

Article

Mill Scale Addition to Reduce Hydrogen Sulfide Production in Anaerobic Digestion

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Abstract: Direct addition of sulfur-reducing agents during anaerobic digestion (AD) is very effective in controlling hydrogen sulfide (H₂S) content in biogas, although one major problem is the high operational cost due to the large amount of chemicals used. The objective of this study was to remove H₂S using a waste mill scale (MS) as a sulfur-reducing agent. To evaluate its feasibility, MS was added to AD fed with food waste (FW) at concentrations between 0 and 160 g MS/kg total chemical oxygen demand (TCOD) during the batch test, and the experimental results were compared to those of the batch test with the addition of iron chloride (FeCl₃). Both FeCl₃ and MS played an important role as electro-conductive materials in improving methane productivity by promoting direct interspecies electron transfer. An increase in H₂S removal efficiency was observed with increases in both materials. In total, 30%, 60%, and 90% of H₂S production based on the maximum sulfur in the form of H₂S (control) was 3.7, 9.4, and 23.8 g FeCl₃/kg TCOD and 13.3, 34.1, and 86.2 g MS/kg TCOD, respectively. This finding indicates that MS can be used as a sulfur-reducing agent substitute for H₂S removal in AD fed with FW.



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Keywords: anaerobic digestion; food waste; hydrogen sulfide production; mill scale; sulfur-reducing agent

1. Introduction

Sustainable organic waste management has become one of the greatest challenges worldwide. Anaerobic digestion (AD) is recognized as a well-established technology for the treatment of a wide range of organic matter (such as food waste, sewage sludge, agricultural residues, and livestock manure) but also for the production of biogas, which has been utilized for a combination of heat and electricity generation [1–4]. Currently, the use of biogas is moving toward new applications, such as vehicle fuels and injection into the natural gas grid. However, to utilize it widely, biogas purity is critical, which can often compromise its true economic potential [5].

Biogas mainly consists of methane (CH₄) and carbon dioxide (CO₂), but it also contains trace contaminants, such as hydrogen sulfide (H₂S), moisture, siloxane, and ammonia, which greatly affect its purity. The most common contaminant is H₂S, and its level can vary from 10 ppm_v to approximately 20,000 ppm_v, depending on the composition of the feedstock. H₂S is mainly produced by sulfate-reducing bacteria (SRB) during the degradation of sulfur-containing organic compounds (methionine and cysteine) [6–9]. H₂S is a highly corrosive and deleterious compound that causes significant damage to pipes and generators when combined with moisture [5]. Moreover, the combustion of H₂S results in sulfur dioxide emissions if not removed prior to biogas utilization. H₂S removal is thus necessary for the eventual utilization of biogas to protect downstream equipment and avoid the formation of harmful compounds. To date, common H₂S removal technologies include physicochemical approaches either during digestion or from crude biogas [5,10–13].

H₂S can be removed by the direct addition of chemical compounds such as iron salts in the form of FeCl₂ or FeCl₃ into the digester. These react with the produced H₂S to form iron sulfide (FeS), which is an insoluble precipitate. This approach is very effective in controlling H₂S content (>99%) in biogas, although one major problem is high operational costs due to the various fresh chemicals required and difficulties in recycling the used iron salt [10,14].

Recent studies have proposed that metallic iron-rich waste is a potential alternative reagent for H₂S removal from biogas [15]. Mill scale (MS) is an abundant and unavoidable waste produced by the rolling mill in the steel industry (accounting for 2% of the total steel produced) [16]. According to the World Steel Association, global crude steel production in 2020 reached 1864 million tons (Mt), from which 37.3 million tons of mill scale were generated [17]. It is a very valuable metallurgical material containing approximately 65–70% of iron. It consists of mixed FeO, Fe₂O₃, and Fe₃O₄, and its chemical composition varies depending on the type of steel produced and process employed [18]. If the addition of MS effectively controls H₂S levels in biogas and does not negatively affect methane productivity, it is expected to be an alternative way to reduce the operational costs of biogas desulfurization.

