



# Acid-Base Pretreatment of Sugarcane Bagasse for Anaerobic Digestion into Biogas in the Presence of Cowdung Mesophically to Remove H<sub>2</sub>S Through Adsorption on XFe<sub>2</sub>O<sub>3</sub>-Cement Sand

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The objectives of this investigation were to employ an acid-base pretreatment technique for extracting sugars from bagasse and to explore anaerobic biogas production within a 1-liter bio-digester utilizing cow manure as the substrate, maintaining a C/N ratio of 22–30 at a controlled temperature of 35 °C for a hydraulic retention time (HRT) of 30 days. The study revealed that the acid-base pretreatment was highly effective in disrupting lignin linkages, thereby enhancing cellulose accessibility. This approach also yielded the highest biogas production of 84.84 mL/g after 16 days, compared to only 76.09 mL/g from untreated bagasse. Furthermore, the acid-base pretreated bagasse demonstrated superior biomethane production, achieving approximately 357.33 mL/g of volatile solids (VS), whereas untreated bagasse yielded 325.34 mL/g of VS. The initial pH of the anaerobic digestion process plays a pivotal role in influencing methanogenic activity, which is critical for methane generation. Notably, methanogens present in cow manure were capable of producing methane even under highly acidic conditions over the sixteen-day period. Additionally, the xFe<sub>2</sub>O<sub>3</sub>/cement-based sand absorbents exhibited a limited hydrogen sulfide (H<sub>2</sub>S) absorption capacity of 57.7%, whereas the xFe<sub>2</sub>O<sub>3</sub>-based sand absorbents achieved a remarkable removal efficiency of 95% to 100% for H<sub>2</sub>S.

The optimal absorber was identified as cementitious sand with a 4%wt Fe<sub>2</sub>O<sub>3</sub> content, effectively eliminating H<sub>2</sub>S at gas flow rates between 59 and 89 mL/min. Moreover, the reusability of the Fe<sub>2</sub>O<sub>3</sub>/cement-based sand could be substantially improved through a washing process followed by exposure to atmospheric oxygen.

**Keywords:** Biogas, cement-based sand, Ferric oxide, Hydrogen sulfide removal, Sugarcane bagasse.

## 1. Introduction

The demand for refined petroleum products in Thailand, particularly jet fuel, is projected to escalate in 2024, with an anticipated average growth of 24.2%, reaching 16.8 million liters per day, compared to 13.5 million liters per day in 2023. Similarly, diesel consumption is expected to experience a modest increase of 0.4%, reaching 69.1 million liters per day, while gasoline consumption is forecasted to ascend by 3.7%, culminating at 32.6 million liters per day (Srisatabusaya, 2024). This upward trajectory underscores a consistent amplification in energy utilization. Within the Thai demographic, agricultural activities, particularly sugarcane cultivation, remain predominant. It is forecasted that sugarcane production will attain 105.86 million tons during the 2022-2023 period (S.R. Department, 2023). The residual by-products of sugarcane processing, notably 26.8% bagasse, hold significant potential for biogas generation, thus contributing to a reduction in dependence on gasoline and liquefied petroleum gas (Paulose, 2020; Prasad, 2020).

Several strategies can be implemented to improve the efficiency of utilizing sugarcane bagasse, with anaerobic digestion (AD) being recognized as a promising approach for biogas production (Smith, 2022; Jones & Lee, 2021). Nevertheless, the complex molecular structure of bagasse, which includes hemicelluloses, cellulose, and lignin, presents a significant obstacle for anaerobic digestion. As a result, various pretreatment methods are necessary to enhance microbial degradation (Brown & Davis, 2020; Wilson, 2019).

Biogas production typically takes place in anaerobic conditions, where inoculants such as cow dung or rumen fluid are combined with pre-treated sugarcane bagasse. Several factors influence the efficiency of this process, including operational temperature, pH, C/N ratio, and liquid-to-solid ratio (Brown, 2020). The pre-treatment methods applied and the specific inoculum utilized play a crucial role in the breakdown of lignocellulose and hemicellulose, which is comparable to the processing of sugarcane bagasse. This approach softens the biomass and enhances microbial access to cellulose surfaces, thereby facilitating hydrolysis and augmenting biogas production (Jones & Smith, 2019; Wilson & Lee, 2021). Various pre-treatment techniques for biomass, such as lignocellulose derived from sugarcane bagasse, include physical, biological, and chemical methods, each with its respective benefits and limitations (Smith & Davis, 2021; Brown et al., 2020). According to Abraham et al. (2020), these methods can be employed individually or in combination. Anaerobic digestion (AD) is one such method, utilizing efficient microorganisms to recycle bio-waste under anaerobic conditions. This process involves the enzymatic decomposition of organic materials, converting agricultural waste into valuable resources for microbial use. The decomposition is accelerated, leading to the production of bioactive compounds within a

period of two to four weeks. These processes not only reduce greenhouse gas emissions but also avoid the generation of thermal energy, unpleasant odors, and are both cost-effective and efficient.

The anaerobic digestion (AD) process yields biogas, primarily composed of methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), and trace amounts of hydrogen sulfide ( $\text{H}_2\text{S}$ ). However, the presence of  $\text{H}_2\text{S}$  poses a significant challenge as it can corrode engine-generator systems, thereby compromising the efficiency of the combustion process (Brown, 2021). Moreover, reducing  $\text{H}_2\text{S}$  concentrations is crucial not only for optimizing biogas energy output but also for safeguarding human health, as prolonged exposure to  $\text{H}_2\text{S}$  can lead to serious health hazards (Smith & Jones, 2020). Consequently, implementing an effective containment strategy within the anaerobic digestion system to absorb or eliminate  $\text{H}_2\text{S}$  is of paramount importance.

Previous studies have identified numerous methods for the removal of hydrogen sulfide ( $\text{H}_2\text{S}$ ), including dissolution in a liquid medium such as water or a caustic solution, or adsorption onto solid substrates like iron oxide ( $\text{Fe}_2\text{O}_3$ ) (Lien et al., 2014) or activated carbon (Coppola & Papurello, 2018). Additionally, Mrosso et al. (2020) highlighted the use of red rock, notable for its high iron oxide content, to enhance the efficacy of  $\text{H}_2\text{S}$  removal. Cement-based materials are widely utilized in the construction of biogas infrastructure—such as pre-tanks, digesters, post-digesters, and storage tanks—due to their cost-effectiveness. However, there is a lack of comprehensive data on cement-based sand absorbents that offer water resistance, high-temperature stability, and long-term durability, despite their frequent use in cement-based biogas digestion systems (Voegel et al., 2015). Thus, there remains a pressing need to improve absorbent materials that are both economically viable and easily adaptable for  $\text{H}_2\text{S}$  removal.

