p*-values of 0.03558, 0.00513, 0.000019, and 0.000036, respectively. All the *p*-values are less than 0.05, implying that the pretreatment significantly improved compared to the untreated *Xyris capensis* at a 95% significant level. This implies that the cumulative biomethane yield from the pretreated substrate was improved due to the ability of the oxidative pretreatment to alter the structural arrangement of the *Xyris capensis*. Treatment D released the highest cumulative biomethane yield, which was a 48.52% enhancement, followed by treatments C, B, and A, respectively. The least cumulative biomethane yield recorded in treatment A could be traced to the loss of some hemicellulose and cellulose portions during pretreatment with only H_2O_2, which is expected to release biomethane during the anaerobic digestion process. It can be observed that oxidative pretreatment can enhance the biomethane yield of *Xyris capensis*.

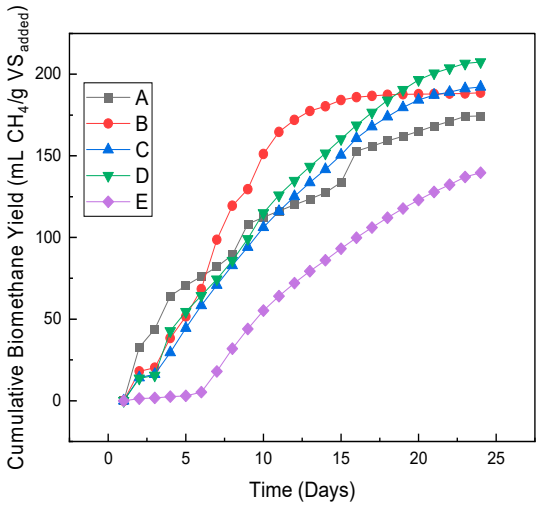


Figure 3. Influence of oxidative pretreatments on cumulative biomethane yield of oxidative pretreated and untreated *Xyris capensis*.

Furthermore, the cumulative biomethane yield of *Xyris capensis* was observed to increase with the increase in the percentage of H_2SO_4 added. As observed from the start of the experiment, the combination of 50% each of H_2O_2 and H_2SO_4 burnt off the entire feedstock. Therefore, a further addition of H_2SO_4 could lead to inhibitory compounds that may hinder biomethane production. Dahunsi et al. observed that H_2O_2 increased the biogas yield of sorghum bicolor stalk by 65% and reduced the lag time by 5 days [17], and this aligned with the result of this study. In a similar study, sweet sorghum bagasse was pretreated with different methods, and it was observed that dilute NaOH released the highest biogas, followed by oxidative pretreatment. It was reported to have improved hydrolysis by 90.9% and total sugar by 19.1%, compared to the untreated feedstock [37]. Oxidative pretreatment of rice straw was reported to enhance the biogas yield, and when the biogas yield and economy of the process were considered, the efficiency was noticed to be 3% [34]. Oxidative pretreatment was observed to improve the biogas of sunflower stalks by 33% during anaerobic digestion [38]. Comparing the result from this result with the previous study, it can be observed that the efficiency of lignocellulose feedstocks differs, and this can be a result of variation in the microstructural arrangement of *Xyris capensis* and the concentration of oxidative agents used. Ammonia pretreatment (10% *v*/*v*) was reported to improve the biogas yield from 100.6 to 163.5 mL/g VS during anaerobic digestion, which represents a 62.52% increase [39]. Alkali pretreatment of groundnut shells was noticed to improve the methane yield by 69.79% when 3% *w*/*w* NaOH was applied for 15 min at 90 °C autoclaved temperature [25]. The methane yield from anaerobic digestion of wheat straw was improved by 45.20% when it was pretreated with urea (1% *w*/*w*) [40]. The results from chemical pretreatment methods of other lignocellulose feedstocks show that some

produce a higher efficiency than in this study [17,41]. Table 3 presents the effects of different pretreatment techniques on the biogas and methane yield of some other lignocellulose materials. It can be observed from the table that the present study performs better than the majority of the studies considered. This indicates that oxidative pretreatment using H_2O_2 and H_2SO_4 at appropriate treatment conditions is more efficient than other pretreatment methods of lignocellulose feedstocks. At the same time, it is more effective than a few of these results. It is not easy to conclude that these other chemical pretreatments are better than this result because they have a different lignocellulosic arrangement, and the pretreatment conditions differ.

Table 3. Effects of different pretreatment methods on biogas and methane yield of some lignocellulose feedstocks.

S/N	Feedstock	Pretreatment Method	Yield	Improvement (%)	Reference
1.	Pearl millet straw	Alkaline	Biogas	45	[42]
2.	Oil palm empty fruit bunches	Wet oxidation	Biomethane	43	[43]
3.	Steam-exploded birchwood	Ultrasonication	Methane	−1.74	[44]
4.	*Arachis hypogaea shells*	Combined particle size reduction and Fe_3O_4 additive	Methane	319.73	[28]
5.	Sorghum bicolor stalk	H_2O_2	Biogas	65	[17]
6.	Digested manure fibers	Thermal-alkaline	Methane	26	[45]
7.	Steam-exploded birchwood	Fenton	Methane	−18.10	[44]
8.	Mixed agricultural wastes	Oxidative	Methane	25	[16]
9.	*Arachis hypogaea* shells	Alkali	Methane	69.79	[25]
10.	*Xyris capensis*	Oxidative	Methane	48.52	This study

4. Conclusions

This study investigated the effect of oxidative pretreatment on the microstructural arrangement and biomethane yield of *Xyris capensis*. The SEM image from the microscopy analysis shows that the pretreatment conditions significantly affect the microstructural arrangement of the feedstock. The severity of the influence was noticed to depend on the percentage of H_2SO_4 added to the treatment solution. It was observed that the oxidative pretreatment of *Xyris capensis* enhances the daily biomethane yield. The optimum daily biomethane peak was released when the treatment was 100% H_2O_2, followed by treatment with 95% H_2O_2 and 5% H_2SO_4. All the pretreatment conditions considered improved the biomethane yield to between 24.84 and 48.52% and reduced the retention time compared to the untreated *Xyris capensis*. The application of oxidative pretreatment using low-cost hydrogen peroxide has not been investigated widely like other strong chemicals until now. It can be observed that hydrogen peroxide with or without the addition of sulphuric acid released better biomethane yield; therefore, the application of oxidative pretreatment presents clear biotechnological means for biomethane production from lignocellulose feedstocks.

Author Contributions: Conceptualization and methodology—K.O.O., original draft—K.O.O., first draft review and supervision—D.M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data are contained within the article and presented in the tables and figures.

Acknowledgments: The authors appreciate the Process Energy and Environmental Technology Station (PEETS), University of Johannesburg, South Africa, for releasing their Automatic Methane Potential Test System during this research.

Conflicts of Interest: Authors declare that there are no conflict of interest.

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