Based on the above research background, the purpose of this study was to investigate the possibility of using MS as a substitute for iron chloride (FeCl₃) in H₂S removal during anaerobic digestion of food waste (FW). Different levels of MS were applied to a batch test to compare its H₂S removal performance with that of the control, in which FeCl₃ was applied. In addition, we demonstrated how MS plays an important role as an electro-conductive material, improving CH₄ productivity by accelerating direct interspecies electron transfer (DIET), and provided the basis for future strategies for biogas utilization.

2. Materials and Methods

2.1. Preparation of Feedstock and Inoculum

The inoculum was obtained from full-scale anaerobic digestion systems located in Cheongju, South Korea, and kept under mesophilic conditions for one week to remove leftover biodegradable matter before seeding. The pH and volatile suspended solids (VSS) of the inoculum were 5.5 ± 0.1 and 14.5 ± 0.6 g/L, respectively. FW was collected from the storage tank of a full-scale anaerobic digestion system in Chungju, South Korea and transferred to the laboratory within 2 h. The FW was ground and strained through a sieve (1 mm × 1 mm) prior to the batch tests. The organic composition of the FW and inoculum are presented in Table 1.

Table 1. Chemical composition of feedstock and inoculum.

| Parameters | Food Waste I | Food Waste II | Inoculum |
|--------------------|--------------|---------------|-------------|
| TCOD (g/L) | 102.5 ± 1.1 | 130.0 ± 0.9 | 26 ± 6 |
| SCOD (g/L) | 71.5 ± 1.0 | 75.0 ± 0.4 | 14 ± 4 |
| SCOD/TCOD (%) | 70 | 58 | 54 |
| TS (g/L) | 98.1 ± 0.6 | 113.1 ± 1.2 | 21 ± 1 |
| VS (g/L) | 85.2 ± 0.2 | 96.5 ± 0.4 | 19 ± 3 |
| Sulfur content (%) | 0.45 ± 0.00 | 0.19 ± 0.02 | 0.27 ± 0.00 |
| pH | 4.1 | 4.1 | 7.2 |

TCOD: total chemical oxygen demand; SCOD: soluble chemical oxygen demand.

2.2. Batch Test

Two sets of batch tests were performed for the desulfurization potential test using 250 mL serum bottles with a working volume of 150 mL. After measuring the concentration of total chemical oxygen demand (TCOD) of the FW, it was added to a feedstock concentration of 7.5 ± 0.2 g COD/L (batch test I with addition of FeCl₃) and 20 ± 0.1 g COD/L (batch test II with addition of MS), and the inoculum was added to each batch test to reach an inoculum/substrate ratio of 2 (VS basis). The rest of the working volume was filled with

tap water, with no external nutrients used. Finally, FeCl₃ (Samjung Co., Seoul, South Korea) was added to obtain FeCl₃ concentrations of 0, 11, 22, 33, 44, 67, and 89 g FeCl₃/kg TCOD in batch test I, while the MS (83% Fe content) powder (Hyundai Steel Co., Seoul, South Korea) was added with a wide range of concentrations (0, 5, 10, 20, 40, and 160 g MS/kg TCOD) in batch test II. The average density of FeCl₃ and MS was 2.9 and 2.3 g/cm³.

After adding all substances, the initial pH was adjusted to 7.5 ± 0.1 by adding 3 N HCl and 3 N KOH solution, and the serum bottles were purged with N₂ gas (99.99% purity) for 5 min to provide an anaerobic condition. A batch test, including a blank (adding only inoculum), was carried out in a shaking incubator (Jeio Tech, Seoul, South Korea) at 120 rpm at 38 °C. All experiments were performed in duplicate, and the experimental results are presented as average values.