## **2. MATERIALS AND METHODS**

### **2.1. Preparation and analysis of substrates**

#### **2.1.1 Preparation of substrates**

The Research and Development division of The Green Millennium Company Limited, located in Prawet, Bangkok, Thailand, provided the sugarcane bagasse used in this study. The bagasse was subjected to dehydration at 55 °C until it reached a consistent mass. Subsequently, it was processed through a laboratory knife mill to standardize its particle size to 1–20 mesh (0.1–2 mm) using a sieve mesh, in preparation for the subsequent chemical pretreatment process.

#### **2.1.2 Analysis of substrates**

The comprehensive study was conducted at Mahasarakham University's laboratory, located in Kham Riang Subdistrict, Kanwichai District, Maha Sarakham, Thailand. The analysis of carbon and nitrogen content in the bagasse, both prior to and following its integration with cow dung, was performed utilizing the Perkin Elmer CHNS/O 2400 Analyzer. A substantial body of research underscores the significance of the carbon-nitrogen (C/N) ratio in facilitating biogas generation through anaerobic digestion (Zheng et al., 2014; Maryana et

al., 2014; Tanimu et al., 2014). Biomass sources exhibit a wide range of C/N ratios, from 32 to 150:1. Moreover, it has been documented that microorganisms involved in fermentation processes exhibit a significantly higher rate of carbon assimilation compared to nitrogen, with a ratio of 25 to 30:1 (Zheng et al., 2014; Tanimu et al., 2014). According to the findings presented by Kaur et al. (2020), the ideal C/N ratio for optimizing biogas production is 30:1. The unprocessed bagasse exhibited a C/N ratio of 130:1, but the ratio decreased to 29:1 when bagasse was combined with cow dung (Kaur et al., 2020).

### 2.1.3 Acid-Base Pretreatment

The sugarcane bagasse was subjected to an acid-alkaline pretreatment protocol as follows: Initially, 10 grams of bagasse were suspended in 200 milliliters of a 1% (v/v) sulfuric acid solution. The suspension was agitated at 100 °C for 40 minutes. Post-treatment, the acid-treated bagasse was filtered and thoroughly rinsed with hot water until the wash water achieved a neutral pH. Subsequently, the neutralized bagasse was treated with 200 milliliters of a 2% (w/v) sodium hydroxide solution, followed by agitation at 100 °C for an additional 40 minutes. Upon completion of the alkaline pretreatment, the bagasse was again rinsed with hot water to neutral pH, followed by a washing step using a 50-mM citrate buffer with a pH of 4.8. Finally, the solid residue was oven-dried at 55 °C until it reached a consistent weight.

### 2.2 Preparation of $x\text{Fe}_2\text{O}_3$ cement-based sand

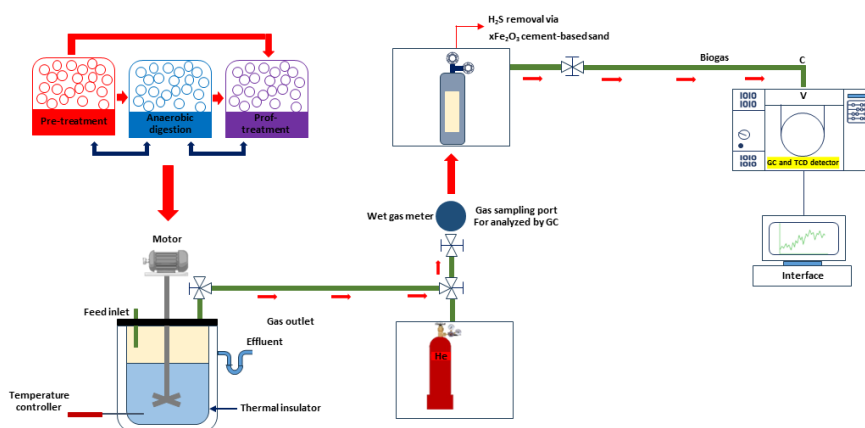
In this study, the absorbent material utilized was a cementitious sand composite, formulated by blending sand, a single component of cement (fine binding powder), and water in a weight-to-volume ratio of 2:1:1, respectively. After the mixture was placed into a cylindrical plastic mold, a central cavity measuring 0.45 cm × 0.45 cm × 0.15 cm was created. The cementitious sand underwent a curing process for forty-eight hours at ambient temperature. Iron (Fe) was incorporated into the cement-based sand at a mass ratio of 8.25 weight percent. During a one-hour period, the cement-based sand exhibited an absorption capacity of 0.486  $\text{FeCl}_3$  and 3.00  $\text{H}_2\text{O}$ . Following a twenty-four-hour drying period in a hot air oven, the iron oxide concentration within the sand was determined to be 8.25 percent. The  $\text{Fe}_2\text{O}_3$ /cement-based sand was subsequently immersed in a 0.36 sodium hydroxide solution containing 3.00  $\text{H}_2\text{O}$  for twenty-four hours, followed by another drying period at room temperature overnight. The sand was then subjected to calcination at 550 °C for six hours. To reduce the presence of  $\text{H}_2\text{S}$  in biogas, a composite sand formulation of  $x\text{Fe}_2\text{O}_3$ /cement was developed, where the weight percentage of  $x$  varied between 1 and 41.8. Comparative experiments were conducted to evaluate the performance of  $x\text{Fe}_2\text{O}_3$ /cement-based sand against a control group consisting of cement-based sand without  $\text{FeCl}_3$  addition.

### 2.3 Experimental procedures

The study employed a laboratory-scale bio-digester constructed from high-density polyethylene (HDPE) and outfitted with four sharp, razor-like stir sticks. The digester had a fixed-bed anaerobic digestion capacity of 1.0 L. To accommodate the release of gas and mitigate the risk of explosion during periods of excessive or sudden gas production, a plastic pipe was connected to one end of the bio-digester and submerged in a 500-mL beaker partially filled with water. The opposite end was connected to a corrosion-resistant metal pipe fitted with a valve, enabling the gas to pass through an  $\text{H}_2\text{S}$  absorber before being

quantified using a gas analyzer. Gas measurements were taken bi-daily over a period of 30 days. Additionally, a stirrer was inserted into the central aperture of the bio-digester to facilitate daily agitation of the slurry (Kulawong et al., 2022).

Figure 1. Schematic of the 5-liter bioreactor contained the absorbent material made of  $x\text{Fe}_2\text{O}_3$ -cement-based sand to make fermented biogas from treated sugarcane bagasse.



A weighing scale was used to determine the required mass of cow manure and chemically treated bagasse. A glass thermometer with a temperature range of 0–110 °C was used to measure the daily temperature of the slurry. The thermometer was placed into the biodigester through the cork. The digital pH meter was utilized to measure the pH of the slurry. There are two distinct categories of digesters: ADR0, employed for the purpose of regulating anaerobic digestion and only comprising unadulterated bagasse, and ADR1, which encompasses bagasse that has undergone treatment with NaOH. The combination of pretreated and untreated bagasse with cow dung is achieved using a 1:2 ratio, which is subsequently followed by a 1:3 ratio when the resulting mixture is combined with water. To maintain a consistent temperature, the digesters were submerged in a water bath maintained at a temperature of 350 °C. To achieve optimal conditions for ADR1,  $x\text{Fe}_2\text{O}_3$ -cement-based sand was supplied to the  $\text{H}_2\text{S}$  removal section in order to purify the produced biogas.