2.3. Analytical Method

The CH₄ content in the biogas was determined by gas chromatography (SRI 310, SRI Instrument, USA) using a thermal conductivity detector and a HayeSep T column (3 ft × 1/8') with N₂ as the mobile phase. The CH₄ content was calculated using the gas composition in the headspace and total volume of biogas produced at each time interval [19]. The cumulative CH₄ production curve was described by the following modified Gompertz equation [20] (Equation (1)) applied to fit the cumulative CH₄ data in order to predict methane production [20]:

$$M(t) = M_o \times \exp\left\{-\exp\left[\frac{R_o \times e}{M_o} \times (\lambda - t) + 1\right]\right\} \quad (1)$$

where $M(t)$ is the cumulative CH₄ production at cultivation time (t) (mL), M_o is the CH₄ production potential (mL), R_o is the CH₄ production rate (mL/d), λ is the lag period (d), and e is the Euler number (2.71828).

The chemical oxygen demand (COD) and pH were measured according to standard methods [21]. For the H₂S analysis during the batch test, a ready-to-use kit (Model GV-100, GASTEC, Kanagawa, Japan) and H₂S detection tubes (KITAGAWA, Kanagawa, Japan) were used, which tightly fit into the glass airlock of the bottle. The sulfur balance was determined by estimating the amount of H₂S_(g) and H₂S_(l) (Henry's constant at 35 °C). Equations (2) and (3) define the H₂S calculation:

$$C = \text{ppm}_v \times \frac{34.08}{22.4} \times \frac{273}{273 + T} \quad (2)$$

$$M = C \times P \times 1/10^6 \quad (3)$$

where C = H₂S compounds (mg/m³), ppm_v = H₂S compounds (ppm_v), T = temperature of batch test (°C), M = amount of H₂S (mg), and P = gas production (mL).

The relationship between H₂S removal and the addition of a sulfur-reducing agent was fitted by Equation (4):

$$y = a + b \times \exp\left(-\frac{x}{c}\right) \quad (4)$$

where y = amount of H₂S; x = amount of injected FeCl₃ and/or mill scale; and a , b , c = constant number.

3. Results and Discussion

3.1. Effect of Iron Chloride Addition on Anaerobic Digestion

The CH₄ accumulation curves were well fitted by the modified Gompertz Equation (1), and all curves of R² were higher than 95% (Figure 1). The reactor performance of batch test I in response to the FeCl₃ addition is summarized in Table 2. The improvements in CH₄ yield and CH₄ production rate with an increase in the amount of FeCl₃ injected were obtained. For example, the sample in the presence of 11 g FeCl₃/kg COD showed a CH₄ yield of 258 ± 4 mL CH₄/g COD and a CH₄ production rate of 23.1 ± 1.1 mL CH₄/d,

and the sample added with 44 g FeCl₃/kg COD resulted in a CH₄ yield of 332 ± 2 mL CH₄/g COD, with a CH₄ production rate of 31.8 mL CH₄/d. Meanwhile, the samples with more than 89 g FeCl₃/kg COD tended to slightly decrease CH₄ productivity. This indicates that FeCl₃ addition positively affected CH₄ productivity. This result is similar to previous studies reporting that FeCl₃ addition accelerated the decomposition and degradation of organic polymers by dissimilatory iron reduction anaerobic digestion [22].