## 2.4 Chemical Analysis

### 2.4.1 Biomethane from Anaerobic Digestion

Over a 30-day period, data were systematically gathered from all digesters, with measurements taken every other day. The total biogas volume was measured using a 100-mL syringe connected to an anaerobic biodigester. Quantification of the biogas was conducted utilizing an Agilent Technologies 6890 N gas chromatograph, equipped with dual columns (Porapak and molecular sieve), flame ionization detection (FID), and thermal conductivity

detection (TCD). For quantitative calibration, standard gas mixtures were utilized, with helium employed as the carrier gas. A 10- $\mu$ L biogas sample was injected into the gas chromatography system through the sample port, with the detection and oven temperatures set at 300 °C and 270 °C, respectively. The flow rates for helium, hydrogen, and air were maintained at 26 mL/min and 80 psi, 30 mL/min and 40 psi, and 300 mL/min and 60 psi (Tanimu et al., 2014; Kaur et al., 2020).

The determination of bagasse biodegradability involved a comparison between the theoretical methane potential and the cumulative methane production observed over the incubation period, as depicted in equation (1).

$$\text{BD\%} = \frac{\text{BMP}_{\text{end}}}{\text{BMP}_{\text{ThOFC}}} \times 100 \quad (1)$$

Where BMP end (mLCH<sub>4</sub>/gVS) is the total amount of methane produced till the incubation period end., and BMP<sub>ThOFC</sub> (mLCH<sub>4</sub>/gVS) is the theoretical methane potential.

At regular intervals of two to four days, hydrogen sulfide levels were measured using a portable gas detector alongside a manual gas pump equipped with rapid-response detection tubes (Jentys et al., 1999). Biogas samples were collected in 2-L Tedlar® gas-sampling bags and quantified using a wet-drum gas meter. To purify the biogas, 99.99% helium carrier gas (HE-HP, Oxygen Tech Co., Ltd., Thailand) was utilized to transport the biogas to the fixed-bed H<sub>2</sub>S remover packed with xFe<sub>2</sub>O<sub>3</sub>-cement-based sand at varying flow rates ranging from 59 to 189 mL/minute (see Figure 1). The purified biogas was subsequently analyzed using a gas chromatograph (Agilent Technologies 6890 N) under the specified conditions, and the removal efficiency of H<sub>2</sub>S was proportionally converted into purified biogas percentages.

#### 2.4.2 Volatile Fatty Acids from Anaerobic Digestion

The Volatile Fatty Acid (VFA) concentration was assessed utilizing the alkali titration method, wherein the sample was diluted with 10 to 100 mL of distilled water. The diluted sample was then transferred into a 20 mL Erlenmeyer flask using a pipette. To this flask, three drops of a methyl orange indicator solution were added. The mixture was subsequently titrated with 0.1 mL of potassium hydroxide (KOH) until the solution developed a faint pink color. The stoichiometric analysis revealed that the VFA concentration in the sample, expressed in grams per liter, was equivalent to the volume of KOH used during titration (Kaur et al., 2020).

### 3. Results and Discussion

#### 3.1 Anaerobic digestion of bagasse for biogas production

The daily biogas production at 35 °C, as illustrated in Figure 2, indicates a substantial increase in biogas yield during the first 16 days of Hydraulic Retention Time (HRT). This surge is likely attributable to the rapid decomposition of soluble sugars within the substrate. Following this initial 16-day period, a marked decline in biogas production is observed, likely due to the extensive conversion of organic material into biogas during this retention phase. The study further reveals that the peak biogas output occurs on the sixteenth day, with

acid-alkaline treated bagasse yielding 84.84 mL/g of volatile solids (VS), compared to the untreated bagasse, which generates 76.09 mL/g of VS, reflecting a distinct difference in biogas productivity (Kaur et al., 2020).

Multiple factors substantiate this assertion. Firstly, acid-alkaline pretreatment has been identified as the most efficacious approach for disrupting lignin's cross-linking structures (Zheng et al., 2014). Secondly, this pretreatment method has been demonstrated to effectively penetrate cellulose crystals and disrupt the microfibrils within the sample (Kim et al., 2020; Pedrosa et al., 2022). Finally, the alkaline process enhances the hydrolysis of hemicellulose, thereby enabling microbial enzymes to more effectively access the cellulose within the sample (Yang et al., 2011; Laca et al., 2019). A thorough comprehension of acid treatments is essential to mitigate corrosive impacts and avert potential damage to cellulose during the acid treatment process (Kargarzadeh et al., 2018).

Figure 2. The total amount of biogas produced by the anaerobic digestion of sugarcane bagasse (with and without acid-base pretreatment) in a 1-L bio-digester at a temperature of 30°C and with cow dung added over 30 days.

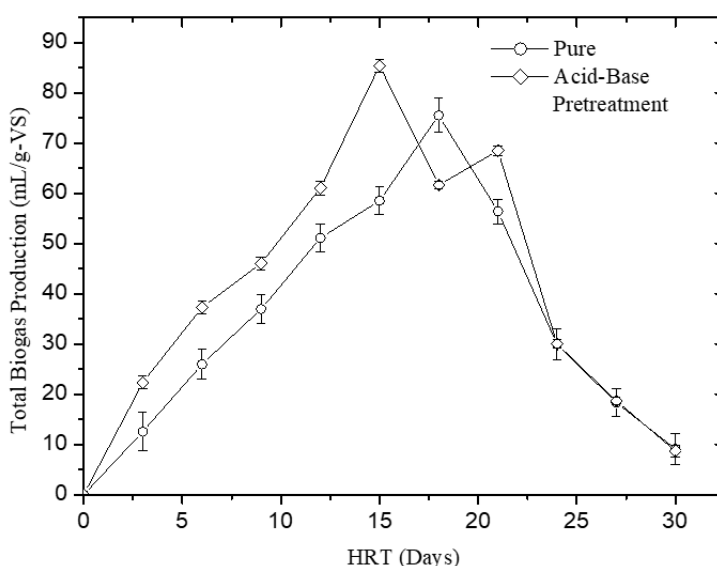
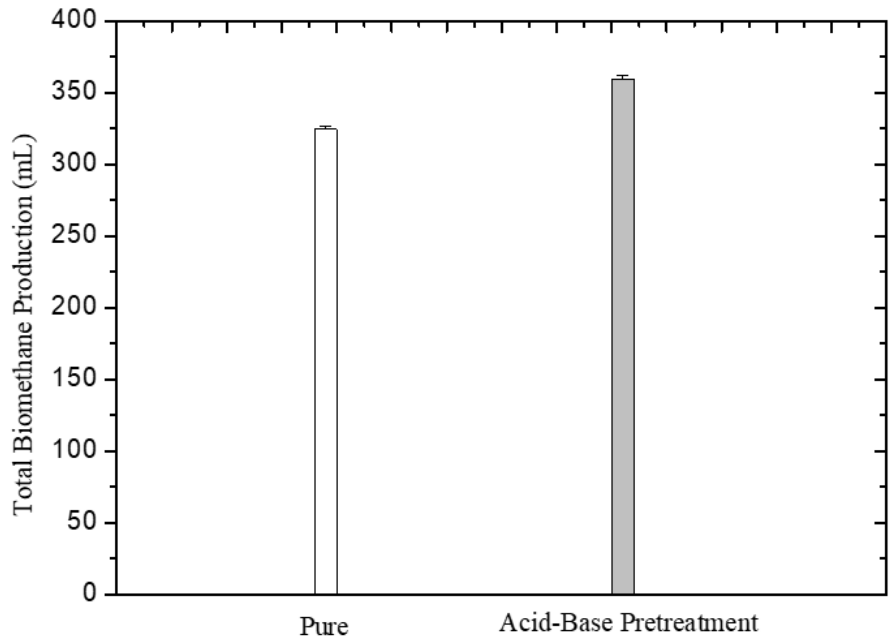


Figure 3 depicts the cumulative biomethane production over a 30-day HRT period. The experimental results reveal that the acid-alkaline pretreatment of bagasse produces the highest biomethane yield, approximately 357.33 mL/g of VS. Conversely, untreated bagasse generates biogas at a rate of 325.34 mL/g of VS at 35 °C. These findings corroborate the previously stated assertion that acid-alkaline pretreatment is markedly more effective in augmenting biogas production from sugarcane bagasse compared to its untreated form. The efficiency of this pretreatment method lies in its ability to effectively break down the structural linkages within the fibrous matrix, thereby substantially enhancing biomethane yield (Zheng et al., 2014; Srisatabusaya, 2024).

Figure 3. The overall biomethane generation from pure and Acis-Base-pretreated sugarcane bagasse at 35 °C throughout a 30-day period of HRT in the present cow dung



3.2 Effects of pH from VFAs evolved

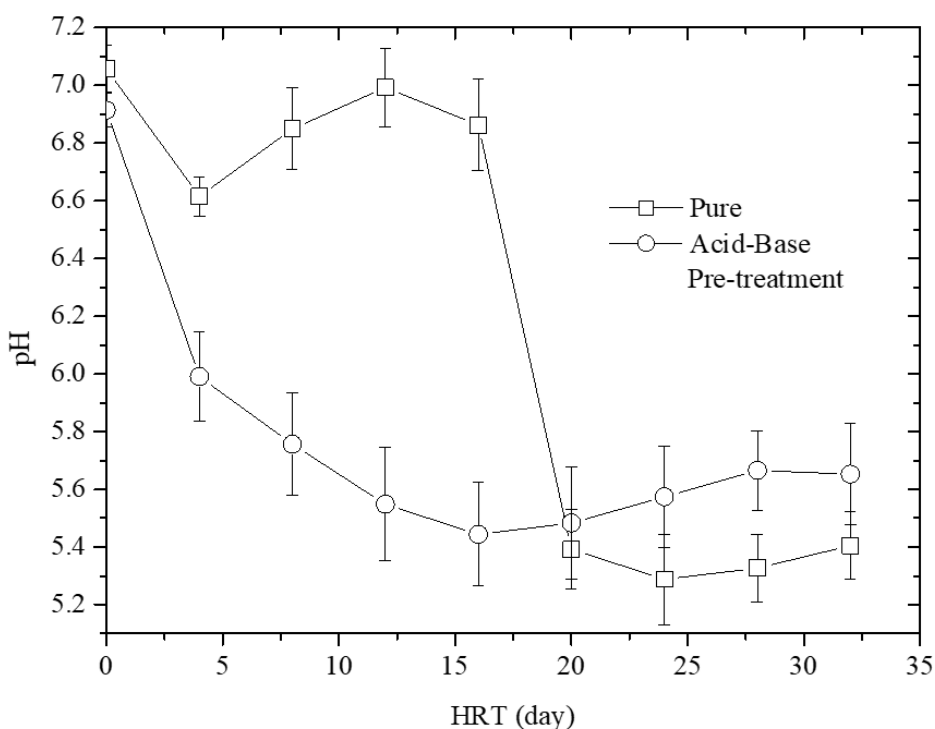
The effectiveness of methanogens, which are crucial for methane generation, is significantly influenced by the pH levels within anaerobic digestion (AD) processes. The initial pH of the fermentation medium ranged between 6.9 and 7.0. Following a 48-hour period of substrate addition, the pH levels dropped to 6.63 for the untreated process and 5.99 for the acid-alkaline treatment, as depicted in Figure 4. This decline in pH is primarily due to the accumulation of volatile fatty acids (VFAs), which are more prevalent in the acid-alkaline process due to the breakdown of glucose into oligosaccharides, subsequently serving as a more accessible substrate for methanogens, thereby enhancing biomethane production (Kaur et al., 2020; Stanley et al., 2022). In contrast, the pH of the untreated process fluctuated between 6.6 and 7.0, reflecting the challenges in decomposing lignin and hemicellulose into fermentable sugars (Poddar et al., 2022; Abraham et al., 2020). Methanogens remain the optimal microorganisms for efficient biomethane production.

As a result, methanogens originating from cow manure exhibited a remarkable capacity to endure the acidic environment within the anaerobic digestion (AD) system (Mrosso et al., 2020), leading to sustained methane production over a 16-day period. Both treatment methods displayed a significant reduction in pH levels, reflecting enhanced substrate digestibility (Coppola & Papurello, 2018). The alkali titration method confirmed the generation of a substantial quantity of volatile fatty acids (VFAs), correlating with a marked increase in biogas output during the first 16 days. Beyond this period, the pH levels

stabilized between 5.27 and 5.68, accompanied by a slight decline in biogas production from day 17 to day 30. This reduction in biogas yield may be attributed to the depletion of critical substrates and the associated pH drop, which signals the terminal phase of certain methanogens' life cycle (Abid et al., 2021; Kaur et al., 2020).

The pH stability during the anaerobic digestion (AD) processes observed in this study aligns with findings from other researchers, contributing to the consistent production of elevated levels of volatile fatty acids (VFAs). Among the prominent VFAs identified are acetic acid, butyric acid, and hexanoic acid (Voegel et al., 2015). As corroborated by the research of Lu et al. (2020), anaerobic digestion conducted under unregulated pH conditions tends to produce higher concentrations of VFAs. A distinct relationship has been established between a pH value of 7 and VFA concentrations ranging from 4.5 to 20 gCOD/L, and from 10 to 45 gCOD/L. Conversely, a pH of 5 is associated with VFA concentrations ranging between 4 to 18 gCOD.