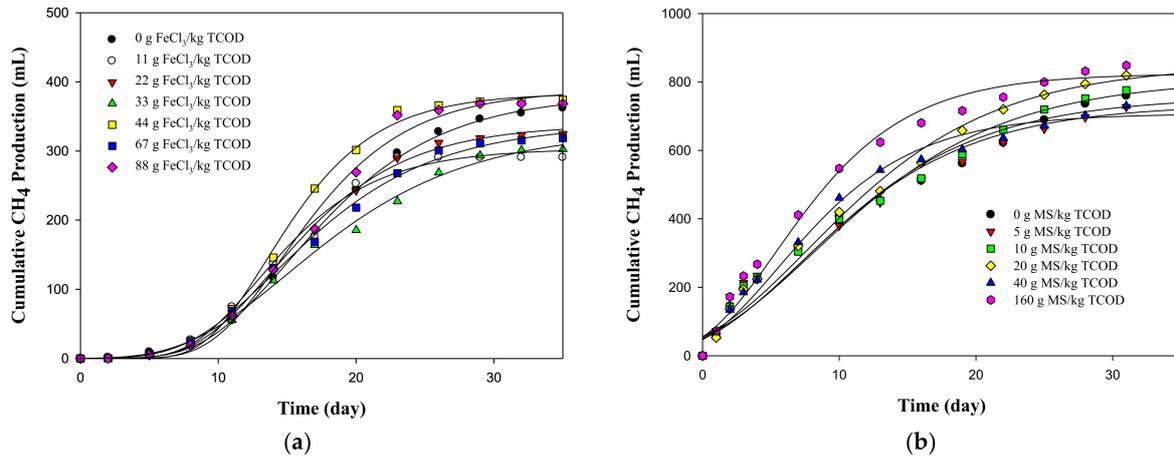


Figure 1. Cumulative methane production of food waste with addition of (a) iron chloride and (b) mill scale.

Table 2. Experimental results obtained from batch test I with the addition of iron chloride.

| FeCl ₃ Dosage (g FeCl ₃ /kg TCOD) | CH ₄ Yield (mL CH ₄ /g TCOD) | CH ₄ Production Rate (mL/d) | λ (d) | H ₂ S Content (ppm _v) | Total Amount of Sulfur Reduced to H ₂ S (mg) | Theoretical Value of Sulfur Reacted with FeCl ₃ (mg H ₂ S/g FeCl ₃) | Final pH |
|---|--|--|-----------|--|---|---|-----------|
| 0 | 211 ± 3 | 18.9 ± 0.3 | 9.0 ± 0.2 | 2,520 ± 426 | 2.37 ± 0.327 | - | 7.4 ± 0.1 |
| 11 | 258 ± 4 | 23.1 ± 1.1 | 8.0 ± 0.0 | 947 ± 267 | 0.95 ± 0.062 | 129 ± 33 | 7.4 ± 0.1 |
| 22 | 289 ± 14 | 22.9 ± 2.1 | 8.4 ± 0.2 | 271 ± 62 | 0.24 ± 0.038 | 97 ± 18 | 7.4 ± 0.2 |
| 33 | 269 ± 11 | 16.4 ± 4.3 | 7.6 ± 0.1 | 88 ± 24 | 0.08 ± 0.020 | 70 ± 13 | 7.4 ± 0.0 |
| 44 | 332 ± 2 | 31.8 ± 0.4 | 9.0 ± 0.3 | 46 ± 22 | 0.05 ± 0.037 | 53 ± 10 | 7.4 ± 0.0 |
| 67 | 283 ± 18 | 19.3 ± 5.6 | 7.7 ± 0.1 | 37 ± 20 | 0.03 ± 0.009 | 35 ± 7 | 7.4 ± 0.0 |
| 89 | 328 ± 16 | 28.2 ± 0.8 | 9.5 ± 0.0 | 19 ± 20 | 0.023 ± 0.004 | 26 ± 5 | 7.4 ± 0.1 |

Another important reason for the observed improvement in CH₄ productivity was that FeCl₃ acted as a selective regulator to reduce the sulfur reduction activities of sulfate-reducing bacteria. The inhibitory effect of H₂S on anaerobic microorganisms in anaerobic digestion has been reported to occur in the range of 50–400 ppm_v H₂S [22]. In this study, the H₂S content was 2520 ± 426 ppm_v in the sample without the addition of FeCl₃, as shown in Table 2. As the addition of FeCl₃ increased, the concentration of H₂S gradually decreased, accounting for 947 ± 267, 88 ± 24, and 19 ± 20 ppm_v in the samples with 11, 33, and 89 g FeCl₃/kg COD, respectively. According to previous study, Andriamanohiarisoamana et al. 2018, the sulfide produced by SRB was directly precipitated by the formation of iron sulfide when FeCl₃ was added to the digester [15]. The amount of precipitated iron sulfide (FeS) can be quantitatively estimated based on the reduced H₂S content in biogas by adding FeCl₃. The amount of H₂S generated in the sample without FeCl₃ addition was 2.37 ± 0.327 mg S. Meanwhile, it gradually decreased as FeCl₃ increased, reaching 0.95 ± 0.062, 0.08 ± 0.020, 0.03 ± 0.009, and 0.023 ± 0.004 mg S in the sample with 11, 33, 67, and 89 g FeCl₃/kg COD, respectively.