Figure 4. The effect of pH solution on AD processes in the biodigester under the mesophilic condition for 30 days

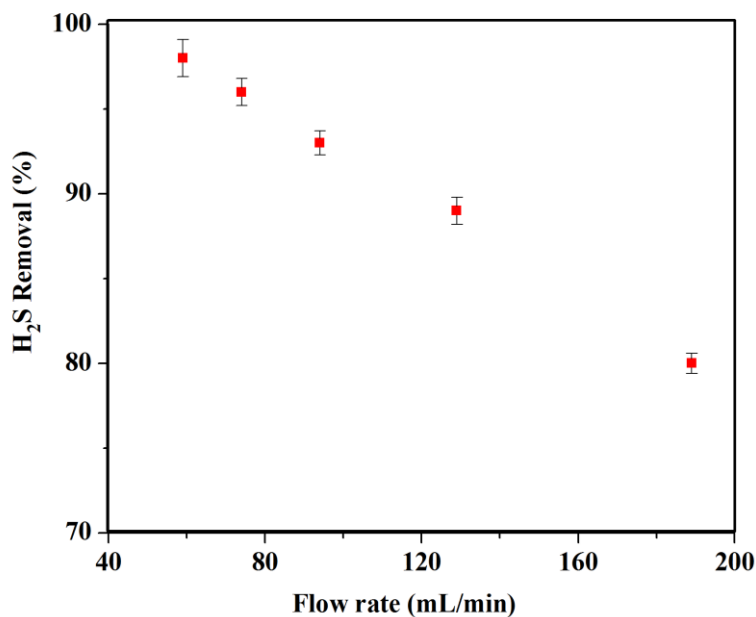


### 3.3 Sand characteristics for H<sub>2</sub>S removal efficiency

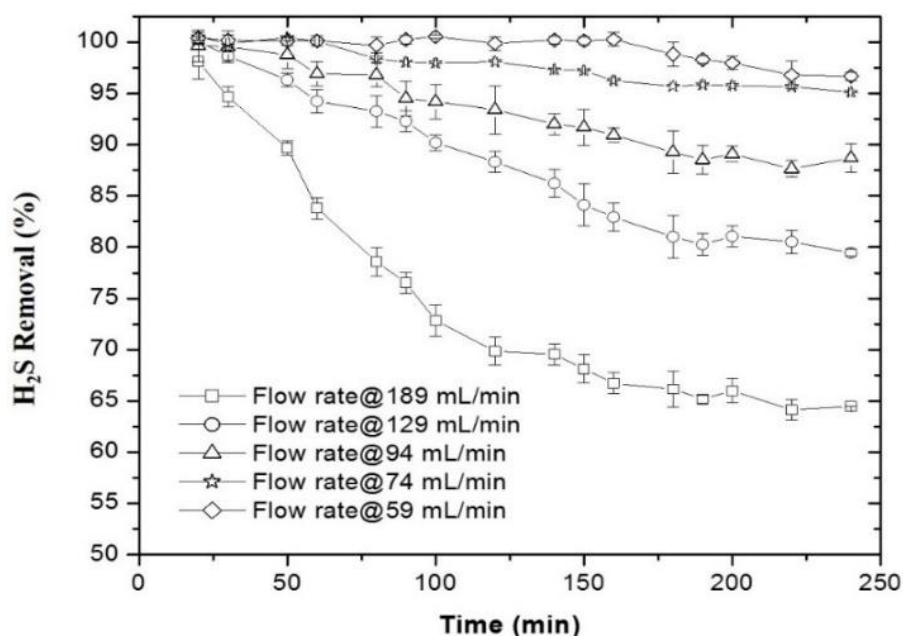
The xFe<sub>2</sub>O<sub>3</sub>/cement-based sand specimen demonstrated a pH value of 6.54, a moisture content of 3.1% (w/w), and a porosity of 44.4%. Here, "w/w" denotes weight per weight. The biogas produced contained a minor concentration of H<sub>2</sub>S, recorded at 11,140 parts per million (ppm). As depicted in Figure 5, the data illustrates the effectiveness of cement-based

sand devoid of  $\text{Fe}_2\text{O}_3$  in the removal of  $\text{H}_2\text{S}$  during a four-hour feeding period with varying flow rates. The cement-based sand achieved an  $\text{H}_2\text{S}$  removal efficiency exceeding 98% at a biogas flow rate of 59 mL per minute. Moreover, a negative correlation was observed between the flow rate and the amount of  $\text{H}_2\text{S}$  extracted from the biogas (Voegel et al., 2015; Lu et al., 2020), as shown in Figure 5. Nonetheless, even at the highest flow rate of 189 mL/min, an 80% reduction in  $\text{H}_2\text{S}$  was attained within a mere four-hour timeframe.

Figure 5.  $\text{H}_2\text{S}$  removal efficiency (%) of cement-based sand without  $\text{Fe}_2\text{O}_3$  during 4 h of feeding time at a flow rate of 59–189 mL/min



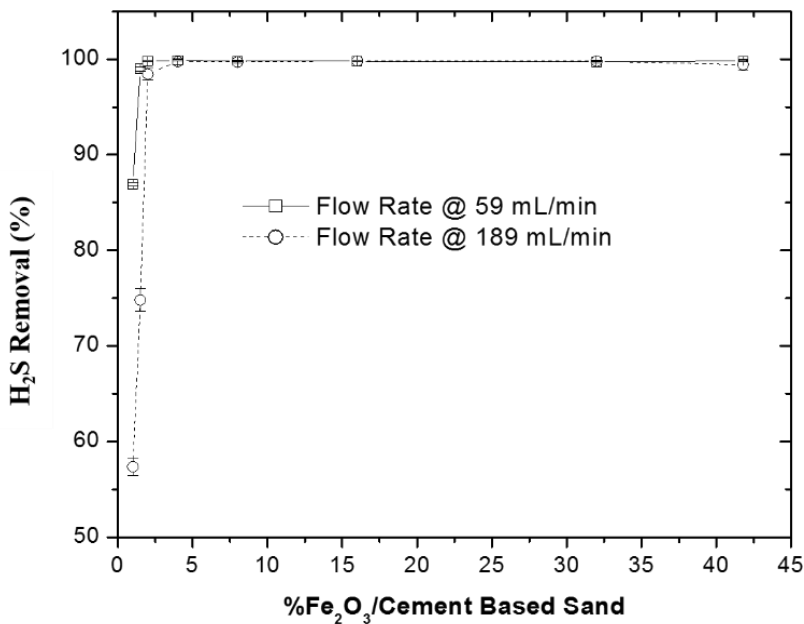
As depicted in Figure 6, a flow rate of 59 mL/min successfully maintained a consistent 100%  $\text{H}_2\text{S}$  absorbance for the first 160 minutes of the experiment. However, this efficiency declined to 96% after 240 minutes. Conversely,  $\text{H}_2\text{S}$  absorbance in the cement-based sand, supplied at flow rates of 74, 94, 129, and 189 mL/min, gradually diminished to approximately 100% after 55, 50, 30, and 25 minutes, respectively, as illustrated in Figure 6. These results align closely with those reported in previous studies (Voegel et al., 2015; Pham et al., 2019), where an 80% reduction in  $\text{H}_2\text{S}$  removal efficiency was observed after a 6-minute water scrubbing process. This variation corroborates findings from earlier research (Lasocki et al., 2015), which demonstrated that the efficiency of  $\text{H}_2\text{S}$  removal using raw sand, acidic sand, typical sand, and podzol soil increased as gas flow rates decreased. Additionally, increasing the thickness of the bog iron ore layer enhanced  $\text{H}_2\text{S}$  removal efficiency, whereas biogas flow rates either decreased or remained stable (Carroll et al., 2016). The rise in biogas flow rate and the extended feeding duration led to the accumulation of  $\text{H}_2\text{S}$  and biogas, intended for household distribution. To achieve more sustainable biomethane production, it is crucial to optimize both  $\text{H}_2\text{S}$  and biogas levels.

Figure 6. H<sub>2</sub>S removal efficiency with increasing feeding time and biogas flow rates

### 3.5 Effects of Fe<sub>2</sub>O<sub>3</sub> on H<sub>2</sub>S removal efficiency

For this experiment, xFe<sub>2</sub>O<sub>3</sub>/cement-based sand was synthesized with varying Fe<sub>2</sub>O<sub>3</sub> concentrations, ranging from 1% to 41.8% by weight. Figure 7 illustrates the effectiveness of H<sub>2</sub>S removal using x Fe<sub>2</sub>O<sub>3</sub>/cement-based sand at two distinct flow rates: a low flow rate of 59 mL/min and a maximum flow rate of 189 mL/min. At a concentration of Fe<sub>2</sub>O<sub>3</sub> below 2.5% in the cement-based sand, H<sub>2</sub>S removal efficiency was less than 80% at the higher flow rate of 189 mL/min. Conversely, the absorbance and removal efficiency of H<sub>2</sub>S ranged between 86% and 98% at the lower flow rate of 59 mL/min. Increasing the Fe<sub>2</sub>O<sub>3</sub> concentration to 2.5% significantly enhanced H<sub>2</sub>S removal at both flow rates (Figure 7). This phenomenon suggests an inverse relationship between the concentration of Fe<sub>2</sub>O<sub>3</sub> in the cement-based sand and the removal efficiency of H<sub>2</sub>S, irrespective of flow rate. H<sub>2</sub>S removal efficiency was comparable between cement-based sand and Fe<sub>2</sub>O<sub>3</sub>/cement-based sand at a flow rate of 59 mL/min. However, Fe<sub>2</sub>O<sub>3</sub>/cement-based sand demonstrated the ability to maintain high H<sub>2</sub>S removal efficiency across a broader range of flow rates (59 to 189 mL/min), whereas cement-based sand did not. The primary mechanism enabling Fe<sub>2</sub>O<sub>3</sub>/cement-based materials to absorb H<sub>2</sub>S is the reaction between ferric iron (Fe<sup>3+</sup>) and the gas (Lasocki et al., 2015). In the Fe<sub>2</sub>O<sub>3</sub>/cement-based sand absorber, the iron oxide (Fe<sub>2</sub>O<sub>3</sub>) reacts with H<sub>2</sub>S as biogas flows through the column, forming iron sulfide (Fe<sub>2</sub>S<sub>3</sub>) and water (H<sub>2</sub>O). The reduced H<sub>2</sub>S removal efficiency in cement-based sand at higher flow rates may be attributed to the low moisture content, which is essential for maintaining Fe<sub>2</sub>O<sub>3</sub> in its hydrated form (Carroll et al., 2016; Wu, 2020).

Figure 7. Tolerance of 4 wt.% Fe<sub>2</sub>O<sub>3</sub>/cement-based sand against H<sub>2</sub>S removal efficiency at the biogas rate of 59 and 189 mL/min



4. Conclusions

This research revealed that the acid-base pretreatment method was found to be most effective in breaking down lignin cross-links and making cellulose more accessible. After 16 days of exposure, it produced the most biogas, 84.84 mL/g, and the highest biomethane output, approximately 357.33 mL/g of VS. The initial pH of anaerobic digestion processes significantly impacts the activity of methanogens, a crucial factor in methane synthesis. The most effective absorber was cementitious sand with a 4% wt Fe<sub>2</sub>O<sub>3</sub> content, effectively eliminating H<sub>2</sub>S at gas flow rates ranging from 59 to 89 mL/min. The reusability of the Fe<sub>2</sub>O<sub>3</sub>/cement-based sand could be significantly enhanced through washing and subsequent exposure to ambient oxygen.

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### Disclosure Statement

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### References

1. Srisatabusaya, P. (2024, February 29). Domestic oil demand set to rise this year. In Y. Praiwan (Ed.), *\*An aerial view of an oil refinery complex operated by Thai Oil in Chon Buri's Sri Racha district\** (Chon Buri's Sri Racha district). © Bangkok Post PCL.
2. S.R. Department. (2023). *\*Production volume of sugarcane in Thailand from 2016 to 2021 with a forecast for 2023\**.
3. Paulose, P. (2020). *\*Anaerobic digestion of sugarcane trash and bagasse for biomethane production\**.
4. Prasad, S. D. (2020). *\*Butanol production from residues of sugar and timber and estimation of butanol production potential in Fiji\** [Master's thesis, University of the South Pacific]. School of Engineering and Physics, University of the South Pacific, Suva.
5. Agarwal, N. K., Kumar, M., Ghosh, P., Kumar, S. S., Singh, L., Vijay, V. K., & Kumar, V. (2022). Anaerobic digestion of sugarcane bagasse for biogas production and digestate valorization. *\*Chemosphere, 295\**, Article 133893. <https://doi.org/10.1016/j.chemosphere.2022.133893>
6. Longati, A. A., Lino, A. R. A., Giordano, R. C., Furlan, F. F., & Cruz, A. J. G. (2020). Biogas production from anaerobic digestion of vinasse in sugarcane biorefinery: A techno-economic and environmental analysis. *\*Waste and Biomass Valorization, 11\**, 4573-4591. <https://doi.org/10.1007/s12649-020-01043-3>
7. Tshemese, Z., Deenadayalu, N., Linganiso, L. Z., & Chetty, M. (2023). An overview of biogas production from anaerobic digestion and the possibility of using sugarcane wastewater and municipal solid waste in a South African context. *\*Applied System Innovation, 6\*(1)*, Article 13. <https://doi.org/10.3390/asi6010013>
8. Poddar, B. J., Nakhate, S. P., Gupta, R. K., Chavan, A. R., Singh, A. K., Khardenavis, A. A., & Purohit, H. J. (2022). A comprehensive review on the pretreatment of lignocellulosic wastes for improved biogas production by anaerobic digestion. *\*International Journal of Environmental Science and Technology\**. <https://doi.org/10.1007/s13762-022-03852-7>
9. Stanley, J. T., Thanarasu, A., Kumar, P. S., Periyasamy, K., Raghunandhakumar, S., Periyaraman, P., Devaraj, K., Dhanasekaran, A., & Subramanian, S. (2022). Potential pre-treatment of lignocellulosic biomass for the enhancement of biomethane production through anaerobic digestion-A review. *\*Fuel, 318\**, Article 123593.