Based on the amount of decreased H₂S in the presence of FeCl₃, the amount of precipitated iron sulfide (FeS) was estimated as 129 ± 33, 70 ± 13, 35 ± 7, 26 ± 5 mg H₂S/g FeCl₃ in the sample with 11, 33, 67, and 89 g FeCl₃/kg COD, respectively. From this, the amount of H₂S generated was reduced as a higher amount of iron salt was injected, whereas the amount of H₂S removed per unit mass of iron salt was decreased. This shows

that it is necessary to inject an appropriate amount of FeCl_3 according to the sulfur content in the substrate.

3.2. Effect of Mill Scale Addition on Anaerobic Digestion

Batch test II, subject to the effect of MS addition on anaerobic digestion, was performed, and the experimental results are shown in Table 3. A slight increase in CH_4 yield was achieved when MS addition increased, showing 260 ± 20 , 277 ± 13 , and 287 ± 8 mL CH_4 /g TCOD at 0, 20, and 160 g MS/kg TCOD, respectively. Meanwhile, it showed a gradual enhancement in the CH_4 production rate as the amount of MS was added. For example, the CH_4 production rate was 36.9 ± 2.0 mL CH_4 /d when MS was not injected (control). On the other hand, it proportionally increased to 39.4 ± 1.6 , 40.3 ± 2.2 , and 56.4 ± 0.1 mL CH_4 /d at 5, 20, and 160 g MS/kg TCOD, respectively. This result clearly shows that the injection of MS has a positive effect on the CH_4 production rate.

Table 3. Experimental results obtained from batch test II after the addition of mill scale.

| Mill Scale Dosage (g MS/kg TCOD) | CH_4 Yield (mL CH_4 /g TCOD) | CH_4 Production Rate (mL/d) | λ (d) | H_2S Content (ppm _v) | Total Amount of Sulfur Reduced to H_2S (mg sulfur) | Theoretical Value of Sulfur Reacted with Mill Scale (mg H_2S /mg MS) | Final pH |
|----------------------------------|--|--------------------------------------|---------------|--|--|--|---------------|
| 0 | 260 ± 20 | 36.9 ± 2.0 | 9.0 ± 0.1 | 801 ± 74 | 1.88 ± 0.010 | - | 7.2 ± 0.0 |
| 5 | 251 ± 47 | 39.4 ± 1.6 | 8.0 ± 0.2 | 783 ± 120 | 1.64 ± 0.003 | 48 ± 2 | 7.2 ± 0.0 |
| 10 | 265 ± 26 | 37.1 ± 0.3 | 8.4 ± 0.0 | 703 ± 80 | 1.60 ± 0.045 | 28 ± 5 | 7.2 ± 0.1 |
| 20 | 277 ± 13 | 40.3 ± 2.2 | 7.6 ± 0.3 | 510 ± 81 | 1.20 ± 0.007 | 34 ± 0 | 7.2 ± 0.0 |
| 40 | 250 ± 51 | 46.5 ± 1.2 | 9.0 ± 0.3 | 262 ± 61 | 0.57 ± 0.092 | 33 ± 3 | 7.2 ± 0.2 |
| 160 | 287 ± 8 | 56.4 ± 0.1 | 9.5 ± 0.5 | 29 ± 29 | 0.08 ± 0.017 | 11 ± 0 | 7.2 ± 0.2 |

The results obtained from batch test II showed that MS effectively reduced H_2S generation during anaerobic digestion. In the biogas, the H_2S concentration in the control was 801 ± 74 ppm_v. A decreased concentration of H_2S was found as MS was added, reaching 703 ± 80 , 510 ± 81 , and 262 ± 61 ppm_v, at 10, 20, and 40 g MS/kg TCOD, respectively. At a concentration of 160 g MS/kg TCOD, H_2S was 29 ± 29 ppm_v, showing that the achieved reduction of H_2S generation was 95.9% compared to the control. A decrease in H_2S content in the presence of MS is linked to a decrease in the total amount of sulfur that was formed into H_2S . The total sulfur reduced by SRB was estimated to be 1.88 ± 0.010 mg in the control, while significantly decreased H_2S was achieved in the samples with MS addition, showing 1.60 ± 0.045 , 1.20 ± 0.007 , 0.57 ± 0.092 , and 0.08 ± 0.017 mg at 10, 20, 40, and 160 g MS/kg TCOD, respectively.

3.3. Performance Comparison between Iron Chloride and Mill Scale Addition

The results obtained from this study showed that both sulfur-reducing agents positively affect CH_4 productivity and H_2S content reduction in biogas. One of the possible reasons for CH_4 productivity enhancement is the promotion of direct interspecies electron transfer (DIET) by adding electro-conductive materials. Numerous studies have demonstrated that CH_4 productivity is enhanced by the addition of a variety of conductive materials that can serve as an electrical bridge to facilitate DIET [3,23–25]. Both FeCl_3 and MS employed in this study are known as electrically conductive materials and may play positive roles on the metabolic pathway of anaerobic digestion. In addition, the improved CH_4 productivity was due to the fact that both FeCl_3 and MS acted as sulfur-reducing agents to decrease the H_2S concentration, which often occurs in the inhibition of anaerobic microorganisms in anaerobic digestion.

However, a discrepancy in the performance between batch tests I and II was observed. This was due to the different compositions of FW used in each test. As shown in Table 1, the chemical characteristics of FW I and FW II employed in batch tests I and II are different. FW I was sampled in the winter of 2019, while FW II was sampled in the spring season of

2020. The seasonal variation in FW composition is a distinctive characteristic producing the chemical differences between FW I and FW II [26].

The SCOD/TCOD in FW I and FW II was 70.0% and 58.0%, while the sulfur content in FW I and FW II was 0.45% and 0.19%, respectively. The higher sulfur content in FW I resulted in 2520 ± 426 ppm_v of H₂S in the control of batch test I, which possibly had an inhibitory effect on methanogenic activity and showed a lower CH₄ yield compared to that of the control in batch test II [27]. However, the enhanced CH₄ yield in batch test I was much higher than that in batch test II when FeCl₃ was added, indicating that the inhibitory effect of H₂S on methanogenic activity gradually decreased. Meanwhile, the lower level of H₂S (801 ± 74 ppm_v) in the control of batch test II was mainly due to the lower content of sulfur in FW II. Its content did not severely inhibit methanogenic activity as much as the control of batch test I, and the increased CH₄ yield was relatively low. However, the CH₄ yield in the presence of FeCl₃ in batch test I was higher compared to that of the batch test with the addition of MS. For example, a methane yield of 328 ± 16 mL CH₄/g TCOD was achieved at 89 g FeCl₃/kg TCOD, while it was 287 ± 8 mL CH₄/g TCOD in the presence of 160 g MS/kg TCOD. This was possibly caused by the different contents of biodegradable compounds or unknown compounds included in the MS, causing microbial toxic effects in the anaerobic digestion. Therefore, further studies focused on solving these issues should be conducted.