- https://doi.org/10.1016/j.fuel.2022.123593
10. Kumar, A., Kumar, V., & Singh, B. (2021). Cellulosic and hemicellulosic fractions of sugarcane bagasse: Potential, challenges, and future perspective. *\*International Journal of Biological Macromolecules*, 169\*, 564-582. <https://doi.org/10.1016/j.ijbiomac.2020.12.182>
11. Blasi, A., Verardi, A., Lopresto, C. G., & Siciliano, S. (2023). Lignocellulosic agricultural waste valorization to obtain valuable products: An overview. *\*Recycling*, 8\*(2), Article 61. <https://doi.org/10.3390/recycling8020061>
12. Abraham, A., Mathew, A. K., Park, H., Choi, O., Sindhu, R., Parameswaran, B., Pandey, A., Park, J. H., & Sang, B.-I. (2020). Pretreatment strategies for enhanced biogas production from lignocellulosic biomass. *\*Bioresource Technology*, 301\*, Article 122725. <https://doi.org/10.1016/j.biortech.2020.122725>
13. Bisaria, V. S. (Ed.). (2014). *\*Bioprocessing of renewable resources to commodity bioproducts\**. John Wiley & Sons.
14. Sibanda, T. N. (2021). *\*Design of an anaerobic digester for electricity generation using a small reciprocating engine\** [Master's thesis, University of the South Pacific].
15. Ghimire, A., Gyawali, R., Lens, P. N. L., & Lohani, S. P. (2021). Technologies for removal of hydrogen sulfide (H<sub>2</sub>S) from biogas. In P. N. L. Lens & S. P. Lohani (Eds.), *\*Emerging technologies and biological systems for biogas upgrading\** (pp. 295-320). Springer. [https://doi.org/10.1007/978-3-030-55933-4\\_13](https://doi.org/10.1007/978-3-030-55933-4_13)
16. Al Mamun, M. R., & Torii, S. (2015). Removal of hydrogen sulfide (H<sub>2</sub>S) from biogas using zero-valent iron. *\*Journal of Clean Energy Technologies*, 3\*(5), 428-432. <https://doi.org/10.7763/JOCET.2015.V3.231>
17. Coppola, G., & Papurello, D. (2018). Biogas cleaning: Activated carbon regeneration for H<sub>2</sub>S removal. *\*Clean Technologies*, 1\*(1), 40-57. <https://doi.org/10.3390/cleantechnol1010005>
18. Mrosso, R., Machunda, R., & Pogrebnaya, T. (2020). Removal of hydrogen sulfide from biogas using a red rock. *\*Journal of Energy*, 2020\*, Article 1-10. <https://doi.org/10.1155/2020/6425734>
19. Voegel, C., Bertron, A., & Erable, B. (2015). Biodeterioration of cementitious materials in biogas digester. *\*Matériaux & Techniques*, 103\*(3), Article 202. <https://doi.org/10.1051/mattech/2015026>
20. Zheng, Y., Zhao, J., Xu, F., & Li, Y. (2014). Pretreatment of lignocellulosic biomass for enhanced biogas production. *\*Progress in Energy and Combustion Science*, 42\*, 35-53. <https://doi.org/10.1016/j.peccs.2014.01.001>
21. Maryana, R., Ma'rifatun, D., Wheni, A. I., Satriyo, K. W., & Rizal, W. A. (2014). Alkaline pretreatment on sugarcane bagasse for bioethanol production. *\*Energy Procedia*, 47\*, 250-254. <https://doi.org/10.1016/j.egypro.2014.01.216>
22. Tanimu, M. I., Ghazi, T. I. M., Harun, R. M., & Idris, A. (2014). Effect of carbon to nitrogen ratio of food waste on biogas methane production in a batch mesophilic anaerobic digester. *\*International Journal of Innovation, Management and Technology*, 5\*(2), 116-122. <https://doi.org/10.7763/IJIMT.2014.V5.499>
23. Kaur, M., Verma, Y. P., & Chauhan, S. (2020). Effect of chemical pretreatment of sugarcane bagasse on biogas production. *\*Materials Today: Proceedings*, 21\*, 1937-1942. <https://doi.org/10.1016/j.matpr.2020.01.287>
24. Kulawong, S., Artkla, R., Sriprapakhan, P., & Maneechot, P. (2022). Biogas purification by adsorption of hydrogen sulphide on NaX and Ag-exchanged NaX zeolites. *\*Biomass and Bioenergy*, 159\*, Article 106417. <https://doi.org/10.1016/j.biombioe.2022.106417>
25. Florendo, P. D., Sharma-Shivappa, V. V., & Fellner, V. (2018). Cattle rumen microorganisms hydrolysis for switchgrass saccharification, volatile fatty acids, and methane production. *\*International Journal of Agricultural Technology*, 14\*(2), 31-43.
26. Sriprapakhan, P., Maneechot, P., & Artkla, S. (2023). Supplement the amount of biogas

- volume by adsorption of VFAs on SiO<sub>2</sub> and MCM-41 from anaerobic fermentation of rice straw. *\*GMSARN International Journal*, 17\*, 447-455.
27. Jentys, A., Kleestorfer, K., & Vinek, H. (1999). Concentration of surface hydroxyl groups on MCM-41. *\*Microporous and Mesoporous Materials*, 27\*, 321-328. [https://doi.org/10.1016/S1387-1811\(98\)00225-5](https://doi.org/10.1016/S1387-1811(98)00225-5)
28. Wang, W., Gu, Y., Zhou, C., & Hu, C. (2022). Current challenges and perspectives for the catalytic pyrolysis of lignocellulosic biomass to high-value products. *\*Catalysts*, 12\*(12), Article 1524. <https://doi.org/10.3390/catal12121524>
29. Karimi, K., & Taherzadeh, M. J. (2016). A critical review of analytical methods in pretreatment of lignocelluloses: Composition, imaging, and crystallinity. *\*Bioresource Technology*, 200\*, 1008-1018. <https://doi.org/10.1016/j.biortech.2015.11.022>
30. Pedrosa, J. F. S., Rasteiro, M. G., Neto, C. P., & Ferreira, P. J. T. (2022). Effect of cationization pretreatment on the properties of cationic Eucalyptus micro/nanofibrillated cellulose. *\*International Journal of Biological Macromolecules*, 201\*, 468-479. <https://doi.org/10.1016/j.ijbiomac.2021.12.033>
31. Yang, B., Dai, Z., Ding, S.-Y., & Wyman, C. E. (2011). Enzymatic hydrolysis of cellulosic biomass. *\*Biofuels*, 2\*(4), 421-449. <https://doi.org/10.4155/bfs.11.116>
32. Laca, A., Laca, A., & Díaz, M. (2019). Hydrolysis: From cellulose and hemicellulose to simple sugars. In A. Pandey, R. D. Tripathi, P. C. Sharma, & D. P. Singh (Eds.), *\*Second and third generation of feedstocks\** (pp. 213-240). Elsevier. <https://doi.org/10.1016/B978-0-444-64203-7.00012-7>
33. Kargarzadeh, H., Mariano, M., Gopakumar, D., Ahmad, I., Thomas, S., Dufresne, A., Huang, J., & Lin, N. (2018). Advances in cellulose nanomaterials. *\*Cellulose*, 25\*(4), 2151-2189. <https://doi.org/10.1007/s10570-018-1723-5>
34. Prabakar, D., Manimudi, V. T., Sampath, S., Mahapatra, D. M., Rajendran, K., & Pugazhendhi, A. (2018). Advanced biohydrogen production using pretreated industrial waste: Outlook and prospects. *\*Renewable and Sustainable Energy Reviews*, 96\*, 306-324. <https://doi.org/10.1016/j.rser.2018.07.031>
35. Quintana Najera, J. (2022). *\*Augmentation of biochar in anaerobic digestion\** [Master's thesis, University of Queensland].
36. Ennaert, T., de Beeck, B. O., Vanneste, J., Smit, A. T., Huijgen, W. J. J., Vanhulsel, A., Jacobs, P. A., & Sels, B. F. (2016). The importance of pretreatment and feedstock purity in the reductive splitting of (ligno)cellulose by metal supported USY zeolite. *\*Green Chemistry*, 18\*(7), 2095-2105. <https://doi.org/10.1039/C5GC03025B>
37. Kim, T. H., Kwak, H., Kim, T. H., & Oh, K. K. (2020). Extraction behaviors of lignin and hemicellulose-derived sugars during organosolv fractionation of agricultural residues using a bench-scale ball milling reactor. *\*Energies*, 13\*(2), Article 352. <https://doi.org/10.3390/en13020352>
38. Abid, M., Wu, J., Seyedsalehi, M., Hu, Y.-y., & Tian, G. (2021). Novel insights of impacts of solid content on high solid anaerobic digestion of cow manure: Kinetics and microbial community dynamics. *\*Bioresource Technology*, 333\*, Article 125205. <https://doi.org/10.1016/j.biortech.2021.125205>
39. Chandel, A. K., Antunes, F. A. F., Anjos, V., Bell, M. J. V., Rodrigues, L. N., Polikarpov, I., de Azevedo, E. R., Bernardinelli, O. D., Rosa, C. A., & Pagnocca, F. C. (2014). Multi-scale structural and chemical analysis of sugarcane bagasse in the process of sequential acid–base pretreatment and ethanol production by *\*Scheffersomyces shehatae\** and *\*Saccharomyces cerevisiae\**. *\*Biotechnology for Biofuels*, 7\*, Article 1-17. <https://doi.org/10.1186/s13068-014-0161-y>
40. Li, Y., Chen, Y., & Wu, J. (2019). Enhancement of methane production in anaerobic digestion process: A review. *\*Applied Energy*, 240\*, 120-137.

- <https://doi.org/10.1016/j.apenergy.2019.01.243>
41. Schnürer, A. (2016). Biogas production: Microbiology and technology. In J. Sing (Ed.), *\*Anaerobes in biotechnology\** (pp. 195-234). Elsevier. <https://doi.org/10.1016/B978-0-12-803791-4.00009-6>
  42. Cheah, Y.-K., Vidal-Antich, C., Dosta, J., & Mata-Álvarez, J. (2019). Volatile fatty acid production from mesophilic acidogenic fermentation of organic fraction of municipal solid waste and food waste under acidic and alkaline pH. *\*Environmental Science and Pollution Research*, 26\*(35), 35509-35522. <https://doi.org/10.1007/s11356-019-06823-3>
  43. Lu, Y., Zhang, Q., Wang, X., Zhou, X., & Zhu, J. (2020). Effect of pH on volatile fatty acid production from anaerobic digestion of potato peel waste. *\*Bioresource Technology*, 316\*, Article 123851. <https://doi.org/10.1016/j.biortech.2020.123851>
  44. Achak, M., Boumya, W., Elamraoui, S., Asdiou, N., Taoufik, N., Barka, N., Aboulkas, A., & Lamy, E. (2023). Performance of olive mill wastewater treatment using hybrid system combining sand filtration and vertical flow constructed wetlands. *\*Journal of Water Process Engineering*, 53\*, Article 103737. <https://doi.org/10.1016/j.jwpe.2023.103737>
  45. Lien, C.-C., Lin, J.-L., & Ting, C.-H. (2014). Water scrubbing for removal of hydrogen sulfide (H<sub>2</sub>S) in biogas from hog farms. *\*Journal of Agricultural Chemistry and Environment*, 3\*(1), 1-6. <https://doi.org/10.4236/jacen.2014.31001>
  46. Pham, C. H., Saggarr, S., Berben, P., Palmada, T., & Ross, C. (2019). Removing hydrogen sulfide contamination in biogas produced from animal wastes. *\*Journal of Environmental Quality*, 48\*(1), 32-38. <https://doi.org/10.2134/jeq2017.08.0328>
  47. Lasocki, J., Kołodziejczyk, K., & Matuszewska, A. (2015). Laboratory-scale investigation of biogas treatment by removal of hydrogen sulfide and carbon dioxide. *\*Polish Journal of Environmental Studies*, 24\*(3), 1427-1434. <https://doi.org/10.15244/pjoes/40416>
  48. Wu, L. (2020). *\*Recycling mine waste to improve the acid resistance of cement-based composites for underground structures\** [Doctoral dissertation, University of British Columbia].
  49. Carroll, S., Carey, J. W., Dzombak, D., Huerta, N. J., Li, L., Richard, T., Um, W., Walsh, S. D. C., & Zhang, L. (2016). Role of chemistry, mechanics, and transport on well integrity in CO<sub>2</sub> storage environments. *\*International Journal of Greenhouse Gas Control*, 49\*, 149-160. <https://doi.org/10.1016/j.ijggc.2016.01.010>