It was found that the H₂S removal efficiency increased with increasing sulfur-reducing agents. However, the H₂S removal efficiencies of FeCl₃ and MS were different, and FW1 and FW2 had different sulfur content. Therefore, an indirect comparison by using the theoretical value of sulfur reacted with both the sulfur-reducing agents is needed, indicating the amount of precipitated iron sulfide (FeS) based on the amount of decreased H₂S in the presence of both sulfur-reducing agents. We estimated the theoretical amount of H₂S reduction based on a gram of FeCl₃ and MS added, and similar patterns of decreased efficiency at higher levels of both sulfur-reducing agents were observed. For example, batch test I showed 129.0 ± 32.8 , 69.5 ± 12.8 , and 26.4 ± 5.0 mg H₂S/g FeCl₃ at 11, 33, and 89 g FeCl₃/kg TCOD, while 47.7 ± 1.8 , 33.9 ± 0.2 , and 11.2 ± 0.1 mg H₂S/mg MS at 5, 20, and 160 g MS/kg TCOD, respectively. We further investigated the relationship between H₂S removal and the addition of sulfur-reducing agents fitted by Equation (3), and the R² values of both curves were over 0.98 (Figure 2). In total, 30%, 60%, and 90% of H₂S production based on the maximum sulfur in the form of H₂S (control) was 3.7, 9.4, and 23.8 g FeCl₃/kg TCOD and 13.3, 34.1, and 86.2 g MS/kg TCOD, respectively. Comparing the amount of sulfur-reducing agents required for each target amount, the amount of MS to be added to reduce 30% of H₂S production was approximately 3.6 times higher than that of FeCl₃ addition.

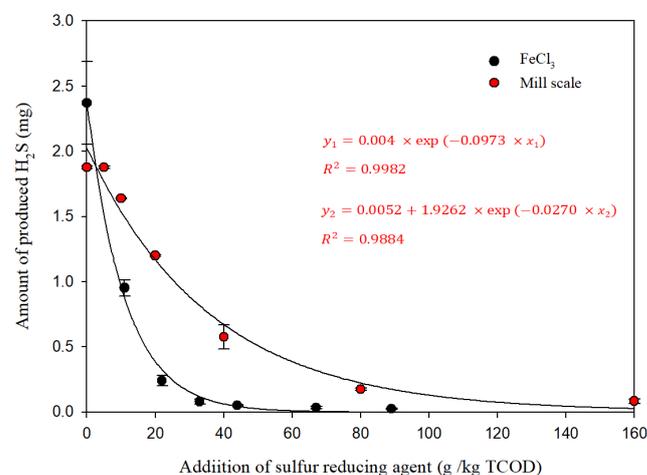


Figure 2. Change in hydrogen sulfide generation at various concentrations of FeCl₃ and mill scale during anaerobic digestion.

The results of this study showed that MS can be used as a substitute for sulfur-reducing agents for H₂S removal in anaerobic digestion fed with FW. However, introduction of MS into AD of FW could lead to enriching metals in the digestate, which is supposed to be spread on farming land. More research is needed to investigate the effects of MS addition on digestate and crop growth.

4. Conclusions

This study was conducted to investigate the feasibility of using waste MS to reduce the H₂S content in biogas. The results showed that MS positively affected the AD process. It was found that MS plays an important role as an electro-conductive material, improving CH₄ productivity by accelerating DIET—showing that the CH₄ production rate was 36.9, 39.4, 40.3, and 56.4 mL CH₄/d at 0, 5, 20, and 160 g MS/kg TCOD, respectively. In addition, the reduction in H₂S is crucial, which increased with increasing MS content, showing 48 ± 2, 34 ± 0, and 11 ± 0 mg H₂S/mg MS at 5, 20, and 160 g MS/kg TCOD, respectively. This finding indicates that MS can be used as a substitute for sulfur-reducing agents in H₂S removal in anaerobic digestion fed with FW. However, a larger amount of MS is needed to achieve a compatible H₂S removal efficiency obtained by the addition of FeCl₃. Further studies are required to analyze the economic feasibility of MS as a sulfur-reducing agent.

Author Contributions: Writing original draft: B.-K.A.; data curation, T.-H.K.; data curation J.S.; data curation, S.-K.P.; supervision, Y.-M.Y. All authors have read and agreed to the published version of the manuscript.

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